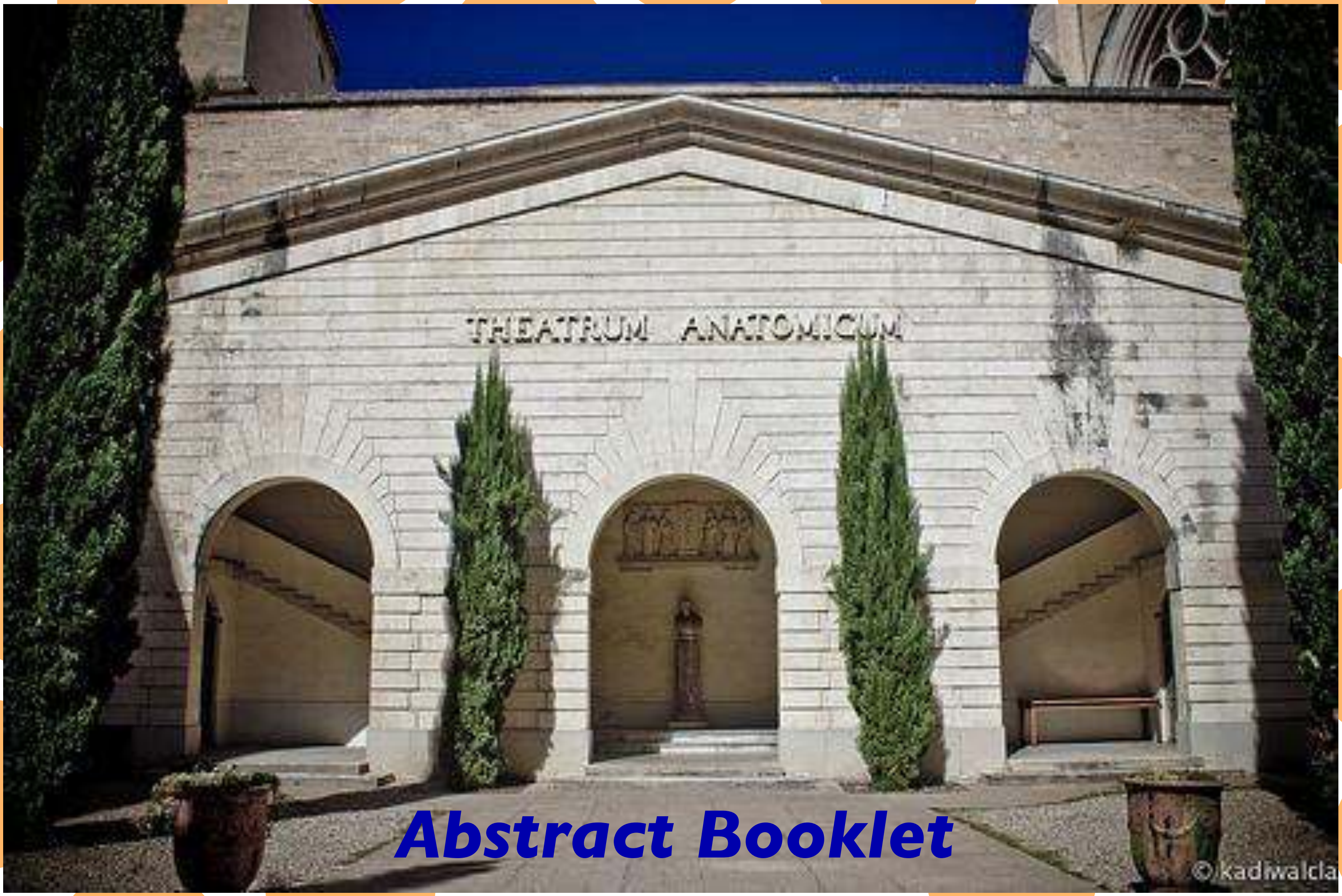
Workshop on Dynamics in Viscous Liquids IV

Theatrum Anatomicum
Montpellier
May 4 – May 7, 2015



Abstract Booklet

International Workshop on Dynamics in Viscous Liquids IV

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Programme

Organization
Ludovic Berthier, Luca Cipelletti, and Thomas Voigtmann

Contents

Introduction

It is our pleasure to welcome you to the 4th International Workshop on Dynamics in Viscous Liquids in Montpellier. It continues the series of previous workshops in Munich (2004, organized by Andreas Meyer and Thomas Voigtmann), Mainz (2006, organized by Jürgen Horbach and Wolfgang Paul), and Rome (2011, organized by Emanuela Zaccarelli, Thomas Voigtmann, and Giorgio Parisi).

This workshop series brings together the leading experts on theoretical and experimental advances in the field of viscous liquid dynamics (from glass-forming liquids, viscous metallic or oxide melts, and polymers to dense colloidal suspensions and other soft-matter model systems, granular and active matter).

Our aim is that the oral presentations at the workshop reflect the latest developments in the field, and stimulate fruitful debate. At the same time, the workshop shall also provide a platform especially for young researchers working in this field. Hence, the workshop's programme contains no invited talks and is completely determined by a programme committee that bases its decision on the one-page abstracts submitted by all contributing participants. These are the abstracts collected in this booklet. We, the organizers, wish to thank the committee for spending its time and for a very stimulating meeting with many in-depth discussions. We have received around 170 submissions, all of which were carefully read and judged by the committee members. They had to undergo the hard task of selecting only 48 talks for an oral presentation.

The workshop location is in the heart of the medieval Montpellier center, an enjoyable pedestrian area burgeoning with social life, typical restaurants and historical buildings. Oral sessions will take place in the Theatrum Anatomicum of the Medical School of the University of Montpellier. This hall, originally built at the beginning of the 19th century for the Anatomy and Dissection classes at the University, is located in the court of an historical palace, built to host a monastery by Guillaume Grimoard, who was later to be elected Pope under the name of Urban V (1362–1370). The poster sessions will be held in the Urban V palace.

We cordially thank the Research Unit (Forschergruppe) FOR1394, “Nonlinear Response to Probe Vitrification” (funded through the German Science Foundation / Deutsche Forschungsgemeinschaft, DFG) for financial support. Special thanks go to Christelle Eve for her help in organizing this workshop.

We hope that this workshop will, as its predecessors, prove to be a stimulating, entertaining, and productive meeting for all of us. We wish you all a pleasant stay in Montpellier,

Ludovic Berthier
Luca Cipelletti
Thomas Voigtmann

1 Useful Information

Programme Committee

Daniele Coslovich	Université de Montpellier, France
Olivier Dauchot	ESPCI Paris, France
Thomas Franosch	Universität Innsbruck, Austria
Peter Harrowell	University of Sydney, Australia
Andreas Heuer	Universität Münster, Germany
Alois Loidl	Universität Augsburg, Germany
Wilson Poon	University of Edinburgh, UK
Itamar Procaccia	Weizmann Institute, Rehovot, Israel
Peter Sollich	King's College London, UK
Gilles Tarjus	Université Paris 6, France
Emanuela Zaccarelli	Università di Roma La Sapienza, Italy

Organization

Ludovic Berthier	Université de Montpellier
Luca Cipelletti	Université de Montpellier
Thomas Voigtmann	Institut für Materialphysik im Weltraum, DLR, Köln

Conference Secretary

Christelle Eve

Conference Office

Laboratoire Charles Coulomb
UMR 5221 CNRS-UM2
Université Montpellier 2
Place Eugène Bataillon – CC026
34095 Montpellier Cedex 5
France
e-mail: office@viscous-liquids.de

Co-Funding

Research Unit FOR1394
Nonlinear Response to Probe Vitrification
funded through Deutsche Forschungsgemeinschaft (DFG)

Useful Addresses

* Conference location: 2 Rue de l'École de Médicine
tram stop "Albert 1er", lines T1, T4

Restaurants

1 Pasta, Place Albert 1er (pasta, pizza, lasagna: good & quick)

2 Boulangerie Lo Monaco, 8 rue JJ Rousseau (take away pizza, quiches, tartines)

3 Atypik, 15 rue JJ Rousseau (french cuisine)

4 Vert anglais, Place Castellane

5 Comptoir de l'Arc, Place de la Canourgue (very nice location, good food)

6 La terrasse, Black cat, Place Candolle (very nice location, terrasse)

7 La morue, La girafe, Rue du palais Guilhem (small terrasses)

8 Esprit vin, Place Chabaneau (large terrasse)

9 Burger et Blanquette, Place du Marche aux Fleurs (large terrasse, several others nearby)

10 Le Pre Vert, 10 rue Sainte-Anne (quick salads, nice terrasse)

11 Le petit Nice, Place Jean Jaures (large terrasse, several others nearby)

12 Pizza pizzetta, 1 Rue Ferdinand Fabre (pizza, good & quick)

13 Rebuffy (beer bar)

Husser Brasserie Le Corum, Esplanade Charles De Gaulle
Tram Stop "Corum", lines T1, T2, T4
conference dinner

Hotels

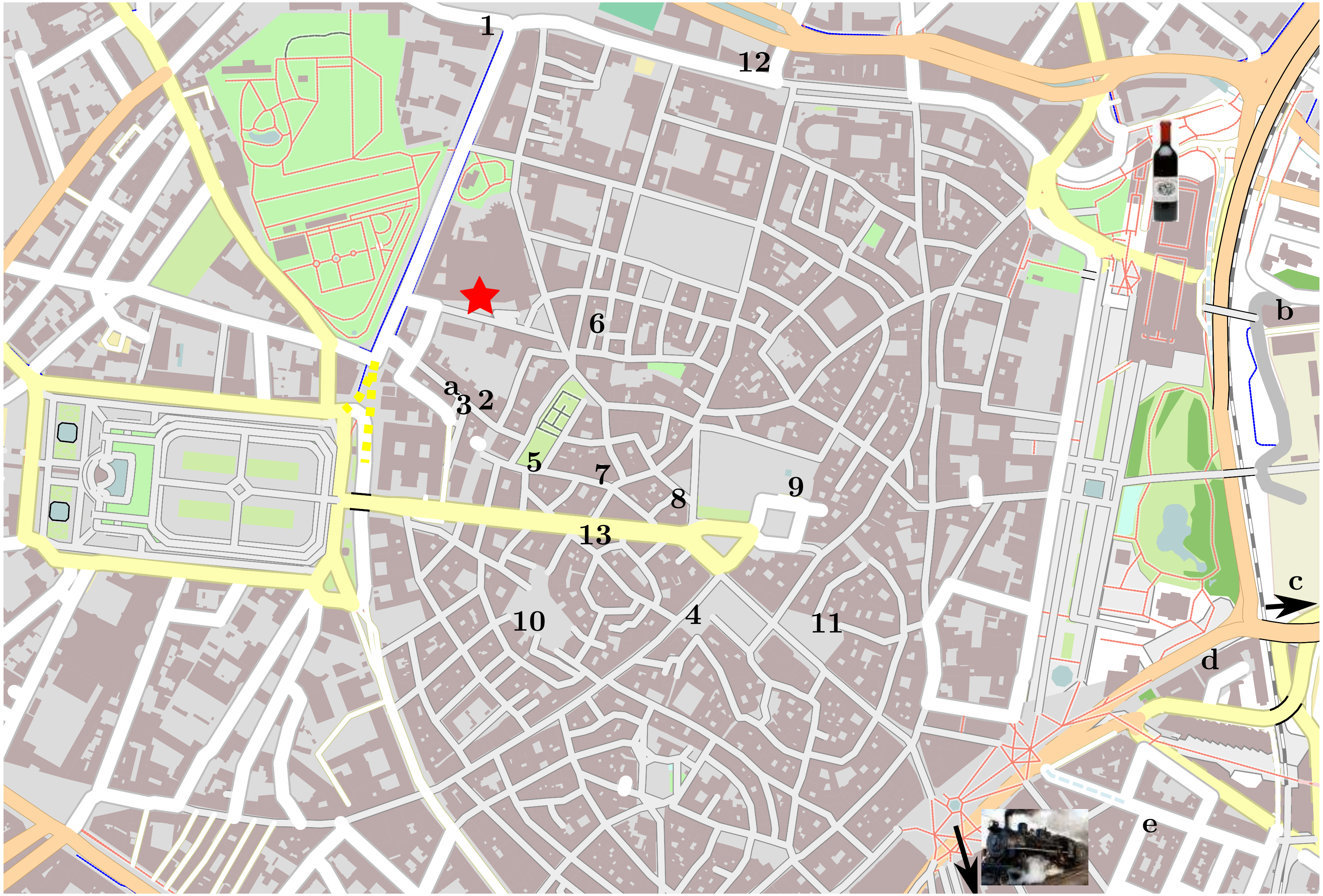
a Best Western Le Guilhem

b Crown Plaza

c ibis Montpellier Centre

d ibis Montpellier Centre Comédie

e D'Aragon



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2 Programme

	Mon 04/05	Tue 05/05	Wed 06/05	Thu 07/05
08:00–08:45	Registration			
08:45–09:00	Opening			
09:00–10:20	J. Kurchan	R. Jack	M. Blank-Burian	G. Biroli
	J. P. Garrahan	J. Russo	C. Dasgupta	J. Horbach
	C. P. Royall	Y. Jin	G. Abade	V. Krakoviack
	G. Szamel	P. Charbonneau	M. Siebenbürger	C. Cammarota
10:20–10:50	coffee			
10:50–12:10	S. M. Bhattacharyya	A. Amon	A. Sarracino	H. Delanoë-Ayari
	J. C. Dyre	G. Foffi	S. Mandal	T. Kawasaki
	N. Gnan	E. E. Ferrero	P. E. Ramírez-González	V. Roger
	Y. Shokef	L. Isa	M. Laurati	S. Papenkort
12:10–14:00	lunch			
14:00–15:30	Poster group A	Poster group A	Poster group B	Poster group B
15:30–16:00	coffee			
16:00–17:20	C. Cottin-Bizonne	T. Rizzo	A. Pons	M. Michl
	A. Solon	F. Giavazzi	A. Lemaître	P. Gadige
	C. Valeriani	B. Ruzicka	B. Chakraborty	E. Del Gado
	C. Maggi	F. Lequeux	P. Urbani	D. Vandembroucq
				Closing remarks
18:00–	Wine & Cheese Party			
19:00–			Conference Dinner	

Monday, May 4

08:00	**Registration**
08:45	**Welcome Note** *L. Berthier, L. Cipelletti, and Th. Voigtmann*
	Session 1, Chair: L. Berthier
09:00	**J. Kurchan**, LPS-Ecole Normale Superieure *On the origin of multiple timescales and effective temperatures in glasses*
09:20	**J. P. Garrahan**, University of Nottingham *Glasses and large deviations: from classical to quantum*
09:40	**C. P. Royall**, University of Bristol *Piecing together the Jigsaw of Thermodynamic Transitions in Glassformers*
10:00	**G. Szamel**, Colorado State University *Differences between dynamics in two and three dimensional glass forming fluids*
10:20	**Coffee break**
	Session 2, Chair: G. Biroli
10:50	**S. M. Bhattacharyya**, CSIR-National Chemical Laboratory India *Role of Pair and Many Body Correlations in Determining the Entropy and Dynamics in Glass Formers*
11:10	**J. C. Dyre**, Roskilde University *Origin of the quasiuniversality of simple liquids*
11:30	**N. Gnan**, CNR Roma, Italy *Multiple singularities and iso-dynamics in a simple glass former*
11:50	**Y. Shokef**, Tel Aviv University *Jamming Percolation in Three Dimensions*
12:10	**Lunch**
14:00	**Poster Session A**
15:30	**Coffee break**
	Session 3, Chair: L. Cipelletti
16:00	**C. Cottin-Bizonne**, Université Claude Bernard Lyon1 *Nonequilibrium equation of state in suspensions of active colloids*
16:20	**A. Solon**, Université Paris Diderot *What is the Pressure of an Active Particle Fluid?*
16:40	**C. Valeriani**, Universidad Complutense de Madrid *Self-propelled particles: self-assembly and active depletion*
17:00	**C. Maggi**, Università di Roma “Sapienza” *Generalized Energy Equipartition and Multiple Effective Temperatures in Harmonic Oscillators Driven by Active Baths*
18:00	**Wine & Cheese party**

Tuesday, May 5

Session 4, Chair: D. Coslovich

09:00 **R. Jack**, University of Bath
Information-theoretic measurements of coupling between structure and dynamics in glass-formers

09:20 **J. Russo**, University of Tokyo
The origin of glass forming ability in a system with competing orderings

09:40 **Y. Jin**, Sapienza Università di Roma
Numerical detection of the Gardner transition in simple structural glass formers

10:00 **P. Charbonneau**, Duke University
Cavity point-to-set correlations: recent advances

10:20 **Coffee break**

Session 5, Chair: E. Zaccarelli

10:50 **A. Amon**, Université Rennes 1
Emergence of Cooperativity in Plasticity of Soft Glassy Materials

11:10 **G. Foffi**, Université Paris-Sud
Dynamic transition and memory encoding in glass-formers under shear

11:30 **E. E. Ferrero**, Université Grenoble Alpes
Relaxation in yield stress systems through elastically interacting activated events

11:50 **L. Isa**, ETH Zurich
Colloidal monolayers under steady shear at the liquid-liquid interface

12:10 **Lunch**

14:00 **Poster Session A**

15:30 **Coffee break**

Session 6, Chair: A. Heuer

16:00 **T. Rizzo**, IPCF-CNR and Università “Sapienza”
Times, Lengths and the Nature of the Glass Crossover

16:20 **F. Giavazzi**, Università degli Studi di Milano
On the microscopic origin of anomalous relaxation in soft glassy materials

16:40 **B. Ruzicka**, Sapienza Università di Roma
Glass-glass transition in an charged colloidal suspension

17:00 **F. Lequeux**, ESPCI/CNRS/UPMC/PSL Research University
The Role of Dynamical Heterogeneities on the Mechanics of Polymer Glasses

Wednesday, May 6

Session 7, Chair: Th. Voigtmann

09:00 **M. Blank-Burian**, Westfälische Wilhelms-Universität Münster
The Potential Energy Landscape of Sheared Supercooled Liquids

09:20 **C. Dasgupta**, Indian Institute of Science, Bangalore
Activity-induced Fluidization in Dense Glassy Systems

09:40 **G. Abade**, Universität Konstanz
Active microrheology in a colloidal glass: mode-coupling theory and molecular dynamics simulations

10:00 **M. Siebenbürger**, Helmholtz Zentrum Berlin
History dependent mechanical properties of colloidal glasses

10:20 **Coffe break**

Session 8, Chair: T. Franosch

10:50 **A. Sarracino**, Sorbonne Universités
Microscopic theory for negative differential mobility in crowded environments

11:10 **S. Mandal**, Leopold-Franzens-Universität Innsbruck
Multiple reentrant glass transitions in confined hard-sphere glasses

11:30 **P. E. Ramírez-González**, Chinese Academy of Sciences
Probing the Existence of Partially-Arrested States in Ionic Liquids.

11:50 **M. Laurati**, Heinrich-Heine University Düsseldorf
Localization and caging in binary glasses

12:10 **Lunch**

14:00 **Poster Session B**

15:30 **Coffee break**

Session 9, Chair: P. Charbonneau

16:00 **A. Pons**, UMR CNRS 7636 and Université Paris 6 & Paris 7
Mechanical fluctuations suppress the threshold of soft-glassy solids

16:20 **A. Lemaître**, Université Paris-Est
Structural relaxation is a scale-free process

16:40 **B. Chakraborty**, Brandeis University
A Theoretical Framework for Shear Induced Rigidity in Athermal Materials

17:00 **P. Urbani**, CEA, Saclay
Critical exponents of the jamming transition

19:00 **Conference Dinner** (Husser Brasserie Le Corum, Esplanade Charles De Gaulle)

Thursday, May 7

Session 10, Chair: I. Procaccia

09:00 **G. Biroli**, CEA, Saclay
Continuous Glass Transitions, Activated Dynamic Scaling and the Random Field Ising Model

09:20 **J. Horbach**, Heinrich Heine-Universität Düsseldorf
Rounded delocalization-to-localization transition of soft-disk fluids in a porous medium

09:40 **V. Krakoviack**, École Normale Supérieure de Lyon
Structure and dynamics of a fluid in a quenched disordered potential

10:00 **C. Cammarota**, “Sapienza” Università di Roma
Fluctuations and Shape of Cooperative Rearranging Regions in Glass-Forming Liquids

10:20 **Coffee break**

Session 11, Chair: P. Royall

10:50 **H. Delanoë-Ayari**, Université de Lyon
Rheology of cellular aggregates.

11:10 **T. Kawasaki**, Laboratoire Charles Coulomb, Montpellier, France
Diverging viscosity and soft granular rheology in non-Brownian suspensions

11:30 **V. Roger**, Laboratoire Charles Coulomb (L2C), Montpellier, France
Viscosity and Microscopic Dynamics in Concentrated Suspensions of Colloidal Microgels

11:50 **S. Papenkort**, Deutsches Zentrum für Luft- und Raumfahrt, Köln
Lattice Boltzmann Simulations of Glass Forming Liquids

12:10 **Lunch**

14:00 **Poster Session B**

15:30 **Coffee break**

Session 12, Chair: G. Tarjus

16:00 **M. Michl**, University of Augsburg
Nonlinear dielectric spectroscopy in plastic crystals

16:20 **P. Gadige**, CEA, Saclay
New control parameter for the glass transition of glycerol

16:40 **E. Del Gado**, Georgetown University
Cooperative processes, stress localisation and yielding in colloidal gels

17:00 **D. Vandembroucq**, Laboratoire PMMH, 75231 Paris cedex 05, France
Viscous coarsening and fragmentation in phase separating oxide glasses

List of Poster Contributions

A1 **A. A. Aerov**, Universität Stuttgart
Theory of rheology in confinement

A2 **B. Riechers**, Georg-August-Universitaet Goettingen
Time Dependent Nonlinear Response in Glassy Systems

A3 **C. F. E. Schroer**, Westfälische Wilhelms-Universität Münster
Non-equilibrium kinetics determine non-equilibrium thermodynamics in microrheologically driven supercooled liquids

A4 **D. Truzzolillo**, Laboratoire Charles Coulomb (L2C)
Off-equilibrium surface tension in driven colloidal suspensions

A5 **E. Agoritsas**, Univ. Grenoble Alpes, LIPHY, F-38000 Grenoble, France
Role of yield energy distributions in athermal amorphous materials under shear

A6 **F. Turci**, University of Bristol
Mechanical Response of Local Motifs in Deeply Supercooled Liquids

A7 **F. Varnik**, Ruhr-Universität Bochum
Correlated motion and diffusion in sheared athermal suspensions of deformable particles

A8 **G. P. Shrivastav**, Universität Düsseldorf
On the origin of shear bands in a model glass former

A9 **H. Cárdenas**, Deutsches Zentrum für Luft- und Raumfahrt, Köln
Continuum Mechanics Simulations in Glass Forming Liquids

A10 **J. Rottler**, University of British Columbia
Spatiotemporal correlations between plastic events in the shear flow of amorphous solids: from molecular dynamics to mesoscopic models

A11 **K. Martens**, Université Grenoble Alpes
Universal features in the rheological response of yield stress materials beyond critical exponents

A12 **L. Jørgensen**, Institut Lumière Matière (Université Claude Bernard Lyon 1 / CNRS)
Yield stress and elasticity influence on surface tension measurements

A13 **M. Braibanti**, University of Fribourg
Rheology and internal dynamics of dense nanoemulsions across the glass and the jamming regimes

A14 **M. Gruber**, Universität Konstanz
Active microrheology below the delocalization transition

A15 **M. Pierno**, Università di Padova
Sliding of viscoelastic Non-Newtonian drops

A16 **M. Priya**, Deutsches Zentrum für Luft- und Raumfahrt, Köln
Shear induced melting in repulsive systems with short-ranged attractive interactions

A17 **M. S. van Deen**, Leiden University
Rearrangements and plasticity in two-dimensional sheared foams

A18 **F. Varnik**, Ruhr-Universität Bochum
Non-locality of effective temperature in a shear driven model glass

A19 **N. Segall**, Tel Aviv University
Jamming vs Caging in Three Dimensional Jamming Percolation

A20 **P. Chaudhuri**, Institute of Mathematical Sciences
Yielding of soft glasses under applied shear

A21 **P. K. Jaiswal**, Weizmann Institute of Science
Shear transformation zones: State determined or protocol dependent?

A22 **P. Keim**, University of Konstanz
Discontinuous behaviour of the shear modulus defines the glass transition temperature

A23 S.U. Egelhaaf, Heinrich Heine University
Groups of Mobile Particles Determine the Creep Response of Colloidal Glasses

A24 F. Varnik, Centre for Advanced Materials Simulation
Sensitivity of the correlation of plastic rearrangements to the microscopic dynamics in sheared disordered solids

A25 S. Jabbari-Farouji, Université Grenoble Alpes
Tensile deformation of amorphous and semi-crystalline polymers

A26 R. Hartkamp, Massachusetts Institute of Technology
A constitutive framework for the non-Newtonian pressure tensor of a simple fluid under planar flows

A27 S. Sastry, Center for Advanced Scientific Research
Sheared frictionless sphere packings and shear jamming

A28 V. V Vasisht, ETH Zurich
Making jammed particle suspensions flow: slow and high shear rate cooperative rearrangements

A29 G. Bossis, Université de Nice Sophia Antipolis Nice
Abrupt shear thickening and stick-slip behavior of concentrated suspensions in the presence of fluidizer molecules

A30 M. Y. Nagazi, Universite Montpellier II
Microscopic precursors of fracture in amorphous solids

A31 A. M. Philippe, Université Montpellier 2 - CNRS
Anomalous dynamics of concentrated PNiPAM suspensions

A32 Y. M. Joshi, Indian Institute of Technology
Phase behavior of aqueous suspension of Laponite: A rheological perspective

A33 Y. Saruyama, Kyoto Institute of Technology
Temperature Modulated Dielectric Measurement: a Non-linear Technique for Kinetic Study on the Response of the Relaxation Time to Quick Temperature Change

A34 C. Liu, Université Grenoble Alpes
The nature of avalanche dynamics in the flow of yield stress materiels

A35 D. Donnarumma, Université Montpellier 2 & CNRS UMR 5587
Bronchial mucus characterization by macro- and micro-rheology

A36 E. Clement, Laboratoire de Physique et Mecanique des Milieux Heterogenes (PMMH UMR 7636 CNRS-ESPCI-P6-P7)
Viscosity of bacterial suspensions

A37 G. Briand, CNRS, Paris
Dense regimes of self-propelled hard disks

A38 K.-D. Nguyen Thu Lam, PSL Research University
Self-propelled hard discs: non-conservation of momentum, effective alignment and transition to collective motion

A39 R. Cerbino, Università degli Studi di Milano
Viscoelasticity of self-assembled liquid crystals of DNA

A40 D. Levis, Universitat de Barcelona
Effective thermodynamics of self-propelled particles

A41 A. Liluashvili, Deutsches Zentrum für Luft- und Raumfahrt, Köln
Active Microrheology of Dense Microswimmer Suspensions

A42 T. Schilling, Université du Luxembourg
Non-equilibrium aspects of the crystallization process

A43 C. P. Royall, University of Bristol
Crystallisation in a Modified Kob-Andersen Glassformer

A44 **C. Valeriani**, Universidad Complutense de Madrid
Exposing a dynamical signature of the freezing transition through the sound propagation gap

A45 **J. Gerges**, BAT P5 Université Lille 1
A predictive calculation of the crystallization tendency of model pharmaceuticals in the supercooled state from molecular dynamics simulations

A46 **P. Holmqvist**, Lund University
The short time dynamic signature of the liquid-crystal-glass transition in charged spherical colloidal suspension

A47 **R. Beyer**, Johannes Gutenberg Universität Mainz
From Nuclei to Micro-structure: investigating intermediate length scales by small angle laser light scattering

A48 **T. Odagaki**, Tokyo Denki University
Free energy landscape approach to the crystallization of super-cooled liquids

A49 **A. P. Cohen**, Bar-Ilan University
Fluids of colloidal ellipsoids: trading free volume for freedom of rotation

A50 **E. Secchi**, Laboratoire de Physique Statistique de l'Ecole Normale Supérieure
Ionic current noise across individual carbon and boron-nitride nanotubes: Hooge's law and beyond

A51 **M. Isobe**, Nagoya Institute of Technology
Dynamical Faciliation in Binary Hard Disk Systems

A52 **A. L. Thorneywork**, University of Oxford
Dynamics of quasi-two-dimensional binary colloidal hard spheres: self-diffusion, 'no' hydrodynamics and collective transport

A53 **P. Nadal**, Université Montpellier II
Simulation of hard sphere suspensions of fluctuating sizes

A54 **R. Bandyopadhyay**, Raman Research Institute
A light scattering study of the dynamical slowing down in Laponite suspensions: similarities with supercooled liquids

A55 **E. Zaccarelli**, Università di Roma "Sapienza"
Casimir-like forces close to the percolation transition

B1 **C. Crauste-Thibierge**, Ecole Normale Supérieure de Lyon (ENS/CNRS UMR 5672)
Fluctuations and aging at the critical point of a binary mixture

B2 **D. Bonn**, University of Amsterdam
Direct Measurement of the Free Energy of Aging Hard-Sphere Colloidal Glasses

B3 **G. F. Julien**, Laboratoire Polymère et Matériaux Avancés
Phase separation in polymer blends close to and below T_g*: aging and rejuvenation*

B4 **H. R. Schober**, Forschungszentrum Jülich
Aging rates in Glasses and their melts

B5 **Q. Tang**, Georg-August-Universität
Slowing Down of Accelerated Physical Aging in Ultrathin Polymer Films

B6 **A. Scagliarini**, University of Rome "Tor Vergata" and INFN
Plastic flow of foams and emulsions in a channel: experiments, theory and simulations

B7 **C. Rohwer**, Max Planck Institute for Intelligent Systems
Linear response of correlated fluids in confinement

B8 **K. Fukao**, Ritsumeikan University
Translational and rotational motions in thin films of polyamide random copolymers

B9 **L. Bocquet**, Ecole Normale Supérieure
Subcontinuum mass transport of hydrocarbons in nanoporous media and long-time kinetics of recovery from unconventional reservoirs

B10 **M. Kohl**, Heinrich-Heine University Düsseldorf
Relation of structure and dynamics of a bidispere sphere systems close to a wall

B11 **S. Tatsumi**, Kyoto Institute of Technology
New phase transition of confined cyclohexane in measoporous silica

B12 **A. Bérut**, Université de Lyon
External forces acting on micro-particles trapped with optical tweezers

B13 **A. Grzybowski**, University of Silesia
Variety of density scaling law manifestations

B14 **S. Sastry**, Centre for Advanced Scientific Research
Kinetic and thermodynamic fragilities of model fluids with variable barriers to bond breaking

B15 **A. Zaccone**, Technische Universität München
Valence-band Repulsion Controls the Fragility of Supercooled Metallic Melts

B16 **B. Abou**, UMR CNRS 7057 & Université Paris Diderot
Susceptibility χ_4 *fails to capture significant increase of dynamic correlation length near glass transition*

B17 **J. de Pablo**, University of Chicago
Structural and energetic features of two-dimensional vapor deposited glassy films

B18 **H. J. Schöpe**, Eberhards Karls Universität Tübingen
Experimental determination of structural and dynamical heterogeneities in a metastable colloidal fluid

B19 **I. Elyukhina**, South Ural State University
Exact and approximate analytical solutions for oscillating-cup viscometer

B20 **D. Long**, Laboratoire Polymères et Matériaux Avancés - UMR 5268 CNRS/Solvay
Heterogeneous dynamics and polymer plasticity

B21 **M. D. Alaimo**, Politecnico di Milano
Spatially–resolved heterogeneous dynamics in colloidal gels

B22 **M. Paluch**, University of Silesia
Temperature-density scaling of configurational entropy rationalized in terms of the Adam-Gibbs theory

B23 **O. Czakkel**, Institut Laue-Langevin, Grenoble
Glassy state dynamics of poly(lactic-acid) as seen by neutron spin-echo spectroscopy

B24 **R. C. Ball**, University of Warwick
Complex interactions with the surroundings dictate tagged chain dynamics in unentangled polymer melts

B25 **S. Hosokawa**, Kumamoto University
Transverse phonon excitations in a Pd-based metallic alloy in the liquid and supercooled liquid phases

B26 **Z. Evenson**, Deutsches Zentrum für Luft- und Raumfahrt, Köln
Dynamics of Binary Zr-Cu Liquids with Minor Additions

B27 **A. S. Ninarello**, UMR 5221 CNRS Université Montpellier 2
Heterogeneous Glassy Dynamics near a Random Critical Point

B28 **A. M. Puertas**, Universidad de Almería
Diffusion of a hard tracer in an ideal gas

B29 **A. Piscitelli**, Nanyang Technological University
Mean Square Displacement from a jumper model

B30 **A. Widmer-Cooper**, University of Sydney
Defect-mediated relaxation in the random tiling phase of a binary mixture: Birth, death and mobility of an atomic zipper

B31 **C.J. Fullerton**, University of Bath
Investigating Amorphous Order in Stable Glasses Through Random Pinning

B32 **C. Rainone**, Sapienza Università di Roma
Evolution of metastable glassy states in mean field hard-spheres: a replica approach

B33 **E. Tjhung**, CNRS and Universite Montpellier 2
Dynamic heterogeneities close to a non-equilibrium phase transition

B34 **E. Teomy**, Tel Aviv University
Jamming by Shape in Kinetically-Constrained Models

B35 **F. Leoni**, Tel Aviv University
Entropic selection within higly degenerate ground states: colloidal and deformable Ising antiferromagnets

B36 **G. Gradenigo**, CNRS et Université Paris-Sud 11
From Kinetically Constrained Models to the ideal glass transition: a thermodynamic study of the Triangular Plaquette Model

B37 **H. Ikeda**, Nagoya University
A One-dimensional Kac Model of Dense Amorphous Hard Sphere in High Dimension

B38 **H. L. Peng**, Deutsches Zentrum für Luft- und Raumfahrt, Köln
Length scale for transport coefficients in glass-forming liquid

B39 **A. Ikeda**, Kyoto University
Replica theory analysis of the glass transitions of complicated systems: Network-formers and ellipsoids

B40 **I. Procaccia**, Weizmann Institute of Science
The Static Lengthscale Characterizing the Glass Transition at Lower Temperatures

B41 **M. Leocmach**, Ecole Normale Supérieure de Lyon
Importance of many-body correlations in glass transition:an example from polydisperse hard spheres

B42 **M. Medina-Noyola**, Universidad Autónoma de San Luis Potosí
Non-equilibrium Statistical Thermodynamic Theory of Arrested Spinodal Decomposition

B43 **M. Ozawa**, University of Tsukuba
Tuning of Pairwise Potential Can Control the Fragility of Glass-Forming Liquids: From Tetrahedral Network to Isotropic Soft Sphere Models

B44 **R. Pastore**, Universitá di Napoli Federico II
Hopping and dynamical phase coexistence in supercooled liquids

B45 **N. Chtchelkatchev**, Russian Academy of Sciences
Glass formation and local quasicrystal order in dense liquids with repulsive two length scales potential

B46 **S. M. Hernández-Hernández**, Universidad Autónoma de San Luis Potosí
Ultrasoft systems and the hard-sphere dynamic universality class

B47 **T. Egami**, University of Tennessee
Anisotropic Stress Correlations in Simple Liquids

B48 **T. S. Ingebrigtsen**, University of Tokyo
Effect of size polydispersity on a Roskilde-simple liquid

B49 **T. Maimbourg**, École Normale Supérieure
Exact solution of hard spheres dynamics in high dimension

B50 **U. Buchenau**, Forschungszentrum Jülich
Probing cooperative liquid dynamics with the mean square displacement

B51 **V. N. Novikov**, University of Tennessee
Quantum effects in glass transition

B52 **A. Ninarello**, UMR 5221 CNRS Université de Montpellier
Observable-dependence of the effective temperature in off-equilibrium diatomic molecular liquids

B53 **C. Zhang**, University of Fribourg
Structure of marginally jammed polydisperse packings of frictionless spheres

B54 **S. Ciliberto**, École Normale Supérieure
Colloidal particles interactions near a critical point

B55 **A. J. Soininen**, Forschungszentrum Jülich GmbH
Water dynamics in carbon nanohorns: the apparent fragile-strong transition is a crossover from localized to diffusive motion

3 Abstracts

3.1 Talks

– space for notes –

On the origin of multiple timescales and effective temperatures in glasses

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– space for notes –

Glasses and large deviations: from classical to quantum

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The dynamics of many-body systems is often richer than what one can directly infer from their static properties, glass formers being a typical example. This dynamical richness is revealed by considering strictly dynamical observables. The full statistical characteristics of such quantities encode the dynamical properties of the system at hand. By considering their large deviations it is possible to derive a statistical mechanics of trajectories, which is to trajectories of the dynamics what equilibrium statistical mechanics is to configurations of the statics. In this talk I will describe this approach and how it can be applied to the glass transition problem. I will show how the underlying kinetic phenomenon of glass formation is a novel class of order-disorder transitions in trajectory, rather than configuration, space. I will consider the connection between the inactive dynamical phases this approach reveals and glasses prepared by more standard means. A significant prediction from this approach is the emergence of non-trivial correlations that distinguish glass from its reversible melt.

The ideas behind this "dynamical facilitation" perspective on the classical glass transition problem can be extended to account for collective non-equilibrium dynamics in quantum many-body systems as well. One such situation is the case of strongly interacting Rydberg gases. In these systems the so-called Rydberg blockade between excited atoms gives rise to collective non-equilibrium physics that due to excluded volume effects is analogous to what occurs in classical soft-matter systems at high densities, something we call "Rydberg soft-matter". Time permitting I will also discuss connections between the dynamical large-deviation properties of classical glass models and the problem of many-body localisation in closed quantum systems.

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– space for notes –

Piecing together the Jigsaw of Thermodynamic Transitions in Glassformers

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The fundamental nature of the glass transition is a major outstanding question in condensed matter, in particular the dramatic super-Arrhenius slowdown in relaxation time so far eludes comprehensive explanation. An important question is whether such dynamical behaviour is accompanied by some kind of thermodynamic transition and what nature that transition might take [1]. Here we make two contributions to this debate : firstly, using an information theoretic approach we address the conundrum that exists in identifying a suitable lengthscale to characterise the approach to any transition [2]. Second we develop a reweighting technique that allows us to approach the transition much closer than hitherto possible [3].

A new dynamic lengthscale — Recently geometric motifs have been identified in glassy liquids, but a causal link between these motifs and solidification remains elusive. One "smoking gun" for such a link would be identical scaling of structural and dynamic lengthscales upon approaching the glass transition, but this is highly controversial. Here we introduce an information theoretic approach to determine correlations in displacement for particle relaxation encoded in the initial configuration of a glassforming liquid. We uncover two populations of particles, one inclined to relax quickly, the other slowly. Each population is correlated with local density and geometric motifs knows as locally favoured structures (LFS). Our analysis further reveals a dynamic lengthscale similar to that associated with structural properties which may resolve the discrepancy between structural and dynamic lengthscales [Fig. 1(a)] [2].

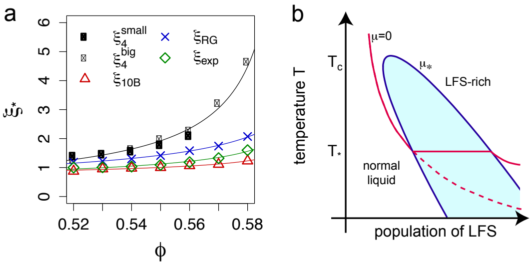

FIG. 1. (a) Structural and dynamic correlation lengths as a function of ϕ in hard spheres. Dynamical lengths ξ_4 are calculated in conventional microcanonical simulations of different sizes of $N = 1372$ and $N = 10976$ respectively. The new dynamical lengthscales $\xi_{\rm exp}$ and $\xi_{\rm RG}$ correspond to significantly correlated particles in the isoconfigurational ensemble. $\xi_{\rm 10B}$ is a structural length scale based on "10B" LFS. (b) Liquid-liquid transition in the Kob-Andersen mixture in the temperature-LFS population plane. Below the critical temperature T_c phase coexistence is possible (shaded area bounded by μ_*). The case that the dynamical biasing potential μ is set to zero corresponds to experiments (red line). The dashed line indicates the metastable liquid branch below T_*. At T_* a liquid-liquid transition is found for $\mu = 0$.

Reweighting : the ideal glass and a liquid-liquid transition — The timescales inherent in the glass transition present a great challenge to computer simulation which might otherwise pick up hints of any thermodynamic transition. Here we address the challenge of limited time-windows in simulation of a model atomistic glassformer by introducing a technique of trajectory reweighting. Our approach allows access to equilibrated configurations at significantly lower temperatures than has been possible until now. We report two findings. Firstly, that our analysis indicates a minimum entropy amorphous configuration reminiscent of an "ideal glass" at finite temperature $T_k \approx 0.28$. Secondly, at a rather higher temperature $T* \approx 0.425$ we find a peak in the specific heat capacity which corresponds to liquid-liquid transition to a state rich in LFS [Fig. 1(b)]. The dynamics of this LFS-rich liquid are very much slower than the normal liquid [3].

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– space for notes –

Differences between dynamics in two and three dimensional glass forming fluids

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We use computer simulations to compare the structural relaxation and heterogeneous dynamics in two and three dimensional glass-forming fluids. We find significant differences between two and three dimensions. First, in Newtonian dynamics simulations of two dimensional glassy fluids we see no evidence of an emerging plateau in the self-intermediate scattering function and the mean-square displacement. However, we see an emerging plateau in a correlation function quantifying time-dependence of orientational correlations. Also, we find that the relation between a dynamic correlation length measuring the spatial extent of dynamic heterogeneity and the relaxation time is very different in two and three dimensions. Finally, in two dimensions we see strong dependence of the structural relaxation on the underlying microscopic dynamics. This is in contrast with the three dimensional case, where for strongly supercooled fluids Newtonian and Brownian dynamics lead to the same long-time structural relaxation.

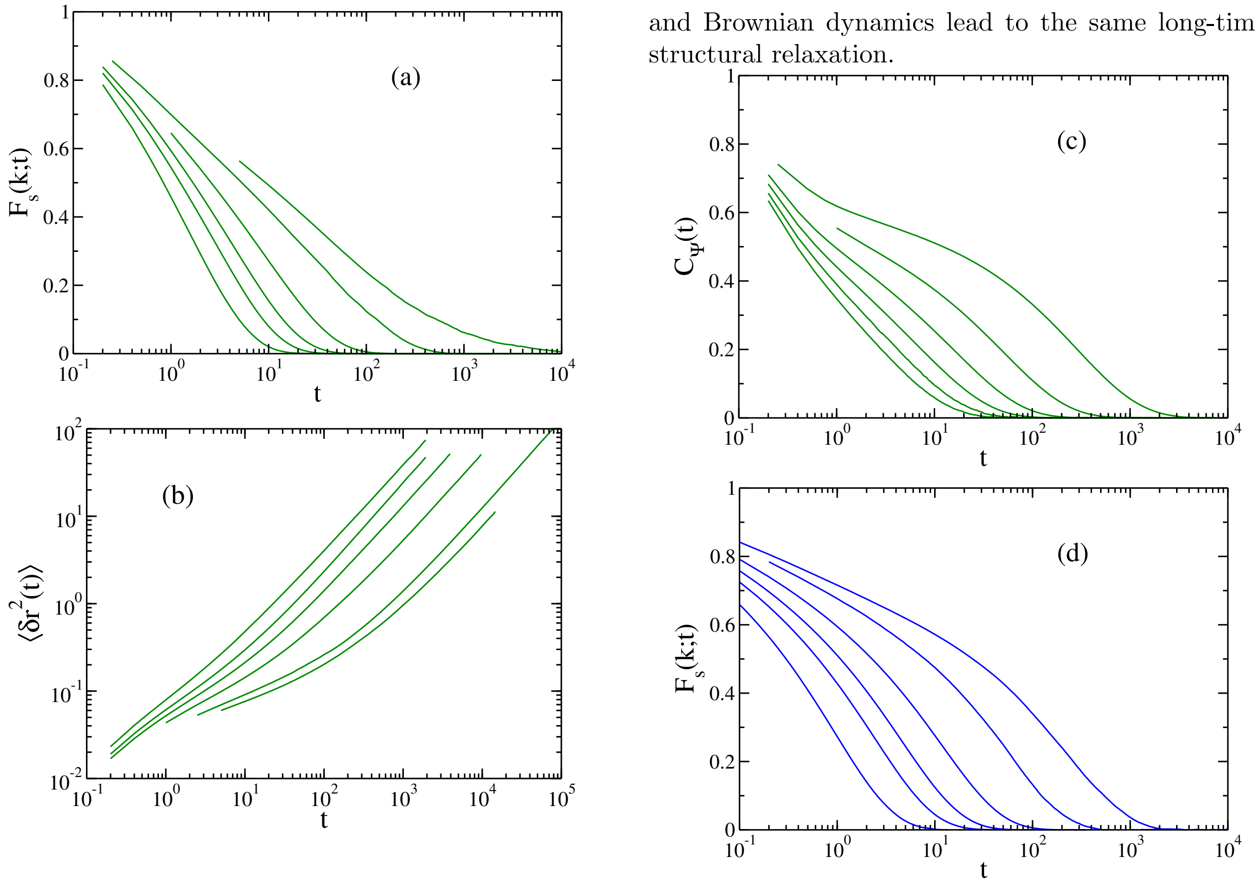

FIG. 1. (a-c) Relaxation in a two-dimensional glassy fluid with Newtonian dynamics at $T = 1.0, 0.8, 0.7, 0.6, 0.5$ and 0.45, from left to right. In (a) we show the self-intermediate scattering function $F_s(q;t) = \left\langle e^{-i\mathbf{q}\cdot\mathbf{r}_j(t)} e^{i\mathbf{q}\cdot\mathbf{r}_j(0)} \right\rangle$. In (b) we show the mean-square displacement $\left\langle \delta r^2(t) \right\rangle = \left\langle (\mathbf{r}_j(t) - \mathbf{r}_j(0))^2 \right\rangle$. In (c) we show the bond orientation correlation function $C_\Psi(t) = \left\langle \Psi_6^j(t) \left[\Psi_6^j(0)\right]^* \right\rangle / \left\langle \left|\Psi_6^j(0)\right|^2 \right\rangle$. (d) Self-intermediate scattering function $F_s(q;t)$ for a two-dimensional glassy fluid with Brownian dynamics at $T = 1.0, 0.8, 0.7, 0.6, 0.5$ and 0.45, from left to right. Note that all panels show the exact same temperature sequence.

We gratefully acknowledge the support of NSF grant CHE 1213401. This research utilized the CSU ISTeC Cray HPC System supported by NSF Grant CNS 0923386.

– space for notes –

Role of Pair and Many Body Correlations in Determining the Entropy and Dynamics in Glass Formers

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We present a study of two model liquids, Lennard Jones (LJ) and its repulsive counter part (WCA), exhibiting similar structure but significantly different dynamics at low temperatures [1]. The observation raises questions about the role of structure and thermodynamics in determining the dynamics. The well known Adam-Gibbs (AG) relation, $\tau(T) = \tau_o \exp\left(\frac{A}{TS_c}\right)$, expresses relaxation times τ in terms of a thermodynamic quantity, the configurational entropy S_c. By evaluating S_c, we show that the AG relationship quantitatively captures the differences in the dynamics between the LJ and WCA systems thus predicting that the differences in the dynamics of these systems can be understood in terms of their thermodynamic differences [2]. In order to analyze the independent role of pair and many body correlations we re-express the AG relation as follows: $\tau(T) = \tau_2^{AG}(T) * \exp\left(-\frac{A*\Delta S}{TS_{c2}S_c}\right)$ where $\tau_2^{AG}(T) = \tau_o \exp\left(\frac{A}{TS_{c2}}\right)$. Although the τ_2^{AG}s diverge at higher temperatures reminiscent of the well known mode coupling theory (MCT) behaviour, they capture the corresponding differences in $\tau(T)$ of the two systems [2]. Thus similar structures of the two systems predict different pair configurational entropy (S_{c2}) values, indicating a strong sensitivity of the later to changes in the former[2]. However, as expected the pair entropy is not enough to explain the correct dynamics and the residual multiparticle entropy (ΔS) arising from many body correlation is essential. But an interesting observation is that the ΔS, speeds up the dynamics at low temperatures (note in Fig.1, $\tau < \tau_2^{AG}$), which is at odds with the notion that stronger multiparticle correlations are responsible for the stronger temperature dependence of the relaxation times [2].

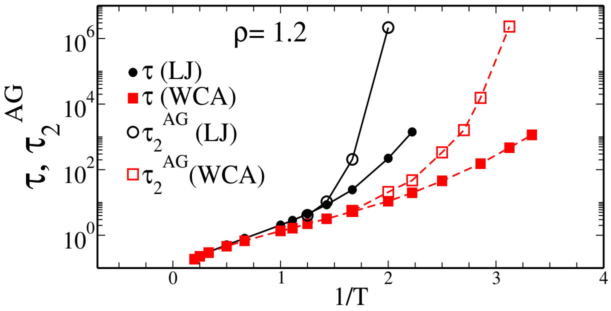

FIG. 1. τ, τ_2^{AG} vs. $1/T$ for LJ and WCA systems.

We further show that the AG theory which is based on activation dynamics can completely describe the MCT power law behavior in the region where the latter is found to be valid (Fig. 2) [3]. Since the configurational entropy has a finite value at the MCT transition temperature, T_c, the AG relation is not expected to predict any avoided transition in this regime. Our study reveals that although S_c is finite, S_{c2} vanishes at T_{K2} and in the MCT regime provides a dominant contribution to the total configuratonal entropy. We further find that $T_{K2} \simeq T_c$ (see Table I), thus concluding that the avoided transition at T_c observed in the AG relation is due to the vanishing of S_{c2} [3]. We also show that although both AG coefficient (A) and pair thermodynamic fragility (K_{T2}) are dependent on density and temperature, but their ratio is density-temperature independent and is related to MCT critical exponent (γ) [3].

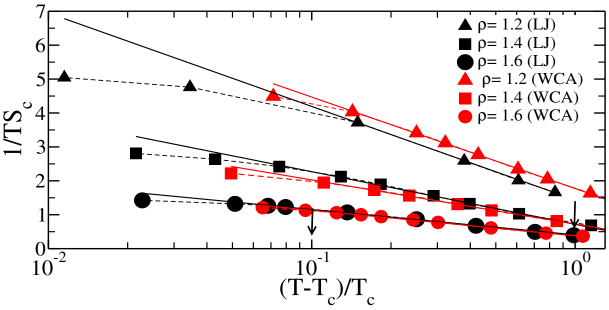

FIG. 2. $\frac{1}{TS_c}$ is linear when plotted against $\ln(\frac{T}{T_c}-1)$ in the region $10^{-1} \leq (\frac{T}{T_c}-1) \leq 10^0$.

TABLE I. *T_c and T_{K2} values are tabulated below.*

	$\rho=1.2$		$\rho=1.4$		$\rho=1.6$	
	T_c	T_{K2}	T_c	T_{K2}	T_c	T_{K2}
LJ	0.435	0.445	0.93	0.929	1.76	1.757
WCA	0.28	0.268	0.81	0.788	1.69	1.696

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– space for notes –

Origin of the quasiuniversality of simple liquids

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Quasiuniversality refers to the empirical fact that many simple liquids in simulations and experiments have surprisingly similar structure and dynamics [1–5]. A number of empirical freezing melting rules like the Lindemann criterion [6] likewise points to quasiuniversality. Examples of quasiuniversal systems are Lennard-Jones type system for different exponents, inverse-power-law systems with exponents ranging from infinity to unity (the latter is the one-component plasma), the Yukawa system, etc. Not all single-component pair-potential model liquids are quasiuniversal, however; counterexamples include the Lennard-Jones Gaussian, the Gaussian-core, and the Jagla models.

The usual explanation of quasiuniversality is based on the hard-sphere (HS) reference system. It is difficult to intuitively understand, however, why this idealized and unphysical model has the same physics as, for instance, the low-temperature one-component plasma. Moreover, the HS argument for quasiuniversality cannot explain all the above-mentioned exceptions to quasiuniversality. Finally, it would be nice to have an analytical reference potential instead of the discontinuous HS potential.

This paper [7] argues that the simple exponentially repulsive potential $v_{\rm EXP}(r) \equiv \varepsilon\exp(-r/\sigma)$ is the "mother of all pair potentials." The argument is based on the fact that this "EXP" system has strong virial potential-energy correlations in the low-temperature part of its phase diagram, compare the figure. This implies [8] that functions $h_{\rm EXP}(\rho)$, $g_{\rm EXP}(\rho)$, and $\tilde{\Phi}_{\rm EXP}(\tilde{\mathbf{R}})$ exists such that the potential-energy function obey the approximate identity

$$U_{\rm EXP}(\mathbf{R}) \cong h_{\rm EXP}(\rho)\tilde{\Phi}_{\rm EXP}(\tilde{\mathbf{R}}) + g_{\rm EXP}(\rho)\,. \qquad (1)$$

The presentation shows how Eq. (1) implies quasiuniversality for all pair potentials that can be approximated as follows (in which the tildes refer to so-called reduced units)

$$\tilde{v}(\tilde{r}) \cong \sum_j \Lambda_j e^{-u_j\tilde{r}}\ ,\ |\Lambda_j| \gg 1\,. \qquad (2)$$

We show that this provides a straightforward explanation of the above-mentioned quasiuniversality of some systems – as well as of the violation of quasiuniversality for other systems. Basically, all pair potentials of the above form have approximately the same potential-energy surface.

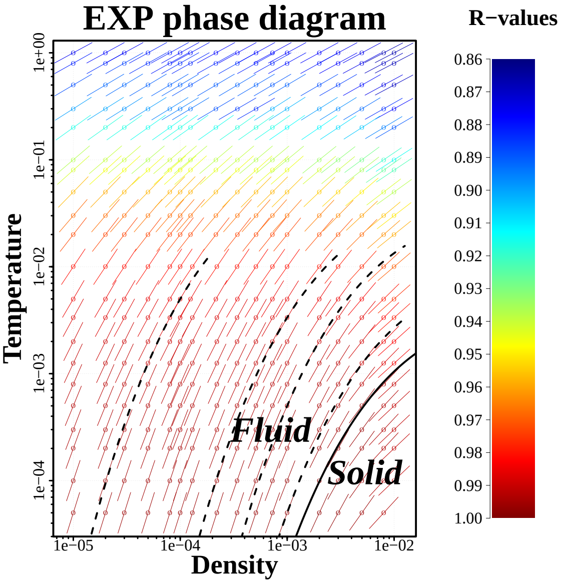

FIG. 1. Density-temperature thermodynamic phase diagram of the EXP pair-potential system. The colors indicate the value of the virial potential-energy correlation coefficient R. The slope of each line segment is that of the isomorph through the state point in question (the curve along which structure and dynamics are almost invariant in reduced units). The full curve marks the melting isomorph.

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– space for notes –

Multiple singularities and iso-dynamics in a simple glass former

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Almost fifteen years ago the mode coupling theory (MCT) allowed to predict the existence of a rich dynamical behaviour in colloidal systems with short-range attraction [1]. For specific values of the attraction range the theory described the presence of multiple liquid-glass transitions and of a glass-glass line with one endpoint that could influence the dynamics of the system in the fluid phase. Such theoretical curiosity is nowadays a useful and well-established concept fully confirmed by numerical simulations[2] and extensive experimental measurements [3].Only recently, systems with two repulsive length scales in the interaction potential have been indicated as good candidates for displaying a similar dynamical behaviour [4]. In particular we have focused on the theoretical predictions of the Square-Shoulder (SS) system i.e. a model of core-softened particles having a purely repulsive potential consisting of a hard-core part complemented by a step-like shoulder. Differently from all previously investigated models, MCT predicts for the SS system a disconnected glass-glass line, completely buried within the glass region and terminating with two endpoints (see Fig. 1 (a)). The two endpoints can be considered as "critical points" beyond which the transition between the two glasses becomes continuous and are named A_3 singularities. Upon increasing the shoulder width Δ the glass-glass line progressively moves towards the fluid-glass one and the two lines eventually merge (Fig. 1(b),(c)). While this happens, each A_3 point moves in the three-dimensional control parameter space (temperature T, packing fraction ϕ, shoulder width Δ), until it coalesces with the fluid glass-line giving rise to a higher-order (A_4) singularity. Such singularity is the only endpoint accessible from the fluid phase, i.e. in equilibrium conditions. According to MCT, the SS model is characterised by two distinct A_4 points (Fig.1 (b),(c)). Interestingly, such type of glassy critical points have been recently predicted to occur in generic glass forming liquids after randomly pinning a fraction of particles in the system[5]. The presence of A_4 points can be detected in the nearby fluid region since they lead to a logarithmic relaxation of the density correlators and to a subdiffusive behaviour of the mean-squared displacement, as found by MCT. By means of extensive numerical simulations we verify, for the first time, the existence of both A_4 singularities for a $50 : 50$ non-crystallising binary mixture of SS particles, providing one of the most stringent test of previously formulated MCT predictions [6]. In addition we report the observation of a new, unexpected behaviour. We find the presence of special loci of points in the fluid phase along which the self and collective dynamics is identical at all time- and length-scales. We call such loci iso-dynamics lines and attribute their existence to the competition between two higher-order singularities. Our study provides a model system (i)with competing singularities that give rise to a novel phenomenology (iso-dynamics) not described by MCT, (ii) that can be used to to test recent predictions based on the inhomogeneous MCT formalism on the dynamics close to A_3 and A_4 singularities [7] and (iii) that can stimulate experimental search for anomalous dynamics and multiple glass transitions in repulsive systems with two competing length scales.

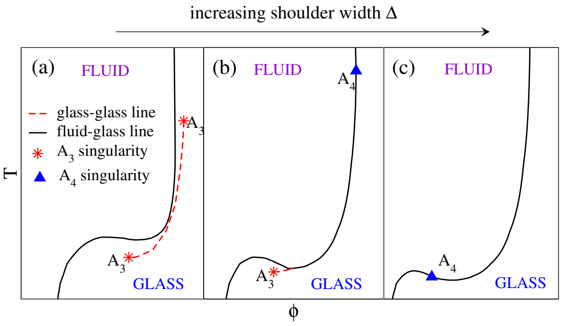

FIG. 1. Schematic evolution of the MCT dynamic state diagram of the SS system for increasing values of the shoulder width Δ. (a) For small Δ, beside the fluid-glass line (solid line), a disconnected glass-glass line is predicted (dashed line), ending in two A_3 singularities (stars). (b) On increasing Δ, the glass-glass line merges with the fluid-glass line and an A_4 singularity appears when one of the two A_3 points meets the fluid-glass line (filled triangle). (c) At even larger Δ also the second A_3 point eventually intersects the fluid-glass line generating a distinct A_4 singularity (filled triangle).

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– space for notes –

Jamming Percolation in Three Dimensions

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Kinetically-constrained models [1] provide a promising framework for describing the cooperatively slow relaxation dynamics in diverse systems such as glass-forming liquids, colloidal suspensions and granular materials. Due to their mapping to bootstrap percolation, most kinetically-constrained models become jammed, or nonergodic only either at the limit of zero temperature (Ising spins) / full occupation (lattice gas) [2, 3], or when considering finite-sized, confined systems [4]. An interesting exception is the spiral model [5], which by mapping to directed percolation was proven to undergo an ergodicity-breaking transition at a finite density (or temperature). Having such a simple, single-species lattice model at hand is very useful, and there is recent interest in such jamming percolation models [6–8].

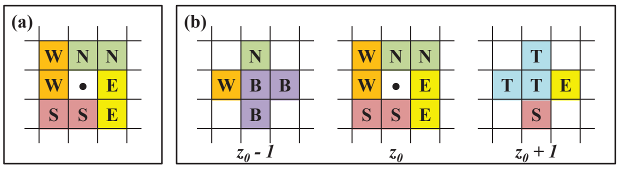

FIG. 1. (a) The 2D spiral model is defined on the square lattice such that site (•) is unblocked if its ((W *or* E) *and* (S *or* N)) sets are completely empty. (b) Our 3D model is defined on the cubic lattice by requiring that the sets ((W *or* E) *and* (S *or* N) *and* (B *or* T)) are completely empty. Here slices from three consecutive layers are shown side by side.

We introduce [9] a three-dimensional kinetically-constrained model (see Fig. 1), for which we prove that the fraction of frozen particles is discontinuous at the directed-percolation critical density. In agreement with the accepted scenario for jamming- and glass-transitions, this transition has mixed nature; the discontinuity is accompanied by diverging length- and time-scales. Our static results in three dimensions (Fig. 2,b,d) are qualitatively similar to those previously obtained for the two-dimensional spiral model (Fig. 2,a,c). However, we identify that because one-dimensional directed-percolation paths comprise the backbone of frozen particles, the unfrozen rattlers may use the third dimension to travel between their cages. Thus in three dimensions the dynamics are diffusive on long-times even above the critical density for jamming (Fig. 2f), in contrast with the two-dimensional spiral model, in which the diffusion ceases with the appearance of frozen particles (Fig. 2e).

Diffusion vanishes in three dimensions only at some higher density at which the one-dimensional strings of blocked particles become thick enough to close the windows in the mesh that they form. Culling, or pruning enables us to identify the backbone of particles that will never move, and we analyze their structure in order to determine the diffusivity without running the entire dynamics.

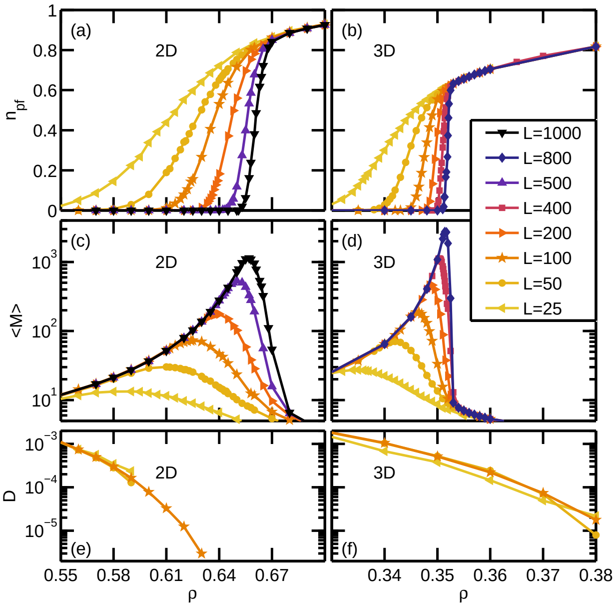

FIG. 2. For the simulated system sizes (see legend), the fraction of permanently frozen particles (a,b) rises and the mean culling time (c,d) peaks around $\rho_c^{2D}(L) = 0.65$ in the 2D spiral model and $\rho_c^{3D}(L) = 0.35$ in our 3D model. The diffusion coefficient (e,f) vanishes there in 2D, yet in 3D it stays finite above $\rho_c(L)$.

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Nonequilibrium equation of state in suspensions of active colloids

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Active colloids constitute a novel class of materials composed of colloidal-scale particles locally converting chemical energy into motility, mimicking micro-organisms [1, 2]. Evolving far from equilibrium, these systems display structural organizations and dynamical properties distinct from thermalized colloidal assemblies. Experimentally, active colloidal systems have been mostly characterized so far through detailed single particle studies in the dilute gas limit, where particles only interact with the solvent. In this regime, a mapping from nonequilibrium active systems to equilibrium passive ones was established in the presence of a gravitational field, where activity renormalizes the value of the effective temperature [3, 4]. Much less is understood at finite densities when particle interactions and many-body effects cannot be neglected. Several new phases of active matter have been observed experimentally in synthetic self-propelled colloids [5–7], from active cluster phases at relatively low density to gel-like solids and phase separated systems at larger density, suggesting that active colloids tend to aggregate when self-propulsion is increased.

Here, we experimentally characterize the phase behaviour and equation of state of a system of active colloids and of a model of self-propelled hard disks, extending previous work on active colloids performed in the dilute regime [3] and at low density [5], to a much broader range of densities. We use sedimentation experiments to probe the nonequilibrium equation of state of a bidimensional assembly of active Janus microspheres. We compare those results to computer simulations of sedimentation of a model of self-propelled hard disks [8, 9].

In Fig. 1, we show the sedimentation images for the experimental system, for different activity levels. The passive case reveals equilibrium configurations from a dilute fluid to a dense homogeneous amorphous phase, while active systems exhibit much richer structures. The dilute gas spreads over larger altitudes, finite size clusters are observed at moderate densities, gel-like configurations are found at larger densities, and dense phases exist at the bottom of the cell.

More quantitatively we show that self-propulsion profoundly affects the equation of state, but these changes can be rationalized using equilibrium concepts [10]. We show that active colloids behave, in the dilute limit, as an ideal gas with an activity-dependent effective temperature. At finite density, increasing the activity is similar to increasing adhesion between equilibrium particles. We quantify this effective adhesion and obtain a unique scaling law relating activity and effective adhesion in both experiments and simulations. Our results provide a new and efficient way to understand the emergence of novel phases of matter in active colloidal suspensions.

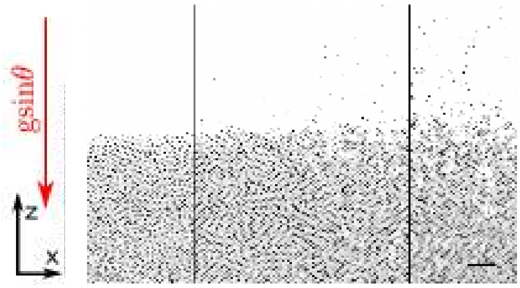

FIG. 1. Imaging sedimentation profiles. Snapshots of phoretic gold-platinum Janus colloids under gravity for activity increasing from left to right. The scale bar is 20 μm,

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What is the Pressure of an Active Particle Fluid?

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For fluids in thermal equilibrium, the concept of pressure, P, is familiar as the force per unit area exerted by the fluid on its containing vessel. This primary, mechanical definition of pressure *seems* to require knowledge of the interactions between the fluid's constituent particles and its confining walls. But we learn from statistical mechanics that P can also be expressed thermodynamically, as the derivative of a free energy with respect to volume, and therefore obeys an equation of state involving only bulk properties of the fluid. Hydrodynamics provides a third definition of P, as the trace of the bulk thermodynamic stress tensor, whose microscopic definition in terms of momentum fluxes is again well known. In thermal equilibrium, all these definitions of pressure coincide.

Purely thermodynamic concepts, like temperature, are well known to be ill-defined in systems far from equilibrium [2]. However, one could hope that mechanical properties, like pressure, are less problematic. Here we investigate this question for active fluids (assemblies of self-propelled particles (SPPs)), in which energy dissipation at the microscopic level drives the motion of each particle to give strong non-equilibrium effects [3].

We define the mechanical pressure P of an active fluid as the mean force per area exerted by its constituent particles on a confining wall. This was studied numerically for a number of active systems, showing some surprising effects for finite-size, strongly confined fluids [5–7]. Alternatively, when describing the dynamics of such active fluids at larger scales, some authors have introduced a bulk stress tensor and defined pressure as its trace [3, 5], leading to recent experimental measurements [4]. But since we are far from equilibrium, the usual equivalence between these different definitions should generically not be relied upon.

In this presentation [1], we will show that the pressure P exerted on a wall by active fluids *can depend* on the microscopic interactions between the fluid and the wall. In other words, there is in general no equation of state relating the mechanical pressure to bulk properties of the fluid (see fig. 1), so that all connections to thermodynamics and to bulk stress tensor are lost. To appreciate the remarkable consequences of this result, consider the quasi-static compression of an active fluid by a piston. Since the mechanical pressure depends on the piston, compressing with a very soft wall—into which particles bump gently—or with a very hard one require different forces and hence different amounts of work to reach the same final density.

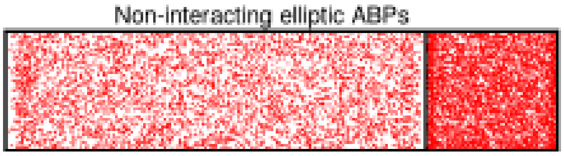

FIG. 1. Active Browninan elliptic particles (SPPs reorienting via rotational diffusion) in a cavity divided by an asymmetric mobile wall (stiffer on the right side). Due to the lack of equation of state, steady-state is attained with different densities in the two halves.

We shall however explore some limiting models for interacting and non-interacting SPPs in which an equation of state is recovered. Even in such cases, thermodynamic intuition can fail. First, pressure can be anisotropic. Second, we show that both interacting and non-interacting active particles admit flux-free steady-states where the pressure is not homogeneous.

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– space for notes –

Self-propelled particles: self-assembly and active depletion

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In our work, we simulate a dilute suspension of attractive self-propelling spherical particles and address the problem of the formation of living clusters and crystals of active particles [1]. We observe the formation of fluid-like "living" clusters and explain this general feature in terms of the balance between active forces and regression to thermodynamic equilibrium [1, 2]. We also discuss how active motion affects the kinetics of crystal formation.

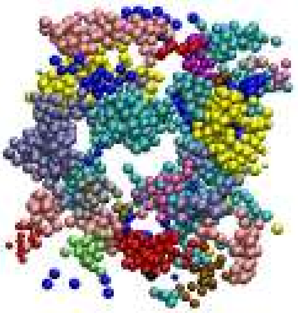

FIG. 1. Typical snapshot of living clusters from Ref.[1].

Next, we study how a solution of small active disks, acting as depletants, induces effective interactions on large passive colloids. Specifically, we analyze how the range, strength, and sign of these interactions are crucially dependent on the shape of the colloids.

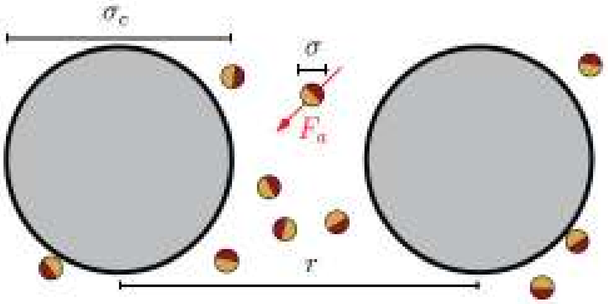

FIG. 2. Schematic representation of two colloidal disks in a bath of active particles.. The persistent force Fa acts along a defined axis (as shown by the arrow as well as the colors, where red corresponds to the back of the particle and yellow the front). From Ref. [3].

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– space for notes –

Generalized Energy Equipartition and Multiple Effective Temperatures in Harmonic Oscillators Driven by Active Baths

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A remarkable result of equilibrium statistical mechanics is the theorem of energy equipartition. In its simplest form, the theorem states that each quadratic term in the Hamiltonian contributes with the same amount of energy $k_B T/2$ to the average energy of the system [1]. In the case of a harmonic oscillator this applies to both kinetic and potential energies. For colloidal particles, whose motion is significantly overdamped, the value of kinetic energy imposed by the equipartition theorem is reflected by the Einstein relation: $D_T = \mu k_B T$ (μ being the mobility of the particles). Therefore, for a colloidal harmonic oscillator, the equipartition theorem establishes a link between the thermal diffusion constant D_T and the average potential energy $U = D_T/2\mu$, independently on the elastic constant k of the oscillator.

However this theorem is not supposed to hold in out of equilibrium system such as those found in the study of *active matter*. In these systems the Einstein relation has been used to *define* the effective temperature by knowing the diffusivity ($T_{\text{eff}} = D/\mu$). In some limiting cases this T_{eff} can be used to predict the statics of the systems in presence of external fields [2–4]. In this talk I will show that this simple scenario breaks down even in the simple case of an harmonic oscillator. I will focus on the off-equilibrium dynamics of one single colloidal particle immersed in a bath of dense swimming *E. coli* bacteria and subject to an external harmonic potential [5]. The elastic force field is obtained experimentally by placing the micro-spheres in a cylindrical microcapillary. Sedimenting colloids fluctuate near the bottom of the capillary where they experience a near-perfect harmonic potential (Fig. 1). The same system is also studied numerically by means of extensive computer simulations. I will demonstrate that, for this active harmonic oscillator, the dynamics is well described by a set of stochastic differential equations whit two noise sources: the standard Langevin thermal (white) noise and an "active" time-correlated noise originated by the collisions with swimming bacteria.

In this model the average value of potential energy is still linked to the diffusivity by a simple generalization of the equipartition theorem:

$$U = \frac{D_T}{2\mu} + \frac{D_A}{2\mu}\frac{1}{1+\mu k \tau} \tag{1}$$

where D_A and τ are, respectively, the amplitude and the characteristic relaxation time of the colored noise acting on the colloids (in absence of the external field).

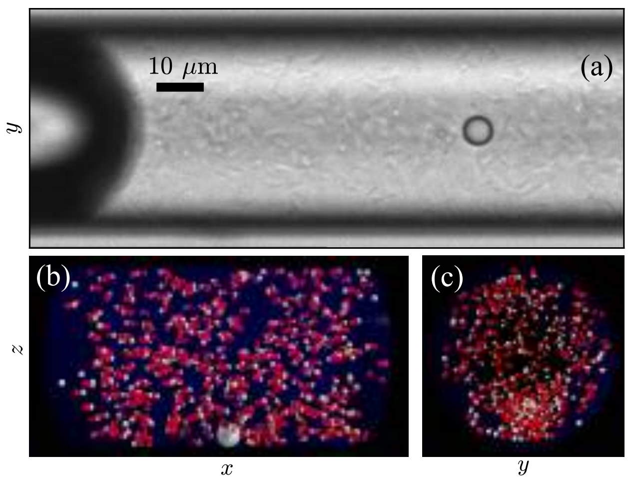

FIG. 1. (**a**) A 3.5 μm radius silica bead is suspended in a bath of motile *E. coli* bacteria filling a 25 μm radius capillary glass tube. (**b**),(**c**) Snapshots from the numerical simulation.

As a consequence the effective temperature, that can be associated with the potential energy, depends directly on the elastic constant k and is always *lower* than the one obtained from the free diffusivity via the Einstein relation.

Finally I will discuss how Eq. (1) is generally valid for all the active-matter systems characterized by an exponentially time-correlated noise such as Janus self-propelled particles and the "run and tumble" swimming microorganisms [6].

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Information-theoretic measurements of coupling between structure and dynamics in glass-formers

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On approaching their glass transitions, supercooled liquids exhibit strong dynamical heterogeneity. That is, in a given trajectory, some particles are much more mobile than others, and these particles are clustered in space. Many theories of the glass transition aim, in one way or another, to connect the clusters of mobile (or immobile) particles to local structural features of the liquid.

Analyzing these connections quantitatively is a challenging task. The *dynamical propensity* of Harrowell and co-workers [1] allows the structural component of the dynamical heterogeneity to be measured accurately, in computer simulation. Here we introduce a method that uses the propensity to compare the predictive power for dynamics of different structural observables.

The method is based on *information theory* [2]: it yields a numerical estimate of "the average amount of information about a particle propensity μ_{it} that is provided by a measurement of some structural measurement s_i". This quantity is measured in *bits*, where one bit is the universal unit of information. This allows direct comparison of the predictivity of different observables s_i. We consider two glass-forming liquids and several choices for s_i, including properties of normal modes, locally-preferred structures, and local energy and density. Fig. 1 illustrates this idea by showing the predictive power of a normal mode analysis in a glass-forming mixture, as a function of the dynamical time scale considered.

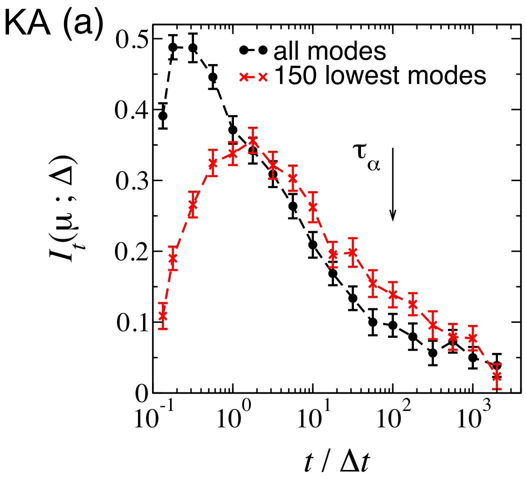

FIG. 1. Mutual information between particles' propensity and their local participation in normal modes, in a glass-forming mixture of Lennard-Jones particles.

Our results reveal a subtle picture, in which different structural observables allow accurate predictions on very different time scales, with normal modes being most predictive on short time scales, and local energy (or density) giving strong predictions at longer times. We discuss the consequences of these results for theories of the glass transition, as well as the methods used to estimate the mutual information, and the possibility of using similar ideas to analyse the quality of predictions in other situations.

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The origin of glass forming ability in a system with competing orderings

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Glasses are formed when the transition to the stable equilibrium phase is avoided and the relaxation time of the disordered state drastically increases. Glass formation is often associated to *frustration* effects, which can have different origins [1, 2]. For example, it has long been known that systems in which the stable structure is competing with different local orderings are more easily vitrified, but this connection is understood only in terms of empirical rules which lack a microscopic explanation. In order to gain precise insights on the origin of glass forming ability, we run computer simulations of a model system with tetrahedral interactions (modified Stillinger-Weber potential) in which a tendency to form locally open structures competes with that to form compact (bcc-like) structures. The advantage of this model is that by tuning the strength of the tetrahedral interactions (described by a scalar parameter λ), one can continuously control the glass forming ability. At intermediate values of λ, this system is known to display glassy behaviour, where both the melting temperature is suppressed and where the dynamics of the liquid becomes less fragile. [3]. With a broad spectrum of simulation techniques, we exploit the simplicity of the model to fully unveil the thermodynamic and dynamic properties of the system as it transforms to a glass-former [4].

We first focus on the suppression of the nucleation process, and isolate all independent contributions to the glass forming ability. Contrary to expectations, we show that the glass forming ability originates only from a steep increase of the surface tension in the glass forming region, and that it is not due to a slowing down of mass transport or thermodynamic driving force to crystallization. We further demonstrate that the thermodynamic origin of the increased surface tension is linked to an increase of the configurational entropy of the supercooled liquid state in the glass-forming region, and that the barrier to nucleation can be almost entirely ascribed to the loss of this configurational entropy. The surface tension is a measure of the free energy penalty of forming a liquid/solid interface, and from a microscopic point of view is linked to a progressive loss of medium-range crystalline order in the supercooled liquid. Locally ordered regions act as precursors to crystallization and, by wetting small crystalline nuclei, effectively decrease the surface tension [5]. The decrease of crystal precursors is shown in Fig. 1, where the glass forming region, located at intermediate values of λ, coincides with a region of minimum of medium-range order in the fluid.

Our study provides a consistent thermodynamic description of the glass forming ability for a broad class of glass-formers, i.e. the so-called tetrahedral liquids such as Si, Ge, C, water, and SiO_2, all of which are extremely important in nature and materials science. Given the simplicity of the scenario, we believe that our study will offer insights for understanding the glass forming ability of systems where glassy behaviour stems from a competition between competing orderings and a disorder effect, as for example metallic glasses in the proximity of an eutectic point [6].

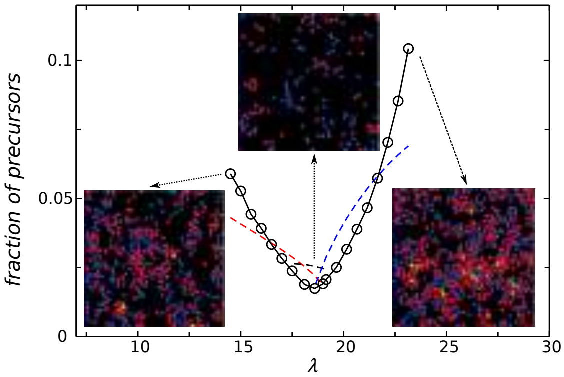

FIG. 1. Fraction of medium-range crystalline ordered regions (symbols) as a function of the λ, the parameter that controls the global ordering of the system. Dashed lines are the superimposed phase diagram of the system, showing that the eutectic region corresponds to a minimum in the number of precursors. Insets are snapshots of typical configurations in which only precursors particles are displayed.

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Numerical detection of the Gardner transition in simple structural glass formers

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A supercooled liquid becomes sluggish upon cooling, and forms a glass below the glass transition temperature. If a glass is further quenched to the zero temperature, its molecules become jammed such that each one is in close contact with its neighbours and mechanically stable. Interestingly, recent theoretical advances [1, 2] predict that there should exist a novel transition, called *Gardner transition*, between the glass and the jamming transitions. At the Gardner transition, a glass state splits into many marginal and fractal sub-states. The main objective of this study is to show supportive numerical evidence for the existence of this phase transition in simple glass formers.

We consider systems with (i) An equimolar binary mixture of hard spheres (HS) in dimension $d = 3$, with diameter ratio $6 : 5$ and mass ratio $1 : 1$, (ii) monodisperse HS in $d = 4$, and (iii) mono-disperse Mari-Kurchan (MK) particles [3] in $d = 3$. The MK particles are HS that interact with an additional quenched random shift pairwisely, and by construction mean-field. In particular, the MK and the HS models become equivalent in the large dimensional limit $d \to \infty$.

To study the Gardner transition, we compress an initial equilibrium state at volume fraction φ_0 (above the dynamic glass transition $\varphi_{\rm d}$) to a desired density $\varphi > \varphi_0$, using the modified Lubachevsky-Stillinger algorithm [4]. During this process, the system falls out of equilibrium but remains in the same metastable free energy basin. A *restricted* thermodynamic equilibrium is reached within the basin, when the compression is sufficiently slow. Our simulation protocol thus corresponds to the adiabatic *state following* construction considered in earlier theoretical calculations [2].

Deep in the glass phase, we observe that a followed state undergoes a Gardner transition at $\varphi_{\rm G}$, with typical critical behaviors as in a continuous phase transition. We focus on the behaviors of the caging order parameter Δ, which is the long time limit of the mean squared displacement (MSD), $\Delta(t) = \frac{1}{N}\sum_{i=1}^{N}\langle|\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2\rangle$, and the mean squared distance Δ_{AB} between two followed states in the same metastable basin. We show that the exact location of the Gardner transition can be determined consistently from three independent approaches (Fig. 1):

(i) Dynamically, $\Delta(t)$ grows slower and slower approaching to $\varphi_{\rm G}$, which is associated to a diverging time scale $\tau \sim |\varphi - \varphi_{\rm G}|^{-\gamma_\tau}$.

(ii) Statically, the susceptibility $\chi = N\frac{\langle\Delta^2\rangle - \langle\Delta\rangle^2}{\langle\Delta\rangle^2}$ also diverges at $\varphi_{\rm G}$, $\chi \sim |\varphi - \varphi_{\rm G}|^{-\gamma}$.

(iii) The probability distribution $P(\Delta_{AB})$ develops an exponential tail at the transition, due to rare samples. This behaviour is characterized by a maximum of the skewness of $P(\Delta_{AB})$ at $\varphi_{\rm G}$.

In general, we find quantitatively (MK model) and qualitatively (HS model) good agreements between our simulation results and theoretical predictions.

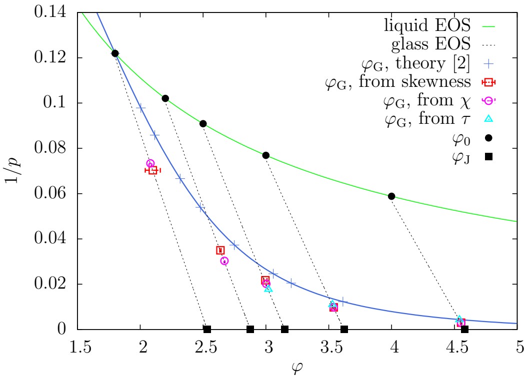

FIG. 1. Phase diagram of the MK model in $d = 3$. We plot the inverse reduced pressure $1/p$ as a function of ϕ. The equation of state (EOS) of the liquid is $p = 1 + 2^{d-1}$. The evolution of a glass state follows the glass EOS from φ_0 to the jamming density $\varphi_{\rm J}$. The Gardner transition density $\varphi_{\rm G}$ determined from our numerical simulations are compared to theoretical predictions [2] of the infinite dimensional HS/MK models (properly rescaled to $d = 3$).

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– space for notes –

Cavity point-to-set correlations: recent advances

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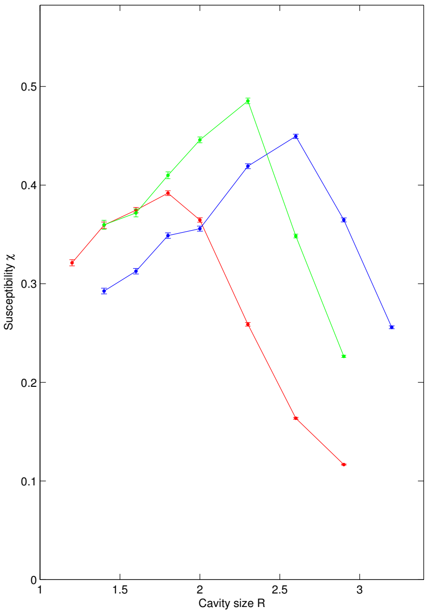

FIG. 1. PTS susceptibility $\chi(R)$ as a function of cavity size R, for temperatures $T = 0.80$ (red), 0.60 (green), and 0.51 (blue) (in standard Lennard-Jones units).

A relatively modest cooling of glass-forming liquids results in a dramatic dynamical slowdown, as is captured by their shear viscosity and structural relaxation time growing by orders of magnitude. This slowdown is thought to be controlled by cavity point-to-set (PTS) correlations, whose correlation length diverges together with the relaxation time. Yet efficiently measuring and interpreting PTS correlations remains an open computational challenge.

To measure these important correlations, we have developed a numerical approach based on parallel-tempering. In this scheme, the cavity is coupled to replica cavities immersed in high-temperature and otherwise less frustrated environments, in order to overcome barriers in the free-energy landscape. For small cavities, relaxation can be efficiently achieved with a relatively small number of replicas. This scheme is thus especially effective for small cavities, for which conventional methods for measuring PTS correlations run into sampling difficulties. The consistency and convergence of numerical results is further validated by relaxing the cavity configuration starting with two different configurations – one with the original equilibrium configuration, and another with a randomized configuration.

A model-free way to extract the PTS length can then be obtained from the radial-dependence of the PTS susceptibility of the core overlap Q,

$$\chi(R) \sim \left[\langle\langle Q^2\rangle\rangle\right] - \left[\langle\langle Q\rangle\rangle\right]^2 , \qquad (1)$$

where $[\ldots]$ denotes averaging over the disorder created by pinning particles outside the cavity, and $\langle\langle\ldots\rangle\rangle$ thermal averaging for a given pinning disorder. Sample results for the Kob-Andersen binary Lennard-Jones model as a function of cavity radius R are provided in Fig. 1. The peak at $R^*(T)$ serves as proxy for the growing cavity PTS correlation length.

With these various computational and conceptual advances, we can reliably extract cavity PTS correlations in a regime well beyond that previously accessible. Various new physical insights are then accessible, including the role of bimodality and of replica-symmetry breaking in finite systems.

We acknowledge financial support from NSF No. DMR-1055586, the Alfred P. Sloan foundation, and the European Research Council under the European Union's Seventh Framework Programme (FP7/2007-2013)/ERC Grant Agreement No. 306845.

– space for notes –

Emergence of Cooperativity in Plasticity of Soft Glassy Materials

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Summary We present an experimental study of the strain fluctuations in a granular material submitted to a homogeneous stress. We observe a self-organisation of the plastic flow well before the failure of the material which corresponds to the formation of a permanent shear-band. At the beginning of the loading, the strain organizes in transient bands of mesoscopic size and a well-defined orientation which is different from the angle of the macroscopic shear band that appears at the failure. The orientation of the micro-bands may be interpreted as the directions of stress redistribution given by Eshelby tensors.

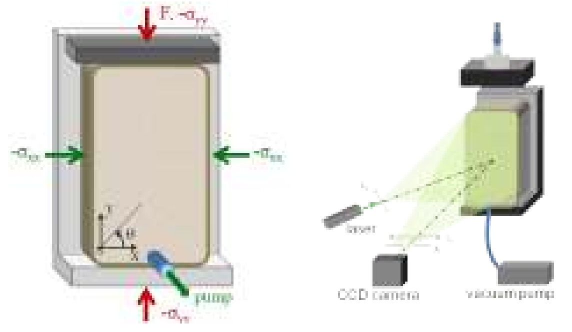

FIG. 1. Schematic view of the biaxial compression apparatus with the dynamic light scattering detection of small strain [1].

For this study we designed a biaxial compression apparatus with a strain detection based on dynamic light scattering [1]. The experimental setup is schematically shown on Figure 1. The granular samples, composed of glass beads of diameter 90 μm, is placed into a latex membrane in contact with a glass plate. A partial vacuum is applied to the sample and creates a confining stress. The sample is then slowly compressed and the stress versus axial strain characteristics are measured. The strain near the glass plate is measured with a dynamic light scattering setup. For this an expanded laser light illuminates the material and the scattered light is recorded with a camera. The correlation functions of the scattered intensity are calculated for small zones of the image, giving access to map of correlations. This method is very sensitive and gives access to values of strain in the range $10^{-6} - 10^{-4}$. Typical maps of correlations in Figure 2 (top row of pictures). We observe a heterogeneous strain pattern, with large fluctuations before failure. After the failure a permanent band appears that may be identified as a shear band.

The analysis of the strain fluctuations is performed with the computation of the spatial correlation function of the measured deformations. Such spatial correlations are shown in Figure 2 (bottom pictures). At the beginning of the loading, we find a spatial correlation function which is correlated along two given directions. Those directions are inclined along an angle θ_E (doted line) which is different from the angle θ_{MC} at which the failure occurs (solid line).

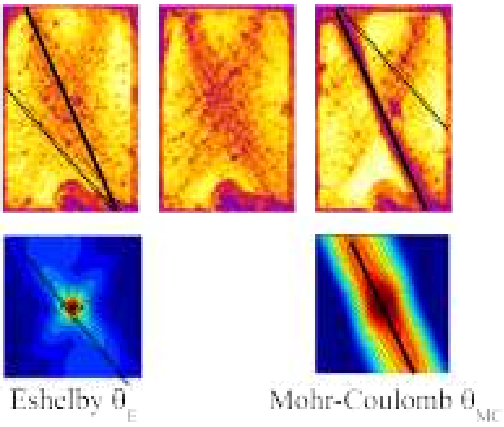

FIG. 2. Top: Maps of correlations observed at different loading. Bottom: Spatial correlations of the deformations showing two distinct orientations.

The occurrence of correlations in directions θ_E may be interpreted as the consequences of micro-reorganizations occurring into the granular material [2]. We expect that such reorganizations redistribute stress into the material along directions given by the Eshelby stress tensor. The presence of such events are confirmed by our numerical simulations [3, 4]. The stress redistribution triggers new events into the material, creating the fluctuating structures that we observe in the deformtaion maps. This observation and this description are in agreement with the observations of correlated structures of deformation that have been observed in numerical studies of other athermal amorphous systems [5].

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– space for notes –

Dynamic transition and memory encoding in glass-formers under shear

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Understanding the behavior of glasses under mechanical deformation is of primary importance in applied science and, at the same time, it still presents a major problem for basic science. As a matter of fact, while the deformation behavior of crystals is theoretically well understood, no universally accepted framework exists to rationalize mechanically driven amorphous systems. I will present some recent numerical work on the strain deformation of a model glass former under periodic shear deformations. I will show that after a transient, the glass enters a stationary state whose nature depends dramatically on the amplitude of the deformations. For large amplitudes, the system will be diffusive, but below a certain threshold it will enter a cyclic orbit in phase space and the system will be not diffusive [1]. Interestingly, since the nondiffusive state is also non-ergodic, it retains memory of its initial stage and this fact can be used to store and read information by a simple shear protocol [2]. Both the dynamic transition and the memory effects discussed here have a strong analogy to what have been observed in sheared dilute suspensions [3, 4]. This is a quite surprising result given the profound differences between the two systems. I will try to rationalize such universal behavior with the help of few toy models [5].

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– space for notes –

Relaxation in yield stress systems through elastically interacting activated events

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Relaxation of the microscopic structure in glasses, and more generally in soft yield stress materials, is a topic of long-standing interest and great complexity. Broad ranges of time, energy and length scales are involved, together with nonequilibrium aspects such as aging and a strong dependence on the sample preparation scheme. As a result, no unique scenario has emerged to describe the relaxation of density fluctuations in systems that, quenched from a liquid into a glassy (solid) state, still display internal dynamics strong enough to produce structural relaxation on a measurable time scale. The complexity of the relaxation is usually quantified by the manner in which it deviates from exponential. In many cases, stretching, corresponding to a broad distribution of relaxation times, is observed. However, the opposite situation of compressed relaxation (i.e., faster than exponential) has emerged in the last years as a new paradigm. In this work, we confirm through the numerical study of a simplified model that this behavior can result from thermally activated plastic events akin to the shear transformations observed in yield stress solids undergoing external deformation.

We propose a minimalistic two-dimensional model [1] at the mesoscale for thermally activated relaxation dynamics in yield stress materials. The mean-square displacement and the dynamical structure factor for tracer particle trajectories are taken into account. Moreover, we measure the distribution of particle displacements and the distribution of waiting times for consecutive plastic events at the same point.
To discriminate correlation effects, we compare our thermal model with an analogous *random* (mean-field like) model, where plastic activations have no local stress dependence, ergo do not depend on spatial interactions.

Our results can be classified in *elasticity effects*(**E**) and *correlation effects*(**C**), as follows:

E1 At each temperature we observe for $D(t)$: an initial ballistic regime independent of the model, of duration ruled by the typical event lifetime, and a long time diffusive behavior (Fig.1a)

E2 We fit $S(q,t)$ in the ballistic regime with a compressed exponential of shape parameter close to expected mean-field value in 2d $\gamma_{MF} = 2$ (Fig.1b), in the diffusive regime we obtain a pure exponential decay on q^2t, as expected (Fig.1d).

E3 Regarding the distribution of particle displacements (independent on the model) we confirm the expected mean-field scalings for low temperatures.

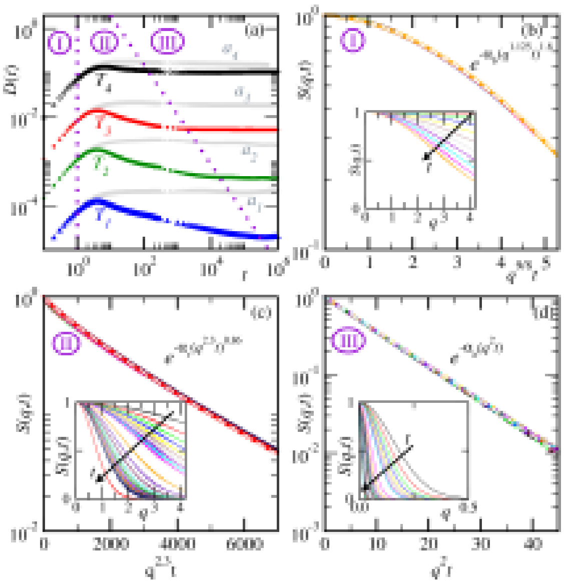

FIG. 1. *Tracer particle dynamics* – (a) Diffusion coefficient $D = \langle(\Delta r)^2\rangle/(4t)$ as a function of time t for different temperatures $T_i = 0.05, 0.07, 0.1, 0.2$. Three dynamical regions: (I) ballistic, (II) crossover, (III) diffusive. (b) Dynamical structure factor $S(q,t)$ for $T = 0.2$ for time intervals corresponding to the ballistic regime (I), fitted by an compressed exponential. (c) $S(q,t)$ for $T = 0.07$ for the crossover regime (II), fitted by a stretched exponential. (d) $S(q,t)$ for $T = 0.2$ for the diffusive regime (III), fitted by a pure exponential. Insets in (b,c,d) show raw data.

C1 In the thermal model, we observe for $D(t)$ an intermediate sub-diffusive regime with a duration ruled by T (Fig.1a). During this regime, the relaxation time scales as $\tau_r \sim q^{-n}$ with $n > 2$. Relaxation curves collapse onto a stretched exponential master curve $S(q,t) = exp[-a_s(q^nt)^\gamma]$ with $\gamma < 1$ (Fig.1c).

C2 The displacements distribution $P(u)$ is identical in both models, the change of the dynamics for the thermal model is rather due to negative correlations in the two-time auto-correlation function of the vectorial displacements *(not shown)*.

C3 The distribution of waiting times $\Psi(\tau_{ev})$ (trivially exponential in the random model) shows a power-law form with an exponential cutoff in the thermal model *(not shown)*.

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– space for notes –

Colloidal monolayers under steady shear at the liquid-liquid interface

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The macroscopic response of colloidal systems to shear and deformation is directly coupled to their microscopic structural evolution. Non-linear flow phenomena, including “shear thinning” or “shear thickening”, are paradigmatic examples of this fundamental interplay. Unfortunately, in most cases the use of macroscopic rheometers does not allow in-situ access to the system’s microstructure at the single-particle level. In this work we investigate the steady shear response of dense monolayers of charged colloids spread at a water/oil interface. In addition to 2D confinement, the presence of a liquid-liquid interface triggers the formation of crystalline regions with large lattice constants [1]. Following a novel active microrheological approach [2], a micro-fabricated magnetic disk is placed at the interface and rotated in a controlled fashion by external magnetic fields. Simultaneously, the structure of the sheared interface is imaged by optical microscopy and individual colloids are tracked.

Our observations emphasise the coupling between flow and structure in the sheared monolayer. We measured the velocity profiles of the sheared suspension at different area fractions, shear rates, particle sizes and binary mixture compositions. Upon rotation of the microdisk, three flow regimes are reported. At small shear rates, the monolayers flows via discreet hopping of the particles, i.e., the shear-induced motion is defect-mediated. At larger applied rates, the flow induces ordering of the colloidal suspension around the disk, in the form of concentric rings. In the presence of binary mixtures, alternate layers of smaller and bigger particles are found. This flow-structure coupling is reminiscent of layering transitions in bulk shear-thinning fluids [3]. Finally, increasing the shear rates even further, the bulk phases are also set significantly in motion and impose the flow field measured at the interface. We identify a regime where the microrheological tool is sensitive to interface properties.

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Times, Lengths and the Nature of the Glass Crossover

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Stochastic Beta Relaxation (SBR) is a rather intuitive dynamical model of the glass crossover that has been derived by a dynamical-field theoretic treatment of Mode-Coupling-theory (MCT) near its dynamical singularity [1]. We have performed a detailed numerical study of the solutions of SBR obtaining a comprehensive characterization of the glass crossover [2].

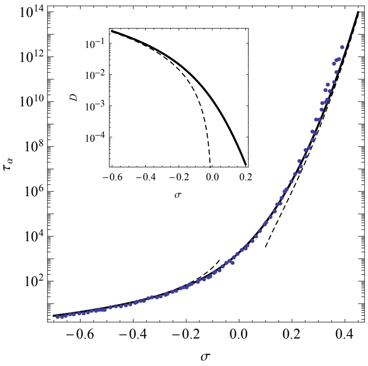
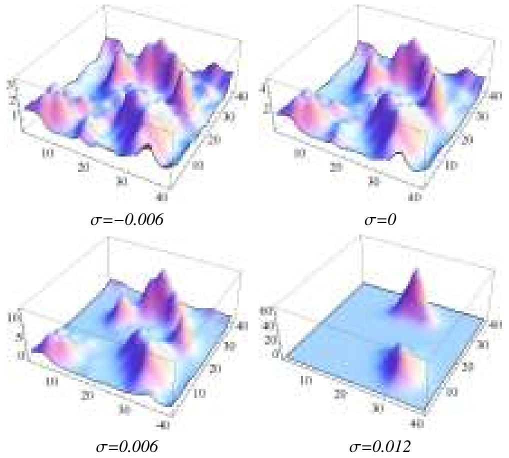


FIG. 1. Relaxation time τ_α from SBR, as a function of the distance σ to the ideal MCT glass transition at T_{MCT} ($\sigma < 0$: liquid, $\sigma > 0$: glass). Inset, diffusion coefficient D obtained from the theory. Symbols are dielectric-spectroscopy data for propylene carbonate from Lunkenheimer *et al.* (2000).

Both above and below the dynamical arrest temperature T_{MCT} the density-density correlator decays from the plateau value as $-B(x)t^b$, where b is the same of MCT while the space-dependent prefactor $B(x)$ is due to the local random fluctuations of the temperature that are the main feature of SBR. From the $B(x)$ profile one can extract many important quantities, the α-relaxation time, the diffusion coefficient and the correlation length, see *e.g.* fig. (1). We see that, approaching T_{MCT} things changes with respect to ideal MCT: (i) dynamical arrest is avoided *but* (ii) the relaxation time starts to grow much faster, from power-law to exponential. Note that there was no *ad hoc* assumption on nucleation or activated processes in the derivation of SBR, actually the initial assumption is that T_{MCT} marks a genuine phase transition.

Dynamical fluctuations are naturally associated to fluctuations of the B-profile: regions where the correlator is decaying faster are associated to the peaks of $B(x)$ and the dynamical correlation length can also be extracted from it. Figure (2) shows that the structure of dynamical fluctuations also displays an important qualitative change upon crossing T_{MCT}. Above T_{MCT} ($\sigma < 0$) there is a power-law increase of dynamical fluctuations and of the dynamical correlation length. Below T_{MCT} ($\sigma > 0$) strong *Dynamical Heterogeneities* appear as rare faster regions that dominate the global relaxation. Note that dynamics slows down because these regions are rare in space, but not because they are larger. Indeed the dynamical correlation length *decreases* slightly below T_{MCT} and decorrelates from the relaxation time. Overall the structure of dynamical fluctuations changes from being scale-invariant above T_{MCT} to being activated-like below T_{MCT}. As a consequence observables that scaled similarly above T_{MCT} decouple below T_{MCT} and this is reflected *e.g.* in deviations from the Stokes-Einstein relationship.


σ=−0.006 σ=0

σ=0.006 σ=0.012

FIG. 2. Normalized B-profile $B(x)/\overline{B}$ on a plane sliced from a cubic box for different values of σ (σ-scale different from fig. 1).

We note that SBR cannot sustain too large fluctuations and could fail well below T_{MCT}. There it could be replaced by activated dynamics characterized by elementary events with an intrinsic time and length scales of an unusual large (but not necessarily increasing) size (mesoscopic vs. microscopic).

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– space for notes –

On the microscopic origin of anomalous relaxation in soft glassy materials

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Many disordered solid-like systems exhibit residual structural relaxations that slowly evolve in time, which is known as aging. For 'glassy' soft matter systems (like colloidal gels and suspensions, concentrated emulsions, clay...) aging dynamics seems quite ubiquitously characterized by compressed exponential decays and a 'ballistic' type scaling of the scattering wave vector dependence of the relaxation times [1]. These features are commonly explored in dynamic light scattering experiments and have been attributed to a peculiar displacement field generated by a large number of randomly distributed dipolar stress sources, relaxing with a given average rate [2, 3]. Although this microscopic scenario is widely accepted to be at the origin of anomalous relaxations in aging soft matter systems, direct experimental evidence of its validity is still missing.

In this contribution we focus on the relation between the anomalous q-dependent relaxation processes and the microscopic dynamics of a coarsening foam. In foams, stress imbalances are continuously generated by the coarsening process and relax through intermittent bubble rearrangements leading to a complex, spatially heterogeneous dynamics [4]. To capture all these features we use time resolved microscopy to acquire movies of the relaxing foam. The movies are first analyzed with the recently introduced methods of Digital Fourier Microscopy [5, 6]. Consistent with the aging dynamics described above, we find that the intermediate scattering functions are well described by compressed exponential decays: $g(q,t) = e^{-(t/\tau)^{\beta}}$, as shown in Fig.1. The relaxation times scale as $\tau \sim q^{-1}$ over a wide range of q and the compressing exponents are $\beta \simeq 1.35$. The same movies are then used to investigate the dynamics in real space, by tracking single particles (bubbles) along their trajectories and by monitoring the dynamic activity associated with intermittent rearrangements.

Our results provide the first direct experimental evidence for the validity of the scenario proposed in [2, 3], namely the power-law tail of the distribution of displacements (Fig.2), the Poissonian statistics of the rearrangement events and the strong persistence in the motion of the particles despite its intermittent nature. However, our experiments also reveal that the model holds only over a limited range of q. The dynamics exhibit a qualitatively different behavior on large spatial and time scales, indicative of a characteristic length scale, the bubble radius, over which the constituent of the system have to move to completely rejuvenate the stress configuration. Above such length-scale the system relaxes 'diffusively' (inset in Fig.1) with an effective 'diffusion coefficient' that matches that describing the increase in bubble size due to coarsening.

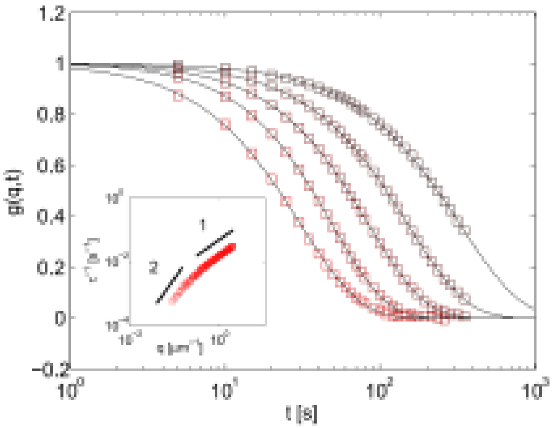

FIG. 1. Main panel: Representative intermediate scattering functions obtained at q -values of, from right to left: 0.47, 0.74, 1.18, 1.88 and 2.98 μm^{-1} . Solid lines are compressed exponential fits to the data. Inset: Decay rates τ^{-1} as a function of q. Solid lines indicates power-laws with the indicated exponents.

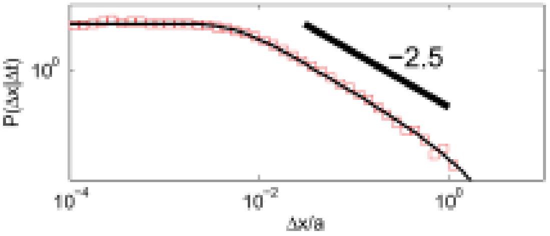

FIG. 2. Probability distribution function of bubble displacements obtained within a time interval of $\Delta t = 5s$ (symbols). Displacements are normalized by the average bubble radius a. The continuous line through the data corresponds to a fit with a function of the form: $P(\Delta x|\Delta t) = \frac{A}{\Delta x_0}\left[1 + (\Delta x/\Delta x_0)^{\alpha}\right] e^{-\frac{\Delta x}{L_0}}$. The solid line indicates a power-law with an exponent of -2.5.

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Glass-glass transition in an charged colloidal suspension

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Ageing dynamics from a liquid phase to an arrested state (gel and/or glass) is a very common feature of viscous liquids. In particular recent advances in the study of soft materials have led to a deeper knowledge of the slowing down of the dynamics and to the discovery of new phases and states besides the ones commonly experienced in atomic or molecular systems. Here we show the evidence, in a charged colloidal suspension, that the dynamics of the system still evolves even in the arrested glassy state: increasing waiting time a spontaneous *glass-glass* transition is observed.

The dynamics and the structure of the system have been investigated well beyond the glass transition at very long waiting times through respectively X-ray Photon Correlation (XPCS) and Small Angle X-ray Scattering (SAXS) measurements performed at the European Synchrotron Radiation Facility (ESRF). Moreover macroscopic properties of the sample, obtained through dilution and rheological experiments, have been measured. All the experimental results clearly indicate the existence of two different behaviours before and after a critical time (t_c ≈3 days) as indicated in Fig. 1 by the black and red curves/symbols respectively [1]. The existence of a spontaneous transition between two distinct dynamically arrested states, i.e. a *glass-glass* transition, is confirmed by Monte Carlo simulations that also permit to gain a microscopic understanding of this transition and to clarify the nature of the interactions. In particular the first arrested states, obtained after an aging process from a fluid to a glassy state due to repulsive electrostatic interactions, evolves in a different glassy state thanks to attractive interactions. We believe that these findings are not peculiar of the investigated system but could be a generic feature of heterogeneously charged or patterned [2] systems with competing attractive- and repulsive electrostatic interactions when driven out-of-equilibrium towards an arrested state.

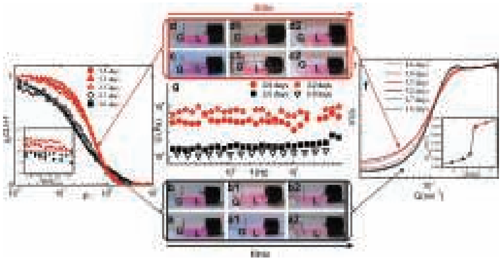

FIG. 1. **Experimental behaviour of glassy Laponite suspensions at concentration C_w=3.0 %. a-d** Photographic time sequence of a dilution experiment for Laponite suspensions. The initially glassy sample (**G**) is added with the same volume of dyed water (**L**) 1-day (**a**), 2-days (**b**), 3-days (**c**) and 4-days (**d**) after arrest takes place. The samples **a** and **b** (water added before t_c ≈ 3 days) start to fluidize (**a1**, **b1**) until the whole sample is completely liquid (**a2**, **b2**). The samples **c** and **d** (water added after 3 days) do not show any macroscopic change of their solid like state (panel **c1-c2**, **d1-d2**). **e** XPCS intensity autocorrelation functions for rejuvenated aqueous Laponite suspensions at different rejuvenation times before (black symbols) and after (red symbols) t_c. In the inset the β exponent is shown as a function of Q. **f** Static structure factor as obtained from SAXS measurements for rejuvenated aqueous Laponite suspensions at different rejuvenation times before (black lines) and after (red lines) t_c. In the inset the peak position as a function of the rejuvenation time t_R enlightens a transition between two different structures. **g** Frequency dependence of the storage modulus G' at different times before (black symbols) and after (red symbols) t_c

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– space for notes –

The Role of Dynamical Heterogeneities on the Mechanics of Polymer Glasses

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The Role of Dynamical Heterogeneities on the Mechanics of Polymer Glasses

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If dynamical heterogeneities in glasses have been evidenced about 20 years ago, their roles on the mechanical properties of polymer glasses remain unclear. Here we study the mechanics of polymer glasses in their glass transition regime to reveal the importance of dynamical heterogeneities on their non-linear mechanics.

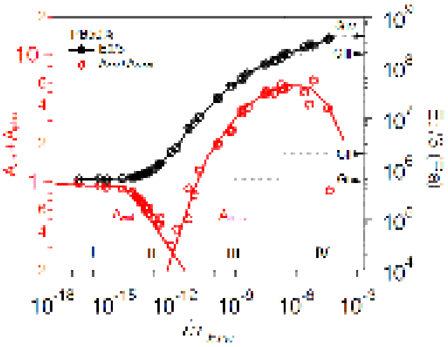
Indeed, if cross-linked elastomers are able to undergo elastic deformation of large amplitude– up to a few unities - glassy polymer exhibit a plastic behavior a few per cent deformation. The non-linear mechanical behavior in the crossover between the glassy and the rubber behavior remains however not described in the literature.

We have precisely measure the non-linear behavior of polymer glasses, using indeed perfectly miscible blends (PB/SBR) to enlarge the glass transition domain. We have taken a lot of care in quantifying the eventual self-heating. We have shown previously quantitatively that the linear visco-elastic properties of these blends behave like a tiling of domains with different glass transition temperatures that can be easily measured by calorimetry [1].

We show from a non-linear mechanical study in the glass transition domain that:

1) if the entanglement slipping model [2] described well the mechanical response above the glass transition, when approaching the glass transition, the entanglement sliding is slow down, and as the results the mechanical response tends to be exactly the one predict by the Gaussian affine model.

2) Slightly below the glass transition, a plastic behavior appears, extremely similar to the Payne effect. We show that this phenomenon appears at the percolation threshold of the slow domains – i.e. the polymeric domains with a relaxation time slower than the inverse of the frequency.



Indeed, we have also observed also these properties in the single component polymers.

We will explain how these properties are a precise signature of the dynamical heterogeneities, evidencing that the onset of the Payne effect corresponds exactly to the percolation of the slowest domains.

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The Potential Energy Landscape of Sheared Supercooled Liquids

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In [1], the effects of shear cycles on glasses have been analysed with athermal simulations. These cycles display an initial stress overshoot in the ensemble average as well as a finite shear stress in the plastic flow regime. The shear stress is subject to aging and therefore decays with time. In single simulations one can see that while the system is strained, the stress relaxes through sudden jumps, while increasing continuously elsewhere. These jumps result from vanishing local minima in the potential energy landscape (PEL).

In our current work, we perform molecular dynamics simulations at very low temperature ($T = 0.01$) in a small system ($N = 260$) and at relatively high shear rate ($\dot{\gamma} = 0.005$). We use Lees-Edwards boundary conditions to shear the system. To describe effects in the PEL, it is best to use a small system. We can show that finite size effects have only limited influence on the major observables like the stress overshoot and viscosity for our system size. To compare the PEL properties to previous results [2], we perform periodic minimization of the potential energy.

The energy minimization is performed in two steps. In the first step, we keep the strain γ constant. The results are comparable to athermal simulations [1]. In the second minimization step we also vary the strain. We call the configurations at these minima inherent structures (IS_γ and IS respectively). Fig. 1 shows a sketch of this new minimization scheme. In Fig. 2 we see that after this minimization, we always have a zero shear stress. These IS are thereby comparable to IS from simulations of unsheared systems at higher temperature, which was previously impossible using only IS_γ.

Fig. 2 shows that even in a single run, we see the stress overshoot. The corresponding potential energies are shown in Fig. 3. Surprisingly, even significantly beyond the overshoot the system is still in the attraction regime of the initial IS, as extracted from the new minimization scheme.

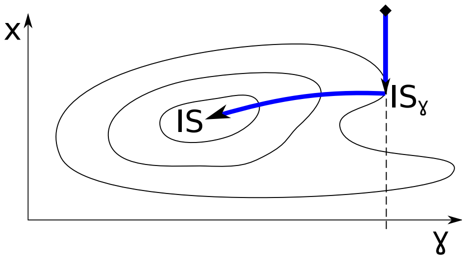

FIG. 1. Schematic representation of the minimization scheme used to determine the inherent structures in a strained system

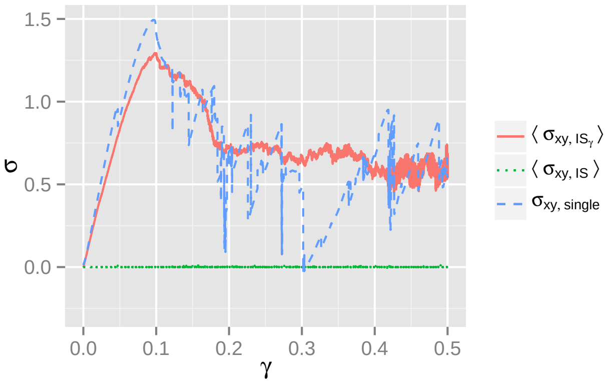

FIG. 2. Ensemble averaged shear stress σ_{xy} (solid/dotted) compared to a single run (dashed)

We also see that the ensemble averaged IS energy stays roughly the same until we reach the maximum overshoot point at $\gamma \approx 0.1$. In the single run we also observe a continuous stress relaxation until the first IS jump, which occurs much later at $\gamma \approx 0.14$

In the PEL picture we argue as follows:
At $E_{\mathrm{IS}_\gamma} \geq -4.55$ the system reaches the outer part of the initial IS. In this region, the system has an increased mobility, which allows shear stress relaxations and IS jumps.

We also analyse IS transitions statistically in the plastic flow regime. There, we follow a CTRW approach [2], since the IS are comparable with unsheared simulations despite Lees-Edwards boundary conditions.

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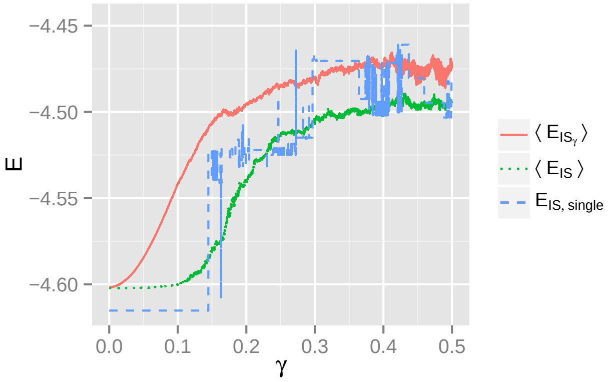

FIG. 3. Ensemble averaged IS energy E_{IS} (solid/dotted) compared to a single run (dashed)

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Activity-induced Fluidization in Dense Glassy Systems

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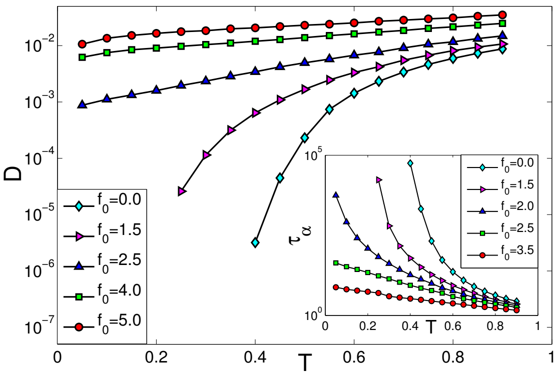

FIG. 1. The diffusion constant (D) has been plotted as a function of temperature (T) for different values of the self-propulsion force (f_0) for $\tau_P = 4.0$ and $\rho_a = 1.0$. The plot shows that the dependence of the diffusion constant on the temperature becomes weaker with increasing f_0. The inset shows the α-relaxation time for $\tau_P = 4.0$ and $\rho_a = 1.0$ as a function of temperature (T) for different f_0, illustrating a qualitative change in the behavior with increasing f_0 and a reduction in the (putative) glass transition temperature.

Investigations of the effects of activity on the collective dynamics of soft glassy systems have received much attention in the last few years [1, 2]. This interest is driven in part by experiments on biological systems, such as bacterial cytoplasm [3], cytoskeleton-motor complexes [4, 5] and cell nuclei [6], in which chemical activity is found to fluidize a glassy state that exhibits characteristic glassy features such as caging, non-ergodicity and dynamical heterogeneity in the absence of activity. To develop a theoretical understanding of this activity-induced non-equilibrium glass transition, we have studied, using molecular dynamics (MD) simulations, the effects of active driving in a generic model glass former, the Kob-Andersen binary mixture [7]. Activity is introduced by assuming that a fraction ρ_a of one kind of particles in the binary system experience a random active force f_0 that is correlated over a persistence time τ_p.

Our main results are : (i) Tagged particle dynamics shows cage-hopping resulting in a late time diffusion coefficient that is weakly dependent on the temperature in the limit of large activity (see Fig. 1); (ii) Activity fluidizes the glass and dramatically reduces the glass transition temperature (see Fig.2); (iii) The phase diagram in the $(T - f_0)$ plane (Fig.2) shows the complete disappearance of the glass phase beyond a threshold value of the activity; (iv) The effect of activity on dynamical correlation functions in the liquid state is determined by a specific combination of f_0, τ_p and ρ_a that provides a measure of the relative magnitude of the "active" stress with respect to the stress arising from interparticle forces; (v) The presence of activity decreases the kinetic fragility of the liquid; and (vi) Activity leads to local clustering of the self-propelled particles induced by the passive particles in the glassy medium. We present simple analytic arguments, based on a heuristic Langevin description of the dynamics of a particle in the cage formed by its neighbors, which provide rationalizations of the shape of the phase boundary between fluid and glass phases in the $(T - f_0)$ plane and other features observed in the dynamics of the system in the presence of activity.

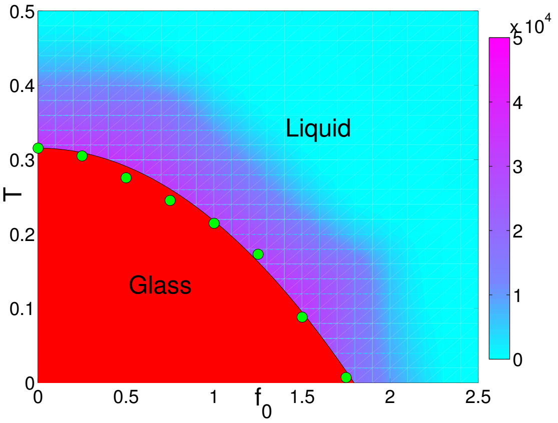

FIG. 2. Phase diagram in the $(T - f_0)$ plane. The glass transition temperatures (green filled circles) have been obtained by fitting the computed α-relaxation time τ_α to the Vogel-Fulcher-Tammann form to extract T_{VFT} for different values of f_0. Both dimensional considerations and heuristic arguments based on a Langevin model suggest that the phase boundary has the form $T_{\mathrm{VFT}}(f_0) = T_{\mathrm{VFT}}(0) - A\,\rho_a \tau_P {f_0}^2$, where A is a constant of order one. The phase boundary (thin black line) represents a fit of the data for $T_{\mathrm{VFT}}(f_0)$ to this form. The variation of τ_α in the liquid phase is displayed by the color plot.

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Active microrheology in a colloidal glass: mode-coupling theory and molecular dynamics simulations

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Active microrheology, viz. driving a probe particle through a complex material, allows to resolve the spatio-temporal evolution of its nonlinear response and of the underlying structural processes. We use molecular dynamics simulations and mode-coupling theory (MCT) to study the dynamics of a tracer particle embedded in a glass-forming colloidal dispersion under the action of a constant force. On the MCT side, this work extends previous approaches [1, 2] to the regime of strong applied forces. We focus on the structure of the probe particle displacements, described by means of van Hove correlation function $G_s(z,t)$ in force direction.

MCT results for the long time limit of the van Hove function of the probe in a glassy host at $\phi = 0.516$ are shown in Fig. 1 for strong forces F_{ex} close to the threshold, $F^c_{ex} \approx 24 k_B T/d$ (d is the particle diameter). They exhibit a Gaussian central part and a long exponential tail in force direction. The tail becomes more pronounced for larger forces. Two length scales emerge from this picture: the cage size (width of the Gaussian part) and the correlation length of the exponential tail. Their dependence on the force is shown in the inset of Fig. 1. This structure reproduces computer simulations results, shown in Fig. 2 for a glassy polydisperse hard-sphere system at $\phi = 0.62$. We relate this to the coexistence of two types of trajectories of probe particles: those localized inside the cage, contributing to the Gaussian part, and those probe particles that perform jumps to other cages, generating the tail [3, 4]. This residence in the cage and jumping from cage to cage is illustrated by typical probe trajectories (inset of Fig. 2) for F_{ex} close to the force threshold in a glassy binary hard-disk system at $\phi = 0.81$.

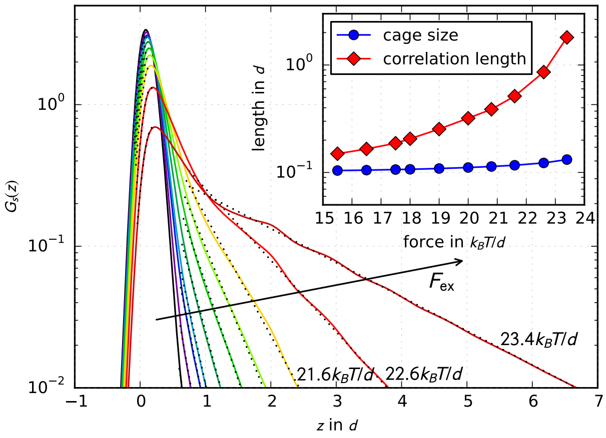

FIG. 1. MCT results for the long time limit of the van Hove function of the pulled probe in a glassy host ($\phi = 0.516$) and different F_{ex}. Inset: cage size and correlation length as a function of F_{ex}.

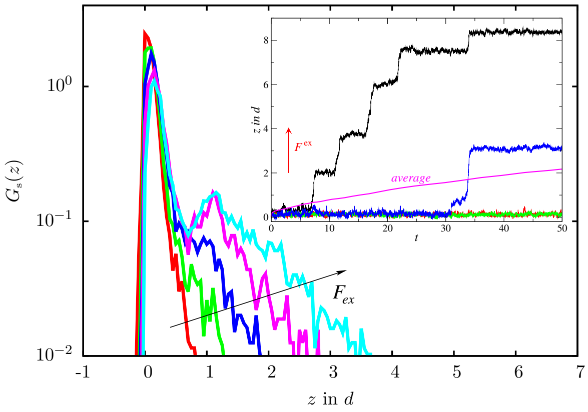

FIG. 2. Simulation results: van Hove function of the pulled probe in a glassy polydisperse hard-sphere system ($\phi = 0.62$) and different F_{ex}. Inset: probe trajectories in force direction in a glassy binary hard-disk system ($\phi = 0.81$) close to the simulated force threshold ($\approx 50 k_B T/d_{small}$). Four individual runs are shown together with the average.

In the delocalized regime, simulation and MCT results for the probe displacements indicate strong anisotropy in the probe dynamics. In the direction perpendicular to the force, the motion of the probe is diffusive, with diffusion enhanced by increasing the applied force. This force-induced transverse diffusion exceeds the intrinsic one for large forces. Parallel to the force, the linear force-induced displacements exhibit caging and a sub-linear crossover to the final steady drift.

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History dependent mechanical properties of colloidal glasses

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Colloidal dispersions offer unique experimental access to study the emergence of solidity at the glass transition. Here, we use an aqueous suspension of core-shell microgels [1] to investigate the history-dependence of the mechanical properties of glass and support our analysis by schematic mode-coupling theory (MCT) and computer simulations.

The first experiment is shear reversal during start-up flow (named Bauschinger effect, see Fig. 1). The overshoot arising from start-up is age-dependent, which was already shown and is not topic of this work. Preshear which induces plastic rearrangements can soften the glass and strongly affect the stress-release during yielding, as seen in simulations [2] and described in a two-times MCT model.

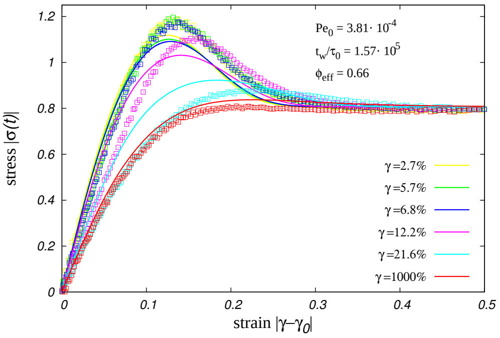

FIG. 1. Shear reversal at different strains for the start-up at $\mathrm{Pe}_0 = 3.81 \cdot 10^{-4}$. The experimental curves (symbols) are measured at $\phi_{\mathrm{eff}} = 0.66$ and a waiting time time of $t_w/\tau_0 = 1.57 \cdot 10^5$, the lines mark the MCT results.

The second experiment focuses on creep in glass under load which depends on the temporal and shear history [3]. A schematic MCT captures the latter, including the existence of a static yield stress, the superdiffusive strain-growth at intermediate times, and plastic flow. Oscillations due to inertial effects can also be rationalized.

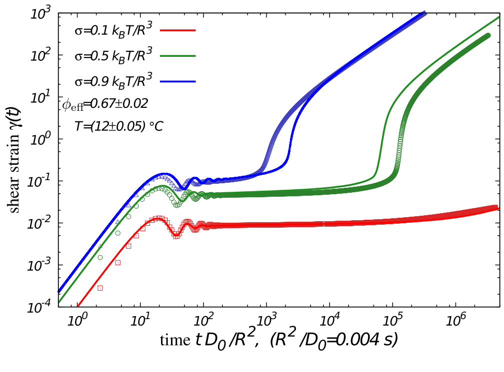

FIG. 2. Experimental creep data from Ref. [3] indicated by symbols for different stresses. Lines are results of a schematic MCT model.

In the last experiment, shear cessation, the stress relaxation (after setting the strain to zero) characterizes the material and clearly indicates a glassy or a fluid state. Whereas the stress in the fluid state relax completely after some time, in the glass residual stresses remain (see Fig. 3). These residual stresses found in experiment, in Brownian dynamics simulations of binary hard disks (see inset left), and in MCT influence as well the mechanical properties of the glassy state further on. With increasing cessation time in the glassy state G'' decreases (see right inset in Fig. 3) as well with decreasing Pe_0 in the sheared steady state (not shown here).

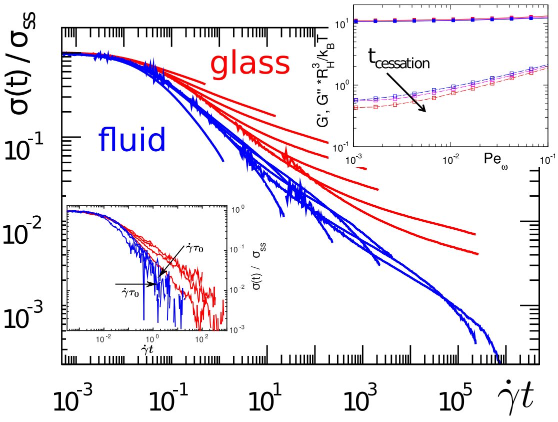

FIG. 3. Stress relaxation during cessation from the sheared steady state of the colloidal suspension (taken from Ref. [4]) for the fluid (blue) and glassy state (red). The left inset shows simulations of binary Brownian disks, the right inset the influence of history on the linear viscoelastic spectra; here a preshearing was performed at $Pe_0 = 1.0 \cdot 10^{-4}$, followed by different cessation times: $t_{\mathrm{cessation}}/\tau_0 = 5.0 \cdot 10^3$, $5.0 \cdot 10^4$ and $5.0 \cdot 10^5$ (blue, magenta, red).

Experiment, MCT and simulations give a broadly consistent picture of the evolution of stresses in glasses.

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Microscopic theory for negative differential mobility in crowded environments

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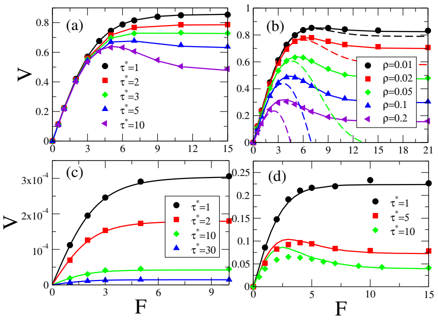

FIG. 1. $V(F)$ in a square lattice: (a) $\rho = 0.05$, $\tau = 1$; (b) $\tau = 1$, $\tau^* = 10$; (c) $\rho = 0.999$, $\tau = 1$; (d) $\rho = 0.5$, $\tau = 1$. Analytical prediction (lines) and numerical simulations (symbols).

A fundamental result of statistcal mechanics is the fluctuation-dissipation theorem, which relates system response and spontaneous fluctuations. Recently, a great effort has been devoted to generalizations of this theorem to nonequilibrium situations [1, 2], and also to elucidating the effects of the higher order contributions in the external perturbation. Theoretical understanding of the latter issues is of an utmost importance in the field of active microrheology [3, 4].

A striking example of anomalous behavior beyond the linear regime is the negative response of a particle's velocity to an applied force, observed in various physical contexts. Here, we study the behavior of the stationary velocity of a driven particle in an environment of mobile hard-core obstacles. We consider a discrete model where a hard-core tracer particle (TP) performs a random walk of mean waiting time τ, biased by an external force F, on a lattice containing a bath of hard-core particles (or "obstacles") of density ρ, which perform symmetric random walks of mean waiting time τ^*.

Using a decoupling of relevant correlation functions, we demonstrate analytically that the drift velocity can exhibit a nonmonotonic dependence on the applied force, see Fig. 1, and show quantitatively that such negative differential mobility (NDM) is controlled by both the density and diffusion time scale of obstacles [5]. Our study unifies recent numerical and analytical results obtained in specific regimes [6, 7], and makes it possible to determine analytically the region of the full parameter space where NDM occurs, see Fig. 2. Our solution reveals and quantifies a minimal physical mechanism responsible for NDM, which is based on the coupling between the density of obstacles and the diffusion time scales of the TP and obstacles.

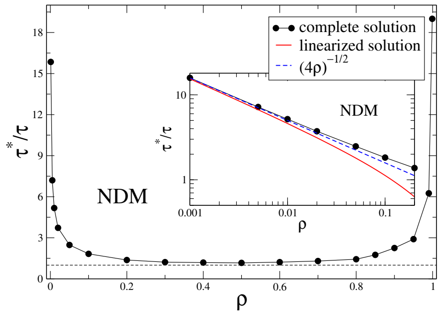

FIG. 2. Region of NDM in the plane τ^*/τ vs ρ (black circles). Inset: zoom of the low density region.

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Multiple reentrant glass transitions in confined hard-sphere glasses

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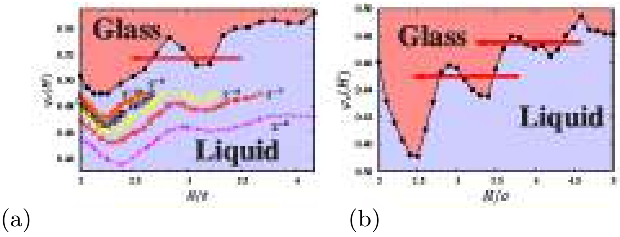
Glass forming liquids exhibit a rich phenomenology under confinement. This is often related to the effects arising from wall-fluid interactions. Here, we focus on the strong confinement limit (wall-to-wall separation of the order of a few particle diameters). A recent theoretical work predicts that if a hard-sphere fluid is sandwiched between two planar hard walls (slit geometry), its glass-transition line may be a non-monotonic function of the distance between the walls [1]. Such a prediction is very interesting since it indicates that a purely geometric effect may be used to induce the transition from the liquid to glassy state as a function of the wall separation (H).

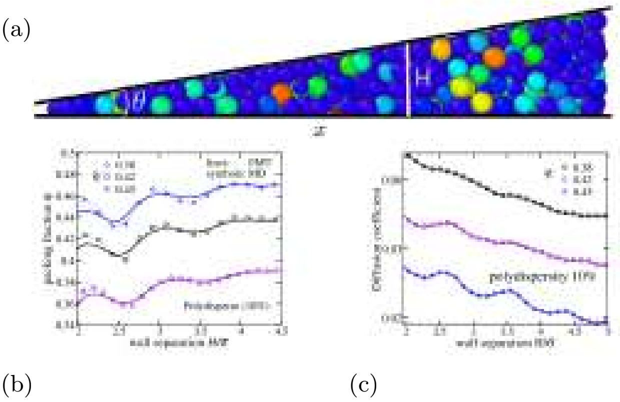
Motivated by this idea, we performed event driven molecular dynamics (EDMD) simulations of model polydisperse hard sphere liquids in a slit geometry. This strong confinement induces structural changes due to competing length scales, for example, a non-monotonic variation of the first diffraction peak with the wall separation. For the distances investigated, the first diffraction peak is maximal for non-commensurate wall distance. As expected, this must have a strong impact on the dynamics of a liquid. Indeed, a non-monotonic dependence of the self diffusion coefficient (D) on plate separation is observed. By increasing the packing fraction, the self diffusion coefficient varies by a factor of 1000 upon variation of H at $\varphi = 0.49$. This dramatic amplification is one of our principle results [2]. We find that the self diffusivity exhibits power-law behavior ($D(\varphi) \propto (\varphi_c - \varphi)^\gamma$) for a fixed wall distance, which is asymptotically predicted by the mode-coupling theory (MCT) [1]. The state diagram obtained from the simulation is compared to the MCT calculation in Fig. 1. The most prominent feature is the variation of the glass-transition line with a period comparable to the hard sphere average diameter, $\bar{\sigma}$. As a consequence, along such paths, first a transition from a confined liquid to a non-ergodic glass state occurs, followed by a melting to a fluid state upon further shrinking the dimension.

In the second part of our work, we consider the experimentally more accessible confined geometry, i.e., a wedge-shaped channel. By transferring the slit geometry results using thermodynamic relations, we are able to predict that the above reentrant effect also persists here. This effect may find interesting applications in nano-technology, for example, fluids confined in a nano-scale roughness. To provide direct evidence, we performed a number of EDMD simulations of a polydisperse hard-sphere system in a wedge-shaped geometry with a tilt angle of 9°. These simulations clearly demonstrate that the self diffusion coefficient in a wedge exhibits variation as a function of the distance from the corner of the wedge (see Fig. 2(c)). This strongly suggests that a liquid-glass phase coexistence may occur at a sufficiently high external pressure.



(a) (b)

FIG. 1. (a) State diagram of a confined 10% polydisperse hard sphere liquid as obtained from the simulation data. (b) Prediction from the MCT for a confined monodisperse hard-sphere liquid. The arrow indicates constant density paths where (multiple) reentrant behavior occurs.



(b) (c)

FIG. 2. (a) A snapshot of polydisperse hard sphere system in a wedge-shaped channel. The height obeys $H = x\tan(\theta)$. (b) Packing fraction variation in a wedge. (c) The self diffusion coefficient variation in a wedge as a function of the wall separation.

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Probing the Existence of Partially-Arrested States in Ionic Liquids.

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Recently, the Self-Consistent Generalized Langevin Equation (SCGLE) theory was used to investigate the dynamically arrested states in the context of the primitive model of molten salts [1]. The most important result of the cited work was the prediction of low-temperature regions where the bigger ions are fluid and the small ions are arrested. For instance, in the Fig. 1 we show the dynamic arrest lines calculated with the SCGLE theory for a molten salt with no charge asymmetry ($\zeta = |q_{cation}/q_{anion}| = 1$) and size asymmetry $\delta = 3.5$ ($\delta = \sigma_{cation}/\sigma_{anion}$, with σ_α being the diameter of the corresponding ion). Inside the F-G region the anion is dynamically arrested and the cation is fluid. The region G-G corresponds to fully arrested states in which both ions are arrested.

Probably, those kind of partially-arrested states may be hard to observe in simple ionic liquids due to the inherent difficulty of avoiding crystallization. However, a novel class of ionic liquids, known as Room-Temperature Molten Salts (RTMS), possess a glassy-behavior at more accessible temperatures and offering a better opportunity for probing the theoretical predictions. RTMS are organic salts with melting temperatures less than 100^oC [2]. The study of this compounds has becoming a very active field due to their potential applicability on industry. Despite all the work done, the exact amount of similarities between these systems with the classic examples of ionic liquids, as halide molten salts, is still not clear.

With the aim of probing the reliability of the theoretical predictions, the glassy-behavior of the 1-ethyl-3-methyl- imidazolium tetrafluorborate (EMIM-BF4) RTMS is studied using molecular dynamics (MD) simulations. As shown in Fig. 2, we have found a singular behavior in which the BF4 anion has a less diffusion coefficient compared with the EMIM cation. The intuitive idea that bigger particles have slower diffusion, contrast with the faster diffusion of the bigger EMIM in our MD simulations. Despite the complexity of the ions, our observations are in complete qualitative agreement with the predictions of the SCGLE theory.

In this work, a qualitative comparison between theory and simulation is presented in order to check the general picture given by theoretical predictions. We can conclude that the theoretical prediction about the existence of partially-arrested states in ionic liquids is consistent with our molecular dynamics simulations of EMI-BF4 RTMS.

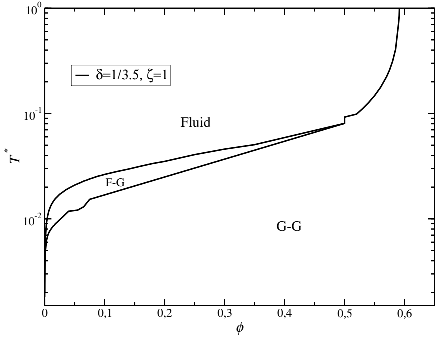

FIG. 1. Arrest lines predicted by the SCGLE theory for the primitive model of molten salts with a size asymmetry adequate for our RTMS (1:3.5). Inside the F-G-region the small ions are arrested but the big particles are still fluid. The G-G-region corresponds to fully arrested states.

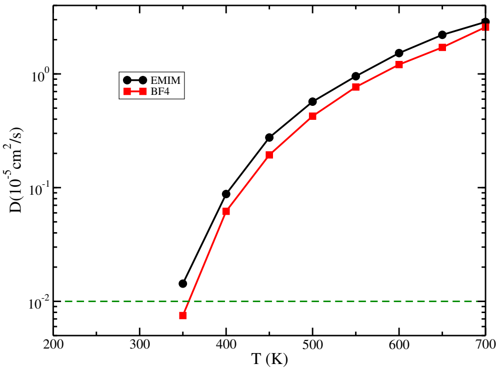

FIG. 2. Diffusion coefficients as a function of the temperature of the EMIM-BF4 system. Strong tendency to dynamic arrest is observed at low temperatures. Besides, lower diffusion coefficients was observed for the BF4 anion. Using D=10^{-7}cm^2/s as our dynamic arrest criterion for simulation, we observe the arrest of the anion are arrested at larger temperature than the cation.

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– space for notes –

Localization and caging in binary glasses

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Anomalous diffusion is observed for proteins moving in the crowded environment of the cell, or for fluids confined in porous matrices. To microscopically investigate these complex dynamical processes, the dynamics of a colloidal dispersion in a matrix of frozen larger particles has been the subject of several studies. In particular, it has been shown that two different kinds of dynamical arrest mechanisms of the fluid exist, depending on the volume fraction of the fluid and of the host matrix. For a dilute fluid, a localisation transition occurs when the particles in the fluid are confined in a concentrated matrix [1]. On the other hand at larger fluid volume fractions, dynamical arrest is a consequence of a caging-like transition of the mobile particles in the decreasing free volume within the matrix. The transition between these arrest mechanisms is predicted to result in a A3 singularity by mode coupling theory (MCT) [2], which is signalled by anomalous diffusion in the MSDs and logarithmic relaxations of the collective dynamics.

Here we experimentally study the case of dynamical arrest of a dilute fluid in a dense, almost frozen matrix, as a function of the size asymmetry between the fluid and matrix particles. As model system we use binary mixtures of colloidal hard spheres with different total volume fractions ϕ and two different size ratios $\delta = R_s/R_L = 0.19$ and 0.28, with R_s and R_L the radii of the small and large spheres, respectively [3]. The relative volume fraction of the small spheres is kept fixed at $x_s = \phi_s/\phi = 0.01$, with ϕ_s the volume fraction of small spheres. We use a recently developed technique, differential dynamic confocal microscopy, combined with fluorescence labelling, to selectively measure the wave vector q-dependent dynamics of the small spheres.

For $\delta = R_s/R_L = 0.19$ we observe that the dynamics of the small spheres indicate effects of confinement and localisation for $\phi > 0.60$, i.e. at ϕ significantly larger than the glass transition volume fraction $\phi_g \approx 0.58$. This is signalled by the growing intermediate plateau of the intermediate scattering function $f(q, \Delta t)$ at fixed q with increasing ϕ (Fig. 1, top). For $\delta = 0.28$ and comparable ϕ we observe instead, in a certain q range, logarithmic relaxations of $f(q, \Delta t)$ (Fig. 1, bottom).

These anomalous relaxations indicate a competition between different arrest mechanisms: localisation due to confinement and caging. These results suggests that a transition between localisation due to confinement and caging can be controlled by varying the size ratio between the matrix and fluid particles. Moreover the occurrence of a localisation transition for the small spheres at large size disparity confirms predictions of MCT and self-consistent generalised langevin equation (SCGLE) theories for the glass transition in binary colloidal systems.

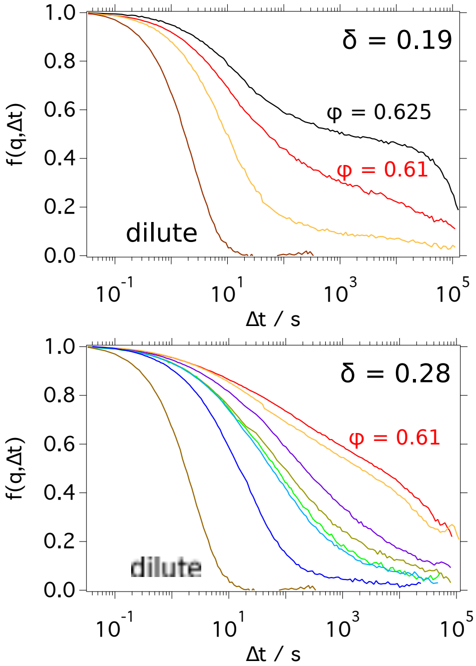

FIG. 1. Experimental intermediate scattering functions $f(q, \Delta t)$ for $qR_L = 1.75$, describing the dynamics of small spheres in binary mixtures with (top) $\delta = 0.19$, $\phi = 0.60$, 0.61 and 0.625, from bottom to top, (bottom) $\delta = 0.28$, $\phi = 0.52$, 0.56, 0.57, 0.58, 0.588, 0.604 and 0.61, from bottom to top. The $f(q, \Delta t)$ of a one-component dilute dispersion of small spheres is also shown for comparison.

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– space for notes –

Mechanical fluctuations suppress the threshold of soft-glassy solids

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In this work, propose a dynamical mechanism leading to the fluidization of soft-glassy amorphous material driven below the yield-stress by external mechanical fluctuations. The model is based on the combination of memory effect and non-linearity. We show that small stress modulations around a mechanical reference state lead to the dynamical destruction of the yield stress and to the emergence of a liquid-like behaviour. As, this viscous response is linearly related to the inverse of the stress modulation rate, it does not appear as an activated process where mechanical fluctuations are described as an effective temperature as it was suggested previously [1].

We test this scenario on a granular packing driven mechanically below the Coulomb threshold. We designed the experimental system as an Atwood machine to avoid introduction of uncontrolled mechanical perturbations from motorized engine. The set-up (Fig. 1(a)) consists in a shear cell filled with glass beads at a well-defined packing fraction. Shear is obtained by applying a torque on a four-blade vane using a mass m suspended from a pulley partially hanging in a water tank. Modulations of the torque is obtained by varying the Archimede's forces on the mass by vertical oscillatory displacements of a water tank. In addition, we obtain a spatially resolved map of the top surface deformations by using diffusive wave spectroscopy (DWS) [2].

When a constant stress σ_0 smaller than the yield stress is applied, a creep behaviour is observed with a logarithmic dependence of the strain with time (red curve of Fig. 2) [3]. Figure. 2 shows also typical deformations for two experiments performed at the same mean stress and oscillation amplitude but for two oscillation frequencies (blue and green curves). During the constant stress phase, a slow increase of the deformation, $\gamma(t)$, is observed corresponding to the beginning of the logarithmic creep. Then, when submitted to oscillations, the system will transit to a linear creep regime characterized by a constant mean strain rate, $\dot{\gamma}_\infty$, which increases with the oscillation frequency. The slope of this linear creep allows to define an effective viscous response. It is shown that the effective viscous response directly related to small stress modulations in agreement with the theoretical prediction of a generic secular drift.

DWS technique had already shown that the macroscopic plastic deformation can be quantitatively related to the rate of apparition of dynamical local heterogeneities ("hot spots") [4]. We observe the same feature even varying penetration depth of the vane which indicates that the localized relaxation process is spreading over the whole material. Moreover, the liquid-like regime is accompanied by a radical change in the "hot spots" apparition dynamic which might be explained by our set-up geometry.

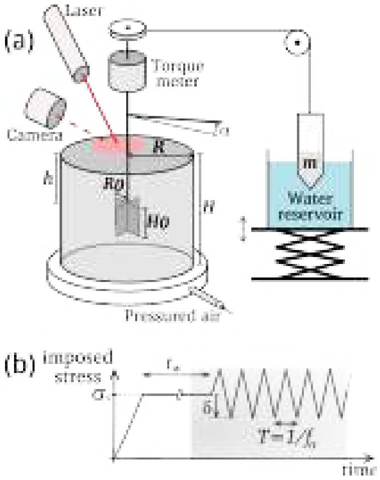

FIG. 1. (*a*) Experimental set-up. (*b*) Imposed stress during an experiment: stress ramp to reach mean stress, σ_0, constant stress during t_w and stress modulation characterized by a frequency f_σ and an amplitude δ.

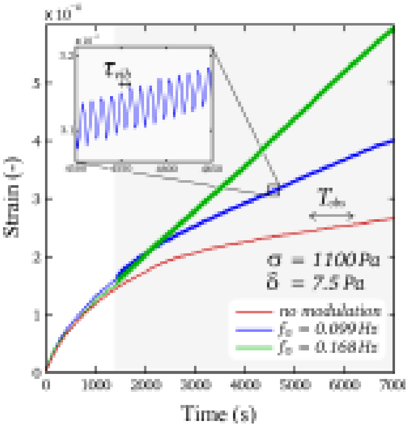

FIG. 2. Strain as a function of time for three experiments performed at $\sigma_0 = 1100$ Pa, and $\delta = 7.5$ Pa, and for various oscillations frequencies. The oscillations start at t = 1500s (grey area).

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– space for notes –

Structural relaxation is a scale-free process

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We show that in deeply supercooled liquids, structural relaxation proceeds via the accumulation of Eshelby events, i.e. local rearrangements that create long-ranged and anisotropic stresses in the surrounding medium. Such events must be characterized using tensorial observables and we construct an analytical framework to probe their correlations using local stress data. By analyzing numerical simulations, we then demonstrate that events are power-law correlated in space, with a time-dependent amplitude which peaks at the alpha relaxation time τ_α. This effect, which becomes stronger near the glass transition, results from the increasingly important role of local stress fluctuations in facilitating relaxation events. Our finding precludes the existence of any length scale beyond which the relaxation process decorrelates.

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A Theoretical Framework for Shear Induced Rigidity in Athermal Materials

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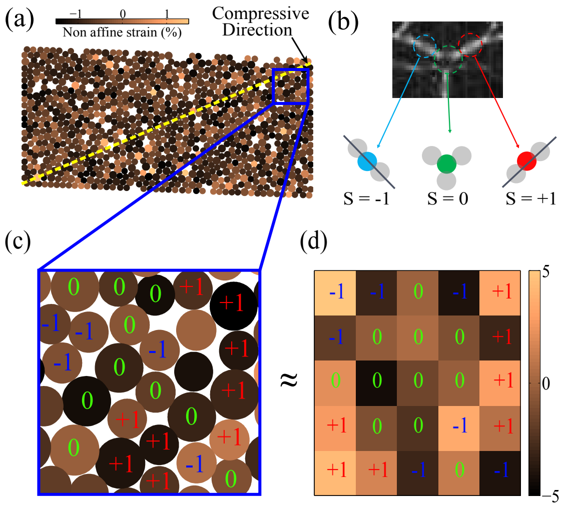

FIG. 1. **Mapping to spin model:** (a) The disordered nature of the granular packing leads to the creation of non-affine strains at the granular level, which are mostly uncorrelated. (b) Under the application of shear strain, the stress tensor of these grains evolve like spins under external magnetic field, subject to local magnetic disorder. This allows us to map the stress tensor of a grain to a spin-1 system: if the stress tensor is isotropic, then it's mapped to zero spin, otherwise it's mapped to ±1 spins. (c) A small subsection of the packing shows this spin mapping. (d) Making further simplifying assumptions, we map this real packing to a square lattice with quenched random field in each lattice site, on which the spins evolve as the external field (not shown) is varied. The colorbar indicates the value of the random field. This is the model on which we base all our calculations and predictions.

Recent studies[1–4] of non-Brownian systems such as dry grains and dense, non-Brownian suspensions have shown that shear can lead to solidification through the process of shear jamming in grains and discontinuous shear thickening in suspensions. The similarities observed between these two distinct phenomena suggest that the physical processes leading to shear-induced rigidity in athermal materials are universal. We will present a unified statistical mechanics framework for understanding these non-equilibrium transitions. The approach focuses on the importance of frictional contact forces, and the collective behavior induced by the constraints of force and torque balance. Our analysis identifies the crucial physical processes underlying shear-driven rigidity transitions, and clarifies the distinct roles played by shearing forces and the density of grains.

This work has been supported by NSF-DMR 1409093 and by the W. M. Keck Foundation. We are indebted to the Behringer group for sharing their data. Also, we acknowledge extended discussions with Dapeng Bi, Eric Brown, R. P. Behringer, Jie Ren, Joshua Dijksman, Dong Wang.

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Critical exponents of the jamming transition

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Continuous Glass Transitions, Activated Dynamic Scaling and the Random Field Ising Model

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Recent works have shown that the glass transition can be made second-order by tuning certain control parameters, e.g. by randomly pinning a fraction of particles [1, 2] or introducing quenched disorder as done in studies of super-cooled liquids in porous media [3, 4]. These continuous glass transitions are possibly related to the logarithmic relaxation found in attractive colloids for special values of the control parameters [5]. Remarkably, by combining mode-coupling theory, activated dynamics scaling and field-theoretical approaches one can go much farther than usual in their analysis and obtain an almost complete theoretical description for three dimensional systems.
In this talk, after an introduction to these new kind of glass transitions, I will present such a description and the key theoretical approaches that play a very important role in the analysis, in particular Inhomogeneous Mode Coupling theory [6] and the mapping to the Random-Field Ising model [7, 8].
Our main results are that at continuous glass transitions configurational entropy does not play any role, dynamical correlation functions show logarithmic instead than two-step relaxation, time and length-scales are related by activated dynamic scaling and several critical exponents are the same ones of the Random Field Ising model.

This talk mainly focuses on the work presented in Ref. [6]. Some results of [8] will also be discussed.

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– space for notes –

Rounded delocalization-to-localization transition of soft-disk fluids in a porous medium

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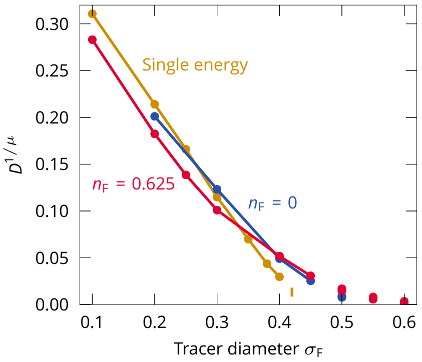

FIG. 1. Rectification plot of the self-diffusion coefficient D as function of the fluid diameter σ_F with the expected exponent for the Lorentz gas, $\mu = 1.31$, for single energy (orange), confined-ideal-gas particles (blue), i.e. $n_F = 0$, and interacting fluid particles with $n_F = 0.625$ (red).

The Lorentz model is a paradigm for the understanding of fluid transport through heterogeneous media [1]. In its simplest two-dimensional (2D) version, a point tracer explores the space between randomly distributed hard-disk obstacles which may overlap and are uncorrelated. This model system exhibits a localisation transition with respect to the diffusive motion of the tracer, i.e. the long-range diffusive transport of the tracer ceases to exist as a critical obstacle density n^c is approached. The localization transition is associated with a non-linear power-law growth of the mean-squared displacement (MSD), $\delta r^2(t) \sim t^{2/z}$ with a universal dynamic exponent z.

Recently, Skinner *et al.* [2] have presented an experiment of a 2D colloid system that differs from the original Lorentz model with respect to soft interactions between the tracer and the matrix particles as well as a correlated matrix structure. Complementary molecular dynamics (MD) simulations of an ideal gas fluid in a soft host matrix [2, 3] have demonstrated that for the case of soft interactions the localisation transition is rounded, i.e. the critical singularities, as seen at the critical density n^c in the hard-disk Lorentz gas, are avoided. This rounding originates from the energy distribution of the ideal-gas tracer particles; however, an effective interaction distance can be assigned to each tracer according to its energy, thereby providing a mapping to the hard-core case. Thus, only for a system where all the tracer particles have the same energy, a localisation transition as in the original hard-disk Lorentz model occurs.

Here, MD simulations are used to investigate the diffusion of a fluid of interacting particles through frozen host structures. The host structures are obtained from independent snapshots of an equilibrated liquid of polydisperse particles at a moderate density. Interactions between particles are modeled via a WCA potential [3]. The fluid is driven towards a localisation transition by increasing the effective diameter [3], σ_F, of the fluid particles. The number density of the fluid is varied from $n_F = 0$ (ideal gas) to $n_F = 1.25$ (with n_F given in units of σ_F^{-2}).

As for the ideal gas fluid ($n_F = 0$), the localisation transition of the interacting tracer particles is rounded (cf. Fig. 1 for $n_F = 0.625$) while non-interacting tracer particles with a single energy show a localization transition as in the hard-disk Lorentz gas. This is indicated by the rectification plot of the self-diffusion coefficient D (Fig. 1), testing the asymptotically expected power law for the Lorentz gas, $D \propto (\sigma_F - \sigma_F^c)^{1.31}$ (with σ_F^c the critical fluid particle diameter).

There are however qualitative differences between the ideal gas case and the case of interacting tracer particles. Around $\sigma_F = 0.5$, the MSD shows anomalous diffusion, $\delta r^2(t) \sim t^\alpha$ with $\alpha < 1$, over three to four orders of magnitude in time. An effective exponent α is obtained that increases with increasing n_F; at $n_F = 0$ the exponent is below the one expected for the hard-disk Lorentz gas (and the single energy case), $\alpha_L \equiv 2/z \approx 0.659$. Surprisingly, for values of σ_F larger than about 0.4, the interacting tracer particles exhibit a faster diffusive motion than the non-interacting ones in the ideal gas case. This is due to the gain of energy of individual particles due to the collisions with other particles. Our findings indicate that the soft systems show similarities to the original Lorentz gas with respect to anomalous diffusion and the approach of a localized state. However, due to the rounding of the transition, asymptotic power laws with universal exponents (see above) do not exist for the case of the interacting soft-disk fluid.

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– space for notes –

Structure and dynamics of a fluid in a quenched disordered potential

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Inspired by recent fundamental studies [1] and proposed applications [2, 3] of the effects of random optical fields on the dynamics of colloidal systems, we have undertaken a theoretical investigation of the structure and dynamics of a classical hard-sphere fluid plunged in an external quenched disordered potential energy landscape modeled as a Gaussian random field (for early work on this type of model, see Refs. [4, 5]).

Structural properties are studied in the framework of integral equation theories, using different approximation schemes (hypernetted chain closure, optimized cluster theory). Two interesting observations follow. First, some aspects of the structure are found to be extremely sensitive to the presence of the excluded volume interactions and, as a result, dramatically change with the fluid density. Second, an unusual breakdown of the hypernetted chain closure, resulting in the violation of fundamental properties of correlation functions, is uncovered. We will discuss its probable origin which is of interest, since this approximation is quite popular for studies of quenched-disordered systems and amorphous solids.

Dynamics is investigated in the framework of the mode-coupling theory (MCT) that was first developed for the study of fluids adsorbed in disordered porous solids [6] and is easily shown to be applicable to the present case as well. The main predictions of the theory, which take the form of dynamical phase diagrams such as the one shown in Fig. 1, for instance, will be reviewed and critically discussed. Indeed, some predicted features are manifestly incorrect if taken literaly, but hint at evolutions that can be understood on the basis of percolation concepts and in the light of recent computer simulations [7]. It eventually results that the phase diagrams predicted with MCT are qualitatively very different from the ones obtained within a mean-field-like replicated liquid approach [5].

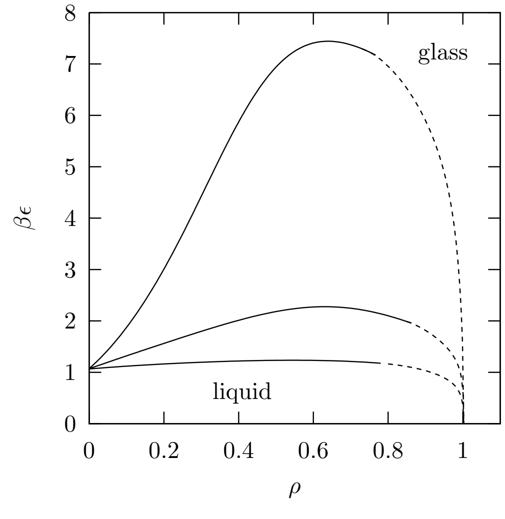

FIG. 1. MCT dynamical phase diagrams of hard-sphere fluids plunged in quenched disordered potential energy landscapes modeled as Gaussian random fields with correlation function $K(r) = \varepsilon^2 e^{-(r/\sigma)^2}$. The fluid density is denoted by ρ and the inverse temperature by β. From bottom to top, $\sigma = 0.25$, 0.5, 0.75. The full and dashed lines correspond to continuous and discontinuous ideal glass transitions, respectively. The structural input has been obtained with the hypernetted chain closure.

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Fluctuations and Shape of Cooperative Rearranging Regions in Glass-Forming Liquids

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Developing a theory of the glass transition remains one of the most fundamental challenge of statistical physics and condensed matter. Recent years have witnessed important and substantial progress in its understanding[1, 2]. In particular the original idea of the Random First Order Transition (RFOT) theory, introduced by Kirkpatrick, Thirumalai and Wolynes, that super-cooled liquids are in a mosaic state, a kind of micro phase separated state in which the number of possible phases is huge[3], has been made concrete and testable in analytical computations and numerical simulations. We understand now how to define and measure the spatial extent of a single micro-phase region[4], also known as cooperative rearranging region, even if each single micro-phase is characterised by an apparently chaotic, amorphous order. Numerical simulations have shown that this length, called point-to-set (PS), grows upon super-cooling and plays an important role in the static and dynamical behaviours.

In this talk I shall present our recent result that unveils the existence of a second static length-scale that together with the PS length is central to the physics of super-cooled liquids and rules the equilibrium relaxation mechanism within the RFOT picture[5]. These results are obtained through the development of a theory of amorphous interfaces within the micro-phase coexistence picture of glass-forming liquids. I will show that the statistical properties of surfaces which separate different cooperative rearranging regions coincide with the ones of domain walls in the random field Ising model. As a major consequence, beside the spatial extent of a single cooperative rearranging region, i.e. the classical PS length, the micro-phase coexistence is characterised by the fluctuation properties of their interfaces and by a new length-scale $\xi_\perp$ that measures the interface thickness (see Fig.1). This second length scale also grows when approaching the glass transition, but slower than the PS length.

The results I will present strengthen the relationship with the random field Ising model found following different theoretical approaches[6, 7]. They are in agreement with previous numerical studies of amorphous interfaces[8] and provide a theoretical framework for explaining numerical and experimental findings on pinned particle systems and static lengths in glass-forming liquids[9, 10]. Moreover the interplay between these two length scales opens new perspectives at the onset of glassy behaviour where we expect that the interface thickness will become comparable or even dominant with respect to the PS length.

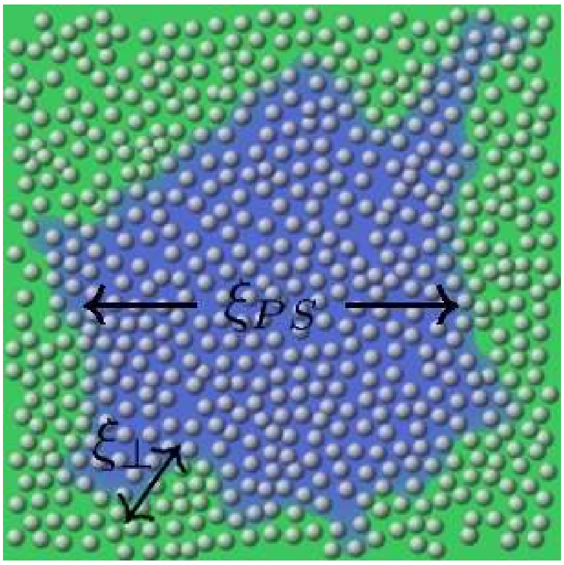

FIG. 1. Cartoon of interface fluctuations of a cooperative rearranging region as detected in numerical simulations of a soft spheres system. The linear spatial extent represents the PS length, ξ_{PS}, wheres the external shape is rough and fluctuating over the length-scale $\xi_\perp$.

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– space for notes –

Rheology of cellular aggregates.

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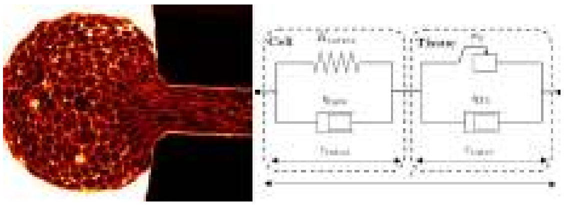

FIG. 1. A : Two photon image of an aggregate flowing in a 60 microns wide channel. B : Rheological diagram for the tissue.

During embryogenesis, cells divide, change of size, shape, migrate and exchange neighbors. All these processes generate active forces. To understand how the embryonic tissues deform and flow in response to these forces, it is necessary to characterize the embryonic tissues rheology. Cellular aggregates, that are tridimensional auto-aggregated spheres of adherent cells, are a good model system to study the mechanics of embryonic-like tissues. It has been shown in macroscopic rheology experiments that cell aggregates behave like visco-elasto-plastic materials [1]. The effective viscosity of the tissue has been found to be many orders of magnitude higher than the single cell viscosity. In this study, we apply a controlled shear stress to cellular aggregates and look at the dynamics of individual cell deformation and cells rearrangements, in order to understand the link between the tissue effective viscosity and the cell scale. For that, we make these multicellular aggregates flow and deform through narrow microfluidic channels. We observe at the same time the individual cells dynamics using 2 photon microscopy (see Fig. 1). This access to the microstructure of the tissue enables us to construct a rheological model combining intercellular and intracellular rheology.

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– space for notes –

Diverging viscosity and soft granular rheology in non-Brownian suspensions

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The peculiar rheology observed close to the jamming transition has been widely studied in dense disordered systems such as granular materials, emulsions, suspensions of large colloids and foams. For these systems it is commonly believed that thermal fluctuations do not play important roles in their dynamics; these systems are called non-Brownian or athermal. Thus the jamming transition is controlled by packing fraction rather than temperature. Below the jamming packing fraction φ_J, the system flows with a finite viscosity when an external force is applied. When the external force is a steady shear flow, the shear viscosity is represented as $\eta = \sigma_{xy}/\dot{\gamma}$, where σ_{xy} is the shear stress and $\dot{\gamma}$ is the shear rate. On approaching φ_J from below, the viscosity η increases dramatically and the system eventually develops a solid-like behavior above φ_J. According to large number of experimental and numerical works, it is generally believed that the viscosity of a hard sphere suspension shows a power law divergence

$$\eta \approx (\varphi_J - \varphi)^{-\beta}. \tag{1}$$

where $\beta \sim 2$. However it is not clear whether this scaling function is asymptotically correct or not because in experiments it is difficult to get enough accuracy and in numerical simulation the conventionally reported data range is too narrow to assess this issue.

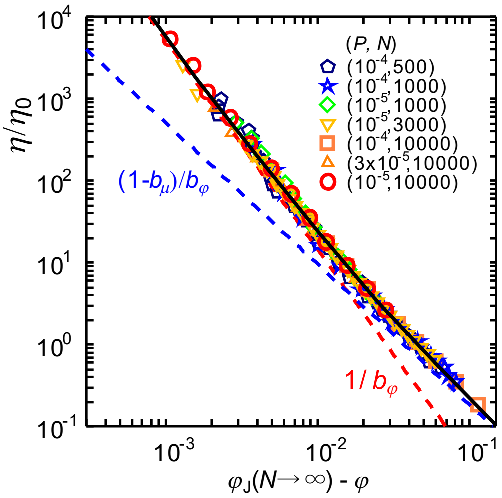

FIG. 1. Shear viscosity after the hard sphere ($P \to 0$) and the large system size ($N \to \infty$) limits are taken. Symbols are measurements for different N and P which satisfy the $N \to \infty, P \to 0$ limits. The black line represents Eq. (4) with parameters taken from the scaling. Red and blue dashed lines separately represent the two power law contributions in Eq. (4).

To clarify this, we study the shear rheology of dense three-dimensional suspensions of frictionless non-Brownian particles in the vicinity of the jamming transition by using large scale computer simulations and finite size scaling analysis. We perform simulations of soft repulsive particles at constant shear rate $\dot{\gamma}$, constant pressure P, and finite system size N, and study carefully the asymptotic limits of large N and infinitely hard particle repulsion. We aim to investigate the asymptotic behavior of the shear viscosity in the hard particle limit by extending earlier analysis by several orders of magnitude. To this end, we first get the hard sphere limit of the two dimensionless numbers $\mu \equiv \sigma_{xy}/P$ and φ. They are simultaneously scaled by the viscous number $J \equiv \dot{\gamma}\eta_0/P$ (where η_0 stands for the solvent viscosity), such that:

$$\varphi(P \to 0, J, N) = \varphi_J(N) - C_\varphi J^{b_\varphi}, \tag{2}$$

$$\mu(P \to 0, J, N) = \mu_J(N) + C_\mu J^{b_\mu}, \tag{3}$$

with the estimated asymptotic ($N \to 0$) values: $\varphi_J = 0.6474$, $\mu_J = 0.108$, $b_\varphi = 0.391$, and $b_\mu = 0.346$. Combining these results with the relation $\eta = \mu/J$, we obtain the behavior of η in the hard sphere limit ($P \to 0$) and large system size limit ($N \to \infty$). It is given by the sum of two power law functions:

$$\frac{\eta}{\eta_0} = \mu_J \left[\frac{C_\varphi}{\varphi_J - \phi}\right]^{\frac{1}{b_\varphi}} + C_\mu \left[\frac{C_\varphi}{\varphi_J - \phi}\right]^{\frac{1-b_\mu}{b_\varphi}}, \tag{4}$$

where the exponents of the power laws are given by: $1/b_\varphi = 2.55$ and $(1 - b_\mu)/b_\varphi = 1.67$. In Fig. 1, the wide range data on φ dependence of η with double limits ($P \to 0$ and $N \to \infty$) are shown. We can see that they are well described by Eq. (4) rather than Eq. (1). Additionally, our finite-size scaling analysis suggests that this divergence is accompanied by a growing correlation length scale, which also diverges algebraically as the jamming transition is approached.

Finally, we can also study the effect of soft repulsion, and propose a natural extension of the standard granular rheology to account for softness effects, which we validate from simulations. Close to the jamming transition, this 'soft granular rheology' offers a detailed description of the non-linear rheology of soft particles, which differs from earlier empirical scaling forms based on Eq. (1).

The details of this study are available in Ref. [1].

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– space for notes –

Viscosity and Microscopic Dynamics in Concentrated Suspensions of Colloidal Microgels

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Introduction Colloidal suspensions have been widely used as model systems to study physical properties of molecular systems such as liquids, glasses and crystals [1]. In colloidal suspensions, the key parameter is the volume fraction occupied by the particles, ϕ. Upon increasing ϕ, both the viscosity η and the structural relaxation time τ of a suspension strongly increase. Indeed, η and τ are closely related quantities: "for a fluid to flow, its structure must relax, and this relaxation is reflected directly in its viscosity" [2]. While the relation between η and τ has been extensively investigated in molecular glass formers, much less is known about the behaviour of these two quantities and their possible decoupling in supercooled colloidal suspensions. This is due mainly to two experimental issues: i) measurements of the zero-shear viscosity by traditional rheometry only extend over 3-4 decades in η, much less than the data available for τ; ii) it is very difficult to control and measure the absolute volume fraction of a colloidal suspension with the accuracy required to compare the ϕ dependence of τ and η as measured in separate experiments.

The most complete set of data to date is probably that of *Segrè et al.*, who measured $\eta(\phi)/\eta_0$ and $\tau_\alpha(\phi)/\tau_0$ in the range $0 < \phi \leq \phi_f = 0.5$ for hard sphere suspensions [3]. They found that there is no decoupling between these two quantities (see fig.1), provided that $\tau(\phi)/\tau_0$ is measured at a q vector corresponding to the first peak of the structure factor (here η_0 and τ_0 are the viscosity of the background solvent and the relaxation time of the suspension at infinite dilution). Unfortunately, these data cover a limited range in η and τ, barely up to the onset of the supercooled regime. Therefore, the question remains open as to what is the behaviour of these quantities for $\phi > \phi_f$, up to the deep supercooled regime where the dynamics dramatically slows down. Does the Segrè-Pusey scaling $\eta \sim \tau$ still hold in this regime?

Our Experiment To address this question, we present viscosity and microscopic dynamics measurements for pnipam microgel particles of radius $a = 170$ nm, in a wide range of volume fraction. To circumvent the experimental difficulties mentioned above, we use a novel setup where viscosity and microscopic dynamics measurements are performed simultaneously on the very same sample, by means of original light scattering techniques. On the one hand, Multispeckle Dynamic Light Scattering is used to measure the microscopic dynamics at various scattering vectors. On the other hand, a combination of scattering and imaging is used to measure the sedimentation velocity of a small amount of large (radius $R = 2$ μm silica probe particles added to the suspension. The suspension viscosity is then obtained from the sedimentation velocity of the probe particles. We are therefore able to directly compare the viscosity and the relaxation time of our suspensions, with no concern about the absolute error on the determination of the suspension volume fraction (see [4]). We find that for our microgels the Segrè-Pusey scaling holds in the deeply supercooled regime, thereby extending previous results by more than 3 decades (fig.2). Ongoing measurements at low q will allow us to obtain the diffusion coefficient D and to test whether the $\tau \sim \eta$ scaling also extends to D^{-1}.

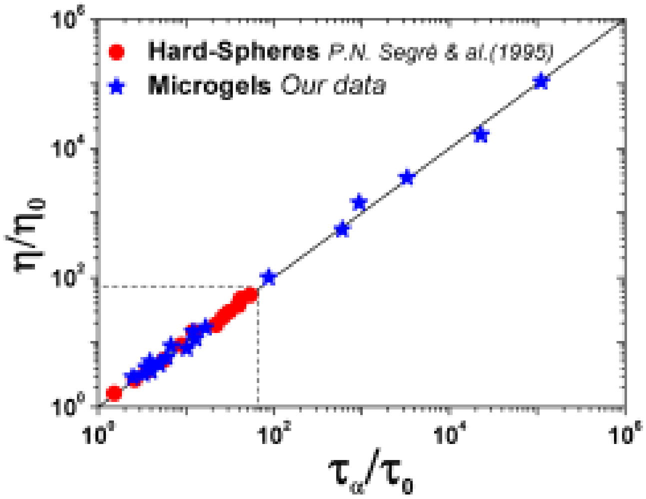

FIG. 1. Relative viscosity vs normalized relaxation time (measured at the first peak of $S(q)$). Full circles: *Segrè et al.* for Hard-spheres [3]. Stars: our data for PNIPAM microgels.

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– space for notes –

Lattice Boltzmann Simulations of Glass Forming Liquids

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The rheology of complex fluids undergoing a glass transition, is highly nonlinear. The interplay between slow structural dynamics on the microscopic scale and a mesoscopic flow field gives rise to non-Newtonian flow effects. Prominent examples are shear thinning, dynamic yield and residual stresses. In confined flow geometry, the shear rates, and thereby the fluid properties, can vary considerably in space and over extremely long time spans. The modeling of such material properties thus requires a multi-scale approach combining macroscopic continuum mechanics with microscopic theory that allows to capture the pronounced temporal history effects (usually in terms of integral equations).

Starting from first principles, mode coupling theory of the glass transition (MCT) is able to provide constitutive equations [2] that describe the history effects determining the flow of glass-forming fluids based on a microscopic description of structural-relaxation phenomena. The Lattice Boltzmann (LB) method is a modern simulation scheme to solve the Navier-Stokes equations even for complex flow geometries. We introduce a new LB model [1] which is able to include memory-integral effects in fluid-mechanics simulations and provides a link between both regimes. We implement a combined LB-MCT algorithm that accounts for long-lasting temporal history (via MCT) on every lattice point in space (as treated by LB).

A simple test case is pressure-driven channel flow. Its transient dynamics is very much affected by the non-Newtonian properties of the fluid. Fig. 1 shows the stopping flow after removing the pressure gradient. To relax residual stresses, the fluid is forced to reverse flow direction and comes to an oscillatory stop, a characteristic sign of viscoelasticity. We find the transient dynamics to dependent sensitively on the channel diameter and even to undergo a qualitative change. We can trace this effect back to a competition between the time scales of structural relaxation and the ones of hydrodynamic momentum transport.

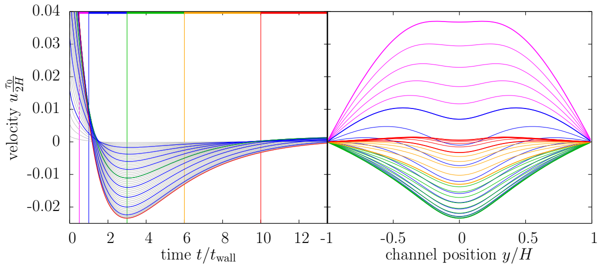

FIG. 1. Decay of the velocity profile in a channel after switching off the driving pressure. Lines in the left panel correspond to various positions y across the channel (red: center, green: half-center). t_{wall} is a hydrodynamic time scale set by the channel diameter. Profiles (right panel) are shown for different times (vertical lines left).

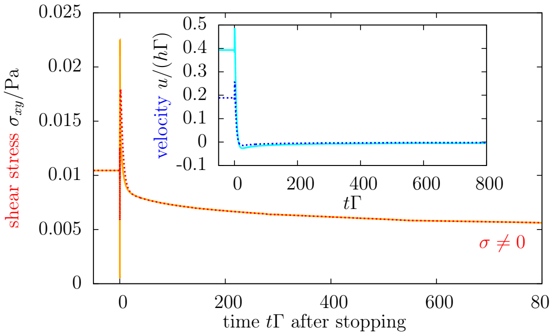

FIG. 2. Velocity (red; main panel) and shear stress (blue; inset) evolution after the cessation of simple shear flow at $t\Gamma = 0$, calculated using lattice-Boltzmann simulations combined with MCT.

A qualitative influence of the macroscopic flow geometry on the microscale properties is seen in the formation of residual stresses. The latter often arise in casting followed by quenches, and dramatically influence the material properties used in applications, i.e., for scratch-resistant smartphone covers (impressively demonstrated by exploding Prince Rupert drops) [3]. As shown in Fig. 2, our combined LB-MCT algorithm is able to capture the emergence of finite residual stresses for an initially shear-molten glass, after the driving force is removed. The same algorithm demonstrates, that for the quench performed in pressure-driven channel flow, no residual stresses can remain due to the symmetry imposed by the Navier-Stokes equation and the boundary conditions. In general, the combination of a Navier-Stokes solver with a constitutive equation capturing the temporal-history dependence of a glass former allows us to study more complex flow scenarios.

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– space for notes –

Nonlinear dielectric spectroscopy in plastic crystals

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– space for notes –

New control parameter for the glass transition of glycerol

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Most of our everyday life materials are glasses, yet our understanding of the formation of glasses is far from being complete. Upon fast enough cooling, most liquids do not crystallize, but instead enter in a supercooled regime where their viscosity dramatically increases upon a quite modest lowering of the temperature T. In this supercooled regime, evidence has mounted over the two last decades that the dynamics of molecules is heterogeneous both in space and in time. Relaxation occurs by groups of N_{corr} molecules, some groups relaxing faster than other; hence the name of Dynamical Heterogeneities (DH) for these groups. It has been argued, both theoretically [1] and experimentally [2] that nonlinear cubic responses χ_3 give access to some features of the DH's.

Here, we study the dielectric nonlinear response of glycerol by applying an electric field which is the sum of a static field E_{st} and of an ac field E_{ac} of angular frequency $\omega = 2\pi f$. Our two sample bridge technique allows to efficiently suppress the linear part of the polarisation P_{Lin} and to study accurately the 1ω component of the nonlinear third order polarisation $\delta P_{1\omega}$. By measuring $\Delta P_{1\omega} \equiv \delta P_{1\omega}(E_{ac}, E_{st}) - \delta P_{1\omega}(E_{ac}, 0)$, one obtains the third order susceptibility of interest -noted $\chi_{2;1}^{(1)}$- which is given by:

$$\Delta P_{1\omega} = 3\epsilon_0 E_{ac} E_{st}^2 |\chi_{2;1}^{(1)}| \cos(\omega t - \delta_{2;1}^{(1)}) \qquad (1)$$

where ϵ_0 is the dielectric vacuum constant and $-\delta_{2;1}^{(1)}$ is the phase of the cubic susceptibility $\chi_{2;1}^{(1)}$.

Fig. 1 shows the modulus -left axis- and phase -right axis- of $\chi_{2;1}^{(1)}$ as a function of f/f_α where f_α is the relaxation frequency of the liquid -given by the peak of the out of phase part of the linear susceptibility χ_{Lin}-. For the four T's reported in Fig. 1, one observes that: (i) the phase $-\delta_{2;1}^{(1)}$ follows a universal function of f/f_α; (ii) the modulus $|\chi_{2;1}^{(1)}|$ has a peak in the vicinity of f_α; (iii) the height of this peak significantly increases when lowering T. These three features are similar to what was reported over the last few years for two other cubic susceptibilities -namely the first and third harmonics cubic responses obtained with a pure ac field-. One can argue [1], that these features are a signature of the DH's, and that one can draw the T-dependence of N_{corr} from that of the height of the peak of Fig. 1.

With respect to other cubic susceptibilities, Fig. 1 shows a new feature: over a wide range in frequency, $\chi_{2;1}^{(1)}$ is found to be related to the temperature derivative of χ_{Lin} as summarized by the following equation:

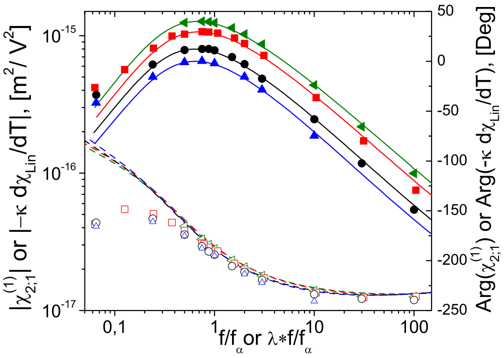

FIG. 1. Comparison of $\chi_{2;1}^{(1)}$ (symbols) and of $-\kappa(\partial\chi_{Lin}/\partial T)$ -lines-. Left axis: moduli (full symbols or plain lines). From top to bottom $T = 197$K, 202K, 211K, 218K, which amounts -at $E_{st} = 0$- to $f_\alpha = 0.27$Hz, 2.1Hz, 60Hz, 520Hz. Right axis: phases (open symbols or dashed lines).

$$\chi_{2;1}^{(1)}(f, T) = -\kappa \left(\frac{\partial \chi_{Lin}}{\partial T} \right)_{f/\lambda_{\text{eff}}, T, E_{st}=0} \qquad (2)$$

where $\kappa \simeq 1.18 \times 10^{-16}$Km^2/V^2 and $\lambda_{\text{eff}} \simeq 0.80$ for the four T's studied. This establishes an important quantitative link between the two methods -$N_{corr} \propto \partial\chi_{Lin}/\partial T$ and $N_{corr} \propto \chi_3$- put forward theoretically [1, 3] to relate N_{corr} to macroscopic observables. Besides [2], from Eq. 2 one may argue that a static field E_{st} increases the glass transition temperature T_g by an amount $\delta T_g = 3\kappa E_{st}^2$.

Apart from the above we will show the recent results of $\chi_{2;1}^{(1)}(f \ll f_\alpha)$ exhibiting the "trivial" response, depending neither on T nor on f since no glassy correlations exist at low frequencies. Electric field induced aging studies are in progress to understand the glassy dynamics. This illustrates how much we may deepen our understanding of the glass transition by using the fact that static electric field is a new control parameter of the glass transition.

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– space for notes –

Cooperative processes, stress localisation and yielding in colloidal gels

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Colloidal gel networks are disordered elastic solids that can form even in extremely dilute particle suspensions. With interaction strengths comparable to the thermal energy, their stress-bearing network can locally restructure via breaking and reforming interparticle bonds. This allows for yielding, self-healing, and adaptive mechanics under deformation. Designing such features requires controlling stress transmission through the complex structure of the gel and this is challenging because the link between local restructuring and overall response of the network is still missing. We have used numerical simulations of a minimal model and analyzed the cooperative dynamics emerging from the mesoscale organization of the network and the mechanical response of the material to shear deformation [1–3]. Our results indicate that consequences of local bond breaking propagate along the gel network over distances larger than the average mesh size. Under deformation, our space-resolved analysis of strains and stresses unravel how a strong localization of tensile stresses (Fig.1) may trigger the yielding of the gel and eventually damage its structure. This strain-induced reorganization of the gel and the flow inhomogeneities developed upon yielding are closely reminiscent of experimental observations [4] and strongly affected by the shear rate.

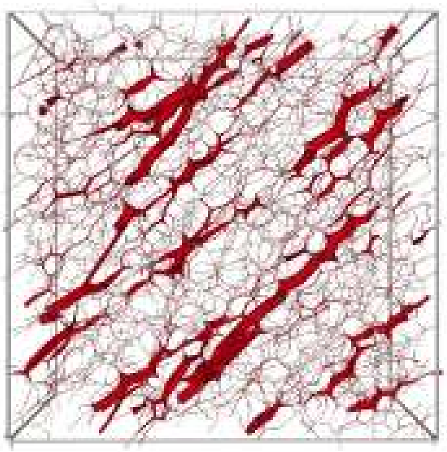

FIG. 1. A snapshot of the gel network under shear: the thicker strands are the ones where the tensile stress intensity is larger than 60% of the maximum tensile stress.

Our analysis of the gel restructuring at rest and under deformation aims at disentangling the role of thermal fluctuations and of relaxation of internal stresses [5] in the complex dynamics detected in colloidal gels in various experiments, where faster than exponential decays of time correlations have been detected [6], and in the mechanical behaviour of other poorly connected soft solids [7].

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– space for notes –

Viscous coarsening and fragmentation in phase separating oxide glasses

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When a homogeneous liquid is suddenly brought into a phase coexistence region, phase domains appear by nucleation or spinodal decomposition. This early stage of phase separation is followed by a coarsening stage: domain growth driven by surface tension. The characteristic size of these domains increases as a power law of time: $\xi(t) \propto t^{\alpha}$ where α depends on the transport mechanism (diffusive, viscous, inertial). While phase separation has recently been mainly discussed in the context of soft matter studies, it has also early been a subject of interest in glass science[1]. Many oxide glass compositions indeed present a large domain of phase separation. Depending on the composition, the critical temperature of phase separation may lie well above the temperature of glass transition or in the supercooled regime. In the latter case the dynamics of coarsening directly competes with the viscous slowing down associated to glass transition.

We discuss here recent in-situ X-ray tomographic experiments on a ternary oxide glass system, a barium borosilicate glass. The two phases, barium-rich and silica-rich respectively, present a high density contrast, which enables a good quality segmentation of the 3D images. The two separating phases are also characterized by a strong viscosity contrast[2].

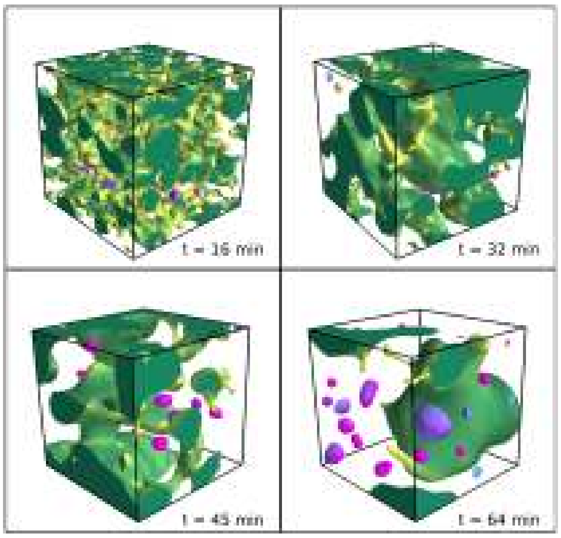

FIG. 1. X-ray tomography of a barium borosilicate glass under coarsening at 1130°C (after 16mn, 32 mn, 45mn and 64mn). The lateral size of the cube is 140μm. Only the minority (barium-rich) phase is represented. The percolating domain is represented in shades of green, following the mean local curvature. Isolated domains are represented in shades of purple.

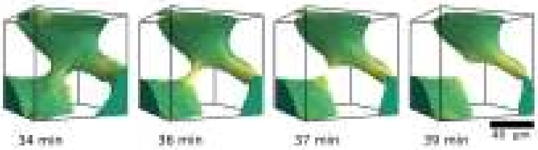

FIG. 2. Capillary break-up in the less viscous phase

Experiments have been performed on the beam-line ID19 at the European Synchrotron Radiation Facility (ESRF). Glass samples 2 mm in diameter were studied at high temperatures (in the range [1000°C-1300°C]), well above glass transition. Volumes of size up to 700μm×700μm×350μm were reconstructed with a voxel of micrometric size.

As evidenced in Fig. 1 the use of 3D imaging enabled us to directly follow the domain growth. The linear character of the time dependence of the characteristic size of the domains was establihed quantitatively, in agreement with Siggia's prediction for viscous coarsening[3]. The hypothesis of dynamic scaling invariance was tested on the distribution of local slopes measured on the domains. Limits to dynamic scaling invariance could be observed and were attributed to an original phenomenon: the gradual fragmentation of domains of the less viscous phase. Interestingly, we could show that the distribution of isolated domains induced by fragmentation inherits from the self-similar character of the coarsening structure: a power-law distribution of droplets is obtained[2].

As shown in Fig. 2, in conditions of viscous coarsening, domain growth results from series of hydrodynamic pinch-off events at small scale. However, the fragmentation at play here seems rather to be related to another hydrodynamic phenomenon, end-pinching[4] that strongly depends on the viscosity contrast between the two fluids. In the present context of phase separation, we could check that fragmentation was indeed due to the viscosity contrast. Only low viscosity domains show fragmentation[5].

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3.2 Posters A

Theory of rheology in confinement

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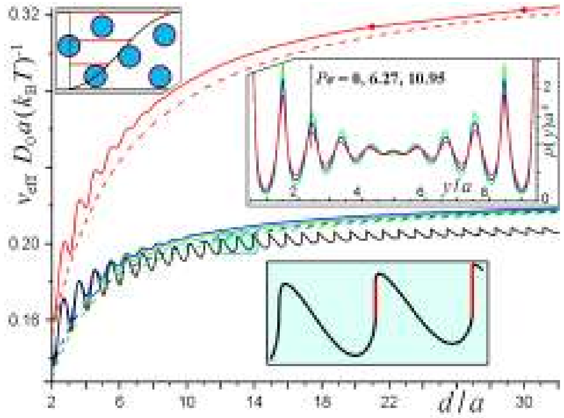

FIG. 1. Effective viscosity of a hard sphere fluid sheared between two walls as a function of the distance d between them for $Pe = 0, 6.27, 10.95, 20$ (full curves, top to bottom). Dashed curves represent corresponding estimates via the slip length computed for an isolated wall, Eq. (1). The lower inset shows enlarged segment of the lowest curve, where discontinuities as a function of d develop. $\Phi = 0.45$.

The viscosity of fluids is generally understood in terms of kinetic mechanisms, i.e., particle collisions, or thermodynamic ones as imposed through structural distortions upon e.g. applying shear. Often the former is less relevant, and (damped) Brownian particles are considered good fluid model systems. We formulate a general theoretical approach for rheology in confinement, based on the many particle diffusion equation, evaluated via classical density functional theory. We exemplify how simple closures yield the generic behavior of the viscosity in the case of a fluid between parallel hard walls, which had not been accessible by first principles theories before. We discuss how the effective viscosity between two parallel walls depends on the distance between the walls, and on driving velocity, and analyze how it may be understood in terms of a slip length of the fluid at the walls.

The Figure shows the resulting effective viscosity for hard spheres of average packing fraction $\Phi = 0.45$ for different Peclet numbers $Pe \equiv va^2/D_0 d$; v is the velocity of the moving wall, a and D_0 are respectively the spheres' diameter and diffusion coefficient. The upper curve shows the case of small Pe, i.e. linear response. The effective viscosity approaches a distance independent bulk value for $d \to \infty$, while it consistently reduces to smaller values for small d. For $d \lesssim 8a$, oscillations start to be visible.

In Ref. [1], using the model, we computed a slip length L of the suspension at a single wall under shear. A geometrical consideration suggests the following effective viscosity for the case of two parallel walls,

$$\nu_{\rm eff}(d) = \nu_{\rm eff}(d \to \infty)\frac{d}{d+2L}, \tag{1}$$

a function of L and of the viscosity for large d (bulk). The outcome of Eq. (1) is shown by dashed curves, where for small Pe, we have $L = 1.27$ [1]. Despite the mentioned oscillations in the curve, which are not reflected by Eq. (1), Eq. (1) gives an astonishingly good result for d as small as 2 particle diameters. We note that e.g. for $d = 3a$, the density of particles is rather inhomogeneous, while the effective viscosity is still well described by the estimate of Eq. (1).

Upon increasing the driving velocity, the asymptote for large d decreases, which is due to the well known phenomenon of shear thinning in bulk systems at intermediate values of Pe. Apart from this, the overall qualitative features are very similar to the discussed ones, in particular, Eq. (1) gives a very good estimate of the overall trend for larger rates as well. Regarding $Pe = 10.95$, we see that the oscillations in the viscosity extend to larger values of d. This is a clearly non-linear effect, as the higher rate causes changes in the density (see the upper inset), which for increasing rates develop the more pronounced oscillations, extending to larger d.

As found in simulations [2, 3], bulk suspensions show layering for certain densities and shear rates. The behavior of the viscosity in confinement is hence nontrivial. The considered model [1, 4] shows a layering instability for large Peclet numbers, upon which the particle density develops oscillations along the direction perpendicular to shear direction for arbitrarily large distances d. The lowest curve shows a state in which the bulk is layered ($Pe = 20$). In that case, we see that the effective viscosity is *unsteady* as a function of d, showing discrete jumps for $d \gtrsim 12a$ (see the lower inset), which can be understood by the underlying density profiles. At the jumps of $\nu_{\rm eff}(d)$, the density is discontinuous as well, as the number of layers is changed by one. Our analysis thus predicts that this discontinuity is also found in the viscosity. Last, we note that the relative height of the discontinuities decays as $1/d$, since for large d each individual layer contributes less to the total viscosity.

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Time Dependent Nonlinear Response in Glassy Systems

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Non-equilibrium kinetics determine non-equilibrium thermodynamics in microrheologically driven supercooled liquids

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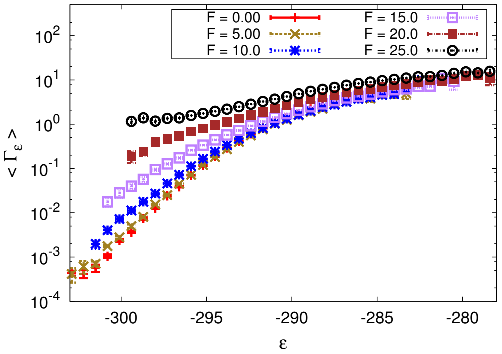

FIG. 1. Local escape rates Γ_ϵ to leave a basin of energy ϵ at different forces F.

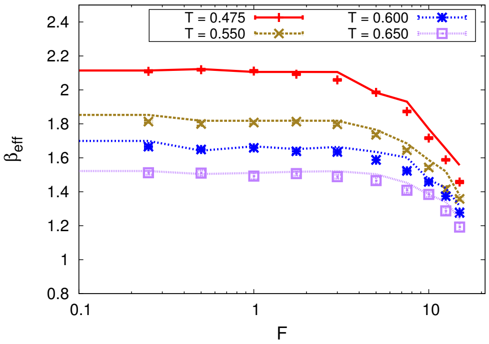

FIG. 2. Effective inverse thermal energy $\beta = \frac{1}{k_B T_{\text{eff}}}$ versus the external force F for different (bath) temperatures T.

In active microrheology, an external force field is applied on a small fraction or even single particles embedded in a complex material. In the last few years, this method has been extensively used to study the properties of glass forming system via experiments, theoretical methods as well as computer simulations [1]. In this field, one of the main challenges is the understanding of dynamical response at large field strengths at which the probed material falls out of equilibrium.

We study the dynamical response of a single probe particle pulled by an external force through a supercooled model liquid via computer simulations. Therein, we are particular interested in the path the system takes through its underlying Potential Energy Landscape (PEL) and how it is altered by the external forcing.

In our previous work we have analyzed the dynamics of the pulled particle in terms of hopping events between adjacent basins of the PEL, characterized by spatial displacements and local hopping rates [2, 3]. We could observe, that while the spatial displacements is exclusively responsible for the linear response at low force strengths, the main source of nonlinearity can be traced back to an nonlinear increase of the average hopping rate $\langle\Gamma\rangle_P$ [2].

The microscopic origin of the average hopping rate $\langle\Gamma\rangle_P$ relies in the structure of the PEL

$$\langle\Gamma\rangle_P = \int d\epsilon \; \Gamma_\epsilon(\epsilon) P(\epsilon) \tag{1}$$

where $\Gamma_\epsilon(\epsilon)$ denotes the escape rate of a basin of energy ϵ and $P(\epsilon)$ the probability that a basin of energy ϵ is visited. Understanding the force dependence of these quantities thus enables the understanding of the nonlinear response of the pulled particle dynamics in general.

In this talk, we demonstrate, how the application of the external force leads to a facilitation of the escape process from single basins which is as more pronounced as deeper the energy of basin is (Fig. 1). This energy-dependent increase of local escape rates leads to a redistribution of the basin population so that higher energies become more favorable. The resulting energy distribution is identical to an equilibrium distribution of the system at a higher temperature, so that it can be characterized by a force-dependent effective temperature $T_{\text{eff}}(F)$. By using the non-equilibrium escape rates, we are able to quantitatively predict the non-equilibrium temperature (see FIG. 2) [4]. We further put the effective temperature based on PEL arguments in relation to the effective temperature discussed in the context of non-equilibrium fluctuation-dissipation relations [5].

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Off-equilibrium surface tension in driven colloidal suspensions

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Surface tension between immiscible fluids is a well-understood and well-characterized phenomenon. By contrast, much less is known about the effective, off-equilibrium surface tension that arises when a (transient) interface is created between miscible fluids. This effective surface tension plays a key role in many driven phenomena, from jetting and drop formation and coalescence to precipitation and deposition, as it was already recognized more than 100 years ago by Korteweg [1], who first hypothesized that effective surface tensional stresses must be at work between two miscible fluids at contact. However, experimental investigations in this field remain scarce and the theoretical predictions by Korteweg have not quantitatively tested so far, to the best of our knowledge. We present a thorough experimental investigation of the Saffman-Taylor instability arising when a simple fluid (the solvent of a colloidal suspension) is pushed through a miscible, more viscous one (the colloidal suspension itself). We show [2] that the resulting interface pattern can be accounted for by the non-linear rheological properties of the suspension and an effective surface tension. By measuring the effective surface tension for suspensions at a variety of particle volume fractions, we successfully test Korteweg's theory. We moreover find that the effective surface tension increases with the size of the colloidal particles, a surprising result at odd with the typical behavior in atomic or colloidal systems at equilibrium, where the surface tension usually decreases as the squared particle size [3]. We rationalize this finding by showing that for our particles, microgel spheres composed of cross-linked polymers, the surface tension is dominated by the entropic contribution associated with the internal degrees of freedom of the polymers. Finally we present new data on the effective surface tension between suspensions of hard, compact particles and their own solvent. While we find little variation of the bulk rheological properties with particle kind, microgels and hard particles exhibit vastly different effective surface tension properties. We discuss this surprising result in view of available models for both bulk and interfacial stresses.

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Role of yield energy distributions in athermal amorphous materials under shear

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Encompassing very dissimilar systems (such as foams, pastes, or metallic glasses), amorphous materials are composed of particles that can have very different shapes and sizes, such as grains of sand in a sandpile or bubbles in a soap foam. Lacking a crystalline structure, they exhibit a structural disorder that turns out to play a determinant role in their mechanical properties, while challenging their very description. Several elastoplastic models have been developed at the mesoscopic scale, in order to account for the plasticity in such amorphous systems, such as the Soft-Glassy-Rheology (SGR) model [1, 2] and the Hébraud-Lequeux (HL) model [3]. These two mean-field models have proven to be rather successful in reproducing certain features observed in amorphous systems, but not all at once. Moreover, a consistent picture connecting these models is still missing.

Here we discuss the role of structural disorder in the mechanical properties of athermal amorphous materials under shear. We first argue, using a toy model, that the standard SGR model should be interpreted as a model for systems with *thermal* dynamics, while mean-field *athermal* dynamics, on the contrary, can be accounted for by the HL model, in which the mechanical noise stems explicitly from the plastic activity in the sheared medium. Then, focusing on the HL model, we show that the inclusion of structural disorder, by means of a distribution of yield energy barriers, has no qualitative effect on its predictions for the macroscopic stress σ_M at low shear rate $\dot{\gamma}$, while such a disorder is known to be one of the key ingredients leading kinematically to a finite macroscopic yield stress in the SGR model. More specifically, the possible scalings of σ_M with respect to $\dot{\gamma}$ are robust, and only their prefactors are modified. We characterize furthermore the dynamical distribution of local yield stress σ_c in the limit of low shear rate, as illustrated in Fig. 1 for its mean value $\overline{\sigma_c}$ as a function of the single control parameter of HL-like models, α_{eff}, that couples the amplitude of the mechanical noise to the plastic activity in the sheared material [4].

We conclude that the statistical mechanisms at play in amorphous materials at low shear rate are different, already at a mean-field level, depending on the thermal versus athermal nature of their underlying dynamics.

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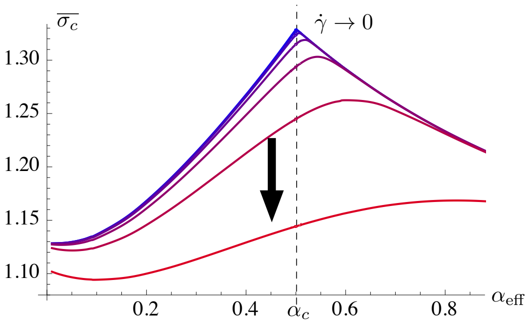

FIG. 1. Mean value of the dynamical distribution of local yield stress, in the stationary case at very low shear rate $\dot{\gamma}$. The different curves corresponds to increasing constant shear rates (blue to red) over six orders of magnitude.

Mechanical Response of Local Motifs in Deeply Supercooled Liquids

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Locally Favoured Structures (LFS) in supercooled liquids and glass formers consist in local particle motifs that are energetically favourable and that are a manifestation of transient short range order [1, 2]. These motifs have been observed in many different systems but the specific mechanism connecting such structural changes to the slow dynamics typical of glassy systems is still unclear.

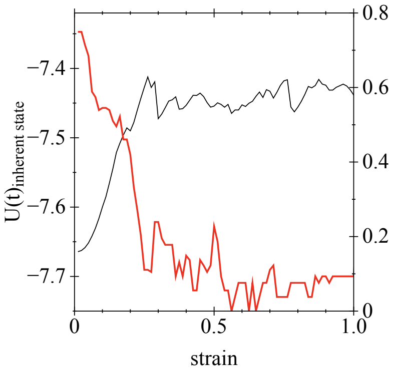

FIG. 1. Dependence of the inherent states potential energy on the applied strain (black curve) compared to the response in the structural parameter corresponding to the fraction of icosahedral particles (n_{13A}, red curve).

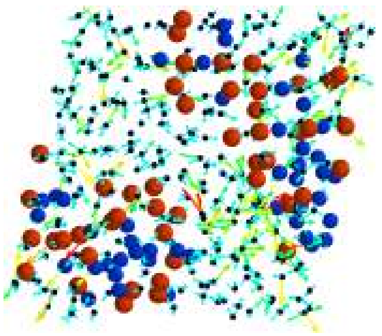

FIG. 2. A snapshot illustrating the distribution and the magnitude of soft modes (coloured arrows) with respect to the big (red) and small (blue) particles forming icosahedral clusters in a sheared configuration of the Wahnström binary mixture.

Employing biassed sampling techniques in trajectory space [3], we manage to obtain LFS-rich configurations (more than 40%) of a classical binary Lennard-Jones glass-former, presenting structural and dynamical properties typical of low temperature regimes that are inaccessible to standard molecular dynamics techniques. The role of the LFS in the increase of the solidity of the glass is explored via a simulated shearing experiment where, in the athermal quasi static limit [4–6], we are able to contrast the rise of shear transformation zones with the presence of connected clusters of icosahedrally ordered regions via local deformation and normal modes analysis . Plastic events and soft-modes of the density of states distribution are used in order to identify the localized events and rearrangements leading to the relaxation of the lateral stresses. We therefore quantify the emergence of the solid behaviour of the glass, associating its elastic response to the deformation of extensive regions in locally preferred clusters.

Our study shows that our "deeply supercooled" configurations are significantly more solid than conventional simulations. The emergence of solidity is shown via the analysis of local non-affine deformation to be strongly related to the LFS domains and that plastic events occur outside these regions.

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Correlated motion and diffusion in sheared athermal suspensions of deformable particles

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Athermal suspensions of deformable particles occur manifold in nature and technology. A statistical description of these far from equilibrium systems is, however, a challenging task. Central to the understanding of these systems is the fact that they can 'jam', i.e., they acquire a solid-like character above a certain critical particle concentration, yet often remain amorphous in structure [1, 2]. The jamming transition is typically associated with the emergence of correlated particle motion and dynamical heterogeneities [3]. While this issue has been the subject of numerous studies in the case of Brownian systems and athermal granular suspensions, concentrated soft particle suspensions consisting of vesicles or capsules have received less attention with regard to dynamic correlations and shear induced fluctuations [4, 5].

In view of the above mentioned theoretical interest and their relevance for biological and technical applications, we study here via computer simulations fluctuations of particle displacements and stresses in a sheared athermal suspension of deformable particles, covering volume fractions from the dilute up to the deeply jammed regime. Particles have the shape of red blood cells and interact only via hydrodynamics and short-range repulsive forces [6, 7]. Fluctuations are found to be generally anisotropic and the flow organizes into temporary shear bands at large particle concentrations. Fluctuation variances and relaxation times scale canonically with shear rate in the Newtonian regime and show a characteristic power-law scaling in the jammed state [8].

The statistical properties of the displacement and stress fluctuations are intimately related to the rheology and can be rationalized in terms of a dissipation balance that relates the variance of the instantaneous velocity fluctuations to the power injected by the shearing [9, 10]. Within this simple picture, the dependence of shear rate $\dot{\gamma}$ of the velocity fluctuations $\langle u^2 \rangle^{1/2}$, diffusivity D and velocity relaxation rate $1/\tau_v$ are all predicted to scale as $\propto \dot{\gamma}\eta^{0.5}$, with η being the effective viscosity. Simulation results are consistent with this theoretical expectation [10].

Useful discussions with Claus Heussinger and financial support by the DFG (project VA205/5-2) are acknowledged.

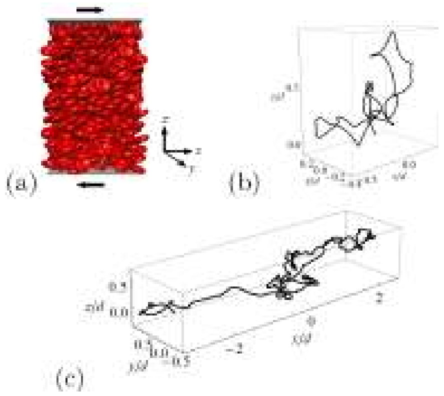

FIG. 1. (a) Sketch of the simulation setup. Walls move with constant velocity in ±x-direction to impose shear. (b) and (c) Typical particle trajectories for volume fractions of (b) $\phi = 24\%$ and (c) $\phi = 78\%$. The capillary number is in both cases Ca= 10^{-4} (Ca=$\eta_0 \dot{\gamma} r/\kappa$, where η_0, $\dot{\gamma}$, r and κ are the solvent viscosity, shear rate and the particle's radius and bending elasticity, respectively). In the both cases shown, the particles start off at the coordinate origin.

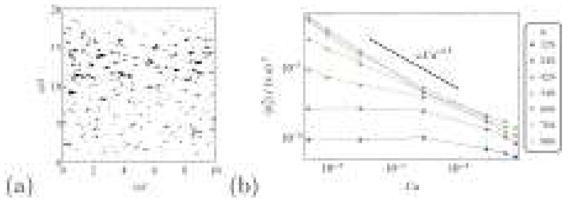

FIG. 2. (a) Typical snapshots of the particle velocity fluctuations in the shear plane for $\phi = 78\%$ (the average flow velocity is subtracted from displacements). It is visible that particles move in a strongly correlated manner. The capillary number is 10^{-4}. (b) Variances of the instantaneous velocity fluctuations in the vorticity direction (u_y) in dependence of the capillary number.

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On the origin of shear bands in a model glass former

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We study the mechanical response of a binary Lennard-Jones glass [1] by shearing with a constant strain rate via Lees-Edwards boundary conditions [2]. The observed steady-state flow curve is monotonic. However, the onset of flow is associated with spatial heterogeneities [3]. Highly mobile regions form a long-lived shear-band-like structure. The dynamical heterogeneities can be captured very well in the spatially resolved mean square displacement of particles.

To investigate the origin of these shear bands we identify the local events which are observed to be localized to one or two particles and generate quadrupolar strain fields.

We have also studied the effect of aging on the transient dynamics of the system. We find that the height of the stress overshoot in the stress-strain curve increases with longer waiting times. High temperature fluid state influences the stress peak, with its height decreasing with increase in the quenching temperature.

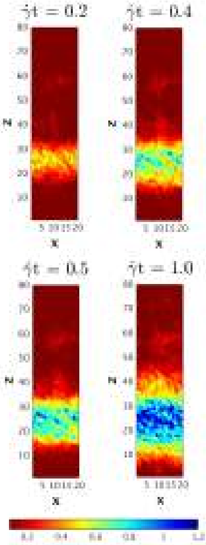

FIG. 1. Displacement maps for different strains. This sample is aged at temperature $T = 0.2$ until $t_\mathrm{w} = 10^4$ and sheared with a constant strain rate $\dot\gamma = 10^{-4}$.

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Continuum Mechanics Simulations in Glass Forming Liquids

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Dense liquids and glasses typically show complex nonlinear non-Newtonian flow behavior [1]. Typical effects of this nonlinear glassy rheology are shear thinning and yield stresses.

A phenomenological model to discuss the non-stationary non-linear rheology by incorporating the interplay of slow structural relaxation and flow-induced rearrangements, is so-called fluidity model. It relies on a Maxwell-type constitutive equation for the stress $\boldsymbol{\sigma}(t)$,

$$\overset{\triangledown}{\boldsymbol{\sigma}}(t) = G_\infty \boldsymbol{D}(t) - f(t)\boldsymbol{\sigma}(t), \tag{1}$$

where $\boldsymbol{D}$ and G_∞ are the symmetric shear-rate tensor and the low-frequency Maxwell plateau modulus, respectively. The symbol $\overset{\triangledown}{\boldsymbol{\sigma}}$ is the upper-convected derivative taking into account the change of the tensorial stresses due to flow advection.

The fluidity $f(t)$ is a local inverse relaxation time [2, 3]. We propose a variant of existing models where the fluidity is governed by the differential equation

$$\tau_f \dot{f}(y,t) = -\left(f(y,t) - \frac{1}{\tau_M(t)} \right) + D_f \nabla^2 f(y,t). \tag{2}$$

The steady-state relaxation time defined by $1/\tau_M = 1/\tau + |\dot{\gamma}|/\gamma_c$ includes shear thinning as the competition between the structural relaxation rate $1/\tau$ and the flow rate $\dot{\gamma}$ (where γ_c is a dimensionless model parameter).

The effect on the dynamics of a heterogeneous fluidity value is included by using the diffusion term $D_f \nabla^2 f$ in Eq. (2) [2]. D_f is related to a cooperativity length that describes to what extend a fluidized region spreads along its neighbors during flow, accounting for spatial heterogeneities [3].

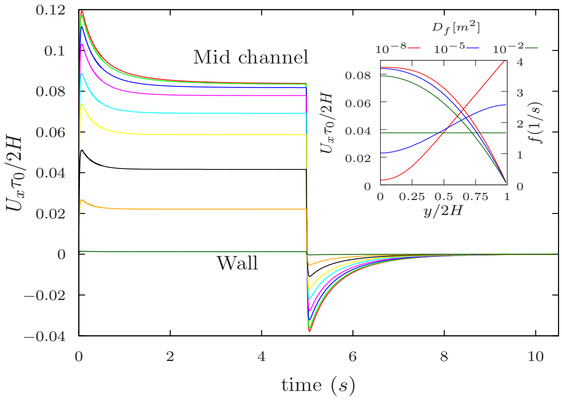

FIG. 1. Velocities centerlines at different positions of presure-driven flow in a channel. Inset: fluidity (right axis) and velocity (left axis) profiles for different D_f in steady state for half channel.

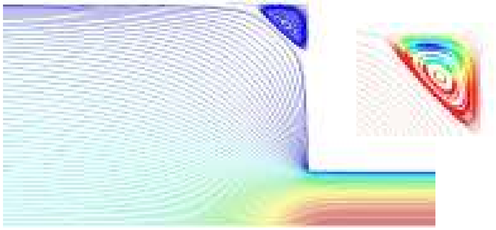

FIG. 2. Stream lines pattens and vortex found for a higher relaxation time fluid in a 4:1 contraction flow.

We use a computational fluid dynamics (CFD) tool based on finite volume method (FVM) to combine the resulting constitutive equation with Navier-Stokes equations. Diverse geometries like pressure driven flow, simple shear, and abrupt contractions during start-up flow and cessation flow are studied, henceforth they can be adapted to more complex systems.

Figure 1 shows the evolution of velocity in start-up and cessation flow at different positions in a planar channel. Fluidity and velocity profiles are in the inset for different diffusion coefficients D_f.

For low diffusion coefficients ($D_f \simeq 0$) typical non-Newtonian velocity low shear profile is formed in the center of the channel. This effect decreases for higher D_f making the profile parabolic-like. In this case the fluidity spreads uniformly along the channel becoming almost constant.

Other effects like vortex patterns found in abrupt contractions have also being studied for different time-dependent parameters. Velocity stream lines in steady state for a 4:1 contraction flow develop according to Fig. 2. Color map shows higher velocities with red color and lower velocities with blue. A close-up of the vortex indicates how the lowest velocities are distributed in that area.

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Spatiotemporal correlations between plastic events in the shear flow of amorphous solids: from molecular dynamics to mesoscopic models

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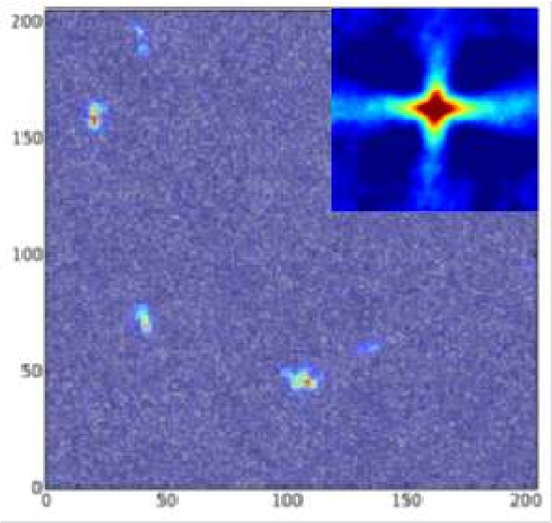

FIG. 1. Main figure: snapshot of particle configurations in a molecular dynamics simulations of a 2D amorphous packing under simple shear. Color indicates the amount of residual nonaffine displacements D^2 as a measure of plastic activity. The inset shows a map of the correlations between plastic events separated by a finite lag time.

The slow flow of dense amorphous solids exhibits striking heterogeneities: swift localised particle rearrangements take place in the midst of a more or less homogeneously deforming medium as can be seen in Fig. 1. Correlations and interactions between plastic events that involve of order 25 particles (in 2D) control the evolution of the strain field on much longer length and time scales. This contribution summarizes recent efforts by our group to develop a mesoscopic (coarse-grained) model of plastic flow that is systematically linked to atomistic molecular dynamics simulations. We first determine the time-dependent elastic response of an amorphous medium to an isolated plastic event and show that, despite large fluctuations, it can be modeled with the picture of 2D Eshelby inclusions with an elastic Green's function displaying quadrupolar symmetry, viz. $G(\mathbf{r},\mathbf{r}') \sim \cos(4\Theta)/(\mathbf{r}-\mathbf{r}')^2$ [1]. We then determine the full spatiotemporal correlation functions between elementary plastic events in a sheared athermal glassy solid,

$$\mathcal{C}_2\left(\Delta r, \Delta t\right) \equiv \left\langle \overline{D^2\left(r,t\right) D^2\left(r+\Delta r, t+\Delta t\right)} \right\rangle - \left\langle \overline{D^2\left(r,t\right)} \cdot \overline{D^2\left(r,t+\Delta t\right)} \right\rangle, \qquad (1)$$

where D^2 is the local residual non-affine displacement of a particle. The inset of Fig. 1 shows an example of these correlations, which build up throughout the material with a rate consistent with the velocity of shear waves. Our mesoscopic description builds upon the picture of localized, short-lived and highly dissipative events observed in the MD simulations by considering elastoplastic blocks of size of a rearranging region. Upon reaching a local yield stress drawn from a disorder distribution, elastic interactions occur instantaneously and the local stress evolves according to

$$\dot{\sigma}(\mathbf{r}) = \mu\dot{\epsilon} + 2\mu \int dr' G(\mathbf{r},\mathbf{r}')\dot{\epsilon}_{\mathrm{pl}}(\mathbf{r}'). \qquad (2)$$

We achieve excellent agreement for all aspects of bulk rheology between atomistic simulations and this class of mesoscopic models. Quadrupolar plastic correlations (see Fig. 1) are also successfully reproduced, but we find that the mesoscopic simulations overemphasize buildup and anisotropy of the correlations seen in molecular dynamics. Achieving quantitative agreement therefore requires considering additional physics. In particular, including the effect of elastic heterogeneity on the propagation of shear waves, their finite propagation speed, and distributions of the shear angles of plastic events appears to be required. Preliminary results from a dynamical finite element formulation of the mesoscopic model that takes these points into account will be discussed.

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Universal features in the rheological response of yield stress materials beyond critical exponents

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In order to establish a better understanding of the necessary ingredients for coarse grained models of athermally sheared yield stress materials, we explore within molecular dynamics simulations of a bidisperse Lennard-Jones system several assumptions that are commonly incorporated in mean field descriptions. We focus here on the Hébraud-Lequeux Model [1], that we believe to be a good candidate to describe the underlying athermal dynamics [2, 3].

Within our analysis we probe a constant relation predicted by this model between the macroscopic dynamical yield stress σ_Y and the prefactor A in the Herschel Bulkley law for the rheological response to steady shear, $\sigma_{xy} = \sigma_Y + A\dot{\gamma}^{1/2}$. This nonlinear relation links the macroscopic stress σ_{xy} to the imposed shear rate $\dot{\gamma}$.

The mean field calculations suggest that this constant relation, once adimensionalized, should only depend on the coupling constant α between the rate of plastic activity and a resulting diffusion in the mesoscopic stresses. We find that in a regime where the flow curve can be well fitted through the suggested Herschel Bulkley form (see Fig. 1(a)), the effective noise in the coarse grained shear stress can indeed be approximated by a diffusion process. Further the constant relation seems to be well represented through the mean-field model predictions (see Fig. 1(b)). The only discrepancies we find can be explained to be a result of oversimplifications of the relaxation dynamics. But interestingly, both the constant relation as well as the coupling constant α between activity and stress diffusion appears to be density independent.

This points towards a possibly universal relation between these quantities in systems with homogeneous flow transitions and a tempting qualification of sheared disordered systems through the coupling constant α.

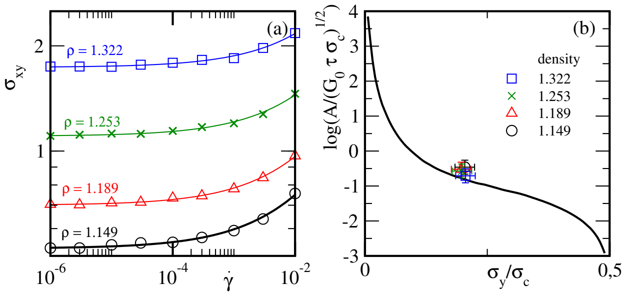

FIG. 1. Left panel: Flow curves, that is macroscopic stress as a function of applied shear rate, obtained for different densities in the microscopic dynamics simulations. Straight lines are fits with Herschel Bulkley curves $\sigma_{xy} = \sigma_y + A\dot{\gamma}^{1/2}$ Right panel: Prefactor in the Herschel-Bulkley fit as a function of the macroscopic yield stress in adimensional units compared to the Hébraud-Lequeux prediction (straight line).

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Yield stress and elasticity influence on surface tension measurements

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Yield stress fluids are present in many fields of everyday life and industry. The bulk flows are well characterized by the empirical Herschel-Bulkley or Bingham laws. But in numerous applications (coating, droplets, imbibition…), the fluid is confined by interfaces, either solid or fluid, so that its behavior does not quite comply with the bulk models [1].

Among other factors, reducing the scale implies an increase of the surface to volume ratio and of the role of the surface tension γ which competes with the yield stress σ_Y. However, at small scales $L \ll \gamma/\sigma_Y$, we expect the yield stress to play a negligible role on the shape of the system, which allows static measurements of the surface tension. Surface tension measurements have already been made with yield stress fluids, but for the same fluid, different values can be found in the literature [2, 3].

We have used a capillary bridge tensiometer (home-made setup) to measure the surface tension of carbopol gels of different concentrations and yield stresses, keeping $\sigma_Y L/\gamma$ between 0.01 and 0.5. It appears that what is measured is an effective surface tension depending on the yield stress of the fluid and on the flow history. More precisely, the effective surface tension measured after stretching of the bridge is always higher than after compression and the difference is greater when the yield stress increases.

The experimental results have been compared to a simple elastoplastic model. With only few physical ingredients, the experimental curves can be faithfully reproduced (see Fig. 2). As the geometry of the bridge is always intermediate between a filament and a flat cylinder, both approximations were tested, without any qualitative difference. Moreover, the shape of successive stretching-compression cycles can be described taking into account the elasticity of the fluid.

This work highlights several points. First, capillary bridges are convenient systems to study both surface tension and rheological properties of complex fluids, and this in spite of their apparently complicated geometry. Secondly, the influence on equilibrium properties measurements of physical characteristics maintaining the system out of equilibrium cannot be evaluated by such a simple dimensionless number comparing energies. Here, even if the dimensionless number introduced above is small, the influence of the yield stress can hinder the measurement of surface tension. Finally, in surface tension measurements of complex fluids, the flow history must be taken into account to explain different values for the same fluid.

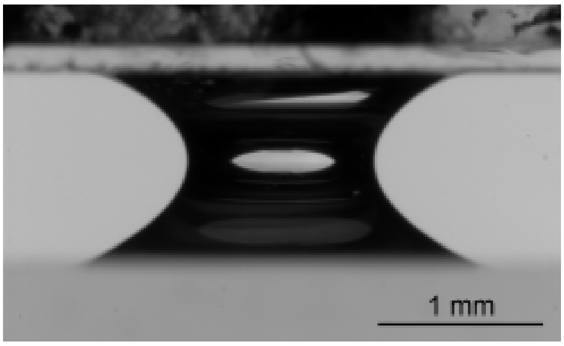

FIG. 1. Capillary bridge of carbopol gel with yield stress $\sigma_Y = 19\,\text{Pa}$ between two horizontal glass plates. The white stain in the middle is only a reflect.

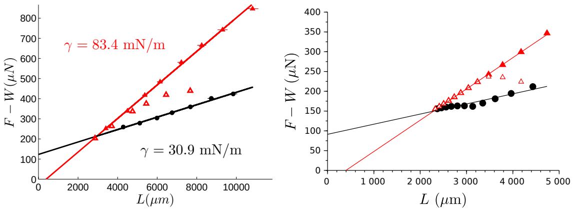

FIG. 2. Left: typical experimental curve, for $\sigma_Y = 16$ Pa and $G' = 80$ Pa. The slopes of the two linear fits represent the effective surface tension while stretching the bridge (red) and compressing it (black). $F - W$ is the measured force minus a correction for the weight of the droplet. L is a length combining the radius and the curvature of the bridge at the neck.
Right: typical curve from the model, with $\sigma_Y = 5$ Pa and $G' = 10$ Pa.

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Rheology and internal dynamics of dense nanoemulsions across the glass and the jamming regimes

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We discuss rheology and local internal dynamics of concentrated silicone oil-in-water emulsions, amorphous disordered solids composed of repulsive and deformable soft colloidal spheres. Based on recent results from simulation and theory, we derive quantitative predictions for the dependences of the elastic shear modulus and the yield stress on the effective droplet volume fraction [1]. The remarkable agreement with experiments we observe supports the scenario that the repulsive glass and the jammed state can be clearly identified in the rheology of soft spheres at finite temperature while crossing continuously from a liquid to a highly compressed yet disordered solid [2]. We show that the onset of elasticity due to entropic contribution can be described by a quasi-equilibrium analytical model of linear elasticity that includes energetic contributions from entropy and soft interfacial deformation [3] .

For emulsions of nanoscale droplets, known as nanoemulsions, the radius R begins to approach the Debye screening length, λ_D. Such charge-stabilized nanoemulsions, after having been repeatedly fractionated using ultracentrifugation to provide uniform droplet sizes, can become elastic solids at very low droplet volume fractions, even as low as about $\phi \simeq 0.2$ [4, 5]. By changing the droplet size and/or the electrolyte concentration the stiffness of the interaction potential can be tuned over a significant range.

Using dynamic light scattering at $\Theta \sim 160°$ we study the internal dynamics of uniform concentrated nanoemulsions. The mean size of the droplets is chosen to be of the order of $d = 200 \pm 30$nm such that the scattering wave number q lies close to or above the first peak of the static structure factor. The size polydispersity is roughly 20%, thus sufficiently high to suppress crystallisation. We monitor the self- intermediate scattering or field correlation function $g_1(t)$ of singly scattered light across the glass and the jamming transition by varying the droplet concentration in small steps.

Figure 1 shows preliminary results for the evolution of the correlation function $g_1(t)$. The hallmarks of the glass transition are clearly present such as the divergence of the structural long relaxation time and the increase of the plateau height for concentrations above dynamical arrest [6]. Experiments are currently underway, and should be completed by the end of April 2015, to carefully map out the transition and thus investigate the properties of the glass and jamming transition for interaction potentials of different stiffness across all relevant regimes.

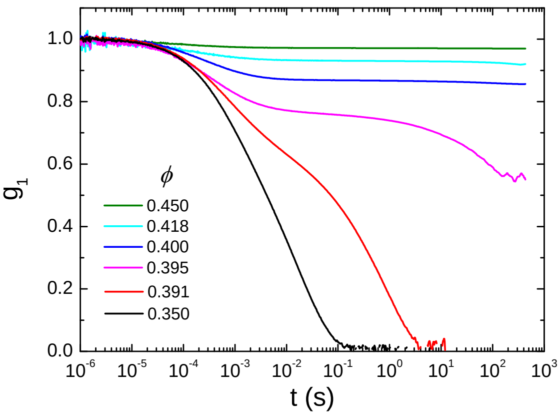

FIG. 1. Internal dynamics of dense nanoemulsions with a mean droplet size $d \sim 200$nm: Self-intermediate scattering function from a dynamic light scattering experiments near backscattering for different droplet volume fractions ϕ (see legend).

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Active microrheology below the delocalization transition

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In active microrheology, a strong external force is applied to a colloidal probe immersed in a complex fluid. As a result, the probe particle is displaced, yielding information about the local viscoelastic properties. For soft solids there is a delocalization transition when the force on the probe particle is large enough to pull it free [1]. We study the long time limit of the spatial probability distribution of a tracer particle in a glassy host as seen by active microrheology in constant force mode (cf. Fig 1).

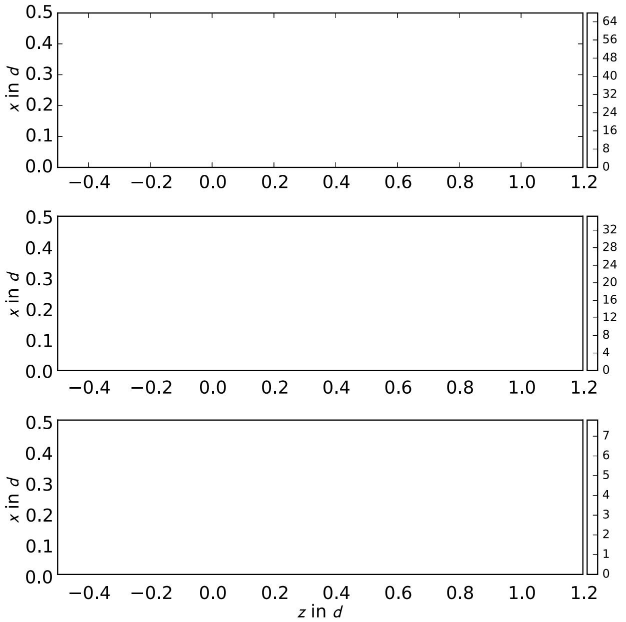

FIG. 1. Long time limit of the self part of the van Hove function $G_s(\boldsymbol{r}, t \to \infty)$ of the tracer particle in the localized state for a packing fraction of $\phi = 0.516$ (slightly above the MCT glass transition) for different external forces acting in positive z-direction. A delocalization transition occurs at an external force of about $24\,k_\mathrm{B}T/d$.

Our model system is a bath of hard spheres of diameter d performing Brownian motion and an actively pulled hard sphere tracer particle of diameter d_s. The spatial probability distribution is obtained from mode-coupling theory (MCT) refining the previous model [2] by decomposing the mobility-tensor kernel as suggested by [3]. This procedures enables us to reach even larger forces maintaining physically meaningful results.

There show up highly nonlinear effects already below the critical force, for example in mean and mean square displacements are (cf. Fig. 2). We attribute this behaviour to the emergence of exponentially decaying tails of the probability distribution in the direction perpendicular and parallel to the applied force (cf. Fig 3), which can also be found in molecular dynamic computer simulations.

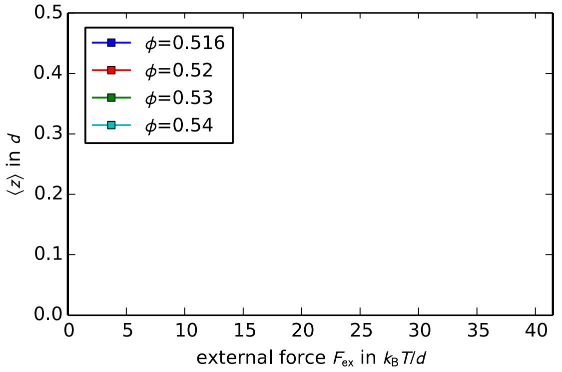

FIG. 2. Mean displacement of the tracer particle for different forces and packing fractions. The white symbols are the values taken from [2].

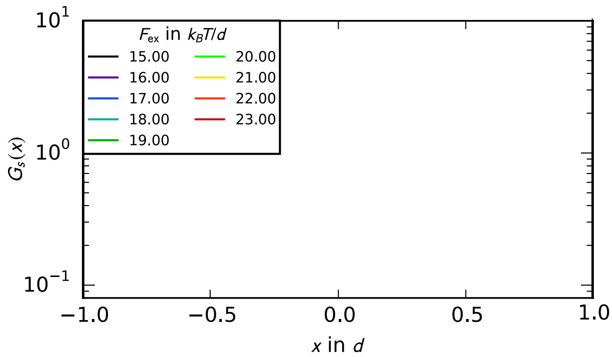

FIG. 3. Marginal distribution of G_s in direction perpendicular to the direction of the external force for a packing fraction of $\phi = 0.516$.

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Sliding of viscoelastic Non-Newtonian drops

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Moving droplets, coating flows and spreading films are ubiquitous in nature and technology: they are frequently recurrent in a huge variety of situations which are relevant not only for fundamental research, but also for an ample variety of concrete applications (see [1–3] and references therein).

The spreading and motion of a droplet on a smooth solid surface has also received much attention because of the singularity that occurs at the contact line, where the competition between capillary forces and viscous dissipation results in a singular problem [4, 5].

Most complex fluids encountered in practice exhibit a number of different non-Newtonian properties. Notably, concentrated polymer solutions often exhibit both shear-thinning and normal stress effects [6]. Shear thinning was even proposed as mitigating the moving contact line singularity: if the viscosity of the liquid decreases monotonically with increasing shear stress, then there will still be an infinite shear stress, but the stress singularity will be integrable, yielding a finite force at the substrate Some experimental studies analyzed the spreading of a polymer solution [7], focusing on the role of a shear-rate dependence of the viscosity and the existence of normal stresses. For the former, the spreading behaviour was found not to deviate strongly from the Newtonian laws.

In this study we perform an experimental study to characterize the motion of drops of polymer solutions of PAA and Xanthan at different polymer concentrations, sliding over homogeneous and inclined surfaces We systematically investigate the effect of polymer concentration on the macroscopic motion of the droplets above the critical Bond number, i.e. the critical dimensionless force needed to depin the drop before it starts to move. Beyond the critical Bond number, we characterize the motion of these droplet by studying the relation between the average dimensionless velocity and the applied volume forces (see Fig. 1). Results from experiments are complemented with numerical simulations for the "idealized" problem of a FENE-P droplet. The numerical simulations are quite useful to study the average speed of the droplet and address systematically the importance of the various free parameters in the FENE-P model and visualize the distribution of the polymer feedback stresses during the motion of the droplet, thus correlating the distribution of those stresses to the interface shape and the resulting macroscopic velocity.

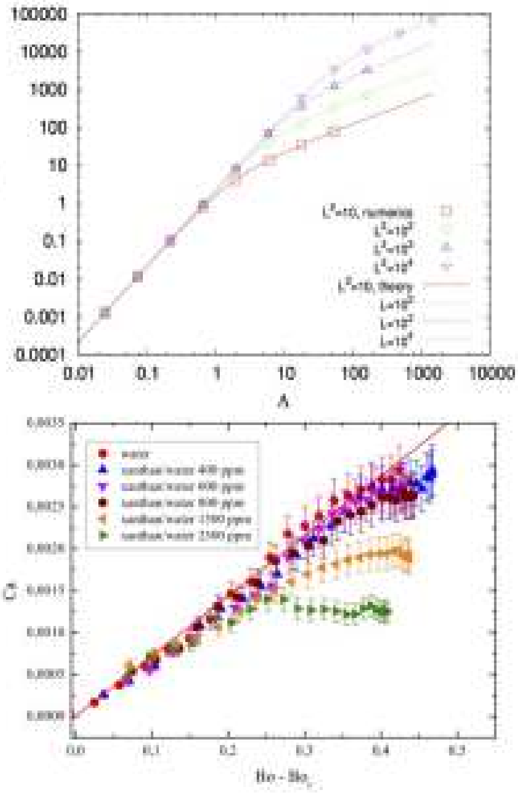

FIG. 1. Top Panel: Normal Stress Difference as a function of the dimensional shear.the polymer shear viscosity η_S developed in steady shear flow as a function of the dimensionless shear $\Lambda = \dot{\gamma}\tau_P$, with $\dot{\gamma}$ the shear rate and τ_P the polymer relaxation time. Different values of the finite extensibility parameter L^2 are considered. Bottom Panel: Bottom panel: dimensionless Ca vs $Bo - Bo_c$ trend for water and Xanthan/water solutions.

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Shear induced melting in repulsive systems with short-ranged attractive interactions

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The relaxation behavior of an arrested colloidal suspension, on application of a steady shear is investigated using the mode-coupling theory (MCT) of glass transition [1]. We study the rheological properties of a system of mono-dispersed particles interacting via a hard-sphere potential plus a short-ranged attraction. The theoretical model established by Fuchs and Cates using MCT via integration through transients approach (ITT-MCT) [2] is used for studying a square-well system (SWS) [3] in details by varying the relevant parameters: packing fraction φ, attraction range δ and attraction strength Γ.

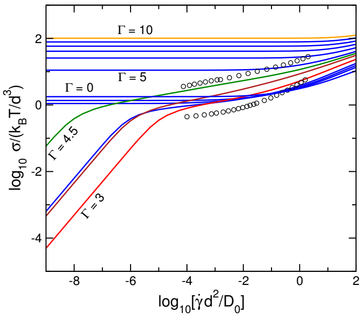

FIG. 1. Steady-state shear stress σ in response to shear rate $\dot{\gamma}$ (flow curves), for a square-well system at packing fraction $\varphi = 0.525$, attraction range $\delta = 0.04$, and attraction strengths $\Gamma = 0$, 1, 1.5, 2, 3, 4, 4.5, 5, 6, 7, 8, 9, and 10. Symbols are experimental data from Ref. [4].

The quiescent glass transition diagram for a SWS shows that for a fixed attraction range δ if the attraction strength Γ is increased at a fixed packing fraction φ, a reentrant behavior is observed: for small attractions a repulsive glass is formed due to caging of the particles which melts upon increasing the attraction strength. However, at high enough attraction strengths attractive glass is formed due to bonding between the colloidal particles. In Fig. 1, we mark the signature of this reentry phenomenon in the flow behavior of the system by obtaining the response of the steady-state shear stress σ to the applied shear rate $\dot{\gamma}$. A non-vanishing yield stress $\lim_{\dot{\gamma}\to 0} \sigma = \sigma_y > 0$ develops characterizing the strength of the glass: for a repulsive glass σ_y is of the order of k_BT/d^3, set by entropic energy-density scale while for attractive glass σ_y is of the order of $(k_BT)\delta/d$, set by attraction-dominated energy-density scale and is much larger as compared to the repulsive counterpart. The yield stress vanishes for intermediate attraction strength. Experimental data for a colloid–polymer mixture [4] (symbols) agree reasonably well with our model.

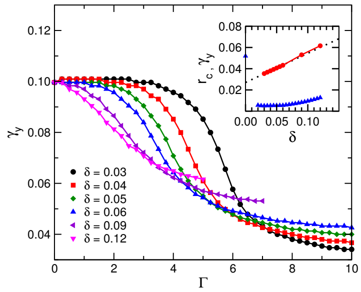

FIG. 2. Yield strain γ_y for different attraction range δ at packing fraction $\phi = 0.535$, as a function of attraction strength Γ (for a shear rate $\dot{\gamma} = 0.1d^2/D_0$, where D_0 is the free-diffusion coefficient of the particles). The inset shows the dependence of the large-Γ asymptote on δ (circle). A dotted line indicates a linear relation. The triangles indicate the equilibrium single-particle localization length r_c at the same state points.

In Fig. 2, we investigate the yielding behavior of the SWS extensively for the states dominated by repulsion and attraction and observe that the attractive glass is marked by a much smaller yield strain as compared to the repulsive glass. The observation is consistent with experiments [4], where it is observed that the repulsive glasses yield around 10% of particle diameter satisfying the Lindemann's criterion while attractive glasses yield at smaller yield strains. Experiments also report a two-step yielding for an attractive system, which is beyond the scope of the MCT model considered here.

In an ongoing work, we have extended the ITT-MCT model to study the nonlinear rheology of a binary mixture. Some recent experiments indicate that highly asymmetric binary mixtures, *i.e.*, mixtures with size-ratio $\delta \sim 0.1$, are expected to exhibit properties similar to attraction dominated colloid-polymer mixtures. Thus, the model formulated will be used to investigate highly asymmetric binary mixtures and to test the above mentioned experimental observation.

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Rearrangements and plasticity in two-dimensional sheared foams

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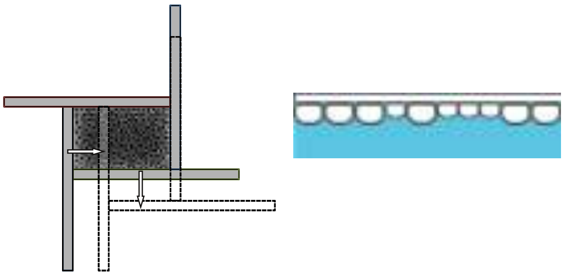

FIG. 1. Schematic of our bi-axial shear setup. (left) Illustration of the application of a pure shear deformation to a two-dimensional packing of foam bubbles. (right) Sideview, illustrating the bi-disperse monolayer of bubbles.

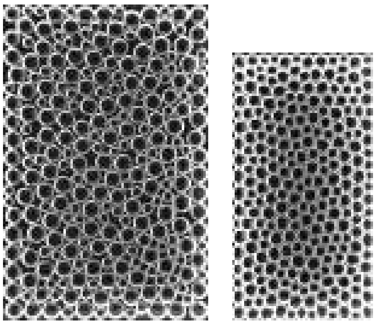

FIG. 2. Two examples of foam samples. (left) Low-density foam, $\phi \approx 0.87$. (right) High-density foam, $\phi \approx 0.99$.

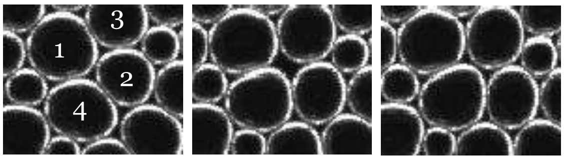

FIG. 3. An example of a T1 event in a high-density sytem. Bubbles 1 and 2 are initially nearest neighbors and become next-nearest neighbors after the event. Bubbles 3 and 4 are initially next-nearest neighbors and become nearest neighbors.

We experimentally apply a slow pure shear deformation to a quasi-two-dimensional foam under glass-liquid boundary conditions (Fig. 1) [1]. Most research has focussed the behavior of dense systems, such as Lennard-Jones glasses [2–4] and densely packed foams [2, 5–7]. We have focussed on varying the packing density (Fig. 2), and compare the behavior of wet foams, near the jamming transition, to that of dry foams.

The behaviour close to jamming is qualitatively very different from that of dense systems: While localized T1 events (Fig. 3) dominate the behavior of dry foams, for wetter foams the rearrangements become less localized and events lose their quadrupolar nature. We quantify the response using the temporal and spatial structure of rearrangements, as well as by measuring the onset of plasticity and irreversibility.

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Non-locality of effective temperature in a shear driven model glass

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The issue of effective temperature for driven out of equilibrium systems has been the subject of a number of theoretical and numerical studies [1]. The effective temperature reflects the fluctuations of the system at large time scales, relevant for the slow structural relaxation [2]. In this study, a massive tracer particle, whose average kinetic energy reflects the temperature associated with its momentum fluctuations, is used as a thermometer [1]. To asses the reliability of the obtained effective temperature, we first show that the immersed massive tracers hardly affect the inherent structural relaxation. Moreover, it is shown that the use of atomistically rough solid walls removes the conceptual problem related to the violation of the equipartition theorem in molecular dynamics simulations with PBC in systems with a heterogeneous mass distribution [3, 4].

The focus of this talk is on the non-local character of the effective temperature studied in a binary Lennard-Jones glass [5]. We propose a model which relates the effective temperature at a given point in space to the plastic activity and correlations thereof in the surrounding medium. In such a system, fluctuations have two distinct source: (i) quiescent fluctuations and (ii) fluctuations induced by the imposed shear. Correspondingly, effective temperature is thus written as,

$$T_{\rm eff}(\boldsymbol{r}) = T_{\rm eff}^{\rm quiescent}(\boldsymbol{r}) + T_{\rm eff}^{\rm shear}(\boldsymbol{r}) \ , \qquad (1)$$

where $T_{\rm eff}^{\rm quiescent}(\boldsymbol{r})$ and $T_{\rm eff}^{\rm shear}(\boldsymbol{r})$ represents temperature associated with (i) and (ii), respectively. $T_{\rm eff}^{\rm quiescent}(\boldsymbol{r})$ is obtained in the absence of the external shear and it has a uniform profile in the channel. This term dominates $T_{\rm eff}$ in the supercooled and equilibrium states, as shown in the inset of Fig. 1. In contrary, deep in the glassy state, $T_{\rm eff}^{\rm shear}(\boldsymbol{r})$ is the dominant term, which reflects shear-induced stress fluctuations mediated by the elastic medium,

$$T_{\rm eff}^{\rm shear}(\boldsymbol{r}) = \Big(c\dot{\gamma}^{\alpha}(\boldsymbol{r})\Big)^2 + \sum_{\boldsymbol{r}'\neq\boldsymbol{r}} \left(c\frac{\dot{\gamma}^{\alpha}(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|^3}\right)^2 , \qquad (2)$$

where c incorporates information about the stress associated with an elementary unit of rearrangement and its size, $\dot{\gamma}^{\alpha}(\boldsymbol{r}')$ represents frequency of the rearrangements at $\boldsymbol{r}'$, and $1/|\boldsymbol{r}-\boldsymbol{r}'|^3$ is associated with stress propagation from $\boldsymbol{r}'$ to $\boldsymbol{r}$. It is shown that including non-local effects in $T_{\rm eff}^{\rm shear}$ via Eq. (2) is necessary for an adequate description of the simulation results on $T_{\rm eff}$ (Fig. 1) [6]. In particular, a model which neglects the non-local term in Eq. (2) shows significant deviations at low shear rates, where glassy dynamics is most prevalent.

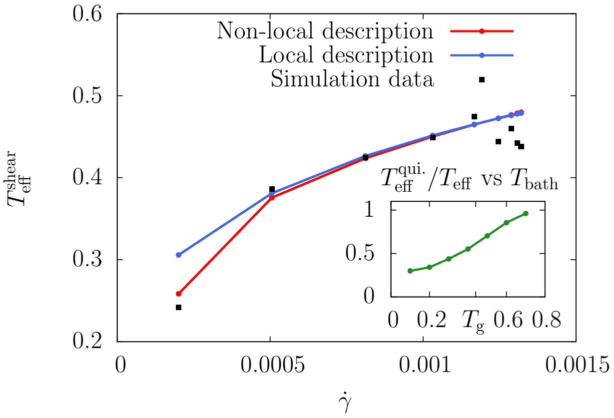

FIG. 1: Comparison of the non-local description $T_{\rm eff}$, Eq. (2), and simulation results. The local description refers to only the first term of Eq. (2). The inset depicts the contribution of the quiescent fluctuations to $T_{\rm eff}$ as a function $T_{\rm bath}$, the ambient temperature.

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Jamming vs Caging in Three Dimensional Jamming Percolation

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Kinetically-constrained models (KCM) [1] are widely used in the study of jamming and glass transitions in granular and amorphous materials. These lattice gas (or Ising) models are characterized by having a restricting set of rules for particle movement (or spin flip) which depends on the state of a given site's neighbors. Due to their simplicity KCM provide a convenient framework for both numeric and analytic work, and allow qualitative analysis of complex systems. Most KCM become jammed only at the limit of zero temperature (Ising spins) or equivalently full occupation (lattice gas) [2] or when considering finite-sized [3] or confined systems [4].

An interesting exception is the Spiral Model [5], which has been proven to undergo a directed percolation phase transition at $\rho_J^{2D} \approx 0.65$. We have extended the rules of the Spiral Model (Fig. 1a) to a three dimensional model [6] (Fig. 1b) in which a similar phase transition occurs at $\rho_J^{3D} \approx 0.35$. At these critical densities percolating clusters of jammed particles form in the shape of one dimensional strings that span the entire system. In the 2D spiral model cages are formed, confining mobile particles from traversing the system. However in our 3D model just above ρ_J^{3D} most cavities remain connected and mobile particles use the third dimension to travel between them and thus exhibit long-time diffusive behavior [6], hence caging does not play a substantial role at ρ_J^{3D}.

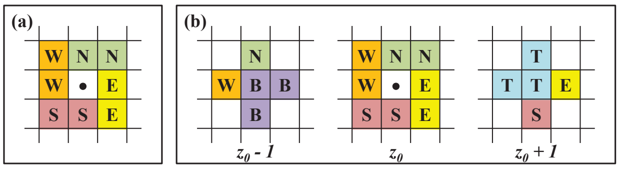

FIG. 1. (a) The 2D spiral model is defined on the square lattice such that site (•) is unblocked if its ((W *or* E) *and* (S *or* N)) sets are completely empty. (b) Our 3D model is defined on the cubic lattice by requiring that the sets ((W *or* E) *and* (S *or* N) *and* (B *or* T)) are completely empty. Here slices from three consecutive layers are shown side by side.

To investigate this diffusive behavior we avoid running long dynamic simulations and instead use a culling algorithm; by removing all mobile particles from the system we remain only with the jammed clusters. This enables us to consider very large systems and to reach arbitrarily close to the transition on both of its sides. We study about the dynamics of our model by understanding the static geometric structures that form and eventually confine the mobile particles above some second critical caging density ρ_C^{3D} , which differs from the previously studied critical jamming density ρ_J^{3D} .

In our 3D model slightly above ρ_J^{3D} the system mostly consists of one large cavity, with a size that scales with the volume of the system (Fig. 2). We investigate the second critical density ρ_C^{3D} at which the jammed one-dimensional paths become thick enough to break the major cavity into multiple smaller cages. By choosing the order parameter to be the maximal cage size in the system we observe two phase transitions - the first at ρ_J^{3D} where jammed particles begin to appear and the second at ρ_C^{3D} where the major cavity is divided into smaller cages which have a typical size that does not scale with system size.

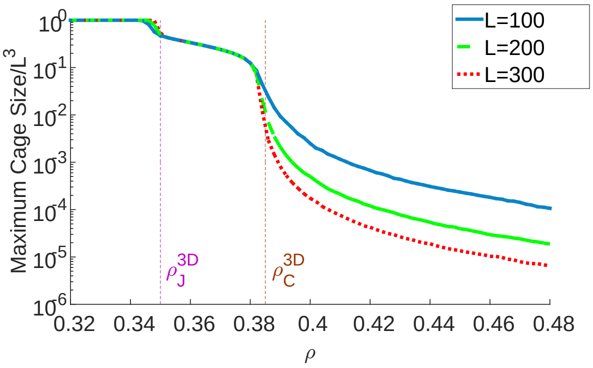

FIG. 2. For different system sizes (see legend) the maximum cage size undergoes two phase transitions. Before the first critical density for jamming ρ_J^{3D} the maximum cage size consists of the entire system. After the first critical density the maximum cage size is smaller but scales with L^3 . After the second transition at ρ_C^{3D} the maximum cage size no longer scales with the system's size.

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Yielding of soft glasses under applied shear

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Introduction. Understanding the rheological properties of soft amorphous materials, from a microscopic point of view, remains a challenging problem. In particular, an important question is how a quiescient glass yields under applied mechanical perturbation and whether the nature of that perturbation determines the yielding scenario. Using numerical simulations, we have studied the onset of flow in model soft glasses. Our studies investigate the yielding scenario for the case when the developed stress field is spatially uniform, e.g. in Couette flow, as well as where it is spatially non-uniform, e.g. in Poiseuille flow.

Couette Flow. When a spatially uniform shear stress is imposed on a confined glass, we observe that the time scale for the onset of steady flow diverges with decreasing stress [1]. The transient regime, prior to onset of steady flow, is characterised by long-lived spatial heterogeneities, the extent of which depends on the age of the glass. Below the yield threshold, persistent creep in the form of shear-banded structures is observed; see Fig. 1(a). By combining simulations and experiments, we have further studied this increasing mobility under applied stress, which has revealed the existence of quantitative correlations between macroscopic strain and single particle displacements in the transient regime [2]. In our ongoing work, we consider the case of using imposed strain rate as a control parameter and characterise the transient dynamics which are characteristic of the yielding process [3].

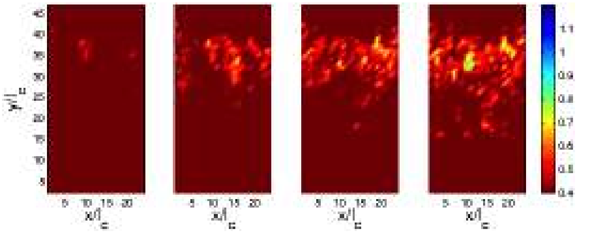

FIG. 1. Maps showing the time evolution of local displacements during creep flow in a Couette setup. From Ref. [1].

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Poiseuille Flow. To investigate the nature of the yielding process when a non-uniform stress field is imposed, we have studied the onset of Poiseuille flow in confinements corresponding to typical microfluidic channels [4]. Here, too, diverging timescales with decreased forcing is observed. However, the divergence occurs at a stress larger than the bulk value, with the gap increasing with decreasing channel width. For narrow channels, yielding happens via a rapid transition with the simultaneous fluidization of regions having different local stresses; see Fig. 2.

Summary. Our studies elucidate the spatio-temporal evolution of the local dynamics as a quiescent glass yields under different shear protocols. We demonstrate that dynamical heterogeneities are characteristic to the yielding process and can be temporally persistent around yielding thresholds. Further, if the applied stress is spatially non-uniform, an interplay with spatial confinement can deviate the yield threshold from the bulk value. In all these cases, the history of sample preparation plays a role in determining the transient dynamics, even leading to hysteretic effects.

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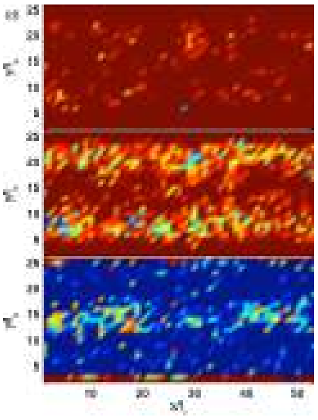

FIG. 2. Maps showing the time evolution of local displacements during onset of Poiseuille flow. From Ref. [4].

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Shear transformation zones: State determined or protocol dependent?

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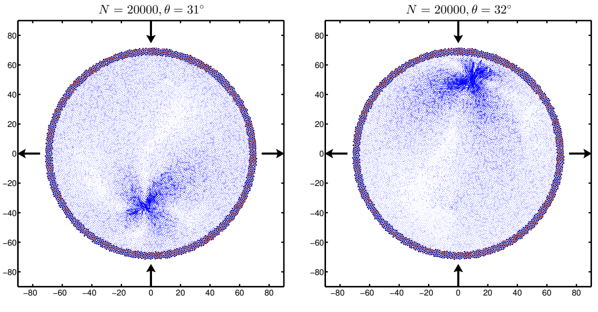
A shear-transformation-zone (STZ) is visualized as a localized group of molecules in an amorphous solid that undergoes a plastic event when an external mechanical load is applied. In the development of the theory of plasticity in amorphous solids, it is still not well understood whether an STZ is a *region* existing in the material that can be determined from the analysis of the unloaded material or it is an *event* that depends on the loading protocol, where small changes in the protocol lead to a different event. In this work we present strong evidence that the plastic events are protocol dependent and any infinitesimal changes in it result in a macroscopic change in the position of the first plastic event [1].

There are two approaches to study plastic response in amorphous materials. The first considers plasticity resulting from the existence of STZs in the material that are more sensitive to external load [2]. The other approach is to think of plasticity as an instability resulting from a protocol of an increase in the external load [3, 4]. This instability can be understood by analyzing the Hessian matrix of the material with the lowest eigenvalue approaching to zero. We perform simple numerical simulations that can decide between the two possibilities.

We consider a 2-dimensional binary (glass forming) Lennard-Jones mixture of N particles with circular symmetry, the details of which can be found in Ref. [1]. The system is loaded athermally and quasi-statically, pulling along the x-axis and compressing along the y-axis. The area preserving affine step is:

$$x' = x(1+\delta\gamma) \; ; \quad y' = y/(1+\delta\gamma) \; . \qquad (1)$$

We annul the forces between the bulk particles (excluding the wall particles) using gradient energy minimization after every affine step of loading. The system then undergoes a non-affine step bringing the system back to mechanical equilibrium. This quasi-static loading is continued until we hit the first plastic event and the lowest eigenvalue approaches to zero. Moreover, the associated eigenfunction localizes on a typical quadrupolar structure. An example of this phenomenon is shown in Fig. 1a which is obtained by selecting the x-axis in Eq. (1) to be at 31° with respect to the horizontal direction of the original square box. It can be assumed to be an STZ, but let us consider the situation where the x-axis is at 32° with respect to the horizontal direction (Fig. 1b). A relatively small change in the strain protocol (1° in the chosen direction of the principal stress axes) gives rise to a big change in the position of the first plastic event.



(a) (b)

FIG. 1: The first plastic event for (a) 31°, (b) 32°.

Figure 2 shows how the dependence of the protocol becomes stronger and stronger for larger systems. Thus, we conclude that a priori prediction of the site of the plastic response is impossible in the thermodynamic limit.

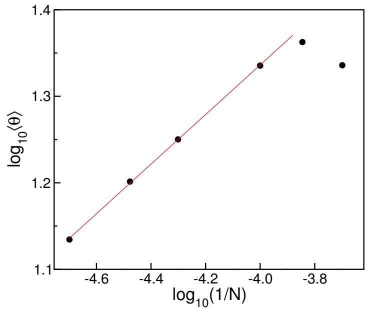


FIG. 2: The average angle required to observe a major change in the position of the first plastic event as a function of the system size.

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Discontinuous behaviour of the shear modulus defines the glass transition temperature

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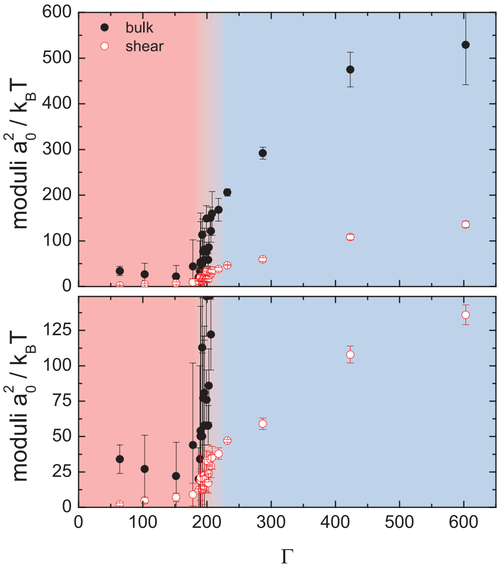

FIG. 1. A discontinuous behavior of the moduli as function of (inverse) temperature Γ defines the transition to solidity. In the lower plot the ordinate is zoomed in to focus on the shear.

Using positional data from video-microscopy of a colloidal monolayer we determine the wave-vector-dependent normal mode spring constants ('dispersion' relation) in the supercooled fluid and glassy state from the particle displacements $u(\vec{r},t)$. The confinement to two dimensions is realized by sedimentation on an otherwise interaction free substrate which is given as water/air interface of a flatly spanned interface in hanging droplet geometry. Continuum elastic theory is used in the limit of long wavelengths to analyse the elasticity of the monolayer [1]. In an isotropic solid, the elasticity tensor possesses only two independent elements, e.g. the bulk and the shear modulus which can be expressed via the Lamé coefficients μ and λ.

$$\frac{a_0^2(2\mu+\lambda)}{k_BT} = \lim_{\vec{q}\to 0}[q^2\langle|u_{\|}(\vec{q})|^2\rangle]^{-1}\,, \qquad (1)$$

$$\frac{a_0^2\mu}{k_BT} = \lim_{\vec{q}\to 0}[q^2\langle|u_{\perp}(\vec{q})|^2\rangle]^{-1}\,. \qquad (2)$$

Figure 1 shows the moduli as function of temperature. The onset of a finite static shear modulus upon cooling marks the fluid/solid transition. This provides an opportunity to determine the glass transition temperature in an intuitive and precise way [2].

Basis of the method is the decomposition of the acoustic excitations into plane waves by the fourier transform of the displacement field. Therefore we compute the covariance matrix C_{ij} from the particle displacements $u_i(t)$. Diagonalizing the covariance matrix serves the principal components of the spectrum with the eigenvectors being the amplitudes of the mode pattern and the eigenvalues gives the density of states (DOS). Figure 2 b-f) shows the mode pattern. For the largest amplitudes (with frequencies given in inverse length), plane waves are clearly resolved. Figure 2 a) shows the density of states and the arrows mark the frequencies of b-f)

$$C_{ij} = \langle u_i(t)u_j(t)\rangle_t\,, \qquad (3)$$

The linear increase of the (DOS) for small frequencies marks Debye behaviour in two dimensions and the extrema coincides with Van-Hoove singularities of classical solids. From an experimental point of view it is important to note that working on solid substrates, where a fraction of about an per cent of the particles is pinned, the plane wave behaviour can not be resolved [3].

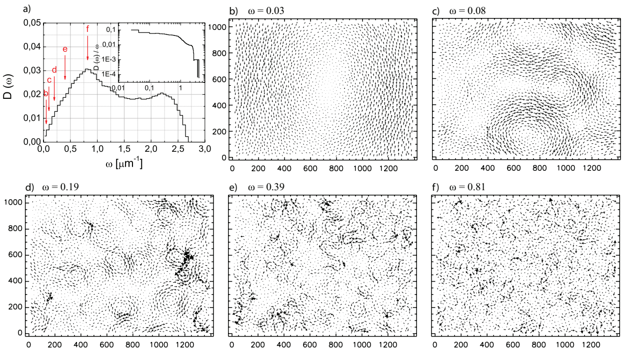

FIG. 2. Graph a shows the spectrum of Eigenvalues of the displacement field covariance matrix. By scaling with ω, the inset reveals convincing Debye behavior. The red arrows indexed b-f indicate positions in the spectrum where the mode structure is shown in graphs b-f.

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Groups of Mobile Particles Determine the Creep Response of Colloidal Glasses

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We investigated colloidal glasses after constant stress is suddenly applied [1]. The microscopic origin of the rheological creep response is investigated by confocal microscopy and computer simulations using binary mixtures of sterically stabilized PMMA spheres and Yukawa particles, respectively. This is possible due to developments in simultaneous rheology and confocal microscopy.

First, we compare the macroscopic rheological response to the particle dynamics, namely the mean squared displacement Δy^2. If the applied stress σ is below or near the yield stress $\sigma_{\rm y}$, a creep response is observed with the strain γ growing sub-linearly with time t without reaching a steady state. At the same time, also Δy^2 increases sub-linearly, i.e. the particle dynamics is sub-diffusive. In contrast, if $\sigma \gg \sigma_{\rm y}$, the strain response shows a transient regime between the initial elastic regime and the steady flow with $\gamma \sim t$. Similarly, transient super-diffusion, i.e. a super-linearly increasing Δy^2 is observed before diffusion with $\Delta y^2 \sim t$ prevails in the steady state. All in all, Δy^2 is found to be proportional to γ (Fig. 1a), despite the non-equilibrium and non-linear conditions during creep and the transient regime prior to the onset of steady flow.

Note that in the present situation, i.e. the sudden application of stress σ, no time scale is imposed and flow regimes below yielding can be investigated. This is in contrast to the case of imposing a constant shear rate $\dot{\gamma}$, where the bulk stress $\sigma(t)$ is monitored [2–4]. In this case, $\Delta y^2 \sim \gamma(t)$ cannot hold in the transient regime, where Δy^2 increases super-linearly with t while $\gamma(t)$ increases linearly. The choice of control parameter, i.e. constant σ or constant $\dot{\gamma}$, hence determines the intermediate flow states through which a glass evolves from the quiescent state to steady flow.

We also determined the distribution of displacements, namely the self part of the van Hove function $p(\Delta y)$. It exhibits a nearly Gaussian shape for small Δy together with moderate and more significant exponential tails for creep and the transition to steady flow, respectively. The tails reveal the existence of very mobile particles. The time-dependence of the fraction of these very mobile particles $\Phi_1^*(t)$ closely follows that of the instantaneous strain $\gamma(t)$, up to $\Phi_1^*(t) = 1$ (Fig. 1b). After spatial coarse-graining into larger regions, i.e. groups of particles, the evolution of the fraction of very mobile regions, $\Phi_N^*(t)$, follows $\Phi_1^*(t)$ and hence $\gamma(t)$. Thus, γ is not only proportional to Δy^2 but also the fraction of individual mobile particles or groups of mobile particles, i.e. dynamical activity, both, below and above the yield stress.

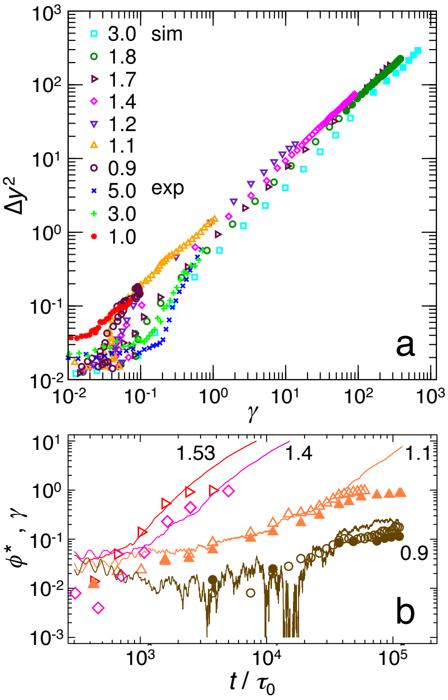

FIG. 1. (a) Mean squared displacement in vorticity direction, Δy^2, as a function of strain γ for different values of the applied stress $\sigma/\sigma_{\rm y}$ (as indicated) obtained in experiments (multiplied by a constant factor) and simulations. (b) Fraction of individual mobile particles $\Phi_1^*(t)$ (solid symbols) and groups of mobile particles $\Phi_N^*(t)$ (open symbols) and instantaneous strain γ (lines) determined by simulations at stresses $\sigma/\sigma_{\rm y}$ as indicated.

Heterogeneities in the location of these dynamical activities are present for applied stresses below and above the yield stress. For $\sigma \lesssim \sigma_{\rm y}$, i.e. during creep, *localised* regions of enhanced dynamical activity allow only for sub-diffusive dynamics. Increasing σ beyond $\sigma_{\rm y}$, the active regions grow heterogeneously and super-diffusive transients emerge, finally leading to sample-spanning mobile regions, and particle diffusion with steady flow setting in. Therefore, the spatial distribution of dynamical activity determines the onset of flow.

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Sensitivity of the correlation of plastic rearrangements to the microscopic dynamics in sheared disordered solids

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Plasticity in amorphous solids has been the subject of a number of recent studies focusing on issues such as non-locality [1], avalanche-like evolution of plastic events [2], and the system-size-scaling of their correlations [3–5].

In contrast to experiments, where the rate of heat generation due to plastic deformation is often negligibly small, the orders of magnitude difference between experimental studies and MD simulations gives a more pronounced role to MD thermostat at finite temperature simulations [6]. As the microscopic dynamics, per se, is distorted by the use of a thermostat, some effect on the system dynamics can also be expected. However, while the dependence of the structural relaxation on the coupling of the microscopic dynamics to a thermostat has been addressed in the case of equilibrium supercooled liquids [7, 8], we are aware of no systematic study of this issue in the context of spatio-temporal correlations of plasticity in sheared amorphous solids (see, however, Ref. [5] for the possible role of viscous damping).

Here, we investigate this issue via molecular dynamics simulations of a binary Lennard-Jones glass under steady shear. For this purpose, we choose a simulation setup with two atomistically rough walls and select a sufficiently low shear rate so that the heat produced via viscous dissipation can be conducted towards the walls with a relatively weak temperature gradient. This provides our reference system with unperturbed dynamics. For the same geometry and exactly the same set of initial configurations, we then perform simulations (i) of Newtonian dynamics (no thermostat), (ii) using the Nosé-Hoover thermostat and (iii) with a dissipative particle dynamics (DPD) thermostat.

In these studies, while single particle dynamics hardly depends on the thermostat (not shown), spatial correlations of plastic events appear to be more sensitive to it. As seen from Fig. 1, the use of the DPD-thermostat has the strongest effect on the correlation function. Interestingly, however, the qualitative trends are similar with and without thermostat. In particular, a power-law decay is observed in all the three cases investigated. On the *quantitative* level, however, differences are not negligible. The most important quantitative effect regards the apparent dependence of the power-law exponent on the specific type of the thermostat. This finding is of great importance when it comes to a comparison of simulation results to the predictions of a theory of amorphous plasticity.

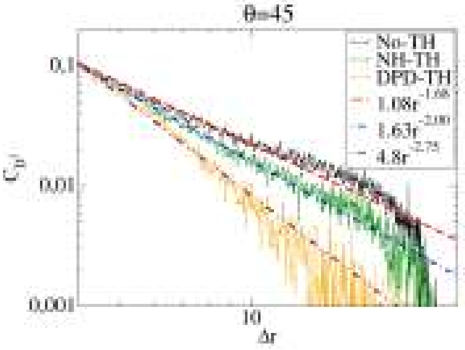

FIG. 1. Effect of thermostat on the spatial correlation of plastic activity. Results from simulations without thermostat are compared to those obtained with Nosé-Hoover (NH) and dissipative particle dynamics (DPD) thermostats.

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Tensile deformation of amorphous and semi-crystalline polymers

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Upon slow enough cooling, crystallisable polymers form partially crystalline structures that consist of ordered chain folded lamella and amorphous regions. This combination of amorphous and crystalline regions leads to particular mechanical properties of semicrystalline polymers and at room temperature, they usually have a larger stiffness and toughness compared to their amorphous counterparts. Although there is a wide agreement on their structure [1] mechanisms of deformation, especially in the non-linear regime of response, are poorly understood. In order to gain an insight into plastic deformation mechanisms in semi-crystalline polymers, we perform large-scale molecular dynamics simulations for a coarse-grained model for semiflexible polymers (CG-PVA) [2]. This model displays both crystallisation and glassy behaviour via changing the cooling rate, see Fig. 1. We investigate the mechanical response of polymers via uniaxial tensile tests [3]. We address two key issues: i) How do ordered and amorphous regions transform under uniaxial tension in semicrystalline polymers? ii) How do mechanical properties of semicrystalline polymers differ from their amorphous counterparts at temperatures above and below glass transition? We obtain the stress-strain curves for both amorphous and semicrystalline polymers of various sizes $50 \leq N \leq 1000$ at temperatures above and below the glass transition temperature T_g . The response beyond the elastic limit encompasses strain softening and strain hardening regimes. To understand the underlying mechanisms of plastic deformation, we analyse conformational and structural changes of polymers as shown in Fig. 2. In particular, we characterise the volume distribution of crystalline domains along the stress-strain curve. The strain-softening regime is dominated by deformation of crystallites via reorientation of chain-folded lamellae towards the tensile axis, fragmentation of largest crystalline domains and a partial loss of crystallinity. The strain hardening regime coincides with unfolding of chains and recrystallisation as a result of strain-induced chains alignment. These observed deformation mechanisms are consistent with experimental findings. We compare the tensile behaviour of semicrystalline polymers with their amorphous counterparts at temperatures above and below the glass transition temperature. In a good agreement with experimental findings, the Young modulus of semicrystalline samples is higher than the amorphous polymers. However, the strain-hardening modulus of amorphous polymers is higher than the semicrystalline ones as it is dominated by alignment of amorphous polymers with tensile axis. Finally, we will discuss the effect of polymer length and density of entanglements on Young and strain-hardening modulus of semicrystalline and glass polymers.

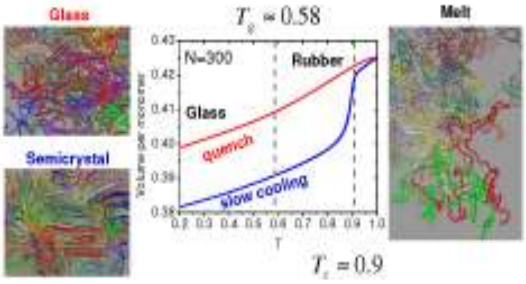

FIG. 1. Volume per monomer as a function of reduced temperature T for chains of length 300 obtained at a slow cooling-rate $10^{-6}\tau^{-1}$ and a rapid quench $10^{-3}\tau^{-1}$ leading to semicrystalline and glassy states, respectively. The conformations of polymers in the melt (right), glassy and semicrystalline states (left) are also depicted.

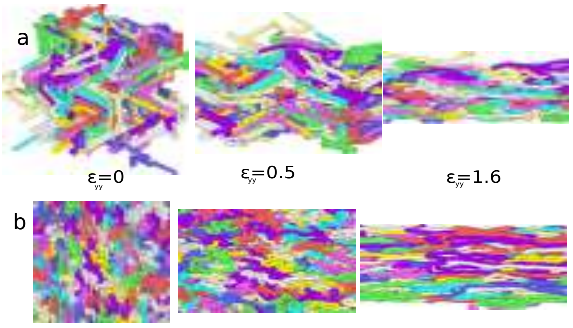

FIG. 2. Snapshots of polymer configurations of a) semicrystalline polymers b) glassy polymers at different strain values.

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A constitutive framework for the non-Newtonian pressure tensor of a simple fluid under planar flows

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Planar Couette flow (PCF) and planar elongational flows (PEF) have been simulated extensively due to their relative simplicity and relevance. The class that combines PCF and PEF, referred to a planar mixed flow (PMF), was difficult to study due to a lack of reproducible periodic boundary conditions. This problem has recently been solved, resulting in various studies of this interesting flow type [1–3]. These studies treat PCF, PEF and PMF as individual cases that are thought to be different because the stress responses appear different.

We find that the non-Newtonian stress response for monoatomic (WCA) fluid under various different planar flow fields can be completely described by a single equation.

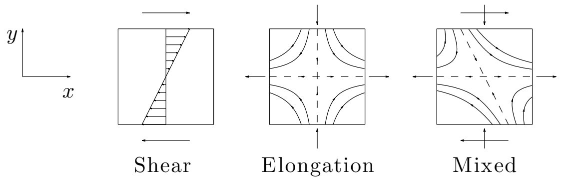

FIG. 1. A schematic of planar flow types: PCF (left), PEF (middle), and PMF (right).

Fig. 1 shows a schematic of three planar flow types. These flows can be imposed on a fluid by coupling a velocity gradient to the SLLOD equations of motion. The generalized velocity gradient is given by:

$$\nabla\mathbf{u} = \begin{bmatrix} \dot{\epsilon} & 0 & 0 \\ \dot{\gamma} & -\dot{\epsilon} & 0 \\ 0 & 0 & 0 \end{bmatrix} , \qquad (1)$$

where $\dot{\gamma}$ is the shear rate and $\dot{\epsilon}$ the rate of elongation. The viscosity under various flow types can be analyzed via a generalized expression $\eta = -\mathbf{P} : \mathbf{S}/(2s^2)$, in terms of the strain rate tensor $\mathbf{S} = \nabla\mathbf{u} + (\nabla\mathbf{u})^T$, the pressure tensor $\mathbf{P}$, and the magnitude of the strain rate tensor $s \equiv \sqrt{\frac{1}{2}\mathbf{S} : \mathbf{S}}$. The fact that the viscosity is independent of the planar (mixed) flow type is demonstrated in Fig. 2, in which PCF, PEF, and PMF simulation results collapse onto the same viscosity profile.

In Ref. [4] it is demonstrated that not only viscosity, but the whole pressure tensor $\mathbf{P}$ for steady-state planar flows can be expressed in terms of the flow field. The pressure tensor is written as the sum of an isotropic tensor, a tensor representing the phase lag due to shear, and a tensor describing the out-of-plane anisotropy:

$$\mathbf{P} = p\,\mathbf{I} - \frac{\eta}{\cos(2\phi)}\mathbf{R}(-\phi)\cdot\mathbf{S}\cdot\mathbf{R}^T(-\phi) + a\,\mathbf{I}_a\ . \qquad (2)$$

where $p = p_0 + p_a$ is the isotropic pressure composed of the equilibrium pressure, p_0 and the pressure dilatancy p_a due to the applied flow field. $\mathbf{I}_a \equiv \frac{1}{\sqrt{6}}\mathbf{I}\cdot(1,\ 1,\ -2)^T$ is a diagonal traceless tensor and $\mathbf{R}$ is a rotation matrix. This model contains four (flow-dependent) state variables: pressure dilatancy p_a, viscosity η, viscoelastic lagging angle ϕ, and out-of-plane anisotropy a. Each of these can be expressed in terms of the flow strength s and the magnitude of the shear $\dot{\gamma}$. This allows us to predict the pressure tensor for a wide range of field strengths and flow types without the need to explicitly simulate each of them.

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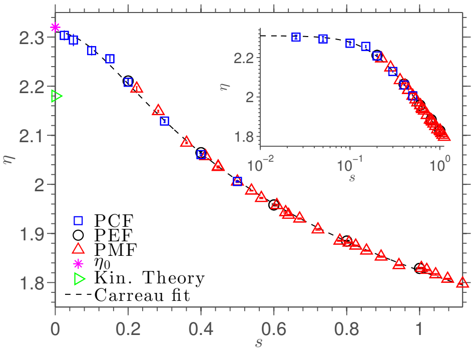

FIG. 2. Viscosity of a WCA fluid under shear (PCF), elongation (PEF) and mixed flow (PMF) at state point $\rho = 0.8442$, $T = 0.722$. The inset contains the same data as a semi-log plot.

Sheared frictionless sphere packings and shear jamming

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Amorphous packings of spheres have been intensely investigated in order to understand the mechanical and flow behaviour of dense granular matter, and to explore universal aspects of the transition from fluid to structurally arrested or jammed states. Considerable attention has recently been focussed on anisotropic packings of frictional grains generated by shear deformation leading to *shear jamming*, [1] which occurs below the jamming density for isotropic packings of frictionless grains. With the aim of disentangling the role of shear deformation induced structures and friction in generating shear jamming, we study sheared assemblies of *frictionless* spheres computationally, over a wide range of densities, extending far below their jamming point.

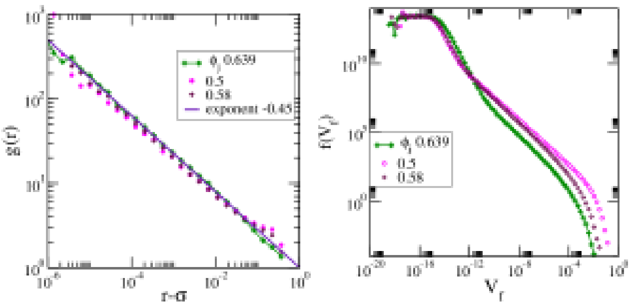

FIG. 1. (a) The pair correlation function near contact in the steady state demonstrating the emergence of a power law even at low densities under shear, observed previously to characterizd jammed packings. Shown for comparison is the pair correlation function for a jammed frictionless sphere packing at packing fraction 0.639. (b) Free volume distribution for sheared configurations at different packing fractions, indicating a power law tail observed previously [3] for jammed packings.

We consider [2] a system of equal-sized frictionless soft spheres, which are sheared thermally using the athermal quasistatic shearing protocol, *i. e.* in such a manner that the sphere assembly always resides in a local energy minimum. We study a number of geometric features in the steady state, and compare them with previous studies of jammed configurations, with and without the presence of friction. We observe (Fig. 1(a)) that under shear, even at packing fractions well below the jammed density for frictionless spheres, sphere configurations develop a near-contact power law singularity observed previously to characterize jamming. Similarly, (Fig. 1(b)) the free volume distribution develops a power law tail, previously observed for nearly jammed packings[3]. A comparison with previous studied of frictional packings reveals that the parametric relationship between the coordination number and the packing fraction for the sheared configurations we study is very close to that observed for frictional packings [4, 5] (Fig. 2). Thus, sheared frictionless packings appear to attain a structure that is reminiscent of jammed packings, in particular frictional packings, under shear. We discuss the implications of these observations to shear jamming. We also present results of the behavior observed under finite shear rates.

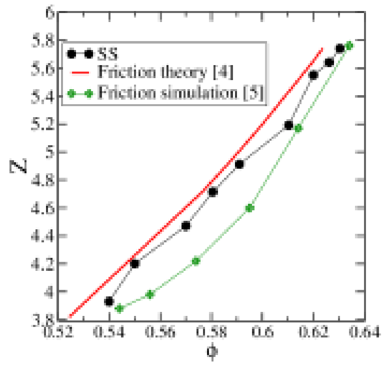

FIG. 2. Comparison of the parametric relationship between coordination number and packing fraction for frictional spheres and for sheared frictionless configurations.

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Making jammed particle suspensions flow: slow and high shear rate cooperative rearrangements

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We have combined confocal microscopy imaging of jammed emulsions under shear with molecular dynamics simulations of dense soft sphere suspensions. The experiments performed at volume fractions above the jamming transition, for various shear rates, follow the Hershel-Bulkley flow curve. The confocal microscopy measurements carried out in tandem with the shearing unravel important features at the droplet level. They indicate that at low enough shear rates, the flow becomes localized and the rearrangements of the emulsion droplets are slow and intermittent. Increasing the imposed shear rate makes the emulsion flow with an increasingly linear flow profile but the local rearrangements remain cooperative in nature. Using extensive numerical simulations of a model soft sphere suspension with a polydispersity of 10%, we have attempted to understand these experimental results. The simulations support the idea that, at sufficiently high volume fractions, particle mobility strongly depends on the accumulated local shear strain, both at low and high shear rates. The local changes in displacements of the particles are analyzed by computing the non-Gaussian parameter and cage correlation function. Using these results, we understand the rearrangement of particles at various local shear strains. We have also computed the local structural order parameter to understand the correlation between dynamical cooperativity and structural changes.

Abrupt shear thickening and stick-slip behavior of concentrated suspensions in the presence of fluidizer molecules

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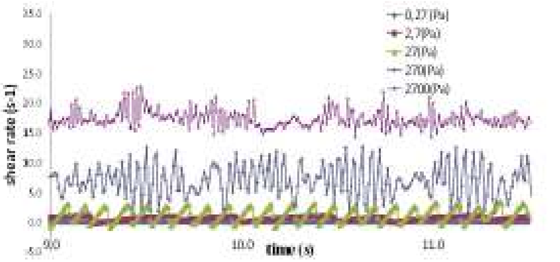

FIG. 1. Time dependent shear rate fluctuations for five fixed values of the applied stress. Suspension of calcium carbonate at 68% volume fraction in the presence of a fluidizer molecule

The fluidizer molecules which are used in cement industry allow to increase the maximum volume fraction of mineral particles in order to improve the mechanical properties of the concrete, still keeping a good fluidity for facilitating the molding of the cement slurries. We study both experimentally and theoretically the effect of fluidizer molecules on the critical shear rate where an abrupt shear thickening transition occurs. A detailed analysis of the forces between polymer molecules adsorbed on the surface of the particles versus their gyration radius allow to predict the value of the critical shear rate. These predicted values are in quite good agreement with the experimental ones obtained in microgravity to rule out the effect of sedimentation. Interestingly, a novel kind of very regular stick-slip instability where ,at constant imposed stress, the shear rate increases slowly and then falls to zero abruptly before starting again, is observed before the jamming transition. This instability is interpreted t hrough a model taking into account the proportion of frictional contacts between particles as a variable depending on the local stress.

Microscopic precursors of fracture in amorphous solids

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We use space and time-resolved dynamic light scattering in the highly multiple scattering regime (Diffusing Wave Spectroscopy, DWS [1]) to probe the microscopic dynamics of amorphous solids during mechanical tests. Our experiment allows us to measure a coarse-grained map of the microscopic motion in the sample, by measuring the local mean squared displacement down to a resolution of a fraction of nm^2, averaged over regions of interest (ROIs) of typical size of tens of microns. Additionally, we measure the mesoscopic drift of the same ROIs defined for the micrtoscopic dynamics.

We study a semicrystalline polymer (PolyEther Ether Ketone, PEEK) and an elastomer (PolyDiMethylSiloxane, PDMS) charged with particles (Titanium dioxide, TiO2) sized of 300nm, submitted to elongational mechanical tests. The test protocol consists of several stretching steps, each of them followed by a relaxation step during which the elongational strain is kept constant. The test is run until the material macroscopically fractures.

During the stretching step, the measured mesoscopic drift is in agreement with the affine deformation field expected from the imposed strain. During the first few steps, the microscopic displacement can be rationalized as being due to affine deformation, using a formalism developped in [2]. The relaxation steps following these early stretching steps are characterized by microscpic rearrangements that slow down with time, following the relaxation of the macroscopic stress required to keep a fixed strain.

A completely different scenario is observed as the material approaches macroscopic failure. The microscopic dynamics becomes order of magnitude faster than in the previous relaxation steps, unambiguous signalling microscopic rearrangements that eventually lead to macroscopic failure. Remarkably, this strong increase of the microscopic mobility occurs thousands of seconds before macroscopic failure, thereby demonstrating the great potential of these measurements as a way to detect precursor of material failure. Moreover, these dynamical precursor are spatially heterogeneous, the largest increase in microscopic mobility being observed in the region where a macroscopic fracture will occurr.

We can translate this intensity correlation fonction to a mean square displacement over 10s using the equation below[1]:

$$g_1(\tau) = exp(-\gamma k_0 < \Delta r^2(\tau) >^{1/2}) \qquad (1)$$

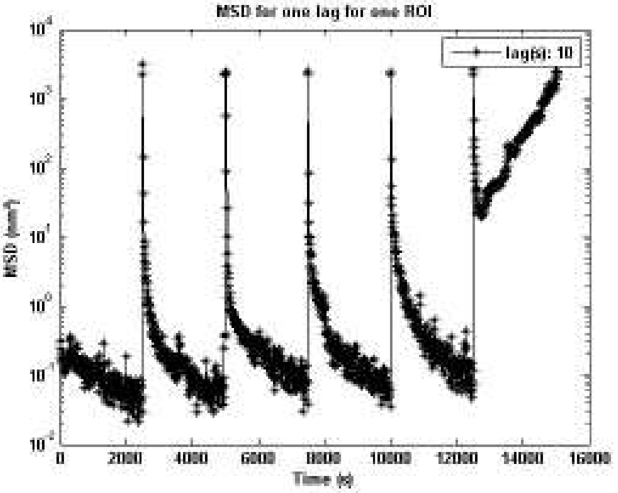

FIG. 1. $\langle \Delta r^2(10) \rangle$ Vs Time.

Than, we build a dynamic mapping (2D) to follow the microscopic dynamic of different region of interst on my sample. This Map indicates that the microscopic rearrangements present heterogeneity at relaxation phases when the sample is perfectly fixed. Moreover, if we compare the map result with an image after failure, we observe that the region with the more important microscopic rearrangements will be the region of failure.
That result allows us to pre-localize the region of the fracture.

These experiments show the interest of this technique as a method to predict and localize an eventual failure of a material.

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Anomalous dynamics of concentrated PNiPAM suspensions

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The present study aims at investigating Poly(N-isopropylacrylamide) (PNiPAM) concentrated suspensions. Microgel particles consist of crosslinked PNiPAM polymer chains, highly swollen by water. Interactions between polymer and water are temperature-sensitive[2] so that particle's size depends on temperature and ranges from 345nm at 20°C (swollen state) to 120nm at 40°C (collapsed state).

We designed an optical set-up allowing us to perform spatially and temporally resolved light scattering experiments (photon correlation imaging)[3] while controlling temperature to within 0.01°C. A laser beam (wavelength λ=532nm) illuminates the sample and the scattered light is collected on a charged couple device (CCD) camera at a scattering angle θ=180°. This backscattering configuration allows us to work at a scattering vector q=$(4\pi n/\lambda)\sin(\theta/2)$ corresponding to a length scale of about 0.2μm, thereby probing microscopic rearrangements at the colloidal particle length scale. Experimentally one measures $g_2(t,\tau)-1$, the two-time autocorrelation function of the temporal fluctuations of the scattered intensity detected by a CCD camera. This intensity autocorrelation function is directly related to the usual intermediate scattering function $f(q,\tau)$ such that $f(q,\tau) \propto \sqrt{g_2(\tau)-1}$ with:

$$g_2(\tau)-1 = \langle g_2(t,\tau)-1\rangle_t = \left\langle \frac{\langle I_p(t+\tau)I_p(t)\rangle_p}{\langle I_p(t+\tau)\rangle_p\langle I_p(t)\rangle_p} - 1 \right\rangle_t$$

where I_p indicates the intensity measured by the $p-th$ pixel of the CCD camera, $\langle ...\rangle_t$ denotes average over time and $\langle ...\rangle_p$ average over pixels.

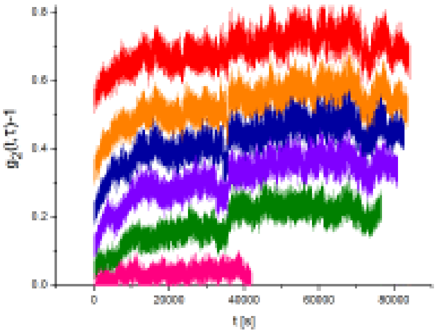

FIG. 1. Two-time correlation function $g_2(t,\tau)-1$ as a function of sample age t. Each line corresponds to a different value of the time delay τ, which increases from 1s to 4.10^{4}s from top to bottom. PNiPAM volume fraction ϕ=0.84.

The evolution of $g_2(t,\tau)-1$ for different lag times τ is shown on figure 1, for a sample at volume fraction ϕ = 0.84. This sample is representative of the behaviour of supercooled suspensions that can reach equilibrium within the duration of the experiments. After an ageing phase (up to τ=3.10^{4}s), the correlation function reaches a stationary state as shown by the fact that the correlation function at a fixed lag τ does not evolve anymore with sample time t. Such a behaviour is similar to that previously observed for hard spheres systems.

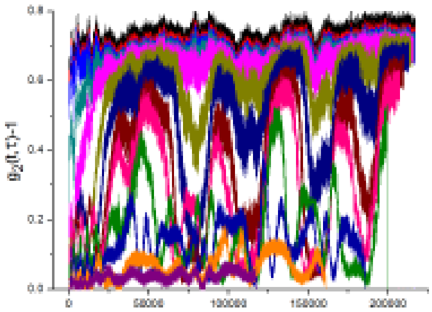

FIG. 2. Same as figure 1 for lag time τ ranging from 1s to 10^{5}s from top to bottom. PNiPAM volume fraction ϕ=1.23.

By contrast, the dynamic behaviour of PNiPAM suspensions at higher volume fraction is surprisingly different. In that case, and as shown on figure 2, the intensity autocorrelation function displays feature crucially different than hard spheres model systems. One can observe intermittent ageing phases followed by large rearrangement events occurring on typical time of 10^{4}s. PNiPAM particles being highly temperature sensitive this intermittent dynamic could be attributed to temporal fluctuations of sample's temperature. We will show that applying on purpose temperature cycles (with amplitude larger than temperature fluctuations measured in constant temperature experiment) does not prevent the intermittent dynamic. For all samples, the time-averaged intensity autocorrelation function $g_2(\tau)-1$ displays a stretched exponential decrease with characteristic time τ_α and exponent β. We will show that, in the regime where anomalous intermittent dynamics are observed, τ_α increases only very weakly with ϕ. Additionally, the shape of the correlation function changes, as indicated by a sharp increase of the stretching parameter β.

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Phase behavior of aqueous suspension of Laponite: A rheological perspective

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Laponite is a disk shaped nanoparticle with diameter 30 nm and thickness 1 nm. In an aqueous media having pH 10, its edge bears a positive charge while the faces have negative charge. Typically dispersion of Laponite beyond 1 weight % are known to enhance viscosity of the same by orders of magnitude over timescale of hours. However, the microstructure responsible for such enhancement is a matter of debate. The scattering studies on Laponite suspension suggest that for concentrations between 1 and 2 weight % and up to 4 mM NaCl there exists an attractive gel state, while beyond 2 weight % and up to 4 mM NaCl suspension is proposed to be in a repulsive Wigner glass state [1]. In this work we investigate Laponite suspensions over a concentration range of 1.4 to 4 weight % and NaCl concentration range of 0 to 7 mM by performing time resolved rheometry, wherein suspension is subjected to cyclic frequency sweep as its structure evolves. We observe that the structural evolution of all the Laponite suspensions is accompanied by an increase in elastic (G') and viscous (G'') moduli and decrease in $\tan\delta$ as shown in Fig.1. It can be seen that the sharpness of decrease in $\tan\delta$, increases with decrease in frequency. Remarkably all the $\tan\delta$ evolution curves pass through a single point as shown in Fig.1. Such point of intersection is known as the crtitical gel state in the rheology literature and is known to be a signature of space spanning percolated network [2].

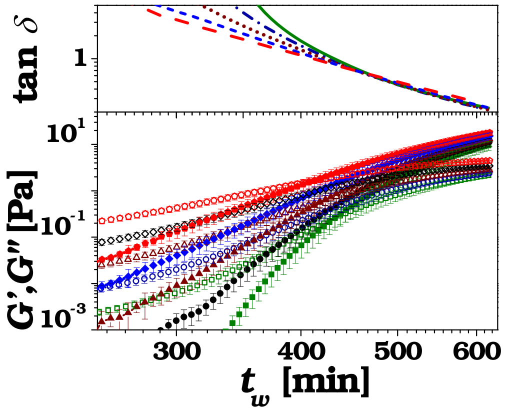

FIG. 1. Evolution of G' (filled symbols), G'' (open symbols) is plotted as a function of frequency for aqueous suspension having 2.8 weight % Laponite and 3 mM NaCl at different t_w (for G' and G'' from bottom to top 0.063, 0.2, 0.63, 2, and 6.3 rad/s. For $\tan\delta$, the rate of decrease weakens with an increase in frequency). Data from Jatav and Joshi [3]

The frequency dependence of G' and G'' can be used to obtain continuous relaxation time spectra $[H(\tau)]$ as shown in Fig.2 [4]. It can be seen that in the initial stage of evolution the relaxation spectra is dominted by the fast modes. However at certain time (457 min), $[H(\tau)]$ demonstrates a power law dependence on (τ) indicating a critical gel state. As suggested by Winter, the power law dependence with a negative slope as shown in Fig.2 is a consequence of percolated gel state [2]. This is opposite to a state of glass at a point of glass transition, which also demonstrates a power law dependence of $[H(\tau)]$ on (τ) but with a positive slope [2]. Therefore, contrary to the scattering studies, the present work clearly suggests Laponite suspensions to be in attractive gel state over the studied concentration ranges. Interestingly we observe that the fractal dimension associated with the critical gel state is independent of concentration of salt but is observed to increase with increase in Laponite concentration.

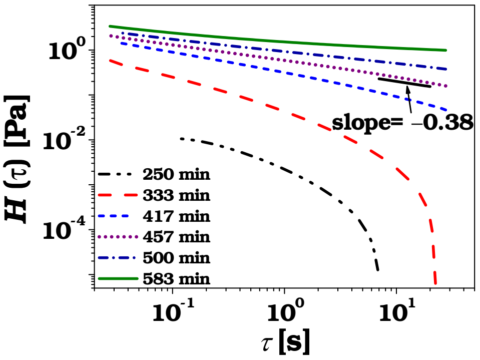

FIG. 2. Relaxation time spectrum $H(\tau)$ obtained by using Tschoegl [4] first order approximation at different aging time (t_w) for the data shown in Fig.1 [3].

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Temperature Modulated Dielectric Measurement: a Non-linear Technique for Kinetic Study on the Response of the Relaxation Time to Quick Temperature Change

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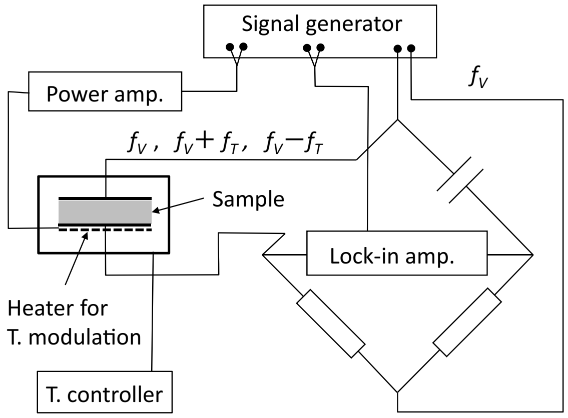

FIG. 1. A schematic diagram of TMDM system.

Glass transition is a typical phenomena showing the complexity of viscous liquids. The relaxation time τ_α measured with the mechanical relaxation, the dielectric relaxation and so on increases rapidly on the cooling process towards the glass transition temperature. Although the temperature dependence of τ_α has been studied extensively, the microscopic dynamics from which the rapid increase of τ_α emerges has not been revealed. In this study a new instrument to measure nonlinear response has been developed to get a new insight into the microscopic dynamics.

A schematic diagram of temperature modulated dielectric measurement (TMDM) is shown in Fig. 1. Conventional Wheatstone bridge was used but the sample temperature was modulated sinusoidally with time. The temperature modulation induced periodic change in τ_α. The electric capacitance of the capacitor including the sample changed at the frequency of the temperature modulation f_T. The input to the lock-in amplifier contains not only the linear component with the frequency of the voltage f_V given to the Wheatstone bridge but also non-linear components with $f_V + f_T$ and $f_V - f_T$. The effects of the modulated τ_α appeared in the nonlinear components. It was found that the response of τ_α exhibited retardation to the temperature modulation. Assuming Debye type response the retardation time τ_τ was calculated from the nonlinear components.

Temperature dependence of τ_τ is shown in Fig. 2[1] with temperature dependence of τ_α. The sample material was poly(vinyl acetate). The amplitude and the frequency of the temperature modulation were 0.8K and 0.05 to 0.3Hz, respectively. Solid circles and open circles show the τ_τ from the spin coat sample and the melt press sample, respectively. The solid curves and broken curves without circles are τ_α of the spin coat sample and the melt press sample, respectively. Temperature dependence of τ_τ is much weaker than that of τ_α. It should be noted that the curves of τ_τ and τ_α cross each other. These results have been confirmed in recent experiments with improved experimental technique which will be explained in the presentation. It is natural to consider that τ_τ, retardation of the change in τ_α to quick temperature change, is attributed to retardation of the structure change. According to this idea temperature dependence of τ_τ is expected to be similar to that of τ_α. However, it does not agree with our experimental results. Results shown in Fig. 2 suggested that the nonlinear components measured with TMDM emerged from microscopic dynamics different from the α process.

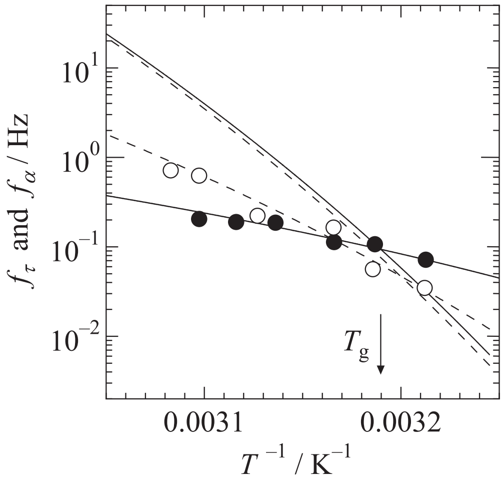

FIG. 2. Temperature dependence of $1/\tau_\tau$ with $1/\tau_\alpha$.

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The nature of avalanche dynamics in the flow of yield stress materiels

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Amorphous solids subjected to an external shear stress larger than the global yielding stress σ_c deform plastically manifesting avalanche type dynamics which can be captured within the fluctuations in the stress time series in both numerical simulations and experimental data [1]. By using a lattice-based elastoplastic model, which is capable to reproduce typical experimental flow curves [2], we found avalanche statistics that are non mean-field and non symmetric avalanche shapes depending on their sizes in the limit of external shear rate going to zero.

The model that we use is implemented as follows: $\partial_t \sigma_i = \mu\dot{\gamma} + \mu\sum_j G_{ij}\dot{\gamma}_j^{pl}$ with $\dot{\gamma}_j^{pl} = \frac{n_j \sigma_j}{\mu\tau}$ where i,j represent the lattice sites, σ_i the local stress, G_{ij} the Eshelby-like elastic propagator, $\dot{\gamma}$ the external shear rate. n_i is either zero or one representing whether the site is elastic or fluidized due to a large local stress with local plastic deformation rate $\dot{\gamma}_j^{pl}$. The disorder of the amorphous medium is implemented in the local threshold $\sigma_{y,i}$, where $\sigma_{y,i}$ is a random variable chosen from a distribution function $P(\sigma_y)$; n_i turns 1 when the local stress $\sigma_i > \sigma_{y,i}$; n_i turns back 0, when the total deformation $\gamma_i^{tot} = |\int_{n=1} \dot{\gamma}_i^{tot} dt|$ reaches a typical value γ_c.

We study this model on both two and three dimensions. We define an avalanche size as the global stress drop multiplied by the system volume $S = \Delta\langle\sigma\rangle L^d$, duration T as the period of each stress strop, and the shape as the absolute value of stress drop rate $|\langle\dot{\sigma}\rangle|$ as a function of time.

In both cases, we find a scaling regime bonded by a lower cut-off and a upper cut-off in the avalanche sizes distribution $P(S)$ as well as in the distribution of avalanche durations $D(T)$. For large values $P(S) \approx S^{-\tau} f(S/S_o)$ and $D(T) \approx T^{-\tau'} g(T/T_o)$ where the upper cut-off scales with system size as $S_o \sim L^{d_f}$, d_f the fractal dimension, and the upper cut-off in durations scales as $T_o \sim \dot{\gamma}^{-\alpha}$. We measured $\tau \approx 1.25$ for 3D and $\tau' \approx 1.23$ for 2D which are distinct from the mean-field prediction $\tau_{MF} = 1.5$ [3].

We define an asymmetric parameter $A_T = \frac{1}{T}\int_{-T/2}^{T/2} \frac{|f(x)-f(-x)|}{f(x)+f(-x)} dx$ for characterizing the symmetry of an avalanche shape. Through the analysis of A_T we show that the shape average over avalanches of duration smaller than T^* becomes more symmetric as T^* becomes larger (see Fig 2), which means average shapes of avalanches becomes more and more symmetric the longer they persist. This may suggest that smaller global stress drops are due to individual avalanches and large global stress drops are rather due to a superposition of many independent avalanches happening at the same time at different places in the system. This makes the average shape of larger avalanches seem to be mean-field like i.e. symmetric.

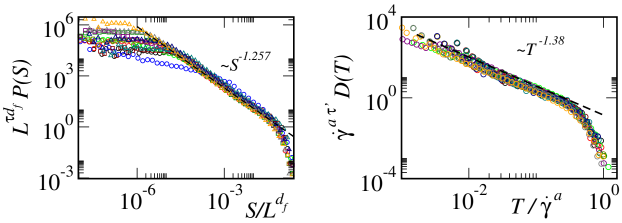

FIG. 1. Left panel: Rescaled probability distribution of avalanche size $P(S)$, with exponent $\tau \approx 1.25$. Right panel: Rescaled probability distribution of avalanche duration $D(T)$, with exponent $\tau' \approx 1.38$.

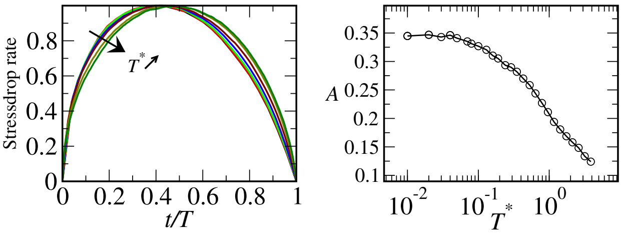

FIG. 2. Left panel: Average shape of avalanches of duration smaller than cursor T^*. The shape becomes more and more symmetric with increasing T^*. Right panel: $A(T^*)$ asymmetric parameter of average shape of avalanches of duration smaller than cursor T^*. $A(T^*)$ decreases with T^*.

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Bronchial mucus characterization by macro- and micro-rheology

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Severe chronic bronchial diseases affect 120 millions of people worldwide. These respiratory diseases are often associated with mucus hypersecretion in the airways, but the distinctive roles of cilia beating and mucus properties and hypersecretion are still to be determined. The project is focused on the physical aspects of mucociliary clearance, and more specifically on the rheological properties of healthy and pathological mucus.

A mucus healthy sample is a complex fluid containing immunoglobulins, antiseptic enzymes, inorganic salts, proteins, glycoproteins known as mucins, and water. It is secreted by goblet cells and it has different functions, the most important one being acting as defense barrier against infectious agents [1]. From the rheological point of view, mucus is a viscoelastic gel-like material, characterized by the presence of a large number of entanglements between glycoproteins and other mucosal components, stabilized by hydrogen bonding and electrostatic and hydrophobic interactions [2].

The mucus samples analyzed in this work were obtained from bronchial epithelium culture. Classical cone/plate rheometry experiments will be compared to microrheology experiments to characterize the heterogeneity of mucus and the different scales of its complex structure. Classic cone-plate frequency sweep provides quantitative measurements of the shear-dependent elastic moduli in the frequency range corresponding to cilia beating. Optical tweezers are used to analyze mucus in a passive or oscillating optical trap. During a passive tracking experiment, a bead is held in place by the trap, and the Brownian motion is recorded. In an active experiment, an oscillating mode is used to simulate the cilia beating. These results will be compared to passive microrheology deduced from a population of beads embedded in the mucus.

This preliminary study will help to better understand how cilia beating is coupled to the viscoelastic properties of the mucus, to generate mucus transport in lungs.

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Viscosity of bacterial suspensions

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The hydrodynamics of active suspensions such a bacterial fluids is currently at the centre of much research partly due to its possible practical importance in medicine, ecology, or biotechnologies, but also as this type of system poses fundamental physical questions on the emergence of a macroscopic description of assemblies of living and moving entities. The assessment of macroscopic transport properties and associated constitutive parameters for such a fluid are currently a much debated issued [1]. For instance, in the dilute regime and for pusher-type swimmers such as bacteria, theories predict [2–4] that the shear-induced swimming orientation should lead to a linear decrease of the apparent fluid viscosity with concentration [2–5]. Moreover, beyond the linear regime, theories based on phenomenology claim that for high activity, a motive macroscopic flow could appear in response to shear[6–8]. Although experimental evidence for viscosity reduction were brought for *Bacillus subtilis* [9] and *E. coli* [10], no full rheological characterization (viscosity *versus* shear rate) exist and furthermore, the phenomenological predictions for the non-linear regime has remained so far unobserved. Here, we present experiments using different techniques (Microfluidics[10], low-shear rheometry[11]) that investigate this question on E.coli suspensions. We obtain in the linear regime a characterization of the viscous response with the shear rate at different concentrations. We show that the rheological curves allow to extract microscopic parameters characterizing the activity. Moreover, in the non-linear regime of concentration, we show a transition akin to a "superfluid transition" where the viscous response vanishes. We discuss these results in terms of implications for the transport properties of active fluids in confined environments.

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Dense regimes of self-propelled hard disks

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Self propelled hard disks, experimentally made of vertically vibrated polar disks, have been shown to exhibit a transition towards collective motion, when the packing fraction exceeds some critical value of the order of thirty percent [1]. In the same situation, isotropic disks behave as a standard hard disk liquid. At larger packing fractions hard disks are known to present a KTHNY scenario towards crystallization, if they are mono disperse [2], and a glass transition [3], if they are enough poly-disperse or bi-disperse with an adequate size ratio. How are these transition altered in the presence of self-propulsion? This question, of a great interest for dense populations of motile organisms, has been recently considered in several numerical works [4, 5].

Here we present the first experimental results addressing this question, which were obtained using the same system of vertically vibrated polar disks for which transition to collective motion has been fully characterized, and systematically compared them to the case of isotropic disks under the same experimental conditions.

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Self-propelled hard discs: non-conservation of momentum, effective alignment and transition to collective motion

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A self-propelled particle borrows energy from its surrounding environment and converts it to translational motion. A system composed of such self-propelled particles is inherently far from equilibrium, in a very peculiar way: the property of detailed balance is broken at the level of every single particle. As of the collective level, such systems are able to take energy from the microscopic scale and inject it into the macroscopic motion of the whole system, thus sustaining an orientationally ordered stationnary state in two dimensions (see Fig. 1b). Such a polar state would be impossible for a system in equilibrium. The giant density fluctuations in this polar state has also attracted much interest. In the polar state, if we increase the orientational noise, the stationnary state becomes isotropic. A polar–isotropic phase transition generically occurs at finite orientational noise.

The current understanding of the polar–isotropic phase transition mostly relies on kinetic theories, from which hydrodynamic equations are derived [2]. Making use of the molecular chaos assumption, these theories are able to describe quantitatively the diluted regime. It is well understood that the phase transition is controlled qualitatively by the competition between the so-called "alignment" of interacting self-propelled particles, which tends to destabilize the isotropic phase, and the orientational noise, which tends to stabilize it.

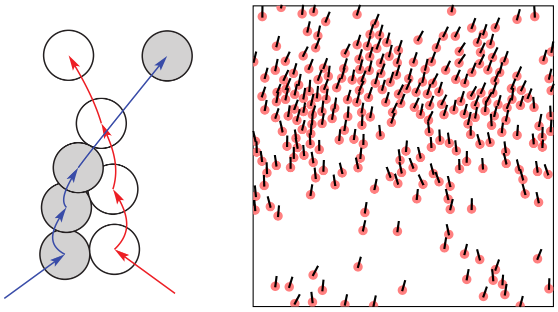

FIG. 1. (a): The scattering of two self-propelled hard discs can be made of several hard-core collisions. (b): Collective directed motion of many self-propelled hard discs.

In a recent work [1], we were able to formulate a kinetic theory in terms of microscopic quantities describing the non-conservation of momentum arising from binary interactions. To be more specific, let us consider two particles that come in interaction, having a pre-scattering summed momentum $\mathbf{p}$. After the interaction, when particles are far enough one from the other, the scattering event is over, both particles go straight and their summed momentum has become $\mathbf{p}'$. The "alignment" resulting from the interaction can be properly defined as the microscopic quantity $\mathbf{p} \cdot (\mathbf{p}' - \mathbf{p})$, which has a nice geometric interpretation. Of course, this quantity depends on the pre-scattering parameters of the interaction (such as the incoming relative velocity and the impact parameter). At the collective level, one needs to consider averages of $\mathbf{p} \cdot (\mathbf{p}' - \mathbf{p})$ over the space of pre-scattering parameters, weighted by the appropriate scattering rate derived from statistical mechanics arguments. Such averages gives access to quantities of interest, providing predictions for the transition, whether it is a continuous or discontinuous one, the scattering rate in the polar state, the fluctuations of the order parameter in the isotropic state.

We will present these results in more details and illustrate them by comparing their predictions to numerical simulations of a model of self-propelled hard discs that was shown to describe very well the data of a recent experiment [3]. This model has a Newton-like dynamics which include the self-propelling mechanism and the hard-core interactions. The study of the binary scattering of this model reveals interesting phenomena. For example, the competition between the time-persistence of the self-propelling mechanism and the steric effect can lead two particles to re-collide many times one against the other (see Fig. 1a). Even though the bare ingredients put by hand in the dynamics do not include any aligning interactions, we will show that the model can indeed have an emerging alignment mechanism. We will also comment on the anomalous departure of the numerical results at finite densities from the theoretical predictions made for vanishing low densities.

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Viscoelasticity of self-assembled liquid crystals of DNA

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Self-assembly of small isotropic molecules may produce anisotropic aggregates, their subsequent orientational ordering and eventually the formation of lyotropic liquid crystals (LC). These LC differ from traditional thermotropic ones, in which the interactions are set by the prescribed molecular properties. Indeed - aggregation being driven by physical rather than covalent bonding - a strong dependence of the aggregate properties on temperature, concentration, ionic force, etc. is usually present. An example is represented by concentrated DNA solutions of short duplexes, in which the formation of chiral nematic (cholesteric) LC was recently observed as a consequence of end-to-end interactions with linear aggregation of the duplexes [1]. Accessing the viscoelastic properties of the LC phase would enable extracting precious information about the underlying interactions between the duplexes, which control the propagation of properties from the microscopic to the macroscopic scale. For instance, the relationship between the handedness of DNA and the chirality of the cholesteric phase is still an open question, with small changes in temperature or concentration causing dramatic changes in the pitch and handedness of the cholesteric LC phase [2].

A classical tool for the determination of the viscoelasticity of thermotropic LC is light scattering, which probes the thermal fluctuations of the LC director in one or more suitable experimental geometries. However, using light scattering with lyotropic LC is a challenging feat, because of the need of controlling the alignment of the director field over the whole size of the light beam. This control is extremely difficult with DNA LC, which requires the development of novel tools for their investigation. A promising method for this task is represented by Digital Fourier Microscopy (DFM) [3], which allows obtaining scattering information from movies of the sample acquired in the real space. The advantage of this approach, recently applied to disordered thermotropics in the nematic phase [4], is that the analysis can be restricted only to the regions where the director is suitably aligned, providing thereby a powerful space-resolved scattering tool. In this work, we develop a new DFM method for cholesteric LC. We first test it with thermotropic LC obtained by adding a chiral dopant to an otherwise nematic LC former. Our results show that a combination of two DFM experiments performed on regions where the helical axis is parallel or perpendicular to the direction of the incident light enables measuring the splay, twist and bend viscoelastic ratios, together with other hydrodynamic modes peculiar of cholesterics [5, 6]. We then study DNA cholesterics, for which we find that the twist and splay viscoelastic ratios are of the same order of magnitude, whereas the bend ratio is about 50 times smaller. In addition, the measured values of the elastic and viscoelastic constants turn out to be relatively insensitive to observed changes in the cholesteric pitch and also in the chirality of the nematic phases. Since the cholesteric pitch is given by the ratio between the molecular chiral torque and the twist elastic constant, our results demonstrate that the cholesteric pitch can be effectively used as a direct, unbiased and quantitative indicator of the chiral interactions at the molecular level.

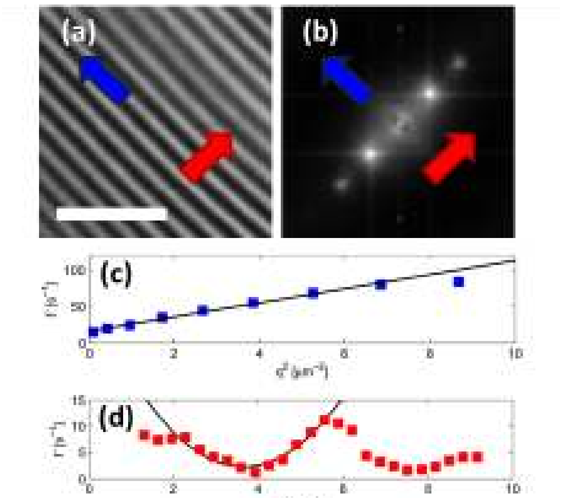

FIG. 1. (a) Image of a fingerprint texture in a DNA LC sample observed between crossed polarizers. Scale bar is 10 μm. (b) Reconstructed two-dimensional scattering pattern from the intensity fluctuations in the region shown in (a). The Bragg peaks corresponding to multiples of $q_0 = \pi/P$ (P is the cholesteric pitch) are well visibile. (c) Decorrelation rate for fluctuations with wave vector perpendicular to the helical axis (undulation mode). The continuous line is a best fit to theory [5]. (d) Decorrelation rate for fluctuations with wave vector parallel to the helical axis (twist mode). The continuous line is a best fit to theory [6].

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Effective thermodynamics of self-propelled particles

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Active matter systems are made of interacting units (active particles) which can convert energy from their environment into mechanical work and, in the situations we consider here, locally produce motion. As a result, these self-propelled particles are intrinsically out-of-equilibrium, giving rise to a plethora of interesting collective behaviour (pattern formation, phase separation, large fluctuations, etc.). Self-propelled particles appear naturally in biological systems where they can be found at very different length scales, from molecular motors inside the cell (~ 10 nm), to bacteria (~ 1 μm) or animals (~ 1 m) [1]. Physicists have recently managed to synthesise non-living active matter at the granular (~ 1 mm) and colloidal scale (~ 1 μm) [2]. Artificial active suspensions made of Janus colloids can now be realised in the lab using state of the art techniques [3, 4], opening the possibility of creating new soft materials with novel functionalities. The systematic characterisation of these non-equilibrium systems clearly needs further theoretical work. Here we present our recent results in this direction, and study how the phase behaviour and dynamics of colloidal matter is affected by the competition between self-propulsion and steric effects. In order to do so, we introduce a model of self-propelled disks where particles perform a persistent random walk characterised by a single parameter, the persistence time [5, 6]. We compare the predictions of the model with the experimental results obtained in suspensions of Janus colloids [4].

Purely repulsive hard disks show the emergence, at any finite density, of complex non-equilibrium structures. Particles spontaneously aggregate into fractal clusters as self-propulsion is increased and, eventually, percolate to form a ramified structure reminiscent of a physical gel. We show that the addition of a finite amount of noise is needed to trigger a non-equilibrium phase separation. These structural changes have a strong impact on the dynamics: the diffusion constant has a non-monotonic behaviour with self-propulsion, with strong deviations from Fickian diffusion that persist over large time and length scales, suggesting that active matter generically behaves as dynamical heterogeneous systems, like colloidal gels made of attractive particles [6].

Suspensions of self-propelled Janus colloids constitute an experimental model system to understand basic general aspects of active colloidal matter. Using sedimentation experiments one can measure the non-equilibrium equation of state of the active suspensions. We conduct Monte Carlo simulations of our model of self-propelled disks in the presence of gravity to discuss the impact of activity in the equations of state. We found a good agreement between simulations and experiments and show that, despite the non-equilibrium nature of the system, the equation of state of active colloids takes a simple form which can be understood as a motility-induced adhesion between the particles. By mapping the active system into the Baxter model of adhesive disks we can associate an effective adhesion to an effective temperature [4]. The latter can be extracted from static and dynamic measurements: from the density profiles in the ideal gas regime and from the diffusion coefficient via the Stockes-Einstein relation. Both determinations give the same result. The equations of state measured in the simulations and experiments are well described by an equivalent effective thermal system of hot adhesive disks.

In order to further investigate which equilibrium thermodynamic quantities, like temperature, can be extended to characterise active matter, we study the applicability of the concept of effective temperature in these non-equilibrium systems. To do that, we extract the effective temperature from the violations of the fluctuation-dissipation theorem in our model of self-propelled disks. This notion of effective temperature has been proved meaningful in the context of glasses and other slowly evolving systems displaying a clear separation of time scales in their dynamics. I will discuss the evolution of the effective temperature over a broad range of densities and activities, and I will show how a unique value, independent of the observable coupled to the linear perturbation, emerges in dense active systems close to dynamical arrest.

We thank all our collaborators in the field: L. Bocquet, C. Cottin-Bizonne, F. Ginot, I. Theurkauff and C. Ybert. We also thank A. Ikeda, I. Pagonabarraga and T. Kawasaki for useful exchanges.

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Active Microrheology of Dense Microswimmer Suspensions

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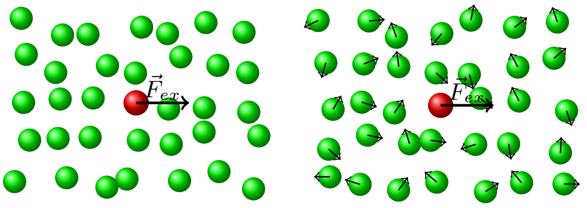

FIG. 1. Left: Schematic representation of passive particles (green balls), and a tracer particle (red ball). Right: Schematic representation of active particles with reorientable velocity (small black arrows), and tracer particle.

We study active microrheology of active self-propelled particles in dense environments, using the mode coupling theory of the glass transition (MCT). A tracer particle (red particle in Fig. 1) is driven by a fixed external force through a glassy suspension of hard-sphere microswimmers with a fixed propulsion velocity v_0 undergoing diffusive reorientation.

A simplified schematic model is constructed [1, 2]: assuming reorientational motion to be much faster than translational rearrangements, the tagged-particle density correlation function ϕ^s of the externally driven probe obeys

$$\begin{aligned} &\partial_t \phi^s(t) = -\omega \phi^s(t) - \int_0^t m^s(t-u)\,\partial_u \phi^s(u)\,du, \\ &\partial_t \phi(t) = -A\phi(t) - \frac{1}{A}\int_0^t m(t-u)\,\partial_u \phi(u)\,du, \\ &\omega = 1 - iF_{ex}, \qquad m^s(t) = v_s \phi^{s*}(t)\,\phi(t), \\ &m(t) = v_1 \phi(t) + v_2 \phi^2(t), \qquad A = 1 + \frac{v_0^2}{8}. \end{aligned} \tag{1}$$

The density correlation function shows slow temporal decay that is modulated by both the external force and the host-suspension activity (cf. Fig. 2).

An experimentally accessible quantity is the force–velocity relation for the driven probe, expressed as a force-dependent nonlinear friction coefficient $\Delta\zeta(F_{\text{ex}})$,

$$\Delta\zeta_s = \int_0^\infty dt \Re \phi^s(t)\,\phi(t)\,. \tag{2}$$

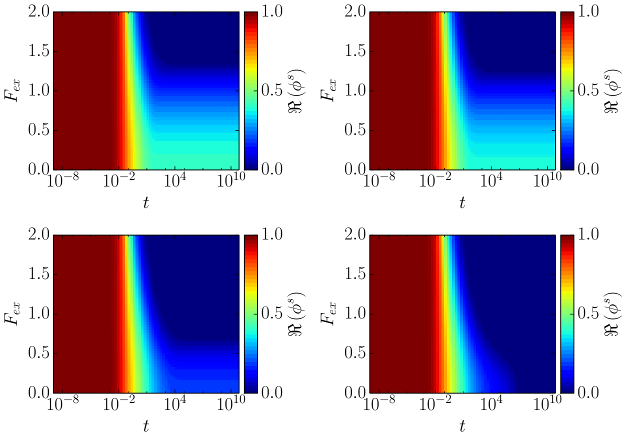

FIG. 2. Real part of the tracer density correlator ϕ^s as a function of time and external force acting on the tracer particle, for a schematic-model glass with different active propulsion velocities v_0 (upper left: $v_0 = 0$; upper right: $v_0 = 0.2$; lower left: $v_0 = 0.4$; lower right: $v_0 = 0.41$).

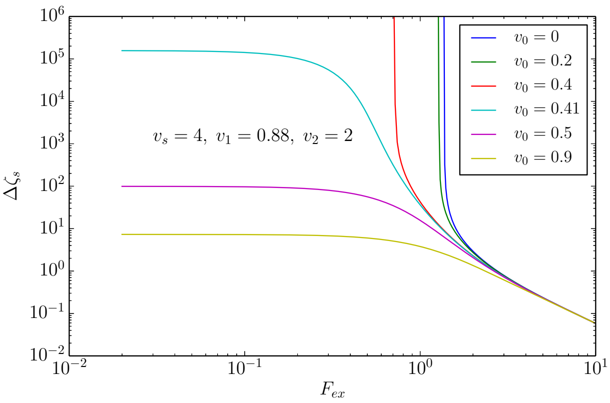

FIG. 3. Friction coefficient $\Delta\zeta$ as a function of external force F_{ex} acting on a probe particle in a glassy suspension of active particles with self-propulsion velocity v_0.

In a glassy suspension, for low external forces, the tracer remains immobile, so that $\Delta\zeta \to \infty$. There exists a critical threshold force above which the tracer becomes mobile; this threshold can be related to a active-propulsion-dependent cage strength. As shown in Fig. 3, by varying the propulsion velocity, the threshold force shifts; in the present model, there is a critical velocity $v_0 \approx 0.41$ above which the active suspension is completely molten. For smaller v_0, the glass remains intact, but is weakened as compared to the passive suspension. This corresponds to macroscopic yield stresses calculated within the same model [1].

As a further step, we present the extension of MCT to include the orientational degrees of freedom.

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Non-equilibrium aspects of the crystallization process

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Crystallization from the undercooled melt is usually described by means of quasi-equilibrium concepts such as transition state theory or kinetic attachment and growth models. We present a computer simulation study of crystallization from the point of view of non-equilibrium thermodynamics and, in particular, quantify the amount of heat dissipated during a crystal nucleation process. As a model system we use Brownian hard spheres. We subject the liquid to an increase in pressure across the liquid-crystal coexistence pressure and compute the volume response of the system. From a large number of sampled trajectories, we obtain the work distribution associated with the crystallization process. As the equilibrium equation of state of the hard sphere system is known very accurately, we can remove all quasistatic contributions from the work distribution and obtain the distribution of dissipated heat. To our knowledge it is the first time that this quantity has been computed. We correlate the dissipated heat with the crystal shape and structure with the aim to construct a coarse-grained description of crystallization processes that takes into account their non-equilbrium nature.

Crystallisation in a Modified Kob-Andersen Glassformer

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Geometric frustration is an approach to the glass transition that proposes that glassiness is caused by a locally favoured structure (LFS) that does not tessellate in Euclidean space. In order to transition between a LFS-rich glassy state and a crystalline one, a large amount of particle rearrangement would be required. This results in a high energy barrier between the metastable glassy state and the thermodynamically favoured one. The Kob-Andersen (KA) binary mixture, a common model glassformer, is a special case however. The locally favoured structure is the KA mixture is a bicapped square antiprism [1] which does geometrically tessellate in Euclidean space to form the Al_2Cu crystal [2].

The KA binary mixture is a model glass former which is homologous to $Ni_{20}P_{80}$, a metallic glass. It is composed of 80% large and 20% small particles that interact with non-additive Lennard-Jones potentials [4]. We are able to identify local structures, in molecular dynamics simulations of the KA mixture using the Topological Cluster Classification (TCC) algorithm. The TCC algorithm uses a neighbour network to hierarchically identify local structures of up to 13 particles and is explained in detail elsewhere [3]. Using the TCC we identified that the LFS for KA has 3 common compositions, each consisting of different proportions of the binary particles, as shown in Fig. 1. Only the A_8B_3 form of the LFS is, a priori, able to tessellate to form the Al_2Cu crystal. However, even though energy minimisation of the structure shows it to be the lowest energy of the three, the A_8B_3 is the least common form of the LFS in a normal KA mixture at 3%. From this result, we propose that the nature of the frustration in the KA mixture is compositional rather than geometric.

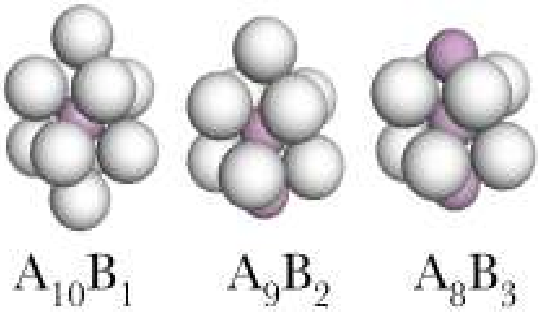

FIG. 1. The three common configurations of the LFS in a KA liquid. Only the A_8B_3 form tesselates

In order to favour the formation of the A_8B_3 form of the LFS and encourage the growth of an Al_2Cu structure, we modified the ratio of large to small particles in the KA mixture from the standard 4:1 to 3:1 and 2:1. This does serve to increase the relative fraction of A_8B_3 LFS in the mixture though the overall amount remains low at 7% and 25% of the total LFS for the 3:1 and 2:1 systems respectively.

We then conducted molecular dynamics simulations using a 2:1 KA liquid and a Al_2Cu crystal seed. For an NPT simulation of 19236 KA liquid particles surrounding a 1500 particle Al_2Cu crystal seed at $P = 0$ and $T = 0.425$, growth of the Al_2Cu crystal is seen. Using a distance based agglomerative hierarchical clustering method we were able to identify the LFS clusters which were members of the Al_2Cu crystal and so track the growth of the crystal over time as shown in Fig. 2. The slowing of growth after 2000 τ_α is a result of the crystal reaching the periodic boundaries of the simulation box in one axis. The crystal growth is anisotropic and so after saturating in one dimension the crystal continues to grow more slowly in the other two dimensions.

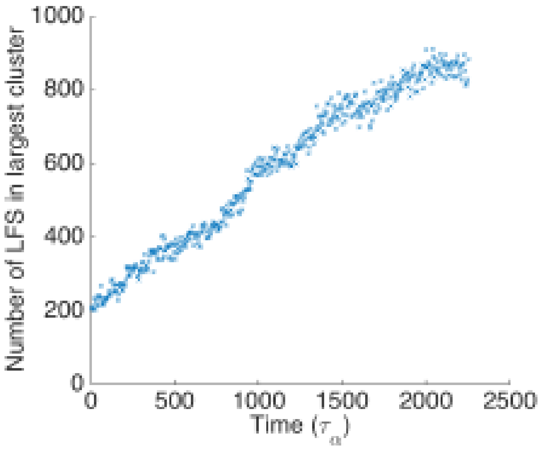

FIG. 2. Graph showing growth of the largest cluster of LFS in a molecular dynamics simulation as a function of the relaxation time of the equivalent KA liquid.

This work was carried out using the computational facilities of the Advanced Computing Research Centre, University of Bristol.

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Exposing a dynamical signature of the freezing transition through the sound propagation gap

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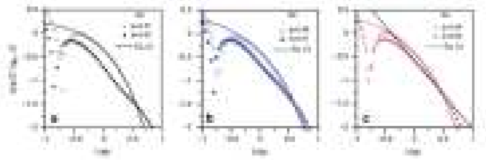
The conventional view of freezing holds that nuclei of the crystal phase form in the metastable fluid through purely stochastic thermal density fluctuations. The possibility of a change in the character of the fluctuations as the freezing point is traversed is beyond the scope of this perspective. Here we show that this perspective may be incomplete by examination of the time autocorrelation function of the longitudinal current, computed by molecular dynamics for the hard-sphere fluid around its freezing point. In the spatial window where sound is overdamped, we identify a change in the long-time decay of the correlation function at the known freezing points of monodisperse and moderately polydisperse systems. The fact that these findings agree with previous experimental studies of colloidal systems in which particle are subject to diffusive dynamics, suggests that the dynamical signature we identify with the freezing transition is a consequence of packing effects alone.



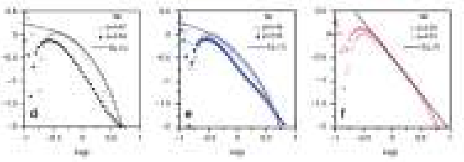


FIG. 1. C(q, t), for packing fractions, ϕ indicated. Only those parts, $\log|C(q, \tau > \tau_m)|$ to the right of the respective maxima are relevant to the discussion; (a–c), are for the one-component hard-sphere fluid, designated S0. (d–f) are for the system with polydispersity 6%, designated S6. Straight lines in c and f are drawn as a guide to locate the dynamical crossover, ϕ_f. Eq.1 is the generalised exponential $C(q,\tau) = K(q)\exp\left[-\tau/\tau_x(q)^{\gamma(q)}\right]$ From Ref.[1].

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A predictive calculation of the crystallization tendency of model pharmaceuticals in the supercooled state from molecular dynamics simulations

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Despite its importance to theoretical models and practical applications, predicting the ability of a given material to vitrify or crystallize remains a challenging problem. This is a very important issue for the development of amorphous pharmaceuticals which particularly requires a fundamental physical understanding of the stability of the amorphous state against crystallization.

The phenomena of crystallization imply the existence of an interface between the crystal and the liquid states. A key property of the liquid-crystal interface is the interfacial free energy, usually denoted γ, which measures the free energy cost of creation of this interface per unit area. There are very few experimental techniques capable of measuring this quantity yet fundamental. Moreover its determination is often indirect and based on some theoretical models such as the classical nucleation theory [1, 2]. The real γ values are not thus known, even for simple cases. Therefore, a reliable determination of γ from molecular dynamics (MD) simulations presents a clear interest.

In the present study, the capillary fluctuation method [3] has been successfully used to determine the interfacial free energy γ of pharmaceutical materials for different crystalline polymorphs. These calculations combined with the determination of the Gibbs free energy difference between the liquid and the crystalline state, and the diffusivity allowed to estimate the transient and steady-state times of nucleation. The results obtained from MD simulation successfully reproduce the experimental tendency of crystallization and have been discussed in the framework of the classical nucleation theory.

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The short time dynamic signature of the liquid-crystal-glass transition in charged spherical colloidal suspension

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We present the short time dynamics of the liquid - crystal - glass transition. By applying dynamic light scattering (DLS) the short time dynamic function, D(q), has been determined from the intensity autocorrelation function, g_2(q,t), at different concentrations in both the crystal and glass regions. From D(q) the short time self diffusion, d_s, was determined as a function of concentration. We found that d_s speeds up in the crystal state but has very similar characteristics in the liquid and the glass region. The general model in which the colloidal crystallization transition in spherical colloidal system is driven by an increase in local entropy is discussed. The experimentally determined structure factor, S(q), will also be presented and we show similarity between the glass and the liquid. This investigation shows that the liquid - crystal and crystal - glass transitions can be identified in addition to the appearance or no appearance of Bragg peaks with the short time dynamics. However, no sharp transition in the short time dynamics or S(q) can be found between the glass and the liquid states.

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From Nuclei to Micro-structure: investigating intermediate length scales by small angle laser light scattering

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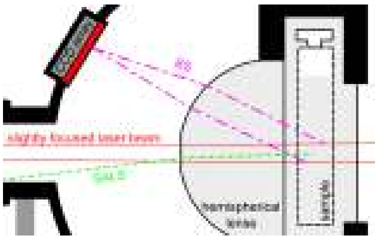

FIG. 1. Light, scattered from the sample, is focused by the hemispherical lens onto CCD arrays, which cover both angular regimes (SALS and BS). The complementary information from two length scales can be compared. The SALS detection unit is not shown.

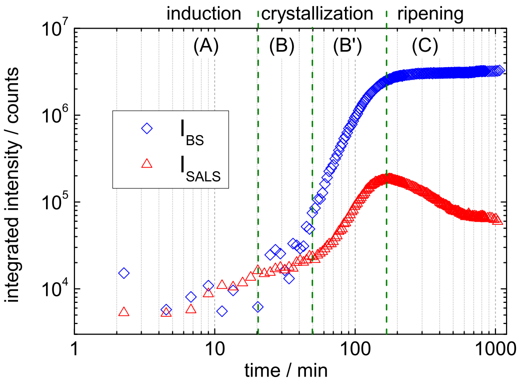

FIG. 2. Temporal evolution of integrated scattered intensities in the BS (blue diamonds) and the SALS (red triangles) regime, showing a strong temporal correlation. (A) to (C) mark the different crystallization stages. The measurements from our other samples show strongly deviating behaviours.

Computer Hard spheres and their experimental counterpart of colloidal hard sphere suspensions are long known to solidify into densely packed crystals. Their crystallization behaviour at the structural length scale has been intensively studied by Bragg and dynamic light scattering and by high resolution microscopy. But what happens to the still molten environment surrounding the growing crystallite? How does the micro-structure evolve during nucleation, growth and coarsening?

To gain a deeper insight into these questions we have developed an improved light scattering apparatus capable of performing simultaneous measurements in the Bragg scattering regime (BS) and in the small angle regime (SALS) (FIG. 1). We demonstrate its performance for several hard sphere and attractive hard sphere suspensions.

A comparison of the small angle to Bragg data allows a calibration of the sequence of crystallization events in time (FIG. 2 displays one example). With the setup we can show, how important complementary information can be gained on the immediate environment of the growing crystals or the global scale crystallite distribution. We further demonstrate that processes on larger length scales have a significant influence on the crystallization kinetics and the final micro-structure.

Free energy landscape approach to the crystallization of super-cooled liquids

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The crystallization time of most super-cooled liquids at a given temperature shows a nose-shaped form when the temperature is plotted against the crystallization time (time-temperature-transformation (TTT) diagram), namely near the melting temperature the crystallization time is an increasing function of temperature and at much lower temperatures it becomes a decreasing function of temperature. The former behavior is believed to be controlled by the thermodynamics and the latter is governed by the slow dynamics. However this belief has not been explained theoretically so far.

In this presentation we discuss a unified theoretical frame work which explains the TTT diagram on the basis of the free energy landscape (FEL) theory for non-equilibrium systems proposed by one of present authors.[1] The FEL is defined as a function of a given configuration of constituents by the partition function for the rapid motion of the constituents around the configuration and the time evolution of the system can be represented by the stochastic motion of the representative point on the FEL. In a reduced representation, we can assume the stochastic dynamics of the representative point among the local minima of the FEL. It is important to note that the FEL depends on the temperature and thus the FEL approach can handle both thermodynamic and dynamic processes in the same frame work.

The FEL of a super-cooled liquid consists of a deep crystalline basin (with $N!$ degenerate ones) and many local minima correspond to non-equilibrium super-cooled states. The crystallization time of super-cooled liquids is then given by the first passage time of a representative point from an initial basin to the crystalline basin.

We denote the crystalline basin by X, the gate basins directly connected to the crystalline basin by O and other basins by I. We assume the stochastic dynamics among O and I basins by the trapping model[2] and the transition from an O basin to the X basin by the hopping motion where the jump rate is determined by the difference of the free energies.

We assume that there are n basins in the super-cooled states I and k basins in the gate basins O. Denoting the state by a vector $\vec{P}(t) = (P(I_1,t),\cdots,P(I_n,t),P(O_1,t),\cdots,P(O_k,t))^t$, we can write the master equation

$$\frac{\partial \vec{P}(t)}{\partial t} = \overleftrightarrow{W}\vec{P}(t) \tag{1}$$

and the formal solution to this equation is given by

$$\vec{P}(t) = \exp\left(\overleftrightarrow{W}t\right)\vec{P}(0). \tag{2}$$

The first passage time distribution $F(X,t)$ to the basin X is given by

$$F(X,t) = \frac{\partial P(X,t)}{\partial t} = \sum_{O_i} w_{O_i,X} P(O_i,t), \tag{3}$$

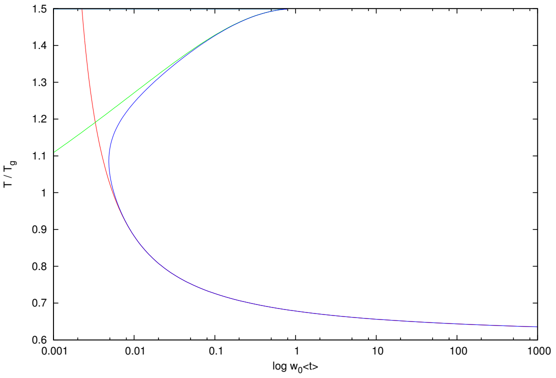

FIG. 1. The TTT diagram obtained for a model FEL structure.

where $w_{O_i,X}$ is the jump rate from basin O_i to basin X and the jumps from X to any other basins are prohibited. The crystallization time can be obtained from the mean first passage time

$$\langle t\rangle = \int_0^\infty tF(X,t)dt. \tag{4}$$

Figure 1 shows the TTT diagram obtained by the present theoretical frame work, where three basins are prepared as basins I together with a gate basin O and the crystalline basin and the relevant distribution was used for thr trapping diffusion.[2] We apply this formalism to various structures of the FEL which include the small world and the scale free network. We show that the TTT diagram is sensitive to the structure of the FEL, indicating the possibility of obtaining the structural information from the TTT diagram.

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Fluids of colloidal ellipsoids: trading free volume for freedom of rotation

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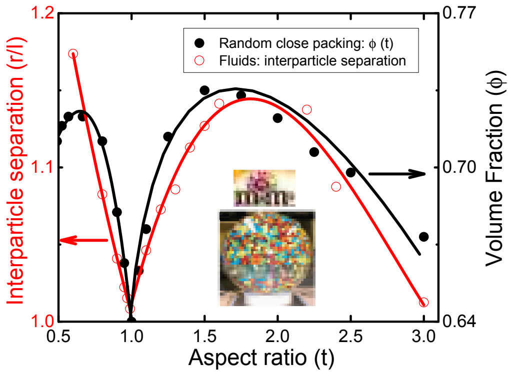

FIG. 1. The most typical separation between nearest neighbors r_{NN} at fluid volume fraction $\varphi = 0.35$ is minimal for the spheres, increasing for the ellipsoids of higher aspect ratio t, and eventually changing the trend for very high $|t-1|$; r_{NN} is normalized by $l = (ab^2)^{1/3}$, where b is the equatorial diameter. Strikingly, the derivative of r_{NN} is discontinuous for $t = 1$, indicating that the physics of ellipsoids is qualitatively different from that of the simple spheres. Interestingly, a similar behavior was observed for densities $\phi(t)$ of random granular packings of macroscopic ellipsoids, such as the M&M candies[3].

The local microscopic structure of fluids of simple spheres is well known. However, the constituents of most real-life fluids are non-spherical, leading to a coupling between rotational and translational degrees of freedom. This coupling does not allow the structure of simple dense fluids of ellipsoids to be obtained by classical experimental techniques, such as light scattering. As a result, the fundamental role played by the rotational degrees of freedom in determination of local fluid structure and fluid dynamics remains unknown.

We determine, for the first time by a direct experimental technique, the structure of dense fluids of ellipsoids[1]. For that purpose, we employ video-rate three-dimensional confocal microscopy of a suspension of colloidal ellipsoids. These μm size particles suspended in a solvent are sufficiently small to explore the phase space by random Brownian motion, yet sufficiently large to be fully visible by optical microscopy. We use simulations and theory to reproduce the experimental structure and estimate the contribution of charge effects to the system[2], achieving perfect agreement between theory, experiment, and simulation. Further, we employ the same theoretical framework to examine the local order in these fluids as a function of the aspect ratio of the constituent particles t. Strikingly, the strength of (short-range) positional correlations $\chi = \int_0^\infty (g(r)-1)^2 r^2 dr$, where $g(r)$ is the radial distribution function, exhibits a non-analytical point for the spheres $t = 1$. Some other characteristics of the local structure, such as the typical interparticle separation r_{NN} at a given volume fraction $\varphi = 0.35$, are non-analytical at $t = 1$, as well; see Fig. 1. This behavior must have an impact on the viscosity of simple fluids. Like in the vicinity of a phase transition, a non-analytical behavior (precluding series expansion in powers of $|t-1|$) is indicative of a qualitative difference between the fluids of spheres, where rotations and translations are decoupled, and the fluids of rotationally-anisotropic particles. Remarkably, the local packing of ellipsoids changes in a discontinuous manner through $t = 1$: the prolate particles pack with their long axes being parallel, like cucumbers, while the oblate ones pack with their *short* axes parallel, like saucers. Surprisingly, the observed scaling of structural characteristics in our thermodynamically-equilibrated fluids matches with the scaling of the volume fraction $\phi(t)$ in non-ergodic packings of ellipsoids, such as the M&M candies[3] (Fig. 1). This suggests a deep connection to exist between the free volume in fluids and the physics of random granular packings, possibly related to the ground-states of matter.

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Ionic current noise across individual carbon and boron-nitride nanotubes: Hooge's law and beyond

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Over the last decade, nanometric sized channels and pores have been intensively exploited and investigated as probes for molecular sensing, thanks to the possibility to achieve low-cost, high-throughput DNA sequencing [1].Techniques based on the resistive-pulse method, also known as Coulter counter method [2], for detection and analysis of single particles or molecules are increasingly popular, applied not only to nucleic acids but also to proteins, polymers and colloidal particles [3, 4]. The resolution of the technique is limited by any noise affecting the ionic current. Low-frequency noise presence has been repeatedly reported in solid state nanopore, without finding a unique and satisfactory explanation [5–7].

In the present work we study the low frequency noise in ionic current in individual transmembrane nanotubes. The systems are obtained by nanomanipulation of individual nanotubes inside a scanning electron microscope, allowing to insert and seal a single nanotube in a SiN membrane. This transmembrane system is then sandwiched between two reservoirs and the electric current is measured. Here we focus on the measurement of the ionic noise with both Carbon and Boron Nitride nanotubes. This offers a unique opportunity to study ion and fluid transport in nanochannel with identical crystallographic structure but radically different electronic properties.

We observe that in both cases the noise exhibits a strong $1/f$ behavior. In semi-conducting systems this is ususally accounted for by the empirical Hooge's law relating the current fluctuation spectrum to the mean current s as:

$$\langle|\Delta I(f)|^2\rangle = \alpha \frac{\langle I\rangle^2}{f} \tag{1}$$

with $\alpha \propto 1/G$, *i.e.* inversely proportional to number of charge carriers.

However, while the spectra recorded in semi-metallic CNT follows the long standing phenomenological Hooge's relation, this is not the case of insulating BNNT. We are able to show that the key of the violation of Hooge's law lays on the surface charge developed at the fluid-solid interface.

In particular, we show that CNT carries a very small surface charge at the fluid-wall interface, more than an order of magnitude lower than what observed in BNNT. By comparing the results obtained on CNT and BNNT for different values of pH, we demonstrate experimentally the impact of the surface charge on the $1/f$ current noise; while systems presenting a very small or negligible surface charge, the frequency can be correctly described by the phenomenological Hooge law, large values of surface charge induce a violation of the commonly used relationship. Highly charged nanofluidic devices present an excess in the current noise that can greatly affect the signal-to-noise ratio with major consequences in the detection of particle translocation and sequencing obtained with solid state nanopores and nanotubes.

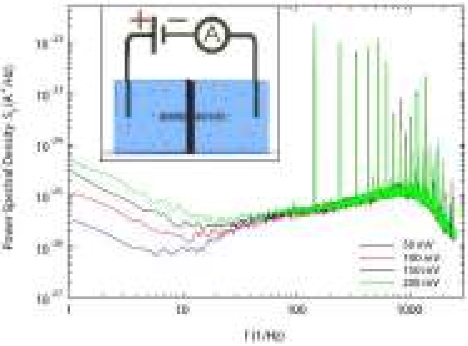

FIG. 1. Main: Noise current power spectra for CNT for different applied voltage. .Panel: Schematic of the experimental set-up for measuring ionic transport through single transmembrane

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Dynamical Faciliation in Binary Hard Disk Systems

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Important predictions of dynamic facilitation theory (DynFT) for structural glass forming materials, results like the parabolic law of transport properties, and the non-equilibirum phase transition in the trajectory space with the s field (i.e., the so-called "s-ensemble"), have been tested with lattice models and continuous force atomistic models [1]. Here, we provide tests and extensions of DynFT to hard disk systems.

It is well known that the rapid decreasing temperature (i.e., quenching) such as the soft disk system show the variety of transitions from liquid state to crystallization or supercooled liquid in which kinetic temperature T is one of the primary control parameter. On the contrary, in the hard disk system, since there is no kinetic temperature (energy) scale, the thermodynamic properties in the system can only be described by the pressure p. As quenching soft disk system, compressing hard disk system have been expected to show the behavior of glass. In this paper, extended dynamic facilitation theory as a function of pressure in the "supercompressed" liquid of additive binary hard disk mixture is numerically investigated.

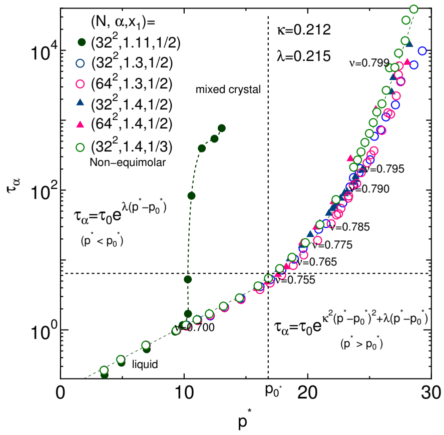

FIG. 1. Structural relaxation time τ_α in terms of reduced pressure p^* with parabolic fittings are shown. Structural relaxation near the monodisperse case ($\alpha = 1.11$;α is size ratio) suddenly increases around $p^* \sim 10$ due to the transition, which is quite different in contrast to the parabolic behavior of structural relaxation.

We consider three equations for facilitated and hierarchical dynamics: the parabolic form of structural relaxation time, the exponential decay of excitation concentration with increasing pressure, p, and the logarithmic growth of excitation free energy with increasing excitation displacement length. In these equations, the usual dependence on inverse temperature, $1/T$, is replaced by dependence on p/T, and onset to correlated dynamics is characterized by an onset value of p/T.

We confirm those generalized DynFT equations numerically by extensive systematic simulations with modern efficient algorithms [2], (i.e., Event-Chain Monte Carlo and Event-Driven Molecular Dynamics). Main results are shown in Figs.1-3.

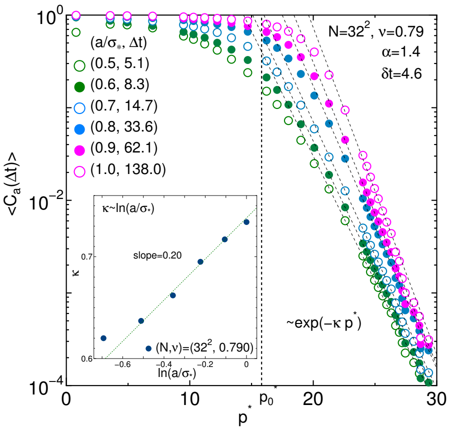

FIG. 2. Averaged excitation rate $\langle C_a(\Delta t)\rangle$ in terms of pressure p^* with typcial spatio-temporal scale of excitation $(a, \Delta t)$. The inset show the slope of exponential decay above onset pressure by changing displacement.

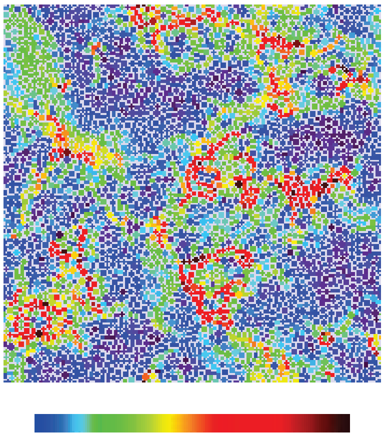

FIG. 3. Typical spatial distribution of excitation in $(N, \nu, x_1) = (64^2, 0.780, 1/3)$ with $(a/\sigma_0, \Delta t) = (0.6, 6.4)$. Specific constraint collective motion emerges above the onset pressure, which are good agreement with the behavior of statistical properties of generalized DynFT.

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Dynamics of quasi-two-dimensional binary colloidal hard spheres: self-diffusion, 'no' hydrodynamics and collective transport

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Transport properties of two-dimensional (2D) fluids are in many respects different to those of their three-dimensional (3D) counterparts. For example, in contrast to 3D the hydrodynamics in 2D is anomalous and is associated with the non-existence of self-diffusion coefficients. With respect to binary colloidal fluids in 2D, many aspects of mass transport are not well understood, including the role of hydrodynamic interactions, the self-diffusion of the differently sized species and the behaviour of collective transport processes such as interdiffusion. In this work, we address these issues using a combination of experiments and computer simulations.

In particular, we study a quasi-two-dimensional binary colloidal hard sphere system at a wide variety of packing fractions and compositions using optical video-microscopy. First, we compare the radial distribution functions from both monodisperse and binary systems to those from fundamental measure theory and Monte Carlo (MC) simulations (see inset of Fig. 1). The observed quantitative agreement demonstrates that our system is an excellent model for a binary hard disk system.

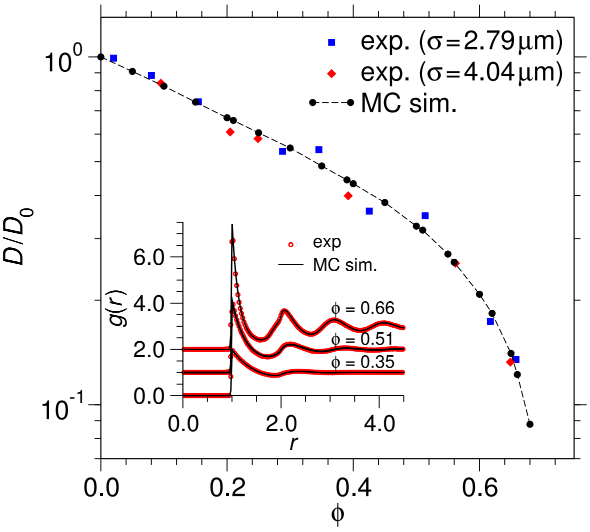

FIG. 1. Long-time self-diffusion coefficient D scaled by the diffusion coefficient at infinite dilution D_0 as a function of the packing fraction ϕ. The inset shows the radial distribution functions for three different packing fractions for the experiments and MC simulations.

Next, we characterise the single particle dynamics via the mean-squared displacement (MSD) and short- and long-time self-diffusion coefficients. We compare the experimental measurements to MC simulations which do not include hydrodynamics. While the short-time dynamics is affected by hydrodynamic interactions, the MSD at long times exhibits quantitative agreement with results from the MC simulation (see Fig. 1), which importantly shows that hydrodynamic interactions do *not* affect the long-time self-diffusion. Consequently, we describe the long-time self-diffusion in the binary systems using an expression dependent upon only the contact value of the radial distribution function to account for direct interactions, and find good agreement with the experimental results.

Finally, we consider collective transport phenomena in our binary hard sphere systems in the form of the interdiffusion coefficient. We develop a new method to measure the interdiffusion MSD from particle trajectories using a centre-of-mass MSD of each component relative to the centre-of-mass MSD of all the particles. We compare the results of this approach to that predicted by the Darken approximation [3], which states that the interdiffusion MSD may be approximated using the self-diffusion MSDs as

$$\left\langle r_{ab}^2\right\rangle = \Phi\left(c_a\left\langle r_b^2\right\rangle + c_b\left\langle r_a^2\right\rangle\right). \qquad (1)$$

Here c_α ($\alpha = a, b$) is the concentration and $\left\langle r_\alpha^2\right\rangle$ the self MSD of component i, and Φ is the thermodynamic factor, where we obtain Φ using a block analysis of the concentration fluctuations. Interestingly we see qualitatively different behaviour for systems at two different size ratios.

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Simulation of hard sphere suspensions of fluctuating sizes

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We introduce and study a simple physical model which aims at capturing the effects of stochastic size fluctuations on the behaviour of hard sphere supensions. As a simplest case, we analyse binary hard spheres mixtures in which the size of each sphere fluctuates randomly between two diameters. Here we have chosen moderate size variations, corresponding to ratios $1.0 < \sigma_B/\sigma_S \leq 1.1$ between the big and the small radii. We explore the fluid phase at number densities $\rho = N/V$ ranging from 0.1 to 0.9, by means of NVT Monte Carlo (MC) simulations. Diameter changes are attempted with probability π_i for an increase and π_d for a decrease, here we mainly focus on systems with $\pi_i = \pi_d$.

For a given diameter ratio, the average equilibrium concentrations of the two types of spheres depend on the number density ρ and the probabilities π_i and π_d only. The structure of a suspension undergoing size fluctuations, as characterised by the radial distribution function $g(r)$, is indistinguishable from that of a non-fluctuating binary mixture at the same composition and number density. By contrast, size fluctuations do affect the dynamical properties: the diffusion coefficient, as computed from the MC dynamics [1], is larger in presence of size fluctuations. For a density of $\rho = 0.9$ and a diameter ratio of $\sigma_b/\sigma_s = 1.05$ the differerence attains an increase of 12.5%.

Further studies will consider fluctuations between more complex shapes and interaction potentials, and explore the relevance of the model for the description of conformation changes and flexibility in protein assemblies [2].

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A light scattering study of the dynamical slowing down in Laponite suspensions: similarities with supercooled liquids

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Two-step response functions are ubiquitous in supercooled liquids approaching their glass transitions and indicate the existence of two simultaneous relaxation processes in these systems [1]. The faster secondary (or β) relaxation process is believed to arise from the diffusion of a constituent particle within a cage formed by its neighbours, while the slower primary (or α) relaxation process is typically attributed to the particle's cooperative diffusion between neighboring cages. The viscosity and relaxation timescales of a glass-former are found to increase sharply when its temperature is quenched rapidly [2]. For fragile glass formers, the α-relaxation time shows a Vogel-Fulcher-Tammann (VFT) dependence on temperature (T), with a fragility index that is solely material-dependent [3].

Colloidal glasses have recently emerged as excellent model candidates for the study of glasses and gels [4]. In contrast to a supercooled liquid that achieves its glass transition when its temperature is decreased rapidly to bypass crystallization, a colloidal suspension can show glassy behavior when its volume fractions ϕ is increased appropriately. In our work [5], we perform dynamic light scattering (DLS) experiments to measure the intensity autocorrelation functions of aging aqueous suspensions of charged, disk-shaped synthetic clay (Laponite) particles. The glass-forming properties of Laponite suspensions have been studied extensively during the last two decades [6]. As expected, the intensity autocorrelation functions, $C(t)$, obtained by us for Laponite suspensions of various ages and particle concentrations, are characterized by two-step decays. The $C(t)$ data are fitted to functions of the form

$$C(t) = \left[a \exp\left\{-t/\tau_1\right\} + (1-a)\exp\left\{-(t/\tau_{ww})^{\beta}\right\}\right]^2 \tag{1}$$

to estimate the relaxation timescales (τ_1 and τ_{ww}) of the aging samples. We observe that both the relaxation processes slow down with increasing sample age t_w, with the slowdown of the primary α relaxation process being far more dramatic than that of the secondary β relaxation process (Figure 1). We fit the τ_1 data to a modified Arrhenius form $\tau_1 = \tau_1^0 \exp(t_w/t_\beta^\infty)$ and the $<\tau_{ww}>$ data to a modifed Vogel Fulcher Tammann form $<\tau_{ww}>=<\tau_{ww}>^0 \exp(Dt_w/(t_\alpha^\infty - t_w))$ (shown by solid lines in Figure 1), where t_β^∞ and t_α^∞ are, respectively, the characteristic timescales describing the β and α relaxation processes and D is the fragility index of the Laponite suspension.

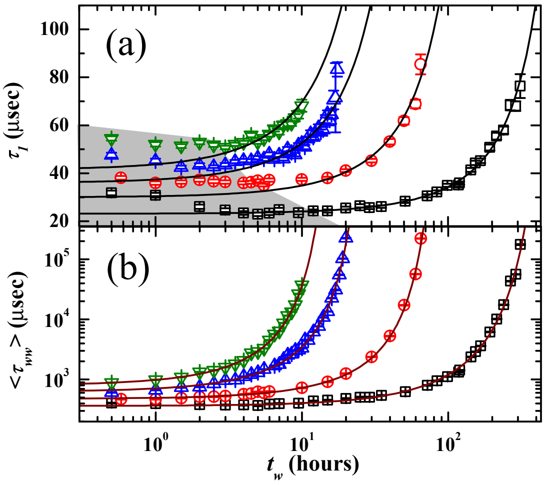

FIG. 1. (a) The fast and the mean slow relaxation times (τ_1 and $<\tau_{ww}>$), are plotted *vs.* waiting time t_w in (a) and (b) for Laponite samples at 25°C and at concentration 2.0% w/v (□), 2.5% w/v (○), 3.0% w/v (△) and 3.5% w/v (▽). The solid lines in (a) and (b) are fits to the modified Arrhenius and Vogel Fulcher Tammann forms.

We compare our dynamical slowdown data with those obtained for fragile supercooled liquids by establishing a one-to-one mapping between the waiting time since filtration (t_w) of a Laponite suspension and the inverse of the temperature ($1/T$) of a rapidly quenched supercooled liquid. Our analysis provides us with new timescales, t_β^∞ and t_α^∞, that can successfully describe the phenomenon of dynamical arrest in Laponite suspensions. Furthermore, we observe a strong coupling between the primary and secondary relaxation processes of aging Laponite suspensions. Finally, our data also demonstrates the self-similar nature of the aging dynamics of Laponite suspensions within the range of sample concentrations studied here.

The authors are grateful to R. Basak for his help with the experiments.

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Casimir-like forces close to the percolation transition

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Geometric percolation and thermal critical phenomena share several features. Clusters in percolation play the same role as thermal critical fluctuations close to a second-order critical point, both being described by scale-free distributions, whose first moment shows a power-law behavior at the transition point [1]. Colloidal particles, immersed in a solvent close to criticality, experience long-range effective forces,named critical Casimir forces. These forces originate from the confinement of the solvent critical fluctuations between the surfaces of two colloids [2].

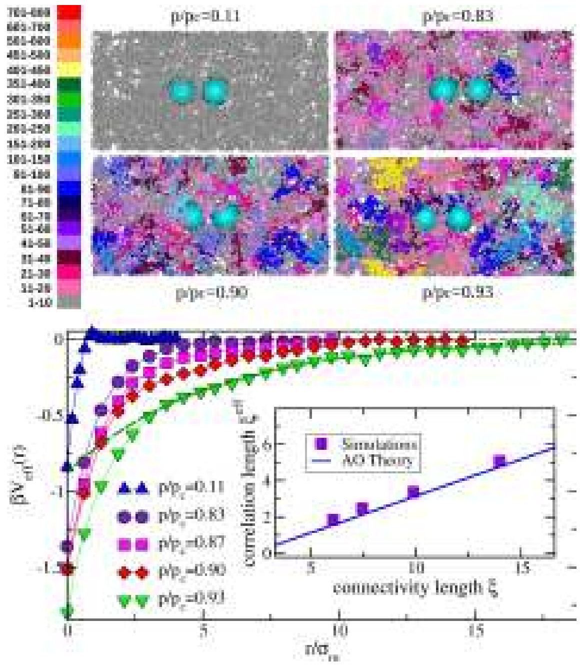

FIG. 1. (a)Snapshots of the simulated system for different mean cluster sizes S on approaching the percolation threshold. Clusters of different sizes are represented with different colors (see the legend). (b) Evolution of the effective potential V_{eff} between two colloids in a gel-forming solution close to the percolation threshold. r is the surface-to-surface distance between the two colloids (in units of the solvent size σ_s). The solid line is the theoretical prediction of the long-distance behaviour of V_{eff}.

Building on the analogy between critical phenomena and percolation, we show that it is possible to observe long-range forces near a percolation threshold. We demonstrate this by performing Monte Carlo simulations of two colloidal particles immersed in a sol of irreversible clusters for different cluster size distributions, on approaching the percolation point. For each cluster distribution we numerically evaluate the effective potential between the colloidal particles and we show that it becomes attractive and long-ranged on approaching the sol percolation transition(see Fig. 1). Our results provide the geometric analogue of the critical Casimir force, since the measured long-range effective potential results from the confinement of the cluster-size fluctuations between the surface of the two colloids. Since we use irreversible clusters to generate such effective interaction, we discuss the effect of the cluster lifetime on the effective potential. Indeed we show that in the case of irreversible clusters (i.e. clusters with infinite lifetime) the range of the potential is controlled by the connectivity length of the system, while for clusters with variable, but finite, lifetime the resulting effective potential has a much shorter range which is controlled by the range of the radial distribution function, which offers a measure of the effective size (dressed by thermal correlations) of the monomer. We also discuss a theoretical description based on a polydisperse Asakura-Oosawa model which captures the divergence of the interaction range. The good agreement between theory and numerical simulations shows that the mechanism controlling the long-range effective interaction close to percolation can be assimilated to a depletion effect [3].

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3.3 Posters B

Fluctuations and aging at the critical point of a binary mixture

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After a sudden change of a thermodynamic parameter, such as temperature, volume and pressure, several systems and materials may present an extremely slow relaxation towards equilibrium. During this slow relaxation, usually called aging, these systems remain out-of equilibrium for a very long time, their properties are slowly evolving and equilibrium relations are not necessarily satisfied during aging. Typical and widely studied examples of this phenomenon are glasses and colloids where many questions still remain open. Thus in order to understand the minimal ingredients for aging the slow relaxations has been studied theoretically in second order phase transitions when the system is rapidly quenched from an initial value of the control parameter to the critical point. Because of the critical slowing down and the divergency of the correlation length the relaxation dynamics of the critical model shares several features of the aging of more complex materials. One of the question analyzed in this models is the validity of the Fluctuation Dissipation Theorem (FDT) during the out of equilibrium relaxation. In equilibrium FDT imposes a relationship between the response of the system to a small external perturbation and the correlation of the spontaneous thermal fluctuations. When the system is out of equilibrium FDT does not necessarily holds and it has been generalized as

$$k_B T \; X(t,t_w) \; \chi(t,t_w) = C(t,t) - C(t,t_w) \qquad (1)$$

where k_B is the Boltzmann constant, T the bath temperature, $C(t,t_w) =< A(t)A(t_w) >$ ($< . >$ stands for average) the correlation function of the observable A and $\chi(t,t_w)$ the response to a small step perturbation of the conjugated variable of A switched on at time $t_w < t$. The $X(t,t_w)$ is equal 1 in equilibrium whereas in out-equilibrium measure the amount of the FDT violation and it has been used in some cases to define an effective temperature $T_{eff}(t,t_w) = X(t,t_w)T$. One experiment has been performed in these conditions in our team [1] in liquid cristals. We propose here to continue this study in another critical system : the demixion transition of a binary mixture of polymer and solvant.

We choose to study a well-characterized mixture of polystyrene and methyl-cyclohexane [2], with a critical temperature T_c a little bit higher than room temperature and a small viscosity allowing easy preparation and quench at the critical point. The correlation length grows like

$$\xi = \xi_0 \left(\frac{T - T_c}{T_c} \right)^{-\nu}, \qquad (2)$$

FIG. 1. Dielectric experiement allowing fast quench at the critical point. A the center, the dielectric cell between two ITO coated electrods.

with ξ_0 can reach 1 nm using high molecular weigth polystyrene, $\nu = 0.63$ is the scaling exponent of the correlation length in the Ising 3 D universality class. Demixion of binary mixtures usually belongs to this universality class.

Dielectric spectroscopy allows the investigation of the molecular dynamics of the relaxation process by means of the polarization of molecular dipoles on the liquid sample. Moreover, the possibility to develop multi-frequency dielectric experiments gives us access to such microscopic information at each aging time over a typical range of $10^{-2} - 10^{2}$ Hz with low noise and high sensibility, see ref. 3. This setup, see Fig. 1, is also adapted to perform very fast quench at the critical point (30 K in typically one minute). Thanks to home-made amplifiers, we are also able to measure dielectric noise comming from the mixture. Dielectric response and noise can be related through a fluctuation-dissipation relation.

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Direct Measurement of the Free Energy of Aging Hard-Sphere Colloidal Glasses

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The nature of the glass transition is one of the most important unsolved problems in condensed matter physics. The difference between glasses and liquids is believed to be caused by very large free energy barriers for particle rearrangements; however so far it has not been possible to confirm this experimentally. We provide the first quantitative determination of the free energy for an aging hard-sphere colloidal glass. The determination of the free energy allows for a number of new insights in the glass transition, notably the quantification of the strong spatial and temporal heterogeneity in the free energy. A study of the local minima of the free energy reveals that the observed variations are directly related to the rearrangements of the particles. Our main finding is that the probability of particle rearrangements shows a power law dependence on the free energy changes associated with the rearrangements, similarly to the Gutenberg-Richter law in seismology.[1]

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Phase separation in polymer blends close to and below T_g : aging and rejuvenation

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We design a spatial model for describing the dynamics of polymer blends close to or below the glass transition. The model incorporates the heterogeneous nature of the dynamics close to T_g on a scale of few nanometers (3-5 nm typically). Spatial dynamics follows then from an Onsager like description and driving forces are derived from an extension of the Flory Huggins model to the case of compressible blends. This model takes also into account the facilitation mechanism which allows for describing the relaxation of a slow dynamic heterogeneity when surrounded by fast ones as due to interdiffusion mechanisms and free volume diffusion. The model is solved on a 2D square lattice corresponding to spatial scales of about a few tens to 100 nm and a resolution corresponding to the scale of dynamical heterogeneities.

We apply this model to study phase separation close to T_g after cooling the system. we observe slow domains building in coexistence with fast ones. Domains are found to grow like the logarithm of time. We study also the reverse process after the temperature is increased again in the totally miscible range. We observe a temporal asymmetry between the aging and the rejuvenation mechanisms : slow domains melt much faster than the elapsed time required to built them during the separation process and total miscibility is recovered after a much shorter time. In particular, we show that glassy morphologies melt thanks to the facilitation mechanism.

Aging rates in Glasses and their melts

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When a liquid is rapidly quenched it takes time to relax to thermodynamical equilibrium. The lower the temperature the longer the relaxation time. Crossing the glass transition temperature, T_g, equilibrium is no longer reached in experimental time scales. The relaxation process affects most physical quantities. It slows down with time and is commonly described by a Kohlrausch-William-Watts (KWW) exponential expression, e.g. [1]. This phenomenological description does not identify the physics behind the process and further violates the invariance to a time shift $t \rightarrow t + t_w$.

We calculated with molecular dynamics simulation the aging rates in the glass and its undercooled melt for a binary Lennard-Jones glass system [2] and for selenium. To check for the effects of the simulation ensemble, the calculations were done for constant volume and for constant pressure with different quench protocols. We monitored the time evolution of the internal energy, the volume or pressure, the diffusivity and the heterogeneity.

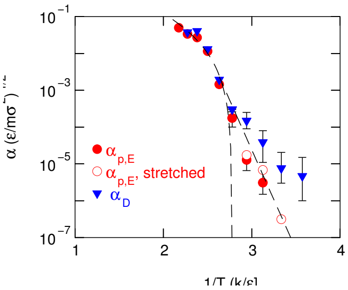

FIG. 1. Aging exponents in the binary LJ-glass for pressure and internal energy (circles) and for the diffusion coefficient and the dynamic heterogeneity (triangles). The solid symbols refer to fits without stretching exponent, the open symbols to a stretching exponent $\beta = 0.5$. The dashed lines show the fits with the MCT and Arrhenius expressions for D_∞, respectively.

At temperatures above the mode coupling theory (MCT) critical temperature T_c pressure or volume, internal energy and diffusivity age with the same rate. Below T_c we find a split of the aging rates into a fast one for the diffusivity and the dynamic heterogeneity and a much slower one for pressure or volume and internal energy. This is shown in Fig. 1 using a KWW expressions for the different quantities $Q(T,t) = Q_\infty(T) + \Delta Q(T) e^{-(\alpha_Q(T)t)^{\beta_Q(T)}}$.

The aging of the diffusivity is well given without a stretching exponent. The stretching of the aging of energy and pressure can be traced to the time dependence of the diffusivity and we get a time shift invariant expression in terms of diffusivity or mean square displacement

$$p(T,t) = p_\infty(T) + \Delta p \cdot e^{-(\langle s^2_{\text{eff}}(t)\rangle - \langle s^2_{\text{ball}}\rangle)/\ell_{p,E}(T)}$$

, where $1/\langle s^2_{\text{eff}}\rangle = 0.8/\langle s^2_A\rangle + 0.2/\langle s^2_B\rangle$ and s^2_{ball} is the ballistic mean square displacement. The aging length ℓ shows a kink near T_c similar to the one observed earlier for the activation volume.

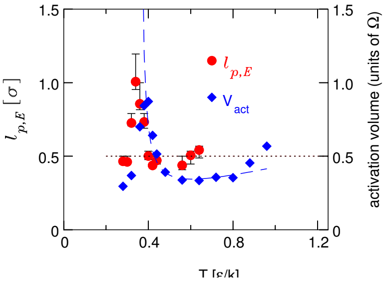

FIG. 2. Red solid circles: aging length against temperature. The dotted line represent the approximate fit with the MCT and Arrhenius expressions in Fig. 1. Blue solid diamonds and dashed line calculated diffusional activation volume and MCT fit [3]. The error bars are estimates of the fit reliability.

In summary we find near T_c a split into fast and slowly aging quantities. This is similar to the violation of the Stokes-Einstein relation at low temperatures [4, 5]. It can be attributed to the dominance of hopping motion over flow. The stretching of the slow relaxation rate stems from the aging of the fast rate.

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Slowing Down of Accelerated Physical Aging in Ultrathin Polymer Films

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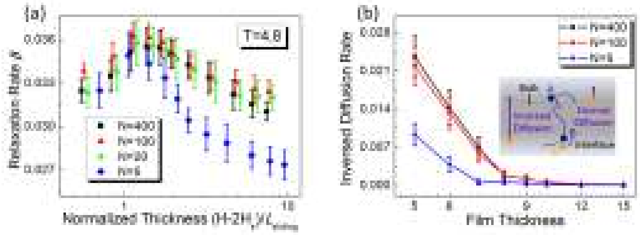

FIG. 1. (a) Variation of aging rate as a function of normalized film thickness $(H-2H_s)/L_{sliding}$. Here H and H_s indicate the thickness of film and surface layer, and $L_{sliding}$ is the average sliding length calculated from the simulation data. (b)Thickness dependence of inversed free volume diffusion rate in ultrathin films. Inset illustrates the IFVD process caused by the sliding motion along chain molecules.

Physical aging in glassy polymer films has attracted great attention in the past two decades due to their strong correlation with the lifetime of polymer-based nano-devices. In recent year, many experiments demonstrated that, upon confinement at the nanoscale level, the physical aging rate was enhanced in comparison to the bulk (see [1] and the references). The occurrence of this accelerated physical aging reduces the lifetime and eventually limits the potential application of polymer-based nano-devices.

Recently we demonstrated that the incorporation of the free volume diffusion and annihilation processes into Monte Carlo simulations could be employed to efficiently study the physical aging in ultrathin polymer films [2]. By using this method, we systematically investigate the influence of film thickness on the aging rate of ultrathin polymer films. Results show that the aging rate increases upon decreasing the film thickness toward specific values, which are consistent with the accelerated physical aging observed in many experiments. Especially, we find that with further reducing the thickness, these accelerated physical aging slows down (see Fig. 1(a)). This phenomena indicate the improved lifetime for ultrathin polymer films, and are of great importance in practical application. We demonstrate that this anomalous slowing down can be attributed to an inversed free volume diffusion (IFVD) process caused by the sliding motion (see Fig. 1(b)) of chain molecules. Our findings provide direct evidence of the relationship between the sliding motion of short chain fragments and the physical aging of ultrathin polymer films, and also verify the existence of a new confinement effect at the nanoscale.

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Plastic flow of foams and emulsions in a channel: experiments, theory and simulations

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Recent studies on foams and emulsions have called approaches in terms of *global* rheology into question [1]. The occurrence of plastic events induces correlations within the material and non-local effects, due to the redistribution of elastic stress in their surrounding. We provide results from the first experimental measurements of the rate of T1 plastic events and of the distribution of their orientations in a Poiseuille flow on a confined foam in a Hele-Shaw geometry. The correlation with independently measured velocity profile is quantified, and that there is still a significant plastic activity towards the centre of the channel. To go beyond the limitation of the experiments, namely the presence of wall friction which complicates the relation between shear stress and shear rate determining the emergence of an extra characteristic length (the *friction* length), we compare the experiments with simulations based on the lattice Boltzmann method [2], which are performed both with, and without, wall friction. Our numerical model enjoys the unique feature of combining two main advantages with respect to conventional methods. From one side, it gives a realistic structure of the emulsion droplets, like in Surface Evolver [3]; at the same time, due to its built-in properties, it provides direct access to equilibrium and out-of-equilibrium stresses, including elastic and viscous contributions, and, in contrast to approaches inspired by the bubble model [4], it naturally incorporates the dissipative mechanisms and the interfacial constraints that lead to plastic events. Our results indicate a correlation between the localisation length of the velocity profiles and the characteristic length of the rate of plastic events (the *plastic* localisation length) [5] , as we show in figure 1. Moreover, we prove that, for particular flow curves, namely for Bingham fluids (for which the shear stress σ, beyond the yield value σ_Y, varies linearly with the strain rate $\dot{\gamma}$), two asymptotic regimes, i.e. close to yield ($\sigma \approx \sigma_Y$) and far from yield ($\sigma \gg \sigma_Y$), can be tackled analytically and exact results can be derived for the dependence of the velocity localisation length on the plastic and friction lengths [6] (see figure 2). Finally, unprecedented results on the distribution of the orientation of plastic events show that there is a non-trivial correlation with the underlying local shear strain. These features, not previously reported for a confined foam, lend further support to the idea that cooperativity mechanisms, originally invoked for concentrated emulsions [1], have parallels in the behaviour of other soft-glassy materials.

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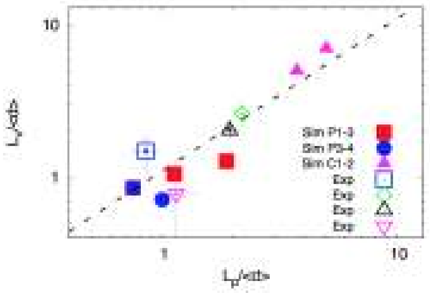

FIG. 1. Scatter plot of the velocity localisation length L_v (computed from a hyperbolic cosine fit of the velocity profiles) vs the plastic localisation length L_p (computed out of an exponential fit of the symmetrised rate of plastic events across the channel) for three sets of data: experiments (empty symbols), simulations of Poiseuille flow with fixed pressure drop and various normalized friction coefficients β^*'s (filled squares) and with fixed $\beta^* = 200$ and various pressure drops (filled circles) and simulations of Couette flow at two β^*'s (filled triangles); both lengths are normalised by the mean bubble/droplet diameter $\langle d \rangle$. The dashed line is the $L_v = L_p$ curve.

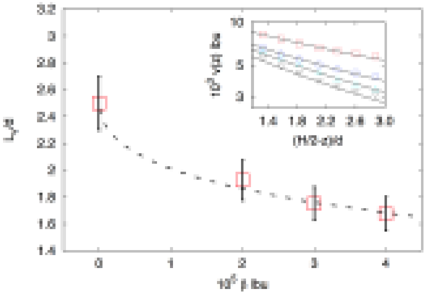

FIG. 2. Localisation length L_v (lengths are given in units of the mean droplet diameter d) vs friction parameter β. The numerical results (bullets) for L_v are compared with the theoretical prediction $L_v(\beta) = \frac{\xi}{1+\beta^{1/2}\xi/K^{1/2}}$ (dashed line) with plastic viscosity of the material $K = 1.7$ lbu (lattice Boltzmann units) and cooperativity length $\xi \approx 2.5\,d$ obtained via an exponential fit of the velocity profile for $\beta = 0$ lbu in the wall proximal region. L_v is extracted from a local fit of the velocity profiles (inset) for various β: $\beta = 0$ lbu (□), $\beta = 2 \times 10^{-5}$ lbu (○), $\beta = 3 \times 10^{-5}$ lbu (△) and $\beta = 4 \times 10^{-5}$ lbu (▽). "lbu" stands for lattice Boltzmann units.

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Linear response of correlated fluids in confinement

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Fluids that undergo phase transitions exhibit a divergence of correlation length- and time scales at the critical point. If such fluids are then confined, the arising competition of length scales can lead to remarkable physical phenomena such as the recently-measured thermal Casimir-type forces [1]. Such phenomena have mostly been investigated in thermodynamic equilibrium in terms of time-independent quantities. Dynamical properties of such systems are less explored — both theoretically and experimentally. Since static near-critical systems are strongly affected even by small perturbations, a better understanding of their non-equilibrium properties is crucial.

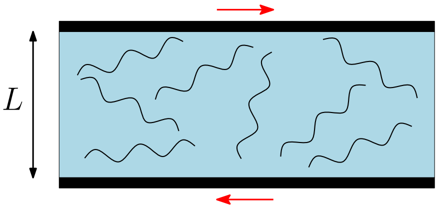

FIG. 1: A correlated fluid in confinement can be driven out of equilibrium, for instance by shearing the confining plates.

Here we consider **forces in confined, correlated fluids that are driven out of equilibrium**, by exploring

1. appropriate linear response relations,
2. an effective theory to include correlations,
3. various dynamical models and their relevance to fluid descriptions, and
4. suitable definitions for forces on confining boundaries out of equilibrium.

Through linear response theory, *non-equilibrium properties* (e.g. transport coefficients) can be related to *equilibrium fluctuations* of dynamical quantities. The well-known Green-Kubo relations establish these exact connections for bulk systems in the linear regime. Linear response theory has also been applied to confined systems, see e.g. works by Petravic and Harrowell [2] and Bocquet and Barrat [3].

Correlations are included in terms of an effective theory for the order parameter field $\psi(\boldsymbol{x})$ which describes, for instance, local concentration deviations in a binary fluid mixture. In this way, a Hamiltonian of the type

$$\mathcal{H} = \int d^{D-1}x \int_0^L dz \left[\frac{1}{2}(\nabla\psi)^2 + \frac{\tau}{2}\psi^2 + \frac{g}{4!}\psi^4\right] + \int d^{D-1}x \left[h_1\psi(\boldsymbol{x})|_{z=0} + h_2\psi(\boldsymbol{x})|_{z=L}\right] \tag{1}$$

may be used to represent a correlated system confined along the z direction by two plates separated by a distance L [4]. $\mathcal{H}$ has bulk contributions as well as surface contributions coupling $\psi(\boldsymbol{x})$ to effective fields at the boundaries. This scenario can be generalised and approximated, and studied under various boundary conditions, depending on the system in question.

We then consider various dynamical models, defined through Langevin equations for $\psi(\boldsymbol{x})$, including a noise term θ,

$$\frac{\partial}{\partial t}\psi(\boldsymbol{x},t) = -\hat{L}_0(\boldsymbol{x})\frac{\delta}{\delta\psi}\beta\mathcal{H} + \theta(\boldsymbol{x},t),$$
$$\langle\theta(\boldsymbol{x},t)\theta(\boldsymbol{x}',t')\rangle_{eq} = 2\delta(t-t')\hat{L}_0(\boldsymbol{x})\delta(\boldsymbol{x}-\boldsymbol{x}'). \tag{2}$$

This can be done for dissipative dynamics ("Model A", where $\hat{L}_0(\boldsymbol{x}) = L_0 = const.$) or conserved order parameter dynamics ("Model B", where $\hat{L}_0(\boldsymbol{x}) = -L_0\nabla^2$) — see [5]. For a realistic hydrodynamic description, however, an additional coupling of ψ to a dynamical velocity field of the fluid is required; this gives "Model H" [5].

We study forces required to perturb the confining boundaries through linear response relations. In particular, the friction force on an object can be found in terms of equilibrium correlations of the forces acting on it, yielding a friction coefficient (in one dimension)

$$\Gamma^{frict} = \frac{1}{k_B T}\int_0^\infty dt\langle\delta F(t)\delta F(0)\rangle. \tag{3}$$

However, a subtlety arises: can standard definitions of forces in terms of the stress tensor be applied in effective theories out of equilibrium? Indeed, this question has been debated extensively [6, 7].

In this submission we explore the above points, and show how results from our linear response approach compare to those obtained for the non-equilibrium Casimir force between vibrating plates [8]. We shall outline different ways to consider shear, and discuss the applicability of various dynamical models to correlated, confined fluid systems.

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Translational and rotational motions in thin films of polyamide random copolymers

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Subcontinuum mass transport of hydrocarbons in nanoporous media and long-time kinetics of recovery from unconventional reservoirs

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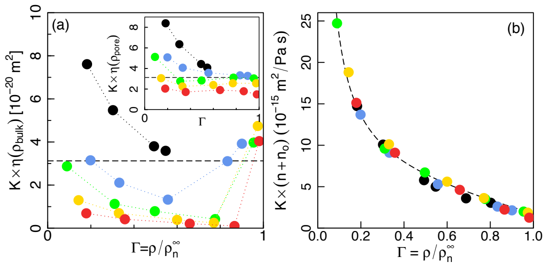

FIG. 1. **Breakdown of Darcy law and permeance master curve for alkane transport.** *(a)* Permeability $\eta \times K = \langle v\rangle/\nabla P$ vs loading Γ ($\Gamma = \rho/\rho_n^\infty$) (from methane to dodecane), showing the breakdown of the hydrodynamic prediction for the permeance. The viscosity is that of the bulk hydrocarbon at the corresponding pressure and temperature. *Inset*: Same plot with the bulk viscosity replaced by the bulk viscosity calculated at the relevant pore density, $\rho_{\rm pores}$. *(b)* Permeance master curve: $K \times (n + n_0)$ (with $n_0 = 2$) versus loading. This demonstrates that $K \sim 1/n$ with n the alkane length. The dashed line is the theoretical prediction.

In this work, we explore the transport of hydrocarbons across nanoporous media and analyze how this impacts at larger scales the long-time kinetics of hydrocarbon recovery from unconventional reservoirs.

First we show, using molecular simulation and statistical mechanics that the continuum description – the so-called Darcy law – fails dramatically to predict transport within a nanoscale organic matrix. The non-Darcy behavior arises from the strong adsorption of the alkanes in the nanoporous material and the breakdown of hydrodynamics at the nanoscale, which contradict the assumption of viscous flow. Despite this complexity, all permeances collapse on a master curve with an unexpected dependence on alkane length. We rationalize this non-hydrodynamic behavior using a molecular description that captures the scaling of permeance with alkane length and fluid density. This is based on a combination of a slip-like friction of the hydrocarbons with the matrix together with a free-volume approximation. This provides an analytical expression for the permeance which allows to rationalize the collapse curve, giving a very good description for the permeance K for all alkanes, at all densities [1].

Then we show that alkane recovery from such nanoporous reservoirs is dynamically retarded due to interfacial effects occuring at the material's interface. This occurs especially in the hydraulic fracking situation in which water is used to open fractures to reach the hydrocarbon reservoirs. Despite the pressure gradient used to trigger desorption, the alkanes remain trapped for long times until water desorbs from the external surface. We estimate the associated energy barrier in the MD simulations using thermodynamic umbrella sampling calculations. The results from simulations are found to be in agreement with a thermodynamic model based on the dewetting cost of the kerogen surface by water, and thus involving the spreading parameter of the alkane-water-kerogen interfaces as a key ingredient. We then explore hybrid interfaces involving a kerogen matrix entrapping the alkanes embedded in a model hydropholic clays. Such composite geometries lead to considerable free energy barriers to desorption, thereby strongly retarding the recovery of the alkanes from the nanoporous kerogen.

In a second step, we explore how this activated desorption mechanism impacts the kinetics of the overall alkane recovery. Based on the picture that unconventional reservoirs are made of collections of kerogen matrices embedded in rocks, we argue that the desorption energy barriers are widely distributed. Using a statistical model to predict the global alkane flux, we show that the flux $Q(t)$ decays algebraically with time, according to a Arps' like law [2]. The decay exponent is larger than 1/2 and typically of order 1, and its precise value depends on the microscale characteristics of the material, ie on the well. Such a behavior is consistent with reported algebraic decays of the flux reported in the litterature [3].

This work was performed in collaboration with K. Falk, T. Lee, R. Pellenq and F. Ulm, at the UMI CNRS-MIT, Massachusetts Institute of Technology, Cambridge, USA.

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Relation of structure and dynamics of a bidispere sphere systems close to a wall

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We study a bidisperse hard sphere system whose isotropy in structure as well as in dynamics is broken due to the presence of a wall. By means of *Brownian dynamics* (BD) simulations and *density functional theory* (DFT) we investigate setups up to very high densities, where glassy dynamics sets in. In contrast to previous studies where monodisperse systems in the vicinity of a wall have been studied [1-3], our system is composed of large and small particles (50:50), whose sizes differ by a factor of 1.4 in order to prevent crystallization effects. Therefore, we are able to explore high densities. We find astonishingly good agreement between the structures obtained in our BD simulations and the predicted strucures, which are calculated by DFT. For example, in Fig. 1 we plot the total correlation function h, which is connected with the well-known pair correlation function g through $h(\vec{r},\vec{r}') = g(\vec{r},\vec{r}')-1$. The shown results are at a packing fraction of $\phi = 0.56$ for both, the BD simulation (Fig. 1a) and the DFT (Fig. 1b). We observe qualitative as well es quantitative agreement for the medium to longer ranged correlations. The short range correlations, which are represented by the contact value (see Fig. 1c), show the same trend and are also at least semi-quantitatively comparable.

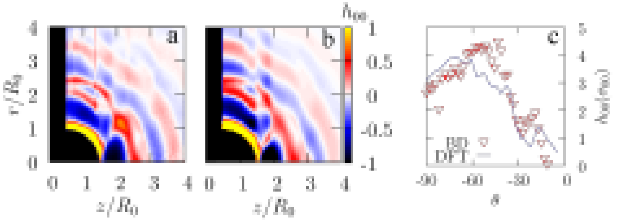

FIG. 1. Total correlation function for the case where one particle is in contact with the wall calculated by (a) BD simulations and (b) DFT at a packing fraction of $\phi = 0.56$. (c) Comparison of the extrapolated contact value in dependence of the polar angle, where $\theta = -90°$ represents the plane and $\theta = 0°$ is the perpendicular direction with respect to the wall.

In our simulations, we observe different particle dynamics for large (Fig. 2a) and small (Fig. 2b) particles. As represented by the self part of the van-Hove correlation function, particles tend to diffuse preferably inside the first layer. As time evolves, they eventually jump into the second layer, whereas the larger particles diffuse mainly in a tilted direction and the smaller particles prefer a perpendicular path. We compared the particle motion in the full system to the motion of a single random walkers, whose steps are chosen according to a diffusion constant

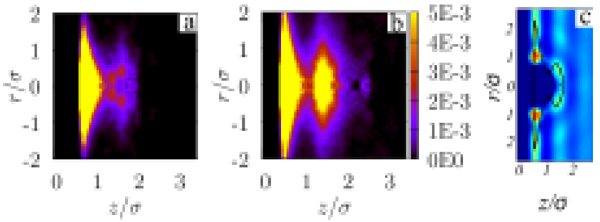

FIG. 2. Self part of the van-Hove correlation function at $7000\tau_B$ for (a) large and (b) small particles. (c) The color code in the background represents the two-particle correlations of smaller particles, whereas the region enclosed by the black line is the van-Hove self-correlation function predicted by the one-particle dynamics of an anisotropic random walk (see text and Eq. 1).

$$D(z,\theta) \propto D_0 \exp\left\{ -\alpha\big(p(z,\theta)\sigma^3\big)/k_BT \right\}, \quad (1)$$

that depends on the distance on the wall z and the direction where it wants to move θ. The spatial dependent pressure $p(z,\theta)$ is obtained from the structural analysis of the simulations, D_0 is the free diffusion coefficient and α is a fitting parameter. Interestingly, we observe a good agreement between the random walk result (Fig. 2c) that are based on structural input and the actual motion (Fig. 2b).

The reason why the prediction of the dynamics close to a wall works much better than in bulk is due to the fact, that the methods employed to obtain structural information of the local cage of a particle is better resolved because the isotropy is broken. Due to the anisotropy, the typical mean correlation functions depend on one more variable. This additional information concerning the position of neighboring particles leads to better mean field approximations of the dynamics in front of a wall in comparison to approximations of the dynamics in bulk. We discover that due to the broken isotropy a random walk of a single particle that is exposed to the force of a mean potential generated by its neighbors yields to a good prediction of the dynamics even if such a method does not lead to good predictions in the isotropic bulk case.

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New phase transition of confined cyclohexane in measoporous silica

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When liquids are cooled rapidly enough to avoid crystallization, molecular motions are getting slower and are stopped at each glass transition temperature, T_g. This slowing down of the molecular motion should be strongly related to the growth of correlation between neighboring molecules in the liquid. In these days, it is suggested that abrupt changes of local correlation might cause the new kind of phase transition in the liquid, which is called as liquid-liquid transition, especially for the molecules with strong interaction between molecules such as water, liquid metals, etc[1–4]. From the thermal dynamical point of view, the scenario that there exists the liquid-liquid transition could be understood by connecting with the breaking of famous Kauzmann paradox[5], the entropy of the over-quenched liquid is less than the one of the crystals. In this study, to investigate the generality of the existence of the liquid-liquid transition, the liquid phase of cyclohexane, which is simple and has less molecular-molecular interaction, was studied by heat capacity measurements and powder X-ray diffraction (XRD).

Since simple molecules such as cyclohexane are very easy to crystallize on cooling, confinement phase was chosen to stabilize the liquid phase of cyclohexane. Confinement conditions were realized by using the highly ordered measoporous substances those are called as MCM-41, SBA-15, and TMPS. Those substances are mesoporous silica-walled materials that exhibit a regularly ordered two-dimensional hexagonal pore arrangement and narrow pore size distributions. The corresponding pore diameters we chose were from 1.9 nm to 6.9 nm.

Heat capacity measurements were carried out by the intermittent heating method with the adiabatic calorimeter in our laboratory. From the heat capacity measurements, apparently different type of 1st order phase transition compared with conventional ones was found in the confined cyclohexane into less than 3.0 nm pores(Fig. 1). The strength of this transition was very weak and the transition temperature did not depend on the diameters of pores. Moreover, these transition temperatures were higher than conventional phase transition from crystal to plastic phase. This result suggested that low-temperature phase might be the liquid phase, which is firstly confirmed at small interaction between molecules.

On the other hand, structural change related to this phase transition was investigated by using XRD. Figure 2 shows laboratory XRD results around phase transition temperature, 154 K. Though the difference caused by new phase transition is supposed to be small, we could find slight difference owing to this new phase transition around the peak $q \sim 15\text{nm}^{-1}$. Corresponding length scale of this q value is about 4 Å and could be thought as distance between molecules. To convince this difference, we are planning to do further investigation by using synchrotron sources in Photon Factory in KEK Instutute in this December. In our presentation, we will show these experimental results and discuss the nature of this new phase.

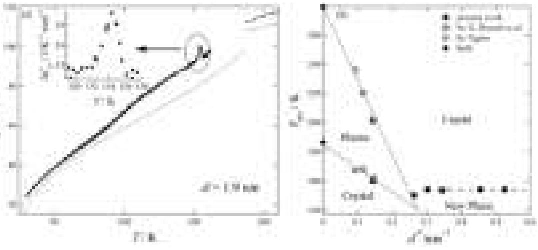

FIG. 1. (a) New phase transition is appeared around 154 K. Inset figure shows the expansion of the phase transition. (b) Transition temperatures of confined cyclohexane as a function of inverse of pore diameters.

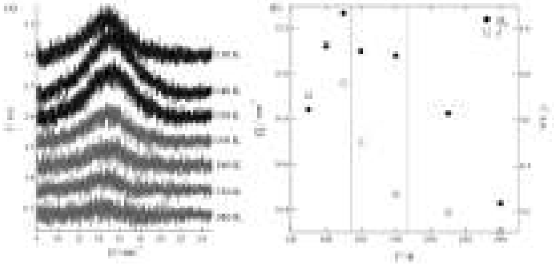

FIG. 2. (a) Temperature dependence of the XRD spectrum around $q \sim 15\text{nm}^{-1}$. These data were based on the difference between sample with MCM-41 and blank MCM-41. (b) Temperature dependence of the peak position (Q_p) and intensity (I) of the hump.

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External forces acting on micro-particles trapped with optical tweezers

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We measure the fluctuations of positions of one or two silica micro-beads ($R = 1\,\mu\mathrm{m}$) trapped with optical tweezers in a microfluidic cell where an external force can be added on the particles. An acousto-optic deflector (AOD) allows us to switch the position of the trap very rapidly (up to 1 MHz) and water flows can be driven by gravitational potential difference.

By random forcing the position of one particle we create a non-equilibrium steady state equivalent to an effective temperature higher than that of the surrounding fluid. By trapping another particle close to the forced one, we study the energy exchange between two particles kept at different effective temperatures [1]. In this situation the equilibrium variances and cross-correlation functions of the bead positions are modified: we measure an energy flow from the "hot" particle to the "cold" one and an instantaneous cross-correlation, proportional to the effective temperature difference between the two particles. A model of the interaction which is based on classical hydrodynamic coupling tensors allows to compute the change of variances and cross-correlation functions with a very good agreement towards experimental data (see figure 1). We also compute the Probability Distribution Function of the heat exchanged between the particles to verify the validity of a Fluctuation Theorem for two sources at different temperatures in our system.

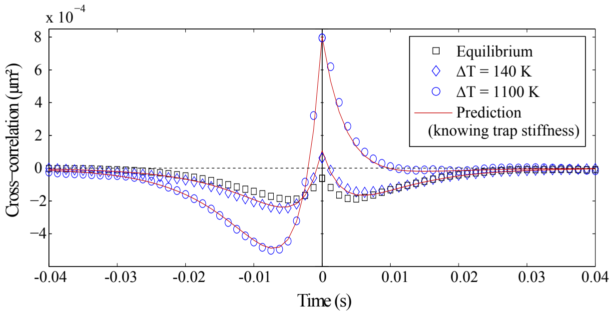

FIG. 1. Cross-correlation of the positions of two particles trapped at different effective temperatures (measured values are compared to the predictions from the hydrodynamic coupling model).

By shearing the fluid, we create a non-equilibrium steady state where the classical Fluctuation-Dissipation Theorem (FDT) is not verified anymore. The shear flow can be simulated by adding an external noise on the position of the optical trap or created by two counter-propagating flows meeting at a junction point [2]. For the latter solution, we use the microfluidic cell shown in figure 2.

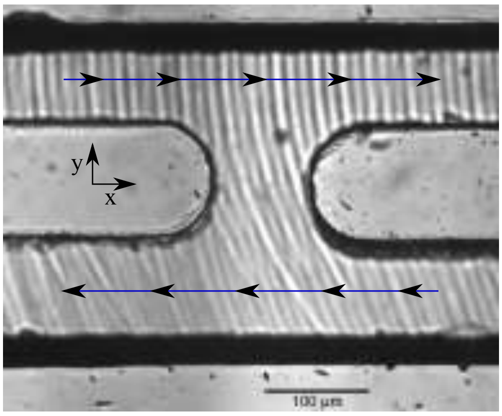

FIG. 2. Picture of the microfluidic channel in the middle of which the particle is trapped. The counter-propagating flows are symbolised by blue arrows.

Preliminary results show that the FDT is clearly violated when a shear is simulated on the system by forcing the position of the particle with the AOD (see figure 3). Our system will allow us to compare these data with the ones obtained in a real shear flow, and to look for the Harada-Sasa equality, linking the violation of FDT to the amount of energy dissipated by the system, in this non-equilibrium sheared steady-state.

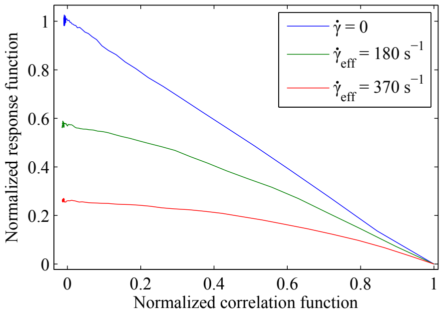

FIG. 3. The violation of FDT is observed when a shear-flow is simulated by adding noise on the position of the trap positions with the AOD (the function are normalized by the variance).

We want to thank Denis Bartolo for his useful advice about microfluidic channels.

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Variety of density scaling law manifestations

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In the last decade, the observed density scaling of molecular dynamics near the glass transition has been constituted as a promising law [1] that is expected to enable us to make progress in a satisfactory formulation of unified theoretical description, which is still sought after for the glass transition and related phenomena. A leading theory that aspires to provide grounds for the phenomenologically established density scaling law is the theory of isomorphs [2], which relies on computer simulation studies of simple models based on the Lennard-Jones potential. According to the first version of the theory of isomorphs [2], molecular dynamics, thermodynamics, and structure of Roskilde simple liquids (i.e., model liquids that comply with the theory of isomorphs) are characterized by some invariants along isomorphic curves in phase diagrams of the liquids if one applies specific reduced units suggested by the theory of isomorphs. Among other things, such isomorph invariants are the structural relaxation time τ, the time-dependent four-point correlation function $\chi_4(t)$, and the excess entropy S_{ex} calculated as the difference between the total system entropy S and the entropy of an ideal gas at the same temperature T and density ρ. As a consequence, in the power law density scaling regime that is typically accessible to high pressure measurements, temperature-density dependences of all the isomorph invariants should be well described by some functions of a single variable ρ^γ/T with the same value of the scaling exponent γ for a given material. Then, the isomorph invariants τ, S_{ex}, and χ_4^{max} (where the latter is the maximum value of $\chi_4(t)$) should be mutually single variable functions, e.g., $\tau = f(\chi_4^{max})$ and $\tau = g(S_{ex})$. Both the predictions have been preliminarily confirmed, however, mainly by simulation studies or using experimental data measured only at ambient pressure. Until recently, any pressure effect on the relationships among τ, χ_4^{max}, and S_{ex} has not been investigated for real glass formers.

Our thorough analyses of high pressure experimental data of various glass formers that belong to different material groups (such as van der Waals supercooled liquids, polymer melts, and supercooled ionic liquids) clearly show that some previous suppositions concerning interrelations between time and length scales of molecular dynamics and entropy near the glass transition require revisiting. This is a consequence of two phenomena of isochronal decoupling, which have been recently observed by us (i) between time and dynamic length scales of molecular dynamics [3–5] (where the former is defined as the structural relaxation time τ and the latter is assumed to be evaluated from the estimates of χ_4^{max} based on enthalpy fluctuations or temperature-density fluctuations [6]) as well as (ii) between the time scale of molecular dynamics τ and the total system entropy S of real materials near the glass transition [7]. We have also established [7] that the density scaling behavior of the excess entropy S_{ex} mimics that of the total system entropy S.

At first glance, these results seem to be disadvantageous to perspectives of finding a simple universal description of the glass transition and related phenomena. However, a very successful application of the density scaling law to both the decoupling phenomena yields a very positive outcome of our investigations. Exploiting high pressure experimental data, we give evidence that τ, χ_4^{max}, S, and S_{ex} obey the power law density scaling law, however, the values of the scaling exponents γ_τ, $\gamma_{\chi_4^{max}}$, γ_S, and $\gamma_{S_{ex}}$ are in general considerably different for the quantites (only $\gamma_S \approx \gamma_{S_{ex}}$). We have proven [3, 7] that such different scaling behaviors imply the experimentally established decoupling phenomena, which can be rationalized by newly derived relationships that can be compactly written as

$$\tau = h_X(\rho^{\Delta_X\gamma} w_X(X)) , \qquad (1)$$

where X denotes χ_4^{max}, S or S_{ex}. The exponent of the additional density power factor, $\Delta_X\gamma = \gamma - \gamma_X$, can be treated as a measure of a given decoupling.

This promising conclusion sheds new light on fundamental problems of the glass transition physics, the successful solution of which can be sought after in terms of the density scaling law that allows different values of the scaling exponent for different physical quantities. What is more, Eq. (1) with $X = S_{ex}$ and the newly reformulated version of the theory of isomorphs [8] seem to converge.

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Kinetic and thermodynamic fragilities of model fluids with variable barriers to bond breaking

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Understanding the fragility of glass forming liquids in terms of the microscopic interactions is an important component of understanding the dynamics of viscous liquids [1, 2]. Fragility is a material parameter which measures the rapidity of change of the viscosity (or relaxation time) with temperature and is a useful organizing principle to understand data for a wide range of glass forming liquids. The fragility parameter, K_{VFT}, calculated from the temperature dependence of viscosity and related quantities (such as diffusion coefficient), fitted to the Vogel-Fulcher-Tammann form, $X(T) = X_0 \exp\left(\frac{1}{K_{VFT}(T/T_0-1)}\right)$ is one of the quantifications of the *kinetic fragility* (K_{VFT}) of a glass former. Using the Adam-Gibbs relation [3], $X(T) = X_0 \exp\left(\frac{A}{TS_c}\right)$ where the temperature variation required to recover the VFT form is $TS_c = K_T(T/T_0 - 1)$, this kinetic fragility may be related to thermodynamic quantifications of fragility (K_T) [4] by $K_{VFT} = K_T/A$. Here A is related to high temperature activation energy [5]. The Arrhenius temperature dependence at high temperatures is characterized by an activation energy E_∞, in terms of which the Adam Gibbs high temperature activation free energy may be written a $A = E_\infty S_{c\infty}/k_B$ where $S_{c\infty}$ is the high temperature limit of the configurational entropy. We examine the role of the high temperature activation energy by studying two model liquids, specified by the following interaction potentials: (a) hard core with square well attractive interactions [6], and (b) the Lennard-Jones interaction with the Kob-Andersen parameterization for a binary mixture. In addition to the above interactions, we introduce barriers of small width to bond breakng, and variable height h, (a) at the outer limit of the square well interaction, as shown in the inset of Fig. 1, and (b) at the location of the first minima of the pair correlation function g(r). Changes in the barrier height change the dynamics of the systems, as shown in Fig. 1 for the square well system, in such a manner that the measured kinetic fragilities change, but the thermodynamics or PEL properties remains largely unaffected Fig. 2. We study the kinetic fragilities of these systems, and analyse them within the framework of the Adam-Gibbs relation, in order to elucidate the role of the high temperature activation energies in governing the kinetic fragility, independently of changes in the thermodynamics of the system as quantified by the temperature dependencde of the configurational entropy.

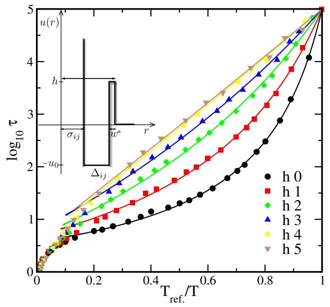

FIG. 1. Angell plot: Logarithm of the relaxation time against rescaled inverse temperature for various barrier heights. As the barrier height increases system exhibits temperature dependent approaching Arrhenius behaviour, and corresondingly, lower fragility. The inset shows a representation of the interaction potential for the square well system. $\sigma_{ij} = 1.2$ or 1.0 is the hard sphere diameter. The square well has depth u_o with attractive shell width $\Delta_{ij} = 0.5\sigma_{ij}$ and bond life time of a pair is controlled by tuning barrier height h.

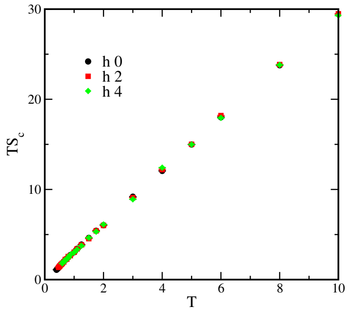

FIG. 2. Thermodynamic fragility: Temperature dependence of TS_c for the square well model which shows that the configurational entropy is not affected by changes in the barrier height.

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Valence-band Repulsion Controls the Fragility of Supercooled Metallic Melts

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Understanding the mechanism which governs the emergence of mechanical stability at the glass transition of supercooled liquids calls for deeper insights into the connection between the fragility index and the interatomic interaction. As many experimental and simulation studies have suggested, mechanical stability in amorphous solids is crucially linked to the repulsive part of the interatomic interaction potential. However, no consensus has been reached about whether interatomic repulsion softness correlates with strong glasses [1] or with fragile glasses [2]. We derived an analytical closed-form relation between the fragility index of metallic glass-formers and the short-ranged, repulsive part of the interatomic interaction (given by pseudopotential theory). This fundamental relation is obtained from a one-parameter theory fit to experimental rheological data of supercooled metallic melts. From this combination of theory and experiments it is established that interatomic repulsion softness in metals goes along with strong glasses and low fragility. Surprisingly, given the huge difference of energy-scales and microscopic interaction, this finding is in full agreement with the correlation observed in the case of soft colloidal particles by Mattsson, Weitz and co-workers [1].

The softness of the interatomic pseudopotential is implemented in the non-affine elastic response [4] through the T-dependence of the atomic connectivity (decreasing with T). An analytical approximation for the short-ranged part of the radial distribution function $g(r)$ leads to a phenomenological expression for the repulsive part of the pseudopotential, $V(r)/kT = -\ln(r-\sigma)^{\lambda}$, with just one semi-empirical parameter λ controlling the repulsion steepness (and its inverse, the softness $\sim 1/\lambda$). The analytical theory for the T-dependent shear modulus, therefore, has only one adjustable parameter, λ, which is extracted from the fit to the experimental data. The analytical expression for the shear modulus versus T can then be used within the elastic (shoving) model of the glass transition, to obtain simultaneous one-parameter fits to the viscosity. The latter are shown in Fig. 1. The theory predicts a double-exponential dependence of viscosity on temperature, in excellent agreement with the data.

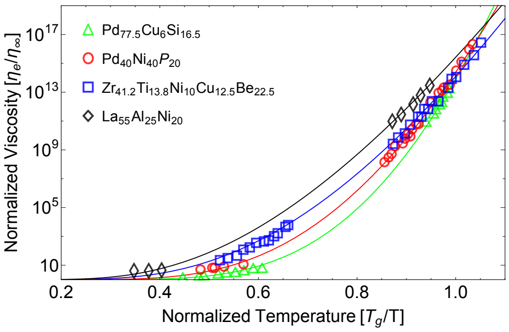

FIG. 1. Experimental data (symbols), from Ref. [3], and the one-parameter theoretical fits (solid lines), of the viscosity of different alloys versus temperature. The only fitting parameter is the steepness of interatomic repulsion.

From the viscosity fits, we also obtain the analytical law connecting the fragility index m to the thermal expansion coefficient α_T and to the repulsion steepness exponent λ, as $m = (V_c C_G/kT_g)[1 + (2+\lambda)\alpha_T T_g]$. Furthermore, the semi-empirical soft potential that we used for the fits to the experimental data, can be mapped with great accuracy onto the standard pseudopotential theory of metals. Using the Ashcroft pseudopotential to account for Thomas-Fermi screening, supplemented with a Born-Mayer term related to valence-electron overlap repulsion, a one-to-one mapping between our semi-empirical soft potential and the pseudopotential theory of metals is established. Using typical values of the Thomas-Fermi screening length and of the Born-Mayer decay-range for amorphous alloys of transition metals, which are not very sensitive to the chemical composition, we found that the steepness of interatomic repulsion is controlled by the energy-scale of the Born-Mayer term. Also, a positive correlation (linear-dependence) between the fragility index and the Born-Mayer repulsive energy-scale is obtained. This finding implies that the physical mechanism which controls the fragility of glass-forming metal alloys is the overlap repulsion between valence electrons of the unfilled d-shells. This is a quantum-mechanical effect resulting from the Pauli exclusion principle, and related to the electronic structure of the material.

The new fundamental law that we discovered opens up opportunities to fabricate alloys with tailored thermo-elastic and glass-forming properties by tuning the interatomic interaction parameters via the electronic structure and chemical composition of the alloy.

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Susceptibility χ_4 fails to capture significant increase of dynamic correlation length near glass transition

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Clusters of fast and slow correlated particles, identified as dynamical heterogeneities (DHs), constitute a central aspect of glassy dynamics [1]. A key ingredient of the glass transition scenario is a significant increase of the cluster size ξ_4 as the transition is approached. In need of easy-to-compute tools to measure ξ_4, the dynamical susceptibility χ_4 was introduced recently [2, 3]. Here, we investigate DHs in dense microgel suspensions using image correlation, and compute both the four-point correlation function G_4 and its associated dynamical susceptibility χ_4. The spatial decrease of G_4 provides a direct access to ξ_4, which is found to grow significantly with increasing volume fraction. However, this increase is not captured by χ_4. We show that the assumptions that validate the connection between χ_4 and ξ_4 are not fulfilled in our experiments. Our findings question the relevance of the broadly used χ_4 (for example [4, 5]) in describing DHs.

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Structural and energetic features of two-dimensional vapor deposited glassy films

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Recent experimental studies have shown that vapor deposited glass films exhibit greater structural and kinetic stability than liquid-cooled glasses [1, 2]. In this work, we present a computational study of two-dimensional binary glassy films prepared by vapor deposition. We find that vapor deposited 2D glassy films exhibit greater stability than their liquid-cooled analogues and, consistent with experiment, lower rates of deposition lead to increasingly stable materials. The 2D glasses considered here exhibit a distinct local order, which is correlated with the inherent structural energy of the films. As the deposition rate is decreased, a transition is observed from mid-sized square-ordered clusters to quasi-crystalline pentagonal arrangements. When the degree of local order of vapor-deposited glasses is compared to that of liquid-cooled samples, we find that the structure of both types of films is equivalent for films having the same inherent structural energies. Previous experimental and computational work has reported that the substrate temperature leading to the most stable vapor deposited films is approximately 15% lower than the glass transition temperature. For the 2D systems considered here, simulations indicate that the ideal substrate temperature decreases significantly with slower deposition rates.

Experiments indicate that glasses prepared by a process of physical vapor deposition (PVD) can reach levels of stability that are equivalent to those of liquid-cooled glasses aged for hundreds of thousands of years[2, 3]. These highly stable PVD glasses are formed by depositing the glass former onto a substrate whose temperature is slightly lower than T_g. It has been proposed that newly deposited molecules can freely explore configurational space on the surface of the growing film, leading to molecular arrangements that lie deeper in the free energy landscape of the material than those arrived at by rapid cooling of a bulk liquid.

In this work, glassy films are prepared through a simulated vapor deposition process using a wide range of substrate temperatures and deposition rates. The system is initialized with a neutral substrate. Then, groups of high-temperature atoms are added to the system and allowed to settle onto the growing film. Atoms are added until the desired film thickness is reached. To mimic experimental physical vapor deposition, atoms in the film and newly added atoms are cooled gradually. The film temperature is maintained through the constant temperature of the substrate. Liquid-cooled films are formed by melting vapor-deposited films, allowing them to reach equilibrium, and then cooling them back to a low temperature at a range of rates.

As shown in Figure 1, vapor deposited films are highly stable relative to their liquid cooled analogues. Using the power law fit shown in Figure 1, we predict that one would have to cool a liquid at a relatively low cooling rate to form a film equivalent to our most stable vapor deposited film. Note that this and all other values are given in reduced Lennard-Jones units.

Due to the computational simplicity of this model, we were able to form vapor deposited films with deposition rates spanning five orders of magnitude. Over this range, the optimal substrate temperature for the deposition, or the substrate temperature yielding the film with the lowest E_{IS}, drops from 86% to 67% of T_g. The minimum energy films formed at slower deposition rates are significantly more stable than those formed more rapidly.

The structures in these films consist of square-ordered clusters and quasi-crystalline arrangements. Bond order parameters q_8 and q_5 are used to analyze the local structure in these films[4], with q_l values that are time-averaged over vibrational timescales; atoms are clustered by averaged q_l value. When comparing the degrees of ordering across films of different types over a range of structural energies, we find that the structural features of a film depend only on inherent structural energy, and not formation style.

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Experimental determination of structural and dynamical heterogeneities in a metastable colloidal fluid

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Solidification of a meta stable melt by crystallization or vitrification is one of the most important non-equilibrium processes in physics. The meta stable melt is not homogeneous and isotropic, it exhibits structural and dynamical heterogeneities [1],[2]. These heterogeneities refer to the appearance of spatially correlated domains of mobile and immobile particles as the temperature crosses the freezing temperature and approaches the glass transition temperature T_GT.

Dynamical and structural heterogeneities are a central aspect in our present understanding of of the crystallization and the glass transition. Crystallization starts, in contrast to the classical nucleation picture, with clusters of highly ordered particles (precursors) [3], [4] and inhomogeneous dynamics play a major role describing a glass [5]. Still, an interesting and open question is: How are dynamical and structural heterogeneities correlated to each other and is the correlation universal for crystallizing and vitrifying metastable fluids. Computer simulations suggest that these dynamical heterogeneities are correlated to structural heterogeneities and it was concluded that particles belonging to clusters of highly ordered particles are less mobile than other particles [6], [7]. However, to date there has been no direct experimental correlation between dynamical heterogeneities and the temporal evolution of structural heterogeneities.

Using advanced space- and time-resolved dynamic light scattering and time-resolved multi angle static light scattering we investigate the dynamical and structural heterogeneities in the simplest model system that shows a first order freezing as well as a glass transition: a colloidal hard-spheres. In a previous report we could show that the temporal evolution of the ensemble averaged dynamics and structure are linked[8]. In addition to this work we analyze the structural and dynamical heterogeneities with subensemble resolution. We find that a super cooled liquid before crystallization as well as the vitrifying liquid is heterogeneous in structure and dynamic and we are able to show that these dynamical heterogeneities and structural heterogeneities display a direct correlation in their temporal evolution. Our results suggest that the emergence of the precursor clusters are the origin for the dramatic slowing down of the dynamics during the glass transition. Furthermore, our work may shed light on the connection between the crystallization and the vitrification processes and help to understand the fundamentals of these two important non-equilibrium processes.

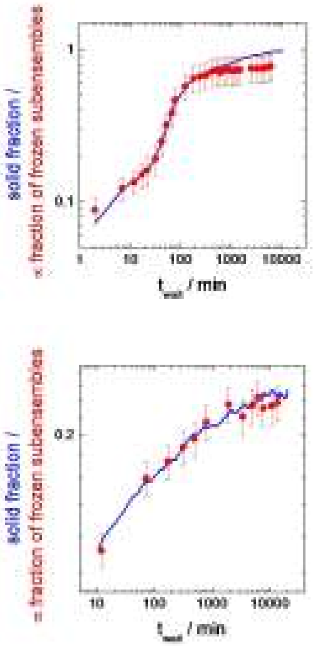

FIG. 1. Comparison between the temporal evolution of the solid fraction and the fraction of immobile particles for a crystallizing sample ($\Phi = 0.563$, left) and for a vitrifying sample ($\Phi = 0.593$, right) at different waiting times.

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Exact and approximate analytical solutions for oscillating-cup viscometer

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Oscillating-cup viscometer is the dominant technique for high-temperature melts (e.g., [1]). Error analysis for this method is widely discussed (e.g., [2, 3]). A systematic approach to choose working equations for data processing has not yet developed. At present, the simplified expressions are usually used that often leads to loss of accuracy and functionality although in the last century some researchers applied more complete exact formulas, numerical methods and digital computer for it (e.g., [4]). In present paper, we give the equations for Newtonian fluids that are optimal for a few problems. It can be also used for linear viscoelastic fluids in terms of complex viscosity.

One of the exact solutions for this fluid mechanics problem leads to the following [5]:

$$\frac{L'}{K} = p\left(1+\frac{p_0^2+q_0^2}{p^2+q^2}\right) - 2p_0,$$

$$\frac{L''}{K} = q\left(1-\frac{p_0^2+q_0^2}{p^2+q^2}\right) - 2p_0 \text{ (i)}$$

$$\text{or } L' + L''\frac{p}{q} = 2K(p-p_0) \text{ (ii); (1)}$$

$$L' = Re(L),\ L'' = Im(L),$$

$$L = -2\nu M\beta\frac{J_2(\beta)}{J_1(\beta)} + 4\frac{M}{H}\frac{k^2}{\nu}\sum_{n=1}^{\infty}\frac{\text{th}(\theta_n H)}{\mu_n^2\theta_n^3},\ (2)$$

where $p = \delta/\tau$, $q = 2\pi/\tau$; p_0, τ_0, etc are ones for $M = 0$; τ and δ is the period and decrement of oscillations; K is the inertia moment at $M = 0$; ν is the kinematic viscosity; M, R and H are the mass, radius and height of the investigated fluid in a viscometer; $\beta = R\sqrt{k/\nu}$; $k = p + iq$; $\theta_n^2 = \mu_n^2 - k/\nu$; J_l is the Bessel function of first kind and order l; μ_n are the roots of the equation $J_1(\mu_n R) = 0$. To numerically solve this transcendental equation, we use the objective function $\Phi = \sqrt{c'F'^2 + c''F''^2}$, where c', c'' are the weight coefficients for the real F' and imaginary F'' parts of the equations in (1i).

Let the experiment parameters: δ_0, τ_0, R, K, M, be given. We minimize Φ on the set of τ and δ: $\Phi{=}\Phi(\tau,\delta)$, in the inverse viscometric task (IT) to model the oscillation law. In the direct task (DT) to estimate rheological constants and, in particular, Newtonian viscosity ν here, the function $\Phi(\nu) \to 0$ or $\Phi(\nu,\rho) \to 0$ for simultaneous measurement of ν and density ρ (e.g., [6]). For rheostable fluids, the approximate analytical solutions along with Eqs. (1), (2) are used [7] but the problem is complicated by a significant number of unknown parameters.

System (1i), (2) is preferred for IT: if $c' \neq 0$ and $c'' \neq 0$, the minimum of Φ on the set of two parameters is more pronounced (Fig. 1a). If $c' = 0$ or $c'' = 0$, at ravine axis as in Fig. 1b, local minima can appear. In model (1ii), (2), there is not the period τ_0 depending on the load on viscometer thread and the temperature T, i.e. it is to be measured over the entire working range of T at the experiment load and is used in (1i). Due to it, Eq. (1ii) takes advantage in the DT. The function Φ built at $c'' = 0$ and from Eqs.(1i), (2) is flatter, i.e. influences of the errors in observable parameters on an estimate of ν is higher. The minimum of $Im(\Phi)$ is more pronounced and shifts stronger due to errors in τ. In Fig. 1, we show the intervals $\tau' \pm (\tau' - \tau_0)$ and $\delta' \pm (\delta' - \delta_0)$, where τ', δ' responds to the minimum of $\Phi(\tau,\delta)$; IT is solved using Eqs. (1i), (2).

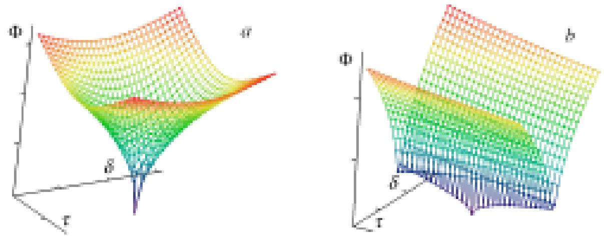

FIG. 1. Surface of Φ (τ,δ) for (2), (1i) (a) or (1ii) (b) ($R = 1$, $\rho = 6$, $\tau_0 = 5$ (CGS); $0.5MR^2/K = 0.15$, $H/R = 2.5$)

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Heterogeneous dynamics and polymer plasticity

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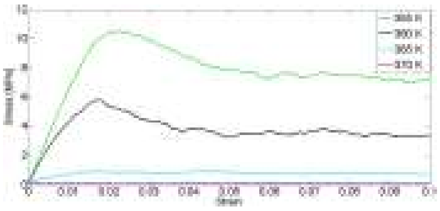

FIG. 1. Stress-strain curves during a shear experiment

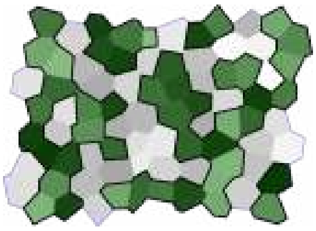

FIG. 2. Dynamical heterogeneities of the system at a given temperature. On the observation duration, the heterogeneities behaving like solids (green) form clusters, surrounded by fluid-like heterogeneities (white).

Experiments have demonstrated that the dynamics in liquids close to the glass transition temperature is strongly heterogeneous, on the scale of a few nanometers. We extend a model which was developed in order to describe mechanical properties of polymers close to their glass transition temperature [1] - [2]. The aim of this work is to understand the consequences of the heterogeneous dynamics of glassy polymers on their non-linear mechanical properties (Fig. 1). We assume that the elastic energy stored on the scale of dynamical heterogeneities effectively reduces the free energy barriers present for internal relaxation. As a consequence, yield appears as the result of an acceleration of the dynamics of subunits with intermediate relaxation times of the same orders of magnitude as the time scale of the experiment: consistently with the percolation picture of the model (Fig. 2), subunits with very long relaxation times are not perturbed by the applied deformation. Our simulations describe the onset of plastic behavior and the reorganization at the scale of dynamical heterogeneities. They allow for calculating the elastic and dissipative moduli as functions of strain amplitude and as functions of temperature. We show that G' decreases by several orders of magnitude at large deformation amplitudes as compared to the linear regime, whereas G'' decreases by a factor of about 3 only. Our simulations predict the appearance of shear bands on the scale of about 10 nm at yield.

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Spatially–resolved heterogeneous dynamics in colloidal gels

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By exploiting a class of novel optical techniques combining the power of microscopy and light scattering, we study two different systems undergoing irreversible and reversible gelation. The aim is to compare their heterogeneous dynamics and to investigate the local rearrangements of their structure induced by the stress accumulated during the gelation process.

First we re–examine the classical problem of the irreversible aggregation induced in suspensions of charged colloidal particles by the addition of destabilizing electrolytes. Even if these kind of strong gels have been extensively investigated, we obtain novel information concerning the strength and the spatial distribution of the rearrangements leading to the decay of gel temporal correlations[1].

An imaging configuration allows to recover the displacement field of the rearranging gel, which shows long spatial correlation and sudden changes in the amplitude of the displacement at long aging times (Fig.1). Even if the amplitude displays an intermittent behavior, the direction of the displacement vectors remains correlated over long times. This evidence supports a model assuming that consecutive events can originate from the same stress source which needs several local rearrangements to fully relax. The overall r.m.s of the gel local displacements as a function of time exhibits two distinct regimes for short and long times, suggesting respectively a diffusive and a quasi-ballist process, in agreement with the time-correlation functions obtained from scattering data.

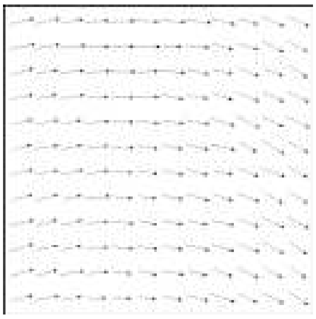

FIG. 1. Normalized displacement field associated to a decorrelation event occurring in a strong gel recovered analyzing two images taken with a delay time of 60 s. The field of view is about 1.5 mm × 1.5 mm and the average displacement is about $2\mu m$.

The second class of gels we investigate is represented by a colloidal suspension with the addition of a non-ionic surfactant which induces short-ranged attractions between the particles known as depletion forces. The depletion mechanism is intimately connected with the critical Casimir effect, which may be regarded as a kind of depletion of long–wavelength fluctuations in the volume comprised by two colloidal particles [2].

The sample is composed of particles with a radius of 90 nm made of MFA, a polytetrafluoroethylene copolymer, suspended in a solutions of a non-ionic surfactant (Triton X100). The surfactant volume fraction is maintained low enough to avoid the phase separation of the MFA at room temperature. Then the strength of the interaction is modified by varying the system temperature driving the system into the coexistence region where a spinodal decomposition usually brings to the formation of an arrested gel. The process is completely reversible and lowering the temperature brings the system back to the original state.

The imaging approach applied to this system allows to investigate the stress propagation in the gel structure and its connection with the strength of the interaction (Fig.2).

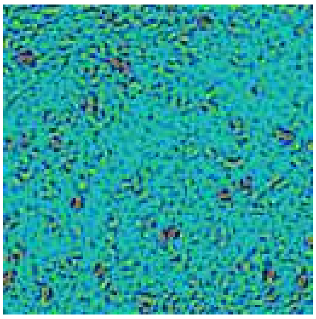

FIG. 2. The difference between two images of the MFA gel taken with a delay time of 30 s shows that the rearrangement events are well localized. The color scales highlights the regions of the gel more displaced (red) and those that did not change position (blue).

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Temperature-density scaling of configurational entropy rationalized in terms of the Adam-Gibbs theory

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The behavior of the molecular dynamics of supercooled liquids approaching the glass transition temperature still remains intriguing research problem in the condensed matter physics. The most of the efforts has been concentrated on finding a model that would be able accurately describe variation of the structural relaxation time, τ_α, with temperature. Among variety of models proposed for description of the temperature dependence of τ_α, the entropy-based model formulated by G.Adam and J.H.Gibbs (AG) [1] is one of the most popular and meaningful because it establishes a connection between thermodynamic and dynamic quantities. According to the AG model, the relaxation time of supercooled liquid is controlled by the configurational entropy $S_c(T)$:

$$\tau = \tau_{AG} \exp\left(\frac{A}{TS_c}\right) . \tag{1}$$

However, it is now common practice to measure the change of τ_α not only with temperature but also with pressure [2–4]. By combining these data, i.e.: $\tau_\alpha(T,P)$ with PVT measurements it becomes possible to analyze the behavior of the τ_α in the full thermodynamic space. Of particular interest is the study of the temperature-volume dependences of τ_α because, as recently demonstrated, they can be transformed into a single curve by plotting the structural relaxation times versus a new variable: TV^γ. This recently recognized property of the molecular dynamics of supercooled liquid state has been called as a temperature-density scaling rule [2–4]. Hence, it is natural to ask whether or not the AG model complies with this scaling rule. Answering this question requires converting Eq. (1) to $T-V$ representation (Fig. 1). In this context, it should be stressed that the conversion of the AG model to $T-V$ variables might be essential for testing its validity in general.

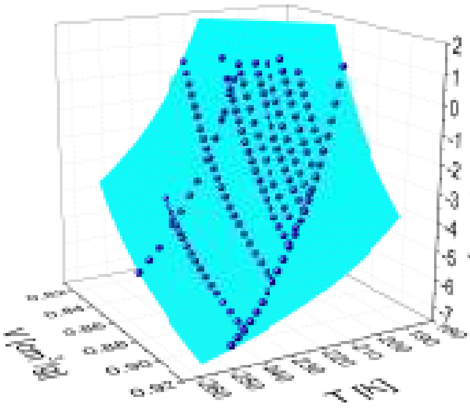

FIG. 1. Plot of a representative temperature-volume dependence of logarithms of structural dielectric relaxation times of a typical van der Waals liquid. Ball symbols denote experimental isobars and isotherms of the structural dielectric relaxation times, whereas the fitting surface results from fitting the experimental points to the Adam-Gibbs model modified by us by finding its temperature-volume representation.

In this presentation, we propose an extension of the original AG model (Eq. (1)), based on newly derived equation of state [5–8], to take into account combined effect of temperature and volume changes and consequently to verify whether or not the concept of temperature-density scaling rule is indeed consistent with Adam-Gibbs model. These considerations lead us to very important result that configurational entropy also satisfies the temperature-density scaling rule.

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Glassy state dynamics of poly(lactic-acid) as seen by neutron spin-echo spectroscopy

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Whereas the glass transition phenomenon of polymers has been widely studied, considerably less attention has been paid to secondary relaxations in the glassy state. This is due to the limited number of techniques that allow a direct study of molecular dynamics at the nanometric lengthscale. The details of the secondary processes are still a matter of controversy, however some are proved to be directly related to the structural relaxation, and therefore play an important role in the widely debated physical ageing process as well.

The interest in using polymeric materials derived from renewable resources has increased significantly in recent years because of improved environmental awareness [1]. Poly(lactic acid) (PLA) is considered to be one of the most promising renewable bioplastics, providing a biodegradable alternative to conventional polymers and thus received much attention recently [2, 3]. Its widespread application is strongly limited by rapid physical ageing (i.e. changes in macroscopic properties with time) at ambient temperature. Overcoming this problem requires a detailed understanding of the occurring dynamics in the glassy state.

Here we show that Neutron Spin-Echo (NSE) spectroscopy may offer a powerful mean to study the glassy state dynamics. In our study, by measuring protonated samples, the hydrogen self-diffusion dynamics has been explored in a temperature range (193 K - 318 K) where the β-relaxation is expected to govern glassy state dynamics. NSE measurements were carried out on the IN11 spectrometer, at the Institut Laue-Langevin (ILL), Grenoble, France. With an incident neutron wavelength of 5.5 $\mathring{A}$ the wave vector (Q) range of 0.7885 - 1.292 $\mathring{A}^{-1}$ and the Fourier time range (τ) of 0.08-0.6 ns has been explored. The obtained incoherent intermediate scattering functions exhibit stretched exponential form and the Kohlrausch-William-Watts (KWW) formula describes the data well (Fig 1). The temperature dependence of the relaxation time (τ_{self}) obeys the Arrhenius law (Fig 1b) while the Q-dependence suggest a non-Gaussian behaviour for the hydrogen motion.

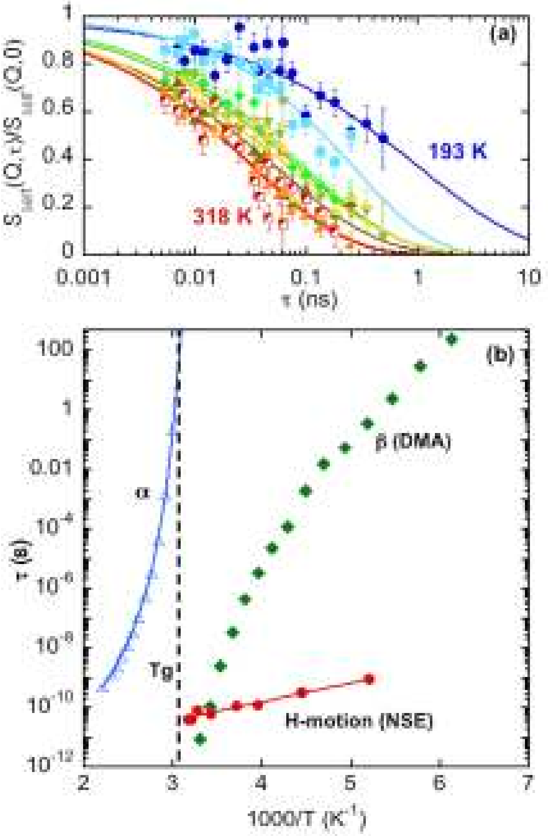

FIG. 1. (a) Incoherent intermediate scattering functions from neutron spin-echo experiments measured on PLA glass (Tg ≅ 333 K) at the maximum of the static structure factor ($Q1 = 1.13\mathring{A}^{-1}$). Solid lines represent KWW fits. (b) Relaxation map of PLA. Circles: H-atom motion from incoherent NSE (values showed for Q1); diamond: β-relaxation from DMA measurements; triangles: α-relaxation from reference [4].

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Complex interactions with the surroundings dictate tagged chain dynamics in unentangled polymer melts

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For more than half a century the theoretical landscape for single chain dynamics for dense polymeric solutions and melts below the entanglement threshold has been dominated by the Rouse model for independent phantom chains[1], supported by ideas of hydrodynamic screening. There exists, however, a large body of literature from experiments, Monte Carlo and molecular dynamics simulations on the deviations from the Rouse behavior for unentangled homopolymer melts, showcased mostly in the subdiffusive behavior of center-of-mass of tagged chains at intermediate times, with the subdiffusion exponent reported in the range 0.75-0.85.

The influence of the surrounding chains of length N_s on the motion of a tagged chain of length N is a key test which we show the Rouse model fails in high-precision numerical simulation of unentangled melts. Our central results are that at intermediate times the tagged chain's center-of-mass moves subdiffusively, $\langle \Delta r^2_{\rm cm} \rangle \propto t^\alpha$ with subdiffusion exponent $\alpha = 0.87 \pm 0.03$ as opposed to $\alpha_{\rm Rouse} = 1$, and that its crossover time to Fickian behavior is directly controlled by the relaxation time of the surrounding chains when the latter are shorter. The terminal relaxation time for the tagged chain $\tau_d \sim \text{Min}[N, N_s]^{2/\alpha}$, and the long time diffusion coefficient $D \sim N^{-1}\text{Min}[N, N_s]^{2-2/\alpha}$ are then sensitive to N_s.

High resolution homopolymer data enables us to show that the observed sudiffusion exponent is a true exponent rather than just a correction to Rouse scaling. We present two-dimensional "exponent flow diagram" in which for the effective exponent $\alpha(t) = d\ln\langle\Delta r^2_{\rm cm}(t)\rangle/d\ln(t)$ we plot its rate of change with logarithmic time $\dot\alpha(t) = d\alpha(t)/d\ln(t)$ vs the exponent $\alpha(t)$ itself. In a normalization group picture this is equivalent to plotting out the "β-function", and an extrapolated zero of $\dot\alpha(t)$ should correspond to a true fixed point exponent.

We have obtained the exponent flow diagrams for the tagged chain centre of mass motion of unentangled melts with chain lengths $25, 50$ and 100 as well as for an entangled chain length 5120 recently published [2]. These diagrams for the effective exponents $\alpha(t)$ of cm msd are shown in Fig. 1. The unentangled chains conform well to a universal curve, and *it should be noted there are no scale factors or fitting parameters behind this agreement.* For the entangled melt, the approach of the effective exponent to 1/2 for the tagged chain cm matches the tube theory due to Doi-Edwards and de Gennes. Most notably however, the exponent data for the unentangled and entangled melt nicely match with unstable fixed point at $\alpha \approx 0.85$. Figure 1 thus stands as clear evidence of our result that in violation of the Rouse model, the cm msd has a *true* subdiffusion exponent approximately 0.85

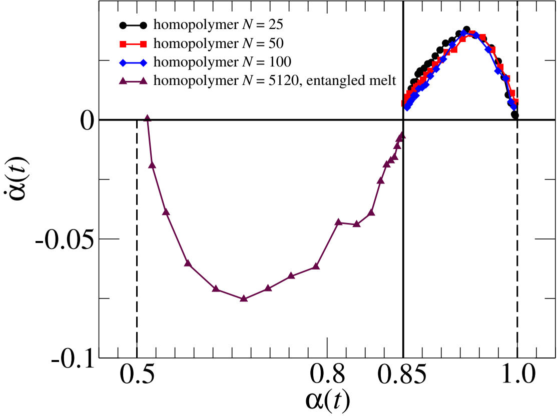

FIG. 1. The measured exponent flow diagrams for unentangled ($N = 25, 50$ and 100) and entangled ($N = 5120$) homopolymer melts for the tagged chain's centre of mass diffusion. All these data share a common fixed point $\alpha \approx 0.85$ corresponding to a true exponent, and distinct flows away from it for the unentangled chains towards fickian and the entangled chains towards effective exponent 1/2 per the tube theory of Doi-Edwards and de Gennes.

Successful blob scaling arguments support the anomalous value of α as a true exponent, and we find the same exponent in the scaling of Rouse mode amplitude correlation functions. Corresponding predictions for the dynamics of a tagged monomer and the chain's segmental orientation autocorrelation function agree very well with rheological measurements and NMR relaxometry experiments. We reflect back on a history of related experimental anomalies and discuss how a new theory might be developed.

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Transverse phonon excitations in a Pd-based metallic alloy in the liquid and supercooled liquid phases

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Lattice modes, or collective modes, are vibration modes of the entire systems. In the long wavelength limit, they can be described by the classical theory of elasticity in which the system is treated as a continuum possessing macroscopic elastic constants. As the wavelength becomes shorter, approaching the distance between atoms, the microscopic structure of the system and the forces between individual pairs of atoms describe the dominant features in determining the nature of the vibrational modes.

In liquids, longitudinal acoustic (LA) phonon modes are experimentally observed by ultrasonic, optical, or inelastic scattering experiments because the density fluctuations can occur due to a strong repulsive force between the atoms when they approach each other. However, transverse acoustic (TA) phonon modes were believed not to be detected in liquids because the shear force in the long spatial range is very weak.

In the terahertz frequency region, there may be a solid-like cage effect on the nanometer scale that acts as a restoring force for TA modes. If this speculation is correct, TA modes could be realised experimentally in dynamic structure factor $S(Q, \omega)$ measurements by inelastic x-ray or neutron scattering (IXS or INS) which cover the terahertz and nanometer ranges of the dynamic properties.

In the previous IXS experiments, $S(Q, \omega)$ spectra of liquid Ga [1], Fe [2], Cu [2], and Sn [3], were measured near the melting points. In each spectrum, low-energy excitations were observed between the quasielastic line and the LA mode. From the detailed analysis for the IXS data, the lifetime of sub-ps and the propagating length of sub-nm were estimated from the TA phonon modes in each liquid metal, corresponding to the lifetime and size of cages formed instantaneously in liquid metals.

Then, a question arises: How do the TA modes change with decreasing temperature, i.e., in supercooled liquids or glasses, where the lifetime of the cages may become drastically longer or infinity, respectively. Unfortunately, simple metals crystallize just below the melting points. On the other hand, $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ alloy is well-known to form the most excellent bulk metallic glass (BMG), and has a wide temperature range of the supercooled liquid. Thus, this system is suitable to investigate the temperature dependence of the TA phonon excitations in non-crystalline materials.

Fig. 1 shows the IXS spectra of liquid $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ at 530°C. Strong LA modes were seen and their dispersion relation was clearly observed as indicated by red arrows. The TA modes also seem to exist between the quasielastic line and the LA peak as shown by blue arrows. Very similar features of the IXS spectra were also obtained for the supercooled liquid at 320°C and glassy state. In addition, optic-like excitations were detected in the glassy state at the higher energies beyond the LA excitations. Detailed analyses are now in progress.

The IXS experiments were performed at the beamline BL35XU in the SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal Nos. 2013A1138, 2013B1298, and 2014A1059).

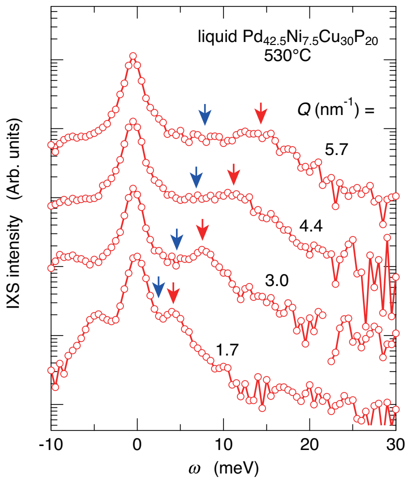

FIG. 1. IXS spectra of liquid $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ at 530°C.

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Dynamics of Binary Zr-Cu Liquids with Minor Additions

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Heterogeneous Glassy Dynamics near a Random Critical Point

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The study of metastable states and the search for growing structural correlations are challenging tasks in glass science, which can be attacked using suitably coupled replicated systems in real glass models[1]. Given two configurations (x,y), it is useful to consider a system where the replica y is frozen and only the replica x can evolve under the influence of the other replica. The total system is described by the following Hamiltonian:

$$H_\epsilon(x,y) = H(x) - \epsilon Q(x,y), \qquad (1)$$

where ϵ is a coupling field and the overlap $Q(x,y)$ between the two replicas is defined as $Q(x,y) = \frac{1}{N}\sum_{i,k=1,N} w(x_i - y_k)$, where $w(x)$ is a smooth function which evolves from one when the interparticle distance is small, to zero when its gets large. Therefore the overlap is of order one when the two copies are in a similar state and close to zero otherwise. In this context, some interesting properties of this systems have recently been revealed. The most important one is the existence of a first-order liquid-to-glass phase transition at equilibrium [2, 3], ending at a second order critical point. After defining an effective potential function as

$$V(Q) = -\frac{T}{N}\ln P(Q), \qquad (2)$$

where T is the temperature and $P(Q)$ the probability distribution of the overlap, it has been shown that by increasing ϵ at constant T, the system presents two different phases (see fig.1).

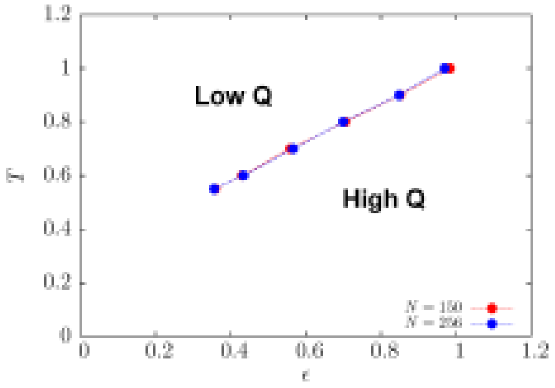

FIG. 1. The phase diagram temperature versus coupling constant for the binary Lennard-Jones system. The curve signals the phase transition between the low-Q phase (top-left corner) and the high-Q phase (bottom-right corner).

For small ϵ, replica x is very different from replica y, the overlap Q is very small. For larger ϵ, replica x is close to replica y and the overlap is large. These two situations are separated by a sharp discontinuity in the (ϵ, T) plane, see Fig. 1. These properties are directly reflected in the evolution of the effective potential $V(Q)$.

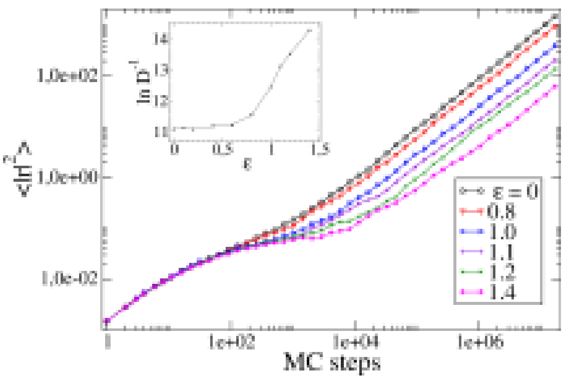

FIG. 2. The mean squared displacement measured at $T = 1.0$ and increasing ϵ values from $\epsilon = 0$ to $\epsilon = 1.4$. The inset shows the behaviour of the inverse of the diffusion constant as a function of ϵ across the phase transition.

In this contribution we study a 80:20 binary mixture of Lennard-Jones particles using the Kob-Andersen potential and implementing a Monte-Carlo dynamics of the Hamiltonian (1) with a system size of $N = 1000$ particles. We carefully analyze the phase diagram in the plane (ϵ, T) both in the high-Q and in the low-Q phases, in order to characterize the dynamical behaviour and its glassy features in equilibrium conditions in the vicinity of the phase transition. We study in particular the dynamical slowing down related to the approach of the random critical point.

We observe a massive change in the dynamical properties of the system when the phase transition is approached. This implies a dramatic slowing down of the mean-squared displacement (see fig.2) and of the relaxation times of density correlation functions. We also focus our analysis on the vicinity of the random critical point, where we find a sudden growth of dynamic heterogeneity. Moreover, we analyse the behaviour of the temporal fluctuations of the microscopic order parameter, the global overlap Q, near the random critical point.

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Diffusion of a hard tracer in an ideal gas

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We study the diffusion of a hard spherical tracer embedded in an ideal fluid bath by means of simulations, varying the volume fraction of the bath, ϕ. The microscopic dynamics is governed by the Langevin equation, which allows us to test the relative importance of inertia with respect to Brownian forces. Given that the tracer-bath particle collisions are uncorrelated, the diffusion of the tracer at all bath densities can be analyzed using models developed for Brownian hard spheres at low density [1], but we have also compared with results from mode coupling theory (MCT).

Zia and Brady [2] simulated this system with Brownian dynamics, showing that the tracer diffusion coefficient decreases with increasing volume fraction of the bath, ϕ. Our results with Langevin dynamics confirm this result for all friction coefficient, but also shows that the normalized diffusion coefficient increases by approaching the Brownian limit ($m/\gamma \to 0$, with m the tracer mass and γ the solvent friction coefficient), as shown in Fig. 1. At low volume fractions, the diffusion coefficient at high γ follows the $1 - 2\phi$ result (dashed line in the figure), obtained from the two particle Smoluchowski equation by Ackerson and Fleishman [1]. The simulation results, however, deviates from this behaviour at intermediate density, making the $1/(1 + 2\phi)$ behaviour a much better approximation (solid line), which agrees with the $1 - 2\phi$ result at low ϕ. The results from MCT, with the structure factor $S_q = 1$ for the ideal fluid bath, on the other hand, show the $1 - 4/3\phi$ behaviour at low density [3], but gives much better qualitative description for the simulation results than the low density calculation.

The $D\gamma = (1 + 2\phi)^{-1}$ behaviour would indicate that friction with the bath increases linearly with the number of collisions with bath particles, given by the bath volume fraction. This is further tested in the inset to the figure, where the linear trend of D^{-1} is tested by plotting $(1/D\gamma - 1)/\phi$ vs. ϕ. The simulation data indeed approaches a constant value close to 2 for all densities, but a slight dependence on ϕ can be detected, which is also observed in the MCT results. This representation also makes clear the evolution with the solvent friction coefficient.

To further understand the tracer dynamics, the velocity autocorrelation functions are studied, which show a shallow negative deep following the relaxation of the momentum at a time scale m/γ, causing the decrease of the diffusion coefficient (the minimum is less conspicuous than for hard spheres at moderate density). The force (from particle collisions) autocorrelation function, or memory function, is monotonous and proportional to the bath volume fraction in the Brownian limit, showing moderate agreement with the calculations from Ackerson and Fleishman: strong deviations are noticed in the short time regime due to the difference from the Langevin dynamics to the true Brownian dynamics and particles softness, but the long time tail is reproduced.

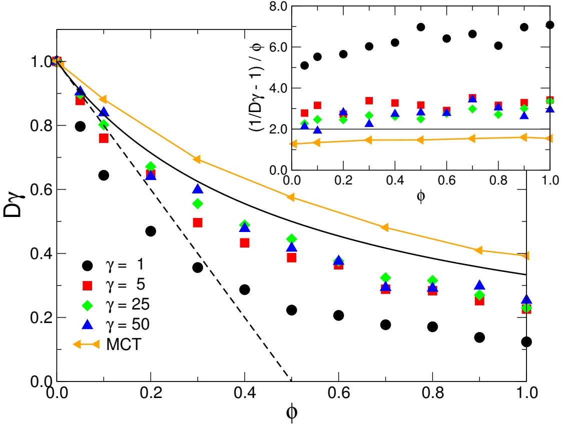

FIG. 1. Self diffusion coefficients normalized with the single particle value as a function of the volume fraction of the bath for different friction coefficients, as labeled. The behaviours $1-2\phi$ and $(1+2\phi)^{-1}$ are also included, dashed and continuous lines, respectively, and the MCT results. The inset presents $(1/D\gamma - 1)/\phi$ as a function of ϕ.

Finite size effects are noticed in the structure of the system, due to the tracer excluded volume in a finite system. The diffusion coefficient is free from finite size effects.

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Mean Square Displacement from a jumper model

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The motion of a particle in a supercooled liquids is characterized by long caging periods, during which the particle is confined by its neighbors, interrupted by fast local rearrangements, known as jumps. This intermittent dynamics is conveniently described within the continuous time random walk approach, that assumes successive jumps of a same particle to be spatially and temporally uncorrelated [3]. This allows to relate the long time diffusion coefficient, D, to the average time particles wait in their cages before performing a jump, τ_w, and to the average squared jump length, l^2, as $D \propto l^2/\tau_w$. Accordingly, the asymptotic behavior of the mean square displacement can be related to simple features of the single particle dynamics. Conversely, it is not yet clear how the whole time dependence of the mean square displacement is related to simple and universal features of particle motion. Indeed, predictions for the time dependence of the mean square displacement are only available at high temperatures, where glassy systems are well described by mode coupling theory.

Here we show that it is possible to describe the whole time dependence of the mean square displacement of supercooled liquids, by integrating the continuous time random walk approach and a model for the short time particle motion. The dynamics is characterized by three dynamical regimes: a ballistic motion with velocity $\propto \sqrt{T}$, a vibrational motion of amplitue r^2_{DW}, and a diffusive motion with diffusion coefficient D. The crossovers between these regimes occur at the ballistic time τ_b, and at the caging, τ_w. We have validated this model against numerical simulations of the Kob–Andersen Lennard-Jones 80:20 binary mixture, of the 80:20 WCA Lennard-Jones mixture, of a 50:50 mixture of particles interacting via a purely repulsive harmonic potential, and of a 50:50 mixture of hard spheres. As an example, we illustrate how the model captures the mean square displacement of one of these systems in Fig. 1.

We consider the temperature/volume fraction dependence of the parameters characterizing the model, and their relation with structural properties of the system. In particular, we have studied the relation between the Debye-Waller factor, r^2_{DW}, and the variance σ^2_g of the first peak of the radial distribution function, which estimates the typical cage size. We have found $r^2_{DW} \gg \sigma^2_g$, which implies that for the systems and temperatures we have considered, it is conceptually wrong to consider the short time behavior of the mean square displacement as determined by the rattling of the particles within the cages formed by their neighbors. Rather, the mean square displacement is dictated by collective oscillations, that involve particles and their cages. However, the cage size results to be related to the dynamics, as in all model systems we find a linear relation between the cage size and the Debye-Waller factor, e.g. for thermal systems $\sigma^2_g(T) = \sigma^2_g(0) + \alpha\, r^2_{DW}(T)$, with α model dependent. Considering that the Debye-Waller factor has been recently related to the relaxation time in the context of elastic models of the glass transition [1], the above relation might allow to link a static structural properties, $\sigma^2_g(T)$, and the relaxation time.

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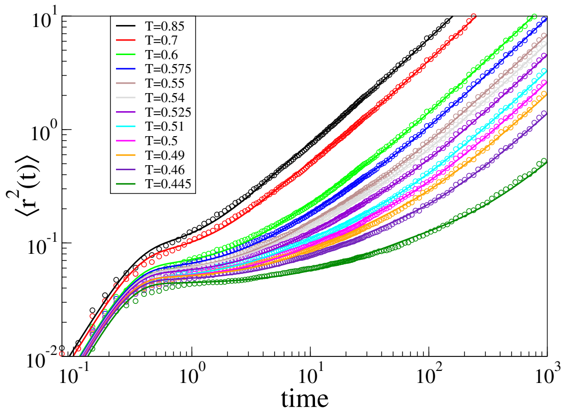

FIG. 1. Mean square displacement of the Kob-Andersen 80-20 mixture at different temperatures. Points are numerical data, lines fits to the proposed model.

Defect-mediated relaxation in the random tiling phase of a binary mixture: Birth, death and mobility of an atomic zipper

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Given the large structural fluctuations present, it is not hard to imagine that relaxation in an amorphous material can proceed via the excitation of local reorganizations ('defects') that can then move the system between distinct configurations. The problem is that, in the absence of any explicit characterization of the localised reorganization, this proposal can only aspire to vague phenomenology. Crystals pose the converse problem. The identification of defects is straightforward but the point defects cannot relax the structure due to the high degree of global constraint imposed by the very structure that made the defects definable. This is the basic dilemma faced by efforts to describe amorphous relaxation. One resolution of this quandary is to find a condensed phase of sufficient order that defects could be explicitly identified and of sufficient disorder that the system has a degenerate manifold of distinct groundstates whose exploration would constitute structural relaxation. We propose that the random square-triangle phase exhibited by some binary mixtures in 2D is just such a phase.

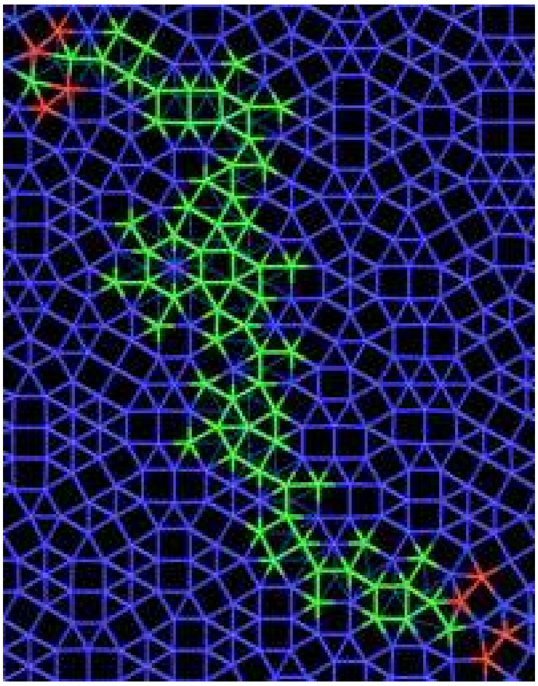

FIG. 1. The passage of a mobile defect through the RT phase. The initial configuration is shown as a purple net whose edges link nearest neighbour large particles. Those large particles that have experienced a change of neighbours by the end of the trajectory, along with the edges of this final net, are indicated in green. The origin of the zipper is indicated by the static defect (red) in the lower right corner and the final position of the mobile defect (red) is at the end of the line of topological change in the top left corner.

In this contribution[1] we describe the mechanism of defect-mediated relaxation in the dodecagonal square-triangle random tiling (RT) phase exhibited by a simulated binary mixture of soft discs in 2D. We examine the internal transitions within the elementary mobile defect (christened the 'zipper') that allow it to move, as well as the mechanisms by which the zipper is created and annihilated (see Fig. 1). The structural relaxation of the random tiling phase is quantified and we show that this relaxation is well described by a model based on the distribution of waiting times for each atom to be changed by the diffusing zipper (see Fig. 2). We make no claim that the mechanism of structural relaxation of the RT phase provides any general account of relaxation in amorphous states. Rather, our goal is to present as complete an account as possible of slow collective structural relaxation in a dense phase characterised by a degeneracy of groundstates. Such a system can provide a valuable test case for general theories of relaxation in complex and disordered materials.

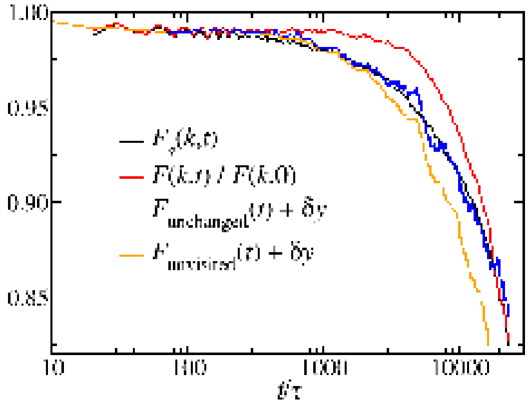

FIG. 2. The total $F(k,t)$ and self $F_s(k,t)$ intermediate scattering functions for the RT phase (summing over large particles only) plotted alongside the fraction of particles $F_{unchanged}(t)$ that have not experienced a local topological change due to the action of the zipper after time t. For comparison we also show the fraction of particles $F_{unvisited}(t)$ that have yet to be visited by the zipper. $F(k,t)$ has been scaled by its value at $t = 0$ and $+\delta y$ indicates that a shift along the y-axis has been applied.

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Investigating Amorphous Order in Stable Glasses Through Random Pinning

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We use random pinning to investigate the structure of stable glassy states as compared to supercooled liquid states [1]. An ensemble of trajectories of a model glass former is biased to have non-typical values of dynamical activity (the s-ensemble). In this ensemble, a dynamical transition is observed between an active (equilibrium) phase and an inactive phase associated with large deviations of the dynamical activity [2]. Configurations taken from these inactive trajectories are very stable, while there is no obvious difference between their structure and the structure of configurations taken from equilibrium trajectories [3]. We therefore refer to these configurations as stable glasses.

By randomly pinning a fraction of the particles in a configuration, and then measuring its overlap with other configurations sharing the same set of pinned particles we can probe many body correlations. When this procedure is carried out for configurations from both phases there is a marked difference in the results, revealing the presence of a length scale in the inactive state comparable to the system size. This is a signature of enhanced amorphous order in the inactive configurations, which helps to explain their stability. Additionally, measuring four-point correlation functions in the presence of random pinning allows a length scale associated with dynamic heterogeneity to be measured [4]. This is an important measurement, as theories of the glass transition make predictions of how it should behave.

Glassy behaviour may be explained using the concept of amorphous order [5], where structure appears to be highly disordered but there are strong correlations between particles. As an alternative it may be explained only using particle dynamics, with no reference to many body correlations [6]. Notably, the stable glass configurations we analyze were produced using a method that selects trajectories with unusually slow dynamics but their stability is linked with strong amorphous order, which is a structural measure. We argue that these two approaches to glasses are not contradictory, and much can be gained by considering them together allowing theories of the glass transition to proceed further.

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Evolution of metastable glassy states in mean field hard-spheres: a replica approach

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The glass transition is one of the great open problems in condensed matter physics. As of now, one of the most promising theories to explain it is the Random First Order Theory (RFOT), which envisions the glass transition as a phenomenon whereupon the relaxation of the liquid is hampered by the presence of a great number of metastable glassy states, which trap the dynamics and prevent the liquid from relaxing and flowing. This approach has led to a number of interesting results, which have recently culminated in the complete statistical-mechanical solution of the glass problem for a model of hard spheres (HS) embedded in a space with infinite dimensions (and so mean-field in the classical sense)[1].

Up to now, the theoretical research effort has mainly focused of the properties of the equilibrium solution. However, the dynamics of glass-formers on human timescales happens actually very far from equilibration, and so the study of this regime is extremely relevant for what concerns experiments (fox example DSC calorimetry [2]) and numerical simulations. In principle, such a study would require solving the dynamics of the glass-former for different preparation protocols, which is as of now an impossible task when starting from first principles.
We present here results obtained from a theoretical scheme which allows us to circumvent this problem and compute many properties of metastable glassy states from first principles, without having to solve the dynamics. We do this by focusing our attention on the in-state free energy of metastable states, as opposed to the liquid, ergodic one. This can be done by restricting artificially the Gibbs measure for the model to a single metastable state [3]. We are able to follow glassy states adiabatically both in compression-decompression (which for HS are equivalent to cooling and heating), compute their equation of state (fig 1) and study their response as a shear-strain is applied to them. Our results reproduce well the behavior of glasses as observed in experiments and numerical simulations. In particular we can reproduce the melting of the glass back into the liquid under heating (onset transition), and the yielding of the glass which takes place when an excessive strain is applied.
We present also similar results [4] for a special HS model which is solvable in dimension three, and allows us to easily obtain thermalized configurations also in the glass phase using the *planting* method, opening the door to an extensive and systematic comparison between theory and simulation.

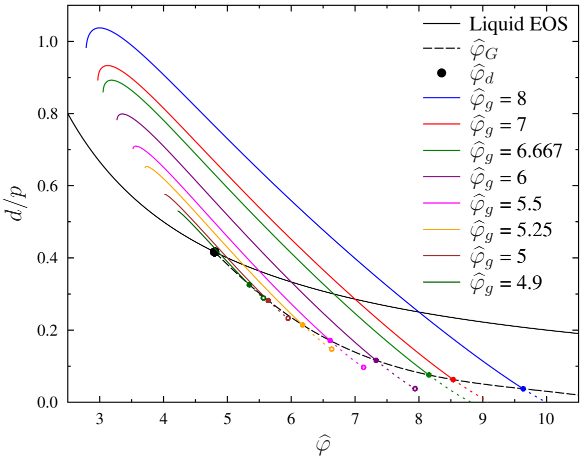

FIG. 1. Equations of state of various glasses. The different $\widehat{\varphi}_g$ are the protocol-dependent densities at which the phenomenological glass transition takes place. The pressure and packing fraction are both rescaled to remain finite as $d \to \infty$.

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Dynamic heterogeneities close to a non-equilibrium phase transition

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Non-equilibrium phase transitions have been studied intensively in recent years. One example is a suspension of colloidal particles driven out of equilibrium by periodic shearing [1, 2]. It has been found that below certain critical point (which depends on the density and shearing amplitude), the system evolves into an absorbing state in which all the particles move reversibly in response to the external periodic driving force. In this work, we use a simplified isotropic 2D model which also possesses the same absorbing phase transition. In this particular type of non-equilibrium phase transition, we detect clear signs of dynamic heterogeneities close to criticality and we suggest a few measurements which can be repeated in experiments.

The model considered in this work is illustrated in Fig. 1. We start from some random configuration at $t = 0$ where some particles are allowed to overlap. Particles which overlap are labelled ‘active’ and are each given an independent random displacement $\vec{\delta}$. On the other hand, particles which do not overlap are labelled ‘passive’ and remain at rest. Below some critical density ϕ_c, the number of active particles will eventually go to zero (no more overlap) and thus all particles will be at rest. This corresponds to the absorbing state in [1, 2]. On the other hand above the critical density ϕ_c, the number of active particles will remain positive and fluctuate around its mean value.

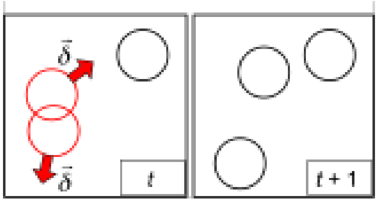

FIG. 1. The model considered in this work. We start from a random configuration at $t = 0$ where some particles are allowed to overlap. Particles which overlap are labelled ‘active’ and are each given a random displacement $\vec{\delta}$. On the other hand, particles which do not overlap are labelled ‘passive’ and remain at rest.

In this model, we observe some clear signatures of dynamic heterogeneities both in time and in space [3]. For instance at short time intervals, the trajectory of any particle will be characterised by a few long waits and very short jumps. (This is analogous to the trajectory of the particles in glassy systems where the particles are caged by their neighbours and there exists a characteristic waiting time for the particles to escape the cage.) However if we look at long enough time intervals, the trajectory of all the particles will eventually look like a Fickian diffusion. Thus we observe dynamic heterogeneity in time. Subsequently, we may define a characteristic timescale τ to be the onset of Fickian diffusion. We found that τ diverges as we approach criticality $\phi \to \phi_c^+$.

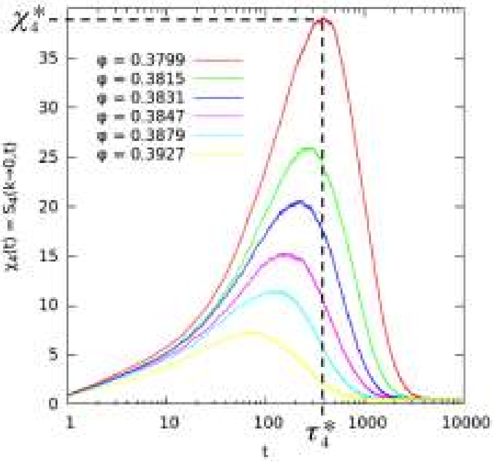

FIG. 2. The dynamic susceptibility $\chi_4(t)$ gives us the correlation between particles which have moved after time t and particles which remain at rest. The maximum correlation ($\chi_4^* = \chi_4(\tau_4^*)$) diverges as we approach criticality ($\phi \to \phi_c^+ = 0.37499$). This indicates a diverging correlation length close to criticality.

Similarly, we can detect dynamic heterogeneity in space by measuring the correlation between particles which have moved and particles which remain at rest during some time interval t. This correlation function is called the dynamic susceptibility $\chi_4(t)$ and is plotted in Fig. 2 for different densities ϕ’s. At $t = 0$, all the particles will be at the same position and thus $\chi_4(t)$ is zero. As t increases, some particles will start to move and thus $\chi_4(t)$ increases before reaching a peak at τ_4^*. Finally as $t \to \infty$, all particles will have been displaced and the correlation function $\chi_4(t)$ will drop to zero again. As we can see from Fig. 2, the maximum correlation χ_4^* also diverges as we approach criticality which indicates a diverging dynamic correlation length close to criticality. Physically, this dynamic correlation length tells us about the domain size of the particles which have moved from their original positions.

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Jamming by Shape in Kinetically-Constrained Models

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In colloidal and granular systems, temperature does not play a major role. The dynamics of such systems are dominated by the geometrical packing fraction of their constituents and may be described by various kinetically-constrained models [1, 2]. The same class of models may also be used to describe the slow dynamics of glasses. We focus on the Kob-Andersen (KA) [3] and Fredrickson-Andersen (FA) [4] models, which are defined as a lattice gas with only on-site exclusion (KA) or an Ising model of non-interacting spins (FA), for which particles (KA) or spins (FA) can move to neighboring sites (KA) or flip (FA) only if they have less than a certain number of occupied (KA) or up (FA) neighbors. Most previous research aimed to understand the thermodynamic limit of infinite system size, while actual experimental systems are finite. We consider finite-size and semi-infinite systems in arbitrary dimension, which are infinite in several directions, but finite in the other directions [5, 6].

By increasing the density of particles in the system (KA) or lowering its temperature (FA), it becomes jammed, i.e. almost all the particles can never move (or flip) according to the kinetic constraints. It has been proven [7–9] that a system which is infinite in all directions, gets jammed only at a density of 1, when all lattice sites are occupied by particles (KA) or all spins are up (FA). We find, analytically and numerically, that finite systems become jammed at some finite, size- and shape-dependent density which nears 1 as the size of the system is increased. We identified that systems are either strongly confined when the number of their effective dimensions, d_{eff}, is smaller than the number of neighboring vacant sites needed for movement, m, or weakly confined otherwise. We find that the critical density scales as

$$1-\rho_c \sim \begin{cases} \left(\ln_{m-1} V^{1/d_{eff}}\right)^{-d_{eff}+m-1} & \text{weak} \\ \left(\ln_{m-2} V_s^{1/(d-t)}\right)^{-d+t+m-1} & \text{strong} \end{cases}, \quad (1)$$

where V is the system's volume, V_s is the volume associated with the $s = d - d_{eff}$ small dimensions, $t < s$ is the number of very small dimensions, and $\ln_k$ is the logarithm iterated k times. The proportionality constant is known exactly at the limit of infinite systems in any dimension [9], but it converges very slowly to that value. Using the fact that in the $m = 2$ models, unjammed clusters must be rectangles, we evaluated this constant numerically for two-dimensional systems of effective size $10^7 \times 10^7$ [10], much larger than the largest systems simulated before ($10^5 \times 10^5$).

Because the jamming density depends on the shape of the system, it is possible to jam or unjam the system just by changing its shape, without altering its total volume or particle density, as seen in experiments [11], and in our simulations (Fig. 1). In the protocol we give here, the jamming transition does not occur by exerting forces on the system, but by performing ensemble averages over systems with fixed shape and density.

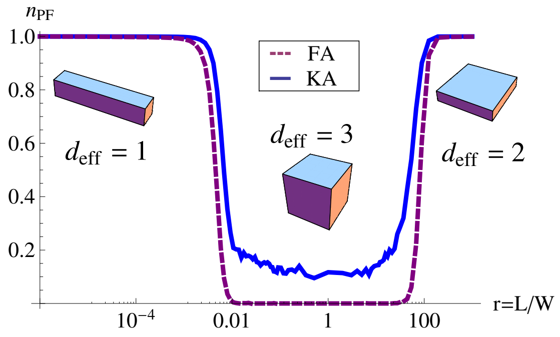

FIG. 1. The fraction of permanently frozen particles, n_{PF}, as a function of the aspect ratio $r = L/W$ for a three-dimensional box of size $L \times L \times W$ in the $m = 2$ models. The total volume of the system is $L^2W = 10^6$ and the density is $\rho = 0.99$. At small r the system is a jammed quasi-one-dimensional tunnel, at intermediate r the system is an unjammed three-dimensional cube, and at large r the system is a jammed quasi-two-dimensional plane.

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Entropic selection within higly degenerate ground states: colloidal and deformable Ising antiferromagnets

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Geometrically frustrated systems [1] like the colloidal [2] and the deformable Ising [3] antiferromagnets have a ground-state degeneracy that is lifted because the zero-temperature entropic differences between configurations in an effect termed order-by-disorder.

Han et al. [2] experimentally studied a system composed of closely packed colloidal spheres confined between parallel walls that are separated by slightly more than a single sphere diameter. The spheres self-assembled into a buckled triangular lattice with either up or down out-of-plane displacements. They found a highly degenerate close-packed state, the maximal density of which is obtained by straight stripes or by any set of parallel stripes that zigzag within the hexagonally packed layer. These zigzagging stripes have subextensive zero-temperature entropy. In order to understand the order-by-disorder effect in this buckled colloidal monolayer, Shokef et al. [3] considered the antiferromagnetic Ising model on an elastic triangular lattice, which shows the same degenerate ground state of zigzagging stripes, but in this case they could exactly calculate the entropy and the free-energy difference between the competing configurations. Using a phonon calculation they found that straight stripes are always favored entropically. However, the free-energy barriers between various ground states are huge compared to this entropic gain, causing the system to fall into a disordered glassy state upon cooling [4].

To better understand the microscopic origin of the entropic difference between the straight and bent configuration in the colloidal and the deformable Ising antiferromagnets and to find out if the same entropic selection mechanism takes place in these two systems, we directly computed the microscopic entropy in the space variables for these two models: hard spheres confined between parallel walls, suitable to describe the colloidal experiments [2], and Ising spins connected with harmonic springs [5], the entropy of which can be exactly computed in the limit of small displacement and low temperature. The approach we used to compute the entropy of the hard-sphere system is similar to the expansion method developed by Stillinger et al. [6] to compute the entropy of the fcc and hcp structure of hard spheres. The main feature of this method relies on computing the entropy of the system in which all the spheres are frozen in the ground state configuration except one. The further step is to allow two contiguos particles to move and so on. For the Ising model we used a similar approach, but doing the expansion as a function of the number of shells, n_s, free to move. Fig. 1 shows that for the deformable Ising antiferromagnet, already at the one free particle level ($n_s = 1$), the entropy difference between the straight and the bent configuration is qualitatively close, at least for angles that are not too large, to the phonon solution found in [3].

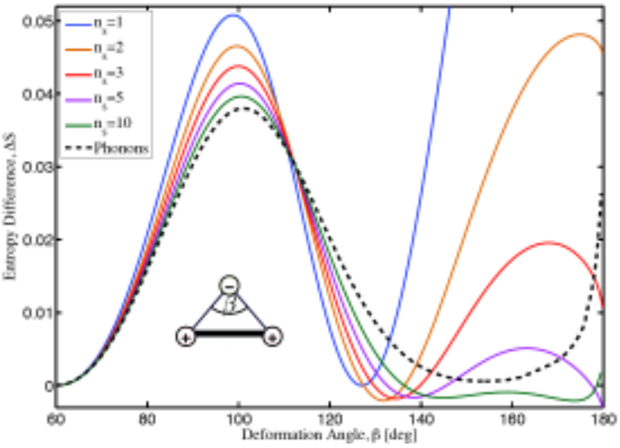

FIG. 1. Entropy difference between straight and bent stripes configuration in the deformable Ising antiferromagnet as a function of the triangular plaquet deformation angle β, for different numbers of free shells.

In the colloidal antiferromagnet, at the one free sphere level there is no entropy difference between the straight and bent configuration, as for the fcc and hcp configuration in 3D, except for large angles. This is a first important difference between the two models we consider. The difference in the entropy we find at the one free sphere level for large angles can be due to the peculiarity of the stripes configuration or to the fact that confinement can change the stability of this kind of systems. We show the effect of allowing more contiguous spheres to move on the entropy difference between these two configurations and demonstrate the connection with the deformable Ising antiferromagnet.

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From Kinetically Constrained Models to the ideal glass transition: a thermodynamic study of the Triangular Plaquette Model

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Two competing scenarios have been proposed since a long time as alternative to explain the critical slowing down of glass-forming materials: the dynamic facilitation scenario, well represented by Kinetically Constrained Models (KCM), where glassiness arise just as a dynamical phenomenon, and the thermodynamic scenario of the Random First-Order Transition (RFOT) theory, according to which the slowing down of dynamics is the signature of a true thermodynamic transition, the glass transition. While the thermodynamic scenario is mainly supported by mean-field results, the strenght of KCMs is that such models often can be exactly solved in finite dimensions, as for instance the two dimensional Triangular Plaquette Model (TPM), in which the relaxation time diverges at zero temperature like $\tau_{\rm rel} \sim \exp(-c/T^2)$ [1]. The TPM consists in spins on a two-dimensional triangular lattice interacting through the Hamiltonian $\mathcal{H}_0 = -\sum_{\langle ijk\rangle} \sigma_i\sigma_j\sigma_k$, the indices $\langle ijk\rangle$ representing triplets of spins lying at the corners of upward pointing triangular cells.

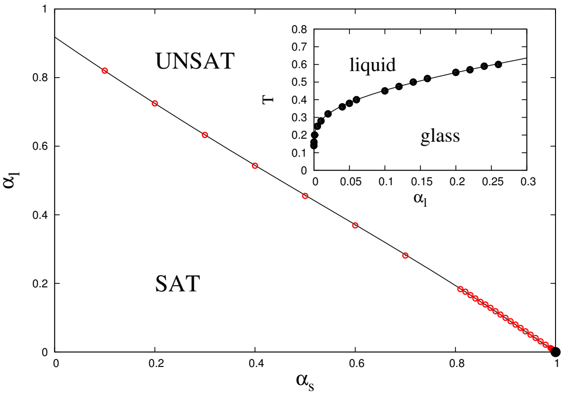

FIG. 1. Main Panel: Sat/Unsat threshold for the Random Dilute Triangular Plaquette Model at zero temperature in the parameter space (α_s, α_l). Inset: liquid/glass phase diagram in the plane (α_l, T). α_s=dilution of the TPM, α_l= concentation of extra random plaquettes.

We present here an extension of the TPM which, changing some parameters, interpolates between the TPM and the diluted non-disorderd p-spin ($p = 3$) model, which has an ideal glass transition at $T_K > 0$ [2]. Our aim is to show that an arbitrary small perturbation of the TPM produces the formation of a glass phase by means of the same mechanism acting in the diluted p-spin. We call our model the Random Diluted TPM (RD-TPM): it is characterized by a dilution parameter $0 \leq \alpha_{\rm s} \leq 1$, which measures the concentration of the original TPM plaquettes, and by the concentration $\alpha_{\rm l}$ of extra *random* plaquettes, contributing an additional term to the Hamiltonian, $\mathcal{H}_1 = -\sum_{\{ijk\}} \sigma_i\sigma_j\sigma_k$, where the triplets of indices $\{ijk\}$ represent in this case a random choice of spins in the 2D lattice. We studied when, varying $\alpha_{\rm s}$ and $\alpha_{\rm l}$, the ground states of the system are frustrated or not, which gives informations on the finite temperature glass transition. We are indeed disregarding the ferromagnetic ground state, but, if the extra plaquettes does not favour local ordering as happens for our model, such state is reached only in infinite time. The appearence of frustrated ground states is related to the unsatisfiability of the system of linear equations representing the constraint of minimum energy for every plaquette. In the main panel of Fig.1 is represented the SAT/UNSAT threshold in the plane (α_s, α_l), as obtained from a numerical study of the model (circles), compared to the analytic predictions on a random regular graph (continuous line). In the UNSAT region the ground states are frustrated and the system is expected to have an ideal glass transition at finite temperature. A quite striking result is that the numerical analysis in finite dimensions (circles in main panel of Fig.1), i.e. when the random plaquettes are added upon the 2D lattice, and the analytic prediction (continuous line) on the random graph, locate the satisfiability threshold on the same line. It is even more remarkable the result that the only dilution $\alpha_{\rm s}$ at which *every* infinitesimal concentration of extra random plaquettes produces frustrated ground states is just $\alpha_{\rm s} = 1$, i.e. the pure TPM. It turns out that the TPM is therefore the only point on the line $\alpha_{\rm l} = 0$ where an arbitrarily small perturbation of the hamiltonian can induce a finite temperature glass-transition. For each point $(\alpha_{\rm s}, \alpha_{\rm l})$ in the unsat region, just asking the energy of the system not to be smaller than that of the frustrated ground states, one can work out the relation $\alpha_{\rm l} \sim \exp(-a/T_K)$ between the Kauzmann temperature and the concentration of extra random plaquettes (a is a constant of the model). Such a relation is fairly verified by the glass/liquid phase boundary in the $(\alpha_{\rm l}, T)$ plane when the model is studied on the random regular graph.

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A One-dimensional Kac Model of Dense Amorphous Hard Sphere in High Dimension

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As the temperature is decreased, the relaxation time and the viscosity of super-cooled liquids show dramatic increase, and eventually overcome the observation time. This phenomenon known as the glass transition is widely observed when liquids are quenched so fast as to avoid crystallization. In the case of super-cooled liquids, driving force of constituent molecules is thermal fluctuation, namely systems are in thermal equilibrium. Interestingly enough, similar phenomena are observed in athermal systems like granular materials where typical size of constituent particles are large enough that thermal fluctuations are negligible. With increase of the density, the viscosity of granular materials under the share strain increase rapidly, and eventually diverges at the jamming density. Both slow dynamics observed in the glass transition and critical behavior of the shear viscosity in the jamming transition suggest that those phenomena can be understood as some kind of critical phenomena.

The first step to understand a critical phenomenon is to construct a mean-field model for the phenomenon. The most simple model for this purpose is the hard-sphere system which shows both the glass transition with infinitely slow increase of the density and the jamming transition with infinitely rapid increase of the density. Recently, exact analysis of the high dimensional hard-sphere system was done, as a consequence a mean-field model and a theory for the unified description of the glass and the jamming transition were established[1]. Especially, for the jamming transition, some of the critical exponents near the jamming transition point calculated by the mean-field theory agree very well with numerical simulations and experimental results.

In order to get deeper understanding of critical phenomena, spacial fluctuation should be considered besides mean value of the order parameter. It is expected that calculating the diverging length scale near the transition points and corrections to mean-field theory will let us argue validity of the mean-field theory in finite dimension. One of the most straightforward way to introduce special structure is to assign a order-parameter to each point of space. In this way, the correlation length of the certain mean-field spin glass model which shows glass transition was calculated. However, for dense hard-sphere system, it is a rather cumbersome method because we have to treat the free-energy of *inhomogeneous* liquid. For this reason, although itself a very curious problem, we use a much easier alternative method. Inspired by Ref [2], we introduce network structure shown in the FIG 1: particles in l th box interact only with particles in $l, l-1, l+1$ th box, all the rest being transparent to it. This model can be analyzed using *homogeneous* $L+2$ component liquids theory, and analytically treatable in high dimension.

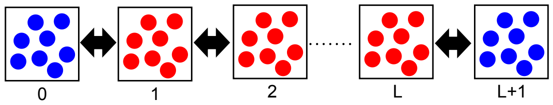

FIG. 1. A schematic figure of our model. The red and blue circles represent mobile and in-mobile particles respectively. Particles in l th box interact only particles in $l-1, l, l+1$ th box.

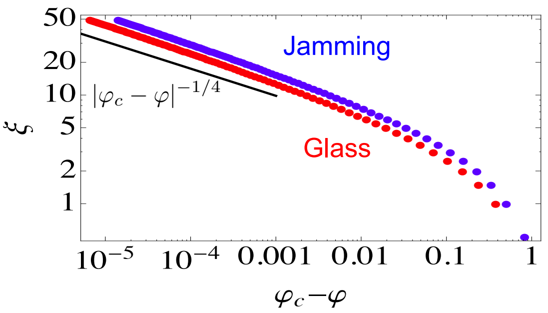

FIG. 2. Correlation lengths calculated by our model using the 1RSB ansatz.

Here, we would like to summarize our results using the 1RSB ansatz which is some kind of approximate solution. In the case of the glass transition, there is two relevant density: the dynamical transition point where dynamical slowing down begin and the ideal glass transition point where the thermodynamics transition from liquid to glass occur. FIG2 shows the correlation length near the dynamical transition point φ_c, we see from this the critical exponent of the correlation length is $\nu_d = 1/4$. On the other hand, near the ideal glass transition point, the analytic form of the correlation length was obtained and we found the critical exponent is $\nu_{id} = 1$. We also estimated correlation lengths in the case of jamming transition, and found two correlation lengths whose critical exponent are 1/4 and 1 respectively.

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Length scale for transport coefficients in glass-forming liquid

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Approaching to glass transition temperature, the dynamic of supercooled liquids drastically slows down and eventually diverges, i.e. the relaxation time of system goes to infinite. Usually this time scale divergence is accompanied by the divergence of length scale. Numerous simulation works also show drastic increase of correlation length, extracted from four-point correlation function. However, how the length scale underlying for transport coefficients grows with under-cooling temperature is still unclear.

We conduct molecular dynamic (MD) simulations for a glass-forming Lennard-Jones mixture using Kob-Anderson parameters at the composition $A_{80}B_{20}$ with fixed pressure (=5.0 in L-J units). Length scale for diffusivity and viscosity are investigated via finite size effect and wave-vector dependent behaviour. Finite size effect for viscosity shows saturated box length at low temperature, while an unsaturated correlation length from wave-vector behaviour. This indicates a finite length scale for Cooperative Rearrangement Region (CRR) of slow relaxation region, but a diverging length scale for clustering of CRR at low temperature. Length scale from size effect of diffusivity shows similar behaviour with the length scale from wave-vector behaviour of viscosity.

Finite size effect is a powerful tool to detect any process involving cooperative movement or long-range interaction. For any thermally activated process:

$$A = A_0 \exp[E(T)/k_B T] \tag{1}$$

where A can be η or $1/D$, and $E(T)$ is corresponding thermal activation energy. For strong liquid, $E(T)$ is a constant, independent of temperature, while for fragile liquid, $E(T)$ increases with cooling degree increase, indicating growth of activation volume. Thus, in fragile liquid, if the simulated box size is smaller than activation volume, the system will derivate from bulk system. From this we can define a critical box length L_c required as the smallest box length to reach its bulk value. L_c acts as the up limit of correlation length for corresponding activation process.

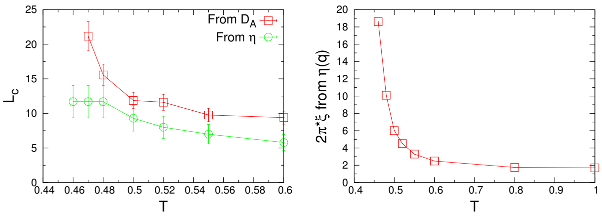

FIG. 1. Left: critical box length extracted from finite size result for diffusivity and viscosity; Right: Correlation length value obtained from q-dependent viscosity.

Left picture in FIG. 1 shows the calculated L_c value for diffusivity and viscosity. There is only slight difference for L_c at small supercooled regime (the onset for breakdown Stokes-Einstein relation is around 0.6), but large difference at highly supercooled regime. The viscosity, which is mainly determined by slow particle's movement, indicates frustrated unit of CRR has a up-limited length size at low temperature.

On the other hand, the length scale for transport coefficients can be investigated by wave-vector dependent behaviour. The q-dependent viscosity is calculated from the transverse current autocorrelation function [1, 2]. Transverse current is defined as: $C_t(q,t) = q^2/N\langle \mathbf{j}_{\vec{q}}^{\perp}(t)\mathbf{j}_{\vec{q}}^{\perp}(0)\rangle$, with $\mathbf{j_q} = \sum_i^N \mathbf{u}_i(t)\exp[-i\mathbf{q}\cdot\mathbf{r}(t)]$. Here, $\perp$ presents wave vector $\vec{q}$ is perpendicular to the velocity $\mathbf{u}$. The generalized viscosity is defined by:

$$\eta(q) = \rho_m k_B T/\tilde{C}_t(q, z = 0) \tag{2}$$

where $\tilde{C}_t(q, z = 0)$ is the Laplace transform of $C_t(q,t)$. In zero-q limit, eq. 2 will give the hydrodynamic value, i.e. $\eta(q \to 0) = \eta_H$, with $\eta_H = V/k_B T \int_0^\infty \langle P_{xy}(t)P_{xy}(0)\rangle dt$. By empirical fitting: $\eta(q) = \eta_H/[1+(\xi q)^2+(\zeta q)^4]$, we can get correlation length for viscosity as $2\pi\xi$. As this length scale is calculated from transverse current, it should coincide with the length scale of transverse wave propagation. In zero-q limit, transverse current decays exponentially as hydrodynamic theory predict. At finite wave vector number, the transverse mode shows negative correlation and damping oscillation as viscous model predict. Thus, there exits a longest wave length which can propagate in the liquid, separating hydrodynamic regime and viscous regime. This longest wave length is a characteristic length scale for supercooled liquid.

Right picture in FiG. 1 shows this calculated length value. At high temperature, the value is in good agreement with finite size result of viscosity, but bifurcates at low temperature. This correlation length indicates a divergence-like behaviour as approaching glass transition temperature. Note the correlation length at lowest temperature is even larger than the box size used to do this calculation. As the argument of frustration [3], this length is not a measure of the size of CRRs, but the clustering of these regions. How these regions aggregate together and influence the diffusivity is still unclear.

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Replica theory analysis of the glass transitions of complicated systems: Network-formers and ellipsoids

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When the crystallization is avoided, the dynamics of liquids slows drastically with decreasing temperature, ending up with the formation of amorphous solids. This glass transition is a highly common phenomenon. Many complicated systems present the glass transition and the associated slow dynamics, everyday examples include window glass, various plastics, optical fibers, etc, which are formed through the glass transitions of molecular liquids, colloidal suspensions, polymeric liquids, and so on.

In experimental studies, the wide varieties of the systems have been studied, and their glass transitions are revealed to have rich phenomenologies [1]. On the other hand in theoretical studies, in order to keep the analysis tractable, the simplified models, such as hard spheres and Lennard-Jones particles, have been focused. An extreme example is the hard spheres in infinite dimensions. Though never exist in reality, this system is the simplest glass former and is playing a great role for the construction of the mean-field theory of the glass transition and the understanding of the universal feature of the glass transition [2].

In this work, we bridge the theoretical and experimental efforts, by extending the microscopic mean-field theory of the glass transition to more complicated systems. In particular we focus on the replica theory [3], that is the theory to calculate the structures and thermodynamics of supercooled liquids and glasses through a replication of systems and liquid state theory calculations of the replicated systems.

Network former.—

Experiments have showed that the increase of the viscosity is strongly dependent on the nature of liquids. The liquids which show a steeper increase of the viscosity are called “fragile”, and the others “strong”. Experimentally liquids tend to become “strong” when the molecules tend to form a network structure in their liquid states, however the theoretical level of understanding on this tendency is still lacking. In this work we apply the replica theory (small cage expansion with the hyper-netted chain theory) to the standard binary mixture of Lennard-Jones particles (BMLJ), and the simple network-forming fluid model (NTW) that was introduced by Coslovich and Pastore [4]. The theory is found to predict that the temperature dependence of the configurational entropy of NTW is much milder than that of usual Lennard-Jones particles. This difference can be mainly attributed to the difference in the temperature dependence of the peak position of the radial distribution function.

Ellipsoids.—

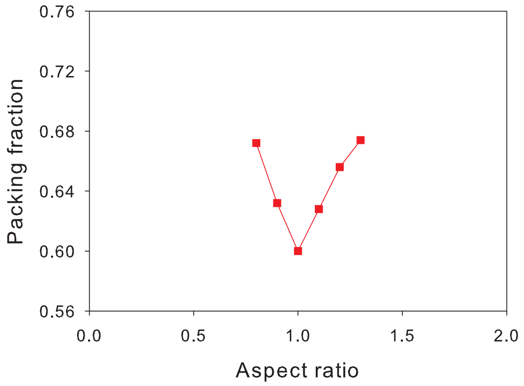

FIG. 1. Dynamical transition density of hard ellipsoids obtained from replicated HNC theory.

To discuss the effect of anisotropy on the glass transition, we develop the replica theory of the glass transition of ellipsoids. A problem for ellipsoids is to include orientational degrees of freedom as well as translational ones. However, this problem can be overcome by using the technique to treat the particle orientation in liquid state theory, that is well developed in the field of molecular liquid state theory [5]. We thus decided to simply apply the scheme of replication to molecular liquid state theory. In practice, we first develop the replicated hypernetted-chain theory [6] of anistropic particles. Fig. 1 shows the dynamic transition density of hard ellipsoids calculated by this theory. The theory reproduces well the fact that the transition density is strongly dependent on the aspect ratio of ellipsoids.

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The Static Lengthscale Characterizing the Glass Transition at Lower Temperatures

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The existence of a static lengthscale that grows in accordance with the dramatic slowing down observed at the glass transition is a subject of intense interest. A recent publication compared two proposals for this length scale, one based on the point-to-set correlation technique and the other on the scale where the lowest eigenvalue of the Hessian matrix becomes sensitive to disorder. The conclusion was that both approaches lead to the same lengthscale, but the former is easier to measure at higher temperatures and the latter at lower temperatures. But even after using both methods together, the range of increase in the observed lengthscales was limited by the relaxation times reachable by standard molecular dynamics techniques (i.e. about 4-5 orders of magnitude). In this lecture I therefore attempt to explore the typical scale at even lower temperatures, testing for this purpose two approaches, one based on the idea of vapor deposition and the other on a swap Monte Carlo technique. I conclude that the first approach does not help in getting to lower temperatures, but the second one does so quite effectively. We can reach a typical lengthscale that grows in accordance with at least 15 orders of magnitude increase in the relaxation time, competing with the best experimental conditions. I will conclude by discussing the relationship between the observed lengthscale and various models of the relaxation time.

Importance of many-body correlations in glass transition: an example from polydisperse hard spheres

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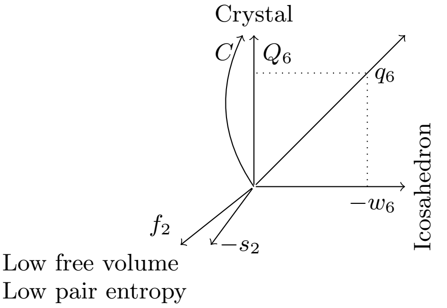

FIG. 1. Schematic order parameter space considered: f_2 and s_2 are two-body, Q_6 and C are many-body sensitive to crystal-like order, w_6 is many-body sensitive to icosahedral order and q_6 is many-boy sensible to both crystal-like and icosahedral orders.

Most of the liquid-state theories, including glass-transition theories, are constructed on the basis of two-body density correlations [1–3]. However, we have recently shown [4–6] that many-body correlations, in particular bond orientational correlations, play a key role in both the glass transition and the crystallization transition.

Here [7] we show, with numerical simulations of supercooled polydisperse hard spheres systems, that the lengthscale associated with any two-point spatial correlation function does not increase toward the glass transition. A growing lengthscale is instead revealed by considering many-body correlation functions, such as correlators of orientational order, which follows the lengthscale of the dynamic heterogeneities. Despite the growing of crystal-like bond orientational order, we reveal that the stability against crystallization with increasing polydispersity is due to an increasing population of icosahedral arrangements of particles. Our results suggest that, for this type of systems, many-body correlations are a manifestation of the link between the vitrification and the crystallization phenomena. Whether a system is vitrified or crystallized can be controlled by the degree of frustration against crystallization, polydispersity in this case.

This study was partly supported by Grants-in-Aid for Scientific Research (S) and Specially Promoted Research from the Japan Society for the Promotion of Science (JSPS) through its "Funding Program for World-Leading Innovative R&D on Science and Technology (FIRST Program)" and a JSPS Postdoctoral Fellowship. ML thank the Region Rhône Alpes and the Programme d'avenir Lyon - Saint Etienne (PALSE NoGELPo) for postoctoral grant.

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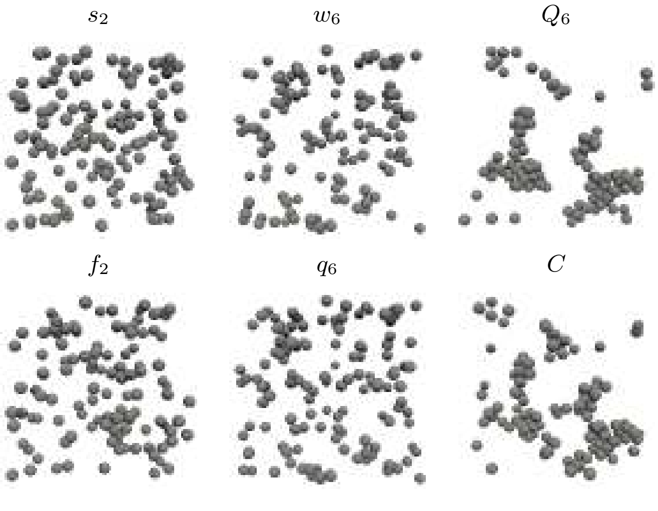

FIG. 2. Visualization of the 10% most ordered particles defined by the various order parameters. All pictures correspond to a thin slice (5σ) of the same configuration at $\beta p\sigma^3 = 23$ and $\Delta = 7\%$. Only Q_6 and C show meaningful spatial fluctuations.

Non-equilibrium Statistical Thermodynamic Theory of Arrested Spinodal Decomposition

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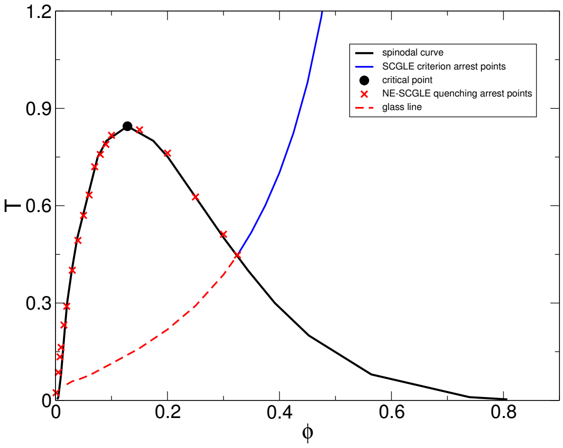

FIG. 1. Equilibrium gas-liquid spinodal line (dark solid curve) in the plane (T^*,ϕ) of the hard-sphere plus attractive Yukawa liquid, calculated from the condition $\mathcal{E}(k=0;\phi,T^*)=0$, with its critical point at $(\phi_c,T_c^*)=(0.13,0.85)$, for the HSAY fluid in Eq. (1) with $z=2$. The blue solid line represents the liquid-glass dynamic arrest line calculated with the *equilibrium* SCGLE theory. According to the *non-equilibrium* SCGLE, this line bifurcates at its intersection with the spinodal curve in a dynamic arrest transition of type B (“×” symbols), which coincides with the spinodal curve, and a glass-glass transition curve of type B (red dashed line).

The Non-equilibrium Self-consistent Generalized Langevin Equation (NE-SCGLE) theory of irreversible relaxation [1] is applied to the description of the non-equilibrium processes involved in the arrested spinodal decomposition of suddenly and deeply quenched simple liquids. This theory predicts that the spinodal curve, besides being the threshold of the thermodynamic stability of homogeneous states, is also the borderline between the regions of ergodic and non-ergodic homogeneous states. Within the non-ergodic region the theory also predicts the existence of a glass-glass transition line buried in the deep-quench regime.

Let us start having in mind a simple liquid whose particles interact through the hard-sphere plus attractive Yukawa (HSAY) potential thus reads

$$u(r)=\begin{cases}\infty, & r<\sigma;\\ -\epsilon\frac{\exp[-z(r/\sigma-1)]}{(r/\sigma)}, & r>\sigma.\end{cases}\qquad(1)$$

For fixed z the state space of this system is spanned by the hard-sphere volume fraction $\phi\equiv\pi n\sigma^3/6$ and by $T^*\equiv k_BT/\epsilon$, the thermal energy in units of the depth of the attractive Yukawa well. In Fig. 1 we present the gas-liquid spinodal line of this system in the state space (ϕ,T^*), defined by the condition $\mathcal{E}(k=0;\phi,T^*)=0$, where $\overline{n}\mathcal{E}(k;\phi,T^*)\equiv 1-\overline{n}c(k;\phi,T^*)$, with $c(k;\phi,T^*)$ being the Fourier transform of the direct correlation function, approximated by the approximate prescription proposed by Sharma and Sharma [2],

Outside the spinodal we determine the liquid-glass transition (blue dots) using the bifurcation equation of the *equilibrium* SCGLE theory [3]. Inside the spinodal we determine the isochoric evolution of the non-stationary static structure factor $S(k;t)$ from its initial equilibrium value $S^{(i)}(k)\equiv\overline{n}\mathcal{E}(k;\phi,T_i^*)$, after the system was instantaneous quenched at $t=0$ to a lower final temperature T_f^*, as prescribed by the NE-SCGLE theory [1], namely, as $S(k;t)=S^*(k;u(t))$, with $u(t)$ being the so-called “internal time” (defined in Ref. [1]), and with the function $S^*(k;u)$ defined as $S^*(k;u)=[\overline{n}\mathcal{E}^{(f)}(k)]^{-1}+\left\{S^{(i)}(k)-[\overline{n}\mathcal{E}^{(f)}(k)]^{-1}\right\}e^{-\alpha(k)u}$. We then input $S^*(k;u)$ in the non-equilibrium bifurcation equation, whose solution for the corresponding squared localization length $\gamma^*(u)$, in principle for $0\leq u\leq\infty$, allows us to monitor the emergence of dynamic arrest during the irreversible isochoric process that follows the instantaneous quench.

The scenario that results from these calculations is represented by the (red) × symbols and dashed line in the figure. The × symbols correspond to a type A transition from the equilibrium liquid region to a (“loose”) glass state, which for a shallow quench will be unable to interfere with the process of classical gas-liquid phase separation, but which for deeper quenches give rise to arrested spinodal decomposition. The red dashed line indicates a type B glass-glass transition from these “loose” glass states to “tight” glassy states, and is the continuation inside the spinodal of the “ordinary” liquid-glass transition located outside the spinodal. We shall describe additional details of this predicted scenario, such as its dependence on the specific form of the potential or on the width of the attractions.

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Tuning of Pairwise Potential Can Control the Fragility of Glass-Forming Liquids: From Tetrahedral Network to Isotropic Soft Sphere Models

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Supercooled liquids show dramatic slowdown of dynamics when they approach the glass transition temperature. According to the concept of the *fragility* [1], the supercooled liquids are classified into two types. One is *strong* glass-forming liquids whose transport coefficients and relaxation times obey simple Arrhenius law. The other is *fragile* glass-forming liquids which show super-Arrhenius behavior. Although it is widely believed that the fragility is a central concept in the study of the supercooled liquids and the glass transition, microscopic origin of the fragility still remains elusive. Computer simulation is an useful tool to investigate such problem since microscopic information is easily accessible. Binary soft-sphere potential mixtures are widely used as a representative model for the fragile glass-forming liquids. On the other side, network-forming models such as the Beest-Kramer-van Santen (BKS) model are often used as a model for the strong glass-forming liquids. These two representative models have been studied rather independently. Constructing a model whose fragility is controlled from the strong to the fragile can be a promising strategy to understand the microscopic origin of the fragility.

In this study, we bridge the gap between the models of the strong and the fragile glass forming liquids by tuning pairwise potential of a tetrahedral network (NTW) model [2]. The model in Ref. [2] is a non-additive binary mixture using the soft-sphere potential for the interaction between same species and the Lenard-Jones potential for the one between different species. We introduce a new parameter, the depth of well, Δ into the Lenard-Jones potential between different species,

$$v_{\alpha\beta}(r) = 24\epsilon\left[\left(\frac{\sigma_{\alpha\beta}}{r}\right)^{12} - \sqrt{\Delta/6}\left(\frac{\sigma_{\alpha\beta}}{r}\right)^{6}\right] \quad (\alpha \neq \beta),$$

where $\alpha, \beta \in \{1, 2\}$. When $\Delta = 6$, the original NTW model is reproduced [2]. When $\Delta = 0$, the model has only the soft-sphere repulsive interaction. We use NVE molecular dynamics simulation to study static and dynamic properties of the model for different Δ.

We confirm that the tetrahedral network structure shown in $\Delta = 6$ is gradually broken and becomes more isotropic with decreasing the Δ through analyzing the radial distribution functions and the coordination numbers. Especially, the coordination number for different species, $Z_{12} \simeq 4$ which is an signal of the tetrahedral structure increases up to $Z_{12} \simeq 9$ when $\Delta \to 0$. The structural relaxation time, τ_α of the model is defined by $F_s(k, \tau_\alpha) = 1/e$, where $F_s(k, t)$ is the self intermediate scattering function. We show the Arrhenius plot for different Δ in FIG. 1. We normalize the temperature by T_0 which is an fitting parameter of the Vogel-Fulcher-Tamman (VFT) low, $\tau_\alpha \propto \exp[1/K(T/T_0 - 1)]$. We find that the Arrhenius behavior shown in $\Delta = 6$ becomes super-Arrhenius with decreasing the Δ. Another parameter, K which quantifies the fragility is obtained for each Δ. We find that the K increases from $K \sim 0.1$ ($\Delta = 6$) up to $K \sim 0.4$ ($\Delta \to 0$). Therefore, we can control the fragility using single parameter, the Δ in the pairwise potential.

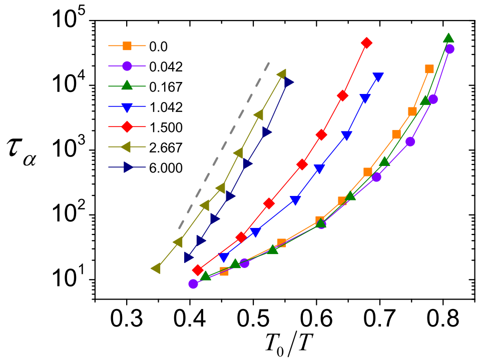

FIG. 1. The Arrhenius plot normalized by the T_0 for different Δ. The grey dashed line is plotted to see the Arrhenius temperature dependence.

In summary, we modified the model in Ref. [2] and bridged the gap between a tetrahedral network model and an isotropic soft-sphere potential model by tuning the pairwise interaction potential. We found that microscopic structure and the fragility are closely related to each other. This model can be a useful tool for further investigation of microscopic origin of the fragility.

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Hopping and dynamical phase coexistence in supercooled liquids

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A controversial hypotheses for explaining the heterogeneous dynamics of molecular and colloidal glasses postulates the temporary coexistence of two phases. In this scenario, two phases with different dynamical features coexist for a time of the order of the relaxation time, and mix afterwards. The validation of this scenario requires the identification of a dynamical order parameter whose distribution acquires a transient bimodal shape. Unfortunately, this dynamical order parameter has not been identified so far. Indeed, it is customary to identify the dynamical phases heuristically, e.g. introducing a threshold on the van Hove distribution to define the 'slow' and the 'fast' particles [1]. An order parameter with a bimodal shape has only been identified in structural glasses driven out of thermal equilibrium introducing a field pinning some of the particles [2], and thus inducing the two phases, or more complex dynamical constraints [3].

Here we provide the first direct observation of the dynamical coexistence of two phases with different diffusion coefficients in equilibrium structural glasses, by showing that in the deeply supercooled regime the distribution of the single particle diffusivities acquires a transient bimodal shape [4]. We obtain this result by quantitatively validating the continuous time random walk [5, 6] (CTRW) description of particle motion against simulations of different model systems, including the Kob–Andersen mixture, a mixture of harmonic spheres, and Kob–Andersen lattice gas lattice model. The validity of the CTRW approach allows to measure the diffusion coefficient of each particle, that in this framework is simply proportional to the number of its 'jumps'.

As illustrated in Fig. 1, the time evolution of the single particle diffusion coefficient depends qualitatively on the temperature. In particular, at low temperature the diffusivity distribution acquires a transient bimodal shape before attaining its expected log–time Gaussian shape. This proves the temporary coexistence of particles with different diffusivities. We relate this distribution to the heterogeneity of the dynamics, by showing that at long times its the variance to mean ratio is fixed by the Stokes-Einstein ratio.

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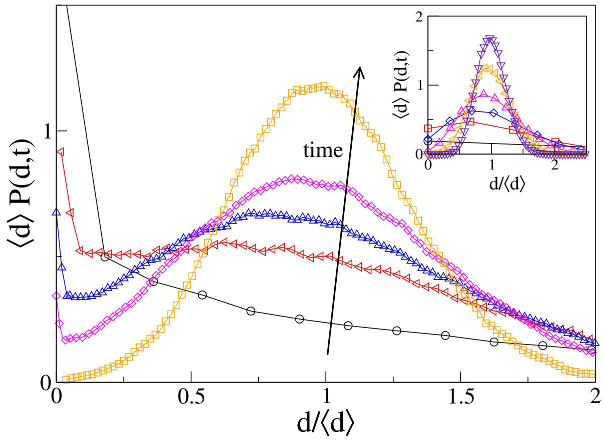

FIG. 1. Probability distribution of the single particle diffusion coefficient at different time, rescaled by the average diffusivity, at $T = 0.6$ (inset) and at $T = 0.45$ (main panel). At low temperature, the distribution acquires a temporary bimodal shape. All data refer to species a of the 80:20 (a:b) KA LJ mixture.

Glass formation and local quasicrystal order in dense liquids with repulsive two length scales potential

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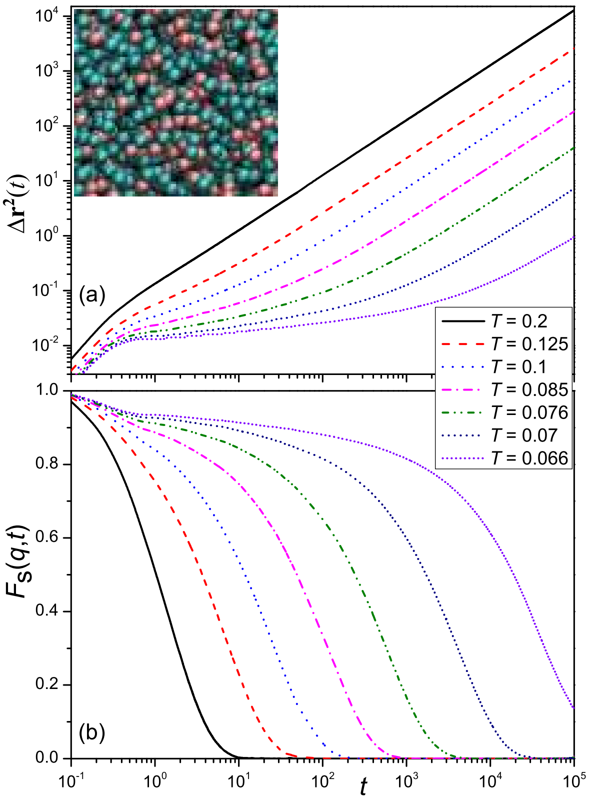

FIG. 1. (a) Mean-square displacement, and (b) Intermediate scattering function showing the glassy behaviour. Inset shows the snapshots. We mark by red (blue) color particles that have a neighbor at distance of the order of the first (second) maximum in rdf.

We investigate glassy dynamical properties and local order of one component three-dimensional system of particles interacting via pair repulsive potential by the molecular dynamic simulation in the wide region of densities, see Fig. 1. We find the glass state and show that it is superfragile and has high glassforming ability. The glass transition temperature T_g has pronounced minimum at densities where the frustration is maximal [1].

It is shown that the same system can be driven to three-dimensional quasicrystalline state rather than to liquid, glass or "ordinary" crystal, see Fig. 2. Note that this is so for *purely repulsive*, isotropic and monotonic interaction pair potential. Molecular dynamic simulations show at certain density-temperature domain the phase with three-dimensional decagonal quasicrystalline order at both the local and the medium scales. It is self-assembled from liquid through the first order phase transition. We suggest that the underlined mechanism of decagonal order formation is the stabilization of large icosahedral-like clusters due to the existence of two effective interparticle distances [2].

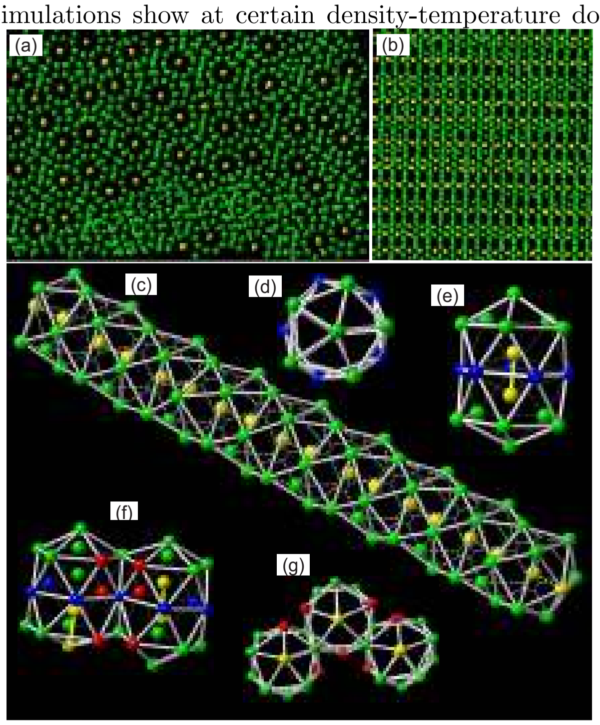

FIG. 2. (a)-(b) Typical snapshots of the particle system demonstrating decagonal order. (c): Decagonal tube; (d,e) The structure of the double icosahedron — the building block of the decagonal tubes. Particles belonging to common face are colored blue. (f,g): Junction mechanism of decagonal tubes. The red particles as well as yellow ones are short-bonded.

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Ultrasoft systems and the hard-sphere dynamic universality class

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The set of soft-sphere systems whose dynamic parameters, such as the α-relaxation time and the long-time self-diffusion coefficient, depend on the density n, the temperature T, and the softness (characterized by some softness parameter ν) only through an effective hard-sphere volume fraction $\phi_{HS} = \phi_{HS}(n, T, \nu)$, is referred to as the hard-sphere dynamic universality class. This concept derives from the structural equivalence established by Andersen, Weeks, and Chandler, between soft-sphere fluids and the hard-sphere liquid, complemented by its recently-proposed dynamic extension [1]. In recent work [2] this concept has been discussed in the context of systems formed by particles interacting with short- and long-ranged, but purely repulsive pair potentials $u(r)$ that diverge at $r = 0$, thus excluding fluid systems formed by ultrasoft particles that allow full overlap between particles (the conceptual opposite of the hard sphere liquid). An open question is then to what extent liquids of ultrasoft particles might or might not exhibit the structural and dynamical behavior characteristic of the hard-sphere dynamic universality class.

Ultrasoft systems display anomalous behavior in the static and dynamic properties in both the liquid and solid phases, mainly due to the facility of the particles to overlap. A simple example that exhibits the typical features of repulsive ultrasoft interactions is the Gaussian core model (GCM), whose pairwise interaction is bounded. Despite its anomalous behavior, we show in this work that the GCM exhibits the characteristic structure and dynamics of hard-sphere fluids for a wide range of conditions, even in the regime of high densities.

Our work is based on the methodology presented in Refs.[1–4], where it is demonstrated that the structural information contained in the static structure factor function, $S(k)$, can be used to identify a structurally equivalent hard-sphere system. For a GCM system at the state point (n^*, T^*), the effective ϕ_{HS} is obtained from the equal-height condition between the main peak of $S(k)$ of the GCM and HS systems; the effective size of the hard particles is then determined from the scaling factor that leads the two peaks to the same position. This procedure is illustrated in Fig.1(a) for a GCM simulated at the state point $(n^* = 0.1, T^* = 0.01)$, to which corresponds the HS system with $\phi_{HS} = 0.392$ and $\sigma_{HS} = 2.02$. We have extended this study for several state points where we simulated static structural and dynamics properties, and determined the functions $\phi_{HS} = \phi_{HS}(n^*, T^*)$, $\sigma_{HS} = \sigma_{HS}(n^*, T^*)$ and $n_{HS} = n_{HS}(n^*, T^*)$.

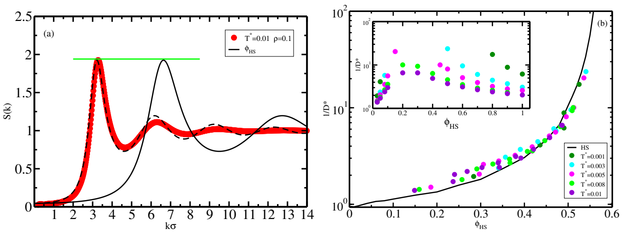

FIG. 1. Static structure factor $S(k)$ determined by Brownian dynamics simulations (symbols) for the GCM at the state point $(n^* = 0.1, T^* = 0.01)$. The solid line corresponds to the Percus-Yevick Velet-Weis correction for the HS system at the effective volume fraction $\phi_{HS} = 0.373$ that matches the first peak of the $S(k)$. b) Inverse of D^* for several temperatures as a function of ϕ_{HS}

To illustrate the scaling of the dynamic properties, in Fig. 1(b) we plot the results for the scaled long-time diffusion coefficient $D^* = D_L/D_0$ for several conditions. The inset displays $1/D^*$ in the natural units of the simulation, illustrating the anomalous behavior of the diffusion coefficient as a function of the density. In the main panel, on the other hand, the data are presented in units of the equivalent hard-sphere systems (in such units, ultrasoft and hard isostructural systems should display the same dynamics, see References.) In this last format we observe that $1/D^*$ first increases with ϕ_{HS} (up to $\phi_{HS} \approx 0.54$) and then loop back, decreasing with ϕ_{HS}. Thus, although the anomalous dynamics is still present in the new units, the transformed data collapses rather well onto the master curve for HS systems (represented by the solid line).

In this work we present further results for the structure and dynamics of equivalent GCM and HS systems, illustrating interesting trends (for instance, we find that σ_{HS} is closely related to the mean distance between particles for a wide range of conditions). As a main contribution, however, it is found that isostructural GCM and HS systems follow basically the same dynamics.

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Anisotropic Stress Correlations in Simple Liquids

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Why the viscosity of a liquid increases so rapidly with decreasing temperature over a relatively small temperature range above the glass transition is one of the major mysteries discussed for a long time. Because viscosity is given in the Green-Kubo equation in terms of the shear stress correlation function, in order to resolve this mystery is it useful to understand the nature and origin of the stress correlations in the liquid.

We have shown earlier that the macroscopic stress can be decomposed into the atomic-level stresses, and the spatial and temporal correlations among the atomic-level stresses determine viscosity [1]. Here we show that the correlation is spatially anisotropic, and follows the symmetry of the Eshelby field created in an elastic body by an insertion which does not fit the hole in which the body is inserted, as shown in Fig. 1. The correlation function oscillates as a function of the distance, r, reflecting the oscillations in the pair-density function (PDF). The Eshelby field decays as $1/r^2$, however, the amplitude of the oscillating correlation function follows the form, $|A(r)| = C/r^2 \exp(-r/\xi)$ where ξ is the screening length. ξ depends on temperature through the power law, $xi(T) = \frac{D}{(T-T^*)^\alpha}$ where T^* is close to the glass transition temperature, $T_g(= 0.4)$, and $\alpha = 0.72$ for a 2D liquid as shown in Fig. 2. The divergence of ξ near T_g is in agreement with the recent calculation which showed that the Eshelby field is unscreened just above T_g [2]. On the other hand the temperature dependence of ξ suggests the presence of medium-range order consistent with the dynamic heterogeneity. We discuss the nature of such order in terms of the *l*=2 and 4 bond orientational correlation and the interaction between the elementary excitations in the liquid [3].

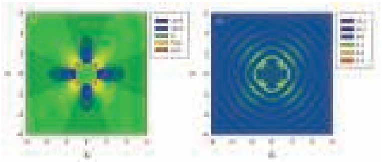

FIG. 1. (a) The x-y shear Eshelby field for an elliptical inclusion, and (b) σ^{xy}-σ^{xy} atomic-level stress correlation in 2D liquid with Yukawa potential. The results for 3D liquid also show the same symmetry as the 3D Eshelby field.

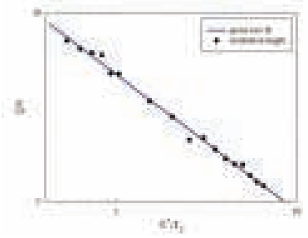

FIG. 2. Temperature dependence of the screening length ξ, following $\xi(T) = D/(T - T^*)^\alpha$ (solid line).

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Effect of size polydispersity on a Roskilde-simple liquid

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Polydisperse fluids are ubiquitous in both biological and industrial processes [1]. Examples of polydisperse systems are: plastic materials, liquid foams, asphalt, micelles, and more. The property that typically varies among the constituent molecules is their charge, mass, and size. The fluids' dispersity naturally induces a rich phenemenology not encountered in their single-component counterparts. As a consequence, polydisperse fluids have been the focus of a number of studies both theoretically [2–4] and via computer simulations [5–7], as well as, in experiments [8, 9].

The former investigations revealed, for instance, that polydisperse fluids exhibit a very rich phase diagram with shifts in critical point and freezing temperatures, as well as, many-solid/fluid coexistence regions. Figure 1 shows the effect that size polydispersity has on the structure of the Lennard-Jones (LJ) liquid.

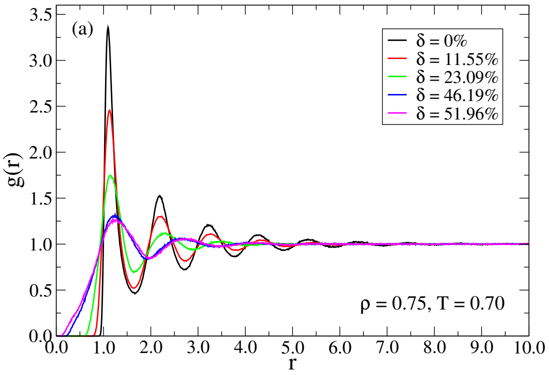

FIG. 1. Effect of size polydispersity (degree of polydisp. is δ) on the structure of the LJ liquid in two dimensions.

We study the effect of size polydispersity on a Roskilde-simple liquid [10, 11] in both two and three dimensions. The class of Roskilde-simple liquids includes most or all van der Waals and metallic liquids, but excludes most or all covalently, hydrogen-bonding, strongly ionic or dipolar liquids. In simulations of model liquids; the LJ liquid, among many others, is identified to belong to the class of Roskilde-simple liquids.

We find in the current study that the polydisperse LJ liquid is a Roskilde-simple liquid, even for very high polydispersities (more than 40% polydispersity), and as a consequence has good isomorphs. Isomorphs are curves in the phase diagram of a Roskilde-simple liquid along which structure, dynamics, and some thermodynamics quantities are invariant in dimensionless units [12]. An isomorph is shown in Fig. 2 for a moderately polydisperse LJ liquid. An excellent invariance is seen along the isomorph whereas no collapse is seen for an isotherm with the same density increase (not shown).

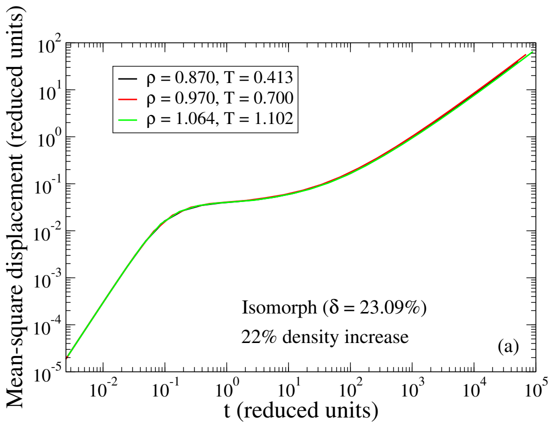

FIG. 2. MSDs for the polydisperse LJ liquid (polydispersity $\delta = 23.09\%$) along an isomorph in three dimensions. Invariance is seen along the isomorph, but not along an isotherm with the same density increase (not shown).

We conclude that the theory of isomorphs is not limited to few-component systems [10–12]. The theory can, in fact, be applied to improve the understanding even further of many realistic systems of both theoretical and industrial interest. The latter such systems are often moderately to highly polydisperse.

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Exact solution of hard spheres dynamics in high dimension

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Glass is made cooling a liquid down to some transition temperature where a dynamical arrest of particles motion occurs. This is due to a dramatic viscosity increase, related to a similar increase of a relaxation time τ_α of the correlations of the system. The hallmark of this dynamics is the emergence of a plateau of duration τ_α on mean square displacements (MSD) of the particles. When the dynamical transition temperature T_D is reached, $\tau_\alpha \to \infty$ and the system becomes stuck in an amorphous state. Unfortunately, in spite of considerable experimental, numerical and theoretical efforts, a theory of this transition from first principles is still lacking. The mode coupling theory (MCT) is one such example, but relies on an approximation which cannot be refined systematically.

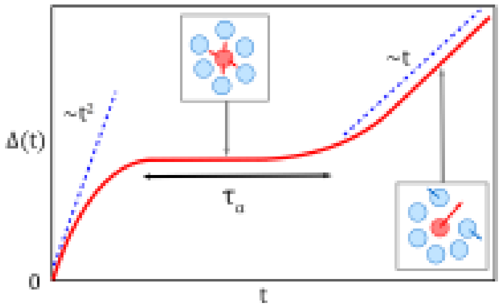

FIG. 1. Mean square displacement of a particle

Recently, breakthroughs about the thermodynamics of hard spheres glasses in infinite spatial dimensions have been obtained [1] and applied to the jamming transition, deep in the glass phase, through replica techniques, as was done for spin glasses 30 years ago. The aim of the present work is to build the dynamical aspect of the problem, needed to understand purely dynamical phenomena such as the increase of viscosity. An exact solution in $d \to \infty$ would be a basis to understand $d = 3$ glasses. Besides, qualitative but also quantitative agreement with $d = 3$ glasses is expected for several key quantities, as a weak dependence upon dimension is seen in simulations [3].

The formulation of the dynamics is guided by the statics results. Starting from an assembly of N hard spheres in the limit $d \to \infty$ or from the Mari-Kurchan (MK) model [2], in which the distance between two hard spheres is submitted to a random shift playing the role of a quenched disorder, we can derive the entropy $\mathcal{S}_\mathrm{stat}$ of the system. This is achieved by the introduction of n replicas of the system and the use of the symmetries of the liquid phase, allowing the expression of $\mathcal{S}_\mathrm{stat}$ in terms of an *order parameter* $\Delta_{ab} = \langle (x_a - x_b)^2 \rangle$ which can be viewed as a MSD between replicas. In both models the same entropy is found, confirming that MK coincides with hard spheres in infinite dimension. Specializing Δ to a Parisi ansatz we recover the entropy of the liquid and replica symmetry breaking glass phases. But if we do not resort to such an ansatz we can use the correspondence between the replica treatment and the dynamical formalism in supersymmetric notation as a guide for the dynamics.

Indeed, we describe the dynamics by a Langevin equation such as :

$$\gamma \dot{x}_i = -\sum_{j \neq i} \nabla V(x_i - x_j) + \zeta_i \tag{1}$$

with thermal noise ζ_i. This can be mapped to a path integral in terms of the trajectories of the particles, giving a generating functional :

$$e^{N\mathcal{S}_\mathrm{dyn}} = \int \mathrm{D}[x_i(t)] e^{\mathcal{A}[\{x_i(t)\}]} \tag{2}$$

From there we can proceed by analogy with the entropy $\mathcal{S}_\mathrm{stat}$ of the statics, and express $\mathcal{S}_\mathrm{dyn}$ in terms of the MSD

$$\Delta(t,t') = \langle [x(t) - x(t')]^2 \rangle \tag{3}$$

The $d \to \infty$ limit is exploited to get a saddle point equation on Δ. Restricting ourselves to equilibrium dynamics we get a single MCT like equation :

$$\ddot{\Delta} + \Omega\Delta + \int_{t_0}^{t} \mathrm{d}u K_\Delta(t-u)\dot{\Delta}(u) = 0 \tag{4}$$

The kernel K_Δ can be interpreted as a difference of correlation functions of two effective 1D one particle Langevin process (non Markovian, with coloured noise), one with potential V and one with pure diffusion :

$$\int_{t_0}^{t} \mathrm{d}u \Gamma_\Delta(t-u)\dot{r}(u) = -\begin{cases} V'(r(t)) \\ 0 \end{cases} + \eta_\Delta(t) \tag{5}$$

The exact computation of K_Δ will answer the question of whether MCT is the right theory in infinite dimension, in which this kernel is approximated. Then, solving the equation for $\Delta(t-t')$, we can get the value of the dynamical plateau Δ_EA and the exponents at T_D (or equivalently packing fraction ϕ_D for hard spheres) e.g. the divergence of τ_α.

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Probing cooperative liquid dynamics with the mean square displacement

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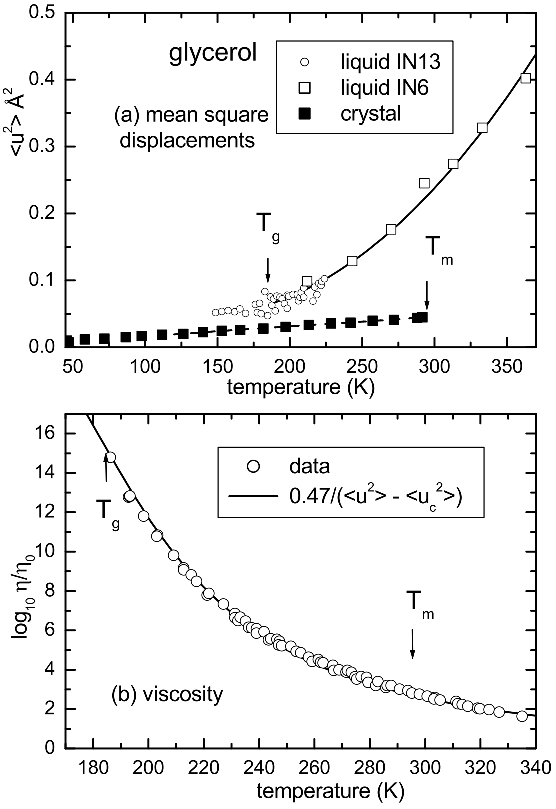

FIG. 1. (a) The mean square displacements in crystalline [5] and liquid [6, 7] glycerol. The lines are the corresponding fits. (b) Proportionality of the logarithm of the viscosity [8] η/η_0 with $\eta_0 = 1.6$ mPas to the inverse difference between liquid and crystalline mean square displacements (the continuous line).

If one models the flow in terms of a thermally activated process, one has to postulate a flow barrier which increases drastically with decreasing temperature. According to one school of thinking [1], this drastic increase is due to the anharmonicity, while others [2, 3] argue that it is due to the Adam-Gibbs mechanism of an increasing cooperatively rearranging region.

One can decide this question [4] by looking at the picosecond mean square displacements of neutron experiments. Fig. 1 (a) shows the mean square displacements $\langle u_c^2\rangle$ of crystalline [5] and $\langle u^2\rangle$ of liquid glycerol [6, 7]. As in earlier work in selenium [9], one finds the relation (see Fig. 1 (b))

$$\ln \frac{\eta}{\eta_0} = \frac{u_0^2}{\langle u^2\rangle - \langle u_c^2\rangle} \tag{1}$$

which describes the viscosity η in terms of the two parameters $u_0 = 1.0$ $\mathring{A}$ and $\eta_0 = 1.6$ mPas. It holds over thirteen decades of viscosity variation, from T_g up to a temperature high above the melting temperature, providing a much better fit of the viscosity than any Vogel-Fulcher law. Note that a linearization of both $\langle u^2\rangle$ and $\langle u_c^2\rangle$ around T_g converts this relation into the Vogel-Fulcher law $\log \eta/\eta_0 \propto 1/(T - T_0)$, thus identifying the Vogel-Fulcher temperature T_0 with the point where the extrapolated mean square displacement of the liquid reaches the crystalline one. The fit parameter η_0 has the value which one expects for a gas of noninteracting glycerol molecules at the liquid density. The parameter u_0 measures the thermal vibration amplitude which has to be reached to make the influence of the interatomic potential negligible. This provides the Vogel-Fulcher law with two parameters which have a well-defined physical meaning.

The good agreement suggests that the number of atoms in a cooperatively rearranging region, which according to Adam and Gibbs is inversely proportional to the structural entropy difference between liquid and crystal, is also inversely proportional to the mean square displacement difference between liquid and crystal. Together with a proportionality of the flow barrier to the anharmonicity coefficient $I_{anh} = \partial \ln \langle u^2\rangle/\partial \ln T - 1$, one obtains eq. (1).

The equation provides excellent fits of the viscosity in glycerol and selenium. In both cases, about half of the fragility is due to the cooperativity and the other half to the anharmonicity, a result which reconciles the two traditional views [1–3].

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Quantum effects in glass transition

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Glass transition is usually considered to be a high temperature phenomenon when cooling a liquid without crystallization below melting temperature T_m leads to formation of a solid glassy state at the glass transition temperature T_g. In contrast, quantum phenomena are believed to play an important role only at very low temperatures, and are known to affect significantly properties of glasses at temperatures below 10K . We show that quantum tunneling effects can broaden significantly the glass transition range in low-temperature glass-formers by decreasing the ratio T_g/T_m from its well known classical value 2/3 [1]. They can lead also to an unusual temperature dependence of the viscosity or structural relaxation time of supercooled liquids: decrease in apparent activation energy (defined as the slope of $\log\tau$ vs $1/T$) with decreasing T close to T_g. This trend is opposite to the usual behavior of the relaxation time in glass forming liquids where the apparent activation energy increases upon cooling. In some cases quantum effects may lead to unusually low fragility. We analyze the dielectric data for structural relaxation of deeply supercooled normal and heavy water and show that both low fragility (14) of water at T_g =136K and high isotope shift of T_g (8K) can be explained by quantum effects [2].

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Observable-dependence of the effective temperature in off-equilibrium diatomic molecular liquids

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When a liquid is brought off-equilibrium, e.g., by quickly lowering the bath temperature T, dynamic properties depend on the waiting time t' , i.e., the system ages. At present a unified thermodynamic approach capable of describing this out-of-equilibrium condition is still lacking. However it has been proposed that by adding as state variables one or more effective temperatures T_{eff} related to the slow modes of the system one could efficiently characterize the aging system [1]. In this theoretical framework the presence of additional temperatures can be revealed by making use of an out-of-equilibrium generalization of the fluctuation-dissipation theorem (FDT). Being t the observation time, it is possible to define a correlation function $C_{A,B}(t,t')$ between the observables A, B and a response function $\chi_{A,B}(t,t')$ of the observable A in respect to a perturbation on the observable B. The FDT out-of-equilibrium is generalized with:

$$\frac{\partial C_{A,B}(t,t')}{\partial t'} = -\frac{T}{X_{A,B}(t,t')}\frac{\partial \chi_{A,B}(t,t')}{\partial t'} \qquad (1)$$

Here a fluctuation-dissipation (FD) ratio $X_{A,B}(t,t')$ is introduced in order to account for the presence of an additional temperature. The (FD) ratio is $|X_{A,B}(t,t')| = 1$ for short times $(t-t')/t' \ll 1$ and $|X_{A,B}(t,t')| = T/T_{eff}(t,t')$ at long times $(t-t')/t' \gg 1$. The hypothesis of one single T_{eff} appears to be particularly appropriate in some classes of systems as for instance weak glass formers [2]. We remark that if T_{eff} can be interpreted as a genuine thermodynamic parameter, it should coincide when measured in coupling with different observables on the same timescale.

In this contribution [3], we study the observable-dependence of T_{eff} , by measuring intrinsically different observables in a system of homonuclear dumbbell molecules out-of-equilibrium respectively related to translational (self-density) and rotational (angular orientation) degrees of freedom. We show that various scenarios can occur as a function of the molecule elongation ζ and that distinct observables can be found in distinct aging conditions during the same temperature quench. This results in a partial decoupling of the translational and rotational degrees of freedom and hence in dissimilar FD ratios.

We perform Metropolis Monte Carlo (MC) simulations of a binary mixture $80:20$ of $N = 500$ homonuclear dumbbell molecules interacting via a LJ potential using the Kob-Andersen parameters. We analyse systems at different ζ in order to characterize the dependence of T_{eff} on the different degrees of freedom.

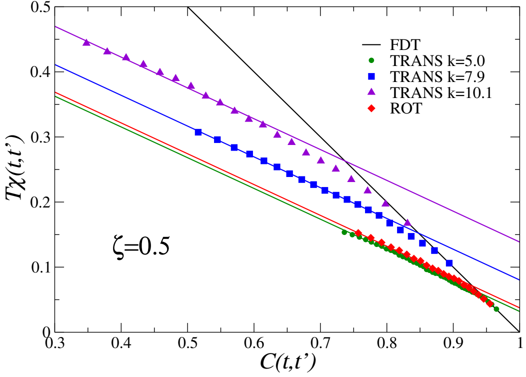

FIG. 1. Self-density FD-plots for wave vectors $\|\mathbf{k}\| = 10.1$ (violet up triangles), $\|\mathbf{k}\| = 7.9$ (blue squares), $\|\mathbf{k}\| = 5.0$ (green circles), together with the angular orientation FD-plot (red diamonds) for elongation $\zeta = 0.5$.

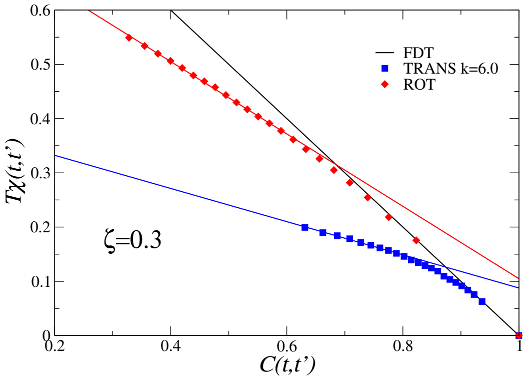

FIG. 2. Self-density FD-plots for wave vectors $\|\mathbf{k}\| = 6.0$ (blue squares) and angular orientation FD-plot (red diamonds) for elongation $\zeta = 0.3$.

In particular we find that at high elongations T_{eff} coincides for the two observables (see fig.1, same FD-ratio). Differently, at low elongations and shallow quenches, the weak coupling between translational and rotational variables results in a breakdown of the description in terms of one single T_{eff} (see fig.2, dissimilar FD-ratio). We show that only for very deep quenches we recover a unique T_{eff} scenario for the two observables.

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Structure of marginally jammed polydisperse packings of frictionless spheres

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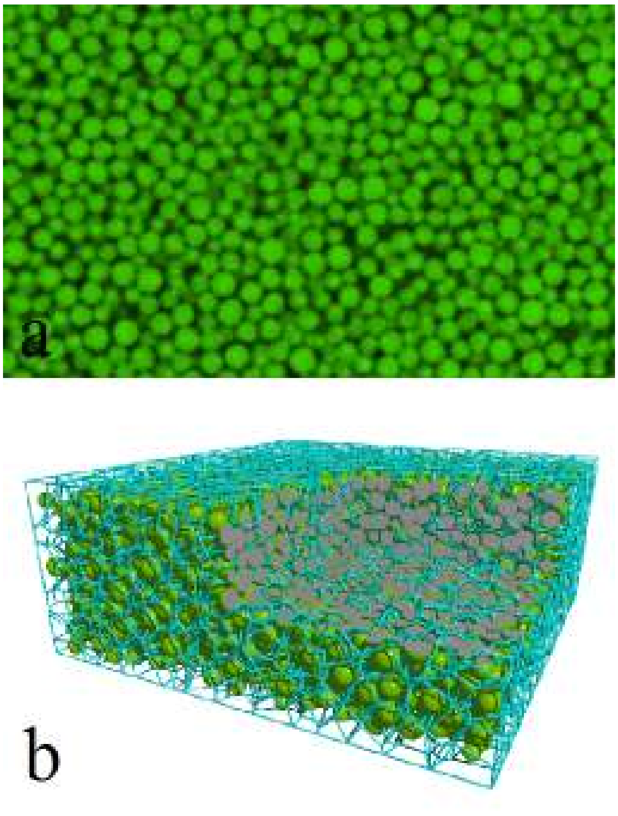

FIG. 1. Three-dimensional imaging of jammed emulsions droplets with an average droplet radius $\bar{a}$ =1.05μm. (a) Raw image of a plane in the bulk of the sample obtained by laser scanning confocal microscopy of light emitted by the fluorescent dye Nile-red at $\lambda = 595$nm. The droplets are marginally jammed and the volume fraction is $\phi \simeq 0.646 \pm 0.014$. (b) Three-dimensional reconstruction of the droplet positions using the sphere matching method (SMM). The lines show the Voronoi radical tessellation around the droplet centroids. The total dimensions are 51.2μm×51.2μm×20.1μm. One corner is cut out to reveal the internal structure of the jammed system.

We model the packing structure of a marginally jammed bulk ensemble of polydisperse spheres. To this end we expand on the granocentric model [Clusel et al., Nature **460**, 611 (2009)] explicitly taking into account rattlers, rather than considering only particles in contact. Then we consider the influence of size correlations[1] between particles and their shell, previously neglected [2]. Next we address the distribution $G_s(s)$ of surface-to-surface separations $s = r - 2a$. We can use the scaling of the excess number of contacts $\Delta Z \sim \sqrt{\bar{Z}_J - 6}$ to derive $G_{sJ}(s) \sim s^{-1/2}$ [3]. For the rattlers we take the simple *ad-hoc* assumption that their neighbors are distributed uniformly $G_{sR} = const.$

The eGCM can be evaluated numerically and we can obtain statistical information directly from the model. We compare the model predictions with experiments on micron scale emulsion droplets under marginal jamming conditions. High resolution images (Figure 1) of the individual droplet positions are obtained using 3D laser scanning confocal microscopy (A1R, Nikon, Japan). 3D-images of size $512 \times 512 \times 201$ pixels are recorded with a resolution of 100nm/pixel in all spatial directions. To track the position of the polydisperse droplets we implement the sphere matching methods (SMM) algorithm. A Voronoi radical tessellation is applied and particles with adjacent cell walls are identified as neighbors.

From an extensive comparison with experimental data and packing simulations, we demonstrate that our extended granocentric approach can deliver accurate predictions for a bulk ensemble of marginally jammed particles covering the full range of polydispersities of practical interest. The observed quantitative agreement opens the path towards a full structural characterization of jammed particle systems for imaging and scattering experiments.

CZ and FS acknowledge financial support by the Swiss National Science Foundation (Project No. 149867). EIC acknowledges the support of the NSF under CAREER Award No. DMR-1255370. M.M. and C.O. acknowledge financial support from the Science Foundation Ireland, grant no. 11/RFP/MTR/3135.

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Colloidal particles interactions near a critical point

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We present a direct measurement of the interaction force of two colloidal particles immersed in a binary mixture close to its critical temperature. A binary mixture at critical concentration is a particular case of systems with a second order phase transition. When the temperature of the system approaches the critical temperature, T_c, the correlation lenght of its thermal fluctuations diverges, $\xi = \xi_0 \epsilon^{-\nu}$, where $\epsilon = (T_c - T)/T_c$ is called the reduced temperature and ξ_0 is its characteristic lenght . The exponent ν is the universal exponent associated to the transition. If the fluctuating field is confined, the system will present the so called critical Casimir force between the walls which confine the mixture. In the case of two walls of surface S at distance d, the critical Casimir force (F_{cas}) reads as follows:

$$\frac{F_{\text{cas}}}{kT} = \frac{S}{d^3}\theta(d/\xi) \tag{1}$$

where kT is the thermal energy and $\theta(d/\xi)$ is the universal scaling function. Critical Casimir forces present a great interest in the nanotechnology area due to its long-range nature, as well as the possibility to be switch on-off in a simple way. A small change in the temperature of the system will power those forces. In the last decade, the experimental study of such a kind of systems has increased exponentially due to the possibility to obtain quantitative measurements in the phenomena scale. The possibility to explore those fluctuating fields locally, to manage nanometric systems and to detect femtoNewton forces allows the first direct observation of these forces only few years ago by Hertlein et al.

In our case, we confine the fluctuating field between two microspheres of silica. The experiment is carried out as follows: the two microsized beads (A, B) are optically trapped in the low critical temperature micelle-solvent solution at a stabilized temperature (±10 mK). The position of the first trap is fixed at position x_A^T while the position of the second trap is driven from a equilibrium position $x_B^T(0)$ to a further one $x_B^T(\tau)$, where τ is the process time. The process is run in such a way that the system goes out from equilibrium. The protocole is repeated several times at the fixed temperature to obtain enough statistics and then, the temperature is increased few milliKelvins. Once the system thermalizs, the scheme is repeated up we achieve the critical temperature. From the experimental data we obtain the *external force profile* by two independent ways. First, from the equilibrium positions, we built the position probability density functions $\rho(x)$, which are directly linked to the total potential $U(x)$, $\rho(x) \sim \exp\left[-U(x)/kT\right]$. On the other hand, the external force is also computed from the non equilibrium process using the fluctuation theorems. In particular, Jarzynski equality allows to obtain equilibrium thermodynamic potential (free energy) from non equilibrium quantities (stochastic work). In Fig. 1, we represent the energy potential extracted from the equilibrium positions defined when both traps are at the further distance. The potential has two main contributions, the optical potential remains constant with the temperature while the *critical potential* increases once the system approaches its critical temperature.

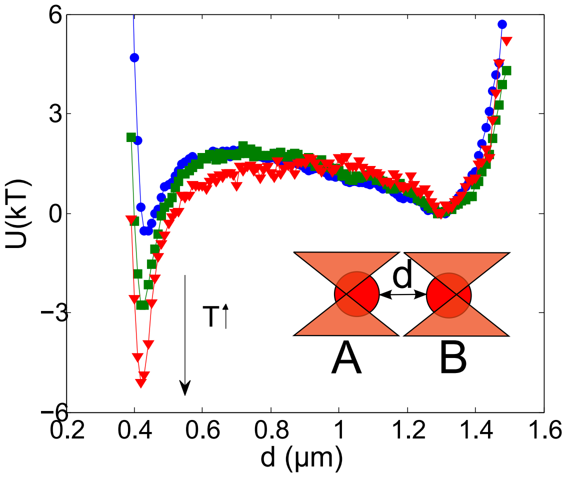

FIG. 1. **Total potential:** Solid circles (27.940°C), solid squares (28.101°C) and solid triangles (28.302°C). The x-axis represents the distance between the colloidal surfaces. The total potential presents two minima, on the right, the optical potential remains constant under temperature changes. On the left, we see how the minima decreases when the temperature approaches to the critical temperature. The potential becomes repulsive at lowest distances due to electrostatic interactions.

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Water dynamics in carbon nanohorns: the apparent fragile-strong transition is a crossover from localized to diffusive motion

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Angell [1] has proposed that water in the “no man's land” below the homogenous nucleation temperature undergoes a *fragile-strong transition* (FST). Theoretical interest in the FST has been fostered by a possible connection [2] with a Widom line emanating from the phase boundary between low and high density amorphous ice.

Experimental support for the FST has mostly come from high-resolution neutron spectroscopy on water confined in various matrices [3]. The FST appears as a kink in the temperature dependence of a mean relaxation time $\langle\tau\rangle$. This interpretation depends critically on the assumption that the experiment sees one and the same relaxation process above and below the kink.

Based on new neutron backscattering data of water in carbon nanohorns we show that in all likelihood the contrary is the case: The apparent FST is a crossover between regimes where localized and diffusive motion, respectively, dominates the quasielastic spectrum.

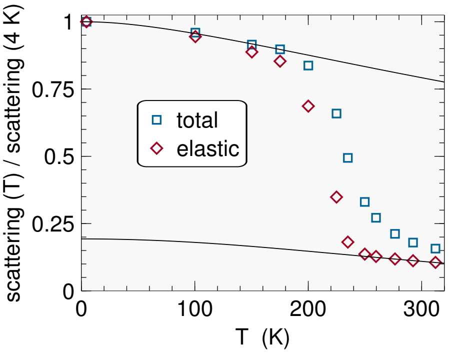

FIG. 1. Total and elastic neutron backscattering intensity at $q = 1.1$ Å^{-1} versus T. Solid lines are extrapolations using a harmonic Debye-Waller factor with fixed Debye temperatures of $\Theta = 1000$ K for the nanohorn matrix, and $\Theta = 220$ K for ice.

Formally, our fit function is the same as regularly used in support of a FST: a sum of a delta line, accounting for elastic scattering by the matrix, and a Kohlrausch spectrum. Except in a small $\langle\tau\rangle$ range, this model suffers from parameter degeneracies [4]. Relaxation times $\langle\tau\rangle$ outside the experimental resolution window depend strongly on constraints imposed upon other parameters. Occam's razor tells us to maximize constraints under minimal physical assumptions.

We use harmonic extrapolations (Fig. 1) of the T dependent scattering intensity to fix the amplitudes in our delta-plus-Kohlrausch fits. Further constraints are determined heuristically: when a parameter shows no systematic variation with q or T, it is kept fixed. It turns out that no single set of constraints strict enough to preclude degeneracies works for all q and T. Instead we identify two q, T regions that admit particularly stringent constraints and a crossover regime in between. Furthermore, at extreme q, T the water dynamics is not resolved within our spectrometer window, and must therefore be exempted from fitting.

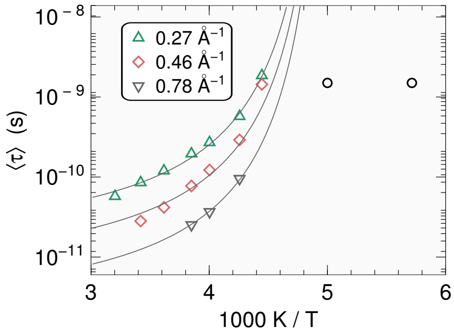

FIG. 2. Temperature dependence of the mean relaxation time $\langle\tau\rangle$. At high T, the q dependent fit results are well described by a Vogel-Fulcher law ($T_0 = 192$ K). At low T, our spectra are consistent with a q independent relaxation time that is not necessarily constant (black circles), but could as well have a weak T dependence.

In this way, we find that quasielastic scattering reveals different physics in different q, T regimes: At low T, it is dominated by localized motion; at high T by diffusive motion (Fig. 2). Our observation of traces of quasielastic scattering down to 150 or even 100 K is consistent with this interpretation, whereas it would be impossible to understand in a primary-relaxation-only scenario.

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4 Author Index

Page numbers in **bold face** indicate corresponding authors of oral contributions. Page numbers in *italic type* indicate coauthors.