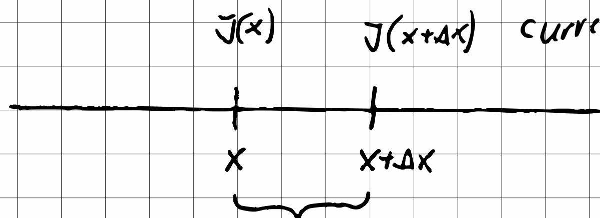
Lecture 30:

Diffusion, Currents & External forces.



current >0 if particles move to the right.

$$\underbrace{}\quad n(x,t) = \rho(x,t)\Delta x$$

number of particles in region.

Particles do not disappear/appear suddenly they have to flow into/or out of the region thru the boundaries.

The change in the number of particles is

$$\Delta n(x,t) = \Big(-J(x+\Delta x,t) + J(x,t)\Big)\Delta t$$

$$\frac{\overbrace{\Delta n(x,t)}^{\rho(x,t)\cancel{\Delta t}\Delta x}}{\Delta t} = -\Big(J(x+\Delta x,t) - J(x,t)\Big)\Big/\Delta x$$

$$\Rightarrow \frac{\partial \rho(x,t)}{\partial t} = -\frac{\partial J}{\partial x}(x,t)$$: Continuity eq.

If now $J = -D \frac{\partial \rho}{\partial x}$ then the continuity eq is

$$\frac{\partial \rho}{\partial t} = + D \frac{\partial^2 \rho}{\partial x^2} \quad : \text{Diffusion eq.}$$

So if particles obey the diffusion eq and if they don't suddenly disappear/appear. i.e. the cont. eq. holds

$$\Rightarrow \quad J = -D \frac{\partial \rho}{\partial x} \quad \text{Fick's law}$$

Particles move away from dense regions.

Note that this does not have to be a consequence of interactions between particles

A pure random walk process combined with the continuity eq. gives this.

External force

Often the random walk is on top of a force causing a steady motion.

Then $X(t+\Delta t) = X(t) + \ell + \overline{\Delta X}$

caused by an external force f

$$\overline{\Delta X} = \underset{\substack{\uparrow \\ \text{average velocity caused by the external force.}}}{V}\Delta t \equiv \underbrace{\overset{\substack{\text{mobility} \\ \downarrow}}{\gamma} f}_{V} \Delta t$$

f is the ext. force.

For a dilute gas we can calculate the mobility γ from the assumption that the particles has a constant acceleration inbetween collisions.

$$\Delta X = V_0 \Delta t + \frac{1}{2} \underbrace{\frac{f}{m}}_{\text{accel.}} (\Delta t)^2$$

long Δt's (Dilute gas)

The average $\overline{\Delta X}$ is gotten by averaging over all initial velocities V_0

$$\overline{\Delta X} \approx \langle V_0 \Delta t \rangle + \frac{1}{2}\frac{f}{m}(\Delta t)^2 \approx \frac{1}{2}\frac{f}{m}(\Delta t)^2$$

$$\Rightarrow V = \frac{\overline{\Delta x}}{\Delta t} = \frac{1}{2}\frac{F}{m}\Delta t \quad \Rightarrow \gamma = \frac{V}{F} = \frac{\Delta t}{2m}$$

Compare this to the Diffusion constant D

$$D = \frac{a^2}{2\Delta t} \qquad a^2 = \int dl\, l^2 \chi(l)$$

$$\gamma = \frac{\Delta t}{2m}\overbrace{D\cdot\frac{2\Delta t}{a^2}}^{1} = \frac{D}{m\left(\frac{a}{\Delta t}\right)^2} = \frac{D}{m\,\bar{V}^2}$$

$\bar{V} = \frac{a}{\Delta t}$: The random walk "velocity" coming from properties of the pure random walk.

Then repeat the derivation of the diff. eq.:

$$P(x, t+\Delta t) = \int dl\, P(x - \overline{\Delta x} + l, t)\,\chi(l)$$

expand P in gradients

$$P(x,t+\Delta t) = P(x,t)\overbrace{\int d\ell\, \chi(\ell)}^{1}$$

$$- \frac{\partial P}{\partial x}(x,t)\int d\ell\, (\overline{\Delta x}+\ell)\chi(\ell)$$

$$+ \frac{\partial^2 P}{2!\,\partial x^2}(x,t)\int d\ell\, (\overline{\Delta x}+\ell)^2\chi(\ell)$$

$$+ \dots$$

$$= P(x,t) - \frac{\partial P}{\partial x}(x,t)\,\overline{\Delta x}$$

$$+ \frac{\partial^2 P}{2!\,\partial x^2}(x,t)\left((\overline{\Delta x})^2 + a^2\right) + \dots$$

$$\frac{P(x,t+\Delta t) - P(x,t)}{\Delta t} = -\frac{\partial P}{\partial x}\underbrace{\frac{\overline{\Delta x}}{\Delta t}}_{\gamma F} + \frac{\partial^2 P}{\partial x^2}\underbrace{\left(\frac{(\overbrace{\overline{\Delta x}}^{\gamma F\cdot\Delta t})^2 + a^2}{2\Delta t}\right)}_{\frac{a^2}{2\Delta t} + \frac{\gamma^2 F^2}{2}\Delta t}$$

$$\approx \underbrace{\frac{a^2}{2\Delta t}}_{D} \quad \text{for small } \Delta t$$

Taking $\Delta t \to 0$

$$\frac{\partial P}{\partial t} = -\gamma F \frac{\partial P}{\partial x} + D \frac{\partial^2 P}{\partial x^2}$$

Or in terms of densities.

$$\frac{\partial \rho}{\partial t} = \underbrace{-\gamma F \frac{\partial \rho}{\partial x}}_{\substack{\text{Drift term} \\ \text{and is caused} \\ \text{by } F.}} + D \frac{\partial^2 \rho}{\partial x^2} .$$

With the external force the current gets an extra term

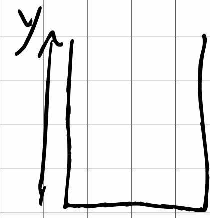
$$J = \gamma F \rho - D \frac{\partial \rho}{\partial x}$$

Cont. eq.

$$\frac{\partial \rho}{\partial t} = -\frac{\partial J}{\partial x} = -\gamma F \frac{\partial \rho}{\partial x} + D \frac{\partial^2 \rho}{\partial x^2} \; ✓$$

Example: Molecules ~~in~~ or earth... $F = -mg$

Steady state distribution $\frac{\partial \rho}{\partial t} = 0$



$$0 = -\gamma \underbrace{F}_{-mg} \frac{\partial \rho}{\partial y} + D \frac{\partial^2 \rho}{\partial y^2}$$

$$\Rightarrow \frac{\partial^2 \rho}{\partial y^2} = -\frac{\gamma m g}{D} \frac{\partial \rho}{\partial y}$$

$$\Rightarrow \frac{\partial \rho}{\partial y} = A e^{-\frac{\gamma m g}{D} y}$$

$$\Rightarrow \rho(y) = \frac{AD}{-\gamma m g} e^{-\frac{\gamma m g}{D} y} + B$$

for $y \to \infty$ we expect $\rho \to 0 \Rightarrow B = 0$

$$\rho > 0 \Rightarrow A < 0$$

$$\rho(y) \sim e^{-\frac{\gamma m g}{D} y}$$

$$\frac{\gamma m g}{D} = \frac{\overbrace{\cancel{D}}^{\gamma}}{m\bar{v}^2}\frac{mg}{\cancel{D}} = \frac{g}{\bar{v}^2}$$

for $\bar{v} \sim 10^3\, m/s$ and $g \sim 10\, m/s^2$

$$\Rightarrow \frac{\gamma m g}{D} = \frac{10\, m/s^2}{10^6\, m^2/s^2} = 10^{-5}\, m^{-1}$$

and

$$\xi \equiv \frac{\bar{v}^2}{g} = 10^5\, m = 100\, km \sim$$ Typical size of atmosphere.

Einstein relation

a random walk in presence of gravity gives

$$\rho = e^{-\frac{\gamma m g}{D} y}$$

In thermal equi'l, we expect:

$$\rho \sim e^{-\beta m g y}$$

comparing these: $\beta = \frac{\gamma}{D} \Rightarrow \boxed{D = \gamma k_B T}$ Eistein relation.

which is also reffered to as a fluctuation dissipation relation as $\frac{D}{k_B T}$ measures a fluctuation while γ is a measure of dissipation.

Solving the diffusion eq.

Green function approach: Green function.

$$\rho(x,t) = \int dy\, G(x-y,t)\, \rho(y,0)$$

Diff. eq.

$$\frac{\partial \rho}{\partial t} = \int dy\, \frac{\partial G}{\partial t}(x-y,t)\, \rho(y,0)$$

$$D \frac{\partial^2 \rho}{\partial x^2} = \int dy\, D \frac{\partial^2 G}{\partial x^2}(x-y,t)\, \rho(y,0)$$

$$\Rightarrow \quad \frac{\partial G}{\partial t}(x-y,t) = D\frac{\partial^2 G}{\partial x^2}(x-y,t)$$

at $t=0$ $\quad \rho(x,0) = \int dy\, G(x-y,0)\,\rho(y,0)$

$\Rightarrow \quad G(x-y,0) = \delta(x-y) \leftarrow$ Dirac δ-function.

Set $z = x-y$

$$\Rightarrow \quad \frac{\partial G(z,t)}{\partial t} = D\frac{\partial^2 G(z,t)}{\partial z^2} \quad , \quad G(z,0) = \delta(z)$$

Lets introduce Fourier-transforms.

$$G(z,t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dk\, \underbrace{G_k(t)}_{\text{fourier coeff.}}\, e^{ikz}$$

$$G_k(t) = \int_{-\infty}^{\infty} dz\, G(z,t)\, e^{-ikz}$$

$$\frac{\partial G(z,t)}{\partial t} = \frac{1}{2\pi}\int_{-\infty}^{\infty} dk \; \frac{\partial G_k(t)}{\partial t} e^{ikz}$$

$$D\frac{\partial^2 G}{\partial z^2}(z,t) = D\frac{1}{2\pi}\int_{-\infty}^{\infty} dk \; G_k(t)(ik)^2 e^{ikz}$$

$$\Rightarrow \quad \frac{\partial G_k(t)}{\partial t} = -G_k(t)k^2 D$$

$$\Rightarrow \quad G_k(t) = A\, e^{-Dk^2 t}$$

for $t=0$ $\quad G_k(0) = \int_{-\infty}^{\infty} dz \, \underbrace{G(z,0)}_{\delta(z)} e^{-ikz} = 1 \Rightarrow A = 1$

$$\boxed{G_k(t) = e^{-Dk^2 t}}$$

$G(z,t)$?

$$G(z,t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dk\, G_k(t)\, e^{ikz}$$

$$= \frac{1}{2\pi}\int_{-\infty}^{\infty} dk\, e^{\overbrace{-Dtk^2+ikz}^{-Dt\left(k-\frac{iz}{2Dt}\right)^2-\frac{z^2}{4Dt}}}$$

Re $Dt>0$ convergent.

$$= \frac{e^{-\frac{z^2}{4Dt}}}{2\pi}\int_{-\infty}^{\infty} dk\, e^{-\widetilde{Dt}\left(k-\frac{iz}{2Dt}\right)^2} \qquad k \to k + \frac{iz}{2Dt}$$

$$= \frac{e^{-z^2/4Dt}}{2\pi}\frac{1}{\sqrt{Dt}}\underbrace{\int_{-\infty}^{\infty} dk\sqrt{Dt}\, e^{-\left(\sqrt{Dt}\,k\right)^2}}_{\sqrt{\pi}}$$

$$= \frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2Dt}}\, e^{-\frac{z^2}{2\cdot 2Dt}}$$

A Gaussian with $\sigma^2 = 2Dt$, just as expected based on the random walk.

$$\rho(x,t) = \int dy \, \frac{1}{\sqrt{2\pi}\sqrt{2Dt}} \, e^{-\frac{(x-y)^2}{2\cdot 2Dt}} \, \rho(y,0)$$

Introducing also the fourier-transforms of the density

$$\rho_k(t) = \int dx \, \rho(x,t) \, e^{-ikx}$$

$$\rho(x,t) = \frac{1}{2\pi} \int dk \, \rho_k(t) \, e^{ikx}$$

Then

$$\rho_k(t) = \int dx \int dy \, G(x-y,t) \, \rho(y,0) \, e^{-ikx}$$

$$= \int dx \int dy \, G(x-y,t) e^{-ik(x-y)} \, \rho(y,0) e^{-iky}$$

$$x \to z+y$$

$$= G_k(t) \, \rho_k(0)$$

$$\rho(x,t) = \frac{1}{2\pi}\int dk\; G_k(t)\,\rho_k(0)\,e^{ikx}$$

$$= \frac{1}{2\pi}\int dk\; e^{-Dk^2t+ikx}\;\rho_k(0)$$

The effect of increasing t is to dampen/weaken the Fourier coeff. with large k^2

at time t, all k modes such that $\boxed{Dk^2t > 1}$ are small

And so Diffusion "smoothes" the density distribution by weakening the largest k^2 components first.