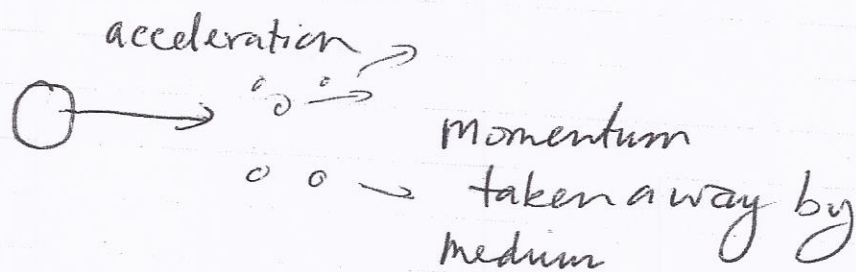


Diffusion and Dissipation

What ^{is} the ^(relation between) ~~the~~ "force" causing the bias and the Velocity?



⇒ terminal velocity

$$v_{\text{drift}} = \overset{\text{mobility}}{\mu} F$$

$$\text{or } F_{\text{drag}} = -\overset{\text{drag coeff}}{\xi} v$$

$F + F_{\text{drag}} = 0$ in the long run.

~~On the average~~

$$m \frac{dv(t)}{dt} = F(t) - \xi v$$

$$v(t) = v(0) e^{-\frac{\xi t}{m}}$$

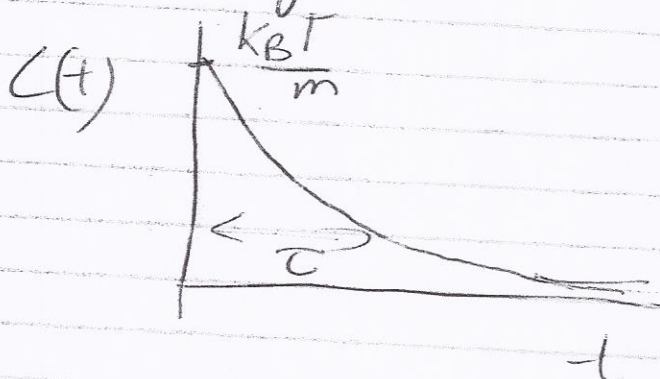
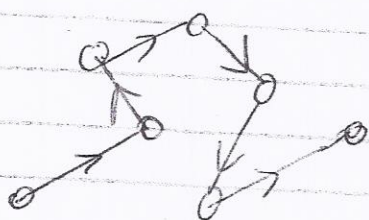
$$+ \int_0^t e^{-\frac{\xi(t-t')}{m}} \frac{F(t')}{m} dt'$$

When $t \gg \frac{m}{\xi} = \tau$ and ~~if~~ F is a constant

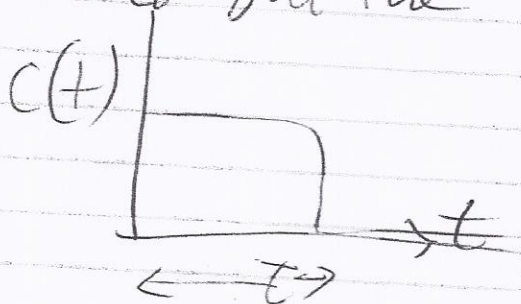
$$\mathcal{V} = \frac{F}{m} \int_0^{\infty} e^{-\frac{t}{\tau}} dt = \frac{F}{\zeta} \quad \boxed{\zeta = \mu^{-1}}$$

The time scale τ is associated with velocity correlation decay.

$$C(t) = \langle v_x(t) v_x(0) \rangle$$



We will pretend that τ is collision time and velocity is completely equilibrated at the collision. As if



Turns out that the conclusions are valid in general, as we will show.

Let us say that just after a collision the x component of the velocity is $v_{0,x}$. With force being applied for time Δt

$$\Delta x = v_{0,x} \Delta t + \frac{F}{2m} (\Delta t)^2$$

The 'extra' velocity is $\frac{F}{2m} \frac{(\Delta t)^2}{\Delta t} = \frac{F}{2m} \Delta t$

If τ is the time scale, after which velocities get 'reset', then

$$v_{\text{drift}} = \frac{F\tau}{2m} \Rightarrow \frac{1}{\tau} = \mu = \frac{\tau}{2m}$$

What about diffusion?

Set $F=0$

$$\Delta x = v_{0,x} \Delta t$$

In time t there are $\frac{t}{\tau}$ periods of motion in one direction

$$\begin{aligned} \langle x^2 \rangle &= \sum \langle \Delta x^2 \rangle = \frac{t}{\tau} \langle v_{0,x}^2 \rangle \tau^2 \\ &= \langle v_{0,x}^2 \rangle \tau t \equiv 2Dt \end{aligned}$$

So $D = \frac{\langle v_{0,x}^2 \rangle \tau}{2}$

Note both D and μ involve τ ,
Something to do with kinetics, not just thermal equilibrium distribution

Note that

$$SD = \frac{D}{\mu} = m \langle v_{0,x}^2 \rangle$$

has lost the timescale of kinetics. At thermal equilibrium

$$m \langle v_{0,x}^2 \rangle = k_B T$$

according to Equipartition Theorem.

Hence

$$SD = \frac{D}{\mu} = k_B T$$

Einstein Relation

or

$$D = \mu k_B T$$

What is the drag coefficient? For 'mesoscopic/macroscopic' objects, we could use Stokes law for spherical objects

$$F = 6\pi\eta a v$$

η is the viscosity of the medium
and a is the radius.

$$\eta = 8.9 \times 10^{-4} \text{ Pa s} \quad \text{around room temp.}$$

For a $1 \mu\text{m}$ radius bead.

$$\begin{aligned} \zeta &= 6\pi\eta a = 6 \times 3.14 \times 8.9 \times 10^{-4} \times 10^{-6} \frac{\text{N}}{\text{m/s}} \\ &= 1.7 \times 10^{-8} \frac{\text{N}}{\text{m/s}} \end{aligned}$$

$$\begin{aligned} D &= \frac{k_B T}{\zeta} = \frac{4.1 \times 10^{-21} \text{ N m}}{1.7 \times 10^{-8} \text{ N s/m}} = 2.4 \times 10^{-13} \frac{\text{m}^2}{\text{s}} \\ &= 0.24 \frac{(\mu\text{m})^2}{\text{s}} \end{aligned}$$

This is what makes Brownian motion observable. Over tens of seconds an μm sized object moves over microns.

If we go down to protein molecule sized objects $\sim 10\text{nm}$, D should be $100-1000$ times bigger. In practice, inside the cell, the observed diffusion constant is orders of magnitude smaller, because cytosol is not just water!