2. Molecules in Motion

*Kinetic Theory of Gases* (microscopic viewpoint)

assumptions

(1) particles of mass $m$ and diameter $d$; ceaseless random motion

(2) dilute gas: $d \ll \lambda$, $\lambda =$ mean free path $=$ average distance a particle travels between collisions

(3) no interactions between particles, except perfectly elastic collisions; particles are hard spheres ($E_K = E'_K$, $'= $ after collision)

(3) $\implies E_p \equiv 0 \implies E = E_{K1} + E_{K2} + \cdots E_{KN} = \sum_{i=1}^{N} E_{Ki}$

pressure: particles bump into the walls of the container $\implies$ change of momentum $\implies$ force

$$P = \frac{1}{3} m \frac{N}{V} c^2$$  \hspace{1cm} (1)

where $N$ is the number of particles and $c$ is the root-
**mean-square velocity** (r.m.s. speed)

velocity \[ \vec{v} = (v_x, v_y, v_z) \]

\[ v^2 = v_x^2 + v_y^2 + v_z^2 \]

speed \[ v = |\vec{v}| = \sqrt{v_x^2 + v_y^2 + v_z^2} \]

\[ c = \langle v^2 \rangle^{1/2} = \left( \frac{v_1^2 + v_2^2 + \cdots + v_N^2}{N} \right)^{1/2} \]

\[ \langle E_K \rangle = \langle \frac{1}{2}mv^2 \rangle = \frac{1}{2}m \langle v^2 \rangle = \frac{1}{2}mc^2 \]

(average kinetic energy of a particle)

\[ c = \left( \frac{2\langle E_K \rangle}{m} \right)^{1/2} \]

Equation (1):

\[ P = \frac{1}{3}m \frac{N}{V} c^2 = \frac{1}{3}m \frac{nN_A}{V} c^2 = \frac{1}{3}m \frac{n\mathcal{M}}{V} c^2 \]
(\mathcal{M} = \text{molar mass of the gas}) or

\[ PV = \frac{1}{3} n \mathcal{M} c^2 \]  

(2)

If the kinetic model correctly describes ideal gases then the ideal gas equation

\[ PV = nRT \]

and (2) must be identical

\[ PV = \frac{1}{3} n \mathcal{M} c^2 \overset{!}{=} nRT \]

\[ \Rightarrow \]

\[ c = \sqrt{\frac{3RT}{\mathcal{M}}} \]

must use SI units here!: \( m \) = mass of a particle in kg; \( \mathcal{M} \) = molar mass of the gas in kg/mol; \( R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \); \( c \) in m s\(^{-1} \)
example: r.m.s. speed of a nitrogen molecule, $N_2$, at room temperature, $25^\circ C$, is $515 \text{ m s}^{-1}$

$$c \propto \sqrt{T}$$

the total energy $E$ (internal energy $U$) of an ideal gas:

$$U = E = N \langle E_K \rangle = \frac{1}{2} N m c^2 = \frac{1}{2} n \mathcal{M} c^2 = \frac{3}{2} n R T$$

$$\langle E_K \rangle = \frac{3}{2} k T$$  equipartition theorem

$$\langle E_K \rangle \propto T$$

distribution of molecular speeds: **Maxwell distribution** $f(v)$

$$f(v)dv = N_{(v,v+dv)}/N = \text{fraction of molecules with a speed in the range } (v, v + dv) = \text{probability of finding a molecule with a speed in the range } (v, v + dv)$$

$$f(v)dv = 4\pi \left( \frac{\mathcal{M}}{2\pi R T} \right)^{3/2} v^2 \exp \left( -\frac{\mathcal{M} v^2}{2 R T} \right) dv$$
qualitative behavior of the Maxwell distribution of speeds:

(1) Since $x^n \exp(-x^2) \to 0$ for $x \to \infty$, we have that $f(v) \to 0$ for $v \to \infty$

(2) Since $\exp(-x^2) \to 1$ for $x \to 0$, we have that $f(v) \sim v^2 \to 0$ for $v \to 0$

(3) The rate of the decrease of the exponential function is governed by the factor $\mathcal{M} / (2RT)$. Therefore large $\mathcal{M}$ or small $T$ lead to rapid decrease, while small $\mathcal{M}$ or large $T$ lead to slow decrease.
The probability of finding a molecule with a speed between $0$ and $\infty$ is one:

$$\int_{0}^{\infty} f(v) \, dv = 1$$

*normalization*
Probability

discrete variable: $u$; takes values $\{u_1, u_2, u_3, \ldots\}$

$P(u_i)$ = probability that $u = u_i$

normalization: $\sum_{i=1}^{N} P(u_i) = 1$ ($N$ can be $\infty$)

mean value (average value, expectation value):

$$m = \langle u \rangle = \sum_{i=1}^{N} u_i P(u_i)$$

$n$-th moment:

$$\langle u^n \rangle = \sum_{i=1}^{N} u_i^n P(u_i)$$

variance (= spread of the probability):

$$\sigma^2 = \langle (\Delta u)^2 \rangle = \langle (u - \langle u \rangle)^2 \rangle = \langle u^2 - 2u \langle u \rangle + \langle u \rangle^2 \rangle$$
\[ = \langle u^2 \rangle - 2\langle u \rangle \langle u \rangle + \langle u \rangle^2 \]
\[ = \langle u^2 \rangle - \langle u \rangle^2 \geq 0 \]

expectation value of a function \( f(u) \):

\[ \langle f(u) \rangle = \sum_{i=1}^{N} f(u_i)P(u_i) \]

example: \( u \) with \( u \in \{0, 1, 2, 3, \ldots\} \)

\[ P(u = i) = \frac{m^i}{i!} \exp(-m) \quad \text{Poisson distribution} \]

\[ \langle u \rangle = m \]
\[ \langle (\Delta u)^2 \rangle = \sigma^2 = m \]
\[ \langle u^n \rangle = \sum_{k=0}^{n} S(n, k) m^k \]

\( S(n, k) \)  Stirling numbers of the second kind

\[ S(n, k) = \frac{1}{k!} \sum_{j=0}^{k} (-1)^{k-j} \binom{k}{j} j^n \]
continuous variable $x$; takes values in $[a, b]$, where $a$ can be $-\infty$ and $b$ can be $+\infty$

$P(x)$ probability density; $P(x)dx =$ probability that $x$ takes a value in the interval $(x, x + dx)$

normalization:

$$\int_{a}^{b} P(x)dx = 1$$

mean value (average value, expectation value):

$$\langle x \rangle = \int_{a}^{b} xP(x)dx$$

$n$-th moment:

$$\langle x^n \rangle = \int_{a}^{b} x^n P(x)dx$$

variance:

$$\sigma^2 = \langle (\Delta x)^2 \rangle = \langle x^2 \rangle - \langle x \rangle^2$$
\[ \langle f(x) \rangle = \int_a^b f(x)P(x)\,dx \]

example \( x \in (-\infty, +\infty) \)

\[ P(x) = \frac{1}{\sqrt{2\pi}\sigma^2} \exp \left( \frac{-(x - m)^2}{2\sigma^2} \right) \quad \text{Gaussian distribution} \]

\[ \langle x \rangle = m \]

\[ \langle (\Delta x)^2 \rangle = \sigma^2 \]

\[ \langle (\Delta x)^n \rangle = \begin{cases} 0 & n \geq 1, \text{ odd} \\ (n - 1)!! \sigma^n & n \geq 2, \text{ even} \end{cases} \]

\[ (n - 1)!! = 1 \cdot 3 \cdot 5 \cdots (n - 1) \]

If one knows the probability or probability density, then all moments of the random variable can be determined (some may be infinite)

the converse is not true: the probability or probability density is in general \textit{not} uniquely determined by its moments
the r.m.s speed represents a typical speed of the molecules in the gas

a second way to define a typical speed is the *average speed*:

\[
\bar{c} = \langle v \rangle = \int_{0}^{\infty} v f(v) dv
\]

\[
= \left( \frac{8RT}{\pi \mathcal{M}} \right)^{1/2} = \sqrt{\frac{8}{3\pi}} \ c \approx 0.921 \ c
\]

\[
\frac{R}{\mathcal{M}} = \frac{N_A k}{N_A m} = \frac{k}{m}
\]

\[
\bar{c} = \left( \frac{8kT}{\pi m} \right)^{1/2}
\]

a third way is the *most probable speed*, location of the peak of the Maxwell distribution:

\[
f'(c^*) = 0
\]

\[
c^* = \left( \frac{2RT}{\mathcal{M}} \right)^{1/2}
\]

\[
c^* = \sqrt{\frac{2}{3}} c \approx 0.816 c
\]
$c^* < \bar{c} < c$

**collision frequency**

determine how often a specific particle collides with other particles in the gas

since this is a representative particle, we can assume that it moves with the average speed $\bar{c}$

we can replace the moving collision partners by stationary particles, if we replace the average speed $\bar{c}$
by the relative average speed $\bar{c}_{\text{rel}}$:

$$
\bar{c} = \left(\frac{8kT}{\pi m}\right)^{1/2}, \quad \bar{c}_{\text{rel}} = \left(\frac{8kT}{\pi \mu}\right)^{1/2}
$$

$$
\frac{1}{\mu} \equiv \frac{1}{m_A} + \frac{1}{m_B}, \quad \mu = \text{reduced mass}
$$

for identical particles

$$
\frac{1}{\mu} = \frac{2}{m} \implies \mu = \frac{m}{2}
$$

$$
\bar{c}_{\text{rel}} = \sqrt{2\bar{c}}
$$

number of stationary particles inside the collision tube: $\mathcal{N} \sigma_0 \cdot \bar{c}_{\text{rel}} \Delta t$, $\mathcal{N} = \frac{N}{V}$ number density, $\sigma_0 =$
$$\pi d^2 = \text{elastic collision cross-section, for collisions between identical particles, } d = 2r$$

**collision frequency** $z = \text{average number of collisions of a particle per unit time}$

$$z = \frac{N \sigma_0 \cdot \bar{c}_{\text{rel}} \Delta t}{\Delta t} = N \sigma_0 \bar{c}_{\text{rel}}$$

$$z = \sqrt{2} N \sigma_0 \bar{c}$$

$$z = \sqrt{2} \frac{N}{V} \sigma_0 \bar{c}$$

$$z = \sqrt{2} \frac{P}{kT} \sigma_0 \bar{c}; \quad (PV = nRT = \frac{N}{N_A} RT = NkT)$$

**mean free path** $\lambda = \text{the average distance a molecule travels between two successive collisions}$

$$\lambda = \bar{c} \cdot \frac{1}{z} = \frac{\bar{c}}{\sqrt{2} N \sigma_0 \bar{c}} = \frac{1}{\sqrt{2}(N/V) \sigma_0} = \frac{kT}{\sqrt{2} P \sigma_0}$$

collisions with walls and surfaces

$$Z_W = \frac{P}{\sqrt{2\pi mkT}}$$
Transport

transfer of matter, energy, charge, momentum, etc., from one place to another

**flux** \( \mathbf{J} = (J_x, J_y, J_z) \)

\[ J_i = \frac{\text{amount of property in direction } i}{\text{area } \perp \text{ to direction } i \cdot \text{time interval}} \]

flux of matter

transport: driven by **spatial gradients**: experiments \( \implies \)

\[ J_x = -\text{const} \cdot \frac{\text{d property}}{\text{dx}} \]

i.e., flux \( \propto \) gradient, if gradient is not too large: linear nonequilibrium thermodynamics
**diffusion**

matter: transport process = diffusion, gradient = concentration

\[ J_x(x) = -D \frac{d\mathcal{N}(x)}{dx} \quad \text{Fick’s first law} \]

\[ D \quad \text{diffusion coefficient}, \quad [D] = \frac{m^2}{s} \]

for liquids, customary units: \[ [D] = \frac{\text{cm}^2}{\text{s}} \]

for small molecules in water at 25°C: \[ D \sim 10^{-5} \text{ cm}^2 \text{ s}^{-1} \]
energy transport: rate of thermal conduction

\[ J_x(x) = -\kappa \frac{dT(x)}{dx} \] Fourier’s law

\( \kappa \) coefficient of thermal conductivity, \( [\kappa] = \frac{J}{K \text{m s}} \)

momentum transport: viscosity

Newton: “Viscosity is a lack of slipperiness between adjacent layers of fluid.”

velocity gradient \( \Rightarrow \) transfer of momentum

\( \vec{p} = (p_x, p_y, p_z) = m \vec{v} = (mv_x, mv_y, mv_z) \)
\[ J_{x,P_x} (z) = -\eta \frac{dv_x(z)}{dz} \]

\( \eta \) is the viscosity (coefficient), \( [\eta] = \frac{\text{kg}}{\text{ms}} \)

1 Poise = 1 P = 1 g cm\(^{-1}\) s\(^{-1}\)

If \( \eta \) is independent of \( v \), then the fluid is a Newtonian fluid.

Kinetic theory: transport parameters

\[ D = \frac{1}{3} \lambda \bar{c} \]

\[ \kappa = \frac{1}{3} \lambda \bar{c} C_V [A] \]

\[ \eta = \frac{1}{3} \lambda \bar{c} M [A] \]

\( \lambda \downarrow \) as \( P \uparrow \quad \Rightarrow \quad D \downarrow \) as \( P \uparrow \)

\( \bar{c} \uparrow \) as \( T \uparrow \quad \Rightarrow \quad D \uparrow \) as \( T \uparrow \)
\[ \lambda \nearrow \text{ as } \sigma_0 \searrow \implies D \nearrow \text{ as } \sigma_0 \searrow \]

\[ \lambda \propto P^{-1} \text{ and } P \propto [A] \implies \kappa \text{ is independent of } P \]

\[ \lambda \propto P^{-1} \text{ and } P \propto [A] \implies \eta \text{ is independent of } P \]

\[ \bar{c} \propto \sqrt{T} \implies \eta \propto \sqrt{T}; \text{ viscosity of a gas increases with temperature} \]

as \( T \nearrow \), molecules travel faster \( \implies \) greater flux of momentum

liquids: \( \eta \searrow \text{ as } T \nearrow \) (typically)

liquids have attractive intermolecular forces, and \( \eta \) decreases with increasing \( T \)

<table>
<thead>
<tr>
<th>( T/°C )</th>
<th>( \eta/P )</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>100</td>
</tr>
<tr>
<td>blood</td>
<td>18</td>
</tr>
<tr>
<td>glycerin</td>
<td>20</td>
</tr>
<tr>
<td>air</td>
<td>0</td>
</tr>
</tbody>
</table>
How does the concentration change due to the diffusive flux?

**non-stationary system:** non-equilibrium state

\[
\frac{\partial c(x, t)}{\partial t} = -\frac{\partial J_x(x, t)}{\partial x}
\]

The continuity equation holds for any type of flux.

In three dimensions:

\[
\frac{\partial c(x, y, z, t)}{\partial t} = -\frac{\partial J_x(x, y, z, t)}{\partial x} - \frac{\partial J_y(x, y, z, t)}{\partial y} - \frac{\partial J_z(x, y, z, t)}{\partial z}
\]

Consider only one-dimensional systems in this class.

\[
\frac{\partial c(x, t)}{\partial t} = -\frac{\partial J_x(x, t)}{\partial x}
\]

Need to close the equation; need a **constitutive equation**:

Fick’s first law: \( J_x = -D_x \frac{\partial c}{\partial x} \)
Drop subscript $x$, since we consider only one-dimensional systems:

$$\frac{\partial c(x, t)}{\partial t} = -\frac{\partial J(x, t)}{\partial x}, \quad J = -D \frac{\partial c}{\partial x}$$

Combine the two equations:

$$\frac{\partial c(x, t)}{\partial t} = D \frac{\partial^2 c(x, t)}{\partial x^2}$$

If $D$ is independent of $c$ and $x$, then

$$\frac{\partial c(x, t)}{\partial t} = D \frac{\partial^2 c(x, t)}{\partial x^2} \quad \text{Fick’s second law}$$

**diffusion equation**

point source: at $t = 0$ all the solute particles are located in a small region of width $\Delta x$ around $x = 0$: concentration $c_0$

$$c(x, t) = \frac{c_0 \Delta x}{\sqrt{4\pi Dt}} \exp \left(-\frac{x^2}{4Dt}\right), \quad t > 0$$
solution of the diffusion equation with $D = 10^{-5} \, \text{cm}^2/\text{s}$ and $c_0 \Delta x = 1 \, \text{mol}$

Figure 1: $t = 1 \, \text{s}$, $x$ in $\text{cm}$

Figure 2: $t = 100 \, \text{s}$, $x$ in $\text{cm}$
Figure 3: \( t = 3600 \text{ s, } x \text{ in } \text{cm} \)

\[
N(x, t) = \text{number of particles in} (x, x + dx) = c(x, t)dx
\]

(one-dimensional system)

total number of particles \( N = c_0\Delta x \)

\[
P(x, t)dx = \frac{N(x, t)}{N} = \frac{c(x, t)dx}{c_0\Delta x}
\]

= probability of finding a particle in \((x, x + dx)\)

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

**Gaussian distribution**
\( P(x, t) \) obeys of course the diffusion equation

\[
\frac{\partial P(x, t)}{\partial t} = D \frac{\partial^2 P(x, t)}{\partial x^2}
\]

integral table: \( \int_0^\infty \exp(-q^2x^2)dx = \frac{\sqrt{\pi}}{2q}, \ q > 0 \)

\[
\int_{-\infty}^\infty P(x, t)dx = \frac{1}{\sqrt{4\pi Dt}} \int_{-\infty}^\infty \exp\left(-\frac{x^2}{4Dt}\right)dx = 1
\]

\( \langle x(t) \rangle = \int_{-\infty}^\infty xP(x, t)dx = 0 \)

integral table: \( \int_0^\infty x^{2n}\exp(-px^2)dx = \frac{(2n-1)!!}{2(2p)^n} \sqrt{\frac{\pi}{p}}, \ p > 0 \)

\( (2n-1)!! = 1 \cdot 3 \cdot 5 \cdots 2n-1 \)

\( \Delta x = x - \langle x \rangle \)

\[
\langle x(t)^2 \rangle = \langle (\Delta x(t))^2 \rangle = \int_{-\infty}^\infty x^2P(x, t)dx
\]

\[
= 2 \int_0^\infty x^2 \frac{1}{\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right)dx
\]
\[ = 2Dt \]

**diffusion:** \[ \langle x(t)^2 \rangle = 2Dt \] in one dimension
\[ \langle x(t)^2 \rangle = 4Dt \] in two dimensions
\[ \langle x(t)^2 \rangle = 6Dt \] in three dimensions
if \( D_x = D_y = D_z = D \)

one dimension: root mean square distance
\[ d = \sqrt{\langle x(t)^2 \rangle} = \sqrt{2Dt} \]

**convective flow:** streaming fluid, carries particles with it, fluid velocity \( \vec{v}(x, y, z, t) \)

**convective flux:** \( J_x = cv_x \)

Consider a one-dimensional system and \( v_x(x, t) = v \), i.e., constant velocity.

\[ J = cv \]
\[ \frac{\partial c(x, t)}{\partial t} = -\frac{\partial J(x, t)}{\partial x} \]
\[
\frac{\partial c(x, t)}{\partial t} = -v \frac{\partial c(x, t)}{\partial x}
\]

*convection equation*

Particles in a fluid flow are generally also subject to diffusive motion:

\[
\frac{\partial c(x, t)}{\partial t} = -v \frac{\partial c(x, t)}{\partial x} + D \frac{\partial^2 c(x, t)}{\partial x^2}
\]

*diffusion-convection equation*

convection: particle velocity \(v \Rightarrow x(t) = v \cdot t\), with \(x(0) = 0\)

diffusion: \(\langle x(t)^2 \rangle = 2Dt\)

convection: \(x(t) \propto t\)

diffusion: \(x_{\text{rms}}(t) = \langle x(t)^2 \rangle^{1/2} \propto \sqrt{t}\)

"Mesoscopic" picture of diffusion

consider a one-dimensional lattice, lattice spacing \(\Delta x\)
solid; in fluids, $\Delta x \approx \lambda$ mean free path

*Simple random walk*: hopping transport, activated transport

particle hops a distance $\Delta x$ during the time $\Delta t$ (= $\tau$ average collision time in fluids)

![Diagram](image)

at each time step the particle jumps to the right with probability $p$ and to the left with probability $q = 1 - p$; particle does not stay in place; the particle has no memory, the jumps are statistically independent

consider unbiased random walk

$$p = q = \frac{1}{2}$$

no systematic force acts on the particle

time $t = n\Delta t$, $n = 0,1,2,\ldots$; position $x = i\Delta x$, $i = \ldots,-2,-1,0,+1,+2,\ldots$ ($i \in \mathbb{Z}$)
statistical formulation: large collection of independent particles

\[ P(x, t) = P(i, n) \]

evolution equation

\[ P(i, n + 1) = qP(i + 1, n) + pP(i - 1, n) \]
\[ = \frac{1}{2}P(i + 1, n) + \frac{1}{2}P(i - 1, n) \]

Solution: Assume the particle starts at \( x = 0 \), i.e., \( i = 0 \)

\[ n = n_R + n_L \]
\[ n_R = \text{number of jumps to the right} \]
\[ n_L = \text{number of jumps to the left} \]
\[ x = i \Delta x = (n_R - n_L) \Delta x \]
\[ n = n_R + n_L, \quad i = n_R - n_L \]

add the two equation
\[ n + i = 2n_R \]
\[ n_R = \frac{1}{2} (n + i) \]

\[ n_L = n - n_R = \frac{1}{2} (n - i) \]

Since the jumps are independent, the probability to observe a walk with \( n_R \) steps to the right and \( n_L \) steps to the left is

\[
\underbrace{p \cdot p \cdots p}_{n_R} \cdot \underbrace{q \cdot q \cdots q}_{n_L} = p^{n_R} q^{n_L}
\]

\[
\frac{1}{2} \cdot \frac{1}{2} \cdots \frac{1}{2} = \left(\frac{1}{2}\right)^{n_R} \cdot \left(\frac{1}{2}\right)^{n_L} = \left(\frac{1}{2}\right)^n
\]

number of different ways of taking \( n \) steps, such that \( n_R \) are to the right and \( n_L \) are to the left:

\[
W_n(n_R) = \frac{n!}{n_R!n_L!}
\]

Consequently

\[
P(i, n) = \frac{n!}{n_R!n_L!} \left(\frac{1}{2}\right)^n
\]
\[ (p + q)^n = \sum_{k=0}^{\infty} \frac{n!}{k!(n-k)!} p^k q^{n-k} \]

\[ \langle i \rangle_n = m_n = \sum_{i=-\infty}^{\infty} i P(i, n) = 0 \quad \text{(by symmetry)} \]

\[ \langle (\Delta i)^2 \rangle_n = \sigma_n^2 = n \]

consider the continuum limit of the simple random walk:

\[ t = n\Delta t, \quad x = i\Delta x \]

\[ \Delta t \to 0, \quad \Delta x \to 0 \]

\[ P(i, n+1) = \frac{1}{2} P(i + 1, n) + \frac{1}{2} P(i - 1, n) \]

\[ P(i\Delta x, (n + 1)\Delta t) = \frac{1}{2} P((i + 1)\Delta x, n\Delta t) + \frac{1}{2} P((i - 1)\Delta x, n\Delta t) \]

\[ P(i\Delta x, (n + 1)\Delta t) - P(i\Delta x, n\Delta t) = \]

\[ \frac{1}{2} P((i + 1)\Delta x, n\Delta t) + \frac{1}{2} P((i - 1)\Delta x, n\Delta t) - P(i\Delta x, n\Delta t) \]
\[
P(i \Delta x, (n + 1) \Delta t) - P(i \Delta x, n \Delta t) =
\]
\[
\frac{1}{2} \left[ P((i + 1) \Delta x, n \Delta t) + P((i - 1) \Delta x, n \Delta t) - 2P(i \Delta x, n \Delta t) \right]
\]
\[
P(i \Delta x, (n + 1) \Delta t) - P(i \Delta x, n \Delta t) = \frac{\Delta t}{\Delta t}
\]
\[
\frac{1}{2 \Delta t} \left[ P((i + 1) \Delta x, n \Delta t) + P((i - 1) \Delta x, n \Delta t) - 2P(i \Delta x, n \Delta t) \right]
\]
\[
P(x, t + \Delta t) - P(x, t) = \frac{\Delta t}{\Delta t}
\]
\[
\frac{1}{2 \Delta t} \left[ P(x + \Delta x, t) + P(x - \Delta x, t) - 2P(x, t) \right]
\]
\[
\frac{\partial P(x, t)}{\partial t} = \frac{1}{2 \Delta t} \left[ P(x, t) + \frac{\partial P}{\partial x}(x, t) \Delta x + \frac{1}{2} \frac{\partial^2 P}{\partial x^2}(x, t)(\Delta x)^2 + \cdots + P(x, t) + \frac{\partial P}{\partial x}(x, t)(-\Delta x) + \frac{1}{2} \frac{\partial^2 P}{\partial x^2}(x, t)(-\Delta x)^2 + \cdots - 2P(x, t) \right]
\]
\[
\frac{\partial P(x, t)}{\partial t} = \frac{(\Delta x)^2}{2 \Delta t} \frac{\partial^2 P}{\partial x^2}(x, t)
\]
\[
\frac{(\Delta x)^2}{2 \Delta t} \rightarrow \frac{0^2}{0} ??
\]

obtain a nontrivial result if \( \Delta x \rightarrow 0 \) and \( \Delta t \rightarrow 0 \) such
that

\[
\frac{(\Delta x)^2}{2\Delta t} = \text{const} = D
\]

\[
\frac{\partial P(x, t)}{\partial t} = D \frac{\partial^2 P(x, t)}{\partial x^2}
\]  \text{diffusion equation}

one can show that the binomial distribution approaches the Gaussian distribution in the continuum limit

Note: the diffusion equation can be obtained either from thermodynamics

\[
\frac{\partial c(x, t)}{\partial t} = -\frac{\partial J(x, t)}{\partial x}
\]  \text{continuity equation}

\[
J(x, t) = -D \frac{\partial c(x, t)}{\partial x}
\]  \text{constitutive equation; Fick’s 1st law}

or from a mesoscopic description, simple random walk

transport equations need to have a solid foundation, either macroscopic (thermodynamics) or mesoscopic (microscopic)
diffusion equation: unrealistic feature of infinitely fast propagation

\[ c(x, t) = \frac{c_0 \Delta x}{\sqrt{4 \pi D t}} \exp \left( -\frac{x^2}{4Dt} \right) \]

no matter how small \( t \) and how large \( x \), the concentration \( c \) will be nonzero, though exponentially small

reason: lack of inertia of Brownian particles; their direction of motion in successive time intervals is uncorrelated

consequences: (i) particles move with infinite velocity; there is some probability, though exponentially small, that a particle will travel an infinite distance from its current position in a small but nonzero amount of time. (ii) motion of the particles is unpredictable even on the smallest time scales.

in most applications, infinitely fast propagation is not a concern, since the density is exponentially small, i.e., zero for all practical purposes

diffusion equation is adequate for aqueous solutions
if infinitely fast propagation is a concern, there are several remedies:

(i) thermodynamics: replace Fick’s first law by the Cattaneo equation

\[ \frac{\partial c(x, t)}{\partial t} = -\frac{\partial J(x, t)}{\partial x} \]  
continuity equation

\[ \tau \frac{\partial J(x, t)}{\partial t} + J(x, t) = -D \frac{\partial c(x, t)}{\partial x} \]  
constitutive eq. = Cattaneo eq.

eliminating \( J \) we obtain the telegraph equation instead of the diffusion equation

\[ \tau \frac{\partial^2 c(x, t)}{\partial t^2} + \frac{\partial c(x, t)}{\partial t} = D \frac{\partial^2 c(x, t)}{\partial x^2} \]  
telegraph equation

The solution of the telegraph equation has the property that

\[ c(x, t) = 0 \text{ for } |x| > \sqrt{\frac{D}{\tau}} t \]

and it converges to the solution of the diffusion equation for \( \tau \to 0 \)
(ii) mesoscopic description: replace the simple random walk by a persistent random walk, where a particle takes steps of length $\Delta x$ and duration $\Delta t$ and the particle continues in its previous direction with probability $\alpha = 1 - \mu \Delta t$ and reverses direction with probability $\beta = 1 - \alpha = \mu \Delta t$; continuum limit $\rightarrow$ telegraph equation

different mesoscopic description

consider a particle of mass $m$, to which a force $\vec{F}$ is applied, moving in a fluid (examples: sedimentation, $F = \text{gravity}$; centrifuge, $F = \text{centrifugal force}$)

$$m \ddot{a} = \vec{F} + \vec{F}_t$$

Newton’s second law; $\vec{F}_t$ force from huge number of collisions with fluid particles

one dimension:

$$m \frac{dv}{dt} = F + \mathcal{F}_t$$
decompose the random force $\mathcal{F}_t$ into its systematic part, the friction force, and its fluctuating part

$$
\mathcal{F}_t = \langle \mathcal{F}_t \rangle + \xi_t
$$

$$
\langle \mathcal{F}_t \rangle = -fv
$$

$$
\langle \xi_t \rangle = 0
$$

fluctuating force $\xi_t$ varies very rapidly compared to $v$, it is statistically independent of $v$, and has very short memory, $\langle \xi_t \xi_{t'} \rangle = 0$ for $t \neq t'$

$$
\frac{mv}{dt} = F - fv + \xi_t \quad \text{Langevin equation}
$$

$$
\frac{m\langle v \rangle}{dt} = F - f\langle v \rangle + \langle \xi_t \rangle
$$

$$
\frac{m\langle v \rangle}{dt} = F - f\langle v \rangle + 0
$$

$$
\frac{d\langle v \rangle}{dt} = -\frac{f}{m}\langle v \rangle + \frac{F}{m}
$$
The solution of the general first order linear ODE

\[
\frac{dy}{dt} = -h(t)y(t) + g(t), \quad y(0) = y_0
\]

is given by

\[
y(t) = \exp[-H(t)] \left\{ \int_0^t g(s) \exp[H(s)] ds + y_0 \right\}
\]

\[
H(t) = \int_0^t h(s) ds
\]

So with \( v(0) = 0 \)

\[
\langle v(t) \rangle = \frac{F}{f} \left[ 1 - \exp\left( -\frac{ft}{m} \right) \right]
\]

\( t \to \infty : \langle v(t) \rangle \to v_\infty = \frac{F}{f} \) \quad \text{terminal velocity or drift velocity}

relaxation time: \( \tau = \frac{m}{f} : \langle v(\tau) \rangle = \frac{F}{f} \left[ 1 - e^{-1} \right] \)

spherical protein with molar mass \( M = 6 \times 10^5 \text{g/mol} \) in
water: $\tau \approx 10^{-11}$ s; cell with radius $r = 10^{-3}$ cm: $\tau \approx 20 \mu$s

$v_\infty = \frac{1}{f} F = \mu F$, $\mu =$ mobility

for an ion in an electric field, $F = ze\mathcal{E}$

$v_\infty = \mu ze\mathcal{E} = u\mathcal{E}$

$u =$ ionic mobility

Stokes law: frictional coefficient $f$ for a spherical particle of radius $a$ in a fluid of viscosity $\eta$:

$f = 6\pi\eta a$

$\mu = \frac{1}{6\pi\eta a}$

$u = \frac{e z}{6\pi\eta a}$

“diffusive” motion: $F = 0$

$m \frac{dv}{dt} = -f v + \xi_t$
\[ x(t) = x(0) + \int_0^t v(s) ds, \quad \text{assume } x(0) = 0 \]

\[ \langle x(t) \rangle = \int_0^t \langle v(s) \rangle ds \]

\[ \langle v(s) \rangle = 0 \text{ for } F = 0 \]

\[ \langle x(t) \rangle = 0 \]

\[ \langle (\Delta x(t))^2 \rangle = \langle x(t)^2 \rangle = ? \]

\[ m \frac{d^2 x}{dt^2} = -f \frac{dx}{dt} + \xi_t \]

\[ m \ddot{x} = -f \dot{x} + x \xi_t \]

\[ m \left[ \frac{d(x \dot{x})}{dt} - \dot{x}^2 \right] = -f x \dot{x} + x \xi_t \]

\[ m \frac{d(x \dot{x})}{dt} = mx^2 - f x \dot{x} + x \xi_t \]

\[ m \left( \frac{d(x \dot{x})}{dt} \right) = \langle m \dot{x}^2 \rangle - f \langle x \dot{x} \rangle + \langle x \xi_t \rangle \]

\[ E_K = \frac{1}{2} mv^2 = \frac{1}{2} m \dot{x}^2 \]

\[ m \left( \frac{d(x \dot{x})}{dt} \right) = \langle 2E_K(t) \rangle - f \langle x \dot{x} \rangle + \langle x \xi_t \rangle \]
\[ \langle x\xi_t \rangle = \langle x \rangle \langle \xi_t \rangle, \ x(t) \text{ and } \xi_t \text{ independent} \]

\[ m\left\langle \frac{d(x\dot{x})}{dt} \right\rangle = \langle 2E_K(t) \rangle - f \langle x\dot{x} \rangle + \langle x \rangle \langle \xi_t \rangle \]

\[ \langle E_K(t) \rangle = \frac{1}{2} kT \quad \text{equipartition theorem} \]

\[ m\left\langle \frac{d(x\dot{x})}{dt} \right\rangle = kT - f \langle x\dot{x} \rangle + 0 \]

\[ \frac{dx}{dt} = -\frac{f}{m} \langle x\dot{x} \rangle + \frac{kT}{m} \]

with \( \langle x\dot{x} \rangle(0) = 0 \) since \( x(0) = 0 \)

\[ \langle x\dot{x} \rangle = \frac{kT}{f} \left[ 1 - \exp\left( -\frac{f}{m} t \right) \right] \]

\[ x\dot{x} = \frac{1}{2} \frac{dx^2}{dt} \]

\[ \frac{1}{2} \frac{d\langle x^2 \rangle}{dt} = \frac{kT}{f} \left[ 1 - \exp\left( -\frac{f}{m} t \right) \right] \]

\[ \langle x^2(t) \rangle = \int_0^t \frac{2kT}{f} \left[ 1 - \exp\left( -\frac{f}{m} t' \right) \right] dt' \]

\[ \langle x^2(t) \rangle = \frac{2kT}{f} \left\{ t - \frac{m}{f} \left[ 1 - \exp\left( -\frac{f}{m} t \right) \right] \right\} \]
two cases:
Case 1: $t \ll \tau = m/f$

$$\exp\left(-\frac{f}{m} t\right) = 1 - \frac{f}{m} t + \frac{1}{2} \left(\frac{f}{m}\right)^2 t^2 + \cdots$$

$$\langle x^2(t) \rangle = \frac{2kT}{f} \left\{ t - m \left[ 1 - 1 + \frac{f}{m} t - \frac{1}{2} \left(\frac{f}{m}\right)^2 t^2 + \cdots \right] \right\}$$

$$\langle x^2(t) \rangle = \frac{2kT}{f} \left\{ \frac{1}{2} \frac{f}{m} t^2 + \cdots \right\}$$

$$\langle x^2(t) \rangle = \frac{kT}{m} t^2$$

$x \propto t$ (ballistic motion for short times)

$$\bar{v} = \sqrt\frac{kT}{m}, \text{ thermal velocity}$$

Case 2: $t \gg \tau = m/f$

$$\exp\left(-\frac{f}{m} t\right) \approx 0$$

$$\langle x^2(t) \rangle = \frac{2kT}{f} t \doteq 2Dt \text{ (diffusive motion for long times)}$$
\[ D = \frac{kT}{f} \quad \text{Einstein relation} \]

example of a fluctuation-dissipation theorem

combine with Stokes law

\[ D = \frac{kT}{6\pi\eta a} \]