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Übungen zu Zeitabhängige Phänomene in der Statistischen Physik
Sommer Semester 2006

Übungsblatt 4: Brownian motion and Langevin equation.

Brownian motion. In 1827 the Botanist Robert Brown observed that pollen grains suspended in water exhibit very irregular motion. Brown found similar behaviour with other suspensions of fine particles, even a powdered fragment of the Sphinx! This phenomena, Brownian motion, remained a mystery until in 1905 Einstein (and independently, Smoluchowski) provided the explanation which simultaneously provided strong evidence for the atomic nature of matter.

1. Einstein argued that the motion of a colloidal particle such as pollen suspended in a solvent arises from the many random collisions with the much smaller solvent molecules. We begin our description by introducing a time interval τ which is very small on the scale of the observation time but large enough that the motion of the particle is uncorrelated within neighbouring time intervals. Discuss the validity of assuming the existence of such a time interval. Give an estimate for τ.

2. We now specify to the case of one spatial dimension. Generalization to higher dimensions is then easy. If there are n non-interacting colloidal particles suspended in the solvent then in interval τ the x-coordinate of particle i changes $x_i \rightarrow x_i + \Delta_i$, where Δ_i is a different positive or negative value for each particle and which is independent from one time interval to the next. The probability density $\phi(\Delta)$ is defined by $dn = n\phi(\Delta)d\Delta$. Make a sketch of $\phi(\Delta)$. Why does ϕ satisfy the condition $\phi(\Delta) = \phi(-\Delta)$? If $\nu = f(x,t)$ is the number of particles per unit volume argue why the following Chapman-Kolmogorov equation should be satisfied
$$f(x, t+\tau) = \int_{-\infty}^{\infty} f(x+\Delta, t)\phi(\Delta)d\Delta.$$

3. By expanding $f(x, t+\tau)$ and $f(x+\Delta, t)$ in series for small values of τ and δ, respectively, show that
$$f + \tau\frac{\partial f}{\partial \tau} = f\int_{-\infty}^{\infty}\phi(\Delta)d\Delta \; + \; \frac{\partial^2 f}{\partial x^2}\int_{-\infty}^{\infty}\frac{\Delta^2}{2}\phi(\Delta)d\Delta,$$
where we have used the symmetry of $\phi(\Delta)$. By defining the diffusion constant $D = \frac{1}{\tau}\int_{-\infty}^{\infty}\frac{\Delta^2}{2}\phi(\Delta)d\Delta$ we arrive at the diffusion equation for $f(x,t)$
$$\frac{\partial f}{\partial t} = D\frac{\partial^2 f}{\partial x^2}.$$

4. Solve the diffusion equation with the boundary conditions $f(x, 0) = \delta(x - x_0)$, $f(x \rightarrow \infty, t) = 0$ to obtain
$$f(x,t) = \frac{n}{\sqrt{4\pi Dt}}\exp\left(-\frac{x^2}{4Dt}\right),$$
and show that the root-mean-square displacement $\lambda_x \equiv \sqrt{\langle x^2\rangle}$ is given by $\lambda_x = \sqrt{2Dt}$

Langevin equation In 1908, following Einstein's original derivation, Langevin presented a new approach to tackling Brownian motion. Langevin's approach introduced the concept of a stochastic differential equation, i.e. a differential equation with a term containing a random process. The colloidal particle is subject to two forces. The first force is a viscous drag $-6\pi\eta\sigma$, where η is the viscosity and σ the particle diameter (we assume a spherical particle). This viscous drag can be calculated from the Navier-Stokes equation of Hydrodynamics. The second force is a fluctuating random force X which reflects the collisions of the solvent molecules with the colloid.

1. What value do we expect for the average of the flucuating force $\langle X \rangle$? Using Newtons second law write an equation of motion for the position of the particle $x(t)$ and show that this can be written
$$\frac{1}{2}m\frac{d^2}{dt^2}(x^2) - mv^2 = -3\pi\eta\sigma\frac{d(x^2)}{dt} + xX,$$
where m is the mass of the particle and $v = \frac{dx}{dt}$. Comment on the effect of the stochastic term upon the solution $x(t)$. Is $x(t)$ deterministic? What kind of information can we expect to obtain from such a stochastic differential equation?

2. By taking averages and using the equipartition theorem show that
$$\frac{1}{2}m\frac{d^2}{dt^2}\langle x^2 \rangle + 3\pi\eta\sigma\frac{d}{dt}\langle x^2 \rangle = k_B T.$$
Where we have assumed that $\langle xX \rangle = 0$. Solve this equation to obtain the general solution $\frac{d\langle x^2 \rangle}{dt} = k_B T/(3\pi\eta\sigma) + C\exp(-6\pi\eta\sigma t/m)$. The term containing the integration constant can be neglected. Why is this? Using this result obtain an expression for the root mean square displacement λ_x. Finally, by combining this result with that from the previous exercise obtain the fluctuation-dissipation result $D = k_B T/(6\pi\eta\sigma)$ which connects the solvent viscosity to the diffusion constant of the colloidal particle. Describe how this result can be used to obtain Avogadro's number from a Brownian motion experiment, given an independent value for the gas constant $R = 8.314\,\text{J K}^{-1}$.

3. Consider again the approximation $\langle xX \rangle = 0$. In making this assumption what are we assuming about the statistical relationship between x and X? Discuss the relationship between this assumption and that of Einstein, who assumed a time interval τ such that the displacements Δ in neighbouring intervals are uncorrelated. Calculate the quantity $\langle vX \rangle$.

4. We now consider the situation in three dimensions. Use Newton's second law to write the equation of motion for this case, noting that the random force is now a vector $\mathbf{X}$. Use the equipartition theorem and the assumption $\langle \mathbf{r} \cdot \mathbf{X} \rangle = 0$ to derive the following equation for the mean square displacement of a colloidal particle initially at $\mathbf{r}(t = 0) = 0$
$$\langle r^2 \rangle = \frac{k_B T}{\pi\eta\sigma}\left[t - \tau_1\left(1 - \exp(-t/\tau_1)\right)\right],$$
where $\tau_1 = m/(6\pi\eta\sigma)$. Expand this result for short times $t \ll \tau_1$ and for long times $t \gg \tau_1$ and comment on the results.