Exercise sheet #9

Problem 1. You release a tiny drop of ink in still water. After some time, the ink spreads out smoothly. This process is described by the diffusion equation:

$$\frac{\partial p}{\partial t} = D\frac{\partial^2 p}{\partial x^2},$$

where $p(x,t)$ is the concentration (or probability density) at position x and time t. What does this equation describe physically, and what does D represent? Why does the ink's spreading slow down over time even as it continues to expand?

For a single Brownian particle starting at the origin, the solution for this equation is Gaussian:

$$p(x,t) = \frac{1}{\sqrt{4\pi Dt}}\exp\left(-\frac{x^2}{4Dt}\right).$$

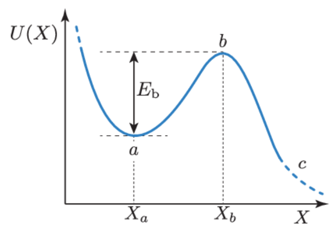
Why does this shape make sense physically, and how does it evolve in time? Give an argument based on this solution for hy the mean squared displacement (MSD) satisfies $\langle x^2(t)\rangle = 2Dt$. What does a graph of $\langle x^2(t)\rangle$ versus t look like, and what does its slope mean?

Problem 2. Now suppose a gentle breeze pushes the Brownian particle to the right. The Fokker–Planck equation describing its behavior becomes

$$\frac{\partial p}{\partial t} = -v\,\frac{\partial p}{\partial x} + D\,\frac{\partial^2 p}{\partial x^2}.$$

What does the new drift term $-v\,\partial_x p$ represent physically? How would the probability distribution evolve compared to pure diffusion? Imagine many identical particles, all starting at $x = 0$. What does $p(x,t)$ represent for this ensemble, and how would a histogram of their positions compare to $p(x,t)$? Why can we think of $p(x,t)$ as a "density of states" in phase space?

Problem 3. In this exercise, following Kramers, you will solve the Fokker-Planck equation for the case of a Brownian particle in a one-dimensional potential well $U(x)$. We assume that the barrier energy E_b is large and that the particle is initially within the well. For a high barrier, the particle has enough time to equilibrate within the well, in other words, we expect the particle to reach a close-to-equilibrium distribution within the potential well before crossing the barrier at b to a state c. The situation is sketched in the figure below. We start the analysis from the Fokker-Planck equation.



a) Demonstrate that equation $\frac{\partial P(x,t)}{\partial t} = \frac{\partial}{\partial x}\left(\frac{U' P(x,t)}{\Gamma M}\right) + D\partial^2 \frac{P(x,t)}{\partial x^2}$ can be rewritten in the form

$$\frac{\partial \mathcal{P}(X,t)}{\partial t} = -\frac{\partial J}{\partial X}$$

with the flux

$$J(X,t) = -De^{-U(X)/k_\mathrm{B}T}\frac{\partial}{\partial X}\left[e^{U(X)/k_\mathrm{B}T}\mathcal{P}(X,t)\right]$$

b) After a very short initial relaxation, the particle at $X < X_b$ will reach a close-to-equilibrium state, and there is only a very small constant probability current J_0 across the barrier, i.e., $\partial \mathcal{P}/\partial t \approx 0$ for $X < X_b$, so that $J(x, t) \approx J_0$. Demonstrate that

$$J_0 = \frac{D e^{U(X_a)/k_\mathrm{B}T} \mathcal{P}\left(X_a\right)}{\int_a^c e^{U(X')/k_\mathrm{B}T} dX'}$$

where c is some point far beyond the barrier (on the dashed part of the curve in the figure). Hint: Use the (rewritten) equation in a) with $J = J_0$ and integrate the equation from X_a to X_c, and the fact that $\mathcal{P}\left(X_c\right)$ is small (think about why this is so).

c) Note that, in the well, the distribution will essentially be the equilibrium distribution

$$\mathcal{P}(X) = \mathcal{P}\left(X_a\right) e^{-\left[U(X) - U\left(X_a\right)\right]/k_\mathrm{B}T}$$

Starting from this result, show that the probability of finding a particle within the well is

$$p = \mathcal{P}\left(X_a\right) \left[\frac{2\pi k_\mathrm{B} T}{\left|U''\left(X_a\right)\right|}\right]^{1/2}$$

Hint: Use the fact that the potential well is very deep, Taylor expand $\mathcal{P}(X)$ around a, and then integrate the resulting Gaussian integral. Note that the first derivative of $U(X)$ vanishes at a.