UNIVERSITÄT KONSTANZ
Fachbereich Physik
Prof. Dr. Matthias Fuchs
Raum P 907, Tel. (07531)88-4678
E-mail: matthias.fuchs@uni-konstanz.de

Übungen zu Zeitabhängige Phänomene in der Statistischen Physik
Sommer Semester 2006

Übungsblatt 7: Kramers' equation, Escape rate problem and Positivity proof

Kramers' equation In previous exercises we have seen that the probability density $P(x,t)$ of the position of a colloidal particle in an external field can be described by the Smoluchowski equation. However, the Smoluchowski equation assumes that the momentum degrees of freedom equilibrate much faster than the positions. This is known as the overdamped limit. In some situations we cannot make this assumption and require the distribution function of both positions and velocities, $P(x,v,t)$. The partial differential equation for this function is Kramers' equation.

1. Consider a colloidal particle suspended in a solvent and subject to an external potential $V(x)$ which give rise to Brownian and deterministic forces, respectively. For simplicity we will work in one spatial dimension. Write a Langevin equation for the particle velocity. Combined with the relation $dx/dt = v$ we have two coupled (stochastic) differential equations.

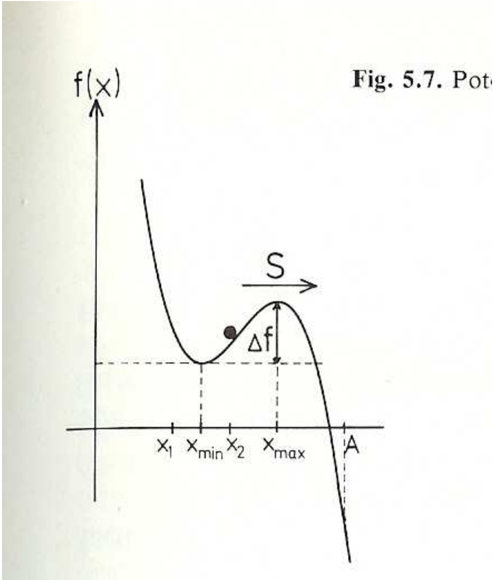
2. The coupled Langevin equations for the position and velocity of the colloidal particle require a two dimensional Fokker-Planck equation to describe the distribution function. The Kramers-Moyal drift and diffusion coefficients in the multi-dimensional are Λ_i and Λ_{ij}, with $i,j = x,v$. Calculate the Fokker-Planck equation corresponding to the coupled Langevin equations and show that this yields Kramers' equation

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial x}(vP) + \frac{\partial}{\partial v}\left(\left(-\frac{F(x)}{m} + \gamma v\right) P\right) + \frac{\gamma k_B T}{m}\frac{\partial^2 P}{\partial v^2},$$

   where $P \equiv P(x,v,t)$, F(x) is the force arising from the external potential, m is the particle mass and γ is proportional to the viscosity, $\gamma = 6\pi\eta d$. Kramers' equation has many applications but was first used by Hendrik Kramers for describing chemical reactions.

3. In the overdamped limit $\gamma \to \infty$ we expect to recover the Smoluchowski equation for the reduced distribution function $P(x,t)$. However, taking this limit from Kramers' equation is delicate and is a problem of singular perturbation theory. Why can these difficulties be anticipated simply from the gamma dependence in Kramers' equation? Assume a series solution in powers of γ^{-1}, $P(x,v,t) = P^{(0)} + \gamma^{-1}P^{(1)} + \gamma^{-2}P^{(2)} + \cdots$. By equating the coefficients of each power of γ we obtain a partial differential equation for each coefficient. The solution for $P^{(0)}(x,v,t)$ involves an arbitrary constant of integration $\phi(x,t)$. The equation for $P^{(1)}(x,v,t)$ requires $P^{(0)}(x,v,t)$ as input and therefore involves $\phi(x,t)$. By integrating the $P^{(1)}$ equation over v we obtain the 'solubility condition' $\partial\phi/\partial t = 0$. The $P^{(1)}$ equation can now be solved. By repeating this procedure higher order terms can be generated. Obtain the series solution to order γ^{-1}. By integrating over v to get rid of the v dependence we finally arrive at the Smoluchowski equation

$$\frac{\partial P(x,t)}{\partial t} = \frac{1}{m\gamma}\left(-\frac{d}{dx}F(x)P(x,t) + k_B T\frac{\partial^2 P(x,t)}{\partial x^2}\right).$$



Kramer's escape rate problem In this problem we consider a Brownian particle sitting in a deep potential well (see Figure 1) and consider the escape rate over the potential barrier.

1. As a first step show that the probability current $S(x,t)$ in the Smoluchowski equation $\partial P(x,t)/\partial t = -\partial S(x,t)/\partial x$ can be rewritten in the following form

$$S(x,t) = -\frac{k_B T}{m\gamma} e^{-\Phi(x)/k_B T} \frac{\partial}{\partial x} \left(e^{\Phi(x)/K_B T} P(x,t) \right),$$

   where the potential is given by the indefinite integral of the force $\Phi(x) = -\int^x F(x')$. If the barrier is high then we expect that $P(x,t)$ changes only slowly with time. This imples that $S(x,t)$ is approximately constant in space. By integrating between x_{min} and A show that

$$S = \frac{k_B T}{m\gamma} e^{\Phi(x_{min})/k_B T} P(x_{min}, t) / \int_{x_{min}}^{A} dx\, e^{\Phi(x)/k_B T}.$$

2. Justify the approximation $P(x,t) = P(x_{min}, t) e^{-(\Phi(x)-\Phi(x_{min}))/k_B T}$ for values of x close to the minimum. Find an expression for the probability p that the particle is located in a region close to the minima between x_1 and x_2. The escape rate r is given by p/S. Combine your results to obtain an expression for the escape rate r.

3. Make Taylor expansions of the potential Φ about the minimum and maximum to obtain Gaussian approximations to the integrals in the expression for Φ to obtain the final result

$$r = \frac{1}{2\pi} \sqrt{\Phi''(x_{min}) |\Phi''(x_{max})|} e^{-[\Phi(x_{max}) - \Phi(x_{min})]/k_B T}.$$

   This result gives the rate at which particles escape over the barrier in the limit that the barrier height becomes large (this result is sometimes called an Arrhenius formula). You might have noticed the similarity to quantum mechanical problems, such as the tunneling of a particle through a finite potential barrier. There is a close correspondence as the Schrödinger equation is also a diffusion equation.

Positivity of solution to the Fokker-Planck equation The probability distribution of the position of a Brownian particle $P(x, t+\tau)$ is related to the transition probability $p(x, t+\tau|x', t)$ by the Chapman-Kolmogorov equation $P(x, t+\tau) = \int dx' p(x, t+\tau|x', t) P(x', t)$. It obeys the Fokker-Planck equation $\partial p(x, t+\tau|x', t)/\partial t = L_{FP}(x) p(x, t+\tau|x', t)$ with initial condition $p(x, t|x', t) = \delta(x - x')$. Find the formal solution to this equation and by expanding your result for small time differences $\tau = t - t'$ derive the following short time expansion of the transition probability

$$p(x,t|x',t') = (1 + L_{FP}(x)\tau + \cdots)\,\delta(x - x').$$

We take the following form for the Fokker-Planck operator

$$L_{FP}(x) = -\frac{\partial}{\partial x}D^{(1)}(x) + \frac{\partial^2}{\partial x^2}D^{(2)}(x).$$

By using $\exp(x) \approx 1 + x$ for $x \ll 1$ and the Fourier integral representation of the delta function derive the following result

$$p(x,t|x',t') = \frac{1}{2\sqrt{\pi D^{(2)}(x')\tau}} \exp\left(-\frac{[x - x' - D^{(1)}(x')\tau]^2}{4D^{(2)}(x')\tau}\right)$$

valid for small time differences τ. Now we consider a starting distribution $P(x_0, t_0)$ and how this evolves to the distribution $P(x,t)$. Divide the time difference into N small intervals of length $\tau = (t - t_0)/N$ and iterate the Chapman-Kolmogorov equation to connect $P(x_0, t_0)$ with $P(x,t)$. The final result is obtained by inserting small τ solution of the Fokker-Planck equation. Using this relation give an argument why the distribution $P(x,t)$ must remain positive, given that we begin with a positive initial distribution $P(x_0, t_0)$.