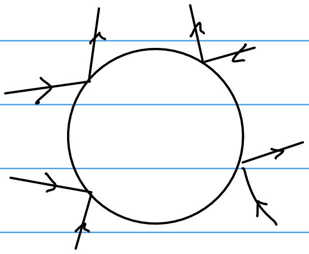
Fluctuations

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.

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

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

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

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

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

Discretiz time : time steps $t_1, t_2, \ldots\ldots$

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

Then
$$P(R_1, \ldots\ldots, R_N) = \frac{1}{(2\pi\langle R^2\rangle)^{N/2}}\, e^{-(R_1^2+\ldots+R_N^2)/2\langle R^2\rangle}$$

$$\simeq \frac{1}{(2\pi\langle R^2\rangle)^{N/2}}\, e^{-\frac{1}{2\pi\langle R^2\rangle\Delta t}\int_{t_1}^{t_N} R^2(t)\,dt}$$

$$\sim e^{-\frac{1}{2q}\int_{t_1}^{t_N} R^2(t)\,dt}$$

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

→ Discrete time

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

Solution of the Langevin equation

Consider $\underline{F} = 0$

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

Homogeneous equation, 1D

$$m\dot{\tilde{v}} = -\gamma \tilde{v} \; ; \; \tilde{v} = \tilde{v}_0\, e^{-\gamma t/m}$$

homogeneous solution.

Particular solution:

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

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

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

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

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

$\langle \quad \rangle = 0$

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

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

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

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

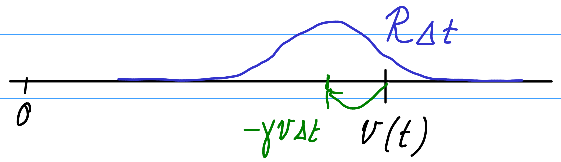
$$\langle v^2(t\to\infty)\rangle = \frac{q}{2\gamma m} = \underset{\neq}{\frac{k_B T}{m}} \Rightarrow \underline{\underline{q = 2\gamma k_B T}}$$

Langevin Equation.

$$m\dot{v} = -\gamma v + R \qquad m = 1.$$

$$P(v,t).$$

$$\underset{v}{v(t+\Delta t)} = \underset{v_{old}}{v(t)} + (-\gamma \underset{v_{old}}{v} + R)\Delta t.$$



$$P(v,t+\Delta t) = \int P(v_{old},t)\underbrace{\mathcal{P}(R\Delta t)}_{\text{Gauss.}}\ \delta(v - v_{old} - (-\gamma v_{old} + R)\Delta t)\, d(R\Delta t)\, dv_{old}$$

$$\delta(\lambda x - a) = \frac{1}{|\lambda|}\,\delta(x - a/\lambda).$$

$$P(v,t+\Delta t) = \frac{1}{1-\gamma\Delta t}\int P(v + (\gamma v - R)\Delta t, t)\,\mathcal{P}(R\ \Delta t)\, d(R\Delta t)$$

$$= \frac{1}{1-\gamma\Delta t}\int\left(P(v,t) + (\gamma v - \underset{\overset{\downarrow}{0}}{R})\Delta t\,\frac{\partial P(v,t)}{\partial v} + \frac{(\gamma v - R)^2\Delta t^2}{2}\frac{\partial^2 P}{\partial v^2}\right)\underbrace{\mathcal{P}(R\Delta t)}_{\text{norm.}}\, d(R\Delta t)$$

to order Δt:

$$P(v,t+\Delta t) = P(v,t)(1+\gamma\Delta t) + \gamma v\Delta t\frac{\partial P}{\partial v} + \frac{\gamma^2 v^2\Delta t^2}{2}\frac{\partial^2 P}{\partial v^2} + \underbrace{\frac{1}{2}\frac{\partial^2 P}{\partial v^2}\int (R\Delta t)^2\,\mathcal{P}(R\Delta t)\, d(R\Delta t)}_{\gamma k_B T\Delta t\,\frac{\partial^2 P}{\partial v^2}}$$

$$\langle R^2\rangle = \frac{q}{\Delta t} = \frac{2\gamma k_B T}{\Delta t}$$

$$\Rightarrow \underline{\frac{\partial P(v,t)}{\partial t} = \gamma\frac{\partial}{\partial v}\left(v\,P(v,t)\right) + \gamma k_B T\,\frac{\partial^2 P(v,t)}{\partial v^2}.}$$

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

In that case: $\underline{P(v) = C\,e^{-mv^2/2k_BT}}$. <u>Maxwell</u>

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:

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

$$\downarrow$$

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

$$m\dot{x}^2 = k_BT \rightarrow$$

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

$$m\frac{d}{dt}\underbrace{\langle x\dot{x}\rangle}_{y} + \gamma\langle x\dot{x}\rangle = k_BT + \underbrace{\langle \cancel{R(t)x(t)}\rangle}_{\substack{\shortparallel\\ 0}}$$

$$\Rightarrow m\langle x\dot{x}\rangle = C + Ae^{-\gamma t/m} \qquad \left(C = \frac{k_BT}{\gamma}\right)$$

$$t\rightarrow\infty: \quad \langle x\dot{x}\rangle = \frac{k_BT}{\gamma}$$

$$t=0: \quad \langle x\dot{x}\rangle = 0 \Rightarrow A = -k_BT/\gamma.$$

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

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

$$\frac{2k_BT}{\gamma}t + 2\frac{k_BT}{\gamma}\frac{m}{\gamma}\left(e^{-\gamma t/m} - 1\right)$$

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

$$= k_BT \frac{\gamma}{m} t^2$$

For $t \to \infty$ $$\langle x^2 \rangle = \frac{2k_BT}{\gamma}\left(t - \frac{m}{\gamma}\right) \simeq \frac{2k_BT}{\gamma} t = 2Dt$$

$$\rightarrow \underline{\underline{D = \frac{k_BT}{\gamma}}} \qquad \gamma = 6\pi\eta \underset{\substack{\downarrow \\ \text{radius}}}{a}, \ \eta = \text{viscosity.}$$

(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 $\langle \Delta x^2(t) \rangle = 2Dt$.

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

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

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

$$\int\left(P(x,t) - \overset{0}{\cancel{\Delta x}} \frac{\partial}{\partial x} P(x,t) + \frac{\Delta x^2}{2} \frac{\partial^2 P}{\partial x^2}(x,t)\right) T(\Delta x)\, dx$$

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

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

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

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

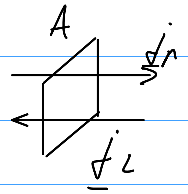
Here we have assumed $\Delta t \gtrsim \frac{m}{\gamma}$, in order to justify the diffusive limit.

On the other hand $\Delta x \lesssim \sqrt{Dt}$; $\quad D = \frac{k_B T}{\gamma}$

Ok for long enough time.

An alternative derivation

Fick's law.



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

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

Particle at $x_0 < 0$ crosses 0 :

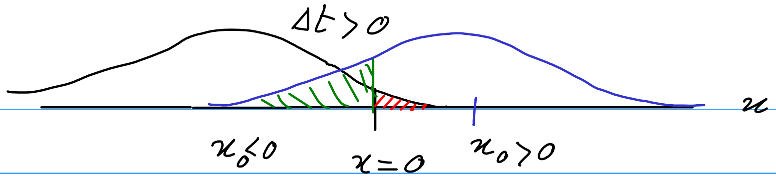
$$\int_0^\infty \frac{e^{-(x-x_0)^2/4D\Delta t}}{\sqrt{4\pi D\Delta t}}\,dx$$

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

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

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

$$x_0 - x = \tilde{x} \qquad \int_0^\infty dx \int_{-\infty}^{-x} \frac{\tilde{x}\,e^{-\tilde{x}^2/4D\cdot\cdot}}{\sqrt{\cdot\cdot}}\,dx_0 = \qquad -\int_0^\infty 2D\Delta t\; e^{-\tilde{x}^2/4D\cdot\cdot}\Big|_{-\infty}^{x}\,dx$$



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

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

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

$$\|$$

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

$$\rho(x_0,t) = \rho(0,t) + x_0\,\rho'(0,t).$$

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

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

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

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

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

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

Consider a volume V with a surface A.
Change in the amount of particles inside V:

$$\int_V \left(\rho(\underline{r},t+\Delta t)-\rho(t)\right) d^3r = \int_A \underline{j}\cdot d\underline{a}\;\Delta t$$

no sources/sinks.

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

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

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

$$\frac{\partial\rho}{\partial t} = \underline{\nabla}\left(D\,\underline{\nabla}\right)\rho$$

(Note: $\rho(\underline{r},t)\sim P(\underline{r},t)$)

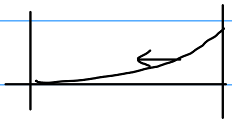
Introduce drift:

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

For F constant:

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

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



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

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

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

Note: $\gamma D = k_B T$

Now we generalize the diff eq, to this case

From $\gamma\langle v \rangle = F$:

$$x = x' + \frac{F}{\gamma}\Delta t + \Delta x$$

Gaussian. $\quad F(x')$

$$P(x, t+\Delta t) = \iint P(x',t)\,\delta\!\left(x - x' - \frac{F}{\gamma}\Delta t - \Delta x\right) T(\Delta x, \Delta t)\, dx'\, d\Delta x$$

$$\langle \Delta x \rangle = 0$$

$$\langle \Delta x^2 \rangle = 2D\Delta t$$

$$= \frac{1}{1 + \frac{dF}{dx'}\Delta t/\gamma} \int P\left(x - \frac{F}{\gamma}\Delta t - \Delta x, t\right) T(\Delta x, \Delta t)\, d\Delta x$$

$$= \left(1 - \frac{dF}{dx}\Delta t/\gamma\right) \int P(x,t) - \left(F/\gamma\, \Delta t + \Delta x\right)\frac{\partial P}{\partial x} + \frac{1}{2}\left(\frac{F\Delta t}{\gamma} + \Delta x\right)^2 \frac{\partial^2 P}{\partial x^2} \Big)\, T(\Delta x, \Delta t)\, d\Delta x$$

$$\Rightarrow P(x,t+\Delta t) = P(x,t) - \frac{dF}{dx}\frac{\Delta t}{\gamma} P(x,t) - \frac{F}{\gamma}\frac{\partial P}{\partial x} + \cancel{\mathcal{O}(\Delta t^2)} + \frac{1}{2}\frac{\partial^2 P}{\partial x^2} 2D\Delta t.$$

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

Einstein - Schmolukowski eqn.

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

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

Solution: $\rho = e^{-W(\underline{r})/\gamma D}$

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

Balance diffusion and drift for electrons:

$$j_{el} = -\rho F/\gamma = -e j_{diff} = -D\frac{\partial \rho}{\partial x} = -D\frac{d}{dx}\Big(\underbrace{Ce^{-eV(x)/k_BT}}_{\rho}\Big)$$

$\rho = en$

$$= \frac{eD\underline{E}}{k_B T} Ce^{-eV(x)/k_BT} = \frac{eD\underline{E}}{k_B T}\rho$$

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

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

Ohm's law. Drude conductivity.

Summary diffusion

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

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

Integrate $\underbrace{x(t) - x_0}_{\Delta x(t)} = \int_0^t v(t)\,dt$

$$\Rightarrow \langle \Delta x^2(t) \rangle = 2Dt, \quad D = \frac{k_B T}{\gamma}$$

Probability density for x satisfies the diffusion equation:

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

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

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

Continuity equ. + Fick's law → diffusion eq.

Introduce drift force F

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

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