will be given by Eq. (4.12) as

\[ \nu_d = \frac{F}{\mathcal{Z}} = \frac{q \mathcal{E}}{\mathcal{Z}} \]

where \( \mathcal{Z} \) is the viscous-friction coefficient of the ion in the fluid.

A concentration \( c \) moving at velocity \( \nu_d \) results in a flux

\[ j = c \nu_d. \]

The present flux

\[ j = c \frac{q \mathcal{E}}{\mathcal{Z}} \]

is called an \underline{electrophoretic flux of ions}.

If the concentration \( c \) of ions is not uniform, then by Fick's law (4.19) there will also be an entropic flux

\[ j_e = -D \frac{dc}{dy}. \]
So the net flux of ions will be

\[ j = q \int \frac{E(x) C(x)}{\mathcal{Z}} - D \frac{dC(x)}{dx} \]

in this example.

If \( q > 0 \) both components of the flux will be in the negative \( x \)-direction.

Now recall Einstein's relation (4.16)

\[ \frac{z}{D} = kT \]

Then \( \frac{z}{D} = D / kT \) and so

\[ j = D \left( -\frac{dC}{dx} + \frac{z}{kT} E C \right) \]

(4.24)

which is the Nernst-Planck formula.
What electric field \( E \) just cancels the entropic force and leads to zero flux, \( j = 0 \)? In the one-dimensional case with everything constant in the \( x - \) and \( y - \) directions, the condition for \( j = 0 \) is

\[
\frac{1}{c} \frac{dc}{dx} = \frac{q}{kT} E = \frac{d \ln c}{dx} \tag{4.25}
\]

which we may integrate to

\[
\ln \frac{c(x_2)}{c(x_1)} = \frac{q}{kT} \int_{x_1}^{x_2} \Sigma(x) \, dx
\]

\[
= - \frac{q}{kT} \left( V(x_2) - V(x_1) \right) \tag{4.26a}
\]

or

\[
\frac{c(x_2)}{c(x_1)} = e^{-\frac{q}{kT} \left( V(x_2) - V(x_1) \right)}
\]

or

\[
c(x) = c_0 e^{-\frac{qV(x)}{kT}}
\]

where \( c_0 \) is some constant.
Now \( q V(x) = U(x) \) is the potential energy of a charge \( q \) at the electrical potential — the voltage — \( V(x) \). So our condition for equilibrium — no flux — is the Boltzmann distribution

\[
C(x) = C_0 e^{-\frac{U(x)}{kT}}.
\]

We may rewrite Eq. (4.26a) as

\[\ln C(x_2) - \ln C(x_1) = -q \left( V(x_2) - V(x_1) \right) / (kT)\]

or as

\[\Delta \ln C(x) = -q \Delta V(x) / (kT), \quad (4.26b)\]

which is the Nernst relation. The subscript "eq" reminds us that this \( \Delta V_{\text{eq}}(x) \) is what is needed to keep \( \Delta C \) in equilibrium.
How big a $\Delta V$ makes $c_2/c_1 = 10$?

$$\Delta \ln c = \ln c_2/c_1 = \ln 10 \approx 2.3,$$

so Neumark's relation (4.266) gives $\Delta V$ as

$$\Delta V = - \frac{\Delta \ln c}{q} kT \frac{q}{e}$$

$$= - 2.3 \frac{kT}{e}$$

$q = e$ the magnitude of the charge of the electron. Now $kT \approx \frac{1}{40}$ eV, so

$$\Delta V = - \frac{2.3}{40} V = -0.058 V = -58 \text{ mV}.$$ 

If the solute is NaCl, then both Na$^+$ and Cl$^-$ ions are present in the solution. The Na$^+$ ions move to the plate of lower voltage; the Cl$^-$ ions go the other way. Nerve and muscle cells
maintain potential differences $\Delta V$ of a few tens of mV across their cell membranes.

Electrolysis

Suppose we put the two plates in a CuCl$_2$ solution. The CuCl$_2$ will be present in the water as Cu$^{++}$ ions and as Cl$^-$ ions. If the plates are maintained at a potential difference $\Delta V$, ...
then the electric field \( E \) between them will be \( \Delta V = EL \) if the distance between the plates is \( L \).

We assume that the concentration of each kind of ion is uniform. Then by the Neuman-Plank formula (4.24),

the field \( E \) is (since \( \mathbf{j} = \mathbf{D} (-\frac{\partial c}{\partial x} + \frac{q c E}{kT}) \))

\[
E = \frac{kT \mathbf{j}}{Dq c}
\]

If the plates have area \( A \) (each), then the current \( \mathbf{I} \) is \( \mathbf{I} = q A \mathbf{j} \) for ions of charge \( q \). So \( \Delta V \) is

\[
\Delta V = EL = \frac{kT \mathbf{l} \mathbf{j}}{Dq c} = \frac{kT}{Dq^2 c} \frac{\mathbf{l}}{A}
\]

which is Ohm's law with \( R = \frac{kT}{Dq^2 c} \frac{1}{A} \).
The geometry of the galvanic cell is involved in \( R \). To avoid mention of \( l \) and \( A \), we define the electrical conductivity of the solution as

\[
K = \sigma = \frac{l}{RA} = \frac{D q^2 c}{kT}
\]

For each species of ion, salt water conducts better than fresh water.

\[4G\]

(a) We try \( c(x, z) = B e^{-x^2/(2Az)} \)

But is it normalized? Recall

\[
\left( \int_{-\infty}^{\infty} e^{-x^2} \right)^2 = \int_{-\infty}^{\infty} e^{-r^2} \int_{-\infty}^{\infty} e^{-y^2} = \pi \int_{0}^{\infty} e^{-u} du = \pi.
\]

So

\[
\int_{-\infty}^{\infty} e^{-x^2} = \sqrt{\pi}, \quad \text{Let } x = y \sqrt{\alpha}. \text{ Then}
\]

\[
\int_{-\infty}^{\infty} e^{-y^2/\alpha} = \sqrt{\pi}, \quad \text{so} \quad \int_{-\infty}^{\infty} e^{-y^2/\alpha} dy = \sqrt{\alpha \pi}.
\]
So,
\[ \int_{-\infty}^{\infty} C(x,t) \, dx = B \int_{-\infty}^{\infty} e^{-\frac{x^2}{2At}} \, dx = B\sqrt{2\pi At} \]

which cannot be normalized unless \( B \) is a function of \( t \), \( B = \frac{1}{\sqrt{2\pi At}} \).

We now replace \( A \) by \( 2D \) and find that
\[ C(x,t) = \frac{e^{-\frac{x^2}{4Dt}}}{\sqrt{4\pi Dt}} \]
is correctly normalized:
\[ \int_{-\infty}^{\infty} C(x,t) \, dx = \frac{1}{\sqrt{4\pi t}} \int_{-\infty}^{\infty} e^{-\frac{x^2}{4Dt}} \, dx = \frac{\sqrt{4\pi Dt}}{\sqrt{4\pi Dt}} = 1. \]

(b) Does \( C(x,t) \) satisfy the diffusion equation
\[ \frac{dc}{dt} = D \frac{d^2c}{dx^2} ? \]
\[ C(x, t) = \frac{1}{\sqrt{4\pi Dt}} e^{-\frac{x^2}{4Dt}} \]

\[ \frac{dc}{dx} = \frac{d}{dx} \left( -\frac{x^2}{4Dt} \right) C = -\frac{2x}{4Dt} C = -\frac{x}{2Dt} C \]

\[ \frac{d^2c}{dx^2} = -\frac{C}{2Dt} + \left( -\frac{2x}{4Dt} \right)^2 C = \left( \frac{x^2}{4D^2t^2} - \frac{1}{2Dt} \right) C \]

\[ \frac{dc}{dt} = \frac{d}{dt} \left( -\frac{x^2}{4Dt} \right) C + \frac{d}{dt} \left( \frac{1}{\sqrt{4\pi Dt}} \right) \sqrt{4\pi Dt} C \]

\[ = \frac{x^2}{(4Dt)^2} 4D C - \frac{1}{2} 4\pi D \frac{1}{(4\pi Dt)^{3/2}} \sqrt{4\pi Dt} C \]

\[ = \frac{x^2}{4D^2t^2} DC - \frac{2\pi}{4\pi Dt} DC \]

\[ = D \left( \frac{x^2}{4D^2t^2} - \frac{1}{2Dt} \right) C \]

\[ = D \frac{d^2c}{dx^2} \]

So \( C(x,t) \) satisfies the diffusion equation

\[ \frac{dc}{dt} = D \frac{d^2c}{dx^2} \]
\[ \langle x^2 \rangle = \int_{-\infty}^{\infty} x^2 c(x,t) \, dx \]
\[ = \int_{-\infty}^{\infty} x^2 \frac{1}{\sqrt{4\pi D t}} e^{-\frac{x^2}{4Dt}} \, dx \]
\[ = -\frac{1}{4Dt} \frac{d}{dx} \int_{-\infty}^{\infty} \frac{4Dt}{\sqrt{4\pi D t}} e^{-\frac{x^2}{4Dt}} \, dx \bigg|_{a = 1} \]
\[ = \sqrt{\frac{4\pi D t}{\pi}} \left(-\frac{d}{dx}\right) \int_{-\infty}^{\infty} \frac{4Dt}{\alpha} e^{-\frac{x^2}{4Dt}} \, dx \bigg|_{a = 1} \]
\[ = 4Dt \left(-\frac{d}{dx}\right) x^{\frac{1}{2}} = 4D t \left(\frac{1}{2}\right) x^{-\frac{3}{2}} \bigg|_{a = 1} \]
\[ = 2Dt. \]
What about three dimensions?
The diffusions in $y$ & $z$ are independent of the diffusion in $x$, so

$$C(r^3, t) = C(x, t) C(y, t) C(z, t)$$

$$= \frac{1}{(4\pi DT)^{3/2}} C$$

for one particle — that is, for $\int C(r^3) dr^3 = 1$.
For $N$ particles,

$$C(r^3, t) = \frac{N}{(4\pi DT)^{3/2}} C$$

(4.2)

where

$$\bar{r} = (x, y, z) \text{ and } r^2 = \bar{r} \cdot \bar{r} = x^2 + y^2 + z^2.$$
Recall that the mean displacement $x_N$ after $N$ steps of length $L$ in one dimension obeys

$$<x_N^2> = NL^2.$$  \hspace{1cm} (4.4)

So in three dimensions, $<\vec{r}_N^2>$ is

$$<\vec{r}_N^2> = 3NL^2,$$

which is true for the end of a model polymer of $N$ links, each of length $\sqrt{3}L$, as we saw in section 4.3. To the extent that polymers are random walks and that random walks are gaussians, the probability distribution for the end $\vec{r}_N$ of a polymer of $N$ links of length $\sqrt{3}L$ is

$$P(\vec{r}_N) = \frac{1}{(2\pi NL^2)^{3/2}} e^{-\frac{\vec{r}_N^2}{2NL^2}}$$

if the first link is stuck at $\vec{r}_0 = 0$.