# 8.512 Recitation 11

- Pset 6 due Monday 05/09

Today: 1) Diffusion equation
2) Random walk in 1D
3) Langevin equation
4) Einstein relation and FDT

Ref: David Tong's lecture notes on kinetic theory

1) Consider the motion of particles in a fluid. Away from equilibrium, the particle density $n(\vec{x},t)$ is not constant, leading to a flow from high to low density regions.

- Number of particles is conserved $\Rightarrow$ continuity equation

$$\vec{\nabla}\cdot\vec{J}(\vec{x},t)+\frac{\partial n(\vec{x},t)}{\partial t}=0$$

- Since $\vec{J}$ is non-zero only in the presence of a particle gradient $\vec{\nabla}n$, one can take a hydrodynamic expansion in small gradients

$$\vec{J}(\vec{x},t)=-\underbrace{D}_{\text{Diffusion constant (yet to be determined)}}\vec{\nabla}n(\vec{x},t)+\ldots$$

Fick's law

- Combining the two yields the Diffusion equation

$$\frac{\partial n(\vec{x},t)}{\partial t}=D\nabla^2 n(\vec{x},t)$$

- If all $N$ particles start at the origin $\vec{x}=0$ then

$$n(\vec{x},t=0)=N\delta(\vec{x})$$

- The solution is a Gaussian in $d$-dimensions

$$\boxed{n(\vec{x},t) = \frac{\mathcal{N}}{(4\pi D|t|)^{d/2}} e^{-\frac{|\vec{x}|^2}{4D|t|}}}$$

$$\int d^d\vec{x}\; n(\vec{x},t) = \mathcal{N}$$

- Note that $\langle \vec{x}(t) \rangle = 0$

$$\langle |\vec{x}(t)|^2 \rangle = \frac{1}{\mathcal{N}} \int d^d\vec{x}\, |\vec{x}|^2 n(\vec{x},t) = 2dD|t|$$

- How is $D$ related to microscopic quantities?

2) First consider a simplified problem for the 1D random walk: after each time step $\tau$, the particle moves by $\ell$ to either right or left w/ equal prob.

$\ell$ = mean free path between collisions
$\tau$ = time between collisions w/ fluid

- Start at $x=0$ and let $P(x,t)$ be the prob. that particle is at $x = n\ell$ at time $t = \mathcal{N}\tau$ ($\mathcal{N} \gg n$)

- Particle made $\frac{1}{2}(\mathcal{N}+n)$ jumps to the right
$\frac{1}{2}(\mathcal{N}-n)$ jumps to the left

$$\Rightarrow P(x,t) = \frac{1}{2^{\mathcal{N}}} \cdot \frac{\mathcal{N}!}{\left(\frac{1}{2}(\mathcal{N}+n)\right)! \left(\frac{1}{2}(\mathcal{N}-n)\right)!} \approx \sqrt{\frac{2}{\pi\mathcal{N}}} \cdot e^{-\frac{n^2}{2\mathcal{N}}} = \sqrt{\frac{2\tau}{\pi t}}\, e^{-\frac{x^2\tau}{2\ell^2 t}}$$

Stirling's approximation

$$\log(\mathcal{N}!) = \mathcal{N}\log\mathcal{N} - \mathcal{N} + \frac{1}{2}\log(2\pi) + \frac{1}{2}\log\mathcal{N}$$

$\Rightarrow P(x,t)$ is a Gaussian and $\langle x \rangle = 0$

$$\langle x^2(t) \rangle = \frac{\ell^2}{\tau} t$$

- For $d=1$ we identify the diffusion constant

- For $d=1$ we identify the diffusion constant

$$\boxed{D = \frac{\ell^2}{2\tau}}$$

- Note that the rms distance $\sqrt{\langle x^2 \rangle} \sim \sqrt{t}$ is a characteristic behavior for random walks!

3) Now consider a less crude approximation for the motion of a particle in a viscous fluid:

$$m\ddot{\vec{x}} = \underbrace{-\gamma\dot{\vec{x}}}_{\text{viscous drag}} + \underbrace{\vec{F}}_{\substack{\text{constant force} \\ \text{(e.g. gravity)}}} + \underbrace{\vec{f}(t)}_{\substack{\text{random force} \\ \text{due to fluid collisions}}} \qquad \text{(Langevin Equation)}$$

- $\mu \equiv \frac{1}{\gamma}$ is called mobility

- This is an example of a Stochastic ODE describing Brownian motion

- The collisions are random so $\langle \vec{f}(t) \rangle = 0$
- At $t_2 - t_1 \gg \tau$, different uncorrelated atoms contribute to collisions $\Rightarrow$ $\langle f_i(t_1) f_j(t_2) \rangle = 0$ at $t_2 - t_1 \gg \tau$

- For fast relaxation times $\tau \to 0$ we have

$$\langle f_i(t_1) f_j(t_2) \rangle = \Gamma \delta_{ij} \delta(t_1 - t_2)$$

- Such an $\vec{f}(t)$ is called white noise

- We can solve Langevin's equation via

$$\frac{d}{dt}\left(m\vec{v}(t)e^{\gamma t/m}\right) = \vec{F}e^{\gamma t/m} + \vec{f}(t)e^{\gamma t/m}$$

$$\Rightarrow \vec{v}(t) = \vec{v}(0)e^{-\gamma t/m} + \frac{\vec{F}}{\gamma}\left(1 - e^{-\gamma t/m}\right) + \frac{1}{m}\int^{t} ds\, \vec{f}(s)e^{\gamma(s-t)/m}$$

$$\Rightarrow \quad \vec{v}(t) = \vec{V}(0)\, e^{-\gamma t/m} + \frac{\vec{F}}{\gamma}\left(1 - e^{-\gamma t/m}\right) + \frac{1}{m}\int_0^t ds\, \vec{f}(s)\, e^{\gamma(s-t)/m}$$

$$\langle \vec{V}(t) \rangle = \vec{V}(0)\, e^{-\gamma t/m} + \frac{\vec{F}}{\gamma}\left(1 - e^{-\gamma t/m}\right)$$

- At $\gamma t \gg m$ the initial conditions are forgotten and we recover the terminal velocity

$$\langle \vec{V}(t\to\infty) \rangle = \frac{\vec{F}}{\gamma}$$

- Similarly $\langle V_i(t_1) V_j(t_2) \rangle = \langle V_i(t_1) \rangle \langle V_j(t_2) \rangle +$

$$+ \frac{1}{m^2}\int_0^{t_1} dt_1' \int_0^{t_2} dt_2' \langle f_i(t_1') f_j(t_2') \rangle\, e^{\frac{\gamma}{m}(t_1'+t_2'-t_1-t_2)}$$

$$= \langle V_i(t_1) \rangle \langle V_j(t_2) \rangle + \frac{\Gamma}{2\gamma m}\delta_{ij}\left(e^{-\gamma|t_2-t_1|/m} - e^{-\gamma|t_2+t_1|/m}\right)$$

- The equal time autocorrelation is

$$\langle |\vec{V}(t)|^2 \rangle = \langle \vec{V}(t) \rangle^2 + \frac{d\Gamma}{2\gamma m}\left(1 - e^{-2\gamma t/m}\right)$$

- In the absense of an external potential $\vec{F}=0$ and at late times $t\to\infty$, the particle should thermalize w/ environment at temperature $T$:

$$\langle \vec{V}(t\to\infty) \rangle = 0$$

$$\frac{m}{2}\langle \vec{V}(t\to\infty)^2 \rangle = \frac{m}{2}\cdot\frac{d\Gamma}{2\gamma m} = \frac{d}{2} k_B T$$

$$\Rightarrow \quad \boxed{\Gamma = 2\gamma k_B T}$$

Also $\langle \vec{V}(0)\cdot\vec{V}(t) \rangle = \langle \vec{V}(0) \rangle \langle \vec{V}(t) \rangle + \cancel{\frac{d\Gamma}{2\gamma m}\left(e^{-\gamma t/m} - e^{-\gamma t/m}\right)}$

$$= |\vec{V}(0)|^2\, e^{-\gamma t/m} = d\cdot\frac{k_B T}{m}\, e^{-\gamma t/m}$$

- We can also solve for

- We can also solve for

$$\vec{x}(t) = \vec{x}(0) + \int_0^t dt' \, \vec{v}(t')$$

$$= \vec{x}(0) + \int_0^t dt' \left[ \vec{v}(0) e^{-\gamma t'/m} + \frac{\vec{F}}{\gamma}(1 - e^{-\gamma t'/m}) + \frac{1}{m}\int_0^{t'} ds \, \vec{f}(s) \, e^{\gamma(s-t')/m} \right]$$

$$\langle \vec{x}(t) \rangle = \vec{x}(0) + \frac{\vec{F}t}{\gamma} + \left(\vec{v}(0) - \frac{\vec{F}}{\gamma}\right) \cdot \frac{m}{\gamma}\left(1 - e^{-\gamma t/m}\right)$$

- At early times $\gamma t \ll m$ the motion is ballistic

$$\langle \vec{x}(t) \rangle \simeq \vec{x}(0) + \vec{v}(0)\, t + \frac{\vec{F}}{m} \cdot \frac{t^2}{2}$$

- At late times $\gamma t \gg m$

$$\langle x_i(t_1) \, x_j(t_2) \rangle = \langle x_i(t_1) \rangle \langle x_j(t_2) \rangle +$$

$$+ \frac{1}{m^2} \int_0^{t_1} dt_1' \int_0^{t_2} dt_2' \int_0^{t_1'} ds_1 \int_0^{t_2'} ds_2 \, \langle f_i(s_1) f_j(s_2) \rangle \, e^{\gamma(s_1 + s_2 - t_1' - t_2')/m}$$

$$= \langle x_i(t_1) \rangle \langle x_j(t_2) \rangle + \frac{\Gamma}{\gamma^2} \delta_{ij} \min(t_1, t_2)$$

$$\langle |\vec{x}(t)|^2 \rangle = \langle \vec{x}(t) \rangle^2 + \frac{d \Gamma t}{\gamma^2} \qquad \text{for } t \geq 0$$

- Recall that for diffusion

$$\langle \vec{x}(t) \rangle = 0$$
$$\langle |\vec{x}(t)|^2 \rangle = 2dD|t|$$

The two eqs. match if $\boxed{D = \frac{\Gamma}{2\gamma^2} = \frac{k_B T}{\gamma} = \mu k_B T}$

Einstein relation

- This tells us that both diffusion and viscosity have the same microscopic origin, i.e. atom collisions.

4) Recall the response function of a damped oscillator

$$\ddot{x}_i + \gamma \dot{x}_i + \omega_0^2 x_i = F_i$$

$$\chi_{ii}(\omega) = \frac{1}{\omega_0^2 - \omega^2 - i\gamma\omega}$$

- The Langevin equation corresponds to the limit $\begin{matrix} \omega_0 = 0 \\ \omega \to 0 \end{matrix}$

$$\Rightarrow \chi_{ii}(\omega) \approx \frac{i}{\gamma\omega} \quad \Rightarrow \chi''_{ii}(\omega) = \frac{1}{\gamma\omega}$$

- On the other hand

$$S_{ii}(\omega) = \int_{-\infty}^{\infty} dt\, e^{i\omega t} \langle x_i(t) x_i(0) \rangle = \underbrace{\int_{-\infty}^{\infty} dt\, e^{i\omega t} \langle x_i(\tfrac{t}{2}) x_i(-\tfrac{t}{2}) \rangle}_{\text{trans. inv.}} = \int_{-\infty}^{\infty} dt\, e^{i\omega t} D|t| = \frac{2D}{\omega^2}$$

- FDT relates the two $\quad S_{ii}(\omega) = \frac{2k_BT}{\omega} \chi''_{ii}(\omega)$

$$\frac{2D}{\omega^2} = \frac{2k_BT}{\gamma\omega^2} \iff \boxed{D = \frac{k_BT}{\gamma}}$$

- This clearly shows that Einstein's relation is an immediate consequence of FDT!