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?

Solution: The diffusion equation describes how an initially localized distribution spreads over time, driven by random microscopic motion that carries material from high- to low-density regions. The diffusion constant D measures how quickly this smoothing occurs and depends on properties such as temperature, viscosity, and particle size.

As the ink spreads, the gradients in concentration become smaller, reducing the driving force for further spreading. Hence, the rate of change slows even though the width continues to grow.

For a single Brownian particle, the Gaussian shape reflects that short random steps are much more common than long ones, most particles stay near the origin, and only a few wander far away. As time increases, the Gaussian flattens and widens while remaining normalized; its width (standard deviation) grows like $\sqrt{t}$. The mean squared displacement follows from the variance of the Gaussian:

$$\langle x^2(t)\rangle = 2Dt.$$

This linear growth means the spreading depends directly on elapsed time, a hallmark of diffusion. A plot of $\langle x^2(t)\rangle$ vs. t is a straight line through the origin with slope $2D$, showing how rapidly randomness increases the spatial uncertainty. □

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

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

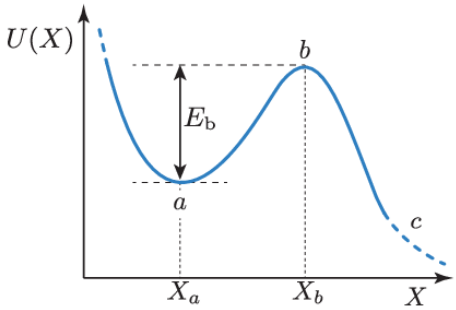
What does the new drift term $-v\,\partial_x p$ represent physically? How would the probability distribution evolve compared to pure diffusion? Imagine many identical particles, all starting at $x = 0$. What does $p(x,t)$ represent for this ensemble, and how would a histogram of their positions compare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

Solution: The new term $-v\,\partial_x p$ describes a uniform drift or convection of the probability distribution in the direction of the flow. While diffusion causes the distribution to broaden symmetrically, drift simply shifts its center by vt without changing its Gaussian form.

If we follow many identical Brownian particles, each one takes a random trajectory, but the ensemble's distribution $p(x,t)$ gives the fraction expected near each position. A histogram of observed positions would approximate the theoretical curve. Each point in phase space represents a particular realization (state) of the system; the density of these points forms the probability density $p(x,t)$, linking the microscopic randomness to the macroscopic smooth behavior.

□

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

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

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

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

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.

Solution: a) The F-P equation for this case can be rewritten as,

$$\frac{\partial P(X,t)}{\partial t} = \frac{\partial}{\partial X}\left(\frac{U' P(X,t)}{\Gamma M} + D\frac{\partial P(X,t)}{\partial X}\right).$$

In other words, we need to check if the definition of J is consistent with the term inside the large brackets on the right hand side. Expanding the derivatives in the definition of J, we get,

$$\begin{aligned}
J(X,t) &= -De^{-U(X)/k_\mathrm{B}T}\frac{\partial}{\partial X}\left[e^{U(X)/k_\mathrm{B}T}P(X,t)\right] \\
&= -De^{-U(X)/k_\mathrm{B}T}\left[e^{U(X)/k_\mathrm{B}T}P(X,t)\right]\frac{U'}{k_\mathrm{B}T} - De^{-U(X)/k_\mathrm{B}T}\left[e^{U(X)/k_\mathrm{B}T}\right]\frac{\partial P(X,t)}{\partial X} \\
&= -\left(\frac{DU'}{k_\mathrm{B}T}P(X,t) + D\frac{\partial P(X,t)}{\partial X}\right) \\
&= -\left(\frac{U'P(X,t)}{\Gamma M} + D\frac{\partial P(X,t)}{\partial X}\right),
\end{aligned}$$

where we used $D = \frac{k_\mathrm{B}T}{\Gamma M}$. This expression is indeed consistent with what we have on the right-hand side. Therefore, Fokker-Planck equation can indeed be rewritten as,

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

b) As it is suggested, after the initial relaxation, we have,

$$\frac{\partial P}{\partial t} = -\frac{\partial J}{\partial X} \approx 0,$$

which implies,

$$J(x,t) \approx J_0 = -De^{-U(X)/k_\mathrm{B}T}\frac{\partial}{\partial X}\left[e^{U(X)/k_\mathrm{B}T}P(X)\right].$$

Rearranging the equation in a convenient way and integrating both sides gives,

$$\begin{aligned}
-\frac{J_0}{D}e^{U(x)/k_\mathrm{B}T} &= \frac{\partial}{\partial X}\left(e^{U(X)/k_\mathrm{B}T}P(X)\right) \\
-\frac{J_0}{D}\int_a^c \mathrm{d}X' e^{U(X')/k_\mathrm{B}T} &= \int_a^c \mathrm{d}X'\frac{\partial}{\partial X'}\left[e^{U(X')/k_\mathrm{B}T}P\left(X'\right)\right] \\
-\frac{J_0}{D}\int_a^c \mathrm{d}X' e^{U(X')/k_\mathrm{B}T} &= e^{U(X_c)/k_\mathrm{B}T}P\left(X_c\right) - e^{U(X_a)/k_\mathrm{B}T}P\left(X_a\right) \\
-\frac{J_0}{D}\int_a^c \mathrm{d}X' e^{U(X')/k_\mathrm{B}T} &\approx -e^{U(X_a)/k_\mathrm{B}T}P\left(X_a\right) \rightarrow \\
J_0 &\approx \frac{De^{U(X_a)/k_\mathrm{B}T}P\left(X_a\right)}{\int_a^c \mathrm{d}X' e^{U(X')/k_\mathrm{B}T}}
\end{aligned}$$

which is indeed the suggested probability current. On the third line we assumed that $P\left(X_c\right)$ is very small, because due to the potential barrier the probability of particle escaping the barrier is very low.

c) As suggested in the problem statement, we can Taylor expand $U(X)$ around $X = X_a$ to obtain an approximate expression for $P(X)$ inside the well, which is

$$\begin{aligned}
P(X) &= P\left(X_a\right)e^{\left(-\left[U(X)-U(X_a)\right]/k_\mathrm{B}T\right)} \\
&\approx P\left(X_a\right)e^{\left(-\left[U(X_a)+U'(X_a)(X-X_a)+U''(X_a)(X-X_a)^2/2-U(X_a)\right]/k_\mathrm{B}T\right)} \\
&= P\left(X_a\right)e^{\left(-\left[U''(X_a)(X-X_a)^2\right]/2k_\mathrm{B}T\right)}
\end{aligned}$$

where we used that $U'(X_a) = 0$, because it is the minimum of the potential well. The probability of finding the particle within the well can be found by integrating the probability distribution over the well, i.e.,

$$p = \int_{a-\Delta}^{a+\Delta} \mathrm{d}X' P\left(X'\right) \approx \int_{a-\Delta}^{a+\Delta} \mathrm{d}X' P\left(X_a\right) e^{\left(-\left[U''(X_a)(X'-X_a)^2\right]/2k_\mathrm{B}T\right)}$$
$$\approx \int_{-\infty}^{\infty} \mathrm{d}X' P\left(X_a\right) e^{\left(-\left[U''(X_a)(X'-X_a)^2\right]/2k_\mathrm{B}T\right)} = \left[\frac{2\pi k_\mathrm{B}T}{|U''\left(X_a\right)|}\right]^{1/2}$$

where on the second line we introduced 2Δ as the range of the potential, and on the third line we extended the range of integration throughout the whole space due to the fact that the probability of having the particle outside the well is very small.

$\square$