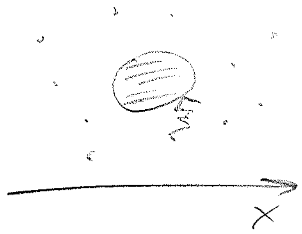
§1 Diffusion

Colloidal particle suspended in fluid.



Eq. of motion for fluid particles

$$\dot{p}_i = -\frac{\partial H}{\partial q_i}, \quad \dot{q}_i = \frac{\partial H}{\partial p_i}$$

Temperature characterises chaotic motion

$$\frac{m}{2}\langle \dot{q}_i^2 \rangle = \frac{k_B T}{2}$$

Stochastic motion of colloid (Newton's 2nd law)

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

$x(t) \equiv$ position of colloid
$f(t) \equiv$ random force

- inertia negligible on long time scales $\tau \gg m/\gamma$.

Statistics of the random force

- Symmetry $\langle f(t) \rangle = 0$.
- Correlation time $\langle f(t) f(t+\tau) \rangle \to 0$ for $\tau \gg \tau_c$

  Exercise: estimate τ_c.
- Stationarity:

$$\frac{1}{\gamma^2}\int_{-\infty}^{\infty} d\tau \, f(t) f(t+\tau) = 2D$$

D indep of t. $[D] = \frac{m^2}{s}$

Aim $x(t)$?

Formal solution

$$x(t) = x(0) + \frac{1}{\gamma}\int_0^t dt_1 \, f(t_1)$$

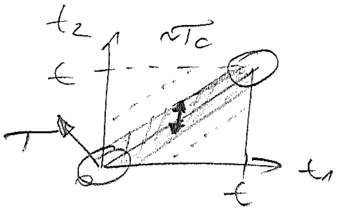
Statistics of diffusive paths.

$$\Delta x(t) = x(t) - x(0)$$

$$\langle \Delta x \rangle = 0$$ by symmetry.

$$\langle \Delta x^2 \rangle = ?$$

$$\langle \Delta x^2 \rangle = \frac{1}{\gamma^2}\left\langle \left(\int_0^t dt_1 \, f(t_1)\right)\left(\int_0^t dt_2 \, f(t_2)\right)\right\rangle$$



$$= \frac{1}{\gamma^2}\int_0^t dt_1 \int_0^t dt_2 \, \langle f(t_1) \, f(t_2) \rangle$$

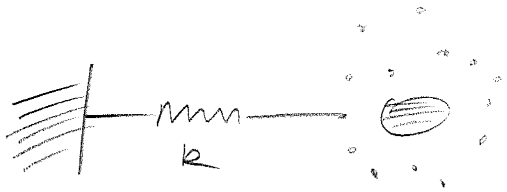
$$= \frac{1}{\gamma^2}\int_0^t dt_1 \int_{-t_1}^{t-t_1} d\tau \, \langle f(t_1) \, f(t_1+\tau) \rangle$$ Change of variables.

$$\approx \; -\,''\,- \; \underbrace{\int_{-\infty}^{\infty} d\tau \; -\,''\,-}_{\gamma^2 2D} \; + O(D\tau_c)$$

$$= 2D \cdot t + O(D\tau_c)$$

Aim $D = D(T)$?

Trick: add elastic spring.



$$kx + \gamma \dot{x} = f(t).$$

Equipartition theorem

$$\langle \tfrac{k}{2} x^2 \rangle = \frac{k_B T}{2}.$$

Pulse response

$$kx + \gamma \dot{x} = p_0\, \delta(t), \qquad x(t) = 0,\ t < 0.$$

$$\Rightarrow x(t) = p_0 \,.\, \chi(t)$$

$$\chi(t) = \frac{1}{\gamma} \exp(-t/\sigma)\, \Theta(t)$$

≡ linear response function

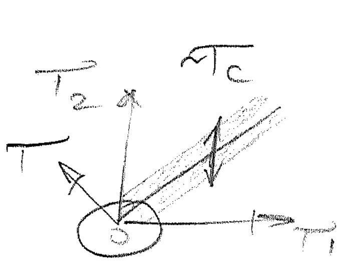
$\sigma = \gamma / k$ ≡ relaxation time scale

$[\sigma] = s$.

Formal solution

$$x(t) = \int_0^\infty dT\, f(t-T)\, \chi(T)$$

$$\langle x^2 \rangle = \left\langle \left(\int_0^\infty dT_1\, f(t-T_1)\, \chi(T_1) \right) \left(\int_0^\infty dT_2\, f(t-T_2)\, \chi(T_2) \right) \right\rangle$$



$$= \int_0^\infty dT_1 \int_0^\infty dT_2\, \langle f(t-T_1) f(t-T_2) \rangle\, \underbrace{\chi(T_1)\chi(T_2)}$$

$$= \frac{1}{\gamma^2} \exp\left(-\frac{T_1}{\sigma}\right) \Theta(T_1) \exp\left(-\frac{T_2}{\sigma}\right) \Theta(T_2)$$

$$= \frac{1}{\gamma^2} \exp\left(-\frac{T_1 + T_2}{\sigma}\right) \Theta(T_1)\, \Theta(T_2)$$

change of variables

$$= \int_0^\infty dT_1 \int_{-T_1}^\infty dT\, \langle f(t-T_1)\, f(t-T_1-T) \rangle \cdot \frac{1}{\gamma^2} \exp\left(-\frac{2T_1 + T}{\sigma}\right)$$

$$\approx \;\text{—''—}\; \int_{-\infty}^{\infty} d\tau \;\text{—''—}\; + O(D\tau_c)$$

$$= \frac{1}{\gamma^2}\int_0^\infty d\tau_1 \exp\left(-\frac{2\tau_1}{\sigma}\right) \underbrace{\int_{-\infty}^{\infty} d\tau \langle f(0) f(-\tau)\rangle \underbrace{\exp\left(-\frac{\tau}{\sigma}\right)}_{\approx 1 \text{ for } \tau_c \ll \sigma}}_{\gamma^2 2D}$$

$$= \underbrace{\frac{1}{\gamma^2}\cdot\frac{\sigma}{2}\cdot\gamma^2 2D}_{\frac{\gamma}{k}D} + O(D\tau_c)$$

$$\frac{k}{2}\langle x^2\rangle = \frac{k}{2}\frac{\gamma}{k}D \overset{(*)}{=} \frac{k_B T}{2}$$

$$\Rightarrow \boxed{D = \frac{k_B T}{\gamma}}$$

= Stokes-Einstein relation

= 1st example of fluctuation-dissipation theorem

Numerics of stochastic processes:

Heuristic example:

$$\gamma \dot{x} = f(t)$$

$x_n = x(t_n)$, $t_n = n \cdot dt$ ≡ discrete time

$u_n = x_{n+1} - x_n$ ≡ updates

$$u_n = \int_{t_n}^{t_{n+1}} dt \; f(t)/\gamma .$$

$\langle u_n \rangle = 0$, $\langle u_n^2 \rangle = 2D \cdot dt$, $\langle u_n \cdot u_{n+1} \rangle \approx 0$

$\longrightarrow$

$u_n \approx \sqrt{2D} \cdot dW_n$

$dW_n \sim \mathcal{N}(0, dt)$ ≡ independent normally distributed random variables.

$$x_{n+1} = x_n + \sqrt{2D} \cdot dW_n$$

≡ explicit Euler scheme

(NB. Be careful if $D = D(x)$.)

$\boxed{\text{Example}}$

- $\frac{m}{2} \bar{v}^2 = \frac{k_B T}{2}$

- m $\qquad m = 1 \text{Da}$

$12 a \cdot N_A = 12 g \quad (C)$

$N_A = 6 \cdot 10^{23}$

$m = 5 \cdot 10^{-26}$ kg

- $k_B T = 4 \cdot 10^{-21}$ J $= 4$ pN $\cdot$ nm

- $\bar{v} = 360$ m/s $=$ speed of sound.
- $a_{H_2O} = 3$ Å

- $T_0 = \frac{a}{v} = 10^{-12}$ s $= \underline{\underline{1 \text{ps}}}$

- Typical diffusion coefficient.

$\gamma = 6\pi \eta r$

$\eta_{H_2O} \quad \frac{1 \text{pN} \cdot 1 \text{ms}}{(1 \mu m)^2} = 10^{-3}$ Pa.s

- $r = 1 \mu m \Rightarrow \gamma = 2 \cdot 10^{-8}$ $N \frac{s}{m}$

$D = \frac{k_B T}{\gamma} = 2 \cdot 10^{-13} \cdot \frac{m^2}{s} = 0.5 \cdot \frac{\mu m^2}{s}$.

- protein $\quad r = 2$ nm $\Rightarrow \gamma = 4 \cdot 10^{-11}$ $N \frac{s}{m}$

$D = \frac{k_B T}{\gamma} = 10^{-10} \frac{m^2}{s} = 100 \frac{\mu m^2}{s}$