12. Diffusion in a Potential

In this section, we extend the concepts of diffusion and Brownian motion into a regime where the time-evolution is not entirely random, but includes a driving force. We will refer to this class of problems as diffusion in a potential, although it is also referred to as diffusion with drift, diffusion in a velocity or force field, or diffusion in the presence of an external force. We will see that these problems can be related to a biased random walk or to motion of a Brownian particle subject to an internal or external potential. Our discussion below will be confined to problems involving diffusion in one dimension.

The common theme is that we account for transport of particles through a surface in terms of two sources of flux, the diffusive flux and an additional driven contribution that arises from a potential, field, or external force experienced by the particle:

$$J = J_{diff} + J_U \tag{1}$$

Here we label the second flux component with U to signify potential. This may be a result of an external force acting on a diffusing system (for instance, electrophoresis and sedimentation), or the bias that results from interactions between diffusing particles. In mass transport through fluid flow the second term is known as the advective flux, $J_U \rightarrow J_{adv}$.

Diffusion with Drift

If diffusion occurs within a moving fluid, the time-dependent concentration profiles will be influenced by the local velocity of the fluid, or drift velocity v_x. The net advective flux density for the concentration passing through an area per unit time is then

$$J_{adv} = v_x C \tag{2}$$

So that the total flux according to eq. (1) is

$$J = -D\frac{\partial C}{\partial x} + v_x C \tag{3}$$

Now using the continuity expression $\partial C/\partial t = -\partial J/\partial x$, and assuming a constant drift velocity the diffusion coefficient is[1]

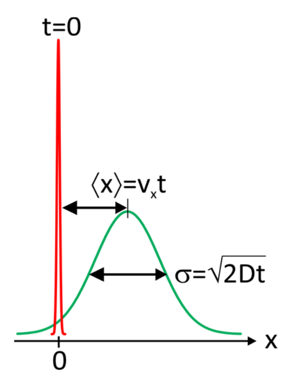
$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v_x\frac{\partial C}{\partial x} \tag{3}$$

This equation is the same as the normal diffusion equation in the inertial frame of reference. If we shift to a frame moving at v_x, we can define the relative displacement

$$\bar{x} = x - v_x t$$

Remember, C is a function of x and t, and expressing eq. (3) in terms of $\bar{x}$ via the chain rule, we find that we can recast it as the simple diffusion equation:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial \bar{x}^2}$$



Then the solution for diffusion from a point source becomes

$$C(\bar{x},t) = \frac{1}{\sqrt{4\pi Dt}}e^{-\bar{x}^2/4Dt}$$

$$C(x,t) = \frac{1}{\sqrt{4\pi Dt}}e^{-(x-v_x t)^2/4Dt}$$

So the peak of the distribution moves as $\langle x\rangle = v_x t$ and the width grows as $\sigma = [\langle x^2\rangle - \langle x\rangle^2]^{1/2} = (2Dt)^{1/2}$.

Let's consider the relative magnitude of the diffusive and drift velocity contributions to the motion of a protein in water. A typical diffusion constant is 10^{-6} cm^2/s, meaning that the root mean square displacement in a one microsecond time period is 14 nm. If we compare this with the typical velocity of blood in capillaries, v = 0.3 mm/s, in the same microsecond the same

[1] In three dimensions: $\mathbf{J}(\mathbf{r},t) = -\mathrm{D}\bar{\nabla}C(\mathbf{r},t) + \mathbf{v}C(\mathbf{r},t)$ and $\dot{C} = \nabla\cdot(D\bar{\nabla}C) - \nabla\cdot(\mathbf{v}C)$.

protein is pushed ⟨x⟩ = 0.3 nm. For this example, diffusion dominates the transport process on the nanometer scale, however, with the increase of time scale and transport distance, the drift term will grow in significance due to the $t^{1/2}$ scaling of diffusive transport.

Péclet Number

The Péclet number P_e is a unitless number used in continuum hydrodynamics to characterize the relative importance of diffusive transport and advective transport processes. Language note:

- Convection: internal currents within fluid
- Advection: mass transport due to convection

We characterize this with a ratio of the rates or equivalently the characteristic time scale for transport with these processes:

$$P_e = \frac{\text{advective flux}\,(J_{adv})}{\text{diffusive flux}\,(J_{diff})} \approx \frac{\text{diffusion timescale}\,(t_{diff})}{\text{advection timescale}\,(t_{adv})}$$

Limits

- $P_e \ll 1$ Diffusion dominated. In this limit, diffusive transport spreads the concentration profile symmetrically about the maximum as illustrated above.
- $P_e \gg 1$ Flow dominated. Effectively no spreading to concentration; it is just carried along with the flow.

If we define a characteristic transport length d and the flow velocity v, then

$$t_{\text{adv}} \approx \frac{d}{v}$$

Given a diffusion constant D, the diffusive time-scale is taken to be

$$t_{\text{diff}} \approx \frac{d^2}{D}$$

So that

$$P_e = \frac{vd}{D}$$

Biased Random Walk

The diffusion with drift equation can be obtained from a biased random walk problem. To illustrate, we extend the earlier description of a walker on a 1D lattice that can step left or right by an amount distance Δx for every time interval Δt. However, in this case there is unequal probability of stepping right (+) or left (–) during Δt: $P_+ \neq P_-$. Probabilistically speaking, the change in position for a given time interval can be expressed as

$$\begin{aligned}\langle x(t+\Delta t)\rangle &= \langle x(t) + \Delta x P_+ - \Delta x\, P_-\rangle \\ &= \langle x(t)\rangle + \Delta x\left(P_+ - P_-\right)\end{aligned} \tag{4}$$

We see that the average position of random walkers depends on the difference in left and right stepping rates. To help link stepping with time, we define rate constants for stepping left or right,

$$k_\pm = \frac{P_\pm}{\Delta t} \tag{5}$$

with $k_+ \neq k_-$. Then eq. (4) can be written as

$$\begin{aligned}\langle x(t+\Delta t)\rangle &= \langle x(t)\rangle + (k_+ - k_-)\Delta t \Delta x \\ &= \langle x(t)\rangle + v_x \Delta t\end{aligned} \tag{6}$$

where the drift velocity is related to the difference in hopping rates

$$v_x = \left(k_+ - k_-\right)\Delta x$$

Expressing eq. (6) as the result of many steps says that the mean of the position distribution behaves like traditional linear motion: $\langle x(t)\rangle = x_0 + v_x t$.

What about the variance in the distribution? Calculating the mean-square value of x from eq. (4) gives

$$\begin{aligned}\langle x^2(t+\Delta t)\rangle &= \left\langle x^2(t) \pm 2\Delta x\, \Delta t\, k_\pm\, x(t) + \left(k_+ + k_-\right)^2 \Delta x^2 \Delta t^2\right\rangle \\ &= \langle x^2(t)\rangle + 2v_x \Delta t \langle x(t)\rangle + \left(k_+ + k_-\right)\Delta x^2 \Delta t\end{aligned} \tag{7}$$

where we used $(k_+ + k_-)\Delta t = 1$.

Using this to calculate the variance in x: $\sigma^2(t) = (k_+ + k_-)\Delta x^2 t$, and then comparing with $\langle x^2\rangle^{1/2} = 2Dt$, leads to the conclusion that the breadth of the distribution σ spreads as it would in the absence of a drift velocity, and the diffusion coefficient for this biased random walk is given by

$$D = \frac{1}{2}\left(k_+ + k_-\right)\Delta x^2$$

When the left and right stepping rates are the same, we recover our earlier result $2D = \Delta x^2/\Delta t$.

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

$$\cancel{m\ddot{x}} = f_d + \cancel{f_r(t)} + f_{ext}$$

$$f_d = -\zeta v_x$$

$$f_{ext} = \zeta v_x$$

$$f = \zeta v_x \tag{8}$$

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

$$J_U = v_x C = \frac{f}{\zeta} C = -\frac{C}{\zeta}\frac{\partial U}{\partial x} \tag{9}$$

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. (3) becomes

$$j = -D\frac{\partial \rho}{\partial x} + \frac{f(x)}{\zeta}\rho \tag{10}$$

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

$$\frac{\partial \rho}{\partial t} = D\frac{\partial^2 \rho}{\partial x^2} - \frac{\partial}{\partial x}\left[\frac{f(x)}{\zeta}\rho\right] \tag{11}$$

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. (9) and the Einstein relation

$$\zeta = \frac{k_B T}{D} \tag{12}$$

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

$$J = -D\frac{\partial C}{\partial x} - \frac{DC}{k_B T}\left(\frac{\partial U}{\partial x}\right) \tag{13}$$

and the corresponding diffusion equation is

$$\frac{\partial C}{\partial t} = D\left[\frac{\partial^2 C}{\partial x^2} - \frac{\partial}{\partial x}\left[\frac{C}{k_B T}\left(\frac{\partial U}{\partial x}\right)\right]\right] \tag{14}$$

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 $U = -f_{\text{ext}}x$. This makes eq. (14) identical to eq. (3), if we use eqs. (8) and (12) to define the drift velocity as

$$v_x = \frac{f_{\text{ext}} D}{k_B T} \equiv \underset{\sim}{f} D$$

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

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

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

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

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

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 $\Phi = 0.3\text{V}$. With $U = e\Phi$

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

Using $d = 4$ nm, $D = 10^{-5}$ cm^2/s, and $e = 1.6\times10^{-19}$ 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. (10), re-writing it as

$$j = -D\left[\frac{\partial\rho}{\partial x} - \frac{\rho}{k_B T}\left(\frac{\partial U}{\partial x}\right)\right] \tag{15}$$

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

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

This is an expression that can be manipulated in various ways and integrated over different boundary conditions.[2] For instance, recognizing that j is a constant under steady state conditions, and integrating from x to a boundary b:

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

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

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

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

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

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