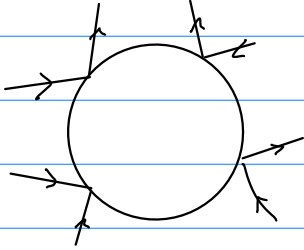


Fluctuations

Brownian motion:



Light particles collide many times with heavy ones.

Collisions have two effects:

- ① they cause drag
- ② Random kicks on top of the drag.

$$m \dot{\underline{v}} = - \underbrace{\gamma \underline{v}}_{\text{drag}} + \underbrace{\underline{R}(t)}_{\text{random kicks}} + \underbrace{F(\underline{r}, t)}_{\text{systematic force}}$$

Properties of $\underline{R}(t)$:

$$\langle \underline{R}(t) \rangle = 0 \quad \text{all } t$$

$$\langle \underline{R}(t) \underline{R}(t+\tau) \rangle = \langle R^2 \rangle \delta(\tau) \rightarrow \text{no time correlations}$$

$$P(R) = \frac{1}{\sqrt{2\pi \langle R^2 \rangle}} e^{-R^2 / 2 \langle R^2 \rangle}$$

Discretize time: time steps t_1, t_2, \dots

$$t_{j+1} - t_j = \Delta t.$$

$$\begin{aligned} \text{Then } P(R_1, \dots, R_N) &= \frac{1}{(2\pi \langle R^2 \rangle)^{N/2}} e^{-(R_1^2 + \dots + R_N^2) / 2 \langle R^2 \rangle} \\ &\approx \frac{1}{(2\pi \langle R^2 \rangle)^{N/2}} e^{-\frac{1}{2\pi \langle R^2 \rangle \Delta t} \int_{t_1}^{t_N} R^2(t) dt} \\ &\sim e^{-\frac{1}{2\eta} \int_{t_1}^{t_N} R^2(t) dt} \end{aligned}$$

$$\langle R(t) R(t+\tau) \rangle = \langle R^2 \rangle \delta(\tau)$$

→ Discrete time

$$\langle R_m R_m \rangle = \langle R^2 \rangle \frac{\delta_{m,m}}{\Delta t} = \frac{q}{\Delta t} \delta_{m,m}$$

Solution of the Langevin equation

Consider $F=0$

$$m \dot{v} = -\gamma v + R(t) \quad \text{Langevin equation}$$

Homogeneous equation, 1D

$$m \dot{\tilde{v}} = -\gamma \tilde{v} ; \tilde{v} = \tilde{v}_0 e^{-\gamma t/m} \quad \text{homogeneous solution.}$$

Particular solution:

$$\text{try } v(t) = v_0 e^{-\gamma t/m} f(t)$$

$$\rightarrow m \left(\dot{f} - \gamma \frac{f}{m} \right) \tilde{v}(t) = R(t) - \cancel{\gamma \tilde{v} f}$$

$$\rightarrow \dot{f} = \frac{R(t)}{m v_0} e^{\gamma t/m}$$

$$\rightarrow f(t) = \frac{1}{m v_0} \int_0^t R(t') e^{\gamma t'/m} dt'$$

$$\Rightarrow v(t) = v_0 e^{-\gamma t/m} + \frac{1}{m} \int_0^t e^{-\gamma(t-t')/m} R(t') dt'$$

$$\Rightarrow \langle v(t) \rangle = v_0 e^{-\gamma t/m}$$

$$\langle v^2(t) \rangle = v_0^2 e^{-2\gamma t/m} + \frac{1}{m^2} \int_0^t \int_0^t \underbrace{\langle R(t_1) R(t_2) \rangle}_{q \delta(t_1 - t_2)} e^{-2\gamma t/m} e^{\gamma(t_1+t_2)/m} dt_1 dt_2$$

$$= v_0^2 e^{-2\gamma t/m} + \frac{q}{m^2} \int_0^t e^{-2\gamma t/m} e^{2\gamma t'/m} dt' =$$

$$= v_0^2 e^{-2\gamma t/m} + \frac{q}{2\gamma m} (1 - e^{-2\gamma t/m})$$

$$\langle v^2(t \rightarrow \infty) \rangle = \frac{q}{2\gamma m} = \frac{k_B T}{m} \Rightarrow \underline{\underline{q = 2\gamma k_B T}}$$

Langevin eq. $m \dot{v} = -\gamma v + R(t)$ is representative for stochastic processes

→ derive an equation for $P(v, t)$. *Probability density for v .*

$$\dot{v} = -\gamma v + R(t)$$

$$v(t) \rightarrow v(t + \Delta t)$$

$$P(v, t + \Delta t) = \int P(v', t) P(R) dR \quad P(R) : \text{probability density for } R \text{ (Gaussian).}$$

$$v' = v - (-\gamma v + R) \Delta t$$

$$P(v, t + \Delta t) = P(v, t) + \int (v' - v) \frac{\partial P}{\partial v} P(R) dR + \frac{1}{2} \int (v' - v)^2 \frac{\partial^2 P}{\partial v^2} P(R) dR$$

$$= P(v, t) + \int (\gamma v - R) \Delta t \frac{\partial P}{\partial v} P(R) dR + \frac{1}{2} \int (\gamma v - R)^2 \Delta t^2 \frac{\partial^2 P}{\partial v^2} P(R) dR$$

$$\rightarrow \Delta t \frac{\partial P}{\partial t} = \gamma v \frac{\partial P}{\partial v} \Delta t + \frac{1}{2} \gamma^2 v^2 \Delta t^2 \frac{\partial^2 P}{\partial v^2} + \frac{1}{2} \left(\frac{2\gamma k_B T}{\Delta t} \right) \Delta t^2 \frac{\partial^2 P}{\partial v^2} + \mathcal{O}(\Delta t^2)$$

$$\underline{\underline{\frac{\partial P}{\partial t} = \gamma v \frac{\partial P}{\partial v} + \gamma k_B T \frac{\partial^2 P}{\partial v^2}}} \quad \underline{\underline{\text{Fokker Planck eq.}}}$$

Stationary solution: $\frac{\partial P}{\partial t} = 0$

In that case: $\underline{\underline{P(v) = C e^{-m v^2 / 2 k_B T}}}$. Maxwell

Diffusion (random walk): $\langle x^2(t \rightarrow \infty) \rangle = 2Dt$.

We try to find $\langle x^2(t) \rangle$

$$x(t) = \int_0^t v(t') dt'$$

$$\left(v(t) = v_0 e^{-\gamma t/m} + \frac{1}{m} \int_0^t e^{-\gamma(t-t')/m} R(t') dt' \right)$$

Simpler method:

$$m \ddot{x} = -\gamma \dot{x} + R(t)$$

Multiply by x :

$$m x \ddot{x} = -\gamma x \dot{x} + R(t) x(t)$$

$$m \left(\frac{d}{dt} (x \dot{x}) - \dot{x}^2 \right) = -\gamma x \dot{x} + R(t) x(t)$$

$$m \dot{x}^2 = k_B T \rightarrow$$

$$m \frac{d}{dt} (x \dot{x}) + \gamma (x \dot{x}) = k_B T + R(t) x(t)$$

$$m \frac{d}{dt} \underbrace{\langle x \dot{x} \rangle}_{\gamma} + \gamma \underbrace{\langle x \dot{x} \rangle}_{\gamma} = k_B T + \underbrace{\langle R(t) x(t) \rangle}_{0}$$

$$\Rightarrow m \langle x \dot{x} \rangle = C + A e^{-\gamma t/m} \quad \left(C = \frac{k_B T}{\gamma} \right)$$

$$t \rightarrow \infty: \langle x \dot{x} \rangle = \frac{k_B T}{\gamma}$$

$$t=0: \langle x \dot{x} \rangle = 0 \Rightarrow A = -k_B T / \gamma$$

$$\text{Now note that } \langle x \dot{x} \rangle = \frac{1}{2} \frac{d}{dt} \langle x^2 \rangle$$

$$\rightarrow \langle x^2 \rangle = \frac{2}{m} \int_0^t \frac{k_B T}{\gamma} (1 - e^{-\gamma t'/m}) dt =$$

$$\frac{2k_B T}{\gamma} t + 2 \frac{k_B T}{\gamma} \frac{m}{\gamma} (e^{-\gamma t/m} - 1)$$

$$\text{For } t \rightarrow 0: \langle x^2 \rangle = \frac{2k_B T}{\gamma} \left(t + \frac{m}{\gamma} \left(1 - \frac{\gamma t}{m} + \frac{\gamma^2 t^2}{2m^2} + \dots \right) - 1 \right)$$

$$= k_B T \frac{\gamma}{m} t^2$$

$$\text{For } t \rightarrow \infty \quad \langle x^2 \rangle = \frac{2k_B T}{\gamma} \left(t - \frac{m}{\gamma} \right) \simeq \frac{2k_B T}{\gamma} t = 2Dt$$

$$\rightarrow \underline{\underline{D = \frac{k_B T}{\gamma}}}$$

$$\gamma = 6\pi\eta a, \quad \eta = \text{viscosity.}$$

radius

(Stokes' law)

Let us now consider the probability for a particle to find itself at position x at time t .

$P(x, t) dx$ = probability to find a particle inside $(x, x+dx)$ at time t .

As v is linear in $R(t)$, also x is linear in $R(t)$.

$R(t)$ is Gaussian $\Rightarrow x(t)$ is Gaussian

We have calculated the width of this Gaussian to be $\langle \Delta x^2(t) \rangle = 2Dt$.

$$\text{Hence } T(\Delta x, t) = \frac{1}{\sqrt{4\pi Dt}} e^{-\Delta x^2 / 4Dt}$$

From this we can derive an equation for $P(x, t)$ as follows.

$$P(x, t + \Delta t) = \int P(x - \Delta x, t) T(\Delta x, t) d\Delta x$$

$$\int \left(P(x, t) - \cancel{\Delta x} \frac{\partial P(x, t)}{\partial x} + \frac{\Delta x^2}{2} \frac{\partial^2 P(x, t)}{\partial x^2} \right) T(\Delta x) d\Delta x$$

$$= P(x, t) + \frac{\partial^2 P}{2\partial x^2} \int \Delta x^2 T(\Delta x) d\Delta x =$$

$$= P(x,t) + D \Delta t \frac{\partial^2 P}{\partial x^2}$$

$$\Rightarrow \frac{\partial P(x,t)}{\partial t} = D \frac{\partial^2 P(x,t)}{\partial x^2} \quad \text{Diffusion } D \text{ constant.}$$

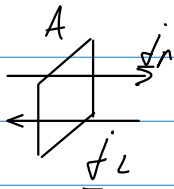
$$= \frac{\partial}{\partial x} D(x) \frac{\partial P(x,t)}{\partial x} \quad \text{General}$$

Here we have assumed $\Delta t \gg \frac{m}{\gamma}$, in order to justify the diffusive limit.

$$\text{On the other hand } \Delta x \leq \sqrt{D\Delta t}; \quad D = \frac{k_B T}{\gamma}$$

Ok for long enough time.

An alternative derivation
Fick's law.



$$\text{Flux: } \underline{j}(\underline{r}, t) = g(\underline{r}, t) \underline{v}(\underline{r}, t).$$

$$\frac{\text{nr of atoms passing through } A \text{ in time } \Delta t}{A \Delta t}$$

Particle at $x_0 < 0$ crosses 0:

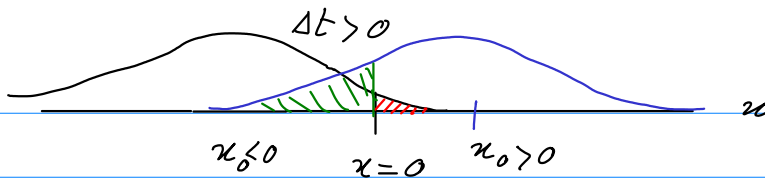
$$\int_0^\infty \frac{e^{-(x-x_0)^2/4D\Delta t}}{\sqrt{4\pi D\Delta t}} dx$$

$$x_0 > 0: \int_{-\infty}^0 \frac{e^{-(x-x_0)^2/4D\Delta t}}{\sqrt{4\pi D\Delta t}} dx$$

$$2p'(0) \int_{-\infty}^0 dx_0 \int_0^\infty \frac{e^{-(x-x_0)^2/4D\Delta t}}{\sqrt{4D\Delta t}} dx = p'(0) D \Delta t.$$

$$\int_{-\infty}^0 dx_0 \int_0^\infty \frac{e^{-(x-x_0)^2/4D\Delta t}}{\sqrt{4D\Delta t}} dx = \int_{-\infty}^0 dx_0 (x_0 - x + x) \int_0^\infty \frac{e^{-(x-x_0)^2/4D\Delta t}}{\sqrt{4D\Delta t}} dx =$$

$$x_0 - x = \tilde{x} \quad \int_0^\infty \int_{-\infty}^\infty \frac{\tilde{x} e^{-\tilde{x}^2/4D\Delta t}}{\sqrt{4D\Delta t}} dx_0 = - \int_0^\infty 2D\Delta t e^{-\tilde{x}^2/4D\Delta t} \bigg|_{-\infty}^x dx$$



$$j(x_0 < 0, t) = \int_0^{\infty} \frac{e^{-(x-x_0)^2/4D\Delta t}}{\sqrt{4\pi D\Delta t}} dx$$

$$j(x_0 > 0, t) = \int_{-\infty}^0 \frac{e^{-(x-x_0)^2/4D\Delta t}}{\sqrt{4\pi D\Delta t}} dx$$

$$\text{Total: } \int_{-\infty}^0 dx_0 \int_0^{\infty} p(x_0, t) \frac{e^{-(x-x_0)^2/4D\Delta t}}{\sqrt{4D\Delta t}} dx - \int_0^{\infty} dx_0 \int_{-\infty}^0 p(x_0, t) \frac{e^{-(x-x_0)^2/4D\Delta t}}{\sqrt{4D\Delta t}} dx$$

$$p(x_0, t) = p(0, t) + x_0 p'(0, t).$$

$$\parallel - \int_{-\infty}^0 dx_0 \int_0^{\infty} p(-x_0, t) \frac{e^{-(x-x_0)^2/4D\Delta t}}{\sqrt{4D\Delta t}} dx$$

$$2p'(0, t) \int_{-\infty}^0 dx_0 x_0 \int_0^{\infty} \frac{e^{-(x-x_0)^2/4D\Delta t}}{\sqrt{4D\Delta t}} dx = -p'(0, t) D \Delta t = j(0, t) \Delta t.$$

$$j(x, t) = -D \frac{\partial p(x, t)}{\partial x}$$

$$\underline{j}_{\text{diff}}(x, t) = -D \nabla p(x, t) \quad \text{Fick's law.}$$

$$j(0, t) = D p'(0, t) = D \frac{\partial p(0, t)}{\partial x} \quad \text{Fick's law}$$

$$\underline{j}_{\text{diff}} =$$

$$\underline{j}_{\text{diff}}(\underline{r}, t) = -D \nabla \rho(\underline{r}, t) \quad \text{Fick's law.}$$

Consider a volume V with a surface A .

Change in the amount of particles inside V :

$$\int_V (\rho(\underline{r}, t + \Delta t) - \rho(\underline{r}, t)) d^3r = \int_A \underline{j} \cdot d\underline{a} \Delta t \quad \text{no sources/sinks.}$$

$$\Rightarrow \int_V \frac{\partial \rho}{\partial t} d^3r = - \int_A \underline{j} \cdot d\underline{a} = - \int_V \nabla \cdot \underline{j} d^3r$$

$$\text{Hence: } \frac{\partial \rho}{\partial t} = -\nabla \cdot \underline{j} \quad \text{Continuity equation.}$$

Using $\underline{j} = -D \nabla \rho$, we obtain

$$\frac{\partial \rho}{\partial t} = \nabla \cdot (D \nabla \rho) \quad \left(\text{Note: } \rho(\underline{r}, t) \sim P(\underline{r}, t) \right)$$

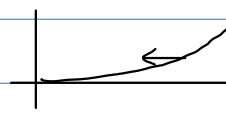
Introduce drift:

$$m \underline{\dot{v}} = -\gamma \underline{v} + \underline{F} + \underline{R}(t)$$

for \underline{F} constant:

$$m \langle \underline{\dot{v}} \rangle = -\gamma \langle \underline{v} \rangle + \underline{F} = 0 \quad \text{for } t \gg m/\gamma.$$

Then $\underline{j}_F = \rho \langle \underline{v} \rangle = \rho \underline{F}/\gamma$



$$\nabla \underline{F} = -\underline{j}_{diff}: \quad D \nabla \rho = \rho \underline{F}/\gamma \Rightarrow \frac{\nabla \rho}{\rho} = \underline{F}/\gamma D$$

Therefore $\nabla \ln \rho = -\nabla U(\underline{r})/\gamma D$

$$\Rightarrow \rho_{eq}(\underline{r}) = \text{Const } e^{-U(\underline{r})/\gamma D} = C e^{-U(\underline{r})/k_B T}$$

Note: $\gamma D = k_B T$

now we generalize the diff eq, to this case

$$P(x, t + \Delta t) = \int P(\underbrace{x - \Delta x}_{x'}, t) T(\Delta x, x', \Delta t) d\Delta x$$

$$\langle \Delta x \rangle = F/\gamma \Delta t = \int T(\Delta x, x', \Delta t) \Delta x d\Delta x$$

$$\langle \Delta x^2 \rangle = 2D \Delta t = \int T(\Delta x, x', \Delta t) \Delta x^2 d\Delta x$$

Multiply left and rhs by $\delta(x - x_0)$ and integrate over x :

$$\rightarrow P(x_0, t + \Delta t) = \iint P(x - \Delta x, t) T(\Delta x, x - \Delta x, \Delta t) \delta(x - x_0) d\Delta x dx.$$

$$\Rightarrow \Delta t \frac{\partial P(x_0, t)}{\partial t} = \iint \left(-\Delta x \frac{\partial P}{\partial x} \delta(x - x_0) T(\Delta x, x - \Delta x, t) + P(x, t) \left(-\Delta x \right) \frac{\partial T}{\partial x}(\Delta x, x, t) \right) d\Delta x dx$$

$$\left(\frac{d}{dx} \langle \Delta x \rangle = \frac{dF/dx}{\gamma} \Delta t = \int \left(\frac{\partial}{\partial x} T(\Delta x, x - \Delta x, t) \right) \Delta x d\Delta x \right)$$

$$= -\frac{1}{\gamma} \frac{\partial}{\partial x_0} \left(P(x_0, t) F'(x_0, t) \right)$$

Assume D const.:

2nd order term $D \Delta t \frac{\partial^2 P(x_0, t)}{\partial x^2}$.

→ Smoluchowski: $\frac{\partial P}{\partial t} = -\frac{\partial}{\partial x} \left(\frac{PF}{\gamma} \right) + \frac{\partial}{\partial x} D \frac{\partial P}{\partial x}$

$$P(x, t) \Leftrightarrow \rho(x, t).$$

→ $\frac{\partial \rho}{\partial t} = \nabla \cdot \left(\frac{\rho \underline{F}}{\gamma} - D \nabla \rho \right) = 0$ for $t \rightarrow \infty$ (equilibrium)

Solution: $\rho = e^{-U(x)/\gamma D}$

Hence $D = k_B T / \gamma$ Einstein relation.

Balance diffusion and drift for electrons:

$$j_{el} = -\rho \underline{F} / \gamma = -e j_{diff} = -D \frac{\partial \rho}{\partial x} = -D \frac{d}{dx} \left(C e^{-eV(x)/k_B T} \right)$$

$\rho = en$ ρ

$$= \frac{e D \underline{E} C}{k_B T} e^{-eV(x)/k_B T} = \frac{e D \underline{E}}{k_B T} \rho$$

We know that $\underline{j}_{el} = \sigma \underline{E}$, σ : conductivity.

Hence: $\sigma = \frac{e D \rho}{k_B T} = \frac{e^2 D n}{k_B T}$ n : number density.

Ohm's law.

Drude conductivity.

Summary Langevin equation and diffusion

Langevin eq: $m\dot{v} = -\gamma v + R(t)$

- ① $\langle R(t) \rangle = 0$;
- ② $\langle R(t)R(t+\tau) \rangle = \langle R^2 \rangle \delta(\tau)$;
- ③ $P(R) = \frac{1}{\sqrt{2\pi\langle R^2 \rangle}} e^{-R^2/2\langle R^2 \rangle}$

Properties of the solution:

$$\langle v(t) \rangle = v_0 e^{-\gamma t/m}$$

$$\langle v^2(t) \rangle = v_0^2 e^{-2\gamma t/m} + \frac{q}{2\gamma m} (1 - e^{-2\gamma t/m})$$

$$t \rightarrow \infty \quad \langle v^2(t) \rangle = \frac{q}{2\gamma m} = \frac{k_B T}{m} \rightarrow q = 2\gamma k_B T.$$

Distribution $P(v, t)$ satisfies the Langevin equation:

$$\frac{\partial P}{\partial t} = \gamma v \frac{\partial P}{\partial v} + \gamma k_B T \frac{\partial^2 P}{\partial v^2} \quad \text{Fokker Planck}$$

$$\frac{\partial P}{\partial t} = 0 \rightarrow P = C e^{-mv^2/2k_B T}$$

Solution for $x = \int^t v dt$:

$$\langle x^2(t) \rangle = 2Dt \quad D: \text{diff. coeff.}$$

$$D = k_B T / \gamma$$

Probability density for x satisfies the diffusion equation:

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial x} D(x) \frac{\partial}{\partial x} P ; \quad P = P(x, t)$$

Fick's law : $\underline{j} = D \underline{\nabla} p$ $p(\underline{r}, t)$: density $\sim P(\underline{r}, t)$

Continuity equ.: $\frac{\partial p}{\partial t} + \underline{\nabla} \cdot \underline{j} = 0$

Continuity equ. + Fick's law \rightarrow diffusion eq.

Introduce drift force F

Schmolukowsky eq. for $P(\underline{r}, t)$:

$$\frac{\partial P}{\partial t} = - \frac{\partial}{\partial x} \left(P \frac{F}{\gamma} \right) + \frac{\partial}{\partial x} D \frac{\partial}{\partial x} P$$