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Übungen zu Zeitabhängige Phänomene in der Statistischen Physik
Sommer Semester 2006

Übungsblatt 5: Sedimentation and diffusion under shear

Brownian motion under gravity The Brownian motion of colloidal particles under gravity, so-called sedimentation, was apparently first considered by Chandrasekhar in 1943 and is still a topic of active research in colloid science (see http://www.deas.harvard.edu/projects/weitzlab/research/Weitz-Sedimentation.htm, for an example of some current work). In this exercise we consider only the simplest case of a single diffusing colloidal particle and seek to emphasise the importance of the boundary conditions when tackling diffusion problems.

1. The probability density function for the position of a colloid at time t is given by the Smoluchowski equation
$$\frac{\partial P(\mathbf{r},t)}{\partial t} = D\nabla^2 P(\mathbf{r},t) + \mathbf{K}\cdot\nabla P(\mathbf{r},t),$$
where D is the diffusion constant and $\mathbf{K} = (0, 0, Dmg/(k_B T))$ with m the particle mass and g the accelleration due to gravity. Gravity thus acts in the z-direction. Comment on the physical meaning of the two terms on the right hand side of the equation. Use the technique of seperation of variables to show that we can write $P(\mathbf{r},t) = f(x,t)f(y,t)w(z,t)$ with
$$f(x,t) = \frac{1}{\sqrt{4\pi Dt}}\exp\left(-\frac{x^2}{4Dt}\right),$$
and where $w(z,t)$ satisfies the equation
$$\frac{\partial w(z,t)}{\partial t} = D\frac{\partial^2 w(z,t)}{\partial z^2} + c\frac{\partial w(z,t)}{\partial z},$$
where $c = Dmg/(k_B T)$. The Diffusion in the xy plane thus takes place in exactly the same way as in the field free case and so we are henceforth only concerned with the diffusion in the z-direction.

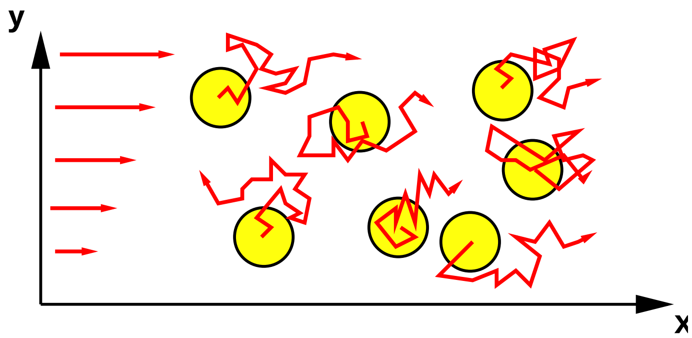
2. The initial height of the particle is taken to be $z_0 > 0$ and we place an impenetrable wall in the xy plane at $z = 0$ representing the bottom of the container. Explain why the following boundary conditions are appropriate
$$w \to \delta(z - z_0) \qquad t \to 0$$
$$D\frac{\partial w}{\partial z} + cw = 0 \quad z = 0 \qquad t > 0.$$
Use the substitution $w = U(z,t)\exp[-c(z-z_0)/(2D) - c^2 t/(4D)]$ to reduce the equation for $w(z,t)$ to a standard diffusion equation for $U(z,t)$ and give the corresponding boundary conditions.

3. The boundary conditions make solution of the diffusion equation for for $U(z,t)$ difficult but analytic solution is possible. The result is

$$\begin{aligned} U(z,t) &= \frac{1}{\sqrt{4\pi Dt}}\left(\exp[-(z-z_0)/(4Dt)] + \exp[-(z+z_0)/(4Dt)]\right) \\ &+ \frac{c}{D\sqrt{4\pi Dt}}\int_{z_0}^{\infty} dz' \exp\left(\exp\left[-\frac{(z'+z)^2}{4Dt} + \frac{c(z'-z_0)}{2D}\right]\right). \end{aligned}$$

This solution follows from using the method of images, familiar from electrostatics. Comment on the application of this method to satisfy boundary conditions in diffusion problems. Obtain the solution for the original variable $w(z,t)$ in terms of the error function and sketch it for few different times. Take the $t \to \infty$ limit of the solution to obtain the equilibrium distribution. This result should be familiar. Finally, use the equilibrium distribution to calculate the average height of the particles.

Brownian motion in a shear field In the previous problem we considered diffusion under an external force field which added an additional term to the diffusion equation to yield the Smoluchowski equation. However, the Smoluchowski equation can also be used to treat diffusion in cases when the solvent has a given velocity field. We now consider the case when the solvent flows in the x-direction with a velocity gradient in the y-direction, so-called simple shear. The Smoluchowski equation for the probability distribution with shear rate $\dot{\gamma}$ is given by:



$$\frac{\partial P(x,y,z,t)}{\partial t} = D\nabla^2 P(x,y,z,t) - \dot{\gamma} y \frac{\partial P(x,y,z,t)}{\partial x}.$$

1. The general form of the Smoluchowski equation is $\partial_t P(\mathbf{r},t) = \boldsymbol{\partial}\cdot[D\boldsymbol{\partial} - \mathbf{F}]P(\mathbf{r},t)$, where $\mathbf{F}$ is the force acting on the particle. Rewrite the above Smoluchowski equation in this form. Can the force be expressed as the gradient of a potential? Use the technique of seperation of variables to show that the distribution can be written as $P(x,y,z,t) = f(z,t)\phi(x,y,t)$, where $f(z,t)$ is the solution of the unsheared one-dimensional diffusion equation and find the equation for $\phi(x,y,t)$. The equation for $\phi(x,y,t)$ is most easily solved in Fourier space. By taking two-dimensional spatial Fourier transform show that the following equation must be satisfied by the transformed variable

$$\frac{\partial \tilde{\phi}(k_x,k_y,t)}{\partial t} = -k^2 D\tilde{\phi}(k_x,k_y,t) + \dot{\gamma} k_x \frac{\partial \tilde{\phi}(k_x,k_y,t)}{\partial k_y}.$$

The solution of this equation is complicated by the coupling between the x and y-directions.

2. Partial differential equations relating first derivatives are often soluble using the method of characteristics. Due to the structure of the transform equation we can regard this as a partial differential equation in two variables, k_y and t, with $D, \dot{\gamma}$ and k_x to be treated as parameters. The independent variables can be parameterized using a parameter r, $t \equiv t(r)$, $k_y \equiv k_y(r)$. Write the expression for the total derivative of $\tilde{\phi}$ and by comparing this with the transform equation show that $r = t$, $k_y = u - \dot{\gamma} k_x t$ and $\frac{d\tilde{\phi}}{dt} = -k^2 D\tilde{\phi}$, where u is a constant of integration. We can now solve the simpler equation $\frac{d\tilde{\phi}}{dt} = -k^2 D\tilde{\phi}$ by expressing the right hand side as a function of t and u and integrating with respect to t (holding u constant). Your solution should include a constant of integration $F(u)$ which is an arbitrary function of u.

3. We can now complete our solution of the transform equation by considering the initial condition $\phi(x, y, t) = \delta(x - x_0)\delta(y - y_0)$. Construct the corresponding initial condition for $\tilde{\phi}(k_x, k_y, 0)$ and use this to obtain the function F. Note that at $t = 0$ we have $u = k_y$. Thus show that the solution of the transform equation is given by

$$\tilde{\phi}(k_x, k_y, t) = \exp\left(-ik_x x_0 - i(k_y + \dot{\gamma}tk_x)y_0 - D\left[k_x^2\left(1 + \frac{1}{3}(\dot{\gamma}t)^2\right)t + k_y^2 t + k_x k_y \dot{\gamma}t^2\right]\right).$$

For one-dimensional diffusion in the x-direction without shear we would find $\tilde{\phi}(k_x, t) = \exp(-ik_x x_0 - Dk_x^2 t)$. The above solution shows that shearing enhances the diffusion constant by a factor $(1 + (\dot{\gamma}t)^2/3)$ in the x-direction. This phenomena is known as Taylor dispersion and was first discussed by G.I.Taylor in the 1940's. In fact, it is this effect which makes stirring Tea an effective method to disperse added milk. The motion of the spoon shears the fluid and leads to enhanced diffusion of the Browian particles (the suspended droplets of milk) in the direction of flow.

4. Perform an inverse Fourier tranform to obtain the distribution $P(x, y, z, t)$ subject to the initial condition $P(x, y, z, 0) = \delta(\mathbf{r} - \mathbf{r}_0)$. The following result for the Fourier transform of a multivariate Gaussian distribution $h(x_1, \cdots, x_N)$ with mean values m_i and standard deviation matrix σ_{ij} is useful

$$\tilde{h} = \exp\left(-i\mathbf{k}\cdot\mathbf{m} - \frac{1}{2}\sum_{ij}\sigma_{ij}k_i k_j\right), \quad h = \frac{1}{(2\pi)^{\frac{N}{2}}|\sigma|^{\frac{1}{2}}}\exp\left(-\frac{1}{2}\sum_{ij}(\sigma^{-1})_{ij}(x_i - m_i)(y_j - m_j)\right).$$

5. The result for $P(x, y, z, t)$ is a Gaussian distribution. It is also possible to obtain this result from an alternative route starting from the Langevin equation. Write down a Langevin equation appropriate for this problem and calculate the first two moments $\langle x\rangle$ and $\langle x^2\rangle$. Using these moments construct the first two cumulants explain how these lead to the desired Gaussian distribution.