12.3: Diffusion in a Potential

Fokker–Planck Equation

Diffusion with drift or diffusion in a velocity field is closely related to diffusion of a particle under the influence of an external force f or potential U.

$$f(x) = -\frac{\partial U}{\partial x}$$

When random forces on a particle dominate the inertial ones, we can equate the drift velocity and external force through the friction coefficient

$$\begin{aligned} \cancel{m\ddot{x}} &= f_d + \cancel{f_r(t)} + f_{ext} \\ f_d &= -\zeta v_x \\ f_{ext} &= \zeta v_x \\ f &= \zeta v_x \end{aligned} \tag{12.3.1}$$

and therefore the contribution of the force or potential to the total flux is

$$J_U = v_x C = \frac{f}{\zeta} C = -\frac{C}{\zeta}\frac{\partial U}{\partial x} \tag{12.3.2}$$

The Fokker–Planck equation refers to stochastic equations of motion for the continuous probability density $\rho(x,t)$ with units of m^{-1}. The corresponding continuity expression for the probability density is

$$\frac{\partial \rho}{\partial t} = -\frac{\partial j}{\partial x}$$

where j is the flux, or probability current, with units of s^{-1}, rather than the flux density we used for continuum diffusion J ($m^{-2}\ s^{-1}$). If the concentration flux is instead expressed in terms of a probability density eq. (12.1.3) becomes

$$j = -D\frac{\partial \rho}{\partial x} + \frac{f(x)}{\zeta}\rho \tag{12.3.3}$$

and the continuity expression is used to obtain the time-evolution of the probability density:

$$\frac{\partial \rho}{\partial x} = D\frac{\partial^2 \rho}{\partial x^2} - \frac{\partial}{\partial x}\left[\frac{f(x)}{\zeta}\rho\right] \tag{12.3.4}$$

This is known as a Fokker–Planck equation.

Smoluchowski Equation

Similarly, we can express diffusion in the presence of an internal interaction potential U(x) using eq. (12.3.2) and the Einstein relation

$$\zeta = \frac{k_B T}{D} \tag{12.3.5}$$

Then the total flux with contributions from the diffusive flux and potential flux can be written as

$$J = -D\frac{\partial C}{\partial x} - \frac{DC}{k_B T}\left(\frac{\partial U}{\partial x}\right) \tag{12.3.6}$$

and the corresponding diffusion equation is

$$\frac{\partial C}{\partial t} = D\left[\frac{\partial^2 C}{\partial x^2} - \frac{\partial}{\partial x}\left[\frac{C}{k_B T}\left(\frac{\partial U}{\partial x}\right)\right]\right] \tag{12.3.7}$$

This is known as the Smoluchowski Equation.

Linear Potential

For the case of a linear external potential, we can write the potential in terms of a constant external force $U = -f_{ext}x$. This makes eq. (12.3.7) identical to eq. (12.1.3), if we use eqs. (12.3.1) and (12.3.5) to define the drift velocity as

$$v_x = \frac{f_{ext}D}{k_BT} \equiv \underset{sim}{f}D$$

$$J = -D\frac{\partial C}{\partial x} + \underset{\sim}{f}DC$$

Here I defined $\underset{\sim}{f}$ as the constant external force expressed in units of k_BT.

The probability distribution that describes the position of particles released at x_0 after a time t is

$$P(x,t) = \frac{1}{\sqrt{4\pi Dt}}\exp\left[-\frac{(x - x_0 - \underset{\sim}{f}Dt)^2}{4Dt}\right]$$

As expected, the mean position of the diffusing particle is given by $\langle x(t)\rangle = x_0 + v_xt$.

To make use of this, let's calculate the time it takes a monovalent ion to diffuse freely across the width of a membrane (d) under the influence of a linear electrostatic potential of $\Phi = 0.3V$. With $U = e\Phi$

$$t = \frac{d}{v_x} = \frac{k_BTd}{f_{ext}D} = \frac{k_BTd^2}{e\Phi D}$$

Using d = 4 nm, D = 10−5 cm^2/s, and e = 1.6×10^{-19} C, we obtain t = 1.4 ns.

Steady-State Solutions

For steady-state solutions to the Fokker–Planck or Smoluchowski equations, we can make use of a commonly used mathematical manipulation. As an example, let's work with eq. (12.3.3), re-writing it as

$$j = -D\left[\frac{\partial\rho}{\partial x} - \frac{\rho}{k_BT}\left(\frac{\partial U}{\partial x}\right)\right] \tag{12.3.8}$$

We can rewrite the quantity in brackets as:

$$e^{-U(x)/k_BT}\frac{d}{dx}\left[\rho e^{U(x)/k_BT}\right]$$

Separating variables, we obtain

$$-\frac{j}{D}e^{U(x)/k_BT}dx = d(\rho e^{U(x)/k_BT}$$

This is an expression that can be manipulated in various ways and integrated over different boundary conditions.[1] For instance, recognizing that j is a constant under steady state conditions, and integrating from x to a boundary b:

$$\begin{aligned} -\frac{j}{D}\int_x^b e^{U(x)/k_BT}dx &= \int_x^b d(\rho e^{U(x)/k_BT}) \\ &= \rho(b)e^{U(b)/k_BT} - \rho(x)e^{U(x)/k_BT} \end{aligned}$$

This leads one to an important expression for the steady state flux in the diffusive limit:

$$j = \frac{-D\left[\rho(b)e^{U(b)/k_BT} - \rho(x)e^{U(x)/k_BT}\right]}{\int_x^b e^{U(x)/k_BT}dx}$$

The boundary chosen depends on the problem, for instance b is set to infinity in diffusion to capture problems or set as a fixed boundary for first-passage time problems.
For problems involving an absorbing boundary condition, $\rho(b) = 0$, and we can solve for the probability density as

$$\rho(x) = \frac{j}{D} e^{-U(x)/k_BT} \left[\int_x^b e^{U(x')/k_BT} dx' \right]$$

If we integrate both sides of this expression over the entire space, the left hand side is just unity, so we can express the steady-state flux as

$$j = D^{-1} \left[\int_0^b e^{-U(x)/k_BT} \left[\int_x^b e^{U(x')/k_BT} dx' \right] dx \right]^{-1}$$

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1. The general three-dimensional expression is $\mathbf{J}(\mathbf{r},t) = -De^{-U(\mathbf{r})/k_BT} \nabla \cdot [e^{U(\mathbf{r})/k_BT} \rho(\mathbf{r},t)]$.