International Workshop on Dynamics in Viscous Liquids

München, March 14 - 17, 2004

Programme

Organization Andreas Meyer and Thomas Voigtmann

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Introduction

It is our pleasure to welcome you in München to the International Workshop on Dynamics in Viscous Liquids.

In this workshop, the latest theoretical and experimental advances in the field of viscous liquid dynamics are discussed. This embraces a wide variety of topics and phenomena, from classical statistical physics to life sciences and geophysics. Above all, this meeting aims at inspiring and encouraging broad discussions between different scientific communities that essentially address similar issues from different points of view.

We hope to facilitate such discussions through the method of organization we have chosen for this workshop. Instead of having invited talks or key note lectures, all of the programme was put together during a meeting of the Programme Committee in December 2003. The decisions were made solely on the basis of the extended abstracts that had been submitted before, and that are collected in this booklet. We are happy to have received such encouraging response by many scientists; and we are deeply indebted to the members of the Programme Committee for the lively and constructive atmosphere during the committee's meeting.

The programme has been laid out to stimulate intensive discussions, especially having no parallel sessions, and poster sessions as a very central part of the meeting. Posters are displayed throughout the entire workshop, so discussions based around them are not limited to the two scheduled poster sessions.

The workshop takes place in the lecture halls of the Geoscience Department of the Ludwig-Maximilians-Universität München, which are within easy walking distance from both the city center of Munich and the famous university district of Schwabing with its unique atmosphere and its numerous pubs, cafes, and restaurants. We thank the Ludwig-Maximilians-Universität for supporting us generously, and Donald B. Dingwell and Kai-Uwe Hess from the geoscience department for their indispensable help during the workshop's preparation.

We wish you all a pleasant stay in München and an interesting, inspiring workshop.

Andreas Meyer and Thomas Voigtmann

Programme Committee:

Universidad del Pais Vasco, San Sebastián, Spain
Université Lyon, France
Chalmers University of Technology, Göteborg, Sweden
Universität Mainz, Germany
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Conference Location:

Geoscience Department Ludwig-Maximilians-Universität München Theresienstr. 41 80333 München

Pubs, Cafes, Restaurants

The map on the right shows the area surrounding the workshop location, indicating some Bavarian pubs and international restaurants. The conference dinner on Tuesday evening is hosted by the Augustiner restaurant, offering a buffet of typical cold and warm Bavarian dishes, and, of course, the world-famous beer.

- 1 Atzinger, Schellingstr. 9 Student pub with Bavarian bar food
- 2 News Bar, Amalienstr. 55 Scene cafe/bar, bar food
- 3 Vinzenz-Murr, Schellingstr. 21 Butchery with excellent Bavarian snacks
- 4 *Cafe Hoelzl*, Schellingstr. 25 Bakery, Cafe, decent cake
- 5 *Engelsburg*, Türkenstr. 49 Traditional pub with atmosphere
- 6 *Lara*, Schellingstr. 30 Döner, Falaffel, fast food
- 7 *Cafe Puck*, Türkenstr. 33 Bar food, nice atmosphere
- 8 Sausalitos, Türkenstr. 50 Mexican cantina, bar, finger food
- 9 Sezgin, Türkenstr. 21 Turkish fast food (Döner)
- 10 *Taverna Olympos*, Türkenstr. 38 Greek restaurant
- 11 *Pizzaria da Claudio*, Amalienstr. 53 Pizza place, Italian food
- 12 Rosi's Schmankerl Kuchl, Amalienstr. 26 Simple Bavarian food, pub
- Odeon, Theresienstr. 19 Cafe, pub, bar food
- 14 Bar Celona, Theresienstr. 38 Snack bar

- 15 *Nido*, Theresienstr. 40 Italian fast food, bar
- 16 Foro Romano, Theresiensstr. 29 Large Italian restaurant
- 17 Cohen's, Theresienstr. 31 Jewish specialties
- 18 Wimmer, Theresienstr. 44 Bakery
- 19 *Tokami Sushi*, Theresienstr. 54 High-standard Sushi bar
- 20 *Bei Meri*, Theresienstr. 56 Greek fast food
- 21 Cyclo, Theresienstr. 70 Vietnamese Restaurant
- 22 Tresznewski, Theresienstr. 72 Brasserie just opposite the Alte Pinakothek
- 23 Deeba, Barer Str. 42 Pakistani restaurant with excellent food
- 24 Cafe in der Pinakothek, Theresienstr. 74 Inside the Pinakothek der Moderne; good lunch specials
- 25 *Bei Raffaele*, Luisenstr. 47 Italian food, good and large pizza
- 26 Kaito, Theresienstr. 47 Traditional sushi place
- 27 Canton, Theresienstr. 49Good Chinese food

Grocery store, Pharmacy, Drugstore, Post office, Bank

- 30 *Tengelmann*, Türkenstr. 25 Grocery store
- 31 *Türkenapotheke*, Türkenstr. 40 Pharmacy
- 32 *KD Markt*, Türkenstr. 44 Drugstore

- 33 *Post*, Amalienstr. 32 Post office
- 34 Deutsche Bank, Barer Str. 62 Bank
- 35 Stadtsparkasse München, Barer Str. 41 Bank



Programme

Sunday

12:00	Registration
13:30	A. Meyer and Th. Voigtmann Welcome note
	Session 1, Chairperson W. Kob
13:35	R. Schilling , Universität Mainz Theory of the glass transition for systems with trivial statics
13:55	SH. Chong , Université Montpellier II Intermediate length scale dynamics of a supercooled molecular liquid
14:15	F. J. Bermejo , Universidad del Pais Vasco, Bilbao Slow dynamics about the glass-transition as explored by Muon Spin Relaxation Spectroscopy
14:35	T. Blochowicz , Universität Bayreuth The Anomaly of the Non-Ergodicity Parameter f as seen by Broadband Dielectric Spectroscopy and Quasielastic Light Scattering
14:55	H. Cang , Stanford University Dynamical Features of Supercooled Liquids, Liquid Crystals and Organic Ionic Liquids: A comparison
15:15	W. Götze , Technische Universität München The β -peak phenomenon in glass-forming van der Waals liquids
15:35	Break
	Session 2, Chairperson: C. Dreyfuss
16:30	T. Franosch , Hahn-Meitner Institut Berlin Recent Progress on the Theory of Light-Scattering and Transient Grating Experiments
16:50	G. Monaco , European Synchrotron Radiation Facility Depolarized Brillouin scattering study of o-terphenyl
17:10	YH. Hwang , Pusan National University The secondary relaxation in sugar-water mixtures
17:30	T. Seydel , Institut Laue-Langevin Statics and dynamics at surfaces of highly viscous liquids and gels studied by X-ray and neutron scattering methods
17:50	G. Dosseh , Université de Paris-Sud Phase transitions in molecular systems on the nanoscale
18:10	D. Leporini , Università di Pisa Hierarchic Cage Dynamics and Confinement in Ionomers Studied by High-Field Pulsed Electron Spin Resonance

Monday

	Session 3, Chairperson: A. Loidl
9:00	L. Berthier , University of Oxford Dynamic criticality and glass formation
9:30	L. Angelani , Università di Roma "La Sapienza" Energy landscape interpretation of critical slowing down in simple liquids
9:50	S. Capaccioli , Università di Pisa Relation between dynamic slowing down and the (isobaric/isothermal) reduction of excess en- tropy in glass-forming systems
10:10	C. A. Angell , Arizona State University Hyperquenching strategies for researching the energetics and dynamics of glassforming liquids, liquid-liquid transitions, and folding proteins
10:30	M. Vogel , University of Michigan Dynamical heterogeneities and mobility propagation in viscous liquids
10:50	Break
11:15	Poster Session A
12:45	Lunch break
	Session 4, Chairperson K. Binder
14:15	M. E. Cates , University of Edinburgh Inhomogeneous shear-thickening and rheological instability
14:45	A. Zippelius , Universität Göttingen Goldstone fluctuations in the amorphous solid state
15:05	H. E. Stanley , Boston University Slow Dynamics of the Complex Fluid, Liquid Water
15:25	B. Ruzicka , Università di Roma "La Sapienza" Gelation in Laponite clay suspensions
15:45	Break
	Session 5, Chairperson P. Gallo
16:30	H. König , Universität Mainz A binary colloidal mixture in 2D: An ideal model system for the glass transition
17:00	W. K. Kegel , Universiteit Utrecht Gravity and the glass transition in colloidal hard spheres
17:20	A. Coniglio , Università di Napoli "Federico II" <i>Cluster and slow dynamics in gelling systems</i>
17:40	S. Ramakrishnan , University of Illinois at Urbana-Champaign Flow of Depletion Gels: Comparisons of Theory and Experiment

Tuesday

	Session 6, Chairperson: F. Sciortino
9:00	S. Yip , Massachusetts Institute of Technology Dynamical Localization of Shear in Structured Matter with Disorder
9:30	F. Varnik , Université Lyon I The static yield stress and flow heterogeneity in a model glass: a molecular dynamics study
9:50	R. Yamamoto , Kyoto University Supercooled Liquids under Shear: A Computational Approach
10:10	M. Fuchs , Universität Konstanz Properties of dense colloidal dispersions under shear: non-linear regime
10:30	Break
11:15	Poster Session B
12:45	Lunch break
	Session 7, Chairperson W. Petry
14:15	G. Hinze , Universität Mainz Single Molecule Rotation in Supercooled Liquids
14:45	H. R. Schober , Forschungszentrum Jülich Diffusion in Metallic Glasses and their Melts: Collectivity, Pressure Dependence and Jumps
15:05	K. Rätzke , Technische Fakultät der Universität Kiel Diffusion in bulk-metallic glass-forming Pd-Cu-Ni-P alloys: from the glass to the equilibrium melt
15:25	M. Paluch , Silesian University Katowice Excess wing versus slow β relaxation process – high pressure dielectric studies
15:45	Break
	Session 8, Chairperson K. Samwer
16:30	J. Horbach , Universität Mainz Test of mode coupling theory for glassformers with a tetrahedral network structure
17:00	S. L. Webb , Georg-August-Universität Göttingen Flow Mechanisms, Structure and Viscosity of Na ₂ O-Al ₂ O ₃ -SiO ₂ Melts
17:20	F. Kargl , Technische Universität München The interplay of microscopic dynamics and structure in sodium silicate melts
17:40	F. Affouard , Université Lille I Comparative study of disaccharide/water solutions by molecular modelling

19:00 Conference Dinner

Wednesday

	Session 9, Chairperson: A. Arbe
9:00	B. Loppinet , IESL Heraklion Dynamics of end-grafted polymer brushes: An evanescent wave dynamic light scattering study
9:30	T. Pakula , Max-Planck-Institut für Polymerforschung Mainz Structure and dynamics responsible for super soft states in bulk polymers
9:50	N. Fatkullin , Kazan State University The Corset Effect of Polymer Dynamics in Pores: Looking for the Crossover from Confined to Bulk Dynamics
10:10	A. Wischnewski , Forschungszentrum Jülich Molecular observation of mechanisms limiting the topological confinement in polymer melts: A Neutron Spin Echo study
10:30	Break
	Session 10, Chairperson: Th. Voigtmann
11:15	A. M. Puertas , Universidad de Almería Attraction driven glass transition in colloidal systems
11:45	G. Foffi , Università di Roma "La Sapienza" Aging in short-ranged attractive colloids: A numerical study
12:05	K. N. Pham , University of Edinburgh Glasses in hard spheres with short-range attraction
12:25	E. Bartsch , Universität Mainz The Glass Transition Dynamics of Microgel Colloids with Short-Ranged Attractions
12:45	Lunch break
	Session 11, Chairperson W. Steffen
14:15	J. Colmenero , Universidad del Pais Vasco, San Sebastián Self-Atomic Motions in Glass-Forming Polymers: Neutron Scattering and Molecular Dynamics Simulations Results
14:45	W. Paul , Universität Mainz Molecular Dynamics simulations of the glass transition in 1,4-polybutadiene melts
15:05	B. Frick , Institut Laue-Langevin Molecular Weight and Temperature Dependence of the Vibrational and Relaxational Modes of Polyisobutylene
15:25	J. P. Wittmer , Université Lyon I Dynamical Properties of the Slithering Snake Algorithm: A numerical test of the activated reptation hypothesis
15:45	Break
	Session 12, Chairperson W. Schirmacher
16:30	D. J. Evans , Australian National University The Fluctuation Theorem
16:50	M. M. Koza , Institut Laue-Langevin Amorphous polymorphism and the supposed glass transition of water
17:10	P. H. Poole , St. Francis Xavier University Relation of phase behavior to crystallization, polyamorphism, and the emergence of tetrahedral structure and complex dynamics in liquid silica
17:30	A. Gray-Weale , University of Oxford Analysis of superionic conductors with theories of viscous liquids

List of Poster Contributions

- A1 F. Audonnet, Université de Paris-Sud Adsorption of molecular liquids in mesopores: from capillary condensation to the glass transition
- A2 P. Gallo, Università Roma Tre Mode coupling behaviour of a Lennard Jones binary mixture: a comparison between bulk and confined phases
- A3 M. Rovere, Università Roma Tre Non-Brownian diffusion regime in confined water
- A4 V. Teboul, Université d'Angers Molecular dynamics investigation of stringlike dynamics in confined water
- A5 F. Varnik, Université Lyon I Confinement Effects on the Slow Dynamics of a Simulated Supercooled Polymer Melt
- A6 M. Beiner, Martin-Luther-Universität Halle-Wittenberg Interrelation between structure and dynamics in nanophase-separated side chain polymers
- A7 A. Rühm, Max-Planck-Institut für Metallforschung Stuttgart Dynamics in thin homopolymer and block-copolymer films
- A8 C. C. Liew, BASF AG Structure and Dynamics in Block Copolymers: Dissipative Particle Dynamics Simulations using a Time-Coarse-Grained Model
- A9 **C. Pareige**, Université de Rouen A new approach to simulate the relaxation in polymers
- A10 M. Kroutieva, Kazan State University A Perturbation Method for the Solution of Integro-differential Equations in Microscopic Models of Polymer Dynamics
- A11 **H. Zapolsky**, Université de Rouen Application of the Random Walk Model to Relaxation Processes in Polymers
- A12 D. B. Kayumova, N.S. Kurnakov Institute of General and Inorganic Chemistry Visco-Elastic Properties of the System Ethylene Glycol – Tetramethylurea
- A13 A. Arbe, Universidad del Pais Vasco, San Sebastián Intermediate length scale dynamics in glass forming polymers
- A14 A. Narros, Universidad del Pais Vasco, San Sebastián Fully Atomistic Molecular Dynamics Simulations of 1,4-Polybutadiene. A Direct Comparison with Neutron Scattering Results
- A15 J. Sacristán, Donostia International Physics Center Self atomic motions in the α -relaxation regime: from simple glass formers to polymers
- A16 **B. Dünweg**, Max-Planck-Institut für Polymerforschung Mainz Hydrodynamic Screening in Semidilute Polymer Solutions
- A17 **P. Papadopoulos**, University of Ioannina Self-Assembly and Dynamics of $Poly(\gamma$ -benzyl-L-glutamate) Peptides
- A18 A. Sagidullin, Kazan State University Dendrimers and Linear Flexible-Chain Polymers: Resemblances and Differences of Self-Diffusion
- A19 A. Blanchard, Forschungszentrum Jülich Quenched polymer dynamics: a structural investigation by means of neutron small angle scattering
- A20 K. Mpoukouvalas, University of Ioannina Effects of temperature and pressure on the dynamics of hydrogen-bonded polymer blends
- A21 S. Pawlus, Silesian University Katowice Nonlinear relaxation dynamics of supercooled siloxane polymers under condition of high compression

- A22 C. Alba-Simionesco, Université de Paris-Sud Local structure and relaxation processes of polybutadiene up to 4 GPa
- A23 G. Kasper, Universität Heidelberg Fragility of glycerol under pressure
- A24 C. Dreyfus, Université Pierre et Marie Curie Light scattering study of an organic glassforming liquid under variable temperature and pressure, and comparison with other van der Waals supercooled liquids
- A25 M. Sekula, Silesian University Katowice Effect of pressure on dielectric relaxation in phthaletes
- A26 P. Rösner, Georg-August-Universität Göttingen Comparison between mechanical and dielectric spectroscopy of poly(methylmethacrylate)
- A27 **P. Rösner**, Georg-August-Universität Göttingen Mechanical spectroscopy of thin $Zr_{65}Al_{7.5}Cu_{27.5}$ films and evidence for an "excess-wing" in metallic glasses
- A28 C. Haon, Commissariat à l'Energie Atomique High Temperature Viscosity Measurements by the Gas Film Levitation Technique: Application to metallic glasses
- A29 A. Griesche, Hahn-Meitner Institut Berlin Diffusion and Viscosity in Pd₄₀Ni₄₀P₂₀ and Pd₄₀Cu₃₀Ni₁₀P₂₀ Melts
- A30 W. Hoyer, Technische Universität Chemnitz Viscosity Investigations on Liquid Sn-Ag-Cu Alloys
- A31 S. Mavila Chathoth, Technische Universität München Microscopic Dynamics and Mass Transport in Pd-Ni based Melts
- A32 S. Hosokawa, Philipps-Universität Marburg Sub-picosecond dynamics in liquid non-simple metals
- A33 H. Knoth, Universität Mainz The Mixed Alkali Effect in ternary Silicates: Computer Simulation Studies
- A34 J. Habasaki, Tokyo Institute of Technology Molecular Dynamics Study of Ion Dynamics in the Nearly-Constant-Loss Region
- A35 M. Pöhlmann, Technische Universität München First-Principles Molecular-Dynamics Simulations and Neutron Scattering on Hydrous Silicate Systems: Structural Properties and Diffusion Mechanism
- A36 S. Ispas, Université Montpellier II Vibrational properties and first principles calculation of NMR spectra for a sodium tetrasilicate glass model: simulated vs. experimental spectra
- A37 N. Zotov, Universität Bonn The Dynamic Structure Factor of Oxide Glasses: A Probe of Mode Localization?
- A38 K. Saito, Toyota Technological Institute Structure, Structural Relaxations and Macroscopic Properties of Silica Glass
- A39 A. Heuer, Westfälische Wilhelms-Universität Understanding the complex transport behavior of supercooled liquids on the basis of their potential energy landscape: a computer study of silica and Lennard-Jones systems
- A40 V. Martín-Mayor, Universidad Complutense Anderson localization in Instantaneous Normal Modes
- A41 **R. Richert**, Arizona State University Heterogeneity of dielectric and thermal relaxation times
- A42 A. Loidl, Universität Augsburg Dielectric spectroscopy of aging disordered matter

- A43 M. Micoulaut, Université Pierre et Marie Curie Reversibility in glass-forming liquids
- A44 N. B. Olsen, Roskilde University Rate constant change following an instantaneous temperature jump
- B1 S. Jabbari-Farouji, Universiteit van Amsterdam Generalized Stokes-Einstein relations and the Fluctuation-Dissipation Theorem in a colloidal glass of Laponite
- B2 I. Saika-Voivod, Università di Roma "La Sapienza" The effect of bond lifetimes on the dynamics of a short-ranged attractive colloidal system
- B3 M. Sperl, Technische Universität München Logarithmic relaxation in colloidal systems
- B4 W. Schirmacher, Technische Universität München Quantum Mode-Coupling Theory and the Boson Peak
- B5 **R. Eramo**, Università di Firenze Supercooled water relaxation dynamics by heterodyne transient grating experiment
- B6 A. Taschin, Università di Firenze Structural relaxation in supercooled bulk water investigated by time-resolved spectroscopy
- B7 W. Petry, Technische Universität München Dynamics of ethanol and methanol: A light scattering study
- B8 W. Petry, Technische Universität München Universal features of relaxation in liquid benzene
- B9 B. Rufflé, Université Montpellier II Relaxation Dynamics of Network Supercooled Liquids: Neutron Spectroscopy and Mode Coupling Analysis
- B10 M. Letz, Schott Glas Light scattering in viscous fluids and its connection to the liquid immersion lithography for structuring microchips
- B11 A. Schulte, University of Central Florida Temperature and Pressure Dependence of Density Fluctuations in Toluene Investigated by Brillouin Scattering
- B12 A. Schulte, University of Central Florida Low Frequency Light Scattering Spectroscopy of Lysozyme in Solution
- B13 A. Lerbret, Université Lille I Influence of sugars on the dynamics of lysozyme
- B14 F. Migliardo, Université Lille I Inelastic Neutron Scattering and Simulation Study on Disaccharides/H₂O Mixtures
- B15 F. Migliardo, Università di Messina Characterization of Fragility in Hydrogen-Bonded Systems by Elastic Neutron Scattering
- B16 J.-A. Seo, Pusan National University A Brillouin Spectroscopy study of relaxation time in sugar mixtures under Shear flow
- B17 **H. Noguchi**, Forschungszentrum Jülich Morphological change of a vesicle under shear flow: A Multi-particle collision dynamics simulation
- B18 **K. Kroy**, Hahn-Meitner Institut Berlin Strain Hardening of Biological Tissue
- B19 C. A. Angell, Arizona State University The transition from crystal to glass by damage, minimum crystal sizes, and the nanogranularity of glasses

- B20 S. K. Das, Universität Mainz Interplay between phase behavior and dynamics in binary liquid mixtures: Computer simulation studies
- B21 Y. Hayashi, The Hebrew University of Jerusalem Dielectric Properties of Supercooled and Crystallized Glycerol
- B22 **T. Psurek**, Silesian University Katowice Analysis of decoupling of DC conductivity and structural relaxation time in supercooled epoxy systems
- B23 E. A. Rössler, Universität Bayreuth Light scattering and dielectric manifestations of secondary relaxations in molecular glassformers
- B24 J. C. Dyre, Roskilde University Minimal model for β relaxation in viscous liquids
- B25 **D. Prevosto**, Università di Pisa Identification of the nature of secondary relaxation processes within the Coupling Model scheme
- B26 J. Matsui, Kyushu University Full picture of incoherent dynamic structure factor in liquid and glassy states
- B27 J. Matsui, Kyushu University Direct measurement of cooperatively rearranging region
- B28 C. Solunov, University of Plovdiv "Paisii Hilendarsky" The Relations between the Configurations in the Cooperative Rearranging Region with Basic Molecular Units and Fragility in Viscous Liquids
- B29 **T. Pakula**, Max-Planck-Institut für Polymerforschung Mainz Cooperative dynamics in condensed molecular and macromolecular systems
- B30 M. Plazanet, Institut Laue-Langevin Neutron scattering studies of the dynamics of the very fragile glass former decalin
- B31 A. Rivera, Universität Bayreuth Low temperature properties in molecular glass formers
- B32 Y. Feldman, The Hebrew University of Jerusalem Slow and Fast Dynamics in Glycerol-Water Mixtures
- B33 **P. Bordat**, Université Lille I Does anharmonicity control fragility?
- B34 J. Bartoš, Slovak Academy of Science Correlations between PALS data and the dynamic properties of small molecular and polymeric glass-forming liquids
- B35 Y. Hiki, Tokyo Institute of Technology Shear Viscosity of Inorganic and Organic Glass-Forming Materials
- B36 **G. Guimbretiere**, Université Montpellier II Brillouin scattering study of hypersonic attenuation in GeO₂
- B37 B. Loppinet, IESL Heraklion Phonon Dispersion in Mesoscopic Self-assembled Soft Matter
- B38 M. Descamps, Université Lille I The entrance of plastic crystals in their glassy crystal state
- B39 **T. Tao**, Kyushu University Specific heat of nonequilibrium systems and the glass transition
- B40 **T. Christensen**, Roskilde University An analysis of boundary-effects in obtaining the frequency dependent specific heat by effusivity measurements
- B41 W. Häussler, Institut Laue-Langevin New developments in Neutron Spin Echo

- B42 **H. Pleiner**, Max-Planck-Institut für Polymerforschung Mainz A Physicist's View on Constitutive Equations
- B43 N. L. Ellegaard, Roskilde University Testing for one Generalized Linear Single Order Parameter
- B44 M. G. Vasin, Ural Branch of the Russian Academy of Sciences Theoretical Model of the Fischer Clusters Formation in Supercooled Liquids
- B45 J. J. Fontanella, U.S. Naval Academy The Defect Diffusion Model and the Physical Properties of Viscous Liquids
- B46 **D. Long**, Université de Paris-Sud Aging in van der Waals liquids: a microscopic model

Oral Presentations

Theory of the glass transition for systems with trivial statics

Rolf Schilling^{*}

Institut für Physik, Johannes Gutenberg-Universität, 55099 Mainz, Germany

Cooling a liquid leads to cage formation accompanied by the growth of static correlations and the slowing down of relaxation. Mode coupling theory (MCT) provides a microscopic theory which relates both phenomenon to each other. It predicts an ideal glass transition, if the static density correlations have reached a critical value [1]. Generically, this transition is described by a *discontinuous* change of the long-time limit of the density fluctuations, the nonergodicity parameter. However, there exist systems where the static correlations vanish. One of these models consist of infinitely thin hard rods with length l on a lattice with lattice constant a = 1. We have proven that the MCT-vertices are zero for all projections of the fluctuating force onto any product of density fluctuation modes. Accordingly, MCT in its present form does not yield a glass transition. Nevertheless, MD-simulations [2] of the rods on a fcclattice have shown quite similar relaxational behavior as for supercooled liquids. The orientational correlator $\phi_1(t) = (1/N) \sum_n \langle \mathbf{u}_n(t) \mathbf{u}_n(0) \rangle$, with $\mathbf{u}_n(t)$ the unit vector along rod n at time t, exhibits a two-step relaxation process with critical nonergodicity parameter close to one. The rotational diffusion constant obeys a power law $D(l) \sim (l_c^{\rm MD} - l)^{\gamma^{\rm MD}}$ with $l_c^{\rm MD} \approx 2.7$ and $\gamma^{M\hat{D}} \approx 4.2$.



FIG. 1: Time dependence of the force-force correlator of an isolated pair of rods for Brownian dynamics. l = 1.8, 2, 4, and 6 from bottom to top (from Ref. [4]).

In a first-step we have derived a self-consistent equation for the frequency-dependent diffusion constant D. It involves as input the time-dependent force-force correlator of a single 2-rod system (Fig. 1). For an fcc-lattice we have found that the static diffusivity is $D(l) \sim (l_c - l)^{\gamma}$ with $l_c \approx 2.20$ and $\gamma = 1$ [3]. However, a detailed analysis proves that the glass transition at l_c is continuous [4], in variance with the numerical finding [2].

To eliminate this important drawback we have returned to the Mori-Zwanzig equation which is the starting point of MCT. But we have performed a different approximation scheme where the memory kernel is factorized in frequency space, in contrast to original MCT. We recover the same structure of the memory kernel but with input quantities (vertices) determined by the Laplace transform of a single 2-, 3-, and 4-rod system at frequency zero. This is a measure of the average number of collision events and equals the area under relaxation curves shown in Fig. 1 for 2 rods. They play the role of the static correlators in original MCT, i.e. the growth of the area drives the glass transition. Since these vertices increase with l, there exists an l_c at which a *discontinuous* glass transition occurs and γ is larger than one. We have also used this approximation scheme for liquids. But the resulting MCT-equations can not be applied to systems with dominating static correlations. In this sense our modified MCT is complementary to the original MCT. The latter is applicable when excluded volume effects are dominant whereas the former one is appropriate for cases where the dynamics is mainly governed by entanglement.

The fact that both approximation schemes lead to the same structure of MCT equations and therefore to the same predictions, suggests that it is the statistics of the trajectories in configuration space which is responsible for the relaxation behavior as predicted by MCT [5].

I am very grateful to W. Götze for many stimulating discussions.

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- W. Götze, in *Liquids, Freezing and Glass Transition*, edited by J.-P. Hansen, D. Levesque, and J. Zinn-Justin, Les Houches Summer School of Theoretical Physics (North-Holland, Amsterdam, 1991), pp. 287– 503.
- [2] C. Renner, H. Löwen, and J.-L. Barrat, Phys. Rev. E 52, 5091 (1995).
- [3] R. Schilling and G. Szamel, Europhys. Lett. 61, 207 (2003).
- [4] R. Schilling and G. Szamel, J. Phys. Condens. Matter 15, S967 (2003).
- [5] W. Götze and L. Sjögren, Rep. Prog. Phys. 55, 241 (1992), see p. 303.

Intermediate length scale dynamics of a supercooled molecular liquid

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We report on computational and theoretical investigations of the intermediate length scale dynamics of a three-site model for orthoterphenyl (OTP) in supercooled states. The intermediate length scales (or wavenumbers) here denote the regime of lengths larger than the nearest-neighbor interparticle distance but smaller than the hydrodynamic regime. Experimental results on the dynamics of glass-forming liquids at this regime are a white area due to experimental difficulties like low scattered intensity and multiple scattering. Also from the theoretical side, the dynamics at this regime are far from understood. The mode-coupling theory (MCT) has been successful in describing the evolution of the structural relaxation driven by the local cage effect, but whether this theory applies also at the intermediate scale is an open question.

We found from the molecular-dynamics (MD) simulations that the three-site model for OTP exhibits interesting dynamical properties at the intermediate wavenumbers. As shown in Fig. 1, besides the peaks located at the static structure factor peak $(q_{\rm max})$ which is related to the nearest-neighbor site-site distance, the critical nonergodicity parameters and the α -relaxation times exhibit unusual peaks near the intermediate wavenumber $(q_{\rm GC})$ which is connected to the overall size of the molecule. Furthermore, these unusual peaks are found to be more enhanced at lower density and higher temperature.

These and related simulation results provide a clean bridge between experimental and theoretical investigations on the intermediate length scale dynamics. For experimentalists, our simulation results, which are free from problems like multiple scattering, serve as a guide to look for corresponding features in their measurements. For theoreticians, they serve as the reference to be compared with their theoretical predictions. We performed in the present work such a theoretical investigation based on the MCT approach.

Using the static structure factor from the MD simulations as input, the MCT equations based on the site representation are solved. We compare the soobtained theoretical results for dynamics with the simulation results. From this comparison, it is found that MCT captures the simulation results at the semiquantitative level, except for the intermediate wavenumbers near $q_{\rm GC}$. Theoretical results at $q \approx q_{\rm GC}$ are found to be improved by taking into account the spatial correlation of the molecule's geometrical center. This implies that unusual dynamical properties at $q \approx q_{\rm GC}$ are basically due to the coupling of the rotational motion to the geometrical-center dynamics. However, there still remain qualitative as well as quantitative discrepancies between theoretical prediction and corresponding simulation results at $q \approx q_{\rm GC}$, which might not be accounted for by MCT. This calls for further theoretical development for understanding the intermediate length scale dynamics.

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FIG. 1: MD simulation results for the wavenumber dependence of various quantities for the three-site OTP at $\rho = 2.71$ molecules/nm³. (a) Solid and dashed lines respectively denote the critical nonergodicity parameters $f_q^{\rm Nc}$ and the critical amplitudes $h_q^{\rm N}$ for the total density correlators $\phi_q^{\rm N}(t)$. $h_q^{\rm N}$ are in arbitrary units. The dotted line refers to the static structure factor $S_q^{\rm N}$, multiplied by a factor of 0.08 for ease of comparison, at T = 190 K. (cf. $T_c^{\rm MCT} \approx 172$ K at this density.) (b) Solid and dashed lines respectively denote the α -relaxation times τ_q and the stretching exponents β_q obtained from the Kohlrausch-law fit of the correlators $\phi_q^{\rm N}(t)$ at T = 190 K.

Slow dynamics about the glass-transition as explored by Muon Spin Relaxation Spectroscopy

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The glass transition of several molecular glassformers is monitored by means of measurements of the spin relaxation rates of implanted muons. The measured data enable us to access the dynamics along the whole range of temperatures comprising the glass and the supercooled-liquid within a time window of about 0.01μ s up to 10μ s. The technique consists in the measurement of the temperature dependence of the relaxation rates of implanted muons onto several samples for which their dynamics about T_q are known in detail. Because of the small muon mass, its motions once implanted will be driven by excitations of its microscopic environment to which it is strongly coupled. The data measured under transverse fields monitor the development of a static component that parallels the behavior of the Lamb-Mößbauer (or Debye-Waller) factor as measured by various other spectroscopies. Analysis of such curves simply involves the fitting of a decaying oscillatory signal arising from the Larmor precession of muons stuck to a diamagnetic environment about the external field (typically 20 G). A preliminary study [1] carried out on a sample along a temperature interval encompassing its glass/liquid and crystal/liquid transitions served to test the capabilities of the technique to monitor in detail the dynamics of both phase transformations. The crystal data could only be reproduced up to some 30 K below T_g . An adequate theoretically-grounded model to explain the strong drop of relaxation rates about and above T_g was found to be provided by the inclusion of a term $\propto (|T - T_c|/T_c)^{1/2}$ following the prediction made by Mode-Coupling Theories (MCT).

Recent results show that the technique can be fruitfully exploited to assess the presence of criticality within the supercooled liquid at micro-second scales.

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The Anomaly of the Non-Ergodicity Parameter f as seen by Broadband Dielectric Spectroscopy and Quasielastic Light Scattering

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Almost 20 years after mode coupling theory (MCT) was presented as a theory of the structural glass transition [1] the experimental verification of its various aspects is still a matter of ongoing debate. MCT predicts a critical temperature T_c at which a particular scaling behaviour of the susceptibility function is expected. Along with that an anomaly in the temperature dependence of the non-ergodicity parameter f(T), *i. e.* the plateau value of the correlation function in between fast dynamics and the structural relaxation, should be observable. Concerning the latter a pronounced crossover from a constant f(T) above T_c to a square root behaviour below is anticipated. The unambiguous identification of that crossover, however, has been a matter of controversy, cf. [2, 3].

In the present contribution we analyze broadband dielectric and light scattering spectra of various glass formers, including dielectric loss spectra of glycerol (GLY) and propylene carbonate (PC) as previously published by Lunkenheimer *et al.* [4], which provide the largest frequency range available $(10^{-5} - 10^{13} \text{ Hz})$. After the temperature dependence of the overall static permittivity is removed and the spectra are scaled to the susceptibility minimum it turns out that the asymptotic MCT scaling law of the minimum region is well fulfilled from T_c surprisingly up to the highest temperatures measured ($\approx 1.5 T_c$), cf. Fig. 1. By extrapolation of the scaling parameters T_c is identified in a consistent manner for all systems studied.



FIG. 1: Dielectric loss data of glycerol as published by Lunkenheimer *et al.* [4], scaled to the susceptibility minimum at temperatures above (full symbols) and below (crosses) T_c . Dashed line indicates the powerlaws occurring above T_c with an exponent parameter of $\lambda = 0.68$.

As is seen in Fig. 1, the low temperature regimes above and below T_c turn out to be easily distinguishable from a phenomenological point of view: Below T_c the so-called high-frequency (HF) wing emerges as an additional spectral feature that seems to destroy the scaling behaviour of the minimum region in $\chi''(\omega)$. In fact a careful quantitative analysis shows, by making use of simple phenomenological model functions, that the high frequency wing evolves in a very similar manner for many different glass formers and that the emergence of the HF wing defines a crossover temperature T_x , which may be obtained from analysing the low temperature susceptibility data, and which happens to agree well with the critical temperature of MCT.

Having a phenomenological description of the full susceptibility spectrum available, it is possible in a straight forward manner to access the quantity f in an almost model independent way by executing the integral over parts of the spectrum. It turns out that the resulting values of f are very close to unity so that rather 1-f has to be considered. And indeed in the temperature dependence of the latter quantity a pronounced change around the critical temperature T_c is identified. It is shown that a similar phenomenological approach can also be taken to consistently analyse susceptibility spectra obtained by dynamic light scattering (LS) so that finally the expected crossover behaviour is identified in five different systems, namely glycerol, 2-picoline, m-tricresyl phosphate, propylene carbonate and toluene, cf. Fig. 2 and a systematic comparison of the non-ergodicity parameter obtained by LS and DS is possible.



FIG. 2: The non-ergodicity parameter as detected by light scattering (LS) and dielectric spectroscopy (DS). The curves are scaled to coincide at temperatures about 100 K above T_c . Around T_c a significant drop occurs in 1 - f, which again levels off to some low value around T_g .

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Dynamical Features of Supercooled Liquids, Liquid Crystals and Organic Ionic Liquids: A comparison

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The results of optical heterodyne detected optical Kerr effect (OHD-OKE) experiments on several complex liquids including van der Waals supercooled liquids, isotropic phase liquid crystals, and organic ionic liquids are reported. For the van der Waals supercooled liquids, the temperatures range from above the melting point T_m down to the mode coupling theory (MCT) critical temperature T_c . For the liquid crystals, the temperatures range from well above the liquid crystal isotropic to nematic phase transition temperature T_{NI} down to approximately T_{NI} . For the organic ionic liquid, the temperatures range from well above T_m down to well below T_m , into the deeply supercooled liquid. In all of the experiments, a wide range of time scales is probed, that is from smaller than 100 fs to tens of hundreds of ns.

The OHD-OKE experiment, a non-resonance pump-probe experiment, examines orientational relaxations in liquids. The OHD-OKE signal is related to the time derivative of polarizability-polarizability correlation functions. A polarized pump pulse introduces an optical anisotropy. The induced birefringence decays because of orientational relaxations. A time delayed probe pulse detects the decay. To maximize the signal to noise ratio, three different pulse lengths are used for different time ranges, and a continuous wave (CW) laser is employed as the probe beam for the longest time scales.

The experiments show striking similarities of the orientational dynamics for all of the liquids. Following oscillatory intra-molecular vibrational contributions to the signal (t < 1ps), a universal power law

decay with power law exponent close to -1 is found in all the liquids starting from about 1 ps, out to several nanoseconds, and in the case of ionic organic liquids, tens of ns. This power law is followed by a second power law decay, the von Schweidler power law in all the liquids. The longest portion of the data is exponential. The range of the two power law decays increase as the temperature decrease.

The OHD-OKE signal decay of all the liquid can be very well described by a fitting function F(t) = $(pt^{-z} + dt^{-b}) \exp(-t/\tau)$. While the exponents of the two power laws, z and b, are temperature independent, the amplitudes of the two power laws, p and d, decrease as the temperature decreases. Agreement with several MCT temperature scaling relations is found. In the supercoolded liquids, there is only one ideal glass transition scaling temperature, T_c . In the liquid crystals, there are two scaling temperatures, T_{CL} and T_{CH} (L=low; H=high). The observed similarities of supercooled liquids and the locally structured isotropic phase of liquid crystals suggest the existence of analogous underlying physical feature of these liquids. The comparisons of the orientational dynamics in these types of liquids provide a new angle from which to examine the problems of dynamics in these liquids.

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The β -peak phenomenon in glass-forming van der Waals liquids

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Using heterodyne detection, optical Kerr-effect (OKE) spectroscopy has provided response functions for structural relaxation of several supercooled van der Waals liquids for time intervals of up to 5 orders of magnitude [1, 2]. The evolution of structural relaxation of Salol could be interpreted within the scaling-law description of the mode-coupling theory for ideal glass transitions (MCT) for temperatures T being 10 K above T_c or higher [1, 3]. However, if T is close to T_c , there opens a time interval of two to three orders of magnitude in size, where the scaling-law description does not account for the data. Within this interval adjacent to the interval for the transient dynamics, the correlation functions exhibit nearly logarithmic decay [1, 2]. It is shown that this hitherto unknown relaxation feature is a manifestation of the β -peak phenomenon, as it was discussed earlier within MCT [4, 5]. This phenomenon appears as result of the strong coupling of the reorientational degrees of freedom, whose dynamics causes the OKE response, with the translational degrees of freedom, whose dynamics causes the MCT-glass-transition singularity. A schematic model, which describes the dynamics by only two correlation functions, one referring to density fluctuations and one to the reorientational fluctuations, yields response functions in agreement with those measured for benzophenone [2] and for Salol [1] for time intervals extending from 2 picoseconds to about 20 and 200 nanoseconds, respectively. The theory [6] implies the prediction of a similar regime of β -peak dynamics for temperatures T near T_c within the Gigahertz interval of frequencies or within the picosecond interval of times for the reorientational correlation functions of liquids consisting of molecules with large anisotropies.

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Recent Progress on the Theory of Light-Scattering and Transient Grating Experiments

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The Navier-Stokes equations have been recently generalized to include the long-wavelength orientational dynamics in order to gain insight into the slow dynamics as observed in light-scattering experiments [1]. In particular, emphasis is put on the interplay of orientational degrees of freedom and the conserved quantities, e.g. density fluctuations, as is implied by the rotation-translation coupling (RT-coupling). Also, this generalization indicated the necessity of introducing frequency-dependent kinetic coefficients in all the terms of these equations. A microscopic justification for these generalized Navier-Stokes equation has been worked out recently, and the consequences of this new mechanism for polarized scattering have been discussed [2–6]. We will present some aspects of the new theoretical results and their implications for the analysis of experimental data.

We shall discuss the role of the various frequencydependent kinetic coefficients in polarized and depolarized scattering and we shall show that a unified description for scattering necessarily contrasts standard textbook results for polarized scattering. In particular, introducing the contributions of mass density and orientation in the detection mechanism, we emphasize the role of the density-orientation crosscorrelation function. We exemplify the influence of the RT-coupling on the Brillouin line shape and briefly discuss the emergence of a 'VV-dip' as a result of the cross-correlation, as recently observed in Salol by Zhang et al. [7]. The microscopic approach reveals that the positivity of all spectra is guaranteed, provided the empirical fit functions for the frequencydependent kinetic coefficients fulfill inequalities similar to Onsager's relations.

Whereas scattering experiments probe thermal fluctuations of the sample, time-resolved transient grating experiment impose modulations of the mass, temperature and orientational density. The decay of this grating can be monitored by the Bragg scattering of an incident probe laser beam. The scattered beam as observed in a heterodyne technique carries information on the dynamics of the supercooled molecular liquid. We show that that the same approach of generalized constitutive equations leads to description of these forced experiments. Since the time scales of the experiment covers the heat diffusion mode neglected for scattering, one has to supplement the equations of Ref. [1] considering the dynamics of temperature variations. This generalization is performed along the lines suggested by Götze and Latz [8] and leads to the introduction of a frequency-dependent tension coefficient and specific heat [9, 10]. The coupling of the dielectric tensor to the orientational degrees of freedom of the supercooled liquid manifests itself in terms of a set of elementary response functions, that generalize the two considered so far, i.e. the *impulsive stimulated* Brillouin scattering (ISBS) and the impulsive stimulated thermal scattering (ISTS). As a consequence of the fluctuation-dissipation theorem the ISBS response functions are directly connected to scattering experiments and can in principle also be obtained as Fourier-Laplace back-transforms of certain scattering data in different scattering geometries. In contradistinction to the ISBS functions, the ISTS signal results from the heat absorbed by the liquid and leads to genuinely new information on the structural relaxation and on the RT-coupling function.

Finally, we show how the generalized constitutive equations have to be modified, once molecules of arbitrary shape are considered, and how one can establish a relation to the Navier-Stokes equations for a liquid of axially symmetric molecules considered so far [11].

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Depolarized Brillouin scattering study of o-terphenyl

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We present light scattering spectra of the fragile glass-former o-terphenyl in the depolarized (VH) configuration. These spectra have been collected at two different scattering angles ($\theta = 60^{\circ}$ and 119°) at temperatures, T, comprised between 290 and 420K. The spectra around room temperature are characterized by the presence of transverse propagating modes. With increasing temperature, these modes gradually disappear in a spectral shape which is still q-dependent, and which shows the classical Rytov dip at the highest probed temperatures.



FIG. 1: Temperature dependence of the structural relaxation time obtained in light scattering experiments. Open squares: orientational relaxation time from VH spectra collected in the backscattering configuration ($\theta = 180^{\circ}$) [2]. Full squares: orientational relaxation time from this experiment. Open circles: longitudinal viscosity relaxation time from isotropic spectra [3]. Full circles: shear viscosity relaxation time from this experiment. Dashed line: shear viscosity scaled on the longitudinal viscosity relaxation time at low temperature.

We use a recently introduced hydrodynamics formalism [1] to describe in detail the θ and T evolution of the spectra. In particular, for each temperature the spectra collected at the two different q values are fitted *globally* using the same set of model parameters, and nice fits are obtained in the whole explored temperature range.

This fitting exercise gives us information – among others – on both the orientational relaxation time and on the shear viscosity relaxation time, as reported in Fig. 1.

The orientational relaxation time, τ_R , is consistent with previous determinations [2]. The shear viscosity relaxation time, τ_s , coincides with the longitudinal viscosity one [3], as also observed in ZnCl₂ [4]. Additionally, τ_s and τ_R are parallel to each other, being $\tau_R \approx 5\tau_s$.

The reliability of the obtained results is strongly supported by the observation that the shear viscosity calculated from the fit parameters is consistent over three decades with its direct measurement results.

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The secondary relaxation in sugar-water mixtures

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Glass will eventually become one of the most widely used man-made materials, but the phenomena underlying the liquid-glass transition and the nature of the glassy state remain incompletely understood. Liquids below their melting temperature are called supercooled liquids and cooling a supercooled liquid below the glass transition temperature produces a glass. In other words, a glassy state can be obtained by cooling a liquid quickly to avoid crystallization.

In the dielectric-loss spectra of molecular glass materials, supercooled liquids usually exhibit at least two relaxation processes, the α - and the β -relaxations. The α -relaxation is related to a long-time scale and corresponds to the overall structural rearrangement of a system. The β -relaxation is related to a short-time scale and corresponds to the local dynamics [1]. In the last two to three decades the experimental techniques in dielectric spectroscopy have strongly developed so that in addition to the α - and β -relaxations, a variety of secondary relaxation processes show up in broadband dielectric spectra [2].

The secondary relaxations are classified into two groups according to the contribution of the peak and the temperature dependence of the relaxation time [3]. When the dielectric loss spectrum exhibits an excess wing on the high frequency side of the α -relaxation peak, we call these glass formers type A systems. The temperature dependence of the secondary relaxation time obeys a Vogel-Fulcher-Tamman equation [4–6]. In contrast, type B glass formers exhibit a well distinguished slow β -relaxation peak and the temperature dependence of the secondary relaxation time obeys an Arrhenius law. The origin of the secondary relaxation in the glass-forming materials has been extensively studied during recent years in theories, experiments, and simulations. However, there is no general agreement about the origin of the secondary relaxation.

We studied the dynamics of glucose-water mixtures that are known to reveal a well-pronounced secondary relaxation by dielectric spectroscopy in the supercooled and glassy states [7]. The α -relaxation and the secondary relaxation were observed simultaneously. As the temperature is lowered, the α -relaxation and the secondary relaxation progressively shift to lower frequencies. At high temperature, the two relaxations overlap, but the secondary relaxation is separated from the α -relaxation with decreasing temperature.

As the weight percent of water is increased, T_q of the glucose-water mixtures is lowered because of the plasitization effect [8]. Figure 1 depicts the effect of water content on the contribution of the α - and the secondary relaxation of glucose-water mixtures. In Fig. 1 it is clear that there is a large variation of the position and the strength of the secondary relaxation,



FIG. 1: The dielectric constants of various glucose-water mixtures at effective temperatures.

indicating that the secondary relaxation is strongly affected by the water contents.

In order to understand the origin of the secondary relaxation, we investigated the temperature dependence of the dielectric relaxation of various sugarwater mixtures, especially concerning the temperature dependence of its relaxation time and amplitude with different water contents.

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Statics and dynamics at surfaces of highly viscous liquids and gels studied by X-ray and neutron scattering methods

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The investigation of dynamics at surfaces is a challenge to scattering methods. The research field is of particular interest as the reduced dimensionality may imply new fundamental insights. In liquids, the microscopic thermal fluctuations in the bulk drive capillary wave fluctuations at the surface and thereby induce long-range lateral correlations [1]. The dispersion of capillary wave fluctuations is determined by the viscosity and surface tension of the liquid. In viscous liquids, the capillary waves may become overdamped. It is not yet fully clear how they freeze in at the glass transition.

New methods using X-rays and neutrons are being explored to investigate dynamics at surfaces. Both Xrays and neutrons are surface sensitive when applied under grazing angles of incidence below the critical angle of total external reflection at the sample. In addition, a large wavevector transfer and a good *q*resolution compared to visible light scattering can be achieved. However, until recently, quasielastic or inelastic measurements at surfaces have not been possible due to limitations in the available flux for both X-rays and neutrons. Therefore, only time-averaged quantities such as the roughness or characteristic lateral correlations of a surface could be obtained.

It has now become possible to study surface dynamics in a direct way using transversely coherent X-rays [2, 3]. When a surface is coherently illuminated, a graininess known as speckle can be observed in the diffraction pattern. On a fluctuating surface, the speckles fluctuate accordingly. X-ray Photon Correlation Spectroscopy (XPCS) can be used to record the fluctuations, and with an adequate setup the intermediate scattering function S(q,t) from a surface can be obtained. Similarly to visible light scattering, hetrodyne mixing is possible to enhance the signal [4]. XPCS is somewhat analogous to the neutron spin echo (NSE) technique in that S(q,t) rather than $S(q,\omega)$ is measured.

XPCS and NSE would complement each other in the accessible dynamic range, NSE probing the faster fluctuations. NSE measurements to probe the dynamics at single surfaces of bulk liquids have, however, not been feasible yet. Nevertheless, interesting developments regarding NSE applied to surfaces are being pursued [5, 6].

We present XPCS experiments [2, 7] as well as, for reference, static measurements with X-rays [8] and neutrons [9] on surfaces of highly viscous liquids, prototypical glass formers and gels. The capillary wave dispersion relation derived from the dynamical measurements yields the viscosity and the surface tension or in the case of overdamped waves the ratio of these quantities. The surface-sensitive experimental methods using X-rays and neutrons will also be explained in detail within this context.

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Phase transitions in molecular systems on the nanoscale

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Despite the large experimental and theoretical activity in the field, no universal picture of thermal properties of confined fluids has emerged to date. The addition of multiple effects such as pore topology (geometry, size and connectivity) or surface properties complicates the interpretation of the results. Nevertheless, the surface properties of the confining media seem crucial. In order to separate this feature from topology effects, a systematic study of thermal properties of confined fluids with variable fluidwall interaction at constant pore topology is essential.

We have investigated confinement effects on thermal properties of several molecular systems – cyclohexane, benzene, toluene, ortho-terphenyl (OTP), and water – confined in highly ordered mesoporous silica MCM-41 and SBA-15, with pore diameters from 2.4 to 14 nm, by ¹H NMR spectroscopy, calorimetry, and neutron scattering. Cyclohexane, benzene toluene and OTP have weak repulsive interactions with silica whereas water molecules may have hydrogen bonds with the OH groups of silica. The importance of fluid-wall interactions and the competition between finite size effects and surface interactions on both melting and glass transition of the confined fluids has been strengthened from our results. The main outputs are the following. In the largest pores (SBA-15, 4.7 nm < d < 14 nm), the melting temperatures of benzene and cyclohexane do not follow the GibbsThomson equation whereas water, that interacts stronger with silica walls than organic substances, does. Fragile glass-forming toluene and OTP never crystallize in pores up to 9 nm. In the smallest pores (MCM-41, 2.4 nm < d < 3.6 nm), benzene and cyclohexane, that never vitrify in their bulk forms, undergo glass transitions. The size dependence of the glass transition temperatures T_g is influenced both by intrinsic properties of the liquid and surface interactions: fragile glass forming liquids like toluene or OTP have a non-monotonic size dependence of T_g whereas the glass transition temperature of benzene increases with decreasing pore size.

In order to change surface properties while keeping the pore topology constant, we have graphted different organic groups at the surface of the mesoporous materials. We will discuss surface modification effects on the thermal behavior of the confined fluids.

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Hierarchic Cage Dynamics and Confinement in Ionomers Studied by High-Field Pulsed Electron Spin Resonance

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Ionic paramagnetic tracers (spin probes) attached by electrostatic interactions to the surface of nanometric ionic clusters (multiplets) in ionomers were used as a model system in which slow cage reorientation can be studied in the glass transition region of the polymer.



A combination of several methodologies based on pulsed high-field Electron Paramagnetic Resonance (EPR) spectroscopy, including continuous wave EPR, saturation recovery measurements, and measurements of the decay of primary and stimulated electron spin echoes was employed to cover time scales from a few picoseconds up to dozens of microseconds.

Three hierarchical reorientation processes of the spin probe were observed on different timescales. The spin probe undergoes fast intramolecular libration on the time scale of a few picoseconds, it experiences a local rearrangement of the cage on the timescale of hundreds of nanoseconds and it performs cooperative reorientation coupled to the structural relaxation over time scales comparable to or longer than several microseconds in the glass transition region. The studies involved both polyisoprene homopolymers, (Fig. 1a) [1], polyisoprene/polystyrene block copolymers with monoionic (Fig. 1b) or zwitterionic functionality (Fig. 1c) [2]. The confinement of the multiplets in the polyisoprene layers of the lamellar phase of the block copolymer and in the polyisoprene/polystyrene interface of the zwitterion lead to clear signatures on the slowest microsecond timescale, whereas they affect dynamics on faster timescales to a much smaller extent.

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FIG. 1: The spin probe attached to the ionic clusters of the polyisoprene homopolymers (a), the polyisoprene/polystyrene block copolymers with monoionic (b) or zwitterionic functionality (c). In case (b) the cluster is confined in the polyisoprene layers of the lamellar phase of the block copolymer. In case (c) the cluster is confined in the polyisoprene/polystyrene interface.

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Dynamic criticality and glass formation

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We summarize the results obtained in a recent series of papers [1–4] where a new theoretical approach to the dynamics and thermodynamics of supercooled liquids and glass formation has been proposed and studied in detail. Although the main ingredients and corresponding simple models have been in the literature for some time [5], it was realized only recently that they contain an extremely rich physics that can be studied to the point that quantitative predictions can be made and confronted to experimental or numerical results.

Our approach relies on two simple ingredients that can be very simply incorporated in a variety of models, generically called "kinetically constrained models" [5]. These are: (i) spatially sparse mobility within a supercooled liquid since most particles are caged by their neighbours; (ii) dynamic facilitation, which expresses the fact that mobility in a localized region tends to excite mobility in a neighbouring region.

The emerging physical picture is illustrated in Fig. 1 where a typical time evolution of mobile/immobile regions represented as black/white dots in the equilibrium dynamics of the one-dimensional version of the Fredrickson-Andersen model [5] at relatively low temperature. This figure strikingly reveals that trajectories of the system are made of spatio-temporal domains of immobility (white surfaces) delimited by mobility excitations (black lines). We have invented the word "bubbles" to describe these domains.

Even at the qualitative level, this bubble picture of the dynamics of supercooled liquids has far-reaching consequences since it explains in a very transparent way the canonical features observed in liquids approaching the glass transition including (i) stretched relaxations; (ii) strong-fragile kinetic and thermodynamic behaviours; (iii) absence of increasing static



FIG. 1: Representative trajectory of the time evolution of mobile (black) and immobile (white) regions in the onedimensional Fredrickson-Andersen lattice model. Vertical direction is space, horizontal direction is time.



FIG. 2: Molecular dynamics verification of a new universal scaling behaviour between a four point dynamical susceptibility χ and the relaxation time τ for various temperatures and physical observables predicted by the theoretical approach described in this talk.

correlations; (iv) existence of dynamic heterogeneity and decoupling phenomena.

It is possible to derive a field theory from the two above physical ingredients that can be studied by the renormalization group. This had led us to propose that the physics of supercooled liquids is governed, as in our theoretical approach, by the existence, at zero temperature, of a dynamic critical point where the temporal and spatial extension of the bubbles in Fig. 1 diverges. Dynamic criticality appears below some onset temperature, T_{onset} , which marks the appearance of dynamic heterogeneity with no other relevant "crossover", "singularity", or "avoided singularity" temperature scale in the problem. This results in a number of quantitative predictions that are supported by numerical simulations, see Fig. 2. Interestingly, this new picture is in qualitative disagreement on some important aspects with most of the alternative theoretical approaches to the glass transition problem, and a careful reading of the literature is favorable to our approach.

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Energy landscape interpretation of critical slowing down in simple liquids

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The enormous increase of viscosity, relaxation times or inverse diffusivity upon cooling in supercooled liquids has been successfully described in the idealized mode-coupling framework [1] as the approach to a dynamical arrest point separating an ergodic to a nonergodic phase. Several works have attempted to connect this dynamic slowing down to the characteristics of the visited Potential Energy Landscape (PEL), defined by the total potential energy function in the 3Ndimensional configuration space. The main question is to find a clear topological change in the PEL related to the transition temperature $T_{\rm MCT}$.

A recent PEL approach [2, 3] has opened the possibility to find a direct numerical observation of the critical slowing down. It is based on the investigation of saddles in the PEL, extending the usual partition in basins of inherent structures (minima) to a generalized partition including saddle points. The way saddles are found is based on a minimization procedure of the pseudo-potential $W = |\nabla V|^2$ (V is the total potential energy): absolute minima of W correspond to saddle points of V. The fact that the majority of sampled minima of W are local minima (corresponding to points in the PEL with an inflection direction) can in principle invalidate the proposed partition of the PEL. However, it is numerically found that this pathology does not affect the results: analyzing true saddles alone (absolute minima of W) or also local minima (we propose the name *quasisaddles* for them) one finds exactly the same behaviors.

The main finding of this PEL approach is shown in Fig. 1, where the temperature dependence of the fractional order n_s at saddle points (the fractional number



FIG. 1: Temperature dependence of the fractional saddle order n_s for a Lennard-Jones model. The value of $T_{\rm MCT}$ for this model is also reported. In the inset the quantity n_s is shown for different model systems investigated, as a function of the reduced temperature $T/T_{\rm MCT}$.

of negative downward curvatures – negative eigenvalues of the Hessian) is reported for a Lennard-Jones model: a well defined T-dependence that extrapolates to zero close the mode-coupling temperature T_{MCT} . A landscape-based description of dynamical structural arrest follows immediately: T_{MCT} marks a crossover in the visited landscape between a saddle-dominated to a minima-dominated dynamics. The fact that the above findings are also found in mean-field p-spin glass models [4] (that are supposed to behave very similar to structural glasses), gives support to the above landscape interpretation of the dynamical arrest.

The analysis of the saddles in the PEL has been also useful to obtain important information about elementary energy barriers (height of order-1 saddles from underlying minima), responsible for the activated dynamics below $T_{\rm MCT}$. The relationship between saddlebarriers and the effective barriers dominating the very low-T dynamics is still an open question. Preliminary results indicate a quantitative relation between them.

A recent saddle-based investigation [5] of different model systems has revealed the existence of a kind of universal shape of the various landscapes: plots for different systems superimpose into master curves once energies and temperatures are rescaled by $T_{\rm MCT}$ (inset in Fig. 1). This allows to establish a quantitative relationship between $T_{\rm MCT}$ and the energy barriers, at least for the model systems analyzed.

The investigation of quite different systems (as for example models with different form of the repulsion pair-potential) could give a better understanding of the above findings.

Moreover one could ask if the landscape concepts introduced in the supercooled liquid investigation (as the saddle-based analysis reported here) are relevant also for the understanding of the rich phenomenology exhibited by colloids, once a suitable PEL is defined for these systems.

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Relation between dynamic slowing down and the (isobaric/isothermal) reduction of excess entropy in glass-forming systems

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According to the Adam Gibbs (AG) model [1] the dynamic slowing down of glass-forming systems can be explained in terms of reduction of the number of available configurations, due to the increasing size of the cooperatively rearranging regions (CRR). So, the configurational entropy SC, i.e. the total entropy of the system apart from the vibrational contribution, was singled out as the key quantity linking dynamics to thermodynamics. The relation $\log(\tau) \propto$ $1/(TS_C)$, predicted by the Adam-Gibbs model, was confirmed by recent numerical simulations [2]. On the other hand, a similar relation was also experimentally proved for several glass-formers at atmospheric pressure in the temperature range between T_q and $1.2 T_q$ [3], but replacing configurational with an experimentally accessible quantity, such as the excess entropy $S_{\rm exc}$ of the melt with respect to the crystal. These results lead to the statement that a proportionality factor must exist between configurational and excess entropy at least along an isobaric reduction. Nevertheless, a heated debate exists in literature concerning the proportionality of configurational and excess entropy and the validity of AG model [4].

Recently, we derived from the Adam Gibbs (AG) model a new equation [5] able to successfully describe the simultaneous temperature-pressure (T-P)scaling of structural relaxation times for several glassformers [5] by using the value of excess entropy determined in the T-P space. In the present study, by making use of both calorimetric and expansivity measurements, S_{exc} was accurately determined over the whole investigated T-P range, allowing a direct comparison with the dielectric relaxation times [6]. The AG relation was proved valid over a broad range of temperature and pressure for simple molecular (o-terphenyl, triphenylchloromethane, glycerol, salol, phenolphtalein dimethyl ether, diphenyl carbonate, epoxy resins) and polymeric (oligomers and derivatives of propyleneglycol; polymethylmethacrylate) glass forming systems, along both isobaric and isothermal paths of entropy reduction. Moreover, our analysis showed that a bilinear relation exists between S_C and S_{exc} , with different proportionality factors (g_P and g_T) in isothermal and isobaric conditions [6]. The ratio g_T/g_P is a constant over the wide T-P range investigated and its value is nearly 0.7 for all the systems. A ratio g_T/g_P smaller than one is reasonably expected, since a compression should reduce more effectively the configurational entropy of the system than a cooling under the same variation of S_{exc} .

Final remarks of the present study concern an extension of the PEAG model in order to take into account many-body effects as indicated by recent developments of the coupling model (CM) by K. L. Ngai [7]. Concerning this issue, new experimental results evidenced a strong connection between the "primitive" and the non-cooperative Johari-Goldstein slow β -relaxation over a wide temperature and pressure interval.

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Hyperquenching strategies for researching the energetics and dynamics of glassforming liquids, liquid-liquid transitions, and folding proteins

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We describe studies, both laboratory and simulation, that take advantage of the intrinsic slowness of relaxation to arrest liquids, and related solutions of biomolecules, in unusually "excited" (high potential energy) states by hyperquenching. After such trapping at high "fictive" temperatures we observe vibrational, structural, and energetic properties as the system evolves at low temperatures, during a controlled annealing procedure. In this manner, events that normally occur during change of temperature may be observed occurring during passage of time, at much lower temperatures. At these low temperatures, the smearing effects of vibrationally excited modes may be greatly reduced.

We find that the high fictive temperature states are characterized by short relaxation times (already known) and considerably more intense boson peaks (less well known) [1]. The thermodynamic consequences of the increased populations of these low frequency modes are examined with the help of computer simulation and normal mode calculations on model glassformers. Behavior in the vibrational DOS at constant pressure is strikingly different from that at constant volume. For glassformers that can exhibit liquid-liquid transitions, one can use the cold equilibration approach to determine the fragility of the high temperature phase, and the enthalpy of the liquid-liquid transition, see Ref. [2].

Finally, for solutions of complex molecules with interesting internal molecular transitions, such as proteins, we can quench in the unfolded states and then, using special non-crystallizing solvents, observe the molecular reorganization to low energy states as it occurs at temperatures far below the normal folding temperature [3]. We describe the "toboggan run" to the folded state characteristic of lysozyme and note, tentatively, some evidence for a "sudden start" to the folding process.

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Dynamical heterogeneities and mobility propagation in viscous liquids

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We use molecular dynamics simulations to study the spatial heterogeneous nature of dynamics in viscous liquids near the critical temperature of the modecoupling theory (MCT), T_{MCT} [1]. In particular, the development of regions containing highly mobile particles and the propagation of the mobile state through space are analyzed. To gain broad knowledge, we compare results for a simple monoatomic liquid derived from the Dzugutov potential [2] and for BKS silica, which shows a crossover from fragile to strong behavior at the studied temperatures [3, 4]. In addition, we investigate a binary Lennard-Jones (BLJ) mixture using a potential energy landscape (PEL) approach.

For BKS silica and the Dzugutov liquid, we find that highly mobile particles during a time interval Δt form clusters that grow upon cooling. At a given temperature, the mean cluster size shows a maximum at times t_C in the late- β /early- α relaxation regime of the MCT. String-like motion, where groups of particles follow one another along a quasi onedimensional path, is a very important channel of relaxation for highly mobile particles in the Dzugutov liquid, whereas it is less important in silica. Thus, this dynamical pattern may be suppressed by the presence of covalent bonds. The transient nature of the strings in both systems is characterized by a maximum of the mean string size at times $t_S \approx t_C \ll \tau_{\alpha}$. These findings for the peak times are consistent with previous results for BLJ mixtures [5] and a polymer melt [6]. Hence, spatially heterogeneous dynamics in various viscous liquids near T_{MCT} show comparable features. To investigate the development of strings in the Dzugutov liquid, we observe the relaxation steps of the individual particles in the strings. For a substantial number of strings, we find nearly simultaneous jumps of 2 to 4 particles, say. As a consequence, the motion within short strings shows a high degree of coherence. For long strings, the motion within small groups of particles is coherent, but different groups or individually jumping particles are active at subsequent times.

Garrahan and Chandler [7] proposed that dynamics in supercooled liquids can be understood via the existence of spatially heterogeneous dynamics and the facilitation of dynamics in the vicinity of mobile regions. Here, we identify the mobile particles in silica during back-to-back time intervals $t_{12} = \Delta t$ and $t_{23} = \Delta t$. It is shown that less than 20% of the mobile particles in t_{12} are still mobile in t_{23} , indicating a short lifetime of this dynamical state. To gain insights into the propagation of mobility, we analyze the probability that a neighbor of a mobile particle during t_{12} becomes mobile during t_{23} . As compared to a random selection of mobile particles, this probability is enhanced by a fac-



FIG. 1: $F(\Delta t)$ characterizing the strength of dynamic facilitation together with the mean cluster size $C(\Delta t)$ and the mean string size $S(\Delta t)$ for the oxygen atoms in silica at T = 3385K.

tor of up to $F(\Delta t) \approx 2$ and, hence, there is evidence that dynamics in the vicinity of mobile particles is facilitated. The effect of dynamic facilitation is maximum at times $t_F \approx t_S \approx t_C$, see Fig. 1, and becomes more pronounced upon cooling. Preliminary results suggest a similar behavior for the Dzugutov liquid.

The PEL of supercooled BLJ mixtures exhibits local minima, or inherent structures (IS), which are organized into meta-basins (MB). We study the particle rearrangements related to IS and MB transitions. We show that IS and MB dynamics are spatially heterogeneous. In particular, "successful" string-like motion enables the system to exit a MB where the mechanism of string formation is comparable to the one observed for equilibrium liquids. Further, we find that the particle rearrangements during two consecutive MB transitions are basically uncorrelated. Specifically, different groups of particles are highly mobile. The relation of IS and MB dynamics to our findings for the equilibrium liquids and to experimental results for the α and slow β -process are discussed.

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Inhomogeneous shear-thickening and rheological instability

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In recent work [1], a very simple model was developed that shows temporal instability in a shear thickening systems with structural memory. This model is inspired by, but not limited to, dense colloidal suspensions in which continuous or discontinuous shear thickening is found, and seems to be accompanied experimentally by a transition to unsteady flow [2], in which steady stress leads to an erratic shear rate or vice versa. The model is scalarized (one shear stress component instead of a stress tensor) and involves an instantaneous nonlinear relaxation and a delayed linear one. These are arranged so that that the flow curve (stress vs. strain rate) would be nonmonotonic (and hence unstable) were it not for the delayed term. If the delay is too long, what appears like a stable flow curve remains unstable to finite frequency perturbations, and spontaneous oscillation sets in.



FIG. 1: Upper figure: Steady-state flow curve (thick line) and underlying short-term curves in a shear thickening model. The latter have negative slopes and would be unstable (to shear banding) if this was the steady state behaviour. Lower figure: very irregular (though periodic) time series of the total stress $\Sigma(t)$ for $\langle \dot{\gamma} \rangle = 4.0$. This is caused by erratic motion of the bands.

The model of [1] contains no spatial coordinates and therefore cannot describe states in which the flow varies in space as well as time. In this work, we extend the model by adding square gradient terms describing stress diffusion. This allows nontrivial spatiotemporal structure to develop [3], and generically this replaces the homogeneous temporal instability of the earlier model. In most cases the resulting behaviour takes the form of 'shear banding' in which layers of viscous and less viscous material form perpendicular to the flow direction (vorticity banding).

Note that this occurs even for parameter values where the steady flow curve is monotonic, whereas the classical scenario of steady state bands requires nonmonotonicity. Indeed the bands we find are always in motion, and a variety of oscillatory patterns, some very complex, can arise (see figure). The issue of whether these patterns can degenerate further into chaotic dynamics (rheochaos) will be addressed. So far there is evidence of rheochaos, but only in quite limited regions of parameter space.

Experimental data strongly resembling rheochaos has been observed in a variety of shear-thinning and shear-thickening systems in recent years [4], and will be discussed if time permits, as will related work by Fielding and Olmsted [5] which addresses a somewhat different rheochaotic scenario. (The latter is a shearthinning model with a nonmonotonic flow curve, in which one of the two bands is destabilized by a memory term.)

The work has benefited from discussions with S. Fielding.

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Goldstone fluctuations in the amorphous solid state

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Goldstone modes in the amorphous solid state, resulting from the spontaneous breaking of translational symmetry due to random localisation of particles, are discussed. Starting from a microscopic model with quenched disorder, the broken symmetry is identified to be that of relative translations of the replicas. Goldstone excitations, corresponding to pure shear deformations, are constructed from long wavelength distortions of the order parameter. The elastic free energy is computed, and it is shown that Goldstone fluctuations destroy localisation in two spatial dimensions, yielding a two-dimensional amorphous solid state characterised by power-law correlations.

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Slow Dynamics of the Complex Fluid, Liquid Water

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Recent experimental and theoretical investigations highlight the central importance of supercooled and glassy states for understanding liquid water, and provide a body of knowledge from which a coherent interpretation of its properties may possibly emerge in the future. For recent reviews, cf. Ref. [1].

Here, I will review some highlights of recent work, experimental [2] and using computer simulations [3]. I will also discuss recent attempts [4] to understand cooperative phenomena in water by investigating the spatially heterogeneous dynamics in the SPC/E model of water by using molecular dynamics simulations [5]. We relate the average mass n^* of mobile particle clusters to the diffusion constant and the configurational entropy. Hence, n^* can be interpreted as the mass of the "cooperatively rearranging regions" that form the basis of the Adam-Gibbs theory of the dynamics of supercooled liquids. Finally, we examine the time and temperature dependence of these transient clusters.

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Gelation in Laponite clay suspensions

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In this work we present a new dynamic light scattering study on different laponite samples at increasing clay concentrations (C_w) from 0.3 to 3 wt % at fixed ionic strength of 10^{-4} M. According to the phase diagram [1] at this ionic strength Laponite can be in two different physical states. Low concentration suspensions $(C_w \lesssim 1.8 \text{ wt \%})$ form a stable, equilibrium fluid phase. Intermediate concentration suspensions $(C_w \gtrsim 1.8 \text{ wt \%})$ are initially fluids, but experience aging and pass into a gel phase after a time that depends on the clay concentration [2-4]. To try to understand the gelation mechanism for this charged colloidal system we have performed accurate and systematic measurements on several samples starting in the low concentration region and increasing clay concentrations.



FIG. 1: Autocorrelation functions (circle points) and corresponding fits with Eq. (1) (continuous lines) for two different samples at increasing waiting times t_w . The waiting times (from left to right) are $t_w=288$, 792, 1128, 1464, 1632, 1800, 1968, 2136, 2328, 2640 hours for sample (A) and $t_w=6$, 30, 54, 78, 102, 126, 150 hours for sample (B).

Autocorrelation functions at increasing aging times t_w for two different samples, one in the low concentration region (Fig. 1a; at $C_w = 1.1$ wt %) and the other one in the higher concentration region (Fig. 1b;

at $C_w = 2.5$ wt %), are reported in Fig. 1. From Fig. 1 it is evident that both samples show aging, a surprising behaviour for the low concentration sample where the state expected is the stable liquid one [1, 4]. Fig. 1a also shows that for the longest waiting time reported (t_w =2640 hours) there is a dramatic change in the autocorrelation function: a crossover between a complete and an incomplete decay, indication of a strong ergodicity breaking and signature of a sol-gel transition. Our dynamic light scattering measurements show that for all the samples studied, up to the lowest concentrated one at $C_w = 0.3$ wt %, there is a typical waiting time, t_w^{∞} , increasing with decreasing clay concentration C_w , at which the system becomes a gel. These measurements indicate that a revisitation of the phase diagram is necessary, suggesting that the equilibrium state also at low clay concentrations is not the liquid but a very fragile gel that takes a long time to appear.

Two different relaxation times, a fast and a slow one, are evident in the autocorrelation functions reported in Fig. 1. In order to describe the two processes quantitatively, $g_2(q,t) - 1$ has been fitted by

$$g_2(q,t) - 1 = (A \exp(-t/\tau_1) + B \exp(-(t/\tau_2)^{\beta}))^2.$$
 (1)

The fits describe the data very well for all the aging times in the liquid (ergodic) phase, as shown in Fig. 1 where they are reported as continuous lines. The fit parameters confirm that the aging process is different for low and intermediate investigated concentrations, as already evident from the comparison of the raw data reported in the two panels of Fig. 1.

The τ_{mean} of the slow relaxation contribution obtained from the fit analysis permits to study the gelation process. In particular the important parameters of the aging, as the gelation waiting time t_w^{∞} , are obtained through a fit of τ_{mean} with a phenomenological law. A scaling law for all the samples at low concentrations is found. A strong indication of a different gelation mechanism for the low ($C_w \lesssim 1.8 \text{ wt \%}$) and intermediate ($C_w \gtrsim 1.8 \text{ wt \%}$) concentration samples is also found.

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A binary colloidal mixture in 2D: An ideal model system for the glass transition

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In the solidification of liquids, crystallization competes with the glass transition. In general, for slow cooling rates crystallization occurs, while a quenched system solidifies in a glassy state. Thus, most materials are available also as glasses which can be described as a solid with liquid-like structure and frozen-in particle dynamics. However, the physical properties of the various glass formers in the supercooled melt, for the glassy state and at the glass transition itself are mostly comparable in spite of the completely different particle interactions [1]. Hence, one might speculate that general features of the glass transition are present in each type of glass formers. Thus it would be satisfactory to explain a glass property for only one single 'model system' in order to understand this attribute for all other glass formers. Using the following line of arguments, we describe several static and dynamic properties of the microscopic structure for a special glass former before postulating that these statements can be transferred to other glass formers.

We investigated a binary two-dimensional (2D) colloidal glass former with a repulsive dipole-dipoleinteraction [2]. During the experiment, the two differently sized superparamagnetic PMMA colloidal particles moved freely on a completely flat water-air interface of hanging droplet geometry, confined to 2D due to gravity. In the suspension, the big (b) and small (s) colloids interacted with their induced magnetic moments, tunable by a homogeneous external magnetic field B, which was applied perpendicular to the water-air interface. The time-dependent particle coordinates were determined by video-microscopy.

During an experiment the room temperature, T, the number density, ρ , the ratio, ξ , of the number n_s of sparticles to the number $(n_b + n_s)$ of all colloids as well as the magnetic susceptibilities $\chi_b = 6.2 \cdot 10^{-11} \text{ Am}^2/\text{T}$ and $\chi_s = 6.6 \cdot 10^{-12} \text{ Am}^2/\text{T}$ of the b and s colloids remain constant. Hence, only B controls the strength of the particle repulsion by the parallel aligned induced magnetic moments. The system is characterized by an interaction parameter, $\Gamma(B)$, that consists of the magnetic energy E_{magn} divided by $k_{\text{B}}T$, given by [2]:

$$\Gamma = \frac{E_{\text{magn}}}{k_{\text{B}}T} = \frac{\mu_0 \sqrt{\pi}}{4} \frac{B^2 \rho^{3/2}}{k_{\text{B}}T} \left(\xi \chi_s + (1-\xi)\chi_b\right)^2.$$
(1)

In order to study the amorphous structure microscopically we calculated three-point correlation functions under the condition that the two fixed particles are defined as nearest neighbors [3]. The distribution of b and s third particles in their vicinity allowed to distinguish for each 3-particle combinations one local density-optimized idealized structure, which we call elementary triangles (ET).

We also distinguished the smallest particle arrange-

ments in the monolayer [3], which are triangles of nearest neighboring particles (TNNP) in 2D, additionally separated into subcategories for the different 3-particle combinations of b and s colloids. Their angle distributions show that the maximum positions are located at the values of the corresponding ET and that for decreasing system temperature the distributions of the geometric properties of the TNNP become sharper, i.e. more ET-like.

Tilings of the different ET describe the complex short-range order in the amorphous 2D sample [3]. Additionally, random tilings of the different ET in the monolayer will not fill up the monolayer completely. Therefore, structural frustrations occur for the TNNP due to the repulsive interaction. Thus, the loss of long-range order in the partial radial pair-distribution functions can be understood by the increasing number of possible ET-combinations with increasing pairdistances as well as by the structural frustrations.

The microscopic structure has been investigated time-dependently by analyzing the modifications of the TNNP [3]. It could be shown that the heterogeneous dynamics in supercooled liquids is related to cooperatively moving regions of stable particle configurations. However, the structural relaxations in the sample take place where the TNNP drastically change their shape in time. This statement is directly connected to the observation that hopping processes are responsible for the increase of the mean-square displacements directly after the plateau, i.e. when the cage-effect starts to weaken.

These structural analyses led us to a novel description of the glass transition. There we qualitatively identify the glass transition by a percolation of stable ET-like TNNP, which form a local density-optimized frame through the whole sample with embedded locally separated less-densely-packed regions of small dimensions and of frozen particle dynamics. We call this approach to the glass transition the *concept of local density-optimized crystallite clusters* [3].

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Gravity and the glass transition in colloidal hard spheres

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The influence of gravity on the mobility of concentrated colloidal suspensions (close to and beyond the glass transition) was investigated by means of realspace fluorescent recovery after photo bleaching, using a confocal scanning laser microscope (CSLM). Our observations indicate a qualitative and quantitative influence of gravity on the long time behavior of the mean square displacement in colloidal glasses.

This is surprising, as the gravitational lengths in the systems are never smaller than many particle diameters. The differences are caused by the time scales in which the systems age: hard sphere glasses in a gravity field age much faster than systems where gravity is negligible.

In systems below the glass transition density, gravity plays no measurable role. This observation qualitatively explains why it is that colloidal systems that are a glass on earth are found to crystallize rapidly in microgravity [1].

If time permits I will also present recent results on the structure and dynamics of concentrated colloidal suspensions near a hard wall. Upon increasing the volume fraction of the colloids, a reentrant phase transition involving an hexatic phase is observed. This behavior is dramatically different from the situation in the bulk (i.e., far away from a wall) and may be a reflection of the two dimensional character of dense matter near walls.

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Cluster and slow dynamics in gelling systems

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At the gelation transition a viscous liquid transforms to an elastic disordered solid. In general this corresponds to the formation of a spanning structure which makes the system able to bear stress. In polymer systems the structure formation is due to chemical bonding, producing a polymerization process [1]. The gelling system typically displays critical power law behaviour in the viscoelastic response and slow dynamics [2]: The relaxation functions show at long times a stretched exponential decay and at the gel point the relaxation process becomes critically slow.

In colloids a strong short range attraction gives rise to a diffusion limited cluster-cluster aggregation process with a gel formation (colloidal gelation) at very low density as a spanning structure is formed [3]. The latter is generally quite different from the one of polymer gels, whereas the viscoelastic behaviour is very similar.

A weaker attraction in colloids is not able to produce a permanent gel but the formation of stable or metastable structures is still detected together with a slowing down in the dynamics [4].

At high densities the short range attraction is able to enhance the caging effect typical of the glassy regime, and to produce a glass-like kinetic arrest at density values lower than the hard-sphere case, and depending on the strength of the attraction [5]. Therefore, for different values of the attraction strength and of the density, colloidal systems should eventually cross over from a gel-like to a glass-like behaviour. How this takes place and which is the role of the formation of stable or metastable structures is still not clear.

In order to investigate this problem we have introduced a minimal model for gelling systems and studied the dynamic behavior by means of numerical simulations [6]. Our results suggest the following scenario: In a gelation phenomenon with permanent bond formation (chemical gelation or irreversible cluster aggregation) the divergence of the relaxation time is due to the formation of a macroscopic critical cluster and the decay of the autocorrelation functions is directly related to the relaxation of such spanning cluster. In the case of non permanent bonds the relaxation time increases due the formation of effective clusters. The size of these effective clusters due to the finite lifetime does not diverge and the relaxation time exhibits a pseudo divergence corresponding to a state which we call pseudo gel or soft gel. As the density increases the clusters will get crowded until a glass transition of clusters is reached. However, in the low density region in general the pseudo-gel and the glass of clusters will interfere with the phase separation curve.

Preliminary results based on molecular dynamics simulations of colloidal hard sphere particles interacting via a DLVO potential will also be discussed within this scenario, in comparison with experimental observations and recent theoretical works [7, 8].

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Flow of Depletion Gels: Comparisons of Theory and Experiment

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Descriptions of the mechanical properties of colloidal gels have largely focused on the mechanics of fractal networks as the basis for explaining the values of exponents in power laws observed in dependencies of yield stresses, and elastic moduli with increasing particle volume fraction. The concepts that colloidal gels consist of interpenetrating fractal aggregates stems from studies at low volume fraction where in diffusion and reaction limited aggregation the resulting particles are fractal in nature.



FIG. 1: Elastic modulus of depletion gels $(R_g/R = 0.078)$ as a function of colloid volume fraction for different values of reduced polymer concentration. The points are experimental data measured at 1Hz and the solid lines are calculations of elastic moduli from MCT-PRISM-2.

Within these fractal models, moduli are predicted to depend on a product of a spring constant and particle volume fraction raised to some exponent. The exponent is predicted on the basis of the fractal microstructure.

In this work, we describe our studies of the mechanics and microstructure of gels produced by the addition of nonadsorbing polymer to hard sphere suspensions and make comparisons with a microstructurally based model where mechanical properties arise from local interactions. This model uses Naive Mode Coupling Theory (MCT) with the two-component nondilute polymer reference site model (PRISM) predictions of the static structure factor (MCT-PRISM-2) [1,2]. MCT is a microscopic local theory that describes particle localization or the elementary bond formation process between a pair of particles. Excellent agreement between theory and experiment is found for the volume fraction and polymer concentration dependence of the elastic modulus.

These results suggest in opposition to fractal microstructure based models in dense gels, power law dependencies of elastic moduli on volume fraction and on strength of attraction result from changes in strength of pair interaction and particle localization distances and not from changes in suspension microstructure.

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Dynamical Localization of Shear in Structured Matter with Disorder

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We offer a perspective for the discussion of the atomistic mechanisms of local shear transformation in ordered and disordered media. Beginning with the affine shear of a single crystal which induces the homogeneous nucleation of slip (dislocation or twinning), we ask what would be the corresponding 'unit process' in the presence of disorder, that is, if the system were instead an amorphous medium, where disorder is distributed throughout, or a nanocrystal, where disorder is localized at the grain boundaries. We will consider molecular dynamics simulation results as reference (model system) behavior to explore possible connections between the current notions of shear deformation in the materials science community and the mechanistic understanding of dynamics of viscous liquids.

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The static yield stress and flow heterogeneity in a model glass: a molecular dynamics study

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Using molecular dynamics (MD) simulations, it was shown in [1] that, unlike Newtonian fluids, a simple model of a binary Lennard-Jones mixture [2] exhibits, at low temperatures, the shear thinning phenomenon (decrease of the viscosity with applied shear rate), commonly observed in many "soft glassy materials" [3]. In the present work, the rheological properties of this model are investigated further. In particular, two prominent new features are found [4, 5]: (i) under an imposed slow shear motion, the system separates into a fluidized shear-band and an unsheared part, see Fig. 1; (ii) when a small stress is imposed, the system does not flow until the stress exceeds a certain threshold value, the yield stress, $\sigma_{\rm v}$, see Fig. 2. Similar observations are also made in experiments on pastes, glass beads, dense colloidal dispersions [6], granular materials [7] and foams [8]. A link between the existence of a yield stress and the flow heterogeneity is suggested. The temperature dependence of the yield stress is studied and its behavior close to the mode coupling critical temperature of the model is discussed.

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FIG. 1: Shear localization in a Lennard-Jones glass. Filled symbols: rescaled velocity profiles, $u(z)/U_{wall}$, from 2 independent simulation runs. In both cases, the left wall is moved with a constant velocity $U_{wall} = 3.33 \times 10^{-3}$ $(\dot{\gamma}_{tot} = 0.83 \times 10^{-4})$. Due to Galilean invariance, the sheared region may be located at either the moving or immobile wall. Open diamonds correspond to a much higher shear rate of $\dot{\gamma}_{tot} = 0.83 \times 10^{-2}$ showing that, at sufficiently high shear rates, the whole system is "fluidized". All quantities are measured in Lennard-Jones units (from [4]).



FIG. 2: The maximum velocity in the system, U_{max} , measured in the layer of closest approach to the left wall during simulations of a binary Lennard-Jones glass for $T = 0.2 < T_c = 0.435$ at imposed stress. The stress is increased by an amount of $d\sigma = 0.02$ once in 4000 LJ time units and U_{max} is measured between two subsequent stress increments. The horizontal dotted line marks the thermal velocity of the wall. Note the sharp increase in U_{max} when changing the stress from $\sigma = 0.6$ to 0.62. Inset: rescaled velocity profiles, $u(z)/U_{\text{max}}$, measured during the same simulations for stresses in the flow regime (for which $U_{\text{max}} \ge U_{\text{thermal}}$). Obviously, once the flow sets in, a linear velocity profile is formed across the system (from [5]).

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Supercooled Liquids under Shear: A Computational Approach

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In the present study [1], we calculate intermediate scattering functions by using the method proposed by Onuki [2] to investigate microscopic dynamics of glassy materials in shear flow. Simulations have been done in 2D to compare the present computational results directly with the theory developed recently in 2D [3]. Our model system is composed of two different particle species 1 and 2, which interact via the soft-core potential $v_{\alpha\beta}(r) = \epsilon (\sigma_{\alpha\beta}/r)^{12}$, $\sigma_{\alpha\beta} = (\sigma_{\alpha} + \sigma_{\beta})/2$, where r is the distance between two particles, and $\alpha, \beta \in 1, 2$. We let the mass ratio $m_2/m_1 = 2$, the size ratio $\sigma_2/\sigma_1 = 1.4$, and the numbers of particles $N_1 = N_2 = 5000$. Simulations were performed in the absence and presence of shear flow with particle density and temperature fixed at $n = (N_1 + N_2)/V = 0.8/\sigma_1^2$ and $k_B T = 0.526\epsilon$, respectively. In the sheared case, we kept the temperature at a constant using the Gaussian constraint thermostat to eliminate the viscous heating effect. Our method of applying shear is as follows: The system was at rest for t < 0 for a very long equilibration time and was then sheared for t > 0. Here we added the average velocity $\dot{\gamma}y$ to the velocities of all the particles in the x direction at t = 0 and afterwards maintained the shear flow by using the Lee-Edwards boundary condition. Simulation data have been taken and accumulated in steady states which can be realized after transient states.

Figure 1a shows the geometry of shear flow in the present simulation. As shown in Fig. 1b, shear flow with the rate $\dot{\gamma}$ advect a positional vector \mathbf{r} as $\mathbf{r}(t) = \mathbf{r} + \dot{\gamma} t r_y \mathbf{e}_x$ in the time duration t, where \mathbf{e}_{α} is a unit vector in $\alpha \in x, y$ axis. A similar advection can be defined in Fourier space for a wave vector \mathbf{k} as

$$\mathbf{k}(t) = \mathbf{k} - \dot{\gamma} t k_x \mathbf{e}_y. \tag{1}$$

The above definition enable us to calculate Fourier component \mathbf{k} of the time correlation function in shear flow. We calculated the coherent scattering functions by using the definition

$$F(\mathbf{k},t) = \frac{1}{N} \left\langle \sum_{i=1}^{N} e^{[-i\mathbf{k}(t)\cdot\mathbf{r}_{i}(t)]} \sum_{j=1}^{N} e^{[i\mathbf{k}\cdot\mathbf{r}_{j}(0)]} \right\rangle, \quad (2)$$

respectively. To examine anisotropy in the dynamics, the wave vector is taken in four different directions with

$$\mathbf{k}_{\alpha\beta} = \frac{k}{\sqrt{\alpha^2 + \beta^2}} (\alpha \mathbf{e}_x + \beta \mathbf{e}_y), \qquad (3)$$

k = 5.8, and $\alpha, \beta \in 0, 1$.

Figure 2 shows $F_{\rho\rho}(\mathbf{k},t)$ at T = 0.526 with and without shear flow. Here the subscript ρ denotes the

linear combination of smaller and larger particle components corresponding to the *density* of an effective one component system. The following has been found: (i) Shear accelerates drastically the microscopic structural relaxation in the supercooled state. The structural relaxation time τ_{α} decreases strongly with increasing shear rate as $\tau_{\alpha} \sim \dot{\gamma}^{-\nu}$ with $\nu \sim 1$. (ii) The acceleration in the dynamics due to shear occurs almost isotropically. There observed surprisingly small anisotropy in the correlation functions even in extremely strong shear $\dot{\gamma}\tau_{\alpha} \simeq 10^3$. This simplicity in the dynamics is quite different from behaviors of other complex fluids such as critical fluids or polymers in shear. Finally we note that the recent mode-coupling theory in shear flow predicts almost the same behaviors [3].



FIG. 1: (a) Geometry of shear flow. (b) Shear advection in real space. (c) Shear advection in Fourier space.



FIG. 2: Intermediate scattering functions under shear. (a) \mathbf{k}_{10} , (b) \mathbf{k}_{11} , (c) \mathbf{k}_{01} , and (d) \mathbf{k}_{-11} are defined in Eq.(3).

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Properties of dense colloidal dispersions under shear: non-linear regime

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Soft materials, such as particle dispersions, exhibit a wide range of rheological properties [1]. While dilute colloids flow with a viscosity only slightly higher than that of the solvent, concentrated dispersions behave as weak amorphous solids and elastically withstand (small) finite stresses. For intermediate concentrations, one generally observes, upon increasing the external shear rate, a strong decrease of the dispersion viscosity ('shear thinning'). While shear induced 'layering' of particle suspensions causes a marked decrease of the viscosity, shear thinning is not always accompanied by a flow-induced ordering. In shearthinning concentrated suspensions of polydisperse colloidal particles the structure remains amorphous during the application of shear. Therefore a mechanism explaining the reduction of the viscosity in disordered systems needs to be discovered.

The framework of linear response theory cannot be used, because the effect of the external driving on the microstructure and its dynamics needs to be understood. The connection to 'glassy melts under strong external drive' arises. We report on the development of such a framework for the non-linear response at arbitrary shear rates. Fundamental starting point is the 'Smoluchowski equation' for the time-evolution of the many-body distribution function Ψ which depends on all of the N particles' coordinates \mathbf{r}_i (with dilute diffusion coefficient D_0 and interparticle forces \mathbf{F}_i):

$$\frac{\partial}{\partial t}\Psi = \Omega^{(\dot{\gamma})} \Psi \tag{1}$$
$$\Omega^{(\dot{\gamma})} = D_0 \sum_{i=1}^N \left[\frac{\partial}{\partial \mathbf{r}_i} \cdot \left(\frac{\partial}{\partial \mathbf{r}_i} - \frac{\mathbf{F}_i}{k_B T} \right) - \dot{\gamma} \frac{\partial}{\partial x_i} y_i \right].$$

Simulations by Strating [2] of hard spheres show that Eq. (1) captures shear thinning in response to the imposed solvent flow, with constant gradient set by the shear rate $\dot{\gamma}$.

Exact projection operator techniques allow to derive general steady state quantities of the sheared system [3]. It is driven far from equilibrium because the shear-dependent term in Eq. 1 causes stationary fluxes, which are absent in thermal equilibrium. As standard 'fluctuation dissipation theorems' (FDT) are known to be violated under shear [4], an important aspect of the projection operator approach is that FDT is neither assumed nor predicted.

Of interest is, e.g., the transverse stress σ , which can be obtained from the stationary average of the microscopic stress tensor element, $\sigma = \langle \sigma_{xy} \rangle^{(\dot{\gamma})}$. It can be connected via an *exact generalized Green-Kubo* expression to the stress auto-correlation function averaged in the quiescent system $\langle \ldots \rangle^{(0)}$ but with $\dot{\gamma}$ dependent dynamics:

$$\sigma = \frac{\dot{\gamma}}{k_B T V} \int_0^\infty dt \ \langle \sigma_{xy} \ e^{\Omega^{(\dot{\gamma})\dagger} \ t} \ \sigma_{xy} \rangle^{(0)} \ . \tag{2}$$

Shear-thinning originates in an acceleration of the structural relaxation reducing the integral in Eq. (2).

In Ref. [3] we argue that advection of wavevectors is the physical mechanism how shearing accelerates the structural dynamics in dense dispersions. While this mechanism should be rather universal, for dense colloidal dispersions, the interesting question arises how it interferes with incipient solidification. Mode coupling approximations are required and lead to closed non-linear equations describing the structural relaxation under shear.



FIG. 1: Steady-state shear stress σ versus shear rate $\dot{\gamma}$ of temperature sensitive Latex colloids (from Ref. [5]) rescaled at high $\dot{\gamma}$ as labeled to eliminate effects of solvent induced interactions. Solid lines are fits using a schematic model from Ref. [3] with separation parameters: $\varepsilon = 0.003$, -0.04, -0.11, -0.20 & -0.32 (from top to bottom); units are converted by $\sigma = 5.8$ Pa $\sigma^{\rm th}$ and $\dot{\gamma} = 280 \, {\rm s}^{-1} \dot{\gamma}^{\rm th}$.

We present extensions of the approach to timedependent fluctuation functions, which allow to address FDT violation. Also, the universal transition between a shear-thinning fluid and a yielding glass will be discussed and compared to experiments on model colloidal dispersions. The qualitative features observed experimentally can be understood from schematic models which focus on the universal aspects, yet even provide a semi-quantitative description of the data, as shown in Fig. 1.

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Single Molecule Rotation in Supercooled Liquids

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One prominent feature of glass forming liquids is the pronounced non-Debye spectral density observed, e.g., in dielectric experiments. In the time domain, this corresponds to nonexponential correlation functions. For the primary process several explanations for the deviation from exponentiallity have been derived, however, details of its origin are still under controversial discussion.

Recently, a number of new experiments have been developed addressing this question. A typical assumption deals with subensembles of variably fast rotating molecules. Often, this kind of 'dynamic heterogeneity' is linked to spatial heterogeneity, although this is not mandatory.

Experimentally, by tracking, e.g., slow rotating subensembles in time, their relaxation back to the equilibrium bulk relaxation can be studied. In this context a new time scale, often called 'exchange' time, has been discussed.

The separation of rotation and exchange could be meaningful if both time scales are well separated, i.e. the exchange is significant slower than molecular rotation. However, from multidimensional NMR experiments on several low weighted organic glass formers and polymers it is found that both, the rotational correlation times and the 'exchange' times are on the same order of magnitude.

In contrast, several optical experiments have given indications for long living heterogeneities close to the caloric glass transition. Here it was found that slow reorienting molecules change to faster rotation and back on a time scale substantially slower than the averaged rotational correlation time.

In most of the experiments probing dynamic heterogeneity ensembles of molecules are monitored. An exception was presented recently by optical tracking of single molecule fluorescence. By analyzing the time dependent polarization of the emitted light of single fluorophores, time traces of molecular orientation could be recorded and analyzed. Again, significantly separated time scales for rotation and 'exchange' (i.e., change of the rotational correlation time) have been found.

We present single molecule studies on fluorophores in amorphous PDE (phenolphthalein-dimethylether) close to the caloric glass transition temperature. By using confocal fluorescence microscopy time traces could be recorded up to several hours. It is common to evaluate the time dependent polarization $P(t) = (I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp})$ in terms of auto-correlating P(t).

In addition to the experimental data, we analyze P(t) analytically and by discrete random walk computer simulations. Surprisingly, even the simplest model of isotropic rotational diffusion leads to non-exponential correlation functions, $C(\tau) = \langle P(t+\tau)P(t) \rangle$. A careful discussion of the dependence of C(t) on the mechanism (geometry) of molecular reorientation is presented [1].

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We report results of molecular dynamics simulations of diffusion both above and below the glass transition. The simulations are done for $Cu_{33}Zr_{67}$, described by a modified embedded potential, and for a binary Lennard-Jones type model glass. Earlier simulations of a soft sphere glass showed that atomic jumps in the glass are highly collective and correlated to quasi-localized vibrations [1]. Both the vibrations and the atomic jumps involve chains of atoms. Similar chain motion was subsequently observed in undercooled liquid $Cu_{33}Zr_{67}$ [2]. This collectivity of motion is in full agreement with experimental findings [3].

Constant pressure simulations of the diffusional isotope effect show that collectivity sets in well above both the glass transition and the mode coupling temperature, T_c . It is mainly driven by the densification upon cooling, but differs quantitatively for different components [4]. From the pressure dependence we find both in the glass and the undercooled melt apparent diffusional activation volumes of around 0.4 atomic volumes, Fig. 1 [5]. This low value is an indication of a collective process above and below T_c . At T_c the activation volume shows a pronounced cusp as predicted by mode coupling theory.

Up to temperatures not too far above T_c it is possible to identify single jumps. We calculated in both glassy and liquid Cu₃₃Zr₆₇ the distribution of jump lengths. It can be described by a temperature independent exponential of the length and an effective activation energy plus a contribution of elastic displacements at short distances. Upon cooling the contribution of shorter jumps dominates. No indication of an



FIG. 1: Calculated activation volume in a binary Lennard-Jones glass (majority *A*-atoms, diamonds, and minority *B*-atoms, circles) versus temperature. The dashed line is a fit with the MCT expression using a common critical temperature for both components.



FIG. 2: Distribution of jumps/second over jump length for Zr (top) and Cu (bottom). Temperatures from top to bottom: 1400, 1200, 1100, 1000 and 900 K. The dotted lines indicate the fit by an exponential jump length distribution, see text. The respective nearest neighbor distances for the two components are indicated by the vertical dotted lines.

enhanced probability to jump over a nearest neighbor distance was found. We find a smooth transition from flow in the liquid to jumps in the glass. The correlation factor of the diffusion constant decreases with decreasing temperature, causing a drop of diffusion below the Arrhenius value, despite an apparent Arrhenius law for the jump probability. The high collectivity of the jumps is reflected in correlation factors larger than one.

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Diffusion in bulk-metallic glass-forming Pd-Cu-Ni-P alloys: from the glass to the equilibrium melt

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Since the discovery of bulk metallic glasses there has been considerable reseach effort on these alloys. On the one hand they allow to prepare fully amorphous metallic samples of at least 10 mm in the smallest dimensions. On the other hand the undercooled melt between melting temperature and caloric glass transition temperature, which has not been accessible before due to the rapid onset of crystallisation, can now be investigated and recent theories can be tested [1]. Here we report on radiotracer diffusion measurements in metallic bulk-glass-forming Pd-Cu-Ni-P alloys.



FIG. 1: Temperature dependence of (top) Co diffusivity and (bottom) isotope effect in $Pd_{40}Cu_{30}Ni_{10}P_{20}$ and $Pd_{43}Cu_{27}Ni_{10}P_{20}$. The diffusivity is plotted on a semilogarithmic scale vs. 1/T. Open squares show data for Cu and Ni diffusion from quasielastic neutron scattering (QNS) in $Pd_{43}Cu_{27}Ni_{10}P_{20}$ [5]. The dashed line represents MCT scaling law using results of QNS for fast β relaxation (see [5]). The liquidus temperature (more precisely, the quasi-eutectic melting temperature) and T_c , determined from the fit to the QNS, data are displayed. Below T_c the tracer diffusivity data were fitted by an Arrhenius law.

Serial sectioning was performed by grinding and ion-beam sputtering. The time, temperature as well as the mass dependence, expressed in terms of the isotope effect E, of Co-diffusion were investigated [2,3,4]. In the glassy state as well as in the deeply supercooled state below the critical temperature T_c , where the mode coupling theory predicts a freezing-in of liquidlike motion, the measured very small isotope effects indicate a highly collective hopping mechanism involving of the order of ten atoms. Below T_c the temperature dependence shows Arrhenius-type behavior with an effective activation enthalpy of $3.2 \,\mathrm{eV}$. Above T_c the onset of liquid-like motion is evidenced by a gradual drop of the effective activation energy, resulting from the decay of hopping barriers, and by the validity of the Stokes-Einstein equation, which is found to break down below T_c . This strongly supports the mode coupling scenario. The Stokes Einstein equation is presently tested for other constituents of the alloy. Co-isotope effect measurements, which have never been carried out near T_c in any material, show atomic transport up to the equilibrium melt to be far away from the hydrodynamic regime of uncorrelated binary collisions.

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Excess wing versus slow β relaxation process – high pressure dielectric studies

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Several relaxation processes can be identified in dielectric spectra of glass-forming systems. The most dominant process becomes the structural α -relaxation which is directly related to the liquid-glass transition. At higher frequencies there is another relaxation process known as the slow β -relaxation. It is considered by many workers to be local and non-cooperative. However, some glass-forming liquids often exhibit instead of the β -peak an excess wing on high frequency side of the α -relaxation peak. This additional contribution to dielectric spectrum can be formally described by a power law $\varepsilon(\omega) \propto \omega^{-b}$. Both phenomena (β -peak and excess wing) are usually observed in the region where the sample is already solid but they can also exist in the equilibrium liquid above T_q .

In recent years, a great deal of efforts is spent on the issue of the slow β -relaxation and the "excess wing". However, despite much discussion, there is no general agreement about the origin of the secondary relaxation in supercooled liquids. In particular the relation between the β -relaxation and excess wing is the focus of attention [1, 2].

Up to now the nature of the high frequency contributions (i.e. slow β -relaxation and "excess wing") to the dielectric spectra has been mainly investigated based on experimental data obtained from temperature-dependent measurements at ambient pressure. However, more definitive postulates concerning the relation between the β -relaxation and excess wing can be obtained from high pressure experiments [3–5]. In addition, pressure studies can also provide important information about the molecular relaxation mechanisms. It results, first of all, from fact that pressure changes intermolecular distances and consequently the height of potential barriers whereas temperature mainly affects the energy of molecules attempting to surmount these barriers. Herein, basing on numerous high pressure dielectric results we try to answer the question whether there are any differences in behavior between the β -relaxation and excess wing when the glass transition is approached via temperature changes or isothermal density changes.

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Test of mode coupling theory for glassformers with a tetrahedral network structure

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Of particular interest for the understanding of the dynamics of structural glasses are systems for which the structure is very different to that of closed packed hard spheres. Examples for such systems are glass-formers with a tetrahedral network structure such as silica (SiO₂) or germania (GeO₂) and mixtures of silica with other oxides (e.g. Al₂O₃, Na₂O, etc.). The latter mixtures exhibit a very rich dynamics: In Al₂O₃–SiO₂ systems, the glass transition dynamics may interfere with phase separation of the oxides. Or in Na₂O–SiO₂ the sodium atoms are much more mobile than the "Si–O matrix" even at typical melt temperatures.



FIG. 1: Lograrithm of the oxygen diffusion constants as a function of 1/T for different systems as indicated.

We investigate the structure and dynamics of SiO_2 , GeO₂ as well as mixtures of SiO_2 with Al_2O_3 and Na₂O. As a model for the silicate mixtures we use a pair potential that is based on the so-called BKS potential for silica [1]. In the case of germania a similar pair potential proposed by Oeffner and Elliott is used [2]. The latter potentials were derived from *ab initio* calculations and we demonstrate that they yield good agreement with experiments both for structural and dynamic quantities. For instance, we find that the considered binary silicates exhibit additional intermediate range order as compared to pure silica where the characteristic length scales stem from the tetrahedral network structure. This is indicated by prepeaks in the static structure factors below wavenumbers of 1 Å⁻¹ [3, 4]. Only recently, in a neutron scattering experiments of various sodium silicates the existence of such a structural feature was confirmed by Meyer *et al.* [5].

Fig. 1 shows the temperature dependence of the oxygen diffusions constant $D_{\rm O}$ for SiO₂, GeO₂, (Na₂O)(2SiO₂) and (Al₂O₃)(2SiO₂). We can infer from this figure that $D_{\rm O}$ for the different systems approaches a value of about 10^{-4} cm²/s around T = 5000 K whereas below this temperature the oxygen diffusion is rapidly slowing down. The slowing down takes place on very different time scales for the different systems. We show that many aspects of the slow dynamics and its subtleties in the considered systems can be well described by mode coupling theory.

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Flow Mechanisms, Structure and Viscosity of Na₂O-Al₂O₃-SiO₂ Melts

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The viscosity of silicate melts is determined by the slowest flow process. In silicate melts, this process is the destruction/creation of Si–O bonds. This mechanism of viscous flow requires the temporary existence of a 5-coordinated Si. To create this unit, one of the oxygens in a Si-tetrahedron must be freed from its neighbouring atom. This may be a Na⁺, Ca²⁺, Fe²⁺, or tetrahedrally coordinated Al³⁺, Fe³⁺ or Si⁴⁺.

The course of such a flow process involves (i) breaking a bond to create an available O^- bond; (ii) creating an SiO₅ unit; (iii) breaking an Si–O bond to reduce the SiO₅ to an SiO₄ unit; (iv) connecting the two broken bonds to each other. Such a flow process requires energy to overcome the barrier of bond breaking. Therefore steps (i) and (iii) are the limiting steps as they require energy. Step (iii) requires the most energy as Si–O bonds are the strongest in the melt structure. The nature of the bond in step (i) is therefore that which predetermines the magnitude of the energy required for flow to occur; if the bond broken in step (i) is a weak Si–O–Na bond, the energy required for flow will be less than that needed if the bond is a strong Si–O–Al connection.

The viscosity of Na₂O–Al₂O₃–SiO₂ melts with a constant SiO₂ content has been determined by the micropenetration technique in the range $10^{8.5}$ – 10^{14} Pa s. The viscosity of these melts increases with decreasing [Na₂O]/[Na₂O + Al₂O₃] (in mole fractions) for melts with [Na₂O] > [Al₂O₃] (peralkaline). The viscosity of melts with [Al₂O₃] > [Na₂O] (peraluminous) remains constant for compositions up to [Na₂O/[Na₂O+Al₂O₃] = 0.35. Arrhenian fits to the data produce a constant value of the activation energy for melts with [Na₂O] > [Al₂O₃] and a constant but higher value of activation energy for melts with [Na₂O] < [Al₂O₃].

Rather than using this activation energy to discuss the flow mechanism and individual bond energies, the $B/S_{\rm conf}(T_g)$ term [1] should be used. Here, B is a constant, and $S_{\rm conf}(T_g)$ is the configurational entropy at T_g . This ratio is related to the size of the rearranging structural units involved in viscous flow, the average potential energy barrier to structural rearrangement and the probability that the rearrangement occurs. The $B/S_{\rm conf}(T_g)$ term increases with decreasing Na₂O content for the present peralkaline melts. This is to be expected as the decreasing number of non-bridging oxygens also decreases the probability of this low energy bond-breaking process.

The $B/S_{\rm conf}(T_q)$ term is constant for the investigated range of peraluminous melts. This implies that the size of the rearranging unit, the energy barrier to structural rearrangement and the probability of the particular structural rearrangement occurring remain constant. These melts contain, however, an increasing amount of a new structure. In the peraluminous composition melts there are not enough Na⁺ to charge balance Al³⁺ in tetrahedral coordination. It is assumed that the excess Al3+ forms charge-balanced tri-clusters of $AlSi_2O_5$ in which an oxygen is the apex of three tetrahedra (one Al- and two Si-tetrahedra). There are now two possible flow mechanisms in this fully polymerised melt: the breaking of an Al-O-Si bond to form either (i) a 5-coordinated Si or (ii) an $AlSi_2O_5$ tri-cluster. Whether the flow mechanism involves a Si^V or tri-cluster will depend upon the average energy barrier associated with each of these structural units. The constant value of the $B/S_{\rm conf}(T_q)$ term implies that the flow mechanism in these peraluminous melts remains the same for the compositional range $0.35 < [Na_2O]/[Na_2O + Al_2O_3] < 0.50$, despite the increasing number of tri-clusters present in the structure.

The addition of iron to these melts introduces tetrahedrally co-ordinated Fe³⁺ and charge-balancing Fe²⁺ to the structure. The changes in flow mechanism due to the presence of Fe²⁺ and Fe³⁺ can be discussed in terms of the changes in viscosity as well as the changes in activation energy and the $B/S_{\text{conf}}(T_q)$ term.

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The interplay of microscopic dynamics and structure in sodium silicate melts

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Observations of highly non-linear macroscopic behaviour in silicates (e. g. the dependance of viscosity on alkali concentration) fitting not together with the picture of a homogeneous distribution of modifying ions in the network, lead to assumptions of preferential pathways for these ions [1, 2]. Here we provide evidence for diffusion channels in the static structure.

We present results of inelastic neutron scattering experiments on Na silicate melts $(Na_2O(SiO_2)_x)$ performed over a broad Na concentration range (x = 1.5, 2, 3, 4) up to 1600 K. Na dynamics was investigated by means of time-of-flight spectroscopy using the spectrometers IN6 and IN5 at ILL. We compare our results with molecular dynamic (MD) simulations [3]. Both methods provide access to similar microscopic timeand length-scales.

The experimentally obtained elastic structure factor $S(q, \omega = 0)$ revealed a prepeak at $q \simeq 0.9$ Å⁻¹ emerging with increasing temperature beyond the first sharp diffraction peak [4]. Its position is independent of Na concentration and its height increases with raising Na content for a fixed temperature in the melt (s. Fig. 1). MD simulations providing access to the partial structure factors connect this prepeak with Na-rich channels percolating in the remaining SiO network [5]. Experimentally found only in the melt the prepeak is verified by MD simulations performed at experimental densities to exist also in the glass, vanishing in $S(q, \omega=0)$ due to a density change.



FIG. 1: $S(q, \omega = 0)$ for NS2, NS3, and NS4 at 1600 K in the melt measured at IN6.

Neutron backscattering at HFBS (NIST) revealed the SiO network dynamics on a ns timescale in the melt decoupled by 3 orders of magnitude of the Na dynamics being on a 10 ps timescale. Since incoherent scattering on sodium is the dominant mechanism towards small momentum transfers giving access to the Na self correlation function, we were able to identify the mechanism of fast Na ion diffusion.

The relaxation rate $1/\langle \tau \rangle$ featuring a q^2 dependance at small wavevectors q and the nearly q independent quasielastic amplitude a represent an experimental proof of Na long-range diffusion. Experimental evidence of all Na atoms participating in this fast diffusion mechanism is given by the elastic amplitude b decaying to 0 for small q. Diffusion coefficients derived from our experimental data compare well with tracer-diffusion coefficients obtained in the melt [6]. We found $D = 3.8 \times 10^{-9} \text{ m}^2/\text{s}$ at 1600 K compared with $D \simeq 5.4 \times 10^{-12} \text{ m}^2/\text{s}$ for the Si and O diffusion expected by rescaling viscosity data via the Stokes-Einstein relation [7]. We observed similar structural and dynamical behaviour on a microscopic scale in Li silicates and K bearing silicates. In NaK-trisilicate we found the mixed alkali effect being absent in the melt. Further, investigations on the ternary Na-aluminosilicates at various concentrations in the melt revealed the prepeak decreasing with increasing Al₂O₃ content. In addition, we observed a slowing down in Na dynamics at a fixed temperature by adding Al_2O_3 .

Thus inelastic neutron scattering on sodium silicate melts together with MD simulations provide an answer to the question how modifier ions are built in the network structure, its consequences for macroscopic behaviour as well as a proof of the microscopic mechanism of fast alkali ion diffusion.



FIG. 2: Density correlation and fit $(b + a \cdot \exp\{-(t/\tau)^{\beta}\})$ at q = 0.4 Å⁻¹ for sodium disilicate (NS2) measured at IN5 at three different temperatures in the melt. Insert: fit paramters a and b at 1600 K.

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Comparative study of disaccharide/water solutions by molecular modelling

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Sugars are often used in pharmaceutical, food and biomedical applications to prepare glassy matrices for long term storage of biological materials. In recent years, trehalose, which is naturally produced by several organisms that are able to survive severe external stresses (temperature changes and/or dehydration), has received considerable attention. Several hypotheses have been suggested to explain the superior effectiveness of trehalose: The 'water-replacement' hypothesis proposed by J. H. Crowe *et al.* [1], the inhibition of biomolecule motions due to the vitrification of the sugar/water solutions advanced by J. L. Green and C. A. Angell [2], and the most efficient inhibition of ice formation by trehalose compared to sucrose and maltose emphasized by S. Magazù et al. [3] and related to its greater 'destructuring effect'. However, none of these assumptions is fully satisfactory regarding the numerous experimental observations as well as numerical simulations. Therefore, we have performed a comparative study [4] of homologuous disaccharides - trehalose, sucrose and maltose - in water solutions at different temperatures and concentrations. We have especially focused our study on the influence of disaccharides on the structure and the dynamics of water.



FIG. 1: Temperature dependence of the relaxation times τ_{α} determined from the incoherent intermediate scattering function of water $F_s(Q, t)$ for the 49 wt.% sugar solutions.

In Fig. 1, we see that the α relaxation times of water in presence of the sugars are 1.2 to 10 times longer than the ones of pure water, depending on temperature. Therefore, it is possible to get a supercooled water liquid when water is in presence of disaccharides, at a temperature for which pure water is a simple liquid. This is confirmed by the observation of a plateau-like region in $F_s(Q,t)$ separating the short (β) and long (α) time regimes. Moreover, we can discriminate the homologuous disaccharides by the relaxation times. Indeed, trehalose slows down the water liquid more efficiently. Hence, trehalose must have a stronger influence than sucrose and maltose on the dynamics of water.



FIG. 2: Distributions of the orientational order parameter q [5] of water molecules not H-bonded to trehalose for different trehalose wt.% concentrations at T = 273 K. The inset presents the distributions of the three 66 wt.% disaccharide solutions at T = 273 K. Sucrose and maltose curves are not normalized in order to show the influence of the hydration numbers.

On the other hand, we have considered the perturbation of sugars on the tetrahedral hydrogen bond network of water by using the order parameter q defined in [5]. In Fig. 2, we see that the high-q peak (structured water) decreases in favour of the low-q peak (unstructured water) as trehalose concentration increases. This trend becomes particularly significant for concentrations above $\simeq 40$ %. It mimics the behaviour of a temperature increase as in [5]. Trehalose is able to perturb the tetrahedral hydrogen bond network of water more deeply than sucrose and maltose because of its more extensive hydration.

This work shows that trehalose has superior effects in 'destructuring' the network of water and in slowing down its dynamics. These two properties could play a key role in the understanding of the microscopic mechanisms of bioprotection.

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Dynamics of end-grafted polymer brushes: An evanescent wave dynamic light scattering study

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The most stable situation of terminally attached soft layers is achieved by covalent bonding of polymer chains at one end to a solid surface. For sufficient high densities σ (d^{-2}) the distance d between grafted sites is less than the size of the polymer coil end the tethered layer falls into the brush regime. While the static properties e.g. density profile of polymer brushes in good and theta solvents have been extensively investigated both theoretically and experimentally, little is experimentally known about their dynamic structure, mainly due to the difficulty of performing relevant experiments.

We present measurements of collective concentration fluctuation in chemically end grafted polystyrene brushes swollen in solvents of various quality as probed by evanescent wave dynamic light scattering [1]. Two PS-brushes with a dried thickness of 8 nm (short) and 95 nm (thick) were used.



FIG. 1: Schematic diagram of the evanescent wave dynamic light scattering set-up. The evanescent light was generated by total reflection of the laser ($\lambda = 532 \text{ nm}$) light at the interface of a semi-cylindrical lense to which polystyrene (PS) chains were covalently attached using the "grafting from" technique [2]. The intermediate scattering function $C(q,t) = \langle c_q(t)c_{-q}(0) \rangle / |c_q|^2$ was recorded under heterodyne conditions by photon correlation over a broad time range.

In the good solvent (dioxane) regime, C(q,t)(Fig. 2a) can be represented by single exponential decay with a diffusive relaxation rate $\Gamma(q) = D_c q^2$ (inset of Fig. 2a; $D_c = 3.8 \times 10^{-7} \text{ cm}^2/\text{s}$ for the thick and $(2.8\pm0.5)\times10^{-7} \text{ cm}^2/\text{s}$ for the short brush). Theoretically [3], $D_c = kT/(6\pi\eta\xi)$ describes the longitudinal mode where η is the solvent viscosity. The relation $D_s \propto 1/\eta$ was confirmed for the same brush in two different good solvents whereas the low value of ξ in these polydisperse brushes is of the order of d.

When the solvent environment changes from marginal to poor, C(q,t) (Fig. 2b) reveals strong effects as compared to the smooth variation of the density profile [4]. On both sides of the theta temper-



FIG. 2: Normalized intermediate scattering functions C(q,t) (a) for the PS-brush in dioxane at 20° C for different q's represented by single exponential functions (solid lines). Inset: the relaxation rate $\Gamma(q)$ vs. q^2 . (b) "thick" PS-brush in cyclohexane at $q = 0.03 \,\mathrm{nm^{-1}}$ for different temperatures $(31 - 58^{\circ}\mathrm{C})$. The solid lines represent the bimodal fit of a single and stretched exponential. Inset: the intensity vs. temperature.

ature $(35^{\circ}C)$ in cyclohexane, C(q,t) is clearly a two step decay and only above 50°C approaches the situation in dioxane. The fast decay is still assigned to the cooperative diffusion albeit slower than in the good solvent regime, and the slow non-exponential but diffusive process probably relates to the self-diffusion of clusters in analogy to gels. As also indicated by the variation of the associated intensities with temperatures shown in the inset to Fig. 2b, based on a current documentation of the structural behavior of brushes [2, 4], the rich and complex dynamic structure is rather unexpected [5].

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Structure and dynamics responsible for super soft states in bulk polymers

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Creating new macromolecular architectures can constitute a challenge for synthetic chemists but can additionally be justified if it can result in new properties of materials. Mechanical properties, which are related to the dynamics of systems with various macromolecular structures will be discussed.

Joining monomeric units into linear polymer chains results in a dramatic change of properties. Whereas, a monomer in bulk can usually be only liquid-like or solid (e.g. glassy), the polymer can additionally exhibit a rubbery state with properties, which make these materials extraordinary for a large number of applications. This new state is due to the very slow relaxation of polymer chains in comparison with the fast motion of the monomers, especially when the chains become so long that they can entangle in a bulk melt. The dynamic mechanical characteristics indicate a single relaxation in the monomer system in contrast to the two characteristic relaxations in the polymer. The rubbery state of the polymer extends between the segmental (monomer) and the chain relaxation times and is controlled by a number of parameters related to the polymer structure. The most important among these parameters is the chain length, determining the ratio of the two relaxation rates. In the rubbery state the material is much softer than in the solid state. If expressed by the real part of the modulus, the typical solid state elasticity is of the order of 10^9 Pa and higher, whereas the rubber like elasticity in bulk polymers is on the order 10^5-10^6 Pa.

It will be demonstrated that some highly branched macromolecular structures can lead to considerably different properties than these obtained by linking monomeric units into linear chains. The examples consider dynamic behavior of multiarm stars in the melt, the melts of brush-like macromolecules and hairy micelles dispersed in linear polymer matrices. In all these systems, there exists a third relaxation process with the longest relaxation time, which is interpreted as related to slow cooperative rearrangements in the structured system. When slow enough, it can create a new elastic plateau with the plateau modulus (10^2-10^3 Pa) by orders of magnitude lower than characteristic for the conventional polymeric rubbery state. We have recently observed properties of this kind in a number of similar systems including block copolymers, which can be considered as super soft thermoplastic elastomers.

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The Corset Effect of Polymer Dynamics in Pores: Looking for the Crossover from Confined to Bulk Dynamics

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On the basis of the general thermodynamic relation

$$\langle n^2 \rangle - \langle n \rangle^2 = k_B T \rho_m \kappa_T \langle n \rangle \,, \tag{1}$$

connecting the fluctuation of the number of particles in a given volume with the isothermal compressibility of the system, κ_T , we investigated the general characteristics of the dynamical behaviour of polymer melts confined in a cylindrical pore with the diameter D.

In the limit of very long chains, i.e. $R_F \gg D$, where R_F is the Flory radius in bulk melts, the polymer molecules are expected to translate inside pores via reptation in an effective tube of diameter $d \propto \sqrt{b^2 \rho_m k_B T \kappa_T}$ in the time limit $t \ll \tau_R$, where τ_R is the (longest) Rouse relaxation time. b is the length of the Kuhn segment, $k_B T$ is the temperature factor, ρ_m is the number density of polymer segments, having a microscopic order of magnitude $d \sim 5$ Å. This microscopically small value of the effective tube diameter d does not depend on the pore diameter D and is the consequence of the corset effect arising due to system features like the chain uncrossability, the low compressibility and the impenetrability of the pore walls. The tube diameter effective under pore confinements is one order of magnitude smaller, than the value predicted by Doi and Edwards for the length scale on which "entanglements" are supposed to become effective, $d_{DE} \sim 50-70$ Å. This value is obtained by fitting tube-reptation model predictions for the viscoelastic plateau with experimentally observed data.

In the opposite limit, $D \gg (b^3/(k_{\rm B}T\kappa_T))^{1/3} R_F$, the transition to bulk dynamics becomes thermodynamically possible. Due to the low value of the compressibility of polymer melts, the prefactor is a large number: $(b^3/(k_{\rm B}T\kappa_T))^{1/3} = \mathcal{O}(10)$. These results are in accord with recent NMR spinlattice relaxation experiments with PEO melts confined in pores of a solid methacrylate matrix. The peculiar frequency dependence characteristic for reptation in the limit $t \ll \tau_R$ was observed for pore diameters up to $D \approx 15R_F$ even for molecular masses below the critical value where bulk dynamics is characterized by the Rouse model, that is, by a totally different frequency dependence of spin-lattice relaxation [1, 2]. The general finding is that under confinements up to about 60 nm predictions for reptation are perfectly fulfilled in our NMR experiments whereas this model fails to account for data measured in bulk melts irrespective of the molecular mass.

Our results are expected to be also important for computer simulations where dense polymer melts of high molecular masses are usually considered for studies of polymer dynamics. The small compressibility, "periodic boundary conditions", and a "sample" size only twice larger at best than the Flory radius suggest that the Corset effect described above applies and bulk dynamics does not yet show up.

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Molecular observation of mechanisms limiting the topological confinement in polymer melts: A Neutron Spin Echo study

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The dynamics of linear polymer chains in the melt depends strongly on the chain length and at the same time shows completely different behaviour at short and long time scales. To study the dynamics of macromolecules, i.e. slow dynamics at large scales, small angle scattering with high energy resolution is required. The method of choice then is neutron spin echo (NSE) spectroscopy, which provides the highest energy resolution compared to all other inelastic neutron scattering techniques. To explore the different dynamic regimes in polymer melts we focussed on the time dependence of relaxation mechanisms in an appropiate time window on the one hand and studied a series of different molecular weights on the other hand.

We report on a direct experimental determination of the time-dependent mean squared segment displacement of a polymer chain in the melt covering the transition from free to constraint Rouse relaxation along the virtual tube of the reptation model. This has been achieved by a NSE measurement of the segmental self-correlation function as conveyed by the spinincoherent scattering from two fully protonated polymer melts, polyethylene (PE) and polyethylene propylene (PEP), with high molecular weight. Within the scenario of de Gennes' reptation model a transition of the time dependence of segmental mean-squared displacements from $\propto t^{1/2}$ to $\propto t^{1/4}$ is expected and clearly corroborated by the incoherent NSE results [1].

While this experiment supports the concept of a tube representing the topological confinement for long polymer chain systems, close comparison of linear rheology data of some long-chain polymer melts with the reptation model indicates the existence of additional degrees of freedom limiting the topological chain confinement. As one candidate, fluctuating chain ends destroying the tube starting from both ends were proposed. This process, called contour length fluctuations (CLF), indeed accounts for the observed power law in the dynamic loss modulus $G''(\omega)$ [2].

In order to study this mechanism on a microscopic scale, we have performed NSE investigations of the single chain dynamic structure factor from polyethylene melts over a large range of chain lengths. This was realized by measuring samples which contain a few percent protonated chains in a matrix of deuterated ones. While at high molecular weight the reptation model is corroborated, a systematic loosening of the confinement with decreasing chain length is found. The dynamic structure factors are quantitatively described by the effect of contour length fluctuations,



FIG. 1: Incoherent NSE data obtained from a fully protonated PE melt in a representation of $-6 \ln[S_{inc}(Q,t)]/Q^2$, i.e. the mean squared displacement $\langle r^2(t) \rangle$ as long as the Gaussian approximation holds. Solid lines describe the asymptotic power laws [1].

establishing this mechanism on a molecular level in space and time [3].

Partly labeled chains allow to switch off the scattering contrast of the chain ends to the matrix chains and therefore the visibility of the CLF process. A comparison of these results with data of fully labeled chains enabled us to separate reptation from additional degrees of freedom. By this key experiment the CLF process was identified unambiguously [4].

A second process which has been incriminated to limit the topological confinement in polymer melts is the relaxation of the tube itself. First measurements of a long polymer chain with fixed length in different matrix molecular weights allow to observe the loosening of confinement with decreasing molecular weight of the matrix. Varying the weight systematically from high molecular weight, i.e. pure reptational behaviour, to short chains, one finally ends up with a long chain which shows simple Rouse behaviour due to the inability of the matrix chains to build a tube [4].

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Attraction driven glass transition in colloidal systems

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Colloidal systems share many properties with simple liquids, but also present some interesting differences, such as aggregation and gelation. Colloids can form a gel when a short range attractive interaction is present, if the interaction is strong enough. The particles get trapped by a web of bonds formed with its neighbours, and the resulting colloidal gel is an amorphous network of particles that spans over the whole system, leaving big voids.

Recently, colloidal gelation has been interpreted as a regular non-equilibrium transition, using Mode Coupling Theory (MCT) [1]. For short range attractions, this theory predicts a glass transition line, which can be divided into two parts; a so-called repulsive glass transition, taking place at low attraction strength and high colloidal density, driven by the steric hindrance, and an attractive glass transition, predicted for all densities and high attraction strength (higher strength for lower density), caused by the particle bonding. At high density and high interaction strength, a high order singularity is predicted, noticed by a logarithmic decay in the correlation functions [2].



FIG. 1: Image of a colloidal gel at $\phi_c = 25\%$.

In this work, we have used computer simulations to study the dynamics of colloidal systems close to the attractive glass transition. This transition is observed at two different colloidal densities, $\phi_c = 0.40$ and $\phi_c = 0.25$, finding analogous properties in both cases. The density-density correlation function and the mean squared displacement are studied, and the results are compared with the predictions from MCT. The time scale diverges according to a power law, with an exponent which implies a von Schweidler exponent compatible with the correlators from the simulations. The wavevector dependence of the time scale also decays according to the predictions from MCT, and the mean squared displacement as well as the correlation functions indicate that bond formation is the mechanism leading to the transition. These results fully confirm that this attractive glass transition takes place in colloidal systems, and its properties are correctly predicted by MCT [3, 4].

However, we will also present here that the system is far from homogeneous. Looking at the distribution of squared displacements, a population of particles that move much faster than average is recognized. The system is then viewed as a network of particles which hardly move and some particles that move in the surface of this network but also in the free space. The number of fast particles decreases as the system approaches the glass transiton. Interestingly, an exchange between the fast and slow particles is also observed.

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Aging in short-ranged attractive colloids: A numerical study

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I present a study of the aging dynamics in a model for dense simple liquids, in which particles interact through a hard-core repulsion complemented by a short-ranged attractive potential, of the kind found in colloidal suspensions. In this system, at large packing fractions, kinetically arrested disordered states can be created both on cooling (attractive glass) and on heating (repulsive glass) due to the presence of a reentrant glass-line. The existence of these two states has been recently confirmed in experiments [1, 2] and simulations [3, 4]. The numerical experiment that I will discuss is sketched in Fig. 1 . From an equilibrated configuration at $T_i = 0.6$ the system is quenched in to the attractive ($T_f = 1.2$) and the repulsive ($T_f = 0.3$) glass.



FIG. 1: Iso-diffusivity curves (i.e. the locus of points in the ϕ , T plane where the normalized diffusion coefficient is constant) for a square-well system for three different values of D/D_0 ($D_0 = \sigma_b \sqrt{T/m}$; data from Ref. [4]). The extrapolated ideal glass-transition line is also reported; data from Ref. [5]. Equilibrium starting configurations at $\phi = 0.608$ and $T_i = 0.6$ (filled circle) are instantaneously quenched at t = 0 to $T_f = 0.3$ and $T_f = 1.2$ (plus symbol).

The possibility of having two distinct glasses, at the same packing fraction, with two different dynamics offers the unique possibility of comparing – within the same model – the differences in aging dynamics. While the aging dynamics of the repulsive glass is similar to the one observed in atomic and molecular systems, the aging dynamics of the attractive glass shows novel unexpected features. I will present results for static structure factors, density-density correlation function and mean square displacements. Connections with recent experimental results [6] will be also discussed.

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Glasses in hard spheres with short-range attraction

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We performed a detailed experimental study of the structure and dynamics of glassy states in hard spheres with short-range attraction [1, 2]. The system consists of nearly-hard-sphere polymethylmethacrylate particles and non-adsorbing linear polystyrene which induced a depletion attraction between the par-Observation of crystallization reveals a reticles. entrant glass transition (Fig. 1) with two different glassy states. Static light scattering shows a continuous change in the static structure factors upon increasing attraction. In contrast, dynamic light scattering results, covering eleven orders of magnitudes in time (Fig. 2), are consistent with the existence of two distinct kinds of glass and give insight into the kinds of particle motion responsible for these observations [2]. The results qualitatively agree with predictions by mode coupling theory [3].



FIG. 1: Equilibrium and non-equilibrium behaviour of a hard-sphere system with short-range depletion attraction. Open symbols are those that reached thermal equilibrium. Other samples did not crystallize: some showed characteristics of hard-sphere glasses at the onset of sedimentation (filled circles), some showed those of attraction-driven glasses and gels (filled squares), and some showed both (pluses). Dashed curves are guides to the eye showing the observed boundary where crystallisation ceased.

In this contribution we will put special emphasis on

aging, which we found in all non-crystallizing samples. The dynamics slowed down with the 'waiting time' – the time interval between cessation of homogenization and the beginning of the measurements. We found that the rate of aging in different glasses are different and that its effects are complex. Repulsive glasses aged only in the first few days, after which they do not evolved within the time window of the measurements. Attractive glasses, on the other hand, showed different dynamics with age for up to more than a week.



FIG. 2: Collective dynamic structure factors at qR = 1.50from marked samples in Fig. 1. The inset show the same plots on an expanded vertical axis. Sample A shows the well-known dynamics of hard-sphere glasses. Sample D in the re-entrant gap has a completely decaying dynamics in its metastable state. Sample G is also a glass and shows an extremely high incipient plateau (inset). Sample J at the region where the two glass transitions are expected to meet shows a logarithmic dynamics.

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The Glass Transition Dynamics of Microgel Colloids with Short-Ranged Attractions

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Polystyrene microgel colloids with nearly hardsphere like interactions have been used to study the effect of short-ranged attraction on phase behaviour and glass transition dynamics. To suppress crystallization, a binary mixture with a size ratio (small:large) of 0.8 and a number ratio of 2.7 has been prepared which shows glassy freezing at a volume fraction $\varphi_{\text{colloid}} =$ 0.595. To switch on attraction, linear polystyrene chains with a size ratio $\delta = R_{\rm g, polymer}/R_{\rm colloid} \approx 0.06$ were added to glassy samples of the binary mixture. By studying the density autocorrelation function we observe the phenomenon of a reentrant glass transition: the glass melts and on increasing the polymer concentration c_p the colloid dynamics first speeds up until the system behaves like a colloidal fluid. On further addition of linear polymer the dynamics slows down again and the particles undergo another glass transition. The latter does not feature the well-known cage effect characteristic of packing-driven glass transitions. This finding is been interpreted in terms of a bonding-driven glass transition. By analyzing the dynamics along cuts through the $\varphi_{\text{colloid}} - c_p$ phase space we establish the glass transition lines. By performing tentative fits with the asymptotic laws of mode coupling theory on samples along the transition lines we find indications of changes of the exponent parameter λ and the plateau value f_q^c which compare favorably with what has been theoretically predicted. Finally, by studying the phase behaviour of a onecomponent microgel system with added linear polymer we demonstrate the reentrant glass transition by a transition from a glassy state via fluid-crystal existence and fluid-gel coexistence to a gel state.

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Self-Atomic Motions in Glass-Forming Polymers: Neutron Scattering and Molecular Dynamics Simulations Results

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Valuable information on the dynamics of the α relaxation can be obtained by quasielastic neutron scattering (NS). For instance, NS on protonated samples is directly related with the self part of the van Hove correlation function $G_s(\vec{r},t)$ corresponding to the hydrogens in the system. $G_s(\vec{r}, t)$ is the probability to find an atom at time t at \vec{r} if it was at $\vec{r}=0$ for t=0. Neutron spin echo (NSE) accesses its Fourier transform $F_s(Q, t)$, and e.g. time of flight or backscattering techniques its counterpart $S_{inc}(Q,\omega)$ ($\hbar Q, \hbar \omega$: momentum- and energy-transfer). As NS delivers the spatial information only in the reciprocal space, the interpretation of experimental results is sometimes not straightforward. Magnitudes as $G_s(\vec{r},t)$ and its moments are not directly accessed. In this direction, computer simulations on fully atomistic polymer models have proven to be an useful complementary tool for unraveling NS data, providing one has realistic enough models [1, 2].

Following these ideas, in this work we have investigated the Q-dependence for the H-self motion in the α -relaxation regime of three glass forming polymers, polyisoprene (PI), 1,2-polybutadiene and 1,4polybutadiene, by a combined effort involving fully atomistic molecular dynamic simulations and NS measurements. The slow decay of $F_s(Q,t)$, due to the α -process, can be well described by the usual KWW function with a Q-dependent characteristic time $\tau(Q)$ and a shape parameter β . By studying the combined NS and simulation results we have established the existence of a crossover from a Gaussian regime of sublinear diffusion to a strongly non-Gaussian regime at short distances. This crossover manifests in a change in the Q-dependence of $\tau(Q)$, as can be seen in Fig. 1a for the case of PI at different temperatures and densities. The crossover occurs at the same Q-value independently of temperature and density. These results can be rationalized taking into account the value of the non-Gaussian parameter $\alpha_2(t)$ calculated at $t = \tau_w(Q)$ for the different $\tau_w(Q)$ included in Fig. 1a. The results obtained are displayed in Fig. 1b. We can see that the data corresponding to different temperatures and densities and those corresponding to different densities at constant temperature, all seem to show the same low-Q asymptotic behavior. Thereby, the crossover for all temperatures and densities always takes place when $\alpha_2[t = \tau_w(Q)]$ takes values of the order of 0.25.

We also show that a simple anomalous jump diffusion model with a distribution of jump lengths captures the main features of such a crossover and leads to an α_2 exhibiting all properties revealed so far from various simulations of different glass forming systems.

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FIG. 1: (a): Q-dependence of the master curves obtained for τ_w^{β} from different starting temperatures (lower curve) and from different starting densities at 513 K (upper curve). Solid lines show the Gaussian behavior. (b): $\alpha_2[t = \tau_w(Q)]$ for all the different starting conditions considered (listed in the figure). The vertical dotted line shows the approximate position of Q_{cross} .

Molecular Dynamics simulations of the glass transition in 1,4-polybutadiene melts

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We present Molecular Dynamics simulations of a chemically realistic united atom model of 1,4polybutadiene (PBD). This model has been validated carefully in simulations of the melt dynamics of PBD and shown to reproduce experimental findings quantitatively. Upon reducing the temperature along the atmospheric pressure isobar, the system is shown to exhibit glassy slowing down. This is shown in Fig. 1 for the mean square displacement of the united atoms for a range of temperatures ranging from a high temperature melt at 400 K to a strongly supercooled liquid at 198 K which is about 20 K above the calorimetric glass transition temperature of PBD as well as 20 K below the best experimental estimate for the mode-coupling critical temperature of PBD.



FIG. 1: Double logarithmic plot of the mean square displacment of monomers as a function of temperature. At low temperatures a time-scale separation between the subpicosecond vibrational dynamics and the long time relaxational dynamics develops.

As can be clearly observed in Fig. 1 a time scale separation between the short time vibrational dynamics and the long time relaxational dynamics develops. At high temperatures the vibrational dynamics directly crosses over to relaxation behavior and Rouse type subdiffusive motion of the monomers (exponent 0.61). Already well above the expected mode-coupling T_c a separation of time scales sets in. Simulations of chemically realistic polymer models can help to understand how much of this time scale separation is entropic in origin (packing effects captured in modecoupling theory) and how much is energetic and due to intramolecuar barriers against local conformational changes of the chains. Comparing simulations of the chemically realistic model to simulations of a freely rotating model with the same liquid structure factor shows that for this polymer the energetics of dihedral rotation barriers are the dominating effect [1]. Consequently the plateau regime in the mean square displacement or the incoherent scattering function and other relaxation functions does not follow the factorization theorem for the β -process of MCT.

Analyzing the momentum transfer, q, and temperature dependence of the α relaxation as observable in the incoherent scattering function over a wide range of temperatures and momentum transfers we come to the following conclusions. Fitting the time dependence of the incoherent scattering in the long time limit with a Kohlrausch-Williams-Watts stretched exponential we find a strong q dependence of the stretching exponent β and the α time-scale $\tau_{\rm KWW}$. The q dependence of β can be qualitatively understood by assuming that the incoherent scattering in zeroth approximation traces the particle mean-square displacement, so that the α -process observed at a given q is most sensitive to particle displacements obeying $q^2 \langle \Delta r^2 \rangle (t)/6 \approx 1$. A detailed study of the importance of non-Gaussian effects for the incoherent scattering shows that this argument is only quantitatively true in the $q \rightarrow 0$ limit. The q dependence of the α time scale is in qualitative agreement with the $q^{-2/\beta}$ behavior found in scattering experiments on different polymers, although we can not assume a q independent β over the range of momentum transfers we studied.

The simulations agree with the conclusions from neutron scattering that the relaxation can not be described by a heterogeneous set of individually Fickian Debeye process, i.e., the scattering qualitatively traces the subdiffusive mean square displacement. An anylsis of the transitions in the torsion potential between different conformational states [2], however, reveals a clearly heterogeneous behavior of the different torsional degrees of freedom with an increasing heterogeneity upon cooling.

This work was done in collaboration with S. Krushev at the University of Mainz and G. D. Smith, D. Bedrov and O. Borodin at the University of Utah, USA.

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Molecular Weight and Temperature Dependence of the Vibrational and Relaxational Modes of Polyisobutylene

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Polymers offer the unique possibility to change with the chain length its conformational entropy and its viscoelastic properties without modifying the intermolecular interactions. Investigation of the glass forming properties and its changes with molecular weight have long tradition by macroscopic measuring techniques, but there is only a limited number of studies applying microscopic techniques.

We have investigated polyisobutylene (PIB) over a wide range of molecular weight, starting from oligomers with $M_w = 390$ up to polymers with molecular weights as high as $M_w = 500000$. Besides the characterisation by thermodynamic methods we have mainly applied incoherent inelastic neutron scattering and recently also high resolution inelastic X-ray scattering.

Thermodynamic measurements were carried out at the LCP, Orsay in order to determine the jump of the specific heat at T_g as a function of molecular weight and also the M_w dependence of the glass transition pressure P_g [1].

The incoherent scattering experiments were carried out at the high energy resolution backscattering spectrometer IN16 and the time-of-flight spectrometer IN6 at the ILL, Grenoble. On IN16 an overview over the influence of M_w on the temperature dependence of the relaxation was gained by elastic scans. At selective temperatures inelastic data were taken in a wide *Q*-range (for $0.2 \text{ Å}^{-1} < Q < 1.9 \text{ Å}^{-1}$). From these backscattering data the intermediate scattering function $S_{inc}(Q,t)$ for PIB was deduced in the nstime range and its Q dependence was compared to recent results from neutron spin echo [2]. For the low molecular weight PIB we also studied the pressure dependence of the intermediate scattering function in the melt. $S_{inc}(Q,t)$ for PIB at $T = 368 \,\mathrm{K}$, shows a characteristic momentum transfer (Q) dependence, which, if fitted by a single stretched exponential relaxation process $S_{inc}(Q,t) = A(Q) \exp(-t/\tau_{\rm KWW})^{\beta}$ and fixed $\beta = 0.55$, shows a Q dependence of the relaxation time $\tau_{\text{KWW}}(Q)$ which is compatible with a crossover from a power law $\tau_{\rm KWW}(Q) \sim Q^{-2/\beta}$ at low Q to $\tau_{\rm KWW}(Q) \sim Q^{-2}$ at high Q [3]. Application of pressure results in an extension of the Q^{-2} -range towards lower Q. A variation of the molecular weight (390 < M_w < 73000) for PIB does hardly influence this characteristic $\tau(Q)$ dependence at T = 368 K [3].

An extended frequency range was investigated at IN6 where we observe the fast ps-relaxations above the glass transition temperature and the Boson peak far below the glass transition temperature. Again PIB with molecular weight between $M_w = 680$ and $M_w = 33000$ was studied. In the glass and for M_w below 4040 we find below the Boson peak frequency the clear presence of low frequency modes, which do not exist at high M_w . Above the glass transition temperature, between T_g to $T_g + 200$ K, we find again a pronounced M_w dependence of the relaxation spectra. In a few cases we can combine the intermediate scattering function $S_{inc}(Q, t)$ with the corresponding S(Q, t), acquired with high energy resolution by neutron backscattering.

Recently we have also started the investigation of the dispersion of low frequency modes by inelastic Xray scattering (energy resolution 1.5 meV; $0.02 \text{ Å}^{-1} < Q < 2.8 \text{ Å}^{-1}$) [4]. The preliminary results for three different molecular weights show again a pronounced M_w dependence of the dispersion at low Q.

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Dynamical Properties of the Slithering Snake Algorithm: A numerical test of the activated reptation hypothesis

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Correlations in the motion of reptating polymers in a melt are investigated by means of Monte Carlo simulations of the three dimensional slithering snake version of the bond-fluctuation model.

Surprisingly, the slithering snake dynamics becomes inconsistent with classical reptation predictions at high chain overlap (created either by chain length N or by the volume fraction ϕ of occupied lattice sites), where the relaxation times increase much faster than expected.

This is due to the anomalous curvilinear diffusion in a finite time window whose upper bound $\tau_+(N)$ is set by the density of chain ends ϕ/N . Density fluctuations created by passing chain ends allow a reference polymer to break out of the local cage of immobile obstacles created by neighboring chains. The dynamics of dense solutions of "snakes" at $t \ll \tau_+$ is identical to that of a benchmark system where all chains but one are frozen. We demonstrate that the subdiffusive dynamical regime is caused by the slow creeping of a chain out of its original correlation hole. Our results are in good qualitative agreement with the activated reptation scheme proposed recently by Semenov and Rubinstein [1].

Additionally, we briefly comment on the relevance of local relaxation pathways within a slithering snake scheme. Our preliminary results suggest that a judicious choice of the ratio of local to slithering snake moves is crucial to equilibrate a melt of long chains efficiently.

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The Fluctuation Theorem

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The question of how reversible microscopic equations of motion can lead to irreversible macroscopic behaviour has been one of the central issues in statistical mechanics for more than a century. The basic issues were known to Gibbs. Boltzmann conducted a very public debate with Loschmidt and others without a satisfactory resolution. In recent decades there has been no real change in the situation. In 1993 we discovered a relation, subsequently known as the Fluctuation Theorem (FT), which gives an analytical expression for the probability of observing Second Law violating dynamical fluctuations in thermostatted dissipative nonequilibrium systems. The relation was derived heuristically and applied to the special case of dissipative nonequilibrium systems subject to constant energy "thermostatting". These restrictions meant that the full importance of the Theorem was not immediately apparent. Within a few years, derivations of the Theorem were improved but it has only been in the last couple of years that the generality of the Theorem has been appreciated. We now know that the Second Law of Thermodynamics can be derived assuming ergodicity at equilibrium, and causality. We take the assumption of causality to be axiomatic. It is causality which ultimately is responsible for breaking time reversal symmetry and which leads to the possibility of irreversible macroscopic behaviour.

The Fluctuation Theorem does much more than merely prove that in large systems observed for long periods of time, the Second Law is overwhelmingly likely to be valid. The Fluctuation Theorem *quantifies* the probability of observing Second Law violations in small systems observed for a short time. Unlike the Boltzmann equation, the FT is completely consistent with Loschmidt's observation that for time reversible dynamics, every dynamical phase space trajectory and its conjugate time reversed 'anti-trajectory', are both solutions of the underlying equations of motion. Indeed the standard proofs of the FT explicitly consider conjugate pairs of phase space trajectories.

Quantitative predictions made by the Fluctuation Theorem regarding the probability of Second Law violations have been confirmed experimentally, both using molecular dynamics computer simulation and very recently in two laboratory experiments [1] which employed optical tweezers.

In this talk we give a brief summary of the theory [2] and a description of the experiments.

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Amorphous polymorphism and the supposed glass transition of water

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One of the most intriguing phenomena found in solid state matter is the so called amorphous polymorphism, i.e. the existence of several distinctly different amorphous states in a single substance. Amorphous polymorphism has been observed for the first time in water at temperatures below 100 K where a high-density amorphous state HDA ($\rho = 1.17 \text{ g/cm}^3$) and a low-density amorphous state LDA ($\rho = 0.93 \text{ g/cm}^3$) can be prepared [1]. Since then amorphous polymorphism has been observed in other glass forming systems like Si, Ge, SiO₂, Triphenylphosphit (TPP), etc. [2, 3].

One possible explanation for the existence of HDA and LDA has been given by molecular dynamics simulations whose results identify the two amorphous states with two distinct, super-cooled liquid phases [4]. The complexity of the amorphous polymorphism has been recently enhanced by the detection of a third, apparently distinct amorphous structure called very high-density amorphous (vHDA) ice with a mass density of $\rho = 1.25 \text{ g/cm}^3$ [5]. Its existence could be equally explained by molecular dynamics simulations in terms of a third deeply super-cooled liquid state [6].

These findings imply, on the one hand, a number of complex transitions between the amorphous systems which could be understood as first order like transformations and, on the other hand, the presence of a glass transition separating the amorphous from the supposed liquid states. Although, some experimental results indicate an endothermic transition in LDA at $T \approx 135$ K they do not give any unequivocal evidence of a glass-transition in water and thus of the validity of the poly-liquid scenario [7]. Moreover, recent cognitions of a shadow-glass transition behaviour question the validity of the so far accepted $T_g \approx 135$ K in water and favour a $T_g \approx 165$ K, i.e. deep in the temperature regime of crystalline ice [8].

To shed light on the supposed glass-transition of water, on the expected relaxation processes, and on the relation between the different amorphous ice phases extensive elastic and inelastic neutron and X-ray scattering experiments have been performed. Here, we primarily focus on the T and Q-dependence of the Debye-Waller factor and the mean-square displacement of HDA, LDA and a crystalline ice I_c as a reference system in their stable states and in the course of the supposed glass transition as seen on a nano-second time scale by back-scattering techniques.

However, since the Debye-Waller factor connects the static and dynamic properties of the system we also present results from diffraction and inelastic experiments which offer compared with the behaviour of the Debye-Waller factor a comprehensive picture of the nature of the amorphous polymorphism of water including the vHDA state.

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Relation of phase behavior to crystallization, polyamorphism, and the emergence of tetrahedral structure and complex dynamics in liquid silica

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We present the results of a comprehensive evaluation of the phase diagram of the BKS potential, a model of silica widely used in molecular dynamics (MD) simulations. To obtain the phase diagram, we conduct extensive MD simulations of the liquid, and three crystals, β -quartz, coesite and stishovite. We determine coexistence boundaries (both stable and metastable) from an evaluation of the total free energy of each phase. The resulting phase diagram (Figs. 1 and 2) is among the most detailed yet to be evaluated for a MD model of a molecular substance: e.g. two melting line maxima, and three triple points involving the liquid phase, are observed. Comparison with experimental phase boundaries (Fig. 1) reveals the quantitative deficiencies of the model, yet also shows that the topology of the real phase diagram is reproduced.

The model phase diagram, combined with information on the molecular structure and dynamics of the simulated liquid, allow us to self-consistently correlate phase behaviour to the complex properties of the liquid phase. In this way, we show the following:

(i) Real liquid silica exhibits a weak density maximum in the supercooled regime. In this regime the liquid is known to have a highly developed tetrahedral network structure and exhibits the dynamics of a "strong" glass-former. Our simulations suggest that a



FIG. 1: Phase diagram of BKS silica in the P-T plane. Coexistence boundaries are shown as solid lines. Metastable coexistence lines (dashed) are also shown that meet at the metastable liquid-quartz-stishovite triple point. In the liquid phase, the locations of a line of density maxima (diamonds) and a line of C_V maxima (circles) are shown. The star locates a state point of the supercooled liquid at which simulation evidence for liquid-liquid phase separation has been found. The inset shows the experimentally determined coexistence lines, and their metastable extensions, for the same phases as in the main panel.



FIG. 2: Phase diagram of BKS silica in the V-T plane. The notation and symbols used have the same meaning as in Fig. 1. The cross locates a state point at which the simulated supercooled liquid spontaneously crystallizes to stishovite.

second and more prominent density maximum occurs well above the melting line, at temperatures T beyond those of current experimental data. Structural analysis shows that this high T density maximum is associated with the initial formation of tetrahedral structure in the liquid, which also correlates to the crossover from "fragile" to "strong" dynamics in the liquid [1].

(ii) The volume V at which liquid-liquid phase separation occurs in BKS silica [2], is coincident with the V of the liquid at a low T metastable triple point where the Clapeyron slope of the melting line changes sign. This is consistent with thermodynamic instabilities that occur in supercooled multi-component liquids under analogous conditions near a eutectic. This highlights the similarity of liquid-liquid phase transitions in single and multi-component systems.

(iii) The onset of spontaneous crystallization of the supercooled liquid to stishovite occurs when the V of the liquid decreases to values within the single-phase stability field of stishovite (Fig. 2). Analysis of the local molecular structure in the vicinity of this onset V reveals how the reorganization of the first coordination shell in the liquid triggers crystal nucleation.

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Analysis of superionic conductors with theories of viscous liquids

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We analyse the dynamics of mobile ions in various superionic crystals using theories developed originally for viscous liquids. Many theories have been developed to deal with the difficult dynamical problems of viscous liquids, but not yet applied further afield. Superionicity occurs when one type of ion in a crystal is free to move, as in a liquid, while the others remain fixed. These materials are not mere curiosities [1], but have found technological application in solid state batteries and sensors, though the mechanism of conduction is not fully understood. We discuss the fluorides of lead and calcium, lithium oxide and strontium chloride. Most previous theories of superionicity were developed around the perfect crystal, and are ill-suited to the disordered superionic; but methods constructed to deal with viscous liquids are forced to treat the collective behaviour of strongly interacting particles in highly disordered environments, and are ideal for superionics. The decrease in the conductivity as ions return to their perfect-crystal sites is similar to the structural arrest of a supercooled liquid as it is quenched into its immobile, glassy state.

Supercooled liquids are metastable, and superionics in equilibrium, but on close examination they have much in common [2]. The similarities include non-Arrhenius temperature dependence of the transport coefficients, anomalies in the heat capacity, twostep relaxation of the time-correlation functions, and the connection between the mobility and entropy described by the Adam-Gibbs equation.

Our main results come from the application of the



FIG. 1: Inherent-structure energies of 324 ions of superionic lead fluoride at several temperatures, relative to the perfect-crystal energy at 800 K. The lines are best fits. The superionic transition is at about $T_c \sim 940$ K in this model. Most of the energy change across T_c is lattice energy (intercepts of lines), and the defect creation energy (slopes) drops sharply. This level of detail is a particular advantage of the inherent structure method.



FIG. 2: A typical lead fluoride inherent structure at 950 K. The large particles are defects, interstitials light, vacancies dark; the others are on-site fluorides (light) and lead ions (dark). Note the clustering of intersitials, which reduces the strain-energy cost of defect creation, and results in mobile and immobile regions.

inherent structure method to superionic conductors (see Fig. 1), though we also discuss kinetic Ising models, and a mode-coupling approach. The inherent structures reveal important features of disorder in the crystal. Defects in lead fluoride, for example, cluster to reduce lattice strain. Since defects are necessary for the motion of charge this implies that the superionic contains mobile and immobile regions; it is dynamically heterogeneous (see Fig. 2). There is also a clue here to the particular tendency of crystals with the fluorite structure to be superionic. The inherent structures give us the characteristics of defect clusters that preserve the mechanical stability of the crystal, their typical sizes and distributions.

Not only does this approach lead to a clearer picture of superionic conduction, it provides a new class of materials and phenomena on which theories originally created for viscous liquids may be tested.

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Poster Presentations

Adsorption of molecular liquids in mesopores: from capillary condensation to the glass transition

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The study of the adsorption of fluids in nanoporous or mesoporous materials is of great interest since these adsorption phenomena play a very important role in a number of industrial processes (catalysis, separation technique, ...). Thus, it is interesting to study the behavior of a confined fluid inside these materials. Indeed, the properties of these confined fluids are different from those in the bulk. During these last years, many studies have shown the existence of a new characteristic length (about some nanometers in supercooled liquids). However, the nature of this characteristic length is still not well defined, and many concepts are associated to it. Nethertheless, it is obvious that this correlation length depends on the properties of the pores (size, rugosity, shape, radius of curvature, surface interactions, \ldots).

Another interesting property is the glass transition (the transition from a supercooled liquid to a glass). Indeed, when a fluid can be supercooled by preventing crystallization (such that it is in a non-equilibrium state), it becomes a glass. In this case, the glass has the macroscopic properties of a solid, keeping the disorganized structure of a liquid. Even if this phenomenom has been well studied, the theoretical explanation of this transition is still not well described.

We have continued current research on the confinement of (molecular) fluids in mesopores, to study changes of the properties between the confined fluid and the bulk (characteristic length, glass transition, ...). These studies are mainly realised on a homemade apparatus able to measure the adsorptiondesorption isotherms. Other experiments (DSC, SANS, ...) are carried out to complete the results obtained by adsorption.

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Mode coupling behaviour of a Lennard Jones binary mixture: a comparison between bulk and confined phases

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Very few computer simulations on the applicability of Mode Coupling Theory (MCT) [1] on supercooled liquids in confined geometries are available. We present a comparative study on the behaviour of a model glass former, a liquid Lennard Jones binary mixture (LJBM), in its bulk and in a confined phase [2]. The bulk phase is known to test many of the predicted features of MCT [3]. Our confined model consists in the same LJBM embedded in a disordered array of soft spheres and it has also been recently found to test MCT [4]. To obtain a quantitative comparison of the dynamical properties of the two systems at equivalent conditions the computer simulations of the bulk liquid have been performed along a thermodynamic path where the (T, P) values follow the isochore of the confined system.



FIG. 1: MSD of bulk and confined LJBM upon supercooling. In the inset a blow up of the plateau region for the MSD of the lowest temperatures investigated for the two systems, T = 0.48 bulk and T = 0.37 confined.

Differences and analogies of behaviour of the LJBM in bulk and in confinement are discussed with respect to MCT predictions. Due to the presence of the soft spheres, A and B particles are trapped in more similar cages than in the bulk, see the plateau of the mean square displacement, MSD, of Fig. 1. The same von Schweidler exponent, b, is found for A and B in confinement while in bulk b is different for each species. Besides, at variance with the bulk, in confinement the high Q value of the Kohlrausch William Watts exponent approaches b. Also as far as hopping is concerned the two types of particles behave more similarly in confinement (see fig.2). We infer that some of the points of slight disagreement with MCT of the LJBM bulk might only be connected to a small ten-



FIG. 2: The non-Gaussian parameter. Thicker lines are associated to T=0.48.

dency to demix still left in its bulk phase in spite of the fact that the LJ crossing parameters have already been tuned with respect to the most commonly used Lorentz-Berthelot rules. On the contrary, in strong confinement the soft sphere repulsive potential might enhance the mixing, forcing both A and B types to a common dynamics.

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Non-Brownian diffusion regime in confined water

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The dynamical properties of water molecules close to an hydrophilic surface are studied by means of Molecular Dynamics simulation.

An anomalous sublinear regime is found in the long time behaviour of the mean square displacement (MSD) of the molecules in the layer closer to the substrate. In the same layer the distribution of the residence times shows an anomalous non Brownian behaviour.



FIG. 1: Log-log plot of the RTD of water molecules in the layer of 6 Å at contact with the substrate at temperatures T = 300 K (open triangles) and T = 240 K (open square). The fits (bold lines) are done with a power law $At^{-\mu}$. A = 0.059, $\mu = 1.50 \pm 0.05$ at T = 300 K. A = 0.026, $\mu = 1.52 \pm 0.05$ at T = 240 K. The inset shows the RTD for the molecules in the internal layer on a linear-log scale.

The residence time distribution (RTD), $\psi(t)$, calculated for the molecules in the layer of 6 Å from the surface and reported in Fig. 1, shows a power law behaviour. For the rest of the molecules an exponential decay is found, as shown in the inset of the same figure. The calculations of the MSD show that after a ballistic regime at short time there is the onset of a cage effect characterized by the presence of a plateau which increases on lowering the temperature. The plateau is determined by the transient caging of the nearest neighbours. At longer times the MSD does not appear to reach the usual Brownian diffusion since the behaviour is sub-linear. The origin of anomalous

diffusion can be traced back to the analytic form of the distribution of the waiting times. Different interaction processes between the water molecules and the sites of the substrate modulate the residence time (RT) of the molecules. Large oscillations of the RT appear to follow the structure of the density profiles. A dispersive transport regime related to temporal disorder shows up in the power law decay of the residence time distribution (Fig. 1) with an exponent μ which determines also the long time tail of the mean square displacement (Fig. 2) with an exponent $\alpha \simeq \mu - 1$.



FIG. 2: MSD of water molecules in the layer of 6 Å at contact with the substrate at temperatures T = 300 K and T = 240 K from above. The long dashed lines are the fits to a sublinear behaviour $\langle r^2 \rangle \propto t^{\alpha}$ with $\alpha = 0.45 \pm 0.05$ at T = 300 K and $\alpha = 0.48 \pm 0.05$ at T = 240 K. In the inset, $\langle r^2 \rangle / t$ is reported.

As a result of our study the transition between the Brownian and the non Brownian sublinear diffusion is related to the amount of water (hydration level) and the distance from the substrate [1].

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Molecular dynamics investigation of stringlike dynamics in confined water

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Using TIP5P intermolecular potential we investigate the modification of the stringlike dynamics for supercooled water confined into different kind of pores or planes. We investigate in particular the orientation of the strings with respect to the surface of the wall and the modification of their average length as a function of the distance from the wall.

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Confinement Effects on the Slow Dynamics of a Simulated Supercooled Polymer Melt

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We present results from molecular-dynamics simulations for a bead-spring model of a supercooled polymer melt which is confined between two completely smooth and pure repulsive walls. We explore the dependence of the structure and the dynamics of the melt on the wall-to-wall separation h (film thickness), as the polymer films are cooled toward low temperatures T. Particular attention is paid to deviations from the bulk behavior introduced by the confinement.

Despite the confinement the supercooled films ex-



FIG. 1: Upper panel: Wave vector dependence of the static structure factor of the melt, S_q , for the bulk and for a film of thickness h = 5 at T = 0.46 ($T_c \simeq 0.45$ in the bulk), showing the suppression of the amplitude of S(q) at $q_{\max} \simeq 7$ in the film with respect to the bulk. Lower panel: Mean-square displacement of the inner monomer of a chain, $g_1(t)$, versus time t for the bulk and for films of different thicknesses h, as indicated, at temperature T = 0.46. R_e is the end-to-end distance of a chain, D the diffusion coefficient of the chain's center of the mass, and $r_{\rm sc}$ the Lindemann localization length. A power law $\sim t^{0.63}$ is fitted to the simulation data in the regime where the connectivity determines the motion of the monomers. Adapted from Ref. [2].

hibit many qualitative features which are also observed in the bulk and can be analyzed in terms of MCT (for a recent review see Ref. [1]). Examples are the two-step relaxation of intermediate scattering functions and Rouse modes, the time-temperature superposition of the α -process or the space-time factorization property on the intermediate time scale of the MCT β -process [2].

Quantitatively, however, there are differences between the bulk and the films, some of which are illustrated in Fig. 1.

We find that the first maximum of the static structure factor S_q is smaller in the film than in the bulk when the same temperatures are compared (upper panel of Fig. 1). By contrast, the intrachain structure factor S_q^p remains essentially unchanged by the confinement. This implies that the confinement alters the intermolecular packing: The "cage" around a monomer cannot "tighten" so quickly, as it is possible in the bulk.

Since this effect becomes more pronounced with decreasing h, we can understand why the dynamics is faster in the films than in the bulk (lower panel of Fig. 1). An immediate consequence of this is that $T_{\rm c}(h)$ decreases with h, in qualitative agreement with the depression of $T_{\rm g}$ found in some experiments.

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Interrelation between structure and dynamics in nanophase-separated side chain polymers

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A nanophase separation of incompatible main and side chain parts is observed for different series of amorphous side chain polymers with long alkyl groups [1]. Alkyl groups - belonging to different monomeric units and chains - aggregate in the melt and form alkyl nanodomains with a typical size of 0.5-2 nm. A consequence of this demixing phenomenon on the one nanometer scale is the coexistence of two relaxation processes with typical features of a dynamic glass transition in these materials. Below the conventional glass temperature T_g an additional polyethylene-like glass transition α_{PE} is observed within the alkyl nanodomains. For the members with long alkyl groups the α_{PE} process obeys non-Arrhenius behavior and is calorimetrically active. This is confirmed by shear and dielectric measurements as well as calorimetry and NMR [2]. A comparison of data for poly(nalkyl methacryates), poly(n-alkyl acrylates), poly(din-alkyl itaconates) and hairy rod polyimides shows that important features of the α_{PE} process are main chain independent and basically determined by the size of the alkyl nanodomains. With increasing nanodomain size the glass temperature of the α_{PE} process, $T_q(\alpha_{PE})$, increases and a strong-to-fragile transition is observed in the steepness index $m(\alpha_{PE})$. These findings are discussed in the context of cooperative motions in self-assembled confinements [1] and will be related to the long and controversial discussion about the size of dynamic heterogeneities in glasses [3]. This is an interesting link between central questions in glass transition research and structural aspects in nanophase-separated materials. The general importance of nanophase separation effects for an understanding of the dynamics of complex materials in nanotechnology and nature will be demonstrated.

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Dynamics in thin homopolymer and block-copolymer films

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Polymeric materials have attracted much attention in the past due to their interesting physical properties and the wide range of technical applications, e.g. in the form of thin-film coatings. Recently we have shown that the dynamics of thin supported homopolymer films can be quantitatively studied using X-ray photon correlation spectroscopy [1]. We have now applied this new technique also to the study of thin block-copolymer films.

We have investigated the dynamics of homopolymer films of poly(styrene) (PS) as well as block-copolymer films of poly(styrene)-*b*-poly(dimethylsiloxane) (PS-*b*-PDMS). The experiments were conducted at beamline 8-ID of the Advanced Photon Source in Argonne, USA, using X-ray photon correlation spectroscopy in grazing angle geometry. The films were examined at temperatures between 120 °C and 190 °C, i.e. above the glass transition temperature $T_{\rm g}$. Film thicknesses ranged from 40 to 300 nm. The lateral length scales examined lie between 600 and 6000 nm, i.e. we could probe much shorter length scales than those accessible by conventional dynamic light scattering in the visible range.



FIG. 1: Scattering patterns recorded on PS-*b*-PDMS with a CCD camera. Left: Bulk sample in capillary. Right: Thin film in grazing angle geometry. The image on the right shows bulk contributions from spherical micelles (as in the left image) as well as surface contributions (horizontal streak) governed by capillary waves.

Fig. 1 shows the static scattering pattern of two samples in bulk and thin-film geometry, respectively. The image on the left exhibits a speckle structure resulting from the illumination with a coherent X-ray beam. The time dependence of the speckle structure is used to unravel the dynamics in the sample. Fig. 2 shows the q-dependence of the surface relaxation times obtained from various PS films, and Fig. 3 shows a single-exponential correlation function obtained from the bulk of a thin block-polymer film.

Our results about the surface dynamics are qualitatively consistent with the theory of overdamped thermal capillary waves on thin viscoelastic films [2]. Moreover we find that the thin film dynamics of PS can be quantitatively explained by its well-known bulk viscosity [1]. Based on our results we can rule out the presence of a potential low-viscosity surface layer as suggested, e.g., in Ref. 3. For the block-copolymer PS-*b*-PDMS we observe diffusion of spherical micelles (diameter approx. 150 nm) in the bulk of the films, whereas the surface undergoes capillary wave fluctuations as in the PS case.



FIG. 2: Surface relaxation times τ obtained on thin PS films at various temperatures. $q_{||}$ denotes the momentum transfer parallel to the surface and h the film thickness.



FIG. 3: Correlation function obtained on a thin PS-b-PDMS film at 190 $^\circ\mathrm{C}.$

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Structure and Dynamics in Block Copolymers: Dissipative Particle Dynamics Simulations using a Time-Coarse-Grained Model

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Block copolymers are potentially suitable for a large number of technological applications. Understanding the interplay of molecular structure and evolution of morphology as a function of temperature and other mechanical variables is essential for further modeling or design of such materials. The dissipative particle dynamics (DPD) method seems to be promising for molecular simulations of slow dynamics in such mesoscale systems [1-3]. In brief, DPD is based on simulations of particles with soft-repulsive and dissipativeand-random forces, which enhanced collisions among particles and hence effectively stretched the characteristic time-scale of the simulated system [2]. The soft-repulsive particle represent a group or segment of molecules [3], and allow larger time-step than molecular dynamics (MD) simulation.

A fundamental problem of DPD using the softrepulsive model, however, is that there is no way to derive a coarse-grained (CG) model for a realistic molecular system. Liew and Mikami have developed timecoarse-grained models that are consistent in phase behavior with Lennard-Jones LJ(12-6) model [4]. They have devised an effective pair potential which has a hardness parameter (β) and a smooth cut-off at r_{cut} . The function is similar to LJ(12-6) when $\beta = 6$, and a model with $\beta = 3$ is analytically representing a timeaveraged effetive potential over a long time span. The resulting model of $\beta = 3$ has a much larger time-scale and allows excellent energy conservation at a very long time-step ($\Delta t^* = 0.02$) in comparison to LJ(12-6). In this work, we have extended the CG model to polymeric systems for DPD simulations of structure and dynamics in block copolymers.

For polymer systems, the CG model-particles are threaded together in linear chains by adding harmonic bonds, and the parameters are chosen in order to avoid unphysical chain-crossing. For comparison with exparimental results, the polymer model can be related to the Flory-Huggins χ -parameter. For copolymeric systems of two components, A and B, that do not favor contact, the $\chi\text{-parameter}$ can be obtained from simulations of polymer segregation as in [3]. Mixtures of homo-polymers with chain lenght $N = N_A = N_B$ is modeled by using model of $\beta = 3.0$ with $\varepsilon = 1.0, r_0 = 1.0$ for both segments of A and B. In this work, however, we are limiting the nonbonded particle interactions to a shorter range by $r_{cut} = 1.8r_0$, and we defined the A - B interaction as $\varepsilon_{AB} = (1 - \Delta)(\varepsilon_{AA}\varepsilon_{BB})^{0.5}$.

We have performed DPD simulations of symmetric di-block and tri-block copolymer of chain length $N = 10 \ to \ 40$ with A - B affinity parameter $\Delta = 0.3 \ to \ 0.5$

at temperature $T^* = 1.0$ to 2.0. From our results of χN -parameters for homo-polymer mixture, we know that the simulated copolmer systems are at the regime of $\chi N > 10.5$ or at temperature lower than the orderdisoder transition (ODT), namely $T < T_{ODT}$.



FIG. 1: Final morphology of a symmetric tri-block copolymer with chain lenght $N = 20 (A_5 - B_{10} - A_5)$.

For a DPD simulation of a 24300 particle system in a simulation cell of $30 \times 30 \times 30r_o^3$ (as in FIG. 1), the CPU time requirement to follow the whole evolution of ODT (ca. $t^* = 4 \times 10^3$ using $\Delta t^* = 0.02$) was only about 20 hours on a Linux-PC with an AMD1800+ processor. We have compared the evolution time taken from disorder to order configulations, and performed analysis of molecular conformation in the simulated morphology. The influence of the number and ratio of loop-bridge conformation on the evolution time of ODT in the tri-block copolymers is one of the key questions to be investigated in this work.

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A new approach to simulate the relaxation in polymers

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Recently, extensive theoretical and experimental efforts have been made to study the slow structural dynamics in glass-forming materials. According to Angell's classification, liquids can be classified into two limiting categories: strong and fragile. This classification is based on the temperature-dependent mechanical or relaxation behavior of the supercooled liquid state. The relaxation aspect of strong and fragile liquids can be described by the Arrhenius and the Vogel-Tamman-Fulcher (VTF) law, respectively. Studies of intermediate liquids, between strong and fragile liquids, have focused attention as a main topic in the study of liquid-glass transitions.

In the present study we introduce new lattice models of glasses with indirect dipole-dipole interaction (IDD). We consider the polymers as a highly polarizable medium (host lattice), doped by randomly distributed dipoles. As is well known, polymers have a high dielectric susceptibility, and some molecular complex can be represented as a dipole. Some recent experimental data show that α relaxation in polymers can be attributed to the reorientation of these dipoles. In our model, a flip of dipoles represents this type of reorientation. In order to calculate the effective pair interaction between the local dipoles, we adopt the Ginzburg-Landau continuum coarse-grained approximation. The interaction between a local dipole and the host lattice polarization is determined by the coupling constant, which is a material constant. We neglect the "direct" dipole-dipole interaction between the local dipoles as well as the interaction between the local dipoles and the applied field. It was shown that their contributions are much less than the corresponding contributions associated with the host lattice polarization induced by local dipoles. The effective Hamiltonian of the IDD interaction is employed for Monte-Carlo simulations of the temperature dependence of relaxation in the polymers. The crucial parameters which determine the kinetics in our system are: the correlation length of interaction $r_{\rm corr}$, the average number of local dipoles interacting with the selected one, n_d , and the reduced temperature. The computer simulation shows (see Fig. 1) that for a small value of $r_{\rm corr}$ and an intermediate value of n_d , a diffusion transition from the liquid to the glass state takes place, and this reflects the non-Arrhenius behaviour of the temperature dependence of the relaxation time. If $n_d \gg 1$, each dipole interacts with a large number of neighboring local dipoles, and this describes a strong liquid. The condition $n_d \ll 1$ indicates that there are practically no interacting local dipoles, and the system behaves as an ideal dilute sys-



FIG. 1: Temperature dependence of the relaxation time.

tem (maximally fragile). Based on this model we give a simple explanation for the set of some thermodynamic parameters introduced in previous models of the liquid-glass transition, such as: the critical temperature, T_c , at which the system loses ergodicity, the temperature of the liquid-glass transition, T_g , and the Kauzmann temperature, T_k .

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A Perturbation Method for the Solution of Integro-differential Equations in Microscopic Models of Polymer Dynamics

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Modern microscopical theories of polymer dynamics lead to integro-differential equations of the form:

$$\frac{\partial C_p(t)}{\partial t} + \int_0^t \Gamma_p(\tau) \frac{\partial C_p(t-\tau)}{\partial \tau} d\tau = -\frac{p^2}{\tau_0 N^2} C_p(t) \,,$$
(1)

where $C_p(t) = \langle \vec{x}_p(t)\vec{x}_0(0) \rangle$ is the autocorrelation function of the normal mode with number p, N is the number of Kuhn's segments per polymer chain, and τ_0 is the relaxation time of Kuhn's segment. $\Gamma_p(t)$ is the memory function covering the whole of the entanglement effects [1–4].

One of the problems of proposed theories is the complex memory function which is the kernel of Eq. (1) and depends on the properties of the model.

We suggest using a simple perturbation method to solve this type of equation. The method implies considering Eq. (1) with an exponential memory function as the zeroth approximation:

$$\Gamma_p^{(0)}(t) = \gamma_p \exp(-tw_p), \qquad (2)$$

which has to satisfy the following conditions: $\gamma_p = \Gamma_p(0)$ is the value of the real memory function at time t = 0; the integrals of the exact memory function and the exponential approximation have to be equal,

$$\int_0^\infty \Gamma_p^{(0)}(t)dt = \int_0^\infty \Gamma_p(t)dt\,,\tag{3}$$

and w_p is calculated from this expression.

Equation (1) with an exponential memory function can be analytically solved by Laplace transform methods. The solution is the sum of two exponential functions:

$$C_p^{(0)}(t) = \alpha \exp(-z_1 t) + \beta \exp(z_2 t),$$
 (4)

where the coefficients α , β , z_1 , z_2 depend on the parameters of the model as follows:

$$\alpha = \frac{1}{2G} (\mathfrak{x}_p - \gamma_p - w_p + G), \qquad (5a)$$

$$\beta = -\frac{1}{2G} (\mathfrak{w}_p - \gamma_p - w_p - G), \qquad (5b)$$

$$z_1 = \frac{1}{2}(x_p + \gamma_p + w_p + G),$$
 (5c)

$$z_2 = \frac{1}{2}(x_p + \gamma_p + w_p - G),$$
 (5d)

where $\underline{w}_p = \frac{p^2}{(\tau_0 N^2)}$ and $G = \sqrt{(\underline{w}_p + \gamma_p + w_p)^2 - 4\underline{w}_p w_p}.$

However, the autocorrelation functions in the intermediate regime are not satisfactorily described by the sum of two exponential functions (see Fig. 1). In the context of perturbation theory, the memory function may be considered as

$$\Gamma_p(t) = \Gamma_p^{(0)}(t) + \delta\Gamma_p(t), \qquad (6)$$

where $\delta\Gamma_p(0) = 0$ and $\int_0^{\infty} \delta\Gamma_p(t) dt = 0$, as follows from Eq. (3). The exact memory function $\Gamma_p(t)$ is complicated and can be evaluated by numerical integration [5].

On the base of the expansion, Eq. (6), we can construct a perturbation theory. To first order the perturbation theory results recover numerical findings [5] obtained for twice renormalized Rouse theory very well, especially at intermediate mode numbers, see Fig. 1.



FIG. 1: Autocorrelation function of normal mode p = 10 calculated by numerical methods (solid line) in twice renormalized Rouse theory [5], and obtained in zeroth, Eq. (4), and first order approximation.

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Application of the Random Walk Model to Relaxation Processes in Polymers

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The mechanisms by which a non-ergodic glassy state is obtained from an ergodic liquid state are at the centre of extensive research. Of particular interest is a better understanding of the temperature dependence of the average relaxation time, which characterises the molecular mobility in these different states. The transition to a non-ergodic state is observed by an increase of the relaxation time τ along with an increase of the average viscosity. For typical cooling rates, τ is of order 10² s at the glass transition temperature, T_g . The temperature variation of the structural relaxation time τ during the glass transition differs for different liquids: it appears to be nearly Arrhenius-like for liquids with covalent bonds and non-Arrhenius for ionic liquids.

The random walk model (RWM) has been applied to explain a non-Arrhenius temperature dependence of the viscosity. In this model, the structural relaxation can be represented as a transition from one configuration to another. This transition may be considered as a structural unit jump within a multidimensional energy landscape. At high temperatures $(T > T_c)$, the energy landscape fluctuates at a frequency that is large enough to allow a unit to jump to an adjacent site in the configuration space without further activation. This supposes that the unit can jump onto the site with lower energy as well as onto one with higher energy. If the temperature decreases, the frequency of the energy landscape fluctuations decreases. For $T < T_c$, the unit jump involves thermal activation over the associated energy barrier. We suppose that the self-energy of the structural units has a Gaussian type distribution with a width kT_0 . In the framework of the RWM in the low-temperature regime $(T < T_c)$, the relaxation time for fragile systems can be written as:

$$\tau = \tau' \left[\frac{\pi}{2(\alpha - 1)} \right]^{1/2} \alpha^{(2\alpha - 3)/2(\alpha - 1)} \left[\Gamma(1/\alpha) \right]^{-1} \times (T_0/T)^{(2-\alpha)/2(\alpha - 1)} e^{\left[(\alpha - 1)(T_0/\alpha T) \right]^{\alpha/(\alpha - 1)}}.$$
 (1)

Here, Γ is the gamma function, α determines the fragility of the system and τ_0 characterises the contribution of structural unit jumps via the fluid state towards the relaxation state. In the high-temperature regime $(T > T_c)$ where 'tunnelling' jumps predominate, the RWM yields:

$$\tau = \tau' 2^{(2\alpha-1)/2(\alpha-1)} (1/\alpha) \Gamma(1/\alpha) (T_0/T) \times e^{[(\alpha-1)(1-2^{-1/(\alpha-1)})(T_0/(\alpha T))^{\alpha/(\alpha-1)}]}.$$
 (2)

Finally, we can obtain the equation for the fragility index m:

$$m_{\rm fit} = \frac{1}{\ln 10} \left[\frac{2 - \alpha}{2(\alpha - 1)} + \alpha \left(\frac{T_0}{\alpha T_g} \right)^{\alpha/(\alpha - 1)} \right] \,. \tag{3}$$

Using this model we explain the dielectric measurements on unsaturated polyester resins. In the framework of this model, we have determined some characteristics of energy landscape, as a function of the styrene content: the width of the density of state kT_0 , the average energy barrier height $\langle E_A \rangle$ that a structural unit must overcome in order to relax, the fragility index, and the value of T_c at which the qualitative change in the dynamics occurs.

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Visco-Elastic Properties of the System Ethylene Glycol – Tetramethylurea

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Ethylene glycol as well as water are solvents with a spatial network of H-bonds. The three dimensional network of H-bonds has some peculiarities: stability, lability and elasticity. Such properties as solvophobic interaction, microstratification on H-bond networks, and microheterogeneity of strongly viscous liquids are connected with the elasticity of this network. A module of all-round compression (a reverse value of isothermal compressibility) is suggested as a characteristic of elasticity. The isothermal compressibility of ethylene glycol, measured by a direct compression instrument with unique precision, is 4 times less than that of liquid alcanes, half of the isothermal compressibility of aliphatic alcohols, and a little less than that of water. Hence, the elasticity of the ethylene glycol's network is sufficiently large.

Diluted aqueous solutions of non-electrolytes (up to 8 mol % show some peculiarities of properties behavior. For instance, aqueous solutions of tetramethylurea have extrema on concentration's dependence of partial molar volume, ultrasound's absorption, coefficient of self-diffusion, intensity of light scattering etc. An anomalous maximum of light scattering intensity can be explained by a precritical state of solution, close to a stratification region.

Solutions of tetramethylurea in ethylene glycol have been investigated by methods of densimetry, viscometry, isothermal compressibility, spin-echo, light scattering and small angle X-ray scattering. The results were compared with the same properties of aqueous solutions of tetramethylurea, and explained by an elasticity of the spatial network of H-bonds of water and ethylene glycol and by a solvophobic character of tetramethylurea's solvation.

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Intermediate length scale dynamics in glass forming polymers

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Neutron scattering (NS) techniques provide a unique tool for deciphering molecular motions in glass forming polymers. For a given system, three correlation functions can be accessed if protonated and deuterated samples are available: the self motion of hydrogens $S_{self}(Q,t)$, the collective motion involving deuterons and carbons $S_{pair}(Q, t)$ and the single chain dynamic structure factor $S_{chain}(Q, t)$. In fact, during the last years, the application of NS to polymers has been very successful, allowing to establish a number of dynamical features for these systems: (i) the study of $S_{chain}(Q, t)$ reveals that the single chain dynamics at large scales (below $\approx 0.2 \text{ Å}^{-1}$) is driven by entropic effects (Rouse model) [1]; (ii) in the α -relaxation regime, the protons perform sublinear diffusion (extensive $S_{self}(Q, t)$ investigations for $0.2 \le Q \le 2 \text{ Å}^{-1}$ [2, 3]) and (iii) the time evolution of the intermolecular correlations observed through $S_{pair}(Q_{max}, t) [Q_{max}: \text{ position of the first peak of the}]$ static structure factor S(Q) fulfills a series of universalities as predicted by the Mode Coupling Theory [4]. However, for the understanding of the complex dynamical behavior of glass forming systems, and in particular of polymers, there is nowadays a region in length scales which remains basically unexplored: that of the so called intermediate length scales (ILS) (several times the intermolecular distances). For polymers, the dynamics under question lies between the Rouse regime and the α -relaxation, universal for glass forming systems. Up to date no theory is available that predicts the dynamical behavior at ILS. With the aim of sheding some light on this question, here we present neutron spin echo (NSE) investigations extending as much as possible the studies of $S_{chain}(Q, t)$ towards short length scales and of $S_{self}(Q,t)$ and $S_{pair}(Q,t)$ towards large length scales for the same polymer, polyisobutylene (PIB). The chain dynamics show a retardation with respect to the Rouse prediction for $Q \ge 0.15 \text{ Å}^{-1}$. This effect can be attributed to the occurrence of local conformational transitions that impose an internal viscosity to the entropy driven dynamics [5]. The effective activation energy for these transitions is of about 0.43 eV. On the other hand, Fig. 1 shows the results obtained for the characteristic timescales of $S_{self}(Q, t)$ and $S_{pair}(Q, t)$ [6]. For collective motions, this time resembles the Q-dependence of S(Q), falling into a kind of plateau in the ILS regime. While the *T*-dependence of collective motion at Q_{max} is the same as that deduced from viscosity measurements, at ILS a weaker dependence is found. Such a thermal behavior coincides with that of the self motion of the protons. In fact, the T-dependence observed there is just the same found for the mechanism producing the deviations of $S_{chain}(Q, t)$ from Rouse

behavior and for the mechanical susceptibility relaxation (see Fig. 1). It seems that the same dynamical process – correlated local conformational transitions – influences self, chain and collective motions at ILS and is behind the stress relaxation in this polymer. In addition to the PIB study we will show new NSE results very recently obtained on poly(vinyl ethylene) that seem to corroborate the above described findings in another glass-forming polymer.



FIG. 1: Result of applying the shift factors corresponding to an activation energy of 0.43 eV to the relaxation times observed for the collective dynamics (empty symbols) and for the self-correlation of hydrogens (full symbols): 335 (circles), 365 (squares), and 390 K (triangles). Reference temperature: 365 K. Arrow: interpolated mechanical susceptibility relaxation time at this temperature.

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Fully Atomistic Molecular Dynamics Simulations of 1,4-Polybutadiene. A Direct Comparison with Neutron Scattering Results

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In this work we present fully atomistic molecular dynamics simulations for a realistic model of an archetypal glass-forming polymer: 1,4-polybutadiene. The simulated model consists of a cubic cell of 25 Åside with periodic boundary conditions and containing one chain of 130 monomers. The simulated microstructure was similar to that of the sample measured by neutron scattering (approximately 50% trans and 50% cis units). The simulations are carried out at three different temperatures (280 K, 300 K, and 350 K) above the glass transition $(T_g = 180 \text{ K})$ and extended until 20 ns. In order to directly compare our results with those from neutron scattering, we calculate the self-part of the van Hove correlation function, $G_s(r,t)$, the mean-squared displacement $\langle r^2(t) \rangle$, the second-order non-Gaussian parameter $\alpha_2(t)$, and the incoherent intermediate scattering function $F_s(Q,t)$ for the hydrogens in the polymer chain. The latter – and its Fourier transform – is the magnitude measured in a neutron scattering experiment on a fully protonated sample where the incoherent scattering from hydrogen atoms dominates. In addition we also calculate the density-density correlation function F(Q,t)/F(Q,0) which can be measured by means of neutron spin echo (NSE) techniques on fully deuterated samples. The results obtained agree quite well with the available neutron scattering results on 1,4polybutadiene as can be seen for instance in Fig. 1. Therefore, we can consider our simulation cell as a good mimic of reality and then we can calculate from the simulations dynamic magnitudes, which cannot be directly measured. In particular, we have separated the contributions to the incoherent scattering from the different hydrogen species: methyne and methylene hydrogens from either cis or trans monomeric units. The analysis of the corresponding magnitudes: $G_s(r,t), \langle r^2(t) \rangle, \alpha_2(t)$ and $F_s(Q,t)$, focuses on the second slow step which is associated to the α -relaxation. As it is usually found experimentally, this decay is well described in terms of a Kohlrausch-Williams-Watts (KWW) function: $A \exp[-(t/\tau_w)^{\beta}]$ – with a Q-dependent characteristic time – for all the hydrogen species and at the three temperatures investigated. However, a direct investigation of $G_s(r,t)$ reveals the presence at the lowest temperature of well defined hopping processes which are not evident in the $F_s(Q, t)$ behavior. These processes can be mainly associated with the dynamics of methyne hydrogens corresponding to the trans units (see Fig. 2).



FIG. 1: Q-dependence of the relaxation time exponentiated to β , τ_w^{β} obtained from simulations at 280 K for all hydrogens (empty symbols) in comparison with those obtained from backscattering measurements at the same temperature (full symbols). A factor 1.4 has been applied to the latter. The line shows the behavior expected from the Gaussian approximation.



FIG. 2: $G_s(r,t)$ calculated from the simulations results at 280 K for the methyne hydrogens of the trans units at the times indicated. The shoulder developing at around 2.5 Å indicates the presence of hopping processes.

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Self atomic motions in the α -relaxation regime: from simple glass formers to polymers

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In a simple glass-forming liquid the α -relaxation at $T > T_c$ is defined as the crossover from decaying to simple diffusion. However, due to chain connectivity, in a glass-forming polymer the long time limit of the α -relaxation is the well-known Rouse regime instead of the simple diffusion. The atomic mean squared displacements in these two regimes are very different: $\langle r^2(t) \rangle \propto t$ for diffusion and $\langle r^2(t) \rangle \propto t^{0.5}$ for Rouse. This implies that the intermediate scattering function, $F_s(Q,t)$, corresponding to the diffusive regime will be close to a single exponential while for the Rouse regime we should observe a stretched exponential $F_s(Q,t) \propto exp[-(t/\tau)^{\beta}]$ with $\beta \approx 0.5$. According to this behavior the Q-dependence of $F_s(Q, t)$ - i.e., $\beta(Q)$ and $\tau(Q)$ - would also be very different for simple glass-forming liquids and glass-forming polymers. In this work, we have investigated this crossover from simple glass-forming liquid like behavior to glass-forming polymer behavior by means of MD-simulations. We have used a fully atomistic model system of polyisoprene previously developed by us [1] and which resulted to be a good mimic of real polyisoprene. The initial model consisted of only one chain of 100 monomers. We have successively *cut* this initial chain to obtain eight different systems where the molecular unit gradually changes from only one to 100 monomers. The MD-simulations were carried out in the NVT ensemble [1] and at a temperature high enough (513 K) to observe the long time limit of the α -relaxation in our dynamic window (2 ns). We have calculated different magnitudes as $\langle r^2(t) \rangle$ and $F_s(Q,t)$. The Q-range covered was from 0.1 to 1 Å⁻¹. In this range, the Gaussian approximation is well fulfilled in this kind of systems [1]. The results obtained are summarized in the figures. Figure 1 shows $\langle r^2(t) \rangle$ for the different systems. The two lines correspond to the simple diffusion behavior and to the Rouse behavior. As can be seen, there is a gradual change from simple glass-forming behavior to glass-forming behavior as the number of monomers in the molecular units increases. Figure 2 summarizes the Q-dependence of both β and $\langle \tau \rangle$ for the two limit cases of 100 monomers per molecular unit (glass-forming polymer) and one monomer per molecular unit (simple glass-forming liquid). The Q-dependence in these two cases is quite different. For polymer like behavior, β hardly depends on Q and $\langle \tau \rangle \propto Q^{-2/\langle \beta \rangle}$. However, for simple glassforming like behavior, the β value changes from one (low Q) to about 0.6 or 0.7 (high Q). Moreover, there are two clear regimes in the Q-dependence of $\langle \tau \rangle$. At low Q, $\langle \tau \rangle \propto Q^{-2}$ and at high Q, $\langle \tau \rangle \propto Q^{-2/\langle \beta \rangle}$. A similar behavior was previously reported [2] from neutron scattering measurements on a low molecular glass-forming system (glycerol). We can conclude that the power law $Q^{-2/\langle\beta\rangle}$ which was previously proposed for the α -relaxation of polymers can also be observed in the case of low molecular glass-forming systems although in a very narrow Q-range due to the crossover to simple diffusive behavior at low Q.



FIG. 1: Mean squared displacement of the protons calculated for the molecular units containing 1,2,4,10,20,33,50 and 100 monomers (top to bottom).



FIG. 2: Q-dependence of the average time (squares) and the β -parameter (dots) for the molecular unit containing 100 monomers (a) and one monomer (b). Lines show the $Q^{-2/\langle\beta\rangle}$ (solid) and Q^{-2} -dependences (dotted).

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Hydrodynamic Screening in Semidilute Polymer Solutions

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We consider a system of neutral flexible polymer chains in good solvent in the semidilute regime. The standard scaling theory of the statics [1] is based on the "blob size" ξ , which controls the crossover between excluded volume statistics at short length scales and random walk behavior at large length scales (above ξ). With respect to the dynamics, there is a crossover from Zimm dynamics at short length scales (fully developed hydrodynamic interactions) to Rouse dynamics at larger length scales (hydrodynamic interactions fully screened). De Gennes has argued [2] that the hydrodynamic screening length ξ_H should scale in the same way as ξ , based on the following reasoning: Employing the picture of Darcy flow through a porous medium of obstacles, one finds $\xi_H^{-2} \sim \zeta c/\eta$, where ζ is the obstacle friction coefficient, c the obstacle concentration, and η the solvent viscosity. Since the obstacles are nothing but the blobs, one has $c\sim\xi^{-3}$ and $\zeta \sim \eta \xi$ (Stokes' law), resulting in $\xi_H \sim \xi$. This prediction has been confirmed by light scattering experiments [3]. However, the phenomenon of "incomplete screening", i. e. the presence of Zimm-like signals on length scales beyond ξ , as observed in neutron spin echo experiments on labeled chains [4], had never been explained properly.



FIG. 1: Normalized dynamic structure factor S(k, t) in the regime of large length scales, using both Rouse and Zimm scaling.

We attack this question by computer simulations, using a new hybrid method [5], where a stochastic Molecular Dynamics simulation of a simple bead– spring system is coupled dissipatively to a background solvent which is simulated via a stochastic lattice Boltzmann equation. Local mometum conservation is explicitly taken into account, and the system can be shown to satisfy the fluctuation–dissipation theorem. The big advantage of this approach is the fact that the solvent is structureless, permitting to equilibrate the chain conformations without solvent.

The results [6] on the single-chain dynamic structure factor S(k,t) show incomplete screening just as the experiments. The data are accurate enough to clearly identify the phenomenon as a short-time effect. On time scales below the blob relaxation time $\tau_{\xi} \sim \eta \xi^3/(k_B T)$, hydrodynamic correlations can propagate freely (the chains are just dragged along with the flow), while on time scales beyond τ_{ξ} the "entanglements" (effective chain-chain collisions) hinder this spreading, such that the Darcy picture starts to apply. This mechanism explains the experimental results, and confirms and completes the de Gennes picture.

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Self-Assembly and Dynamics of Poly(γ -benzyl-L-glutamate) Peptides

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The structure and the associated dynamics have been investigated in a series of oligopeptides of γ benzyl-L-glutamate using DSC, WAXS, FTIR, NMR and dielectric spectroscopy, and rheology, respectively. The peptides with degrees of polymerization below 18 are mixtures of a lamellar assembly of β -sheets and of columnar hexagonal arrangement of α -helices, whereas for longer chains, the intramolecular hydrogen bonds stabilize only the α -helical conformations [1].

Multiple dielectrically active processes were found. Starting from low temperatures, the two Arrhenius processes (γ and β), with apparent activation energies of 20.6 and 50.2 kJ/mol, respectively, associate with the local relaxation of the side-chain methylene units (γ process) and with more cooperative motions of the side chain dipoles sensitive to the 7/2helical packing (α process). The glass transition is manifested in the thermal properties with a step in the heat capacity and with an intense dielectric process bearing characteristics (molecular weight dependence, temperature dependence of relaxation times) known from amorphous polymers. Based on these findings, the α process is attributed to the relaxation of amorphous segments located between and at the end of helically ordered segments. Two slower processes were identified with opposite molecular weight dependence. The weak intermediate mode with an M^2 molecular weight dependence of the characteristic relaxation times suggests amorphous-like chains, whereas the strong slower process originates from the loss of dipole orientational capacity caused by structural defects and reflects the migration of helical sequences along the chains. This identifies the helices as structures extending over rather short fragments of chains (i.e., of low persistence length). The viscoelastic response indicated that the structural defects arise from locally aggregated chains that inhibit the flow of oligopeptides. Further investigation of highly oriented samples using a DC electric field will be presented, showing the dependence of helix dynamics on the existence of defects [2–5].

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Dendrimers and Linear Flexible-Chain Polymers: Resemblances and Differences of Self-Diffusion

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The self-diffusion and nuclear magnetic relaxation of dendritic macromolecules have been experimentally studied with NMR-methods. The solutions of poly(allylcarbosilane) dendrimers (generations from 5 up to 7), poly(butylcarbosilane) dendrimers (generations from 3 up to 7), and PAMAM dendrimers with hydroxyl surface groups (generations 3 and 4) have been examined. It is shown that experimental concentration (φ) dependence of the dendrimer self-diffusion coefficients can be reduced to a unified view – to the generalized concentration dependence of normalized diffusion coefficients, $D'(\varphi)$. The existence of this generalized concentration dependence permits one to discuss on some common laws of the dendrimer diffusivity independent on macromolecular chemical nature, features of dendrimer structure, their molecular mass, and individual properties dendrimer/solvent system.

The obtained dependence $D'(\varphi)$ of dendrimers tends to two characteristic asymptotes predicted within the frames of the dynamic scaling theory [1]: In the limit of an extremely dilute solutions, the asymptote can be described by the relation $D'(\varphi) = 1$, and the second asymptote, $D'(\varphi) \propto \varphi^{-3}$, has been obtained for range of the concentrated solutions.

These asymptotes also characterize the universal concentration dependence of diffusion coefficients obtained for linear flexible-chain polymers [2]. However, in the range of intermediate concentration dependences of self-diffusion coefficients obtained for dendrimers and linear flexible-chain macromolecules are sufficiently different. This last result exhibits that diffusion behavior of these macromolecules differs. It may be explained by non-Gaussian conformation of the dendritic macromolecules and, as a result, by the specific dendrimer interactions differing from those in the typical polymers. The absence of sufficient (long-living) entanglements and penetrations of macromolecules are apparently the dominant factors of interactions for dendrimers.

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Quenched polymer dynamics: a structural investigation by means of neutron small angle scattering

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The time dependence of a structural parameter in polymers can be conveniently studied with the small angle neutron scattering technique (SANS) by quenching a single state. Later states can be reached by heating the sample and freezing-in the new stage. This method complements the inelastic scattering methods. Through the time-temperature superposition the time scales, accessible in such an experiment have recently become roughly between τ_e and τ_d which are both connected to the basic constituents of the tube model for polymers, i.e. the primary tube segment and its chain-end structure. τ_e and τ_d characterize the entanglement Rouse time and reptation time of the chain to leave its tube. Additionally, these length scales of both fit perfectly to the scattering vector range of SANS. We will report on relaxation studies of strongly non-linearly deformed polymer melts after a fast step strain, followed by a quench. The stretching time is adjusted to the microscopic times of the system as to allow the full analysis of dynamic processes. The systems which were investigated were partially labeled H-shaped model-branched polymers, designed in a way to highlight the slow and fast dynamics under strain. Their scattering behaviour is compared to the rheological response from linear shear. The loss modulus $G''(\omega)$ in Fig. 1 clearly witnesses the existence of 2 humps. The hierarchy of time scales as well as the well-discussed tube dilution as a result of the relaxed topology could be shown unambiguously with in situ SANS on a home-built elongational rheometer [1]. This rheometer allows studies and stretching between -100° C and $+200^{\circ}$ C with varying strain rate. The full arm relaxation range which is exponentially activated and therefore broad (see Fig. 1) was accessed. The dynamics of the associated fastest nonlinear retraction process in the arm of the H-polymers can be investigated, however, in much more detail in the simpler blend of linear chains. There, single chain properties are observed [2]. The single chain structure factor $S(\vec{q}, \lambda)$ for a chain with 3-dimensional tube confinement and affinely deformed with strain λ is rescaled by the retraction rate $\gamma(t)$ in its contour length. The time-dependent variables are the orientationally averaged $\gamma(t)$, the tube diameter $d_0(t)$ and tube length. Relaxed chain ends contribute only isotropically to $S(\vec{q}, \lambda)$. Our experiments probe the time scale of about 1% of τ_R , the Rouse time of the chain up to approximately 50% of the reptation time τ_d . We show the comparison to expectations from linear rheology. The analyses in the 2D-detector plane as in Fig. 2 are indicative for non-deformed tubes and confirm the Doi estimates. The retraction is predominantly controlled by the Rouse time as expected and the amount of dangling ends agrees fairly well with renormalized reptation dynamics for contour length fluctuations [3]. As far as already available the relaxation time spectrum as well as elongational modulus will be evaluated from the non-linear step strain.



FIG. 1: Linear shear rheology of a labeled H-shaped polymer. The hierarchy shows up in 2 peaks in $G''(\omega)$.



FIG. 2: Typical 2D-scattering curve (intermediate q) and best-fit using the retraction model. The data correspond to $\lambda = 2$, ≈ 45 entanglements and 50% of the reptation time. The strain direction is vertically.

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Effects of temperature and pressure on the dynamics of hydrogen-bonded polymer blends

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As the blending of two or more polymers has become an economical route to develop new materials to meet the challenging requirements for industrial applications, the understanding of their miscibility is of critical importance.

The dynamics of poly(4-vinylphenol)/poly(vinyl ethyl ether) [PVPh/PVEE] blends, with PVPh content from 10 to 50 wt %, having a very large glass temperature difference between the components, have been investigated using broadband dielectric spectroscopy as a function of temperature (in the range of 173 to 473 K), pressure (0.1-300 MPa) and frequency $(10^{-2} - 10^{6} \text{ Hz})$.



FIG. 1: Comparison of some isokinetical sets of (T, P). Notice the change of slope at high frequencies, associated with an excess of free PVEE segments above the critical temperature. The star symbols indicate the neat PVEE.

Although a single glass transition temperature T_g was observed for all compositions in the DSC measurements, two segmental α -processes for blends with

low PVPh content were found. For $\phi_{\rm PVPh} > 0.2$, the strong hydrogen bonds give rise to a dynamically homogeneous system (unimodal segmental relaxation). For lower PVPh content (i.e., blends with PVPh content 0.1 and 0.2), the weaker hydrogen bonds give rise to two segmental relaxations, i.e. "fast" and "slow" reflecting the unassociated PVEE segments and the intermolecularly PVEE-PVPh hydrogen bonded segments, respectively [1]. We investigated the effect of pressure on the dynamic heterogeneity in the $\phi_{PVPh} = 0.1$ and 0.2 blends. Figure 1 compares the dielectric loss curves of the PVPh/PVEE 10% blend under isokinetic conditions. Pressure [2] is known to have a strong influence on the segmental dynamics [3] and on blend compatibility [4]. We show the existence of a critical temperature T_c (which is independent of pressure) above which there is additional breaking of hydrogen bonds responsible for the slower process, giving rise to an excess of "fast" unassociated PVEE segments [5].

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Nonlinear relaxation dynamics of supercooled siloxane polymers under condition of high compression

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Siloxane polymers are commercially very important, finding applications ranging from lubricants and heat exchange fluids to medical devices and cosmetic products. These materials are also intriguing from a scientific viewpoint. Their low glass transition temperature in combination with excellent thermal stability enables measurements over an enormous range of temperatures. Monodisperse siloxanes are readily available in a range of molecular weights, and with a variety of chemical side-groups. We describe dielectric measurements on polymethylphenylsiloxanes (PMPS) of varying molecular weights, carried out as a function of temperature, pressure and volume and compare the segmental relaxation properties of PMPS with the very similar polymethyltolylsiloxane (PMTS). We report results for PMPS over a molecular weight range of from 7.7 to 121 kg/mol and for PTMS with the molecular weight 35.5 kg/mol. It was found that the shape of the α -relaxation function is invariant to both variables, for temperatures approaching the glass transition; thus, frequencytemperature-pressure superpositioning is valid. Since for PMPS pressure had no effect on the steepness index (fragility), as can bee seen in Fig. 1, the correlation between fragility and the breadth of the relaxation function (non-exponentiality) is preserved under high compression. The measured isotherms were well described by a pressure counterpart of the temperature Vogel-Fulcher law, using a strength parameter that is independent of temperature. Neither dependence exhibited any variation with chain length. Comparing the properties determined from PMPS with PTMS shows that the absence of the pendant methyl on the phenyl side group in PMPS lowers T_a by 15 degrees. Nevertheless, at ambient pressure, the shape of the α -relaxation functions and the fragilities for the two polymers are identical.

However, the application of high pressure brings out differences between their respective dynamics. The relaxation times, T_q -scaled temperature dependence, and T_g itself of PMTS are all more sensitive to pressure than are the corresponding quantities for PMPS.

Furthermore, from PVT measurements it was established that for both polysiloxanes, the respective contributions from volume and thermal energy are comparable. Also the values of E_v/E (ratio of the activation energy at constant volume to the activation energy at constant pressure) for PMPS and PTMS are lower than has been reported for other polymers.



FIG. 1: Relaxation time for PMPS at various molecular weights versus pressure.

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Local structure and relaxation processes of polybutadiene up to 4 GPa

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Raising the problem of the determination of the relative effects of temperature and density on the glass transition depending on the pressure and temperature conditions, local structure and dynamics of the glass-forming polymer polybutadiene are studied, by elastic and inelastic neutron scattering and isothermal calorimetry under very high pressure. Thus we can demonstrate that along an isochore, the ns-timescale relaxation as probed by backscattering, is drastically changing, whereas the static structure factor remains nearly constant. Moreover, the fast, ps-timescale relaxation processes, which are usually observed on time-of-flight instruments near the glass transition, are not constant along the same (P, T)-line. Furthermore, we investigated the spectral changes near the Boson peak frequency (up to its disappearance under pressure at 1.4GPa) on an isotherm in the glass and at room temperature, and we observed that the modes on the low frequency side of the Boson peak appear to be most sensitive to density. Moreover the long time dynamics in the window of the calorimetric or structural experiments is compared to subnanosecond dynamics from QENS, showing a distinct pressure (then density) dependence. Thus we cannot exclude that a change of the coupling between the Boson peak modes and the fast relaxation processes occurs with pressure. At ambient pressure (this is the case of most experimental investigations), the slowing down of the motions, characteristic of the glass transition depends on the thermal energy, more than on density. However, the relative importance of those two factors might change if the experiment imposes a higher relative change of density. Actually, at atmospheric pressure, the change of density between high T and T_q is around 10%. If we impose, thanks to high pressure, a change of 20-30% of density, the glass transition might be driven by different factors, implying more density than thermal energy. The whole phenomenon of the glass transition might be different at much higher densities. None of the studies in the literature covers such a density range, allowing an isotherm variation of the relaxation time along almost 12 decades (from 10^{-9} to 10^{3} s).

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Fragility of glycerol under pressure

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More than 30 years ago an outstanding paper on the dielectric properties of glycerol was published [1]. Since then much progress has been made in extending the frequency and temperature range, respectively. But measurements under elevated pressure are scarce. Based on the old data, Paluch *et al.* found that there is an initial increase of the fragility, the slope at the glass transition temperature in the Angell plot, with pressure [2]. We constructed an apparatus to measure dielectric spectra under constant hydrostatic pressures up to 700 MPa and temperatures down to 130 K, limited by the freezing of the pressure transmitting fluid. Our set-up is similar to that described in [3].

Figure 1 shows the simple scaling $-\varepsilon''_{\rm max}$ describes the maximum value of the dielectric loss at the frequency $\nu_{\rm max}$ – for 99.5% glycerol supplied from Aldrich at 240 K for different pressures in a doublelog plot. The left wings are hardly pressure dependent and increase slightly sublinear with frequency. The slope of the high-frequency wing decreases with increasing pressure. Thus the FWHM of the curves gets broader by 16% between atmospheric pressure and 600 MPa.

In Fig. 2 we plotted $-\log 2\pi\nu_{\rm max}$ versus the $T_{\rm g}$ normalized reciprocal temperature. As shown in the inset the glass transition temperature $T_{\rm g}$ for glycerol varies with pressure in a strongly nonlinear way compared to other glass-formers. We defined $T_{\rm g}$ as the temperature where the maximum of the dielectric loss is at 1 mHz. The curves may be fitted by VFT equations with slightly increasing numerator in the exponent (D parameter) and pre-exponential factor increasing from 6 to $15 \cdot 10^{14}$ Hz with pressure. The



FIG. 1: Masterplot of the imaginary part of the dielectric permittivity for the structural relaxation of glycerol at 240 K for different pressures. Data points are omitted for clarity. The thin solid line describes a mono-exponential Debye process.



FIG. 2: Angell plot of the inverse peak frequency of dielectric spectra of glycerol for different pressures. The asymptote indicates the steepness index. Inset: Nonlinear pressure dependence of the glass transition temperature of 99.5% glycerol.

fragility m, also called steepness index, is 54 ± 2 in our pressure range. This value coincides with the value given for atmospheric pressure [4] but is essentially lower than those derived at elevated pressures in [2]. One reason for this discrepancy may be their extrapolation of the data over an extended range, another the strongly nonlinear dependence of $T_{\rm g}$ with pressure. Interestingly, $T_{\rm g}$ rises approximately linearly with a slope of 18 K/GPa at higher pressures, as measured by a ruby fluorescence technique up to 12 GPa [5]. We supposed that water content of glycerol might play a role. But our measurements of a 85% glycerol-watermixture yielded the same masterplot and the same fragility as the 99.5% glycerol, merely $T_{\rm g}$ was lowered by about 10 K.

In conclusion, in a first approximation the fragility of glycerol derived from dielectric data is pressure independent like those of the few other fragile, small molecule glass-formers measured up to this day.

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Light scattering study of an organic glassforming liquid under variable temperature and pressure, and comparison with other van der Waals supercooled liquids

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Light scattering experiments performed as a function of temperature and pressure [1] on the organic glassforming liquid OTP show that the orientational α relaxation time depends on a unique parameter. The latter can be written as the product of the density and a simple analytic function of the temperature, as shown in Fig. 1.



FIG. 1: α relaxation time of OTP versus $\Gamma = \rho/T^{1/4}$. lines: high pressure data, open squares: data taken at ambient pressure.

Experimental data [1] also allows us to compute the relative contributions of the temperature and of the density to the isobaric relaxation time [2, 3]. They are of the same order of magnitude in the whole experimental domain, although the first contribution is

larger than the second in the vicinity of the glass transition.

Results recently obtained by some of the present authors [4] by light scattering techniques on several van der Waals liquids have been re-examined in the light of this first finding. We show that the relaxation times measured by photon correlation spectroscopy also depend on a similar unique parameter. We discuss the link between this parameter and the relative contributions of temperature and density to the change in relaxation times. We also discuss the validity of the analytical form proposed for this parameter as well as some possible consequences of its very existence.

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Effect of pressure on dielectric relaxation in phthaletes

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Broadband dielectric measurements as a function of both temperature and pressure (up to $1.8 \,\mathrm{GPa}$) are used to investigate the effect of molecular structure on the dynamical properties of supercooled di-n-butylphthalate (DBP) and its isomer, diisobutylphthalate (DiBP). At atmospheric pressure, both the shape of the α -relaxation loss peak and the fragility are essentially the same for the two materials. However, the behavior of their β -relaxations differ. The activation energy for the β -process in DiBP, which is independent of pressure, is larger than for DBP, while the activation volume of the former is about an order of magnitude larger. Moreover, the separation of the α - and β -relaxation times is large in comparison to the breadth of the α -peak, suggesting that the process is not a true Johari-Goldstein relaxation. At elevated pressure, distinct differences between the α -relaxation for the two isomers become evident. The activation volume for the α -relaxation and the pressure coefficient of the glass transition temperature are significantly larger for DBP. On the other hand, the fragility of both liquids is invariant to pressure. This latter observation corroborates recent results from high pressure viscosity measurements on DBP, and is consistent with the invariance of the α peak breadth to pressure.

Related to the small value of the Kohlrausch stretching exponent and its invariance to pressure, there is no decoupling of the α -relaxation times and the dc-conductivity over the investigated range of temperatures and pressures. Finally, a comparison is made of the various characteristic temperatures and relaxation times associated with changes in the dynamics of the supercooled liquids.



FIG. 1: Temperature dependence of the α -relaxation times of DBP and DiBP and the corresponding secondary relaxation times (hollow symbols) at ambient pressure. The solid lines are fits for τ_{α} and to the Arrhenius equation for τ_{β} . Also shown for DiBP are the secondary relaxation times measured at P = 1.8 GPa. The arrows indicate the temperatures at which linear extrapolations of the respective ambient-pressure τ_{β} would intersect the τ_{α} data, at $T_B = 229$ K and 263.5 K, for DBP and DiBP, respectively.

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Comparison between mechanical and dielectric spectroscopy of poly(methylmethacrylate)

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The primary α -process due to viscous flow is not the only relaxation process in poly(methyl-methacrylate), PMMA. The dielectric loss spectrum of this polymer is dominated by a strong β -relaxation. Since the side groups of the molecules carry the main part of the dipole moment, external electric fields force the side groups to rotate. The resulting internal friction can be seen as a strong β -peak in the loss spectrum. The observed merging of the primary α - and the secondary β -relaxation process has been reported [1].

In our work, thin films of PMMA are produced with pulsed laser deposition. The temperature dependence of the dielectric and the mechanical loss are measured at one given frequency. The double-paddle oscillater is used as a substrate for the mechanically investigated films [2]. It is driven in its torsional eigenmode at a frequency of about 5400 Hz. As a result, we get the complex shear modulus of the thin PMMA-films.

Both, dielectric and mechanical losses are compared together. Though the spectra look rather similar, there are some significant differences, that may lead to a further understanding of the merging of the α and the β -relaxation process. The electric field on one and the mechanical twisting on the other hand act in a very different way to the molecules: The electric field interacts with the dipole moments of the side chains and forces them to rotate (β -process). This affects the movement of the whole molecule and leads to viscous flow above the glass transition temperature.

Mechanical twisting of the whole oscillator cannot affect the rotation of individual side chains. In this case, the primary α -process is directly excited. Viscous flow may than also lead to an attendant rotation of side groups.

We assume, that in the merging region, α - and β relaxation in PMMA are coupled together. It is not possible to excite one single process without the other. Since the driving forces in dielectric and mechanical experiments affect the molecules in a very different way, differences in the spectra are expected and can be explained.

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Mechanical spectroscopy of thin $Zr_{65}Al_{7.5}Cu_{27.5}$ films and evidence for an "excess-wing" in metallic glasses

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The double-paddle oscillator is used for the study of mechanical properties of thin amorphous $Zr_{65}Al_{7.5}Cu_{27.5}$ -films in the temperature range from 300 K to 650 K under ultra-high vacuum conditions. The films are prepared by simultaneous electronic beam evaporation from elements of high purity [1]. The oscillator is driven in its secondary torsional eigenmode at about 5400 Hz and the temperature dependence of the complex shear modulus of the film is measured.

At temperatures above the glass transition, the loss modulus can be mathematically described by a Havriliak-Negami function. The characteristic relaxation time is calculated with a Vogel-Fulcher-Tammann temperature behaviour. In the vicinity of the glass transition, our data clearly differ from this mathematical model. The temperature dependence of the mechanical loss modulus is very similar to the dielectric loss modulus of many other glass forming materials, where the deviation from the viscous α -process is described with an "excess wing" [2]. Our experimental results give rise to the assumption that there exists a "wing" also in amorphous metals and could therefore be a universal property of glasses.

One interpretation for the "wing" is to postulate

density fluctuations and dynamic heterogeneities. Cooperative movement of groups of atoms that are called clusters and formed in the vicinity of the glass transition lead to a deviation of the α -process that is due to single-atom movement. The size of these clusters is related to the correlation length of the density fluctuations and is for the Zr₆₅Al_{7.5}Cu_{27.5}-system at about 2 nm [3].

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High Temperature Viscosity Measurements by the Gas Film Levitation Technique: Application to metallic glasses

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To obtain a metallic glass, it is essential to supress the nucleation and growth reaction of a crystalline phase in the supercooled liquid region between the liquidus temperature and the glass transition temperature. Viscosity, which controls the atomic mobility, is an important factor for the transport phenomenoms. Consequently, viscosity measurements are an interesting diagnostic to characterize the glass forming ability (GFA) of a given system.

A contactless technique, namely "gas film levitation", has been developed in our laboratory in CEA-Grenoble [1, 2], the apparatus is shown in Fig. 1.



FIG. 1: Schematic diagram showing the main features of the experiment.



FIG. 2: Drop deformation and relaxation in the gas film levitation process.

The principle of the technique is the following: a flow of inert gas is forced through a porous membrane placed below the sample that is levitated. Heating is achieved by means of a radio frequency system. The specimen is observed by means of a video camera through a hole located opposite to the illumination window. The viscosity measurement is based on the relaxation kinetics of a droplet contactlessly deformed from the top, with the help of a porous membrane similar to the one used for the levitation (Fig. 2). The relaxation kinetics can be studied within the frame of Chandrasekhar s formalism [3], that allows the identification of two types of behavior depending on the value of the Ohnesorge number, $Oh = \eta^2/(R\sigma\rho)$ that relates a typical sample dimension R, the material surface tension σ , density ρ , and the dynamic viscosity η .

At low values of Oh, typical of the metallic glass forming liquids, the return to the equilibrium of the drop apex takes the form of a damped oscillation of characteristic time constant τ proportional to the viscosity of the material. The relation between η and τ is $\eta = (1/5)(\varrho R^2/\tau)C_2(f)$, where $C_2(f)$ is a correction factor tabulated in Ref. [4].

Preliminary experiments were carried out on the glass-forming systems $Pd_{40}Ni_{10}Cu_{30}P_{20}$ (Fig. 3) and $Pd_{40}Ni_{40}P_{20}$.



FIG. 3: Viscosity-versus-temperature curve of the $Pd_{40}Ni_{10}Cu_{30}P_{20}$ metallic glass former.

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Diffusion and Viscosity in $Pd_{40}Ni_{40}P_{20}$ and $Pd_{40}Cu_{30}Ni_{10}P_{20}$ Melts

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Diffusion and viscosity in ordinary single or binary element melts close to the liquidus temperature can be described with help of the hard-sphere model [1]. The resulting temperature dependence of diffusion follows a power-law $D \sim T^n$, with n = 1.7...2.3 [2]. Meyer showed [3] that the mode-coupling theory can describe the dynamic behavior of multicomponent Pdbased melts with a temperature dependence of diffusion $D \sim [(T-T_c)/T_c]^{\gamma}$, with $\gamma = 2.7$ and $T_c \approx 700$ K. T_c denotes a critical temperature at which hydrodynamic motion freezes and only hopping of atoms contribute to mass transfer.

In order to investigate the correlation between diffusion and structure in multicomponent melts, the self diffusion of 62 Ni and the shear viscosity in liquid Pd₄₀Ni₄₀P₂₀ and Pd₄₀Cu₃₀Ni₁₀P₂₀ have been measured [4]. For diffusion measurements the long-capillary technique was used and the gas-filmlevitation technique was used for viscosity measurements. The Stokes-Einstein relation describes well the momentum and mass transport in both melts. The 62 Ni diffusion is equal in both alloys whereas the bulk viscosity is higher in Pd₄₀Ni₄₀P₂₀ (see Fig. 1).



FIG. 1: Ni Diffusion coefficients in liquid $Pd_{40}Cu_{30}Ni_{10}P_{20}$ and $Pd_{40}Ni_{40}P_{20}$ calculated with help of the Stokes-Einstein relation and the Ni covalent radius. The open and closed circles denote calculated diffusion coefficients for PdCuNiP and PdNiP, respectively, the solid lines calculated diffusion coefficients of Vogel-Fulcher-Tammann fits of the respective viscosity data. For comparison the Ni diffusion coefficients of the long capillary diffusion experiments are given (open and closed stars denote diffusion coefficients in PdCuNiP and PdNiP, respectively).

Based on Park's model of the Pd-melt's structure

[5] and based on thermodynamic data of the investigated alloys [6] we assume that localized "network cells" with more or less rigid bounds may fluctuate with time and site. Here, Phosphorous plays an important role as a network former due to its strong covalent bindings. This strong binding character explains the high viscosity compared to ordinary metallic melts.

Substitution of 75% of Ni by Cu $(Pd_{40}Cu_{30}Ni_{10}P_{20})$ replaces some of the strong Ni-P bindings by somewhat weaker Cu-P bindings and thus lowers the viscosity in comparison to $Pd_{40}Ni_{40}P_{20}$.

pair	$\Delta H^{\rm mix}/{\rm kJ/mol}$
Cu-Ni	4
Cu-P	-17.5
Ni-P	-34.5
Cu-Pd	-14
P-Pd	-36.5
Ni-Pd	0

TABLE I: Mixing enthalpies for element pairs calculated for the partial ternary systems in amorphous Pd-Cu-Ni-P [6].

Obviously, the substitution of Ni by Cu does not effect the Ni diffusion. We assume that only a fraction of the Ni-atoms is immobilized in the "network cells" whereas other Ni atoms can move liquid-like through the network.

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Viscosity Investigations on Liquid Sn-Ag-Cu Alloys

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In order to reduce an adverse impact of lead on health and environment, the Sn-Pb solders commonly applied in industry at present have to be put out of use in a recent future. Sn-Ag-Cu alloys are considered as the most potential candidates for new lead-free solder materials. However there appear difficulties concerning practical application of the Sn-Ag-Cu alloys for soldering. These alloys are less efficient and present some mechanical, thermo-mechanical and technological problems as compared to the lead-containing solders.

Only few experimental investigations on liquid as well as solid Sn-Ag-Cu near-eutectic alloys are known from the literature. In order to find the best composition matching the characteristics required by electronic industry a comprehensive study of various physical properties is needed, such as thermodynamic (specific heat, latent heat of fusion, fusion temperature), electrical (resistivity, thermopower), mechanical (hardness, stress-strain, shear strength), flow and adhesion (viscosity, surface tension, wetting), volume change during solidification, solid structure and its stability, etc.

The absolute values of the viscosity are very important for easy flowing of a solder material. We present the experimental results of viscosity investigations carried out in a wide temperature interval on binary Sn-Cu and Sn-Ag eutectic alloys as well as on ternary Sn-Ag-Cu liquid alloys with different Ag and Cu content. The measurements of the viscosity were done with a computer-controlled oscillating-cup viscometer [1]. The dynamic viscosity, η , has been calculated from the logarithmic decrement and the period of oscillations using the modified Roscoe equation [2].

The experiments were performed in an atmosphere of 90% Ar–10% H₂ after initially pumping out the working volume of the furnace to ~ 10 Pa. Accurately weighed (to within \pm 0.1 mg) amounts of the pure components (99.999 %) were initially melted in evacuated and sealed quartz ampoules. The sample compositions of about 70 g were accurate to 0.02 wt. %. Each sample has been weighed before and after the measurements, and no mass loss has been observed. The cylindrical boron nitride crucibles with internal diameter of 20 mm were used. A homogeneous temperature field (\pm 0.3 K) in the range of absolute values up to 900 °C has been created inside a furnace. The sample temperature has been measured with the Pt/PtRh thermocouple arranged just below the crucible and controlled with an electronic regulator. Before the experiments were done, the temperature reading was calibrated by measuring the melting points of pure Sn, Ag and Cu. The samples first were heated up to $800-850^{\circ}$ C and held for about half an hour. Then the measurements were carried out during cooling with rate of 1 K/min up to the alloys solidification. The absolute values of the dynamic viscosity were determined with an accuracy of about 5%.



FIG. 1: Temperature dependences of the dynamic viscosity in liquid Sn-Ag-Cu and Sn-Pb [3] alloys.

The experimental results are plotted in Fig. 1. The temperature dependences of the dynamic viscosity for all investigated alloys can be described with an exponential law. The dynamic viscosity of the eutectic Sn-Pb alloy taken from Ref. [3] is also presented in Fig. 1 for a comparison. It is noteworthy that the dynamic viscosity of the ternary Sn-Ag-Cu eutectic alloy as well as that of binary Sn-Cu and Sn-Ag eutectic alloys is lower than the dynamic viscosity of the liquid Sn-Pb eutectic alloy over the whole investigated temperature interval.

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Microscopic Dynamics and Mass Transport in Pd-Ni based Melts

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Palladium-Nickel based bulk metallic melts can in good approximation be regarded as hard-sphere like systems. As compared to simple liquids, these melts are characterized by a dense packing. As a consequence, their microscopic dynamics are not described by concepts developed for simple liquids. Instead, atomic transport in Pd-Ni based melts is in excellent accordance with concepts developed in the context of glass formation. Pd-Ni-Cu-P melts in quasi eutectic composition [1] exhibit relatively low liquidus temperature at 865 K – as compared to pure liquid Nickel at 1727 K. On approaching the liquidus, structural relaxation becomes well separated from vibrations. This allows us to study the atomic transport mechanism in hard-sphere like, metallic liquids.



FIG. 1: Rescaling of the density correlation function in α relaxation regime (for $t > 1 \,\mathrm{ps}$) using result from fits with a stretched exponential function: time-temperature superposition of structural relaxation holds. Inset: Normalized density correlation function $\Phi(q,t)$ of liquid Pd₄₃Ni₁₀Cu₂₇P₂₀. The lines are fits with a stretched exponential function. Upper right panel: mean relaxation time τ_q of self motion in liquid Pd₄₃Ni₁₀Cu₂₇P₂₀. $1/\tau_q$ shows a q^2 dependence as expected for long range atomic transport for $q \rightarrow 0$. The slope corresponds to the self-diffusion coefficient D.

We investigated microscopic dynamics in PdNiCuP melts with inelastic neutron scattering. The intermediate scattering function displays a fast relaxation process that proceed structural relaxation. The structural relaxation exhibits stretching and obeys timetemperature superposition (see Fig. 1). Liquid Ni, NiP, PdNiP, and PdNiCuP melts exhibit a similar packing fraction although the liquidus and the under-cooling capabilities are quite different. A comparison of the inelastic neutron scattering data shows that neither the absolute value of the Ni diffusivity nor the normalized correlation function of Ni dynamics are affected significantly by the change in the alloys composition (see Fig. 2).

In contrast to simple liquids, atomic transport in dense, glass forming liquids is characterized by a drastic slowing down of dynamics on cooling and a q^2 dependence of the mean relaxation time at intermediate q as a result of a highly collective atomic transport mechanism. At temperatures as high as $2.5 \times T_c$, diffusion in these melts is as fast as in simple liquids at the melting points. However, the difference in the underlying atomic transport mechanism indicate that the diffusion mechanism in liquids is not controlled by the value of diffusivity but rather than that of the packing fraction [2].



FIG. 2: Mass transport in Pd-Ni based melts: Self diffusion coefficient D of Ni in liquid Pd₄₃Ni₁₀Cu₂₇P₂₀, Pd₄₀Ni₄₀P₂₀, Ni₈₀P₂₀ and pure Ni derived from the mean relaxation times (QNS). The inset shows S(q,t) for similar Ni diffusivities. For comparison, diffusivities by ⁶²Ni tracer diffusion are also shown.

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Sub-picosecond dynamics in liquid non-simple metals

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Our recent inelastic X-ray scattering (IXS) experiments on several non-simple metals, such as Si [1], Ge [2], Sn [3], and Ga, have revealed characteristic common features in the collective dynamics. (i) Clear indications for the propagating modes were found as in simple liquid metals, whereas their lifetimes are much shorter. (ii) They exhibit a *positive* dispersion of about 15–25% (except in liquid Ge) again as in simple liquid metals. (iii) A very short time (sub-picosecond) retaining of nearest-neighbour correlation is visualized by a Gaussian component in the quasielastic line shape, which may be related to short-lived covalent species. We review our recent findings by focusing on liquid Si [1] as a typical non-simple liquid metal.

We have investigated the microscopic particle dynamics of liquid Si using high-resolution IXS at BL-35XU/SPring-8, and for the first time obtained the dynamic scattering law, $S(Q, \omega)$, of this metallic liquid. Within the generalized Langevin formalism, the time Fourier-transforms of $S(Q, \omega)$, i.e., the intermediate scattering function F(Q, t), can be determined using a memory function M(Q, t). For M(Q, t), we used a well-known approximation containing two (fast and slow) exponential decay channels for viscous relaxation and one exponential for thermal relaxation.



FIG. 1: F(Q, t) normalized to the initial value S(Q) at selected Q values. The dashed curves represent the Gaussian components.

Figure 1 shows selected F(Q, t) spectra normalized to the initial value, F(Q, t) = S(Q). At the low Q values, the spectra exhibit oscillatory behaviours, which are the time-domain analogue of the inelastic excitations in $S(Q, \omega)$. At 18.9 nm⁻¹, the decay of F(Q, t)is nearly exponential, which reflects the Lorentzian shape of the quasielastic line. However, close to the S(Q) maximum, 27 nm⁻¹, where structural correlations to next neighbours dominate, it is evident that the decays are no longer exponential. The dashed curves represent the Gaussian components in F(Q, t).

We interpret the associated slower decay of F(Q, t)as an additional enhancement of the correlation time between neighbouring particles on the sub-picosecond level. We can estimate the timescale of the corresponding correlation from the width of the Gaussian contribution in F(Q,t) at the S(Q) maximum to be ~ 90 fs. Such short time correlations between neighbours have already been observed in an *ab ini*tio molecular dynamics simulation on liquid Si [4]. It was found that on a time scale of several ten fs, a substantial amount of charge piles up between atoms approaching closer than a critical distance. Their results are in accord the line shape variation found in the present IXS experiment close to the S(Q) maximum. Therefore our observation is the first direct experimental evidence for these sub-picosecond density fluctuations.

Similar anomalies were also found in other nonsimple liquid metals, such as liquid Sn [3] and Ga, which will be also reported in this paper.

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The Mixed Alkali Effect in ternary Silicates: Computer Simulation Studies

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In ternary silicate glasses of the type $[x \cdot A_2 O][(1 - x)B_2 O][y \cdot SiO_2]$ with two different mobile alkalicomponents A and B (e.g. A = Li und B = K) the so-called mixed alkali effect (MAE) is observed. The MAE is the phenomenon that the diffusion of the alkali ions is much slower in ternary systems (e.g. x = 0.5) than in the corresponding binary systems (i.e. x = 0 and x = 1). The MAE is also observed in other glassformers (e.g. borates or phosphates) containing mobile alkali ion components. Based on this universality, many attempts have been made to give insight into the MAE by simple theoretical models, but an understanding of the MAE on a microscopic level is still lacking.



FIG. 1: This figure shows how Debye-Waller and Lamb-Mößbauer factors change from binary (KS2) to ternary (LK2) mixture. Shown here for potassium only.

We examine systems of the types $(K_2O)(2 \cdot SiO_2)$ (dubbed KS2 here), $(Li_2O)(2 \cdot SiO_2)$ (LS2) and $(0.5 \cdot K_2O)(0.5 \cdot Li_2O)(2 \cdot SiO_2)$ (LKS2) via molecular dynamics computer simulations. The potential employed is from Habasaki *et al.* [1]. The simulations are done at constant pressure (p = 0) for systems with 8064 particles at temperatures ranging from 1000 K to 3000 K. While we can fully equilibrate systems at about 1800 K, the systems at around 1000 K only show diffusive behaviour for the alkali ions (systems at 1000 K were relaxed over 78 ns).

The oxygen-neighborhood of the alkali ions is characterised through different mean coordination numbers of the Li- and K-atoms with oxygen (approximately 4–5 with Li and 8–9 for K), as well as different distances for Li–O and K–O next-neighbors. Also, the examined systems show several different intermediate length scales, manifesting themselves through prepeaks in the partial structure factors. The dynamics is analysed by (in)coherent intermediate scattering functions. Preferable sites for the alkali diffusion are found that are located in a network of channels. In the ternary system, each alkali species moves in its own channel network leading to a stronger localization of alkali sites. This is quantified by means of the Debye-Waller factor $f_{\rm KK}(q)$ and the Lamb-Mössbauer factor $f_{s,K}(q)$ which are shown for KS2 and LKS2 at $T = 1000 \,\mathrm{K}$ in Fig. 1. In KS2 $f_{\mathrm{KK}}(q)$ decays much faster than $f_{s,K}(q)$ which means that the correlations between potassium sites is much less localized than the one-particle potassium motion (note that the same behavior is found in LS2 at T = 1000 K). In contrast to that in LKS2 both quantities show a similar decay.

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Molecular Dynamics Study of Ion Dynamics in the Nearly-Constant-Loss Region

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Molecular dynamics simulations of lithium metasilicate (Li₂SiO₃) in the glassy state have been performed at 700 K and 500 K to elucidate the nature of the movements of the ions that give rise to the nearly constant loss experimentally found in ionic conductors of all kinds in the high frequencies/short times regime, when the mobile Li ions are caged.



FIG. 1: Mean squared displacement of Li ions at 700 K.

Several time regimes in the mean square displacement (MSD) of Li ions, $\langle r^2 \rangle$, at 700 K are shown in Fig. 1. At the very short times we see the ballistic motion that has $\langle r^2 \rangle \sim t^2$, followed by an apparent overshoot (oscillation) corresponding to the boson peak observed in neutron and light scattering experiments. At times 0.4 ps to 1.6 ps, there is an extended time regime that the MSD increases very slowly with time approximately as t^{α} with $\alpha \approx 0.11$, which is identified with the NCL. This NCL time region was found to become one order longer at 500 K. This result follows from the relation between MSD and complex conductivity

$$\sigma^*(\omega) = -\omega^2 \frac{N_{ion}q^2}{6H_R kT} \int_0^\infty \langle r^2(t) \rangle e^{-i\omega t} dt \,, \qquad (1)$$

where N_{ion} is the density of mobile ions, q the ion charge, k the Boltzmann constant, H_R the Haven ratio, and T the temperature. For $\langle r^2 \rangle \propto t^{\alpha}$, Eq. (1) gives $\sigma'(\omega) \propto \omega^{1-\alpha}$ or $\epsilon''(\omega) \propto \omega^{-\alpha}$, and hence the NCL because α is small. The properties of the NCL differ in many respects from the ion hopping transport contribution and can be considered to have a different physical origin. Using the self part of the van Hove function $G_s(r,t)$ of Li ions, we conclude that almost ions are still within their cages in this region, although the contribution of jump to MSD is non-negligible. The NCL as defined no longer holds after t_{x1} , as indicated in Fig. 1 when the MSD deviates from the $t^{0.11}$ dependence. The process is followed ($t_{x1} < t < t_{x2}$) by some independent jumps of ions contributing a linear t term to the MSD. Then, cooperative ion jumps start with the MSD initially ($t_{x2} < t < \tau$) having a t^{θ} -dependence ($0 < \theta < 1$) and finally, when $t > \tau$, the steady state diffusion regime is reached and the MSD is proportional to time [1].

In the present work we shall focus our attention on the motions contributing to the NCL from the Li ions most of which remain within their cages. There is a broadening of the first peak of $G_s(r,t)$ in the NCL time regime caused by motion of the Li ions within the cages and the changes with time of the spatial relation between the ion and the matrix atoms. Examples of displacements of individual Li ions indicate the existence of a distribution of displacement amplitudes within the cages, including large amplitudes. The behavior of the van Hove function in the NCL regime $(t_{x1} \approx 40 \text{ ps})$ at 500 K was examined in detail. The difference of the self part of the van-Hove function at t = 9.6 ps and that at $t_v = 1.6$ ps (beginning of the power law region in MSD) has a |r| dependence given by $A|r|^{-\beta-1}$, with $\beta \approx 0.1$ in the region between 0.8 Å and 2.0 Å. That is, the functional form is the tail of a Lévy distribution, where β is the Lévy index $(0 < \beta < 2)$ and $\beta = 2$ corresponds to the Gaussian distribution [2]. The difference of $G_s(r,t)$ for t = 36 ps and t_v was also examined. With increasing t, the prefactor, A, of this distribution becomes larger while β is found to be nearly constant. The motions of the caged Li⁺ ions are correlated with the matrix atoms, particularly the oxygen. In fact, the near constant loss and the accompanying Lévy distribution of length scales disappear if the oxygen atoms are frozen in a simulation. These results suggest that the near constant loss originates from anharmonic interaction of the caged Li⁺ ions with the surrounding matrix atoms executing correlated movements. Our results pave the way for a rigorous treatment of caged ion dynamics by nonlinear Hamiltonian dynamics.

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First-Principles Molecular-Dynamics Simulations and Neutron Scattering on Hydrous Silicate Systems: Structural Properties and Diffusion Mechanism

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In recent years the influence of water on the structure and viscosity of silica (SiO_2) and silicate melts has attracted the interest of many experimental groups due to its importance in geology (e.g., magmatic flow in the earth crust, explosive volcanic eruptions) as well as technology (e.g., glassy optical fibers and semiconductors). These, mostly spectroscopic, measurements suggest that both, water dissolved in the form of Si-OH groups and molecular water are present. The ratio of dissolved and molecular water depends on the temperature and governs the viscosity of the melts above the glass transition temperature T_g . For reviews on the subject see [1].

This project is an attempt to perform a quantumchemical verification of the existing experimental data and hence to obtain a deeper understanding of the dissolution mechanisms of water, in particular in systems containing Al. In a first step we simulate pure (this means Al and Na free) SiO₂ systems with variable content of water. Structural quantities (as the structure factor) and dynamical quantities (as the vibrational density of states) can be directly compared and validated with corresponding quantities obtained from neutron scattering experiments. So far a system of silica containing 3.84wt% H₂O has been equilibrated in its liquid state at temperatures of 3000K and 3500K employing the ab-initio molecular dynamics code CPMD [2].

At the mentioned total water concentration of 3.84wt% we find the water in the liquid state completely dissolved in the form of SiOH groups. Due to the water speciation to SiOH groups, the silica tetrahedral network is broken. Water molecules are only found as transition states and play a role for the hydrogen transport in the liquid. Generally, we find three such intermediate states. These are (i) SiO dangling bonds, (ii) water molecules, and (iii) bridging hydroxyl groups. Figure 1 presents the contribution of each of the mentioned groups to the number of composed OH units per time interval. The formation of new OH bonds gives us an idea of the hydrogen diffusion in the liquid. Statistical quantities like the vibrational density of states and the neutron scattering structure factor can also be extracted from the simulations. We will compare them to recently obtained experimental data.

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FIG. 1: Relative contribution of several intermediate states to the formation of new OH groups.

Vibrational properties and first principles calculation of NMR spectra for a sodium tetrasilicate glass model: simulated vs. experimental spectra

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During the last two decades, significant experimental and theoretical effort have been made in order to provide valuable information on the microscopic structure and the vibrational properties of silicate glasses and melts. These systems represent challenging problems of condensed matter physics, glass and earth sciences.

In this contribution, we present some microscopic characteristics of a sodium tetrasilicate glass $Na_2Si_4O_9$ (called hereafter NS4) which was obtained by combined Car-Parrinello and classical molecular dynamics simulations [1]. The attention given to this system is justified by the fact that it can be used as a prototype for more complicated aluminosilicate and hydrous silicate glasses [2].

Firstly, we present the vibrational properties of NS4 glass model derived using an *ab initio* approach in the framework of the density functional theory, as well as a classical valence force fields one [3]. The total and partial vibrational densities of states (VDOS) are presented, as well as some characteristics of the vibrational modes (participation ratios, correlation lengths). For the low-frequency bands below 500 $\rm cm^{-1}$, we find that the shapes of the two calculated VDOS as well as those of their corresponding partial VDOS are quite similar. For the intermediate- and high-frequency ranges, we observe larger discrepancies between the two calculations. Using the eigenmodes of the dynamical matrix we also calculate the polarized Raman spectra within the bond-polarizability approximation. We find an overall agreement between the calculated parallel polarized (VV) Raman spectra and the corresponding experimental spectrum. Regarding the perpendicular depolarized (VH) Raman spectrum, the comparison of the calculated spectra to the experimental data indicates a need for an adjustment of the VH bond-polarizability parameters.

Subsequently we will present results of first principles calculations of the ¹⁷O, ²⁹Si and ²³Na NMR spectra performed for the NS4 model using the recently introduced gauge including projector augmented wave (GIPAW) method [4]. In contrast to previous studies using modelling clusters, this method probably better accounts for the local environmement that exists in real systems.

The theoretical NMR spectra are in good agreement with the experimental data. Based on these results, we investigate the relationships between the NMR and the structural parameters that exist in such glassy systems. For ²⁹Si, a linear dependence of the $Q^{(4)}$, $Q^{(3)}$ and $Q^{(2)}$ isotropic chemical shift with the mean $\langle \text{Si-O-T} \rangle$ angle has been obtained, in agreement with results of literature. We have also shown that the $Q^{(3)}$ chemical shift anisotropy can be well predicted by a simple linear function of the $\langle \text{Si-O} \rangle_{\text{BO}}$ and $\langle \text{Si-O} \rangle_{\text{NBO}}$ bond length, with errors less than 10 ppm. For bridging oxygens, the quadrupolar coupling constant C_q and asymmetry parameter η_q are primarly influenced by the $\langle \text{Si-O-Si} \rangle$ angle,

For all these nuclei, we also investigate trends between the NMR parameters themselves. We expect that such relationships will simplify the problem of extracting the distributions of NMR parameters from experimental data by reducing the number of unknowns.

Finally, we will discuss the modification of the structural and vibrational properties of our NS4 glass model upon compression.

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The Dynamic Structure Factor of Oxide Glasses: A Probe of Mode Localization?

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The localization of the vibrational modes is an intrinsic property of amorphous solids [1]. Several measures of the degree of localization – participation ratio $p_c(\nu)$ and phase quotient $q_{\Sigma}(\nu)$ – have been proposed in the literature [2]. Previous studies of the vibrational dynamics of amorphous SiO₂ (a-SiO₂) [3] and sodium silicate glasses [4, 5] have shown that the localization of the vibrational modes increases with increasing frequency and with increasing degree of depolymerization [5]. Unfortunately, it is not possible to determine experimentally p_c and q_{Σ} as a function of the frequency. The same is true also for other characteristics of the vibrational modes like their stretching character [6].

The dynamic structure factor $S(q,\nu)$, measured by inelastic neutron and X-ray scattering, is a powerful tool for investigating the dynamics of disordered systems. $S(q,\nu)$ for a-SiO₂ has been calculated by several authors and compared with experiments (Ref. [7] and references therein). First calculations of $S(q,\nu)$ in the harmonic approximation will be presented for depolymerized sodium metaphosphate (NaPO₃) and sodium silicate glasses (Na₂O)_x(SiO₂)_{1-x} (x = 0, 0.2, 0.33 and 0.5) using *ab initio* molecular-like phosphate clusters and molecular dynamics models for the silicate glasses.

However, both the calculation and the interpretation of $S(q,\nu)$ data is difficult because the geometric structure and the correlated motions of the atoms are strongly coupled in $S(q,\nu)$. Following the approach of Carpenter and Pelizzari [8], a new expression is developed relating the one-phonon scattering law $S^{(1)}(q,\nu)$ and modified expressions for the participation ratio, phase quotient and the stretching character of the vibrational modes. This expression allows, from one side, more detailed analysis of the frequency and the wave-vector dependencies of the dynamic structure factor of the investigated glasses and, from the other side, extraction of some information about the mode localization using experimental neutron inelastic data.

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Structure, Structural Relaxations and Macroscopic Properties of Silica Glass

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Silica glass has various basic interesting properties, besides that it has been solely used as a key material in photonics. The group has devoted to elucidate quantitatively the structure, structural relaxations in silica glass, varying temperature, dopant species and its concentration, in conjunction with macroscopic properties such as density and the refractive index. What we have found so far are: (i) The structural relaxation has at least two relaxation processes, or even a distribution of relaxation times. The relaxation processes with the longest relaxation time has the same activation energy as that of the macroscopic viscosity variation as a function of temperature. (ii) Doping of OH, Na, F, Cl etc. very much accelerates the relaxation. For example, doping of F up to 7 mole %can change the relaxation time by the 5–6 orders of magnitude [1]; see Fig. 1. Cl-doping also has a similar outstanding effect on the relaxation. This implies that a proper dopant of a proper concentration can bring silica glass to a more stable structure during a reasonable length of time, giving a great breakthrough to make silica fibers for optical telecommunication much more transparent, as the optical loss in the fiber comes from the Rayleigh light scattering due to the density fluctuations, or the disordered structure of glass, frozen-in at a high temperature at the fictive temperature. (iii) We measure the UV absorption edge of F-doped silica glasses. We then find that the Einstein temperature to describe the variation of the Urbach energy does not seem to depend systematically on F-concentration. (iv) On the other hand, the density of F-doped silica glass very much depends on F-concentration. The density gets larger with increasing F-concentration [2]; see Fig. 2. (v) The refractive index shows a similar F-concentration dependence [3]; see Fig. 3. This result should be interpreted not only by the density variation but also by the polarizability of F atoms. We have concluded from the above results that at least around each doped F atom, probably making a bond with Si atom, a space is made that is more open than the silica glass structure. One can call this space a micro-pore, or a free-volume. The concept 'free volume' has been conveniently used to interpret many experimental results. The present study clearly shows its existence.



FIG. 1: Structural relaxation time in F-doped silica glass.



FIG. 2: Density in F-doped silica glass.



FIG. 3: Refractive index in F-doped silica glass.

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Understanding the complex transport behavior of supercooled liquids on the basis of their potential energy landscape: a computer study of silica and Lennard-Jones systems

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Since the pioneering work of Goldstein [1], it has been realized that the potential energy landscape (PEL) viewpoint is useful for characterizing supercooled liquids and glasses. To this end, one considers the high-dimensional vector of all particle coordinates as a point moving on the surface of the total potential energy [2]. At sufficiently low temperatures, the system resides near the local minima of the highdimensional PEL. It has turned out that the PEL description of thermodynamics starts to work when cooling below approximately $T = 2T_c$, where T_c is the critical temperature of mode-coupling theory [3]. In this temperature regime the statistical properties of PEL minima fully determine all *thermodynamic* properties [4].

Recently, we have employed this concept to obtain a better understanding of the *dynamics*, i.e. of the slowing down of molecular motion upon cooling for the standard binary mixture Lennard-Jones system. For this purpose we have introduced an appropriate coarse-graining of the configuration space, thereby combining individual inherent structures. This gives rise to the concept of metabasins (MBs) [5]. In this framework new insight about the central questions of this workshop can be obtained. (1) Material properties vs. microscopic dynamics. It turns out that the average time τ to escape a MB fully determines the diffusion process for $T < 2T_c$, i.e. $D(T) \propto \langle \tau(T) \rangle^{-1}$. Thus there is a direct connection between the macroscopic (D(T)) and the microscopic $(\langle \tau(T) \rangle)$ dynamics. (2) Underlying transport mechanisms. The escape out of the relevant low-energy MBs can be effectively characterized as an activated processes for temperatures below $2T_c$ with an activation energy E, only depending on the energy ϵ of the MB. Actually, it is possible to identify the relevant saddles which give rise to the functional form of $E(\epsilon)$. (3) Interplay between structure and dynamics. The presence of the energy dependence $E(\epsilon)$ implies that there exits a close connection between the potential energy ϵ , characterizing the stability of the structure, and the dynamics, governed by the activation energy E. In particular this allows one to understand the Non-Arrhenius temperature dependence for a fragile system like the Lennard-Jones system. At lower temperatures the system samples lower regions of the PEL. These low-energy states, however, are more stable and can be characterized by a higher

activation energy. This gives rise to an apparent increase of the activitation energy upon cooling.

Presently, new aspects of this general approach are analysed with respect to two key questions.

(1) What are the properties of the PEL of the strong glass-former BKS silicate as compared to a more fragile glass-former? It turns out that the PEL of BKS silicate is surprisingly similar to that of the Lennard-Jones system. In particular, a similar relation $E(\epsilon)$ can be found. It seems, however, that for BKS silicate the lower end of the PEL is already probed below $T \approx 4000$ K. It is actually the same temperature for which BKS silicate displays a fragile-to-strong crossover. Thus in agreement with the general view a strong connection between the thermodynamics (statistics of minima) and the dynamics seems to exist.

(2) Is it possible to describe the (long-time) transport properties of supercooled liquids in the framework of a generalized version of the phenomenological trap model by Bouchaud and coworkers [6]? It turns out that this is indeed possible and that the parameters for the trap model can be directly extracted (at least for the Lennard-Jones system). Thus, it is indeed justified to view a trap model as an appropriate representation of a complex system like a supercooled liquid. On this basis it becomes possible to analyse, e.g., the applicability of popular equilibration routines like parallel tempering in dependence of the system parameters in great detail.

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Anderson localization in Instantaneous Normal Modes

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A generalization of the Cizeau-Bouchaud [1] cavity equation is proposed for calculation of Instantaneous Normal Liquids in glasses. This amounts to a *randomgraph* approximation to particle correlations [2]. The only structural information used is the pair correlation function, which can be get from simulations or analytical calculations. The localization thresholds (both at real an imaginary frequency) can be obtained from the proposed integral equation solved by a population dynamics algorithm. We check the performance of the method in a binary mixture of soft-spheres simulated down to the Mode-Coupling temperature. Our results are compared with numerics both at the level of density of states and localization properties obtained from the level-spacing distribution.

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Heterogeneity of dielectric and thermal relaxation times

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Dynamical heterogeneity has been recognized as one of the key features regarding transport and relaxation phenomena in supercooled liquids in their viscous regime [1]. One of the experimental approaches to heterogeneity is the technique of dielectric holeburning, where the relaxation behavior of only a subensemble is being modified. These experiments are generally believed to demonstrate dynamical heterogeneity, but a quantitative understanding has not been provided until recently [2]. We have calculated the effects of dielectric hole burning on the basis of the frequency dependent dielectric relaxation $\hat{\varepsilon}(\omega)$ and specific heat $\hat{c}_p(\omega)$ of glycerol and assuming heterogeneous dynamics where the dielectric and thermal relaxation times are spatially correlated quantities. The heat generated in the sample is determined from the time dependent electric field and polarization [3], i.e., without involving steady-state approximations. The calculations mimic the protocol of recent hole-burning experiments on glycerol [4], including the high-field burn-process, the phase-cycle employed to eliminate the linear response to the high field, the detection in terms of the electric modulus M(t), and the signal normalization.

Without using any fit parameters, this model is capable of quantitatively reproducing the amplitudes, shapes, and peak positions of observed dielectric holes, together with their dependence on the burn frequency and the waiting time between the pump and probe processes. A typical picture of how theory and experiments compare is shown in Fig. 1.

The density of states in molecular glass-forming liquids naturally divides into two parts on the basis of their relaxation times. As the temperature approaches the glass transition, the structural degrees of freedom slow down and are effectively decoupled from the vibrational (phonon) modes. It therefore becomes possible to selectively alter the effective temperature of the slow modes and observe their return to equilibrium with the phonon bath, which is the essence of our model.

The calculation addresses the heating and the resulting shift of relaxation times which will occur in these materials. The agreement with the experimental findings tell us that additional non-linearities are not required for understanding dielectric holeburning. The assumption of correlated thermal and dielectric relaxation times establishes a link between the fluctuations of thermodynamic and dynamic quantities. This picture is consistent with the results of frequency resolved specific heat capacity experiments on glass-forming materials.



FIG. 1: Vertical and horizontal representation of a dielectric hole measured in glycerol at T = 187.30 K (symbols) [2]. The experimental conditions are $E_0 = 90$ V/6.4 μ m, $f_b = 0.2$ Hz, n = 6, and $t_w = 1$ s. The lines are calculated results from the present model. Solid symbols refer to the vertical hole, $\Delta M(t)$, while the open symbols reflect the horizontal hole, $\Delta H(t)$.

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Dielectric spectroscopy of aging disordered matter

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During the last decade our understanding of the dynamics of supercooled liquids has increased considerably. This progress was possible due to new experimental techniques and new theoretical approaches. Aside of canonical glass-formers, also experiments on model systems, like spin or orientational glasses, have provided valuable new information on the glass state and glass transition. In recent years the research of glass-forming materials has focused on two main topics, namely the dynamics faster than the structural α -relaxation and the slow out-of-equilibrium dynamics of supercooled liquids at temperatures below the calorimetric glass transition temperature T_g . Concerning the latter, especially the so-called physical aging, i.e. the time-dependent variation of physical properties during the very slow approach of a glass below T_q to its thermodynamic equilibrium, has proven an exciting and intriguing physical phenomenon, which is far from being completely understood until now.

We have performed broadband dielectric spectroscopy for a number of supercooled liquids, glasses, ionic melts, and plastic crystals at temperatures above and below T_g . Specifically, we focus on the different regimes of the relaxation spectra, namely the α - or structural relaxation, the excess wing, and the Johari-Goldstein β -relaxation. We present the results of detailed aging experiments at different temperatures just below the calorimetric glass transition temperature T_q (for an example, see Fig. 1). We consider especially the question how the different regimes of the relaxation spectra recover thermodynamic equilibrium. In addition, various temperature cycling experiments across T_g were performed, revealing the impact of thermal history on the relaxational properties of glasses.

We present a detailed analysis of the time dependence of the dielectric loss for different frequencies and at different temperatures below T_g . The experimental results are discussed in the light of recent theories of aging phenomena in disordered materials. We propose a new description of the time dependence of the aging process taking into account a time-dependent mean relaxation rate.

Among the materials investigated are typical glass formers with an excess wing (e.g. glycerol and propylene carbonate), glass-forming liquids with a welldefined Johari-Goldstein β -process (e.g. xylitol), and a typical ionic melt (calcium-potassium-nitrate). In addition, we investigated model glasses, namely plastic crystals with a crystalline center-of-mass lattice and orientational disorder, which show a well-defined α -relaxation with neither excess wing nor Johari-Goldstein β -process.



FIG. 1: Time-dependent dielectric loss of propylene carbonate (PC) and glycerol for various frequencies at sub- T_g temperatures. The lines are fits with a stretched exponential decay.

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Reversibility in glass-forming liquids

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In the recent years, substantial improvment has been brought to the ordinary differential scanning calorimetry (DSC) by superposing on the usual linear *T*-ramp a small temperature oscillation [1, 2] with a frequency of about 0.01 Hz, i.e. one order of magnitude lower than previous AC calorimetry [3]. This new technique permits separating the usual DSC heat flow endotherm \dot{H}_T into a reversing part \dot{H}_{rev} which follows the initial modulated *T* profile, from the nonreversing part which arises from kinetic events and underlying temperature dependent activated processes. It has been also shown that the latter quantity, once integrated with respect to the sample baseline, yields a non-reversing heat flow ΔH_{nr} .



FIG. 1: Total heat flow (usually determined from DSC) of $As_{20}S_{80}$ together with the reversing (dashed line) and non-reversing heat flow. The area under the curve \dot{H}_{nr} with respect to the baseline defines ΔH_{nr} .

Furthermore, compositional trends in chalcogenide glasses can be studied and reveal the existence of compositional windows accross which the non-reversing heat ΔH_{nr} is found to nearly vanish. In these systems, one has indeed the luxury to change the chemical composition and the mean coordination number \bar{r} of the glass network. These windows are denoted as thermally reversing windows (or reversibility windows) and can have various widths $\Delta \bar{r}$ ranging from 0.14 in $Ge_x Se_{1-x}$ glasses [1] to 0.01 in $Ge_{25}S_{75-y}I_{y}[4]$. The vanishing of ΔH_{nr} can be related to the floppy-intermediate-stressed rigid (FIS) classification of glasses because the window appears close to the mean-field rigidity percolation concentration predicted to occur [5] at the mean coordination number $\bar{r} = 2.4$.

We address some of the issues raised by these new technique. Which physical quantity controlls mostly the non-reversing heat flow? What is reponsable for the width in the reversibility window?

We study MDSC in a simple minded way by considering the dynamics of the random bond lattice model [6]. This model describes the creation of covalent bonding in a glass forming liquid using a bond enthalpy H and an excitation profile (degeneracy) Ω . The analysis shows that under Arrhenius relaxation, the non-reversing heat flow ΔH_{nr} is proportional to the activation energy of the relaxation time, a result that has been observed experimentally on chalcogenide systems [7]. At constant activation energy, ΔH_{nr} is also proportional to $\exp[\Omega]$, while the reversing heat flow (or ΔC_p) is simply proportional to Ω .

To study the structural origin of the width of the reversibility window, we apply [8] a size increasing cluster approximation to construct intermediate range structures containing rings on which we compute the mean number of mechanical constraints n_c . The analvsis reveals that in random structures, there is a single transition for which the number of floppy modes vanishes $(n_c = 3)$ at the mean coordination number $\bar{r} = 2.4$. With the requirement of self-organization (i.e. selecting the elastic nature of the cluster according to the FIS classification), a compositional window emerges which is still bounded on its left side by $n_c = 3$ and on its right side by a stress transition. The latter corresponds to the point beyond which the presence of stressed rigid clusters cannot be avoided anymore. Consequently, the width of the reversibility window appears to be an increasing function of the fraction of small weakly stressed rings.

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Rate constant change following an instantaneous temperature jump

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The non-Arrhenius behavior of the α -loss peak frequency in molecular liquids is studied by aging experiment following an instantaneous temperature jump for the dielectric and shear mechanical response at fixed frequencies (Hz and MHz regions, resp.). Assuming time-aging-time superposition the aging-time dependence of the rate constant and the instantaneous shear modulus can be compared. The results are discussed in terms of the "shoving" model [1].

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Generalized Stokes-Einstein relations and the Fluctuation-Dissipation Theorem in a colloidal glass of Laponite

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Laponite particles charged disk-shaped colloids. Their aqueous solutions are initially liquid. But, with time they go over into a glass state [1]. We study the dynamics of translational and rotational diffusion during the formation of colloidal glass of Laponite [2] using polarized and depolarized dynamic light scattering. In both set of correlations one can observe two modes of relaxation Fig. 1. The fast mode corresponds to rapid diffusion of particles whithin the cages formed by neighboring particles and is independent of aging time for both translational and rotational degrees of freedom. The slow mode corresponds to the escape of particles from the cages: its average relaxation time increases exponentially fast with age of the glass. The rate of evolution for the two degrees of freedom is very similar.



FIG. 1: Evolution of polarized (VV) and depolarized (VH) intensity correlation functions and their corresponding fits with $Aexp(-t/\tau_1) + (1 - A)exp(-(t/\tau_2)^{\alpha})$ for Laponite 3 wt%(pH=10) water, at scattering angle 90, for every 20 minutes $(t_w = 15min - 3h)$.

Combining dynamic light scattering and rheology measurements, we investigate the validity of the generalized Stokes-Einstein (SE) relations as special cases of the fluctuation-dissipation theorem (FDT). Large deviations from the generalized SE relations [3, 4] are observed at low frequencies as the system ages. The evolution of effective temperature Fig. 2 that follows from the application of the FDT [5, 6] for the two degrees of freedom is discussed.



FIG. 2: effective temperature T_{eff}/T_{bath} extracted from translational and rotational degrees of freedom as a function of waiting time.

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The effect of bond lifetimes on the dynamics of a short-ranged attractive colloidal system

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In a recent work [1], Del Gado and coworkers studied a lattice model to explore the influence of bond lifetimes on the dynamics. In particular, for permanent bonds, the correlation times τ diverged as the packing fraction ϕ approached a percolation threshold, while for short-lived bonds, the ϕ -dependence of τ is more typical of a glassy system. At intermediate bond lifetimes, the ϕ -dependence of τ is driven by percolation at low ϕ , but then it crosses over to glassy behaviour at higher ϕ .



FIG. 1: τ as a function of ϕ for different h.

We perform a similar study using molecular dynamics simulations of short-ranged attractive colloid particles modelled by a narrow (3%) of the hard sphere diameter) square well potential of unit depth. For a more detailed description see Refs. [2, 3]. We compare the dynamics of systems with the same thermodyanamics but different bond lifetime, by adding to the square well potential an infinitesimally thin barrier at the edge of the attractive well. Such modification of the potential indeed stabilizes bond lifetimes without changing the thermodynamics. We study the density correlator $f_q(t)$ as a function of time t and extract the barrier and density dependence of the relaxation time τ . By plotting τ as a function of ϕ and barrier height h (see Fig. 1), we recover the crossover from a percolation-governed ϕ -dependence to glassy behaviour.

We will discuss the role of h in the slow dynamic

behaviour of the system, showing that the bond dynamics governed by h only rescale the long-time dynamics (see Fig. 2, where we plot $f_q(t)$ for q near the first peak of the static structure factor for various h, at temperature T = 0.5). This result holds also in the case where two-step relaxation is present when h = 0.

We also perform an analysis of the q-dependence of the percolation-governed dynamics in conjunction with an analysis of the properties of the percolating cluster.

Finally, the implication of the bond lifetime on the modellization in terms of Mode Coupling Theory of the glass transition will be discussed.

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FIG. 2: $f_q(t)$ for $\phi = 0.52$ for various values of h.

Logarithmic relaxation in colloidal systems

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Mode-coupling theory for ideal glass transitions (MCT) predicts in addition to liquid-glass transitions also glass-glass transitions and endpoint singularities for systems with hard core repulsion and a shortranged attraction [1–3]. Close to these endpoint singularities, the correlation functions exhibit logarithmic decay laws [4]. Asymptotic expansion up to nextto-leading order yields wave-vector dependent corrections that divide the three-dimensional control parameter space into distinct regions [5]. For a specific wavevector, the corrections vanish on a two-dimensional surface where logarithmic decay is seen for several orders of magnitude in an experimentally accessible window in time. In the remaining half-spaces the decay is convex or concave in the logarithm of time, respectively. For increasing wave vector, the dividing surface rotates clockwise around the endpoint singularity.



FIG. 1: Logarithmic decay of the correlation function (q = 4.2, 20.2, 24.2, 27.0, 32.2, and 36.2 from top to bottom) and subdiffusive power law for the mean-squared displacement for a state point (×) close to the A_4 -singularity (*) of the square-well system as indicated in the inset, cf. [6]. Dashed lines show the asymptotic approximations.

A similar surface can be calculated for the meansquared displacement (MSD) of a tagged particle, where the relaxation exhibits a subdiffusive power law [6]. Again, characteristic convex and concave relaxation patterns occur upon leaving that surface into different directions. Figure 1 illustrates the logarithmic decay laws close to the higher-order singularity A_4 . Indications of such logarithmic decay have already been seen earlier [7], while the logarithmic decay of the correlation functions in connection with the power law variation of the MSD was found only recently in a molecular dynamics simulation [8].

Even richer dynamical scenarios arise close to a line crossing where three MCT-singularities at once influence the dynamics. Also in this situation, asymptotic expansions of MCT are capable of organizing the complete control-parameter space [9] and provide valuable insight into line crossing scenarios that are found in experiments in colloidal systems [10–12].

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Quantum Mode-Coupling Theory and the Boson Peak

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We present a quantum field theory of vibrational excitations in a disordered elastic medium including anharmonic interactions. From an effective field theory which is obtained by standard field-theoretic techniques we derive a mean-field theory for the singleparticle excitations which turns out to be the quantum version of a mode-coupling theory for the densitydensity correlation function. In the low-frequency limit this theory becomes formally equivalent to the so-called F-1-2 model for the schematic description of glass singularities. Within our theory we obtain (in the weakly anharmonic regime) a continuous (type A) nonergodicity transition if the disorder is increased beyond a critical value. This transition can be interpreted as a global relaxation of the solid due to the instability induced by negative force constants. In the ergodic region a boson peak is obtained in the vibrational density of states which increases with increasing disorder and is shifted towards lower frequencies. In the absence of anharmonicity the theory is equivalent to previous boson peak theories using the coherent-potential approximation if applied to a Debye jellium model. The density of states compares very well to experimental boson peak data. The boson peak is shown to be a precursor phenomenon of the non-ergodicity transition. As further precursor phenomena an anomalous frequency dependence of the density of states below the boson peak as well as an anomalous temperature dependence of the specific heat are obtained.

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Supercooled water relaxation dynamics by heterodyne transient grating experiment

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We performed a measurement of acoustic and thermal relaxation dynamics on supercooled water in the temperature range 42–17°C by heterodyne detected transient grating experiments.

The TG signal shows some particular and interesting features that are produced by the anomalous behaviour of water thermodynamic parameters. In particular the thermal diffusion effects disappear in the TG data for a temperature of about 0°C. We found that this effect has to be ascribed at the combination of two different physical phenomena: (i) One is the anomalous temperature dependence of water density and hence the corresponding variation of the thermal expansion coefficient with the temperature; (ii) a second important effect that has to be considered is the contribution to the TG signal due to the $(\partial \varepsilon / \partial T)_{\varrho}$ term, this term is usually neglected either in the light scattering or TG interpretation. Our data show clearly a non-negligible thermal decay that has to be addressed to the $(\partial \varepsilon / \partial T)_{\varrho}$ effect. The data are analysed using a model based on the linearized hydrodynamic equations in their simplest formulation. Since the structural relaxation time, in the range of temperature analysed, is always smaller than instrumental response time (1 ns), a Markovian approximation for the memory function is used. By using the thermodynamic parameters, such as heat capacity and density, obtained by the literature we have extracted the value of $(\partial \varepsilon / \partial T)_{\varrho}$ in all analysed temperature range.

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Structural relaxation in supercooled bulk water investigated by time-resolved spectroscopy

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Water is one of the most important substance existing, its importance is easily understood by everyone and it spans from life science to technical applications. Despite this paramount interest, the physic proprieties of water are still not fully understood and many relevant questions are open [1]. It is well know that the condensed states of water show anomalous behaviours, where anomalous means that the thermodynamics and dynamics proprieties of water differ strongly from the features of similar molecular materials. In particular in the stable liquid phase, at temperature close to the melting point, and in the supercooled and glass phases, metastable phases below the melting point, several unusual characteristics appear. Specifically several thermodynamics parameters (like for example: thermal expansion coefficient, isothermal compressibility or isobaric heat capacity) and some dynamic proprieties (such as: viscosity and diffusivity) show a common critical behaviour [2]. The analysis of these data substantially agrees individuating a unique "critical temperature" T_s ${\sim}220{-}230$ K, nevertheless the presence and the nature of this singularity is still under discussion and several theoretical models have been worked out to explain it [1]. In order to exclude or to validate the models, a precise characterization of the dynamic structure factors or correlation functions is of fundamental importance. Computer simulations have been able to calculate the timedependent correlation functions of bulk water with a good statistic quality [3]. Vice versa the experimental spectroscopic investigations on supercooled bulk water are difficult due to nucleation phenomena and usually the data are characterized by a very poor quality. Consequently precise measurements of the correlation functions, able to define unambiguously their relaxation features, are not present in literature. The nature of relaxation phenomena in supercooled bulk water has been only partially addressed and no conclusive experimental results have been achieved.

We performed time-resolved optical Kerr effect (OKE) spectroscopy on bulk water measuring the time-dependent correlation function in the supercooled phase, down to 253 K. Data of very good quality has been obtained and they allowed a significant analysis of the relaxation functions. We found that experimental decay is accurately described by the stretched exponential function over a large time window. The stretching parameter is not temperature dependent, confirming the timetemperature superposition principle, and the relaxation times scale with temperature according to a power law, $(T - T_s)^{-\gamma}$, as predicted by the mode-coupling theory (MCT). These results confirm that bulk water, in its weak supercooled phase $(T > T_s)$, behaves as a fragile liquid in all the measured dynamic proprieties and they are properly described by the MCT, so the singularity at T_s can be interpreted as the MCT critical temperature.

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Dynamics of ethanol and methanol: A light scattering study

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We present an analysis on liquid ethanol and methanol over an extensive temperature and frequency range. The dynamic response of these liquids is described by simple approaches of mode coupling theory, which was originally developed for the viscous dynamics around the liquid-glass transition. A schematic two component model describes the dynamics in a frequency range from GHz up to the THz region, and from the glass transition temperature to the boiling point. The microscopic description provides a general understanding of the dynamics of complex liquids from its deeply viscous state up to the boiling point.

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Universal features of relaxation in liquid benzene

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We present an investigation of the dynamics of liquid benzene, as measured by depolarized light scattering, coherent and incoherent neutron scattering and the optical Kerr effect. Although benzene is not a typical glass forming liquid, the relaxation dynamics in the picosecond to nanosecond range can be described by the solutions of a two-component schematic model of mode coupling theory, which was originally developed as a theory of glassy materials. The simultaneous analysis of four different methods in the time and frequency domain is consistent for the entire data set.

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FIG. 1: The mode coupling coefficients v_1 and v_2 in the phase diagram of the F_{12} model. These parameters are identical for all measuring methods. The solid line indicates the ideal glass transition singularity, which is only a little approached on cooling benzene through its entire range of existence. On the glass transition line, the crossing points are indicated for iso-butyl-benzene (ipb), nbutyl-benzene (nbb) and toluene, as obtained from asymptotic mode coupling fits [1, 2].

Relaxation Dynamics of Network Supercooled Liquids: Neutron Spectroscopy and Mode Coupling Analysis

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In the last decades, an increasing number of experimental and numerical results have indicated that the so-called mode-coupling theory of the glass transition (MCT) is able to give a qualitatively correct description of many dynamical features of fragile glass-formers [1].

It is now of considerable interest to explore whether, or not, the MCT scenario is applicable also to stronger glass-forming systems. In particular, very few studies on covalently-bonded network glasses have been performed so far. However, it has been shown that in these more complicated systems, the validity range of the MCT asymptotic laws could be strongly reduced [2]. It is thus advisable in that case to make a direct comparison of the experimental data with the numerical solution of the MCT equations. It is the only systematic procedure if one wants to show that the MCT equations give an accurate description of the structural relaxation dynamics of network glasses. Nevertheless this approach is quite involved and therefore not often done [2–4].

We present such an analysis in two different, low- T_q , supercooled liquids: a multicomponent oxide glass $(Na_2O-Li_2O)-2P_2O_5$ and Selenium, a monoatomic system. For both systems the normalised intermediate scattering function $\phi(Q, t, T)$ measured by neutron scattering experiments on five decades in time [5] is shown to be accurately described by the solution of a schematic MCT model. We conclude that the MCT is indeed able to explain the complex temperature dependence of the relaxation dynamics also in network supercooled liquids above the crossover temperature T_c . On the other hand the wavenumber dependence of the structural relaxation dynamics and how it is related to the structure of the system under study are not really taken into account when using such a schematic MCT model.

However, MCT is also supposed to give a more quantitative description of the relaxation dynamics of supercooled liquids. In particular it is possible to compute from the knowledge of the static structure factor S(Q) the time dependence of $\phi(Q,t)$. These calculations have been done only for very few systems (most are fragile and/or monoatomic simulated systems), since they are quite involved even for binary systems [7]. In a second part, we compare the experimental data with such MCT calculations for viscous (Na₂O-Li₂O)-2P₂O₅. In a first attempt, we directly used the experimental S(Q) to compute $\phi(Q, t)$ as if the system were a monoatomic one. Despite this crude approximation, it is found that the Q-dependence of the calculated intermediate scattering function mimics the one found in the experimental data. In particular, the unexpected minimum of the stretching exponent β which occurs at the location of the first maximum of the structure factor ($Q = 1.2 \text{ Å}^{-1}$ in (Na₂O-Li₂O)-2P₂O₅) is reproduced [6]. More refined analysis, taking into accounts the static structure factor of the phosphate chains only is also discussed.

Finally, the case of supercooled Selenium is addressed. This system presents two advantages over $(Na_2O-Li_2O)-2P_2O_5$. First it is a monoatomic glass, so detailed MCT calculations can be done directly from the measured S(Q) data without any further approximation [8]. Second it is a pure coherent neutron scatterer and thus TOF and NSE experiments directly probe the intermediate coherent neutron scattering function.

We present here the first direct comparison between the solution of the MCT equations, starting from the experimental static structure factor only, and inelastic neutron data.

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Light scattering in viscous fluids and its connection to the liquid immersion lithography for structuring microchips

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During the last decades the ongoing miniaturization of microchips was the driving force for ever increasing computer power. Today structures for the 90 nm lithography node are created on wafers of pure Si using an optical microlithographic process. The further decrease of the minimum feature size on a microchip is possible by increasing the numerical aperture (NA) of the projection lens in lithography exposure tools. Whereas todays exposure tools have "dry" optics with NA limited by optical laws, the use of immersion fluids between the projection lens and the wafer would allow for optics with extremely high NA and will therefore result in a substantial gain in optical resolution. Liquid immersion lithography can extend optical lithography down to the 32 nm lithography node [1]. When investigating fluids for liquid immersion lithography, scattering of light is more crucial than absorption. The reason is that pure absorption can be compensated by an increase of exposure time or light intensity, while scattered light decreases the imaging contrast on the photoresist.

We therefore carefully investigate the scattering of light in a molecular liquid. Light can be scattered due to a number of mechanisms. These are inelastic mechanisms like Raman scattering, elastic scattering on micro- and nano bubbles but also quasielastic scattering on density fluctuations. In addition to the quasielastic scattering on density fluctuations a molecular fluid shows scattering on orientation degrees of freedom. We use the known anisotropic polarizability of water and calculate the microscopic polarizabilities for a number of fluids applying an ab initio method. Based on these anisotropies of the polarizabilities we derive the scattering components due to orientation fluctuations using the results of [2]. Among these the polarization ratio under 90° scattering is calculated and the relation between orientation and center-offmass contributions for different polarization directions of incident and scattered light is evaluated. While the amount of scattering due to molecular orientations seems to be still moderate for water [3] it is expected to be much larger for most fluids, like fluorinated polymers, which are discussed for immersion lithography and which have larger anisotropies of their polarizabilities. We evaluate the overall scattering for a number of fluids, which are candidates for immersion lithography.

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Temperature and Pressure Dependence of Density Fluctuations in Toluene Investigated by Brillouin Scattering

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The density-density correlation function is central to the dynamics of supercooled liquids and the glass transition. In real molecular systems density fluctuations are coupled to the intramolecular degrees of freedom giving rise to both isotropic and anisotropic scattering. The parallel (vv) polarized Brillouin spectra contain contributions from density fluctuations $(I_{\rm ISO}(\omega))$ and also from orientational dynamics and collision induced scattering $(I_{ANI}(\omega))$. Depolarized (vh) spectra are due to $I_{ANI}(\omega)$ only and can therefore be used to remove the contribution from the vv spectra [1, 2] and to obtain the density correlator. Here we present the temperature dependence of the Brillouin spectrum of toluene (melting point 178 K) over the range from $320\,\mathrm{K}$ to $140\,\mathrm{K}$. This allows an assessment of anisotropic contributions and a comparison with incoherent neutron and depolarized light scattering data where accord with mode-coupling predictions has been found [3, 4]. We have measured both vv and vh polarized spectra with a tandem Fabry-Perot interferometer in a 180° backscattering geometry.



FIG. 1: $I_{\rm ISO}$ spectra of Toluene at temperatures from $320\,{\rm K}$ to $140\,{\rm K}$ in $20\,{\rm K}$ steps.

The isotropic spectrum obtained by subtracting the anisotropic scattering $(I_{\rm ISO} = I_{\rm vv} - 4/3I_{\rm vh})$ is displayed in Fig. 1. As the liquid is cooled the width of the Brillouin line increases and reaches a maximum when the timescale of structural relaxation matches this frequency. The lineshape of the spectra will be analyzed with respect to structural relaxations using relevant models.

To reach the glass phase an alternate way to cooling is to raise the pressure at constant temperature. In Fig. 2 we show the evolution of the Brillouin spectrum as a function of hydrostatic pressure from 0.1 MPa to 415 MPa at 295 K.



FIG. 2: Brillouin spectra of Toluene as a function of pressure, measured at a temperature of 295 K. Lorentzian lineshapes (full lines) are shown for comparison.

With increasing pressure the Brillouin line shifts to higher frequency. This corresponds to an increase in sound velocity, the liquid becomes more solid-like. In addition the linewidth broadens, which may be attributed to the interaction of longitudinal sound waves with structural relaxation.

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Low Frequency Light Scattering Spectroscopy of Lysozyme in Solution

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Solvent viscosity and protein bound water are essential variables for protein motions. Upon cooling, the fluctuation rates slow down, and hydrogen bonds associated with the protein water can drive a dynamical transition in myoglobin and lysozyme1. The lowfrequency Raman and Brillouin spectra of proteins in solution provide a probe for dynamic coupling of protein motions to the solvent. We report on polarization resolved measurements of the light scattering spectrum of lysozyme in aqueous solution over the frequency range from 1 GHz to 20 THz and temperatures from 275 and 300 K. The large frequency range was covered by a combination of a U1000 double monochromator and a Fabry-Perot tandem interferometer. Spectra were collected in a 180° backscattering geometry for both vv and vh polarizations. Lysozyme was dissolved at a concentration of 15 mM to avoid aggregation. The vibrational spectrum of the protein was measured in the fingerprint region (30-60THz) to verify the native state of the protein.



FIG. 1: Brillouin spectra of water and lysozyme in aqueous solution.

The Brillouin peaks are observed at 8.2 GHz in the polarized spectra of the lysozyme solution and are shifted by about 400 MHz to higher frequency as compared to water. The shift reflects the change in sound velocity and is attributed to the compressibility of the protein and bound water.

The depolarized spectra normalized by the Bose fac-

tor are displayed in Fig. 2. The dynamics extend over a more than 3 decades and show temperature independent relaxation peaks at 1.5 THz for water and at 2 THz for the protein solution. The α -relaxation peaks are observed between 2 and 40 GHz and these move to lower frequencies with decreasing temperature due to slowing down of structural relaxation. In the frequency range below 2 GHz the protein solution shows an excess of quasielastic scattering as measured on both the Stokes and the Anti-Stokes side of



FIG. 2: Depolarized light scattering susceptibility spectra of lysozyme/H2O and H2O at temperatures of 290 and 275 K.

the Rayleigh line. The excess intensity is discussed with respect to protein rotational motions and waterinduced contributions.

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Influence of sugars on the dynamics of lysozyme

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It is known for a long time that several organisms like plants, spores, fungi or higher microorganisms are able to survive severe external conditions such as high/low temperatures or dehydration. In fact, they pass in a state where their metabolism is greatly reduced by producing sucrose or trehalose, molecules derived from glucose. Once being rehydrated, they resume their normal activity, often within minutes. This phenomenon is called *anhydrobiosis*.

Many other osmolytes have been found to protect proteins, membranes or micelles *in vitro*. However, disaccharides, and in particular trehalose, seem to protect these biomolecules more efficiently.

Several hypotheses have been proposed to explain the mechanisms involved in bioprotection. They may be classified in two main groups. First, the 'waterreplacement' hypothesis, proposed by Crowe *et al.* [1], invokes direct interactions between biomolecules and disaccharides, which act as substitutes of the hydration water. Alternatively, Green and Angell [2] suggested that the dynamics of biomolecules would be slown down by vitrification of the solvent. Presently, none of these hypotheses prevail, and results of experiments and simulations in favour of both are regularly published. Our aim is thus to clarify the current situation and to try to understand the molecular mechanisms involved in bioprotection.

For this purpose, we performed molecular dynamic (MD) simulations of 2 ns in the (N, V, T) statistic ensemble of a lysozyme with three homologuous disaccharides, namely trehalose, sucrose, and maltose $(C_{12}(H_2O)_{11})$ in water, at two concentrations of sugars (22 wt.% and 37 wt.%). The lysozyme is a well-known small globular protein and therefore a lot of experimental [3] and numerical [4] data are available.

In Fig. 1, we present the incoherent intermediate scattering function $S_{inc}(Q,t)$ of the side chains of the lysozyme in presence of sugars in the 37 wt.% solution and in water at 300 K. We see that the side chains of the protein in presence of trehalose are slown down more efficiently than with sucrose and maltose. If we define the relaxational time τ_{α} as the time by which $S_{inc}(Q,t)$ as decreased by a factor of 1/e, we find that the dynamics of the side chains is slowed by about 30 % in trehalose compared to both maltose and sucrose. These results are well in line with our previous simulations of water-sugar solutions [5].

In addition, the number of H-bonds formed between the sugars and the protein was found to be relatively small (between 4 and 10 depending on the simulated system) and thus the dynamics of the lysozyme was not directly related to the number of H-bonds formed. Nonetheless, the sugars were kept far enough from the lysozyme in the initial configuration so that they could



FIG. 1: Incoherent intermediate scattering function of the side chain atoms of lysozyme $S_{inc}(Q,t)$ in the 37 wt.% sugar solutions and in water, at T = 300 K. The inset shows the curves related to sugars in a linear scale and in a magnified way so as to exhibit the discrepancies between the relaxation times τ_{α} .

not form H-bonds. Moreover, the simulation length (2 ns) was probably not long enough to allow many sugars to diffuse towards the lysozyme and then form H-bonds. Therefore, the 'water-replacement' hypothesis cannot be disproved in view of these preliminary results. That is the reason why simulations at higher concentrations are currently carried out to check the respective influence of sugars when they form many H-bonds with the lysozyme.

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Inelastic Neutron Scattering and Simulation Study on Disaccharides/H₂O Mixtures

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In recent years many efforts have addressed to the understanding of the tools used by organisms to survive under environmental stress conditions [1– 3]. Prominent examples of these survival mechanisms are found in some species of frogs able to survive to relatively low temperatures for weeks by means of natural cryoprotective agents such as low-molecularweight substances (glycerol and trehalose) and highmolecular-weight proteins that inhibit ice formation [2].

The TOSCA spectrometer at the ISIS Pulse Neutron Facility (Rutherford Appleton Laboratory, Chilton, UK) has been used to collect inelastic neutron spectra on hydrogen-bonded systems of biophysical interest at T = 20K in order to compare experimental spectra with those obtained by simulation.

The investigated systems were homologues disaccharides (trehalose, maltose and sucrose)/ H_2O mixtures as a function of concentration. The comparison among the spectra of trehalose, maltose and sucrose mixtures emphasises that the addition of trehalose, in respect to the other disaccharides, more effectively destroys the tetrahedral intermolecular network of water, which by lowering temperature would give rise to ice. This result clearly indicates that disaccharides show a noticeable "kosmotrope" character, namely the disaccharide-water molecule interaction strength is much higher in respect to that between the water molecules.



FIG. 1: Comparison among trehalose/H₂O mixture (black line), maltose/H₂O mixture (blue line) and sucrose/H₂O mixture (red line) in the INS bending $(1060 \div 2000 \text{cm}^{-1})$ spectral region. The disaccharides mixtures profiles are shifted for clarity.

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Characterization of Fragility in Hydrogen-Bonded Systems by Elastic Neutron Scattering

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Homologues disaccharides ($C_{12}H_{22}O_{11}$, e.g. sucrose, maltose and trehalose) are cryptobiotic activating substances. Trehalose is nowadays employed for example in the preservation of blood, transplanting organs, in vaccines, food and seeds, as well as in the therapy of the switching off of cancers and viruses. Although the disaccharide crypto-protectant effectiveness is proven, the underlying molecular mechanisms are still cryptic. Green and Angell suggest that the higher value of the glass transition of trehalose mixtures with water explains its bioprotectant effectiveness. However, other similar systems present an even higher T_g value, but do not show comparable bioprotective action.



FIG. 1: Elastic incoherent neutron scattering spectra of trehalose, maltose and sucrose/ H_2O and D_2O mixtures as a function of temperature.

Crowe and coworkers formulated the hypothesis of a direct interaction between the sugars and the object of protection.

As a matter of fact experimental findings obtained by several spectroscopic techniques indicate that the structural and dynamical properties of water, even at relatively low sugar concentration, are drastically perturbed by disaccharides.

Neutron intensity elastic scans on trehalose, maltose, and sucrose/H₂O mixtures as a function of concentration, temperature and exchanged wave vector are presented. The experimental findings show a cross-over in molecular fluctuations between harmonic and anharmonic dynamical regimes [1]. A new operative definition for the "fragility" degree of glassforming systems is furnished by using explicitly the connection between viscosity and mean square displacement. The procedure is tested for the investigated mixtures and for a set of glass-forming systems. In this frame the "stronger" character of the trehalose/ H_2O mixture [2] indicates a better attitude in respect to maltose and sucrose/H₂O mixtures to encapsulate biostructures in a more rigid matrix.

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A Brillouin Spectroscopy study of relaxation time in sugar mixtures under Shear flow

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In this study we measured the polarized component (VV) of Brillouin spectra in trehalose & maltose mixtures with 10% of water with applied shear force. Trehalose and maltose were purchased from Sigma Chemical Co. and were used without a futher purification. The glass phase was made by the microwave method [1]. In the Brillouin scattering experiments, a back scattering geometry was used. The incident beam was vertically polarized 488 nm blue light of Ar ion laser (Coherent 300C) with 500 mW power. The polarized component of the scattered light was measured by using a six-pass tandem Fabry-Perot interferometer (JAS scientific instruments). For the light scattering under shear, we used a couette cell made of glasses.



FIG. 1: Brillouin spectra of trehalose & maltose mixture with 10% of water.

Figure 1 shows a Brillouin doublet of a trehalose & maltose mixture with 10% of water. The Brillouin peak position shifts to the low frequency region as the shear force increased. Figure 2 shows the anti-Stokes part of the Brillouin peaks. The open circles are experimental results and solid lines are fitting results obtained from fitting the data with a simple Lorentzian

form. As the shear force increases, the Brillouin peak positions shift to the lower frequency, and the peak widths are also broadened. These phenomena are similar to those of the Brillouin-peak shift and width broadening with changing temperatures. From these observations, we suggest that shear effects and temperature may play similar roles in this glassy system. In order to understand the shear effect, we qualitatively study the Brillouin-peak shift with shear force in various sugar mixtures.

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FIG. 2: Brillouin-peak shift with different shear forces.

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Morphological change of a vesicle under shear flow: A Multi-particle collision dynamics simulation

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Viscous flows induce morphological changes of dispersed soft, deformable objects. For example, in microcirculation, red blood cells deform and reduce the flow resistance of microvessels. In diseases such as sickle cell anemia and diabetes mellitus, red blood cells have reduced deformability and often block microvascular flow. Therefore, the deformation induced by flow is an important subject not only of fundamental research but also in medical applications.



FIG. 1: Snapshot of a vesicle in simple shear flow. Arrows represent the velocity fields of fluid.

We studied the deformation of a vesicle in simple shear flow using a particle-based hydrodynamics

method, which is called multi-particle collision dynamics. This method was proposed by Malevanets and Kapral [1], and was applied to flow around a solid object [2], polymer dynamics [3], and so on. Two types of vesicular dynamics are known in simple shear flow: a steady state with a tank-treading motion of the membrane, and an unsteady state with a tumbling motion [4, 5]. In tank-treading, the vesicle has a finite inclination angle with the flow direction as shown in Fig. 1. To check the validity of our simulation method, we measured the inclination angles, and found excellent agreement with the previous results of Ref. [4]. We present results for the bifurcation from tank-treading to tumbling with increasing membrane viscosity.

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Strain Hardening of Biological Tissue

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It is an everyday experience that our tissue can easily be stretched to a certain (substantial) extent before dramatic strain hardening painfully prevents any further elongation. Biological (and artificial) tissue owes its characteristic mechanical properties to an entangled and/or crosslinked (visco-)elastic fiber network. In the case of biological tissue, the major scaffolding structures are semidilute to dense assemblies of stiff biopolymers, known as the cytoskeleton (inside cells) and the extracellular matrix. The standard model for the elasticity of (flexible) polymer networks is known as *rubber elasticity*. For various reasons it is inappropriate for the modeling of the polymer networks of interest here. First, it attributes the macroscopic response to the affine deformation of single, non-interacting polymer strands (the length of which is essentially a fudge parameter), and second, the latter are represented as featureless Gaussian chains prevented from collapsing by an external constraint of unspecified origin. In fact, non-trivial predictions for the non-linear elasticity are of purely geometrical origin. In contrast, most recent attempts of a more faithful modeling of artificial (e.g. paper) and biological tissue (cytoskeleton) idealize its dominant structural component as randomly crosslinked rod networks studied numerically. While the latter approach offers fascinating insights into the highly non-trivial mechanics of fiber networks [1, 2], it so far neglects entropic contributions to elasticity and is limited to two dimensions and linear response.

In the present contribution we present an analytical toy model for the non-linear elasticity of stiff polymer networks that rationalizes the above phenomenology in terms of non-affine local deformations of the individual polymers. These are suggested to arise from their mutual *interactions* at length scales where they exhibit a highly anisotropic elastic response. (This is to be contrasted with a naive backfitting of rubber elasticity by replacing the Gaussian elastic response of a single polymer strand by that of a semiflexible polymer.) Guided by an analogy to dilatancy in granular media, we propose a particularly simple schematic ansatz for this non-affinity, which yields simple analytical results for the non-linear modulus and the yield strain as a function of the structural parameters (concentration and stiffness) of the polymers.

It rests on two pillars. The first is the self-consistent (confinement) free energy $\mathcal{F}_c \simeq ck_B T \ell_p^{-1/3} d^{-2/3}$ (ℓ_p persistence length, c polymer length density, $d \ll \ell_p$ effective tube diameter given by $d \propto c^{-3/5} \ell_p^{-1/5}$ in equilibrium) of the polymer solution or gel that attributes the macroscopic compressibility to the caging of the thermal undulations of the polymers by a phenomenological "tube" model [3] that is the direct analog of the common "blob" model for the entanglement of flexible polymers [4]. The second pillar is our ansatz for the non-affinity of the deformations on the interaction length scale $d \ll \ell_p$. As consequence of a "mikado" effect the tubes that make up the polymer solution/gel can access only a certain fraction $d^2c = (1 + X^2)^{-1}$ of the *total* available volume (per polymer length) c^{-1} fixed by the incompressible solvent. This defines what we call the nonaffinity parameter X (= ratio void/tube volume). We suppose that the equilibrium packing is optimized so that the void volume increases upon any macroscopic deformation. For definiteness, we make the ansatz that the void volume (per length) is the square of a linear dimension $\vec{\Delta}$ that deforms affinely. Treating $\vec{\Delta} = \Delta \hat{\Delta}$ as a vector (more highbred variants are currently under investigation to check for universality) we get $d^2 \to {d'}^2 = d^2(1 - 2X^2\hat{\Delta}_i e_{ij}\hat{\Delta}_j)$ and from this via non-linear elasticity theory the nonlinear modulus \mathcal{G} etc. upon averaging over orientation $\hat{\Delta}$. For the particular example of simple shear, we obtain the universal strain hardening behavior

$$\mathcal{G}/G_0 \approx [1 - (\gamma/\gamma_y)^2]^{-2/3}$$

Polymer structural parameters only enter via the linear modulus G_0 and the (formal) yield strain γ_y , respectively,

$$G_0/\mathcal{F}_c = (2/135)X^2(15+8X^2), \ \gamma_y^{-1} = X\sqrt{1+X^2}$$

Despite the simplicity of the model, we thus get nontrivial (possibly generic) predictions about the interdependence of linear and non-linear elastic properties. Qualitatively, these compare very well with data for the linear and non-linear elasticity of a variety of gels and solutions of biopolymers that cover a substantial range of bending rigidities (e.g. various published data by Paul Janmey and collaborators). Further elaboration of the present approach, if combined with a closer examination of its underlying assumptions by experiments and simulation techniques, therefore offers a promising route to an efficient model of a viscoelastic system of considerable complexity.

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The transition from crystal to glass by damage, minimum crystal sizes, and the nanogranularity of glasses

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There are members of each class of substances whose liquid states do not readily crystallize, and so are called glassformers. In these, the difference in energy between amorphous and crystalline packing is not great. We find, like others before, that the glassy state of glassformers can easily be reached at low temperature from the crystal state, by comminution.

The comminution process has elements in common with pressure-induced amorphization in which the crystal is mechanically deformed into an unstable state from which the glass forms spontaneously. To vitrify by comminution, some combination of the following applies: the crystal dimensions are reduced below some critical value, or mechanical damage within crystals accumulates to a critical level. For complete amorphization each granule must reach a free energy that exceeds the free energy of the corresponding granule of glass. By combination of comminution and heat treatment we attempt to separate these effects and to determine the critical length for vitrification from the crystal. We are interested in the possibility of the relation between the critical conditions for spontanesous vitrification under damage and the inhomogeneity length scales of the stable viscous liquid.

Glass formation by mechanical damage has been a recognized preparation technique for some time but there has not been any quantitative enquiry into the relation between disappearance of crystalline character and comminuted crystal size or state. We have chosen selected "good" glassformers, with good Xray scattering ability, for combined calorimetric and X-ray/electron microscope study. We find that crystalline lead germanate changes the XRD pattern from crystal to glass in about 400 min. of comminution in a Spex8000 dual mixer/ballmill, and a glass transition at a temperature slightly below that of the conventional melt cooled glass can be observed in some cases, but not all. A question under study is the relation between observability of the glass transition and intrinsic glass forming ability.

We are exploring the concept of "critical damage". The criterion for critical damage is: (i) the damaged system had an X-ray diffraction pattern that looks superposes on that of the glass; (ii) the damaged system behaves like a normal glass with respect to heat capacity measured by differential scanning calorimetry, i.e. it exhibits a glass transition; (iii) annealing in the range just below this temperature stabilizes the amorphous phase system on a shorter time scale than that of crystal nucleation and growth.

We have recently used low energy neutron scattering (LENS) studies, carried out at NIST using the DCS instrument, to show that a "ubiquitous" characteristic of glasses, the so-called Boson peak (an excess low frequency density of vibrational states) is enhanced when the glass under study has been prepared from the liquid by quenching at very high rates [1]. In view of this finding, which correlates Boson peak strength with level of structural disorder, we expect the strength of the "Boson peak" to be a key marker for the progress of the system towards vitrification under mechanical damage.

Experiments on this question are carried out at NIST. The Disk Chopper Spectrometer (DCS) at NIST is well suited for this purpose because typical Boson peak frequencies match the energy transfers probed using this instrument. Furthermore, the capability of studying the Q dependence of the scattering may provide important information about length scales in these systems. Later experiment using small angle scattering instruments will give more precise information on the grain size necessary to yield the vitreous XRD pattern. We will correlate results from LENS with information to be obtained separately from TEM measurements at ASU.

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Interplay between phase behavior and dynamics in binary liquid mixtures: Computer simulation studies

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Models of binary liquid mixtures are considered to investigate the interplay of the phase behavior with structural and dynamical properties. To this end, we use a combination of Monte Carlo (MC) and Molecular Dynamics (MD) computer simulation techniques. The MC simulations allow to determine the phase diagram and, furthermore, they provide an efficient equilibration of the liquid mixture yielding wellequilibrated configurations. The latter configurations can then be used for MD simulations to analyze structural and dynamic properties.



FIG. 1: Diffusion constants of Al_4Ni as a function of inverse temperature from the simulation and a neutron scattering experiment by Meyer *et al.* [3] as indicated.

First we present the study of a symmetrical, binary Lennard-Jones mixture ($\epsilon_{AA} = \epsilon_{BB} = 1.0$, $\epsilon_{AB} = 0.5$, $\sigma_{AA} = \sigma_{BB} = \sigma_{AB} = 1.0$). The simulations are done at constant density $\rho = 1.0$ where the system is in the liquid state and does not show any tendencies to crystallize at the temperatures under consideration ($T \ge 1.0$). We start with MC simulations in the semigrand canonical ensemble in order to calculate the T x_A phase diagram (x_A : concentration of A particles), i.e. the fluid-fluid coexistence curve. As a "byproduct" fully equilibrated configurations at coexistence are obtained which are the starting point for microcanonical MD simulations to calculate structural quantities such as different static structure factors, transport coefficients such as the self and interdiffusion constants, the shear and the bulk viscosity and time dependent correlation functions such as the intermediate scattering functions. We show that the dynamics exhibits nontrivial features close to and at coexistence that can be described by a subtle interplay of density and concentration fluctuations [1].

We apply the "machinery" that we have developed for the LJ mixture in a "realistic" simulation of an Al-Ni alloy. In this case, an embedded atom potential is used to describe the interactions between the atoms that was very recently proposed by Mishin *et al.* [2] based on *ab initio* calculations. A result of our simulation is shown in Fig. 1: It shows an Arrhenius plot of the diffusion constants for an Al₄Ni mixture in the temperature range $2000 \,\mathrm{K} \geq T \geq 1000 \,\mathrm{K}$ in comparison to neutron scattering data by A. Meyer et al. [3]. Obviously, at high temperatures a very good agreement is obtained between simulation and experiment. The discrepancy at $T = 1000 \,\mathrm{K}$ is due to the fact that in the experiment crystallites in an amorphous matrix are obtained whereas in the simulation the system stays in a metastable liquid phase (this stems from the much smaller accessible relaxation times in the simulation). We analyze the properties of the supercooled Al₄Ni mixture by means of mode coupling theory. Moreover, we discuss in detail structural features in different Al-Ni mixtures such as a prepeak in the total static structure factor that emerges at high Al concentrations.

We thank Andreas Meyer for providing us with the neutron scattering data shown in Fig. 1. The present research was supported by the Deutsche Forschungsgemeinschaft (DFG) under Grant No. Bi314/18 (SPP 1120). One of the authors (J. H.) acknowledges the support of the DFG under Grant No. HO 2231/2-1.

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Dielectric Properties of Supercooled and Crystallized Glycerol

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Although glycerol exists only in liquid, supercooled liquid or glassy states in general, anhydrous glycerol can be crystallized by cooling down below the glass transition temperature ($T_g = 190$ K) and following slow heating [1]. However, the crystallization of glycerol is a very unusual and unstable process that depends on the temperature history and impurities of the sample, therefore almost no experimental studies of crystallized glycerol have been performed.

In this work, we have made an attempt to investigate the main features of glycerol crystallization by comparison between the glass-forming dynamics of anhydrous glycerol and the glycerol that was not specially treated to prevent water absorption.



FIG. 1: The real part of the complex permittivity e of anhydrous glycerol (protocol #1) versus temperature and frequency. The arrows mark temperatures of crystallization (263 K), melting point (293 K), and the main relaxation process before (I) and after (II) the crystallization.

Anhydrous glycerol was obtained from Fluka (Buchs, Switzerland). Glycerol samples for BDS were prepared by two different protocols: (i) all preparation was done under a dry nitrogen atmosphere to protect water absorption from air to the sample; (ii) the sample cells were filled and sealed without the special protection of the water absorption. Broadband dielectric spectroscopy (BDS) measurements of anhydrous glycerol with and without special protection of water absorption were done through wide ranges of temperature (133 to 325 K with interval of 3 K) and frequency (10 m to 3 MHz). The samples were cooled down from room temperature to 133 K quickly, and then BDS measurements were started.

Dielectric permittivity of anhydrous glycerol with the special protection of water absorption displayed significant changes at 263 and 293 K as shown in Fig. 1. The temperature 293 K is known as the melting point of glycerol [1]. It is considered that mobility of glycerol molecules was frozen below the glass transition temperature $(T_g = 190 \text{ K})$ therefore it was impossible to form the crystal structure; even above T_g , the mobility was still not enough and remained a supercooled state; at the specific temperature of 263 K, it became possible to form the crystal structure. In the crystal phase, observed main relaxation process (a-process) indicated by (I) in Fig. 1 disappeared and other process (II) appeared in lower frequency region. In contrast to this, no unusual behaviors were observed in the case of the sample without the special protection of water absorption. Although there is not numerical estimation of water absorption yet, it would be very small, and such small water absorption disabled the crystallization; it may be due to changes of the hydrogen-bonds networks and the dynamic structure of glycerol molecules.

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Analysis of decoupling of DC conductivity and structural relaxation time in supercooled epoxy systems

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Two different types of molecular liquids can be observed in the broadband dielectric spectroscopy. The first of them shows rotational motions of molecules with permanent dipole moments which are observed as the structural relaxation process with the relaxation time (τ). The second type of motions are the translational motions of charge carries (in liquids usually ions) seen as dc-conductivity (σ).

Despite both these processes involve two different kinds of molecules, they seem to be somehow coupled with each other, as it was seen in a number of experiments [1,2]. In low viscosity liquids the coupling is very strong, and the relation between τ and σ can be described by means of a Debye-Stokes-Einstein (DSE) equation:

$$\sigma \tau \simeq \text{const.}$$
 (1)

However, when the viscosity increases, the breakdown of this relation can be observed. Therefore such a breakdown is very often seen in glass forming liquids during cooling or compression [3–8]. To describe the new relation, a modified equation was found:

$$\sigma \tau^s \simeq \text{const.},$$
 (2)

where s is a fractional exponent less than one. The new equation is known as the fractional Debye-Stokes-Einstein (fDSE) equation.

Despite the observation of the decoupling between σ and τ in a number of samples there are a lot of unsolved problems. First of all, as the two processes

are connected with two different types of molecules, is there any influence on the relation with the change of molecular sizes? Does a high size difference cause a big decoupling effect or not?

These questions are the main reason for our dielectric experiments in case of three epoxy systems from the same molecular family with different sizes: DGA, DGGOA, MBDGA [9].

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Light scattering and dielectric manifestations of secondary relaxations in molecular glassformers

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Photon correlation spectroscopic (PCS) data of the molecular glass-forming materials 2-picoline, dimethylphthalate (DMP), and salol are compared with their dielectric loss spectra in the time-frequency range where the dielectric data reveal intermediate relaxation dynamics, namely the "excess wing" in picoline, a Johari-Goldstain process with a temperature activated relaxation rate in DMP, and a relaxation feature of mixed type in salol. We show that in each case the "slow" (kHz–MHz) secondary relaxations are manifested in our depolarized (anisotropic) light scattering (LS) data. As an example, Fig. 1 presents the initial part of a photon correlation function of picoline at $T \approx T_g$, which exhibits an obvious decay between 10^{-8} and 10^{-4} s that precedes the main α -relaxation.

In our LS experiments, we collected the depolarized component of the scattered light. Therefore, for optically anisotropic molecules, our LS data originate chiefly in reorientations of the molecular polarizability tensor. Likewise, dielectric loss spectra reflect reorientations of molecular electric dipoles. Thus, it is the same molecular reorientation dynamics that are detected by LS and dielectric spectroscopy (DS). One then shows [1] that, based on the properties of orientational correlation functions, the dynamics that are significantly faster than the main α -relaxation are expected to be 3 times more intense in LS than in DS data. Experimentally we find that fast dynamics at shorter than 10^{-8} s times are indeed more pronounced in the LS data. The intermediate relaxation dynamics at μ s times exhibit, however, the opposite trend, invariably being more pronounced in the DS data, see Fig. 2 for an example. We also show that the shape of the relaxation spectrum is qualitatively different in the two techniques. We discuss possible sources of these differences in the context of related data from the literature.



FIG. 1: Initial part of PCS data $\phi_{LS}^2(t)$ of picoline at 132 K with a stretched exponential fit.



FIG. 2: (a) PCS data $\phi_{LS}^2(t)$ (\circ) and squared normalized dielectric relaxation function $r^2(t)$ (\cdot) of DMP at 198 K. Solid and broken lines are KWW fits of $\phi_{LS}^2(t)$ and $r^2(t)$, respectively; short-dashed line is an extended fit of $\phi_{LS}^2(t)$ (see text for details). Inset: Dielectric loss spectrum $\epsilon''(f)$ with the same KWW fit as above (broken line) and an extended fit that describes the β -process (short-dashed line). (b) $\phi_{LS}^2(t)$ and $r^2(t)$ transformed into the frequency domain.

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Minimal model for β relaxation in viscous liquids

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Contrasts between β relaxation in equilibrium viscous liquids and glasses are rationalized in terms of a doublewell potential model with structure-dependent asymmetry, assuming structure is described by a single order parameter. The model is tested for tripropylene glycol where it accounts for the hysteresis of the dielectric β loss peak frequency and magnitude during cooling and reheating through the glass transition.

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Identification of the nature of secondary relaxation processes within the Coupling Model scheme

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Supercooled liquids are characterized by a structural relaxation time, τ , that strongly slows down by cooling the system towards the glass transition temperature, T_q (defined such that the structural relaxation time at T_g is 100s). For temperatures $T < T_g$, the structural relaxation process exceeds the usual experimental time window, it is said it is frozen. In this condition usually a further (secondary) relaxation process, often observable from some degrees above T_q , remains; characterized by a relaxation time smaller than 100s also for $T < T_g$, revealed in the dielectric loss spectra as a broad and often symmetric peak. The molecular origin of this process is up to now the center of a heated debate. In fact, it is still unknown if it is an intramolecular [1] or intermolecular [2,3] process, and if it reflects small angle [4] or large angle jumps [5] of molecules. Doubts about the origin of such process originate by the fact that secondary relaxation processes have been revealed both in polymeric glass [6], in which it originate through side groups movements, and in small, rigid molecules [2], in which no internal rotational degrees of freedom are present. A possible explanation in such scenario could be that different types of secondary relaxations exist. This idea is supported by the fact that some glass former systems present two secondary relaxation processes (for example see Refs. [6,7]), which generally present different dynamic characteristic.

Glasses below T_g are characterized by values of thermodynamic properties, such as volume or enthalpy, characteristic of the equilibrium system at higher temperature. Such thermodynamic properties have been shown to evolve with time during isothermal annealing toward the equilibrium value, influencing also the dynamic properties. Although the effects of annealing on



FIG. 1: Effect of annealing on the secondary relaxation process for a dipropilene glycol dibenzoate sample cooled at 173.1 K with a cooling rate q=30 K/min.

structural dynamics are studied, the effect of annealing on the fast dynamics are less investigated but not less important [8,9]. In fact, a significant dependence of β -relaxation properties on annealing time would indicate a similarity in the physical mechanism at the basis of structural and secondary relaxation process, a prominent intermolecular nature of β -process. A great improvement in the understanding of the nature of secondary relaxation, and of dynamic relaxation below T_g can be obtained by studying annealing effects on relaxation spectra in which two different fast relaxation processes are present. We present relaxation spectra on different oligomers of propylene glycol with different terminal groups of the main chain. All systems present two secondary relaxation processes characterized by different dynamic characteristics. In particular, in a dipropylene glycol dibenzoate sample, one secondary process reveals a clear dependence on annealing time of both relaxation frequency and dielectric strength (Fig. 1), thus revealing a strong connection to the structural process. This connection is also confirmed by an analysis based on the coupling model of Ngai [3], which reveals similarities between this secondary relaxation process and the primitive relaxation of the model. Similar conclusions, obtained for the secondary relaxation processes of the other systems led us to infer conclusion on the different molecular nature of the two secondary processes in these systems.

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Full picture of incoherent dynamic structure factor in liquid and glassy states

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The incoherent part of the dynamic structure factor $S_S(q,\omega)$ is exhaustively calculated for both frequency and wave number dependences in wide ranges by molecular-dynamics simulation for a supercooled binary soft-sphere fluid, which reveals the spatial and temporal structure of density fluctuations in full picture.

The difficulty in studying the glass transition is dealing with dynamics distributed in various time and spatial scales; coarse-graining and approximations are difficult to apply in theoretical work, the frequency and wave length windows are limited in experiment and computer simulation. By using such partially obtained dynamic spectra, the glass transition and the accompanying anomalous dynamics are only discussed so far. What is lacking in the glass transition study? It is the dynamic data measured for both time and space in wide ranges which cover the whole dynamics from microscopic to macroscopic scales.

Recent rapid development of computer power allows us to compute the dynamic data in wide range of scales. We calculate the incoherent part of dynamic structure factor $S_S(q, \omega)$ in frequency ranges over 8 decades and wave length over 2 decades at various temperatures. The dynamic structure factor is a common quantity which is well known and studied in scattering experiments and theories. The coherent dynamic structure factor $S(q, \omega)$ will be reported elsewhere.

The model which we employ is a binary softsphere system. The total number of particle is 4000, 2000 particles for species 1 and 2000 particles for species 2. The ratio of mass $m_2/m_1 = 2.0$, diameter $\sigma_2/\sigma_1 = 1.2$. The pair potential is described by $\phi_{\alpha\beta} = \epsilon(\sigma_{\alpha\beta}/r)^{12}$, where $\sigma_{\alpha\beta} = (\sigma_{\alpha} + \sigma_{\beta})/2$ and α,β note the species of particle. The number density is set to 0.8. The simulation box is about $17\sigma_1$ each side. Periodic boundary conditions are applied as usual.

In order to calculate $S_S(q, \omega)$ efficiently, we use the following equation based on Wiener-Khinchin theorem,

$$S_{S}(\mathbf{q},\omega) = \left\langle \frac{1}{T} \left| \int_{0}^{T} \exp\left[i \left\{ \mathbf{q} \cdot \mathbf{r}_{i}(t) - \omega t \right\} \right] \right|^{2} \right\rangle_{i},$$

where $\mathbf{r}_i(t)$ is the position of *i*-th particle at time *t*.

 $\langle \rangle_i$ denotes the ensemble average over particles. The integration time T must be long enough, 6.7×10^7 steps at the glass transition temperature.

The results show how the tagged particle dynamics changes from the ballistic motion in microscopic time and length region to the diffusive motion in macroscopic region. In highly supercooled states near the glass transition temperature T_g , the sub-diffusion regime which exhibits the slow relaxation and anomalous diffusion is clearly observed in $S_S(q, \omega)$.



FIG. 1: The incoherent dynamic structure factor at the glass transition temperature $\Gamma_{eff} = 1.5$.

We discuss (i) which microscopic motion of particles causes such sub-diffusion, (ii) the characteristic wave length at the transition from sub-diffusion to diffusion λ^* exceeding 3 times longer than that at the maximum static structure factor λ_0 at T_g , (iii) the structural entropy estimated by λ^* .

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Direct measurement of cooperatively rearranging region

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The cooperatively rearranging regions (CRR) are directly measured by using the newly developed technique of the interactive molecular-dynamics simulation in which one can controls to constrain each particle motion interactively at any time during simulation. If all particles in CRR are free, the rearrangement occurs. On the other hand, if any particles in CRR are constrained, the rearrangement does not occur. By measuring the distance between the tagged particles and the constrained particles at the border for rearrangement, the direct measurement of CRR can be achieved.

The CRR is originally proposed by Adam and Gibbs, which succeeds to explain the non-Arrhenius behavior in the temperature dependence of viscosity for fragile glass forming liquids. Because of the cage effect, particles cannot diffuse alone at low temperature. The cooperation to the surrounding particles is required for the structural rearrangement. The number of particles in CRR, N_{CRR} , corresponds to the structural entropy. Therefore, N_{CRR} is a key quantity for the glass transition.

We employ the model fluid system of binary softspheres in two dimension, because of the convenience for visualizing the particle configuration and controlling the particle constraint interactively. By clicking mouse button, one can fix the position of the particle pointed by mouse in the simulation window on display.

The size of CRR is measured in the following way: (i) prepare the initial configuration at the favorite temperature and anneal long enough; (ii) constrain the particle situating at the circular shell with the radius r as shown in Fig. 1; (iii) during the time steps corresponding to the diffusion coefficient, if the rearrangement occurs in the inner of shell, the size of CRR is smaller than r, otherwise, it is larger than r; (iv) repeat for different r, such that the border size of the shell is obtained.

The probability of rearrangement is measured for two parameters; the size of confinement $N_{confine}$ and temperature T, as shown in Fig.2. For each data point, the results are averaged over 160 samples. If $N_{CRR}(T)$ is defined at the half-probability of rearrangement, $N_{CRR}(T)$ is equal to the contour line at p = 0.5. $N_{CRR}(T)$ increases rapidly and exceeds to 90 particles upon cooling toward to the glass transition temperature. The obtained result $N_{CRR}(T = T_q)$ is larger than those estimated by heat capacity measurements or the characteristic length scale of dynamic heterogeneity observed by computer simulation. It is understood that $N_{CRR}(T)$ in the direct measurement is the number of particles required for the rearrangement, while $N_{CRR}(T)$ in the indirect measurement is the number of particles which cooperatively have moved during the rearrangement.

It is also remarkable that the dispersion of probability distribution increases upon cooling, which is due to the dynamic heterogeneity significant in the vicinity of T_q .



FIG. 1: Snapshot of the interactive molecular-dynamics simulation; the particles in light gray are constrained particles which figures the circular shell with a certain distance r. The rearranged particles are colored in black.



FIG. 2: Probability of rearrangement for different sizes of confinement and different temperatures.

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The Relations between the Configurations in the Cooperative Rearranging Region with Basic Molecular Units and Fragility in Viscous Liquids

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The relation between macroscopic and molecular equations for the temperature dependence of the relaxation times in the Adam-Gibbs [1] theory is discussed. In comparing molecular Adam-Gibbs and VTF expressions an equation for the size of the cooperative rearranging region (CRR) is obtained [2,3]. An expression for the number of the configurations in the CRR, which make compatible the macroscopic and molecular Adam-Gibbs equations, is obtained.

The temperature range of equivalence of macroscopic Adam-Gibbs equation and free volume theory [4] has been found. The number of configurations in the CRR depends on the way of estimating the configuration entropy [5] and the number of effective thermodynamic "beads" (or rotational bonds) in the molecule. The number of configurations in the CRR at glass-transition temperature has been found to be approximately equal to the number of basic molecular units in the same range, but seem to dependence on the fragility.



FIG. 1: Fragility plot [7] for n-Propanol (n-Pr), 3-Brompentane (3-BP) and o-Terphenyl (OTP).

By measuring the number of configurations in the CRR a possibility for deducing the internal degree of freedom in molecules is discussed. As this is a key problem for understanding the slow dynamic in viscous liquids [6], the estimation of the configurations in the CRRs seems to be promising in this direction. Scaling of the configurations per basic molecular unit to the configurations at glass-transition temperature avoid the uncertainty in measuring their absolute number. It has been obtained that the scaled

number of configurations in the temperature range of validity of the macroscopic Adam-Gibbs theory can be measured by thermodynamic as well by kinetic experiments. From the theory it follows that the scaled number of configurations is larger and increases faster with the temperature in the fragile liquids in comparison to the strong ones.



FIG. 2: The scaled number of configurations per basic molecular unit in the CRRs, $w(T)/w(T_g)$, for the same substances as in Fig. 1.

This finding is supported by experimental results, compare Figs. 1 and 2. The results obtained are in agreement with the conception of the larger number of minima in the potential energy hypersurface for the fragile liquids in comparing to the strong ones.

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Cooperative dynamics in condensed molecular and macromolecular systems

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The concepts concerning cooperativity in dynamics will be discussed on the bases of the DLL (Dynamic Lattice Liquid) model elaborated to describe dynamics in dense molecular and macromolecular liquids.

The model provides a microscopic picture of cooperative molecular rearrangements resulting from system continuity under conditions of excluded volume and dense packing of molecules. The rearrangements are considered as taking place in systems with fluctuating density and with rates dependent on thermal activation barriers which depend on and fluctuate with the local density (intermolecular distances). Dependencies of this kind may include chemical specificity of systems.

It is shown, that the model is able to reproduce the

extreme cases of temperature dependencies of relaxation times represented on one edge by the Arrhenius relation and on the other edge by the Vogel-Fulcher-Tamman relation, as well as, various dependencies filling the gap between these extremes. It reproduces also effects of pressure on the molecular relaxation times in agreement with available experimental observations. The model constitutes a basis for parallel computer simulation algorithms and in this form can be applied for both liquids and polymers.

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Neutron scattering studies of the dynamics of the very fragile glass former decalin

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Decalin is one of the most fragile glass former, with an degree of fragility m = 145. The dynamics of the hyperquenched glass are compared with those of the crystalline sample in the frequency range going from 1 μ eV up to 30 meV. The vibrational density of state is studied during annealing from 2K up to the liquid state (238K). The inelastic peaks broaden strongly when approaching the liquid and are completely smeared out above 240 K. The low-frequency response in the glass is highly anharmonic with quasielastic scattering developing at already rather low temperatures. This quasi-elastic scattering can be well correlated with drops in the Debye-Waller factor. We are currently processing the data in the framework of a Mode Coupling scenario. In the region of excess modes the crystal shows several peaks indicating complex mode patterns. It can be expected that the analysis of this rich experimental information leaves us with an improved understanding of liquids and glass dynamics.

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Low temperature properties in molecular glass formers

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We analyse the dielectric response of several molecular glass formers such as glycerol, propylene carbonate (PC), 4 tertbutylpyridin (4TBP), and Salol, in the low temperature range 5-250 K. The systems studied do not show a Johari-Goldstein relaxation, and are known as type A glass formers. Our objective is to focus on dynamics below T_g , and specifically we want to reach the crossover to the tunnelling regime. We present dielectric data with $\tan \delta$ down to 10^{-5} measured with the new ultraprecision capacitance bridge Andeen Hagerling 2700A in a frequency range 50 Hz-20 kHz. In all systems we observe a nearly constant loss (NCL) behaviour, that is an imaginary part of the permittivity or dielectric loss almost constant in frequency at $T < T_q$ (Fig. 1). Moreover, the frequency dependence of the loss, which extends to more than 5 decades, is not changing below T_g down to 50–80 K.



FIG. 1: Spectrum of the dielectric loss of propylene carbonate, which has a glass transition temperature of 159 K.

In all systems the behaviour below T_g shows very similar features, pointing to a universal response of type A glass formers (Fig. 2): The temperature dependence of the magnitude of the loss is best described by an exponential temperature dependence $\exp(T/T_0)$, with very similar T_0 . This exponential law is identified as a signature of this NCL response because the same NCL temperature dependence has been reported before in other glass formers [1], and also appear as a universal feature in ionic conductors, in both glassy and crystalline materials [2,3].

At the lowest temperatures, below 70 K, there is a crossover to a different regime, that causes a minimum and an increase of the losses. This new relaxation is tentatively attributed to the onset of tunnelling dynamics near 10 K (Fig. 2). In the crossover temperature range, a change in the slope of the frequency dependence of ε'' is observed, turning negative (Fig. 1 below 70 K). In the case of 4TBP we find a different relaxation mechanism that causes a broad maximum in ε'' versus temperature, that may be an indication of thermally activated jumps over energy barriers within double well potential dynamics leading to tunnelling phenomena at lower temperatures.



FIG. 2: Temperature dependence of the dielectric loss of several glass formers at a frequency of 1 kHz.

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Slow and Fast Dynamics in Glycerol-Water Mixtures

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It is well known that the main dielectric relaxation process observed in water/glycerol mixture could be nicely fitted by the Cole-Davidson function. However, the experimental data demonstrate significant deviation from such power law behavior. The presentation of our experimental results in terms of socalled "master plots" in which the data and the correspondent frequency axis were normalized to the value of relaxation peak maximum and the corresponding frequency, shows that all the data for pure glycerol, for example, in the temperature range 196 to 250 K are condensed to a single function in this master plot. It means that both of the excess wing and the dc-conductivity are characterized by the same temperature dependence of the main process, which is described by the Vogel-Fulcher-Tammann (VFT) law. Moreover, the same behavior was also found in glycerol-water mixtures in the glycerol rich region (50 to 100 mole % of glycerol). In addition, it is possible to normalize the frequency dependencies of $\varepsilon^{\prime\prime}$ for different glycerol-water mixtures at a constant temperature. Such normalization demonstrates that the excess wing and the main dielectric dispersion have the same dependency on the composition of glycerolwater mixture over the comparatively wide range of concentrations: from 50 up to 100 mole %. All these results indicate that the dc-conductivity, the main relaxation process and the excess wing reflect an elementary molecular process originating by the same mechanism. Such a mechanism could be related to the formation and transport of H-bond network defects (so-called orientation and ionic defects) similar to that considered in conduction and relaxation of ice.

A further decrease of glycerol content caused the universality in the master plot to disappear. Below 40 mole % glycerol, a different behavior of the main relaxation process and the excess wing was observed. This region with small glycerol mole content has been investigated in detail by Sudo *et al.* who ascribed the main and secondary relaxation processes to the relaxation dynamics of the so-called cooperative domains of glycerol and water, respectively [1]. The likely explanation of this fact is the following: Both glycerol and water are associated liquids with extended hydrogen network structures. At high glycerol concentrations, water molecules may easily penetrate and become incorporated in the glycerol H-bond network without destroying it. At a certain water concentration, however, glycerol molecules cannot provide all water molecules with hydrogen bonds. As a result, water molecules will increasingly interact with each other. Most probably the formation of joint hydrogenbond networks from both constituents provide cooperative glass-forming dynamics for mixtures from 100 to 40 mole % of glycerol, while below this concentration the destruction of such joint hydrogen-bond network reduces the cooperative dynamics.

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Does anharmonicity control fragility?

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All glassy materials are characterised by a common macroscopic property, which is an extraordinary decrease of several orders of magnitude of the mobility in a narrow temperature range under cooling [1]. For a glass-forming liquid, the shear viscosity η or the relaxation time τ exhibits a deviation from an Arrhenius law, which is measured by a fragility index m usually defined as [2]:

$$m = \lim_{T \to T_a^+} \frac{d\log(\eta)}{d(T_q/T)},$$
(1)

where T_g is the glass transition temperature. This parameter enables to classify very different materials such as silica, molecular liquids, polymers, proteins, which are able to show a glassy behaviour. Understanding how a microscopic property is reflected in the macroscopical dynamical behaviour of glass-forming materials is a subject which has been intensively investigated in the last decade [1, 3]. The correlation between macroscopic and microscopic properties must be an essential point to be included in every theory aiming at describing the glass transition problem. This work has not been realised yet but an approach called the Coupling Model (CM) has been proposed by K.L. Ngai [3].

Based on the CM approach, we have investigated the correlation between the fragility, the inter-particle coupling parameter, and the anharmonicity by means of molecular dynamics simulations of simple binary Lennard-Jones liquids (similar to that in [4]). The anharmonicity is controlled by modifying the particle interactions. We have studied three different systems whose species 1-species 1 interaction changes as



FIG. 1: Relaxation time τ_1 of species 1 obtained from S(q,t) for the three studied systems versus $T_{\rm ref}/T$. In the inset, the shape of the potentials of the three studied systems, defining the species 1-species 1 interaction, are shown.



FIG. 2: Non-exponential parameter $\beta = 1-n$ as a function of $T_{\rm ref}/T$ for the tree studied systems. In the inset, the dynamical structure factor S(Q,t) is shown for the three systems at a temperature just above $T_{\rm ref}$.

shown in the inset of Fig. 1. We have determined the α relaxation times of these three systems over a wide temperature range (see Fig. 1), especially at low temperatures when the dynamics slows down considerably. Therefore, we can fix arbitrarily a reference temperature $T_{\rm ref}$ that we identify to a numberical glass transition temperature, in oder to determine a fragility index (like in [5]). We clearly see that the most anharmonic system exhibits the largest fragility.

Moreover, from the dynamical structure factor S(Q, t), we have also determined the stretchedexponential exponent β for the three systems in the investigated temperature range, as shown in Fig. 2. According to the CM approach, $n = 1 - \beta$ is the interparticle coupling parameter. From Fig. 2, we can say that the more anharmonic the system is, the strongest the inter-particle coupling is.

This preliminary study reveals that a fragile system is seen as a system with strongly coupled particles whose effective potential is highly anharmonic.

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Correlations between PALS data and the dynamic properties of small molecular and polymeric glass-forming liquids

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Systematic and detailed positron annihilation lifetime spectroscopic (PALS) investigations were performed on a series of organic glass-formers from 15K up to 370K. This includes both the glassy and liquid states of the supercooled systems. Model compounds of various intramolecular types, such as small molecule and polymeric systems, as well as of different intermolecular forces, such as van der Waals bonded substances [m-tricresyl phosphate (m-TCP), cis-trans-1,4-polybutadiene (c-t-1,4-PBD), polyisobutylene (PIB) and polypropylene glycol (PPG 4000)] or hydrogen-bonded substances [glycerol (GL), propylene glycol (PG), dipropylene glycol (DPG), tripropylene glycol (TPG)] were studied.

The ortho-positronium (o-Ps) annihilation characteristics, i.e., mean o-Ps lifetime, τ_3 , and o-Ps relative intensity, I_3 , as a function of temperature were considered from a phenomenological point of view by comparing the data with various dynamic properties. For example, an abrupt change in the properties is observed at a temperature T_g^{PALS} . This temperature is close to the glass transition temperature, T_g , observed by classical dilatometric and calorimetric methods. Several other empirical correlations are found between the o-Ps response and dynamic phenomena from relaxation spectroscopy depending on the type of glass-former. The observations concerning the variation of τ_3 with temperature are as follows:

(i) As the temperature increases above T_g^{PALS} , an increase in the slope of τ_3 vs. temperature occurs (in the liquid state) at T_{b1}^{lq} . T_{b1}^{lq} is found to be close to the characteristic temperature T_{α} (-6 ± 1), at which the mean relaxation time of the primary relaxation is approximately $10^{-6\pm1}$ s in all of the systems studied. Moreover, in the case of van der Waals systems such as m-TCP and OTP [1, 2] the following relationship is found: $T_{b1}^{lq} \simeq 1.2 \dots 1.3 T_g \simeq T_B^{ST}$, where T_B^{ST} is the Stickel temperature which marks the boundary between distinct dynamic regimes described by two different empirical VFTH equations or by VFTH and

Arrhenius equations [3].

(ii) As the temperature increases above T_{b1}^{lq} , a decrease in the slope of τ_3 vs. temperature occurs (in the liquid state) at T_{b2}^{lq} indicating a crossover to a quasiplateau level. This temperature is characterized by the equality between τ_3 and the relaxation time of the primary α relaxation, τ_{α} . The following relationship is found: $T_{b2}^{lq} \simeq 1.4 \dots 1.7T_g$. In the cases of the associated systems, $T_{b2}^{lq} \simeq 1.4 \dots 1.55T_g$ is in the vicinity of the Stickel temperature T_B^{ST} . However, for PG, DPG, TPG and PPG 4000, T_{b2}^{lq} correlates better with the Schönhals temperature, T_B^{SCH} , at which a change in the relaxation strength, $\Delta \varepsilon_{\alpha}$, occurs. The change in the α relaxation strength is a model-independent characteristic of the α relaxation [4].

(iii) The slope of τ_3 vs. temperature in deeply supercooled liquids is related to the well known Oldekop-Ullmann-Angell fragility, m_g , as well as to the recently defined Richert-Angell fragility, $F_{1/2}$, [5] for all of the compounds in our series of small molecule and polymeric systems. This trend indicates that both thermal activation and free volume are controlling factors in the relaxation dynamics of deeply supercooled liquids in the vicinity of the glass transition temperature.

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Shear Viscosity of Inorganic and Organic Glass-Forming Materials

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We have developed a method for measuring the high shear viscosity of solids [1]. The method is a kind of sandwich method. A cubic specimen of $1 \times 1 \times 1$ cm in size is used, and the lower and upper faces of the specimen are bonded to fixed and movable stainless steel test plates respectively with an adequate bonding material. A constant lateral load is applied to the movable plate by means of a weight and pulley. The lateral displacement of the plate is measured as a function of time by a laser measurement system. The most important point in the method is that the specimen is deformed under almost pure shear mode [1]. The data are analyzed to determine the viscosity of the specimen at temperatures below the glass transition temperature T_g .



FIG. 1: Temperature dependence of shear viscosity of metaphosphate glass near the glass transition.

For obtaining the viscosity data at temperatures above T_g a conventional machine, the dynamic analyzer is used. This machine has been well established for measuring the viscosity in a pure shear mode by the rotation disk method. An example of temperature dependence of viscosity η is shown in Fig. 1. Data obtained by the two methods relate quite smoothly. The viscosity measurements were carried out [2–4] for inorganic glasses: metaphosphate, pyrophosphate, molybdate, fluorophosphates; and organic glasses: polystyrene, poly(methylmethacrylate), polycarbonate. The obtained high temperature data $(T > T_g)$ are well fitted to the Vogel-Tammann-Fulcher (VTF) equation

$$\eta = A \exp[B/(T - T_O)]. \tag{1}$$

The broken curve in the figure is the result of the fit. At low temperatures $(T < T_g)$ the data can well be fitted to

$$\eta^{-1} = \eta_0^{-1} \exp(-E/RT) + {\eta'_0}^{-1} \exp(-E'/RT), \quad (2)$$

where the η s and *E*s are parameters, *R* is the gas constant, and here the *E*s mean activation energies. The solid curve in the figure is the result of the fit. The low temperature behavior, Eq. (2) was precisely analyzed by considering cooperative motions of relaxing elements [5, 6].

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Brillouin scattering study of hypersonic attenuation in GeO₂

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Sound attenuation in glasses is still poorly understood. This is because many competing factors lead to sound-wavedamping. Sorting out different contributions for a given temperature and sound-wave frequency is a difficult task.

A long time ago, strong indication was found that the thermally activated relaxation which explains the ultrasonic attenuation in vitreous silica was not sufficient to account for the measured phonon linewidth Γ in Brillouin light scattering experiments [1]. At these high frequencies, it was proposed to invoke anharmonic 3-phonon interactions, as found in crystals, to explain the hypersonic attenuation in silica. More recently, it was observed that Γ was much lower in permanently densified silica $(d-SiO_2)$ and compares with the one measured in crystalline quartz [2]. Besides, the decrease of the velocity with temperature, observed in normal silica below 70 K and attributed to the relaxational process, is strongly suppressed in densified silica. These results indicate that the increase of density hinders the relaxational process and only anharmonic interactions remain in $d-SiO_2$.

It has also been shown in the past in a somewhat more complicated system that both hypersonic velocity and attenuation measured below the glass transition temperature, T_g , were dependent of thermal history [3]. In particular, a variation of the hypersonic attenuation up to 50% was reported for glasses stabilized at different temperatures covering the whole transformation range. Indeed, when a glass is annealed at a fixed temperature in the transformation range, it may further relax in order to adjust its present molecular configuration to the new configuration corresponding to the annealing temperature. The latter process is called stabilization and the stabilization temperature, the fictive temperature T_f .

To learn more about the sound attenuation origin in glasses, we started high resolution Brillouin light scattering experiments in another simple oxide glass, vitreous GeO₂. In order to establish the relative importance of the different processes responsible for the sound-wave damping we have studied a series of GeO₂ samples of different fictive temperature.

The high resolution Brillouin light scattering experiments have been performed on an especially designed spectrometer [4, 5]. It consists of a controlledthickness planar four-pass Fabry-Perot (FP) interferometer followed by a confocal FP interferometer. The planar FP is used as a monochromator. The frequency corresponding to the maximum of the filter is matched with the frequency of the Brillouin line. The planar FP is stabilized with an electro-optic modulation line set to the Brillouin frequency. The resolving unit is the confocal FP which has a finesse of 50 and a free spectral range of about 1.5 GHz. This spectrometer is then characterized by both a high contrast (10⁷) and a high resolution (HWHM $\simeq 15$ MHz).

All measurements have been carried out in backscattering geometry. The accuracy of the experimental data for the Brillouin shift frequency and its linewidth is ± 3 and ± 5 MHz, respectively. From these data the longitudinal sound velocity and the mean free path of the phonons have been obtained in a wide range of temperature for a series of GeO₂ samples annealed at different fictive temperatures. A strong variation with T_f of both hypersonic velocity and attenuation is found in GeO₂. We discuss these effects in terms of changes in the anharmonic process accompanying the variation with T_f of the density of states.

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Phonon Dispersion in Mesoscopic Self-assembled Soft Matter

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Acoustic excitations in condensed matter are a rich field of the solid state physics. The propagation of sound through inhomogeneous media is of interest since the spatial modulation in density and elastic parameters can give rise to fascinating rich behavior with practical relevance [1]. As more self-assembled mesoscopic structures emerge, long wavelength elastic excitations can be probed by inelastic (Brillouin) light scattering (BS) with direct access to the desired reciprocal space since the wave vector q of the scattered photon matches the characteristic spacing d (of the order of 200 nm) of the structure.



FIG. 1: Polarized Brillouin spectra (left) at $q = 0.025 \text{ nm}^{-1}$ for a 4.5 wt% SI4M solution in toluene at 20°C along with the dispersion relations (right panel). Squares are for the acoustic phonon with $f \propto q$ and the solid lines for the other excitations conform to the cylindrical spacing 355 nm.

Recently, the technique has been employed to study

the phonon dispersion relations in suspension of soft colloids [2] and in two colloidal crystals consisting of high and low elastic constant spherical particles. The nature of the observed optic-like, mixed and Bragg induced phonons was elucidated by theoretical calculations (single sphere scattering cross section and band structure). High molecular weight diblock copolymer is another example of self assembling systems with photonic band gab properties in the visible spectrum.

In concentrated solutions of a symmetric diblock copolymers ordered in 1D lamellar morphology, BS has detected, in addition to the acoustic longitudinal phonon k = q, two further modes due to the interaction of k with the lattice vector $G = 2\pi/d$ [3]. The geometrical characteristics and the mechanical properties of the layered structure are directly related to the observed dispersion.

This study has been extended for an ultra high molecular weight $(3.6 \times 10^6 \text{ g/mol})$ poly(styrene-bisoprene) (SI4M) forming hexagonally arranged cylinders. The BS spectrum clearly depends (Fig. 1) on the cell orientation relative to the q and the experimental dispersion of the phonon spectrum is displayed in the right panel of the figure. Note that for homogeneous systems ($qd \ll 1$) only the acoustic like phonon (f = 5.3 GHz in the figure) with k = q and linear dispersion (q) is observed. The experimental dispersion relations are compared with acoustic band structure calculations for 1D [4] and 3D morphologies.

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The entrance of plastic crystals in their glassy crystal state

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Some rotator ("plastic") phases of molecular compounds can be deeply undercooled in a so-called "glassy crystal" state. They present much of the phenomenological features of the entrance in a conventional glassy state. These include: (i) the dynamical decoupling and caging effects occurring in the high frequency/high temperature regime; (ii) the thermodynamic signature of the glass transition at T_q .

Here we report experiments that turn the underlying crystal structure to advantage. The substituted adamantane family provide single crystals of excellent quality that can be safely undercooled as glassy crystals. The structural and dynamic properties can thus be investigated in great detail. They reveal nanostructural molecular organizations where short range and heterophases fluctuations can be resolved. The temperature changes of their respective relaxation and kinetics near the glass transition could be analysed and dissociated. This provides a clear picture of the vitrifying disordered crystal being on the brink of an absolute metastability limit. The extrapolation of the data in the non-ergodic domain sheds light on the nature of the underlying singularities that are recurrent questions in the physics of glass formers. The specificities of facing a situation of metastability occurring in a crystal state is discussed. What could be learned about the situation of conventional glasses is briefly addressed.

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Specific heat of nonequilibrium systems and the glass transition

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In 1968, Sugisaki measured specific heat of isopentane in various measurement procedures and found the cooling rate dependence of the glass transition temperature T_g [1]. The glass transition temperature T_g is much lower than the critical temperature T_c predicted by MCT, and is higher than the Kauzmann temperature T_K where the configurational entropy becomes zero. From numerical studies, it is known that activation process is dominant in supercooled liquids near T_g . However MCT is a mean-field theory and replica method is an equilibrium theory.

We need a new approach to treat supercooled liquids near T_g . There are some questions on the glass transition temperature T_g . These are questions such as, why does the specific heat (i) change abruptly?, (ii) show $C(T_g+) > C(T_g-)$? and (iii) depend on the cooling rate of the measurements?

To answer these questions, we developed a new formalism to calculate specific heats of nonequilibrium systems. Considering a many-particle system, structural relaxation times abruptly increase near the glass transition temperature. It is known that the abnormal increase of the relaxation time comes from stochastic jump motion of particles. A particle is trapped in a cage which is composed of the other particles. Sometimes a particle jumps out of the cage because of cooperative motion of particles. This can be understood as the stochastic jump motion. To sum up, particles oscillate at their equilibrium positions for some time and occasionally they rearrange their positions by the stochastic jump motions.

We consider a free energy landscape with many basins in the configurational space. A representative point stochastically jumps around basins in the landscape, where a basin corresponds to a state of oscillators system and each basin has a different state from each other. The stochastic jump motion of the representative point among basins corresponds to cooperative jump motion of particles. To study the dynamics near the glass transition point, we calculated the one-particle motion based on the free energy landscape and showed the dynamical characteristics near the glass transition point [2].

We formulated a method of calculating specific heat of nonequilibrium systems. The energy of a nonequilibrium system can be expressed as $e(T,t) = \sum_i p_i(T,t)E_i(T)$, where $p_i(T,t)$ is the distribution function of basin *i* and obeys a master equation, and $E_i(T)$ is the local equilibrium energy of basin *i*. The specific heat of the nonequilibrium system was defined as

$$c(T, t_{obs}) \equiv \frac{e(T + \Delta T, t + t_{obs}) - e(T, t)}{\Delta T},$$

where ΔT is the difference of temperature of heat bath in a measurement procedure, and t_{obs} is the observation time of the specific heat.

We consider a model landscape with many basins, each of which is an oscillator system. The local equilibrium energy of basin i is expressed as

$$E_i(T) = \int_0^\infty \biggl(\frac{\hbar \omega}{2} + \frac{\hbar \omega}{e^{\hbar \omega/k_BT} - 1} \biggr) D_i(\omega) d\omega,$$

where $D_i(\omega)$ is the density of states of basin *i*. We calculated specific heat for the Debye model, $D_i(\omega) \sim \omega^2$. Furthermore, to study the cooling rate dependence of specific heat, we use the Einstein model, $D_i(\omega) \sim \delta(\omega - \omega_E^{(i)})$ [3, 4], for simplicity, where $\omega_E^{(i)}$ is an Einstein frequency of basin *i*.

From these models, we showed the observation time dependence of specific heat. The specific heat changes more abruptly and the transition temperature becomes lower for longer observation time, and specific heat behaves as $C(T_q+) > C(T_q-)$. These behaviors can be understood as follows. We call an "annealed" specific heat, which is measured for infinite observation time at every temperature. For measurements with a finite observation time $t_{obs} > \tau_r$, temperature dependence of the specific heat coincides with the "annealed" one, and is less than the "annealed" one for $t_{obs} < \tau_r$, where τ_r is the relaxation time of the system. We call the latter system a quenched system. The relaxation time depends on temperature, and it increases abruptly near the glass transition point. A system is in annealed state in high temperatures, while it is in a quenched state in low temperatures. Thus the glass transition can be understood as the transition between annealed and quenched states, and it depends on the observation time.

Furthermore, we showed the cooling-rate dependence of the specific heat. The cooling rate dependence can be understood from the fact that different cooling rate corresponds to different initial state for measurements. An initial state of a system is near equilibrium for slow rate of cooling, while it is far from equilibrium for fast rate of cooling. We can understand that the transition in the former system occurs at lower temperature than that in the latter system.

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An analysis of boundary-effects in obtaining the frequency dependent specific heat by effusivity measurements

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The frequency dependent specific heat is a significant response function characterizing the glass transition. Contrary to the dielectric response it is not easily measured over many decades. The introduction of the 3- ω method, where the temperature oscillations at a planar oscillatoric heat generator is measured, made this possible. The method relied on a 1-d solution to the heat diffusion equation. There have been attempts to invoke the boundary effects to first order. However we present the fully 3-d solution to the problem including these effects. The frequency range can hereby be considerably enhanced.

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New developments in Neutron Spin Echo

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Today's Neutron Spin Echo (NSE) instruments [1] access the Fourier time range up to several 100 ns, corresponding to highest energy resolution (sub-neV) of all neutron scattering techniques. In NSE, the spin phase accumulated in magnetic fields before and after the sample is compared. A variant of NSE, the Neutron Resonance Spin Echo (NRSE) technique [2] relies on a similar principle as NSE, while it has the advantage of reducing the dimensions of the magnetic fields. The resolution of NSE and NRSE is mainly limited by the presence of field integral inhomogeneities leading to different spin phases of neutrons moving on different trajectories. New challenges, for example, probing diffusive dynamics of nm-sized biomolecules, require higher dynamical resolution, that is, stronger fields with inevitably increased inhomogeneities. While in NSE the resolution limit is mainly given by field inhomogeneities, NRSE is limited only by the beam divergence allowing for trajectories of different length ("path inhomogeneity"). We have developed a new NRSE variant [3] overcoming this limit. While previously built NRSE spectrometers were not able to correct for the path inhomogeneity, our setup (Fig. 1) is designed in a new longitudinal field geometry and uses correction coils known from NSE. First tests of the new NRSE spectrometer arm have been performed at IN11 (Institut Laue Langevin, Grenoble). The results of the measurements show, that the effect of field integral inhomogeneities could be decreased to large extend and, thus, that a high resolution NRSE spectrometer is feasible.

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FIG. 1: Comparison between one arm of a "conventional" NRSE setup containing two NRSE coils with transversal magnetic fields and, in-between a zero-field region (top). Below, our new NRSE setup using magnetic fields parallel to the neutron beam direction (longitudinal NRSE), making it possible to use "Fresnel" correction coils.

A Physicist's View on Constitutive Equations

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Hydrodynamic equations for various kinds of complex fluids (simple liquids, binary mixtures, liquid crystals, superfluids, crystals, etc.) can be derived rigorously using general physical laws and principles. This hydrodynamic method is generalized to include slowly relaxing quantities, in particular those describing viscoelasticity.

We start with the nonlinear hydrodynamic equations for elastic media derived from basic physical principles. For the Eulerian strain tensor the lower convected time derivative is obtained, unambiguously [1–3]. Adding a relaxation term the permanent elasticity is transformed into viscoelasticity [1, 2], where both, the short time and the long time limit, are given correctly. The dynamic equation for the strain tensor obtained that way still shows the lower convected derivative universally. It covers the usual non-Newtonian effects, like shear thinning, strain hardening, stress overshoot, normal stress differences and Weissenberg effect, non exponential stress relaxation, etc. [4]. When brought into the more familiar form of a dynamic equation for the stress tensor ("constitutive equation"), it comprises most of the wellknown ad-hoc models (Maxwell, Oldroyd, Johnson-Segalman) and is even more general in structure than those [5]. Nevertheless, it imposes also some restrictions on, and reveals some interdependencies of, the various non-Newtonian contributions that are otherwise introduced heuristically. It is shown how these contributions originate from (nonlinear) elasticity, viscosity, strain relaxation and convection. The time derivative for the stress tensor is no longer of the lower convected type, but is material dependent. We also discuss [6] the connection to those descriptions of viscoelasticity that utilize an orientational order parameter.

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Testing for one Generalized Linear Single Order Parameter

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We examine a linear single order parameter model for thermoviscoelastic relaxation in viscous liquids, allowing for a distribution of relaxation times. In this model the relaxation of volume and enthalpy is completely described by the relaxation of one internal order parameter. In contrast to prior work the order parameter may be chosen to have a non-exponential relaxation. The model predictions contradict the general consensus of the properties of viscous liquids in two ways: (i) The model predicts that following a linear isobaric temperature step, the normalized volume and enthalpy relaxation functions are identical. This assumption conflicts with some (but not all) reports, utilizing the Tool-Narayanaswami formalism to extrapolate from non-linear measurements to the linear regime. (ii) The model predicts that the theoretical "linear Prigogine-Defay ratio" is one. This ratio has never been accurately measured, however, as this involves the measurement on an equilibrium liquid of three linear static responses and three linear instantaneous responses. The existing experimental reports of the Prigogine-Defay ratio either fail to measure a truly linear, instantaneous, isobaric and isothermal responses or extrapolate from measurements of a glassy state away from equilibrium.

Starting from a master equation description of inherent dynamics, we calculate the complex thermodynamic response functions. We device a way of testing for the generalized single order parameter model by measuring 3 complex response functions at a single frequency.

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Theoretical Model of the Fischer Clusters Formation in Supercooled Liquids

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Fischer clusters are long-range correlations of density fluctuations [1], which are observed in supercooled liquids (~100 K above the glass-transition temperature T_g). So far these clusters have been revealed in polymers, glass-forming liquids as well as in some one-component liquids. The typical size of these formations is ~100–300 nm while the short-range order size is only ~1 nm. The fractal-like structure and relatively long lifetime are important distinguishing properties of Fischer clusters.

In spite of numerous experimental observations of Fischer clusters and considerable state-of-the-art progress in computer simulation there is no clear enough theoretical explanation of this effect. It is supposed that the cluster formation is concerned with liquid-liquid transition, and that it is the condensation of the atoms formations with the same local-ordering type [2]. For the time being however, this approach does not allow to account for either the fractal-like structure or long lifetime [3].

In this work a theoretical model of liquid-glass transitions is suggested. This model is formulated in terms of theoretical approaches that are well known in the adjacent area of the disordered systems physics, and allows to formulate a consistent explanation of structure formation processes in melts.

The glass transition theories by Nelson and Rivier [4, 5] are the basis of our model. According to this theory the liquid-glass transition is the phase transition in the system of linear defects. Within the framework of this theory there is no fundamental difference between spin-discorded or structural-disordered systems. Both in the first and in the second cases the problem of system description comes to description of interacting disclinations systems. We want to make use of this analogy to make the description of the structural-disordered system as close as possible to the description of the spin-discorded system. It is necessary to make use of the results obtained in the spin-glasses theory.

We suppose that disordered system of topological moments of disclination loops is similar to spin-glass system. The combination of the disclination model of liquid with the modification of the Edwards-Anderson model with large but finite-range interaction is suggested to describe the liquid-glass transition [6, 7]. Within the framework of this approach vitrifying is represented as a "hierarchical" phase transition. The performed estimation allows to conclude, that within the framework of our model the processes of freezing of the degrees of freedom in liquids begin at the temperature that noticeably (several hundreds degrees) exceeds the glass transition temperature T_g . In the temperature range $(T - T_g) \sim 100$ K the clusters form in the liquid's structure, the size of these clusters ~ 100 nm. These results agree with the available experimental data of the Fischer cluster observations. Furthermore, the Vogel-Fulcher law for the relaxation time is obtained in the framework of this approach. Also, it is interesting to note that temperature of appearance of the clusters T_0 can exceed the melting temperature, it allows to suppose that this point can be the reason for skipping and breaking in the viscosity polyterms of some melts at high temperatures [8, 9].

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The Defect Diffusion Model and the Physical Properties of Viscous Liquids

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In the defect diffusion model (DDM), dynamical processes are controlled by defects [1, 2]. For example, a dipole reorients or an ion jumps when it is encountered by a mobile defect. The characteristics of the dynamical processes, then, are determined by the flux of mobile defects into each site. The DDM leads to a relaxation law of the form

$$\phi(t) = \exp\left(-[t/\tau_{DD}]^{\beta}\right), \qquad (1)$$

where β is the stretched exponential parameter and τ_{DD} is the mean relaxation time. When the defects cluster, τ_{DD} , can be written as

$$\tau_{DD} = c^{-1/\beta} \tau_0 \exp\left(\frac{BT_C^{1.5\gamma}}{(T - T_C)^{1.5\gamma}(1 - \delta(T, P))}\right),$$
(2)

where B is given by

$$B = -\frac{L^3 \ln(1-c)}{\beta d_0^3}.$$
 (3)

Here, c is the total concentration of defects, τ_0 is the shortest time for the jump of a defect, γ is a constant that describes local field effects, d_0 is the mean lattice spacing at zero pressure, and $(1 - \delta(T, P))$ is the fractional volume change of the material with temperature and pressure. Inherent in the model is the existence of a defect-defect pair correlation length, ξ , given by

$$\xi(T) \approx L \left(\frac{T_C}{T - T_C}\right)^{1.5\gamma} , \qquad (4)$$

where L^2 is the second moment of the direct correlation function $C(\mathbf{r})$ between the defects (the shortrange Ornstein Zernike correlation length). T_C is the temperature below which mobile defects do not exist. When the defects do not cluster, the DDM leads to an Arrhenius expression for τ_{DD} [3].

It is shown how the model can be used to interpret dielectric relaxation, ionic conductivity and viscosity in viscous liquids. Another application of the model is the fragility of glass-forming liquids defined by

$$m = \left(\frac{\partial \log x}{\partial (T_g/T)}\right)_{T_g},\tag{5}$$

where x is a dynamical quantity such as electrical relaxation time, viscosity or electrical resistivity. It is shown that a necessary condition that a liquid be "fragile" is that there is an attractive interaction between the mobile defects i.e. that the defects cluster with falling temperature. In the defect diffusion model, the fragility is given by [3]

$$m_{DD} = -\frac{0.65T_C^{1.5\gamma}L^3\ln(1-c)\gamma}{\beta d_0^3 T_g^{1.5\gamma} \left(1 - \frac{T_C}{T_g}\right)^{1+1.5\gamma}}.$$
 (6)

Each of the model parameters provides a contribution to and insight into the fragility value. The behavior of exceptional cases, such as orientationally disordered crystals and aliphatic monohydric alcohols, is also naturally accounted for in terms of the model.

Finally, insights based on the model concerning positron annihilation lifetime studies, correlation lengths, the glass transition, the β relaxation and nearly constant loss may also be described.

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Aging in van der Waals liquids: a microscopic model

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It has been shown over the past ten years that the dynamics close to the glass transition is strongly heterogeneous, the typical size of the heterogeneities being of order 2-4 nm in van der Waals liquids. We have recently proposed a model according to which the dynamical heterogeneities correspond to density fluctuations in the liquid [1, 2]. We propose here an extension of this model aimed at describing aging in van der Waals liquids, and more generally the evolution of the microscopic state when the sample is submitted to a varying temperature or pressure, either above or below T_q . This model allows first to show that the dominant relaxation time is a function of the whole spectrum of density fluctuations. Then we describe aging as the relaxation of the density fluctuations spectrum towards equilibrium. Our dynamical equations allow for calculating the evolution of the relaxation time spectrum in the liquid as a function of e.g. a varying temperature. In particular, our description allows for explaining the following features: (i) The dynamics (e.g. τ_{α}) in van der waals liquids is not a function of the average density, but of both the temperature and the density. (ii) Aging can be erased (rejuvenation) by heating the sample in a much shorter time than was allowed for aging. (iii) The evolution of density can be non-monotonous after a temperature jump, depending on the history of the sample: this is one of the Kovacs memory effects. Finally, we compare qualitatively our results to recent experiments probing the relaxation time distribution of liquids during aging.

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