Statistical Physics IV: Non-equilibrium statistical physics
ECOLE POLYTECHNIQUE FEDERALE DE LAUSANNE (EPFL)

Exercise No.5

5.1 Proof of Kramers escape rate [1]:

Kramers famous equation relates the escape rate ($2\pi r = \frac{1}{t_{\text{escape}}}$) of a particle to the curvature of the potential at the bottom and the top (see figure 5.10.1. Risken). Assume that the potential $V(x)$ has a minimum at x_{min} and a maximum at x_{max} so that $0 < x_{\text{min}} < x_{\text{max}} < A$. The escape rate is given by (in the limit of a strongly damped particle and a high barrier compared to the thermal energy):

$$r = (2\pi)^{-1} \cdot \frac{D}{k_B T} \cdot \sqrt{V''(x_{\text{min}})|V''(x_{\text{max}})|} \cdot e^{-(V(x_{\text{max}})-V(x_{\text{min}}))/k_B T} \tag{1}$$

1. Derive this rate. First, assume that the particle is strongly damped and solve the simplified 1-D Fokker Planck equation with a constant probability current ($J(x) \approx J = \text{const}$). Show that with $\Phi(x) = V(x)/k_B T$ the current satisfies:

$$J(x,t) = -De^{-\Phi(x)} \frac{d}{dx}[e^{+\Phi(x)} P(x,t)] \tag{2}$$

2. As outlined above we are treating the problem without reflecting or absorbing boundary conditions, but assume the current to be nonzero even on our boundaries. As such we can neglect the time dependence of $P(x,t)$ and $J(x,t)$ since the solution will become stationary in this case. Why does it become stationary? Obtain an expression for the current by integrating over the interval $x = x_{min}...A$. Find an expression for J and show that it obeys:

$$J = D \cdot e^{V(x_{\text{min}})/k_B T} P(x_{\text{min}}, t) / (\int_{x_{\text{min}}}^{A} e^{V(x)/k_B T} dx) \tag{3}$$

3. Approximate the distribution $P(x_{\text{min}}, t)$ by assuming the stationary distribution of the parabolic well only (i.e. such that particles cannot escape from near x_{min}). This will be an excellent approximation as long as the barrier is high compared to $k_B T$.

4. Obtain an expression for the escape rate r, i.e. $J = pr$, which is defined as the ratio of the probability current J and the absolute probability p to find the particle inside the well.

5. Solve the integrals by considering the regions where the integrals contribute most and by extending the integration limits (0..A) to $\pm\infty$. Use the local Taylor expansion in the potential and use $\int e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}$ to arrive at Kramers escape rate, finally!

5.2 Application of the Kramers escape rate formula: optical tweezers

In optical tweezers a small dielectric particle is trapped in the waist of a focused laser beam by electrical dipole potential. For a spherical particle, this potential can be found as

$$U(\mathbf{r}) = -\frac{2\pi n_0 a^3}{c} \left(\frac{n^2 - n_0^2}{n^2 + 2n_0^2} \right) I(\mathbf{r}), \tag{4}$$

where a and n are the particle radius and index of refraction, n_0 is the index of refraction of the surrounding medium, $I(\mathbf{r})$ is the laser intensity distribution.

[1] cf. Chapter 5.10 Risken: "The Fokker Planck Equation"

Consider the setting of[2], where a particle is trapped in water by two laser beams with Gaussian transverse intensity profiles

$$I_{1,2}(x) = I_{1,2}^{\max} \exp\left(-2\frac{(x \pm \delta x/2)^2}{w_0^2}\right). \tag{5}$$

Here the distributions are given for the beams 1 and 2 in their waists, $w_0 = 1\ \mu$m is the beam width, $I_{1,2}^{\max}$ are the peak intensities (total powers of the lasers 1 and 2 are 80 and 90 mW correspondingly) and the centers of two beams are separated by $\delta x = 1.4\ \mu$m.

Use the Kramers formula to estimate the escape rate of a particle with the radius $a = 100$ nm made of silica ($n = 1.5$, density $\rho = 2650$ kg/m^3) from the 1-st well to the 2-nd. Assume room temperature and the water viscosity $\eta = 8.9 \cdot 10^{-4}$ Pa/s.

Neglect the 3D nature of the problem and, if you prefer, use numerical or approximate methods to calculate the potential curvatures.

5.3 Simulation of Particle Escape(*)

We have recently learned two equivalent descriptions of a diffusion process: the Langevin equation and the Fokker-plank equation. The goal of this exercise is to numerically explore the equivalence of these two approaches. Consider a particle at $x = 2.5$ confined between a reflecting wall at $x = 0$ on one side and a potential barrier on the other side at $x = 5$. Assume that the potential has a Gaussian form of height $h = 1$ and variance of $d = 0.4$, the diffusion coefficient is $D = 0.5$, mass of the particle - $m = 1$ and the damping coefficient - $\gamma = 1$.

Please include your simulation code together with the answers on the following questions. We recommend using Jupyter notebooks.

1. Write down a Fokker-Plank equation and numerically solve it using a programming language of your choice. To impose the boundary conditions, described above, use the fact that the probability current at $x = 0$ has to vanish, and assume the probability density on the right end of the simulation interval [0, 20] to be always 0. Plot the probability density at different moments in time to illustrate the diffusive evolution of particle.

2. Now write an equivalent Langevin equation. Suggest a numerical algorithm to simulate stochastic trajectories generated by this equation. (Hint: you can find such algorithm in Section 2 of this reference [3])

3. Run multiple iterations of your algorithm, and obtain probability densities for the particle at different moments of time. Compare these with the numerical solution of the Fokker-Plank from part 1. Do the two models agree quantitatively? If not, suggest why.

4. Recover the *Arrhenius law* by plotting the escape probability (i.e. the particle being outside of the confined region) over a certain time as a function of the barrier height. Show that the probability scales as $\propto \exp[-V/D]$, where V is the potential barrier height. Can your numerical solution of the Fokker-Plank equation be used to recover the Arrhenius law?

5.4 First passage time and the backward Fokker-Planck equation[4]

It is often of interest to know how long a particle whose position is described by a Fokker-Planck equation remains in a certain region. The solution of this problem can be achieved by use of the backward Fokker-Planck equation.

[2] L. I. McCann *et al* "Thermally activated transitions in a bistable three-dimensional optical trap". Nature 402, 785 (1999).

[3] Grassia PS, Hinch EJ, Nitsche LC. Computer simulations of Brownian motion of complex systems. Journal of Fluid Mechanics. 1995

[4] Handbook of Stochastic Methods for Physics, Chemistry and Natural Sciences, C. W. Gardiner, 2nd ed, Chapter 5.2.7

1. Review: Use Chapman-Kolmogorov equation and Kramers-Moyal expansion to derive the backward Fokker-Planck equation.

2. Consider a one dimensional particle moving along $x - axis$ and a certain interval I on $x - axis$. The particle is initially at x ($x \in I$) at time time $t = 0$. Assume T to be the time that the particle leaves I. Show that the *mean first passage time* ($\langle T \rangle = T(x)$) is given by

$$T(x) = -\int_0^\infty t\partial_t G(x,t)dt, \tag{6}$$

   where $G(x,t) = \int_I dx' p(x',t|x,0)$ is the probability that at time t the particle is still in I.

3. Show that $T(x)$ satisfies the backward, but not the forward Fokker-Planck equation.

4. Consider that the particle with diffusion constant D is moving in a potential field given by

$$V(x) = \begin{cases} \infty & x < 0 \\ h\exp\left\{\frac{-(x-x_0)^2}{2d^2}\right\} & x > 0 \end{cases} \tag{7}$$

   Solve the equation numerically (with a program of your choice) for the parameter values:

   - $h = 1$
   - $x_0 = 5$
   - $d = 0.4$
   - $D = 0.5$

   and plot $T(x)$. Assuming the particle is at $x(0) = 2.5$ at $t = 0$, show that you recover the same result for the mean escape time as for the simulation of the individual trajectories in the exercise "Simulation of Particle Escape". Include your code with the answer.