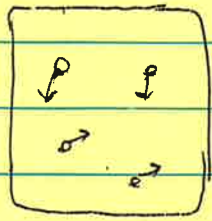
CHEMENG 468. 09/24/2024.

- Elementary Kinetics (gas).

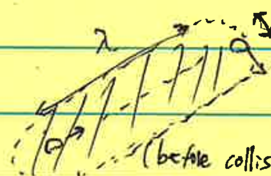


- Velocity distribution : $f(\vec{v}) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \cdot \exp\left(-\frac{m|\vec{v}|^2}{2k_B T}\right)$.

"Collision" is needed to reach equilibrium.
(no collision in ideal gas).

- Transport coefficient of gases : η, k, D
(by Maxwell + collision). viscosity conductivity. diffusivity.

- Mean free path (λ) : $\lambda = \lambda(T, \sigma^2,$



Freely moving volume $\approx \lambda\sigma^2 \Rightarrow \rho \sim \frac{1}{\lambda\sigma^2}$ (density).

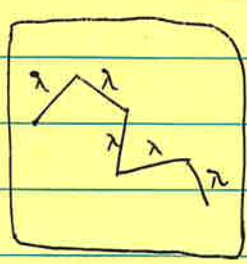
Using $p = \rho k_B T \longrightarrow \lambda \sim \frac{1}{\rho\sigma^2} \sim \frac{k_B T}{p\sigma^2}$

$\therefore \lambda \sim \frac{k_B T}{p\sigma^2} \sim 50\,nm$ (approx).

Then, $t \sim \frac{\lambda}{\langle \vec{v}^2\rangle^{1/2}}$

$\Rightarrow t \sim \frac{k_B T}{p\sigma^2}\sqrt{\frac{m}{k_B T}} = \frac{(k_B T)^{1/2} m^{1/2}}{p\sigma^2}$

Recall $\langle \frac{1}{2} m v^2 \rangle = \frac{3}{2} k_B T$.
so that $\langle \vec{v}^2 \rangle^{1/2} \sim \sqrt{k_B T / m}$
used for both gas & liquid.
Note : $\langle \vec{v} \rangle$ might be zero!



$$\boxed{D = \lambda^2/t \sim \lambda \langle v^2 \rangle^{1/2} \sim \frac{(k_B T)^{3/2}}{p\sigma^2 m^{1/2}}}$$

Gas Kinetics.

09/26/2024.

- $D_{gas} \sim \lambda \bar{v}$ $\left\{ \begin{array}{l} \bar{v} = \langle v^2 \rangle^{1/2} \sim \sqrt{k_B T/m} \\ \lambda \sim \frac{1}{\rho \sigma^2} \end{array} \right.$

$\Rightarrow \boxed{D_{gas} \sim \frac{T^{3/2}}{p\, m^{1/2}}}$

- Scaling (gas).

$\bar{v} \sim 10^2$ m/s (sound, 340 m/s).

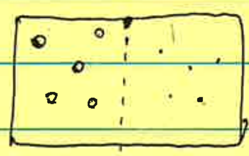
$\sigma \sim 1$ Å

$\lambda \sim 50-100$ nm.

$\tau \sim 1$ ns (upper bound).

3 types of transport.

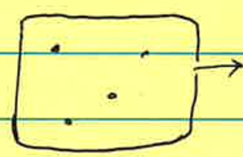
- Diffusion.



$D_{gas} \sim 10^{-5}$ m²/s

E.g.) About 1cm per second.

- Effusion.



$\because$ no collision, (D does not affect)

flux $\sim \rho \bar{v}$

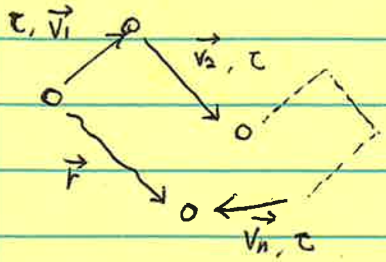
Q) Is it only for pinhole?

What if pinhole increase?

E.g.) propagation of scent (D ~ 1cm/s is not dominant)

- Convection.

- D_{gas} (more precise calculation).



$\vec{r}$ = displacement after n^{th} collision.

Assume all times are τ.

$\Rightarrow$ "Dynamic mean-field distribution."

$$\vec{r} = \left(\sum_{i=1}^{n} \vec{v}_i\right)\tau = \vec{v}_1 \tau + \vec{v}_2 \cdot \tau + \cdots + \vec{v}_n \cdot \tau.$$

Concentration $c(\vec{r}, t) \rightarrow t = n\tau.$

$$c(\vec{r}, t) = \left\langle \delta\left(\vec{r} - \tau \sum_{i=1}^{n} \vec{v}_i\right)\right\rangle \quad \text{(average over collision history)}$$

We introduce Fourier Transform, $(\vec{r} \rightarrow \vec{k})$

$$c(\vec{k}, t) = \int d\vec{r}\; c(\vec{r}, t)\, e^{-j\vec{k}\cdot\vec{r}} = \left\langle \int d\vec{r}\, e^{-j\vec{k}\cdot\vec{r}} \cdot \delta\left(\vec{r} - \sum_{i=1}^{n} \vec{v}_i \tau\right)\right\rangle$$

$$= \left\langle \exp\left(-j\vec{k}\tau \sum_{i=1}^{n} \vec{v}_i\right)\right\rangle = \left\langle e^{-j\vec{k}\tau\vec{v}_1} \cdot e^{-j\vec{k}\tau\vec{v}_2} \cdots e^{-j\vec{k}\tau\vec{v}_n}\right\rangle$$

$$= \left\langle e^{-j\vec{k}\tau\vec{v}_1}\right\rangle \cdots \left\langle e^{-j\vec{k}\cdot\tau\vec{v}_n}\right\rangle = \prod_{i=1}^{n} \left\langle e^{-j\vec{k}\cdot\tau\vec{v}_i}\right\rangle$$

Recall that $\langle e^{\pm jkx}\rangle = e^{-k^2\sigma^2/2}$ when $P(x) = \frac{1}{\sqrt{2\pi\sigma^2}} \cdot e^{-x^2/(2\sigma^2)}$.

Since $P(v_i) \sim$ Gaussian, $c(\vec{k}, t) = \prod_{i=1}^{n} e^{-\frac{k^2\tau^2}{2} \cdot \frac{k_B T}{m}}$ $\left(\because\ \sigma^2 = (\bar{v})^2 = \frac{k_B T}{m}\right)$

$$\Rightarrow c(\vec{k}, t) = \exp\left(-\frac{k^2(n\tau)}{2} \cdot \frac{\tau k_B T}{m}\right) = \exp\left(-k^2 t \cdot \frac{\tau k_B T}{2m}\right)$$

Note $\exp(-k^2 D t)$ $\Rightarrow D = \frac{k_B T}{2m} \cdot \tau = \frac{k_B T}{2m} \cdot \frac{\lambda}{\bar{v}} = \bar{v}^2 \frac{\lambda}{\bar{v}} = \lambda\bar{v}$ (Already from Maxwell!)

Diffusivity

Liquids

$1\,\text{Å} \sim \lambda \sim \sigma \rightarrow$ gas $\rightarrow$ liquid.

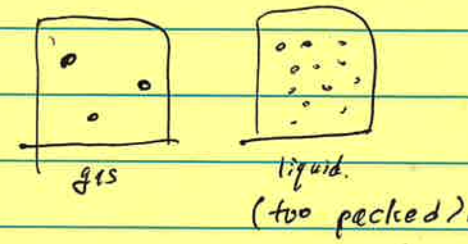
$t_{collision} = \sigma/\bar{v} \sim 10^{-10}/10^{2} = 10^{-12}\,s \sim 1\,ps$ (Experiment, $0.1\,ps \sim h/(k_B T)$)

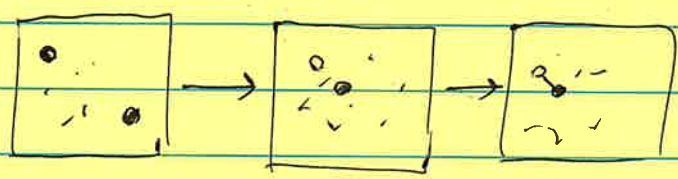
$t_{rotation} \sim 1\,ps$

$t_{diffusion} \sim \sigma^2 / D_{liquid}$ ($D \sim 10^{-9}\ m^2/s$) $\boxed{1\,ns \rightarrow 1\,nm}$

$\sim 10\,ps$

(much slower than collision & rotation)





$A + B \underset{k_d'}{\overset{k_d}{\rightleftarrows}} AB \xrightarrow{k_a} P$

come close　　react.

$k_a \gg k_d'$: diffusion controlled.

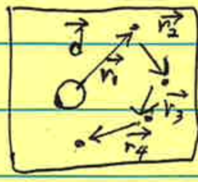
$k_a \ll k_d'$: activation controlled.

(dominated by slow process).

Diffusion.

10/01/2024.

- Brownian motion (1827)



distance.

① $\langle \vec{d} \rangle = 0$

② $\langle \vec{d}^2 \rangle = \langle (\vec{d} - \langle \vec{d} \rangle)^2 \rangle = \sigma^2$

③ Displacement $\vec{R}(t) \Rightarrow \langle R(t) \rangle = 0$

④ $\langle \vec{R}(t)^2 \rangle = \langle \{ \vec{R}(t) - \langle R(t) \rangle \}^2 \rangle \propto t$ (MSD)

(for B.M.)

Note: $\underline{MSD = 2dD \cdot t}$ where $D = \mu k_B T$ (diffusivity). —— (1)

Q) How to prove (show)?

(1) Random walk

$$\vec{R}(t) = \sum_{i=1}^{n} \vec{r_i} \Rightarrow \|\vec{R}(t)\|^2 = \sum_{i=1}^{n} \vec{r_i} \cdot \sum_{j=1}^{n} \vec{r_j} = \sum_{i=1}^{n} \sum_{j=1}^{n} \vec{r_i} \cdot \vec{r_j}$$

$$\Rightarrow \langle \vec{R}(t)^2 \rangle = \langle \sum_{i=1}^{n} \sum_{j=1}^{n} \vec{r_i} \cdot \vec{r_j} \rangle = \sum_{i=1}^{n} \sum_{j=1}^{n} \langle \vec{r_i} \cdot \vec{r_j} \rangle = \sum_{i=1}^{n} \langle \vec{r_i}^2 \rangle$$

(assume $i \neq j$ $\boxed{\text{uncorrelated}}$)

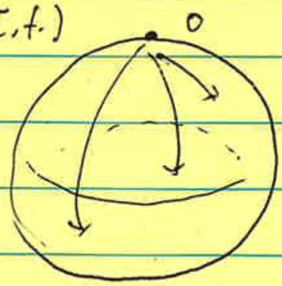
$$= n\sigma^2 = \underbrace{(n\tau)}_{= t} \underbrace{(\sigma^2/\tau)}_{= 2dD}.$$

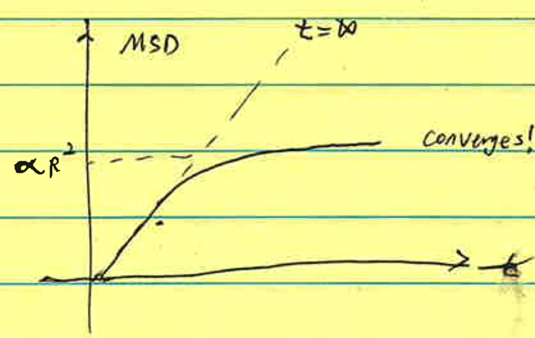
Recall that $\vec{R}^2 = R_x^2 + R_y^2 + R_z^2 \Leftrightarrow \langle \vec{R}^2 \rangle = \langle R_x^2 + R_y^2 + R_z^2 \rangle = d \cdot \langle \vec{R_x}^2 \rangle$

Therefore, $\langle \vec{R} \rangle^2 = d \cdot \langle \vec{R_x}^2 \rangle = d \langle \vec{R_y}^2 \rangle = \cdots$

$\therefore$ In (1), d is multiplied.

c.f.)





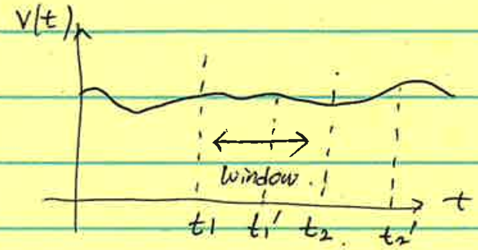
Linear relation in (1) only holds for short time.

As $t \to \infty$ depends on spatial configuration.

(2) Velocity correlation.

$$\vec{R}(t) = \int_0^t d\tau \, \vec{v}(\tau) \Rightarrow MSD = \langle \vec{R}(t)^2 \rangle = \langle \int_0^t d\tau_1 v(\tau_1) \cdot \int_0^t d\tau_2 v(\tau_2) \rangle$$

$$\Rightarrow MSD = \int_0^t d\tau_1 \int_0^t d\tau_2 \underbrace{\langle \vec{v}(\tau_1) \cdot \vec{v}(\tau_2) \rangle}_{\text{velocity correlation. } \boxed{\text{temporal correlation}}} = \int_0^t d\tau \{ \vec{v}^2(\tau) \} \nearrow \text{Wrong!}$$



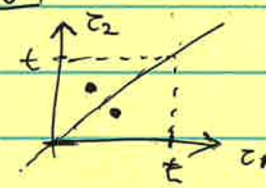
Note: Temporal correlation is well-defined only for stationary states.
For activated states, not well-defined
∵ v(t) profile should be static to measure temporal correlation

Stationary : $\Delta t = t_2 - t_1 = t_2' - t_1'$

$$\Rightarrow \langle \vec{v}(t_1) \cdot \vec{v}(t_2) \rangle = \langle \vec{v}(0) \cdot \vec{v}(t_2 - t_1) \rangle \text{ if system is } \boxed{\text{stationary}}.$$

$$= \langle \vec{v}(0) \cdot \vec{v}(t_1 - t_2) \rangle$$

↳ $\boxed{\text{Time reversal symmetry}}$?



$$MSD = \int_0^t d\tau_1 \int_0^t d\tau_2 \langle \vec{v}(\tau_1) \cdot \vec{v}(\tau_2) \rangle = \int_0^t d\tau_1 \int_0^t d\tau_2 . \langle \vec{v}(0) \cdot \vec{v}(|t_2 - t_1|) \rangle$$

(∵ Time reversal symmetry)

$$= \underbrace{\int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \langle \vec{v}(0) \cdot \vec{v}(\tau_1 - \tau_2) \rangle}_{(\tau_1 > \tau_2)} + \underbrace{\int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \langle \vec{v}(0) \cdot \vec{v}(\tau_2 - \tau_1) \rangle}_{(\tau_2 > \tau_1)}$$

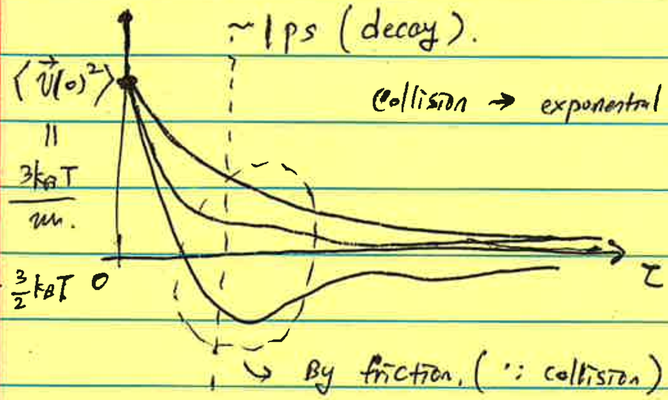
$$= 2 \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \langle \vec{v}(0) \cdot \vec{v}(\tau_1 - \tau_2) \rangle \rightarrow \text{substitute } \tau_1 - \tau_2 = \tau.$$

$$-d\tau_2 = d\tau$$

$$= 2 \int_0^t d\tau_1 \int_0^{\tau_1} d\tau \langle \vec{v}(0) \cdot \vec{v}(\tau) \rangle$$

(2) Vel. corr. continued ...

$\langle \vec{v}(0) \cdot \vec{v}(\tau) \rangle$



Collision → exponential decay (Enskog)

Energy

$\because \frac{1}{2} m \langle \vec{v}_0^{\,2} \rangle = \frac{3}{2} k_B T$

By friction. ($\because$ collision) — depends on structure (intrinsic)

• Diffusion (continued).

10/03/2024.

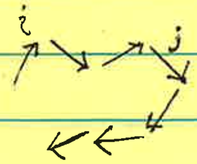
$$MSD = 2\int_0^t dt_1 \int_0^{t_1} dt_2 \, \langle v(\tau)\cdot v(0)\rangle = 2\int_0^t dt_1 \int_0^{t_1} d\tau \, \langle v(\tau)\cdot v(0)\rangle$$

$(\tau = t_2 - t_1)$.

Picture 2 : V - Corr

$$MSD = 2dDt \quad \text{(long term behavior)}.$$

$$2dDt = 2\int_0^t dt_1 \int_0^{t_1} d\tau \, \langle v(\tau)\cdot v(0)\rangle \quad \text{(take derivative)?}$$



Note : For long time, i, j are uncorrelated

However short time they are correlated

$\underline{MSD = 2dDt}$ holds for $\boxed{\text{long - time}}$ only.

Therefore, as $t \to \infty$

$$\lim_{t\to\infty} \frac{d}{dt} MSD = 2dD = \lim_{t\to\infty} \frac{d}{dt}\left(2\int_0^t dt_1 \sim \right)$$

$$\Rightarrow \quad D = \frac{1}{\cancel{2}d} \lim_{t\to\infty} \frac{d}{dt} \cancel{2}\int_0^t dt_1 \int_0^{t_1} d\tau \, \langle \vec{v}(\tau)\, \vec{v}(0)\rangle.$$

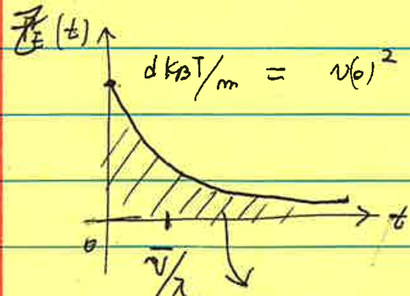
$$\Rightarrow \quad \underline{D = \frac{1}{d}\cdot \lim_{t\to\infty} \int_0^t d\tau \cdot \langle \vec{v}(\tau)\cdot \vec{v}(0)\rangle} \quad \text{(Definition of diffusivity)}$$

$$= \frac{1}{d}\int_0^\infty d\tau \langle \vec{v}(\tau)\cdot \vec{v}(0)\rangle \quad \text{[Green-Kubo Relation]} \quad (1)$$

E.g.) Enskog representation of $\langle \vec{v}(t)\cdot \vec{v}(0)\rangle = Z(t)$.

$$Z_E(t) = d\cdot k_B T/m \cdot \exp\left(-\frac{2\Gamma_E}{3} t\right) \quad \text{where} \quad \Gamma_E = \frac{(k_B T/m)^{1/2}}{\lambda} \quad [1/s]$$

$$= \frac{\bar{v}}{\lambda}$$



Diffusivity (D). (∵ (1))

$$D \sim \int_0^\infty d\tau \; \bar{v}^2 \exp\left(-\frac{2\Gamma_E}{3} t\right)$$

$$\propto \bar{v}^2 \frac{1}{\Gamma_E} = \bar{v}^2 \cdot \frac{\lambda}{\bar{v}} = \bar{v}\lambda$$

Picture 3

Langevin equation.

Picture 1 was displacement x, Picture 2 was velocity $\dot{x}$

now picture 3 is acceleration $\ddot{x}$.

$$m\ddot{x} = \text{force} = \underbrace{\text{friction}}_{\substack{\text{make it stop} \\ \text{after } t\to\infty \\ \text{(slow down)}}} + \underbrace{\text{random}}_{\substack{\text{make it escape} \\ \text{after } t\to\infty. \\ \text{(thermalize)}}} = -\xi\dot{x} + B(t).$$

Solve $\Rightarrow$ $m\ddot{x} + \xi\dot{x} = B(t) \Rightarrow v(t) = v(0)\cdot\exp\left(-\frac{\xi t}{m}\right) + \int_0^t d\tau\, \exp\left(-\frac{\xi(t-\tau)}{m}\right)\cdot R(\tau).$

$\exp\left(-\frac{\xi(t-\tau)}{m}\right)$: after-effect (affects only the future).

Related averages involves two contributions : $\vec{v}(0)$ and $R(t)$.

Now, we can calculate $\langle \vec{v}(\tau)\cdot\vec{v}(0)\rangle$.

$$\langle \vec{v}(0)\cdot\vec{v}(t)\rangle = \left\langle \{\vec{v}(0)\cdot\vec{v}(0)\}\, \underbrace{e^{-\frac{\xi t}{m}}}_{\substack{\text{doesn't depend} \\ \text{on } v(0).}} \right\rangle + \left\langle \int_0^t d\tau\, e^{-\frac{\xi(t-\tau)}{m}}\, v(0)R(\tau) \right\rangle$$

$$= \langle \vec{v}(0)\cdot\vec{v}(0)\rangle\, e^{-\xi t/m} + \int_0^t d\tau\, e^{-\frac{\xi(t-\tau)}{m}} \langle \vec{v}(0)\cdot\vec{R}(\tau)\rangle$$

$$= \underbrace{\frac{d k_B T}{m} e^{-\xi/m \cdot t}} + \underbrace{\cancel{0}}_{\substack{\text{(Random force \& velocity are not} \\ \text{correlated).}}}$$

$$= \frac{d k_B T}{m} \exp\left(-\frac{2\Gamma_E}{3} t\right) \quad \text{(from Enskog).}$$

$\therefore$ collision rate (Enskog) $\equiv$ Friction. #

Since we know that $\langle v(t)\, v(0) \rangle = \frac{d k_B T}{m} \cdot e^{-\xi/m \cdot t}$

~~Substitute to~~

Substitute to $D = 1/d \cdot \int_0^\infty dt\, \frac{d k_B T}{m} e^{-\xi/m \cdot t} = \frac{k_B T}{\xi} = \mu k_B T$

(Einstein relation).

From stoke's relation, $\xi = 6\pi \eta R$ $\quad \boxed{\therefore D = \frac{k_B T}{6\pi \eta R}}$

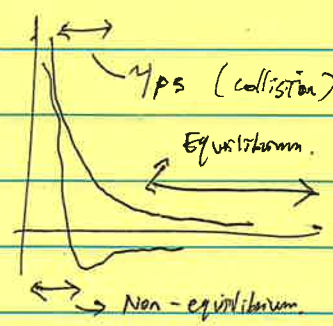
- $t \to \infty$ behavior.

$\langle \vec{v}(t) \rangle = 0$

$\langle \vec{v}(t) \cdot \vec{v}(t) \rangle$ = thermal equilibrium value $= d k_B T / m$.

$\langle \vec{R}(t) \rangle = 0$

Q) $\langle \vec{v}(0) \cdot \vec{R}(t) \rangle = 0$? $\quad \int_0^t d\tau\, e^{-\xi(t-\tau)/m} \langle \vec{v}(0) \cdot \vec{R}(\tau) \rangle$



But $\langle \vec{v}(0) \cdot \vec{R}(\tau) \rangle$ might not be zero at $t \ll 1$ because at the very beginning $\vec{v}(0)$ somehow affects the force (random) $\vec{R}(\tau)$.

Conclusion : The theory only covers $t \gg 1$ps (collision time).

so that you can think $\int_{\delta t}^\infty dt$ (///) where $\delta t \gg 1$ps

So only interested in

the time region way beyond non-equilibrium state ($t \gg$ collide time).

Langevin Equation.

10/08/2024

- Velocity equation.

$m \cdot d\vec{v}/dt = -\xi \vec{v} + \vec{R}(t)$

$\Rightarrow \vec{v}(t) = \underbrace{\vec{v}(0)}_{\text{initial velocity}} \cdot \exp\left(-\frac{\xi}{m} \cdot t\right) + \frac{1}{m} \cdot \int_0^t d\tau \cdot \exp\left(-\frac{\xi}{m}(t-\tau)\right) \cdot \underbrace{R(\tau)}_{\text{random force decay}}$

Goal
{ We showed from $\langle \vec{v}(t)\, \vec{v}(0) \rangle$, that
$\langle \vec{R}(t) \rangle = 0$, $\langle \vec{R}(t)\, \vec{v}(0) \rangle = 0$ and we shall derive,
$\langle \vec{R}(t)\, \vec{R}(t') \rangle = ?$ (Note: From $\langle \vec{v}(t)\, \vec{v}(0) \rangle$, $D = k_BT/\xi$ (Einstein)) }

Let us focus on,

$\langle \vec{v}(t \to \infty)^2 \rangle \leftarrow$ equilibrium statistics (all memory is gone)

$\Rightarrow \langle \vec{v}(t\to\infty)^2 \rangle = d\, k_BT/m$. —— $(*)$

$\Rightarrow \vec{v}(t\to\infty) = 0 + \frac{1}{m} \cdot \lim_{t\to\infty} \int_0^t d\tau \cdot \exp\left(-\frac{\xi}{m}(t-\tau)\right) R(\tau)$. —— ①

Plugging in ① to $(*)$,

$\langle \vec{v}(t\to\infty)^2 \rangle = \left\langle \frac{1}{m^2} \int_0^t dt_1\, e^{-\frac{\xi}{m}(t-t_1)} \int_0^t dt_2\, e^{-\frac{\xi}{m}(t-t_2)} \cdot \vec{R}(t_1) \cdot \vec{R}(t_2) \right.$

$= \frac{1}{m^2} \cdot \int_0^t dt_1\, e^{-\frac{\xi}{m}(t-t_1)} \int_0^t dt_2\, e^{-\frac{\xi}{m}(t-t_2)} \langle \vec{R}(t_1) \cdot \vec{R}(t_2) \rangle$

$\because$ ensemble of R (randomness)!

Recall that system has <u>no memory</u>,

$\langle \vec{R}(t) \otimes \vec{R}(t') \rangle = \gamma\, I \cdot \delta(t-t')$ $\because$ diagonal matrix since no correlation x, y, z.

dyadic product. white noise.

$= \begin{pmatrix} \gamma & 0 & 0 \\ 0 & \gamma & 0 \\ 0 & 0 & \gamma \end{pmatrix} \delta(t-t')$

Therefore, $\langle \vec{R}(t) \cdot \vec{R}(t') \rangle = d\gamma\, \delta(t-t') = tr(\vec{R}(t) \otimes \vec{R}(t'))$

Then, plug into ①,

$\Rightarrow \langle \vec{v}(t\to\infty)^2 \rangle = \frac{d\gamma}{m^2} \cdot \int_0^t dt_1\, e^{-\frac{2\xi}{m}(t-t_1)} \Big|_{t\to\infty}$

$$= \frac{d\gamma}{m^2} \int_0^{\infty} dt_1 \, e^{-\frac{2\xi(\infty - t_1)}{m}}$$ (t_1 also goes to ∞ so we are safe!)

$\Rightarrow -t + t_1 = \tau$. where $\tau \in [t, -t+\infty] = [-\infty, 0]$ (if $t = \infty$)

$$= \frac{d\gamma}{m^2} \cdot \int_{-\infty}^{0} d\tau \, e^{+2\xi\tau/m}$$ [means how history $\tau \in [-\infty, 0]$ affects the time correlation of velocities.]

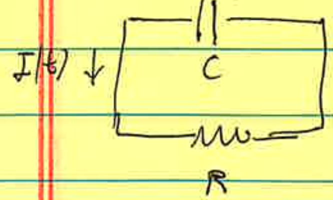
$\Rightarrow \langle \vec{v}(t\to\infty)^2 \rangle = \frac{d\gamma}{m^2} \cdot \frac{m}{2\xi} = d\, k_B T / m$ (from equilibrium).

$\boxed{\therefore \; \underbrace{\gamma}_{\substack{\text{Noise} \\ \text{(fluctuation)}}} = 2 \underbrace{\xi}_{\substack{\text{Friction} \\ \text{(dissipation)}}} \cdot k_B T}$ $\rightarrow$ Fluctuation - Dissipation Theorem. —— (3).

{Note: Noise and friction are both originating from "collisions"
$\Rightarrow$ They are correlated by (3).}

- Example: Johnson noise (1928) $\longrightarrow$ Nyquist theorem

~ noise depends on resistance (R), temperature ($k_B T$)
$\downarrow$ collisions. $\downarrow$ collision $\uparrow$



$I \cdot R + Q/C = V_r(t) \rightarrow$ Random noise.

$\langle V_r(t) \rangle = 0$, $\langle V_r(t) V_r(t') \rangle = \gamma \delta(t - t')$

$$\Rightarrow R \frac{dQ}{dt} = \underbrace{-\frac{1}{C} Q}_{\text{drift}} + \underbrace{V_r(t)}_{\text{source}}$$

$$\Rightarrow Q(t) = Q(0) \cdot e^{-\frac{t}{RC}} + \frac{1}{R} \int_0^t d\tau \cdot e^{-\frac{t-\tau}{RC}} V_r(\tau).$$

(each D.O.F gets $\frac{1}{2} k_B T$)

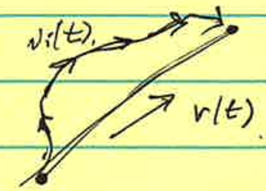
$\Rightarrow \langle Q(t\to\infty)^2 \rangle = \frac{\gamma C}{2R}$ since $\langle E_c = \frac{Q^2}{2C} \rangle = \frac{1}{2} k_B T$ $\because$ equipartition

$\Rightarrow \langle Q(\infty)^2 \rangle = C \cdot k_B T$.

$\boxed{\therefore \gamma = 2 k_B T \cdot R}$

We have shown $\langle \vec{v}(0) \cdot \vec{v}(t) \rangle \rightarrow$ Einstein.

$\langle \vec{v}(t)^2 \rangle_{t \to \infty} \Rightarrow$ FDT.

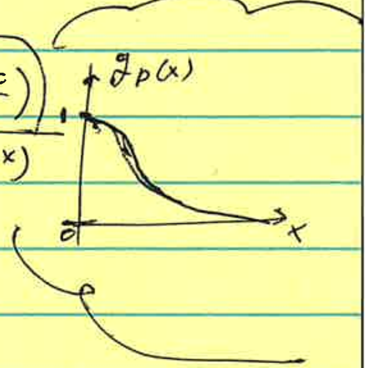


Now we can do $MSD = \langle \vec{r}(t)^2 \rangle = \left\langle \left(\int_0^t d\tau (v(\tau)) \right)^2 \right\rangle$

$\rightsquigarrow$ noise history average $\rightsquigarrow$ $= \boxed{\frac{d k_B T}{m} \cdot t^2 \cdot g_D\left(\frac{\xi t}{m}\right)}$

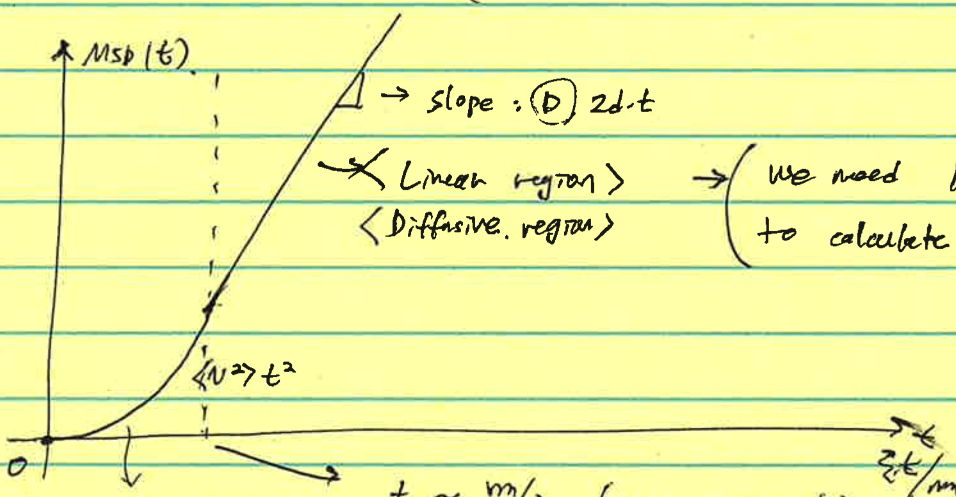
where $g_D = \frac{2}{x^2}(x - 1 + e^{-x})$

$\rightarrow$ Debye function.



Note : $MSD = \underbrace{d k_B T / m}_{\langle v^2 \rangle} \cdot t^2 \cdot g_D(\xi t / m)$

$\langle v^2 \rangle \, t^2 \, g_D(\xi t / m)$



$\rightarrow$ (We need long time regime to calculate D constant).

$t \sim m/\xi$ (memory gone!)

$\sim \langle v^2 \rangle t^2$

physically, $r \approx v t$

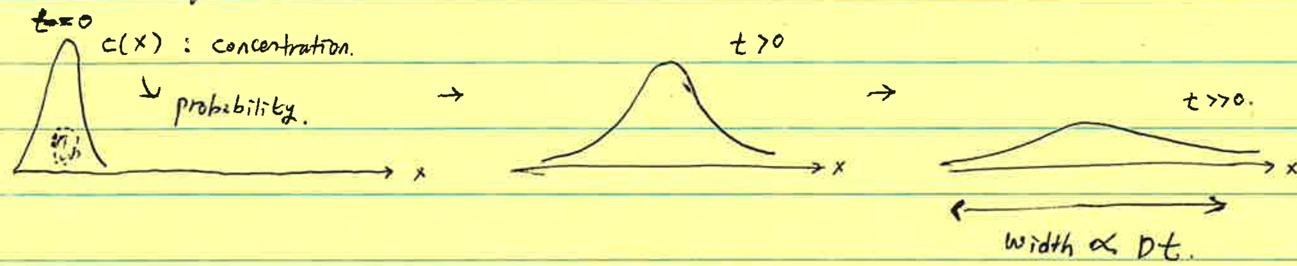
Newton!

<Ballistic region>

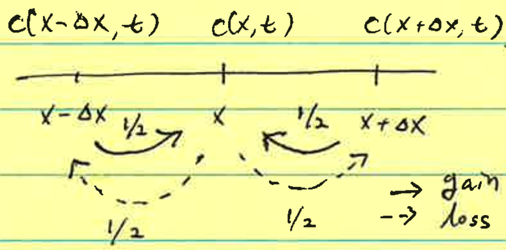
10/10/2024.

We have done, $\underbrace{\text{MSD, Green-Kubo, Langevin + Einstein}}_{\text{single trajectory.}}$ + $\underbrace{\text{Diffusion equation.}}_{\text{collective.}}$

- Diffusion equation.



Assume,



Q) what is $c(x, t+\Delta t)$?

→ use conservation law.

half of them move. (prob = 1/2).

$$\Rightarrow c(x, t+\Delta t) = \frac{1}{2} c(x-\Delta x, t) + \frac{1}{2} c(x+\Delta x, t)$$

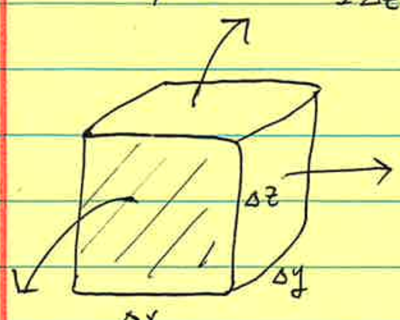
$$\Rightarrow c(x, t+\Delta t) - c(x,t) = \frac{1}{2}\left(c(x-\Delta x, t) - c(x,t)\right) + \frac{1}{2}\left(c(x+\Delta x, t) - c(x,t)\right)$$

$$\Rightarrow \partial c/\partial t \cdot \Delta t = \frac{1}{2}\Delta x \left\{ \partial c/\partial x \left(x + \frac{\Delta x}{2}\right) - \frac{\partial c}{\partial x}\left(x - \frac{\Delta x}{2}\right) \right\}$$

$$= (\Delta x)^2/2 \cdot \left\{ \partial^2 c/\partial x^2 (x,t) \right\}$$

$$\Rightarrow \partial c/\partial t = \frac{(\Delta x)^2}{2\Delta t} \partial^2 c/\partial x^2 \Rightarrow \boxed{\frac{\partial c}{\partial t} = D \nabla^2 c} \quad \left(D = \frac{(\Delta x)^2}{2\Delta t}\right)$$

Diffusivity.



In 'd' dimension, you have 'd' more terms (flux)

$$\Rightarrow \partial c/\partial t = D \nabla^2 c \quad \text{for } c(\vec{r}, t) \ (\vec{r} \in \mathbb{R}^d)$$

where $D = \frac{(\Delta x)^2}{2d\Delta t}$ → diffusivity.

dimension

- Solve for MSD from diffusion equation.

$$MSD = \int_{-\infty}^{+\infty} dx \cdot \underbrace{c(x,t)}_{\downarrow} \cdot x^2 \rightarrow \text{Apply solution of } c(x,t) \quad \text{———} (*)$$

$\| \langle x^2 \rangle$ with I.C., $c(x, t=0) = \delta(x)$

Must be normalized (∵ contribution)

(i) Solve $\partial c/\partial t = D\, \partial^2 c/\partial x^2$

Fourier transform $\mathcal{F}\{c\} = \hat{c}(k,t) = \int_{-\infty}^{\infty} dx\, e^{-jkx} c(x,t)$

$$\mathcal{F}^{-1}\{\hat{c}\} = c(x,t) = \int_{-\infty}^{\infty} dk\, e^{jkx}\, \hat{c}(k,t) \cdot \frac{1}{2\pi}$$

Note that $\hat{c} \cdot (jk)^n = \mathcal{F}\{\frac{\partial^n}{\partial x^n} c\}$

Therefore, $\partial/\partial t\ \hat{c}(k,t) = (jk)^2 \cdot D \cdot \hat{c}(k,t)$

$\Rightarrow \partial/\partial t \cdot \hat{c} = -k^2 D \cdot \hat{c}$ where $\hat{c}(k,0) = 1$

$\Rightarrow \hat{c}(k,t) = e^{-Dk^2 t}\, \hat{c}(k,0) = \underline{e^{-Dk^2 t} \cdot 1}$

Thus,

$$c(x,t) = \mathcal{F}^{-1}\{e^{-Dk^2 t}\} = \frac{1}{\sqrt{4\pi D t}}\, e^{-\frac{x^2}{4Dt}} \quad \text{———} (1)$$

$\left(∵ \langle e^{jkx} \rangle = e^{-k^2\sigma^2/2} \right.$ where $x \sim N(0, \sigma^2)$

in this case, $\left. \sigma^2/2 = Dt. \right)$

(ii) Plug in $c(x,t)$ into $(*)$ to get MSD.

Since $c(x,t) \sim$ Gaussian,

$MSD = \int dx \cdot c(x,t) \cdot x^2$ represents the 'variance' of X.

$\therefore$ $\underline{MSD = 2Dt.}$

- Higher dimension, 'd'

$$c(x,y,t) = \left(\frac{1}{\sqrt{4\pi D t}}\, e^{-\frac{x^2}{4Dt}} \right)^2 \cdots \rightarrow c(x, \cdots, x_d, t) = \left(/// \right)^d$$

• Langevin dynamics — Diffusion equation.

① → $P(x,t)$ finding particle at x at t probability. → Diffusion equation. ⎫ Smoluchowski

② → $P(v,t)$ from Langevin dynamics → Fokker–Plank equation. ⎭

Using ① + ② → $P(v, x; t)$ ⇝ Kramers equation. $\boxed{\text{within potential}}$

↳ In many regimes $\begin{cases} \text{underdamped} & \xi < 1 \\ \text{critical damped} & \xi = 0 \\ \text{overdamped} & \xi > 1 \end{cases}$

E.g.) External $\vec{E}$ ~ potential.

10/15/2024.

Last week),

Diffusion equation : $c_t = D\, c_{xx}$ where $\int c = 1 \rightarrow$ probability.

$$\Rightarrow c(x,t) = \frac{1}{\sqrt{4\pi D t}} \exp\left(-\frac{x^2}{4Dt}\right) \quad (1\text{-}D).$$

$$(\langle x^2 \rangle = \sigma^2 = 2Dt)$$

Expand to N-dimension, $c(x,y,t) = \left(\frac{1}{\sqrt{4\pi D t}} e^{-\frac{x^2}{4Dt}}\right)\left(\frac{1}{\sqrt{4\pi D t}} e^{-\frac{y^2}{4Dt}}\right) \cdots$

Entropy increases,

# of possible config = 1 $<$ # of possible config = ∞

$S_0 < S_t$ (entropy).

$$S(t) = -k_B \cdot \int_{-\infty}^{\infty} dx \cdot \underbrace{c(x,t) \log\left[c(x,t)\, v\right]}_{\text{Gibbs expression of Entropy.}}$$

v → small volume : normalization constant.

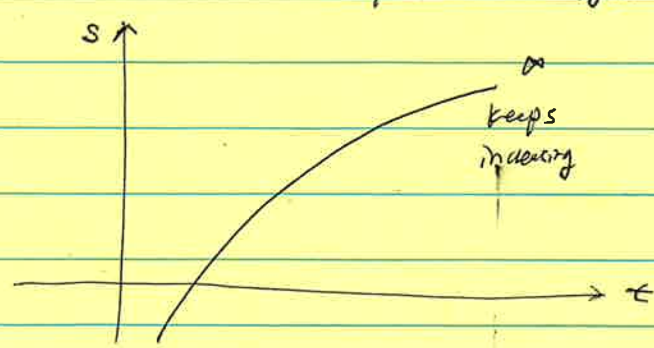
$$= -k_B \langle \log[c(x,t)\cdot v] \rangle = k_B \left\langle \frac{x^2}{4Dt} + \frac{1}{2}\log(4\pi D t)\right\rangle - k_B \langle \log(v) \rangle$$

$$= \langle x^2 \rangle \cdot \frac{k_B}{4Dt} + \frac{k_B}{2}\log(4\pi D t) - k_B \cdot \log(v)$$

$$= 2Dt \cdot k_B/(4Dt) + k_B/2 \cdot \log(4\pi D t) - k_B \log v$$

$$= \frac{k_B}{2}\log(2Dt) + \underbrace{\left(\frac{k_B}{2} + \frac{k_B}{2}\log(2\pi) - k_B \ln v\right)}_{\text{constant.}}$$

↳ Diffusion produces entropy with rate ~ log t



$$\therefore S(t) = k_B \cdot \log\left(\frac{(2Dt)^{1/2}}{v}\right) + k.$$

$$\approx k_B \log\left(\frac{(MSD)^{1/2}}{v}\right) + k$$

$v = R^d$

u

v

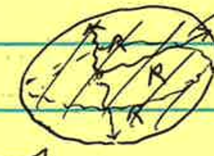
$$\Rightarrow \quad S(t) = k_B \cdot \log\left(\frac{\overset{\text{distance walked}}{R^d}}{v}\right) + \kappa$$

$$= k_B \log(\Omega)$$

v

Within $t > 0$ that $S(t) \nless 0$.

Q) what is R^d and Ω



$\rightarrow R^d$ (volume traveled)

$\therefore \frac{R^d}{v} = \#$ of possible states. $= \Omega$

- Fokker - Plank Equation (FPE) - "conservation of probability"

→ Focus on velocity. $p(v,t)$. s.t. $p(v,t)\,dv$ = Prob finding velocity in $[v, v+dv]$.

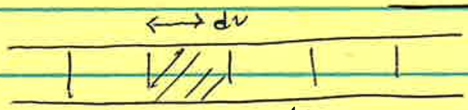
→ Conservation law (1 - dimm)

$$\int_{-\infty}^{\infty} dv \; p(v,t) = 1$$

We can come up with a model,

$\longleftrightarrow dv$

$v = -\infty$



$v = +\infty$

$v - dv$ v $v + dv$

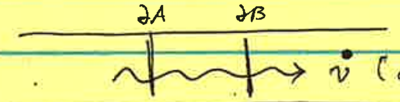
$p(v-dv, t)\,dv$ $p(v,t)\,dv$ $p(v+dv, t)\,dv$

in a short time range,

How does p evolve in t?

Acceleration! → $\dot{v} = dv/dt$.

∂A ∂B



$\dot{v}$ (defined direction).

If $\dot{v}$ is given (directional),*

Gain shall happen at ∂A

Loss shall happen at ∂B

⇒ Loss : $-\dot{v}\, P(v + dv/2, t)$

⇒ Gain : $+\dot{v}\, P(v - dv/2, t)$

$$\Rightarrow \frac{\partial P}{\partial t} \cdot dv = \dot{v}\, P(v + dv/2, t) - \dot{v}\, P(v - dv/2, t) \quad \text{— (1)}$$

From (1), $\frac{\partial}{\partial t} P = -\frac{\partial}{\partial v}\Big(\underbrace{\dot{v}\, P}_{=\text{Flux}}\Big)$: Local conservation (stricter).

→ "Louiville equation."

$$\int_{-\infty}^{\infty} dv \; p(v,t) = 1 \quad : \text{Global conservation. (weak).}$$

- Connection with Langevin Dynamics $\left(m\dot{v} = -\xi v + R. \right)$

$$\left\langle \frac{\partial}{\partial t} P(v,t) = \frac{\partial}{\partial v}\left[(\xi v - R)\, P(v,t) \right] \cdot \frac{1}{m} \right\rangle_R \Rightarrow \text{"FPE"}$$

Observe $P(v,t) \longrightarrow P(v,t+\Delta t)$ and integrate RHS.

$$P(v,t+\Delta t) = P(v,t) + \frac{1}{m}\int_t^{t+\Delta t} d\tau \frac{\partial}{\partial v}\left[(\xi v - R)\, P(v,\tau) \right]$$

Since $\tau > t$, $\rightarrow$ replace $t+\Delta t \rightarrow \tau$ for $P(\tau)$ $R(\tau)$.

$$\Rightarrow \text{LHS} = P(v,t) + \frac{1}{m}\cdot \int_t^{t+\Delta t} d\tau \frac{\partial}{\partial v}\left\{ (\xi v - R(\tau)) \cdot P(v,t+\Delta t) \right\}$$

$$= P(v,t) + \underbrace{\frac{1}{m} \cdot \int_t^{t+\Delta t} d\tau \frac{\partial}{\partial v}\left[(\xi v - R(\tau)) \cdot \left(P(v,t) \right.\right.}_{①} + \underbrace{\frac{1}{m}\int_t^{\tau} dt_2 \frac{\partial}{\partial v}\left((v - R(t_2))\, P(v,t_2) \right)}_{③} \left.\left.\right)\right]$$

① After averaging,

$$\Rightarrow \frac{1}{m}\int_t^{t+\Delta t} d\tau \frac{\partial}{\partial v}\left(\xi v - \cancel{R(\tau)} \right) P(v,t) \quad \text{term goes,}$$

$\cancel{R(\tau)} \rightarrow 0$

$$\Rightarrow \frac{\Delta t}{m}\left(\frac{\partial}{\partial v}\left(\xi v\, P(v,t) \right) \right)$$

② $$\frac{1}{m^2}\underbrace{\int_t^{t+\Delta t} d\tau}_{\Delta t} \underbrace{\int_t^{t_1} dt_2}_{\Delta t} \left\langle \frac{\partial}{\partial v}\left(\xi v - R(\tau) \right) \frac{\partial}{\partial v}\left(\xi v - R(t_2) \right) \right\rangle_R P(v,t)$$

$$\Rightarrow \begin{cases} \xi v \text{ and } \xi v \rightarrow \cancel{O((\Delta t)^2)} \\ \xi v \text{ and } R(\tau) \rightarrow \cancel{O((\Delta t)^{3/2})} \\ \xi v \text{ and } R(t_2) \rightarrow \cancel{O((\Delta t)^{3/2})} \\ R(\tau) \text{ and } R(t_2) \rightarrow O(\Delta t). \end{cases} \rightarrow 0.$$

$$= \frac{1}{m^2}\int_t^{t+\Delta t} d\tau \int_t^{\tau} dt_2 \frac{\partial}{\partial v}\frac{\partial}{\partial v} \langle R(\tau) R(t_2) \rangle \cdot P(v,t)$$

$$\langle R(\tau) R(t_2) \rangle = \gamma\,\delta(t_1 - t_2) = 2\xi k_B T\, \delta(t_1 - t_2)$$

Therefore, ② $= \frac{\gamma}{m^2} \frac{\partial}{\partial v} \frac{\partial}{\partial v} \cdot \int_t^{t+\Delta t} d\tau \int_t^{\tau} dt_2 \, \delta(t_2 - \tau) \cdot P(v, \tau)$

$= \frac{\gamma}{2m^2} \frac{\partial^2}{\partial v^2} \cdot P(v, t)$

Combine ①, ② $\Rightarrow$ $\partial P / \partial t = \frac{1}{m} \frac{\partial}{\partial v} (\xi v P) + \frac{\gamma}{2m^2} \cdot \frac{\partial^2}{\partial v^2} \cdot P$.

$\Rightarrow$

Increase sample size.

10/17/2024.

- Louiville problem + Langevin dynamics.
  (conservation) (dynamics)

$\Rightarrow$ Fokker-Plank equation (FPE)

$$\boxed{\frac{\partial}{\partial t} P(v,t) = -\frac{\partial}{\partial v}\underbrace{\left(\underbrace{-\frac{\xi}{m} v}_{①\ \text{drag}} \underbrace{- \frac{\gamma}{2m^2}\frac{\partial}{\partial v}}_{②\ \text{noise}}\right) P(v,t)}_{=\ \text{Flux}\ (J)}} \equiv \partial P/\partial t = -\partial J/\partial v$$

$$\because \langle R(t_1) R(t_2)\rangle = \underbrace{2\xi k_B T}_{} \,\delta(t_1-t_2) = \gamma\,\delta(t_1-t_2)$$

Note : We will add external force. (drift term).

Ex1) As $t \to \infty$, system will be in equilibrium. ~ Boltzmann distribution.

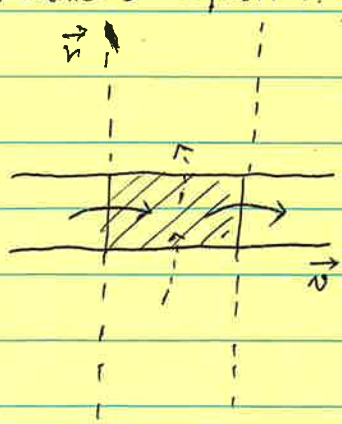
$$\Rightarrow P_{eq} \simeq \left(\frac{m}{2\pi k_B T}\right)^{1/2} \exp\left(-\frac{m v^2}{2k_B T}\right) \rightarrow \text{Flux} = 0.$$

$$\Rightarrow J = \left\{-\frac{\xi}{\cancel{m}} \cdot \cancel{v} - \frac{\gamma}{2\cancel{m^2}} \cdot \left(-\frac{\cancel{mv}}{k_B T}\right)\right\} P(\infty) = 0 \qquad (t \to \infty).$$

$$\Rightarrow \underline{\gamma = 2 k_B T \cdot \xi.} \quad \text{(Fluctuation-Dissipation relation)}$$

Ex2) ?

- Kramer's Equation. $P(r, v, t) \rightarrow$ dist. of pos, vel.



⇢ Flux in coordinate $\qquad \dot{r} = v$

→ Flux in velocity $\qquad \dot{v} = \frac{1}{m}\left(-\xi v + R\right)$

$\downarrow$ $U(x)$ influence

$$\dot{v} = \frac{1}{m}\left(-\xi v + R - \nabla U(r)\right)$$

$+ f_{external}$.

$$\Rightarrow \frac{\partial}{\partial t} P = \Big[\underbrace{-v\frac{\partial}{\partial r} - \frac{1}{m} F \frac{\partial}{\partial v}}_{=\ \text{Flux due to coordinate position}} + \underbrace{\frac{\xi}{m}\cdot\frac{\partial}{\partial v}\left(v + \frac{k_B T}{m}\frac{\partial}{\partial v}\right)}_{\substack{\text{identical to ② of FPE} \\ =\ \text{Flux due to velocity}}}\Big] P.$$

In Kramers' as $t \to \infty$

$$P_{eq}(r,v) \propto \exp\left(-U(r)/(k_BT) - mv^2/(2k_BT)\right)$$

$$\Rightarrow -\frac{v}{k_BT}\left(-\frac{\partial}{\partial v}\right)P_{eq} - \frac{1}{m}\cdot\left(-\frac{\partial U}{\partial r}\right)\cdot\left(-\frac{mv}{k_BT}\right)\cdot P_{eq} = 0$$

- ~~Limitations~~. Limits.

① $\xi = 0$

$$\dot{v} = \frac{1}{m}\left(-\cancel{\xi v}^{\,0} + \cancel{R}^{\,0} + F\right) = \frac{1}{m}\cdot F \rightarrow \text{Conservative!}$$

$$\Rightarrow \frac{\partial}{\partial t}P = \left[-v\frac{\partial}{\partial r} - \frac{1}{m}\cdot F\frac{\partial}{\partial v}\right]P$$

↳ Louiville equation for Newtonian Mechanics.

② $\boxed{\xi \gg 1}$ $\boxed{(\text{overdamped})}$ (e.g. dislocation dynamics)

$$P(r,v,t) \rightarrow P(r,t) = P_{eq}(v)$$

$$\dot{v} = 0 \Rightarrow \dot{v} = \frac{1}{m}\left(-\xi v + R + F\right) \Rightarrow \underline{v = \frac{1}{\xi}(R+F)}$$

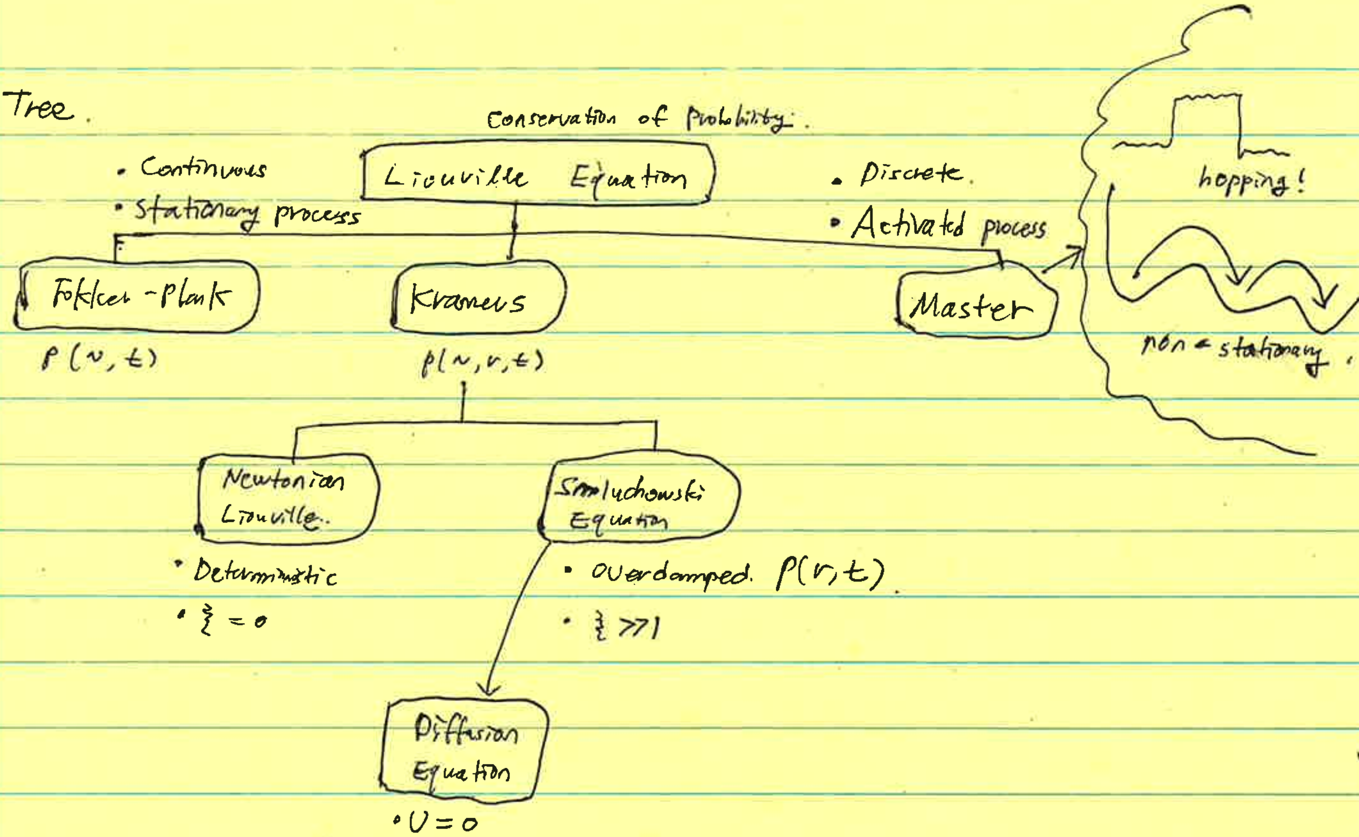
$$\Rightarrow \boxed{\frac{\partial}{\partial t}P(r,t) = \frac{1}{\xi}\cdot\frac{\partial}{\partial r}\left[-F + k_BT\frac{\partial}{\partial r}\right]P(r,t)} \rightarrow \text{Smoluchowski Eq.}$$

overdamped Kramers

↳ $F = 0 \equiv$ diffusion equation.

"Overdamped Kramers = Smoluchowski"

Tree.



Until now, $\langle R(t) R(t') \rangle = \gamma \delta(t-t')$.

But in viscous case (highly) $\delta \rightarrow \gamma(t-t')$ some delay ...

10/22/2024.

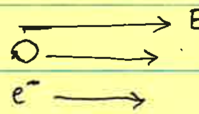
- Smoluchowski Eq.

$$\frac{\partial}{\partial t} P(r,t) = \frac{1}{\xi}\frac{\partial}{\partial r}\Big[\underbrace{-F}_{\text{force (drift)}} + k_B T \frac{\partial}{\partial r}\Big] P(r,t)$$

derived from overdamped Langevin dynamics. such that

$$\cancel{m\ddot{x}}^{\,0} = -\xi \dot{x} + F + R \Rightarrow \xi \dot{x} = F + R \quad (\because \text{ inertia neglected}).$$

Ex). Electrons in electric field.



$$\Rightarrow \langle v\rangle = \langle \dot{x}\rangle = \frac{1}{\xi} eE \quad \left(\because = \left\langle \frac{1}{\xi}(eE + \cancel{R})\right\rangle^{0}\right)$$

$$\Rightarrow \text{Flux}(J) = n\cdot\langle v\rangle e = \underbrace{\left(\frac{n e^2}{\xi}\right)}_{=\sigma} E$$

↘ charge flux

$$\Rightarrow \sigma = ne^2/\xi = \underbrace{ne^2 D/(k_B T)}_{\text{Nernst-Einstein}} \quad \left(\because \xi = k_B T/D\right)$$

Note that RHS of smoluchowski becomes,

$$\frac{\partial}{\partial r}\left(\frac{1}{\xi}\left[\frac{\partial U}{\partial r} + k_B T\frac{\partial}{\partial r}\right]\right) p = \frac{\partial}{\partial r}\left[\frac{1}{\xi}\left(\frac{\partial U}{\partial r} + k_B T\cdot\frac{1}{p}\cdot\frac{\partial p}{\partial r}\right)\cdot p\right]$$

$$= \frac{\partial}{\partial r}\left[\frac{1}{\xi}\cdot\frac{\partial}{\partial r}\{U + k_B T \log(p)\}\, p\right] \quad \text{—— (1)}$$

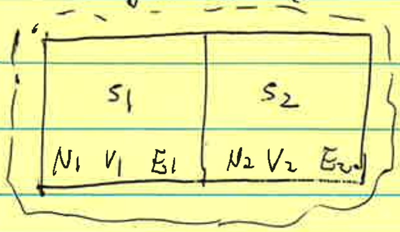
Note) It is known that chemical potential $\mu = k_B T \log c$

If you have additional potential, $\mu' = k_B T \cdot \log c + U$

which is discovered in (1). $= \frac{\partial}{\partial r}\left[\frac{1}{\xi}\cdot\frac{\partial}{\partial r}\mu(r)\; p\right]$

↳ driving force of flux

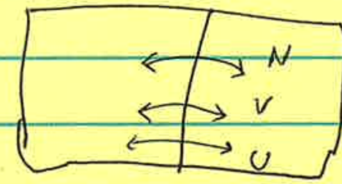
- Thermodynamics. (non-equilibrium). [1930-1950].



Equilibrium : MAX $(S_1 + S_2)$,

$dS = dS_1 + dS_2$.

$$\left.\begin{aligned} dN_2 &= -dN_1 \\ dV_2 &= -dV_1 \\ dU_2 &= -dU_1 \end{aligned}\right\} \text{ for closed system.}$$



From $dS = dS_1 + dS_2$, we have,

$$dS_1 = \underbrace{\frac{\partial S_1}{\partial U_1}}_{=1/T_1} dU_1 + \underbrace{\frac{\partial S_1}{\partial V_1}}_{=P_1/T_1} dV_1 + \underbrace{\frac{\partial S_1}{\partial N_1}}_{=-\mu_1/T_1} dN_1$$

Similar for dS_2 ...

$$\Rightarrow dS = dS_1 + dS_2 = \frac{1}{T_1} dU_1 + \frac{1}{T_2} dU_2 + \cdots$$

$$= \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dU_1 + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2}\right) dV_1 + \left(-\frac{\mu_1}{T_1} + \frac{\mu_2}{T_2}\right) dN_1$$

$$= \left(1/T_1 - 1/T_2\right) dU_1 + \left(P_1/T_1 - P_2/T_2\right) dV_1 - \left(\mu_1/T_1 - \mu_2/T_2\right) dN_1$$

$(\because dU_2 = -dU_1 \cdots)$

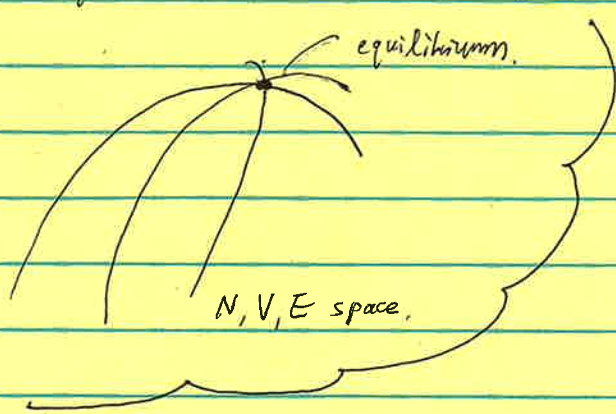
If $T_1 > T_2$, $1/T_1 - 1/T_2 < 0$, $dU_1 < 0 \Rightarrow \underline{dS > 0}$

" $T_1 < T_2$, $1/T_1 - 1/T_2 > 0$, $dU_1 > 0 \Rightarrow \underline{dS > 0}$

Thus, equilibrium is at $T_1 = T_2$.

At $T_1 = T_2$, if $\mu_1 > \mu_2$, $dN_1 > 0 \Rightarrow \underline{-\left(\mu_1/T_1 - \mu_2/T_2\right) dN_1 > 0}$.

$\therefore$ Equilibrium : $T_1 = T_2$, $P_1 = P_2$, $\mu_1 = \mu_2$.



Slight deviation in N, V, E space will cause the force

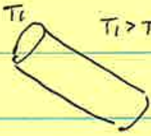
- Rate of Entropy Production

$$\frac{dS}{dt} = \dot{S} = \underbrace{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}_{X_u} \underbrace{\dot{U}_1}_{J_u} + \underbrace{\left(\frac{P_1}{T_1} - \frac{P_2}{T_2}\right)}_{X_V} \underbrace{\dot{V}_1}_{J_V} - \underbrace{\left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right)}_{X_N} \underbrace{\dot{N}_1}_{J_N} \qquad (\sim \text{flux}).$$

X_u: Thermodynamic driving force; J_u: flux. $= X_i J_i$ — (1)

X_i (restoring force).

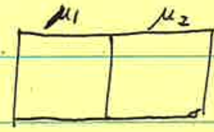
- Fourier & Fick



T_1, $T_1 > T_2$, T_2

$J \propto T_1 - T_2 \propto X_V$

[Fourier's law]



μ_1, μ_2

$J \propto -(\mu_1 - \mu_2) \propto X_N$

[Fick's law]

⟨Linear Response⟩

$\Rightarrow J_i = \underset{\sim}{L_{ij}} X_j$

↳ generalization of thermal conductivity & diffusivity.

"Onsager transport coefficient"

Interestingly, $L_{ij} = L_{ji} \Leftrightarrow L^T = L$ is symmetric.

$\Rightarrow$ Onsager reciprocal principle. — (2)

$\Rightarrow$ Continue (1), we get.

$$\dot{S} = (L_{ij} X_j) \cdot X_i = \underline{X^T \underset{\sim}{L} X}$$

↳ Material tensor.

Since $\dot{S} > 0$, $\underset{\sim}{L}$ is $\boxed{\text{positive-definite}}$.

Q) What does eig. val of L mean?

A).

- Onsager 1931.

Near equilibrium.

$\dot{x}_i = L_{ij} X_j$ where $\dot{x} = \underset{\sim}{L} X$, with $\dot{x}_i \nearrow$ Flux $= J_i$

$\underset{\sim}{L}^T = \underset{\sim}{L}$.

P(x_i) Gaussian.

$$\boxed{\begin{array}{l} \text{① } S = S_{eq} - \frac{1}{2}\beta_{ij} x_i x_j + \dots \\ \text{② Macroscopic law describes} \\ \quad \text{microscopic fluctuation.} \\ \text{③ Microscopic dynamics is reversible.} \end{array}}$$

①

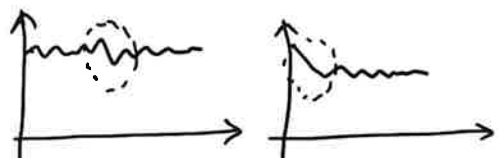
$ds = \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu}{T} dN.$ and $X_i = \frac{\partial s}{\partial x_i} = -\beta_{ij} x_j$

$= -\underset{\sim}{\beta}\, x$

Introduce,

$\dot{x}_i = L_{ij} X_j = -L_{ij} \underbrace{\beta_{jk} x_k}_{= X_j}$ ②

↘ Macroscopic relaxation.



Same functional form (in average).

⇒ Regression Hypothesis.

↓

$\dot{x}_i = -L_{ij} \beta_{jk} x_k$

⟨Correlation Function⟩.

②

$\langle X_i(0) \cdot X_j(t) \rangle$

Since ③ holds, $\langle X_i(t)\, x_j(0) \rangle = \langle X_i(0) \cdot X_j(t) \rangle$.

$\Rightarrow \langle \dot{x}_i(t)\, x_j(0) \rangle = \langle x_i(0) \cdot \dot{x}_j(t) \rangle$

$\Rightarrow \quad -\underset{\sim}{L}_i \underset{\sim}{\beta} \langle x_i(t)\, x_j(0) \rangle = -\underset{\sim}{L}_j \underset{\sim}{\beta} \langle x_i(0) \cdot x_j(t) \rangle$

Since ①, $p(x_i) \sim N \Rightarrow \boxed{\langle x_n(0)\, x_j(0) \rangle = [\beta^{-1}]_{nj}}$ (*)

∴ At $t=0$) $-\underset{\sim}{L}_i \underset{\sim}{\beta} [\beta^{-1}]_j = -\underset{\sim}{L}_j \underset{\sim}{\beta} [\beta^{-1}]_i$

$\Rightarrow L_{ij} = L_{ji} \Leftrightarrow \boxed{L^T = L}$

※ only in linear regime.

↳ (*) holds.

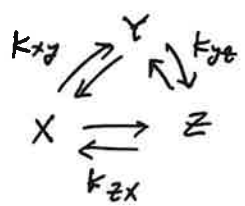
- Reversibility of Microscopic Dynamics.

→ "Detailed Balance" - identical flux

$$A \underset{k_{ba}}{\overset{k_{ab}}{\rightleftarrows}} B \quad \Rightarrow \quad k_{AB}[A]_{eq} = k_{BA}[B]_{eq}.$$

$$\Rightarrow \frac{k_{ab}}{k_{ba}} = \frac{[B]_{eq}}{[A]_{eq}} = k_{eq}. \quad \text{——} \ (*)$$

→ "Cyclic reaction."



$$J_1 = J_{XY} = k_{XY}[X] - k_{YX}[Y].$$

$$J_2 = \dots$$

$$J_3 = \dots$$

$$\Rightarrow \begin{pmatrix} J_1 \\ J_2 \\ J_3 \end{pmatrix} = \begin{pmatrix} k_{XY} & -k_{YX} & 0 \\ 0 & k_{YZ} & -k_{ZY} \\ -k_{XZ} & 0 & k_{ZX} \end{pmatrix} \begin{pmatrix} [X] \\ [Y] \\ [Z] \end{pmatrix}$$

Also, $[X]+[Y]+[Z] = \text{const.}$ and also,

$\dot{S} = \underset{\substack{\uparrow \\ X_i}}{J_i A_i}$ where A_i : chemical potential difference.

$A_i : \dfrac{\mu_X - \mu_Y}{T}$, affinity : driving force of J_i

$$\Rightarrow \dot{S} = J_1 \underbrace{(\mu_X - \mu_Y)}_{A_1} + J_2 \underbrace{(\mu_Y - \mu_Z)}_{A_2} + J_3 \overbrace{(\mu_Z - \mu_X)}^{A_3}.$$

$$= -[\underbrace{(\mu_Y - \mu_Z)}_{A_2} + \underbrace{(\mu_X - \mu_Y)}_{A_1}]$$

$$= (J_1 - J_3)A_1 + (J_2 - J_3)A_2$$

$$\Rightarrow \begin{pmatrix} J_1 - J_3 \\ J_2 - J_3 \end{pmatrix} = \begin{pmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{pmatrix} \begin{pmatrix} A_1 \\ A_2 \end{pmatrix}$$

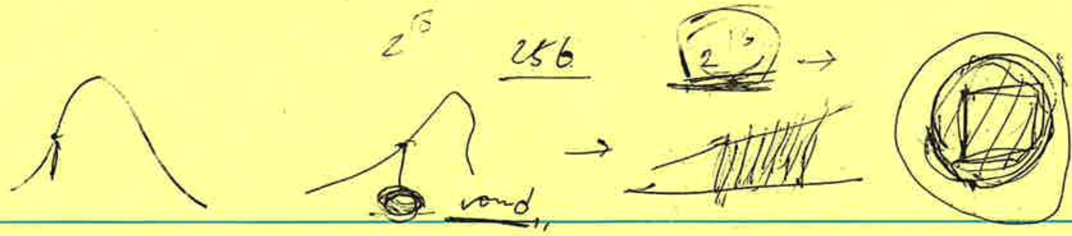
by Linearize rate equation,

$$\begin{pmatrix} J_1 - J_3 \\ J_2 - J_3 \end{pmatrix} = \frac{1}{k_B} \begin{pmatrix} (k_{XY} + k_{XZ})[X]_{eq} & k_{ZX} k_{YZ} [Y]_{eq} / k_{ZY} \\ k_{XZ} [X]_{eq} & (k_{ZY} + k_{ZX})[Y]_{eq} \cdot k_{YZ}/k_{ZY} \end{pmatrix} \begin{pmatrix} A_1 \\ A_2 \end{pmatrix}$$

X_{eq} : $X - X_{eq}$

For $L^T = L \Rightarrow k_{XZ}[X]_{eq} = k_{ZX} \underbrace{\frac{k_{YZ}\,[Y]}{k_{ZY}}}_{=\,[Z]_{eq} \text{ if D.B.}}$

if D.B.



10/07/2024.

- Fluctuation

$$C_{BA}(t) = \langle A(0)\, B(t) \rangle$$

- Response to perturbation $h(t)$. → Linear.

$$B(t) = B_0 + \int_0^t dt'\, \chi_{BA}(t-t')\, h(t')$$

$$H = H_0 - \underbrace{A\, h(t)}_{\text{energy}} \rightarrow \text{"stress/strain."}$$

- Stress relaxation modules.

$$\left.\sigma(t) = \int_{-\infty}^{0} dt'\, \underbrace{G(t-t')}_{Pa} . \underbrace{\dot{\gamma}(t')}_{\text{strain rate}} \right\} \text{: "unit = stress."} \rightarrow \text{"Boltzmann Superposition Principle."}$$

Q) How to know linear works?

A) Decrease ~~dt~~ dt, increase $\dot{\gamma}$ ↑ see convergence.

FDT : $\chi_{BA}(t) = -\beta \frac{d}{dt} C'_{BA}(t)$. (where $\beta = \frac{1}{k_B T}$)

pf).

① static $(t=0)$.

Ex) $\underbrace{\langle (\delta U)^2 \rangle}_{\text{energy fluct.}} = k_B T^2 \underbrace{c_v}_{\substack{\text{heat capacity.} \\ \text{"response"}}}$, $c_v = \left.\frac{U(T+\Delta T) - U(T)}{\Delta T}\right|_{V=\text{const.}}$ —— ①

$$U(T) = \frac{1}{Q}\int dp \int dq . \exp(-H/(k_B T))\, H . = \langle H \rangle$$

$$Q = \underbrace{\int dp}_{\substack{\text{pos.} \\ \text{momentum.}}} \underbrace{\int dq}_{\text{states}} . \underbrace{\exp(-H/(k_B T))}_{\text{partition function.}} \text{ —— ②}$$

② : $Q = \underbrace{\int dp \int dq}_{\substack{\text{momentum} \quad \text{states} \\ \text{micro.}}} \exp\left(-\frac{H}{k_B T}\right) = Tr\left(e^{-H/k_B T}\right)$.

① $\langle H \rangle_0 = \dfrac{Tr\left(e^{\frac{-H}{k_B T}} H\right)}{Tr\left(e^{\frac{-H}{k_B T}}\right)} = U(T)$.

↘ "unperturbed".

Now, perturbed version is given as,

$$U(T+\Delta T) = \frac{Tr\left(\exp\left(-H/(k_B(T+\Delta T))\right) H\right)}{Tr\left(\exp\left(-H/k_B(T+\Delta T)\right)\right)} = \langle H \rangle$$

Calculate $\langle H \rangle - \langle H_0 \rangle = U(T+\Delta T) - U(T)$ when $T \gg \Delta T$

Taylor expansion, ...

$$\Rightarrow U(T+\Delta T) \underset{③}{\cong} \frac{\left\langle e^{-\frac{H}{k_B}\left(\frac{1}{T+\Delta T}-\frac{1}{T}\right)} \cdot H \right\rangle_0}{\left\langle e^{-\frac{H}{k_B}\left(\frac{1}{T+\Delta T}-\frac{1}{T}\right)} \right\rangle_0} \approx \frac{\left\langle e^{\frac{H\Delta T}{k_B T^2}} H \right\rangle_0}{\left\langle e^{\frac{H\Delta T}{k_B T^2}} \right\rangle_0}$$

$$\approx \frac{\left\langle \left(1+\frac{H\Delta T}{k_B T^2}\right) H \right\rangle_0}{1+\left\langle \frac{H\Delta T}{k_B T^2}\right\rangle_0} \approx \left\langle H + \frac{H^2 \Delta T}{k_B T^2}\right\rangle_0 \left(1 - \left\langle \frac{H\Delta T}{k_B T}\right\rangle_0\right) \longrightarrow ④$$

$\frac{1}{1+x} \approx 1-x$

③ is derived by,

$$\frac{Tr\left(e^{-\frac{H}{k_B(T+\Delta T)}} \cdot H\right)}{Tr\left(e^{-\frac{H}{k_B(T+\Delta T)}}\right)} = \frac{Tr\left(e^{\frac{-H}{k_B T}} e^{-\frac{H}{k_B T}\left(\frac{1}{T+\Delta T}-\frac{1}{T}\right)} H\right)}{Tr\left(e^{\frac{-H}{k_B T}}\right)}$$

$$\times \frac{Tr\left(e^{\frac{-H}{k_B T}}\right)}{Tr\left(e^{\frac{-H}{k_B T}} \cdot e^{-\frac{H}{k_B}\left(\frac{1}{T+\Delta T}-\frac{1}{T}\right)}\right)}$$

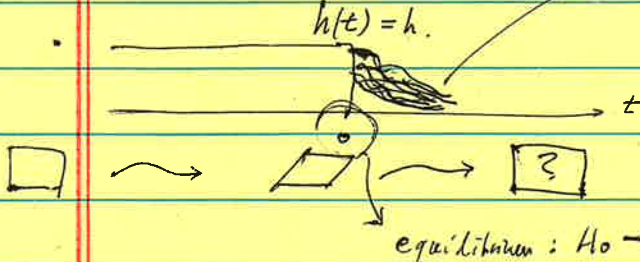
$$④ = \langle H \rangle_0 + \left\langle \frac{H^2 \Delta T}{k_B T}\right\rangle_0 - \langle H \rangle_0 \left\langle \frac{H\Delta T}{k_B T^2}\right\rangle_0 + \sim$$

$$\therefore U(T+\Delta T) - U(T) = \frac{\Delta T}{k_B T^2}\left(\underbrace{\langle H^2 \rangle_0 - \langle H \rangle_0^2}_{= \text{variance}}\right)$$

$$\Rightarrow k_B T^2 C_v = \langle (\delta U)^2 \rangle_0 \quad \#$$

$$H = H_0 - A \cdot h(t) \quad \left(\begin{array}{l} h : \Delta T \\ A : -\frac{H}{T} \end{array}\right)$$

Ensemble average of $\underline{B(t)}$.



$$\langle B(t)\rangle = \frac{Tr\left(e^{-\beta(H_0 - Ah)}B(t)\right)}{Tr\left(e^{-\beta(H_0-Ah)}\right)}$$

$$= \frac{Tr\left(e^{-\beta H_0}e^{\beta Ah}B(t)\right)}{Tr\left(e^{-\beta H_0}\right)} \cdot \frac{Tr\left(e^{-\beta H_0}\right)}{Tr\left(e^{-\beta H_0}e^{\beta Ah}\right)}$$

$$= \frac{\langle e^{\beta Ah}B(t)\rangle_0}{\langle e^{\beta Ah}\rangle_0} = \frac{\langle (1+\beta Ah)\cdot B(t)\rangle_0}{\langle 1+\beta Ah\rangle_0} = \left(\langle B(t)\rangle_0 + \beta h\langle AB(t)\rangle_0\right)\left(1-\beta h\langle A\rangle_0\right)$$

$$= B_0 + \beta h\left(\underbrace{\langle AB(t)\rangle_0 - \langle B(t)\rangle_0\langle A\rangle_0}_{=\mathrm{cov}(A,B(t))}\right)$$

$$= \langle \delta A\cdot\delta B(t)\rangle_0$$

at equilibrium. $A_0 = B_0 = 0$.

$$\langle B(t)\rangle = \beta h\, C_{BA}(t)$$

Fluctuation.

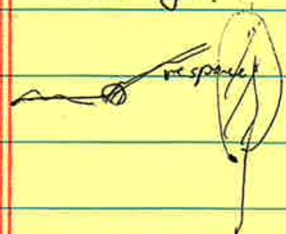
- $\langle B(t)\rangle = h\int_{-\infty}^{0} dt'\,\chi_{BA}(t-t') = \boxed{h\int_t^{\infty} dt'\,\chi_{BA}(t')}$ response.

$$\Rightarrow \int_t^{\infty} dt'\,\chi_{BA}(t') = \beta\cdot C_{BA}(t)$$

$$\Rightarrow \boxed{\chi_{BA}(t) = -\beta\frac{d}{dt}\cdot C_{BA}(t)}$$

Fluctuation Dissipation Theorem.
Response.

- Scattering. • Absorption ~ correlation (relaxation)

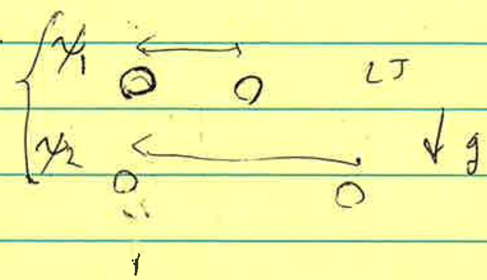


$$H \rightsquigarrow H + \delta H$$

10/31/2024.

$\langle x_0\, x_t \rangle \Leftrightarrow \dot{x} = LX$ — Fluc. Diss. Thm.

corr, equilibrium resp, perturbed.



James Jenkins

Static

① Heat capacity $k_B T^2 c_v = \langle (\delta U)^2 \rangle$.

$\sim C$ in RC circuit. fluct.

② Isothermal compressibility $k_T = -\frac{1}{V} \partial V/\partial p \big|_T \longrightarrow k_B T\, V\, k_T = \langle (\delta V)^2 \rangle$.

③ # fluct. : $k_B T \frac{\partial N}{\partial \mu} = \langle (\delta N)^2 \rangle$

$\langle \delta N_1\, \delta N_2 \rangle = k_B T \frac{\partial N_1}{\partial \mu_2} = k_B T \frac{\partial N_2}{\partial \mu_1}$.

④ polarizability : $\alpha = \frac{p^2}{3 k_B T} \longrightarrow$ 3 is projection. $(1/3)$

⑤ Magnetic susceptibility : $\chi_T = \frac{\mu^2}{3 k_B T}$

⑥ scattering. $I(q, t=0) \propto \langle \delta\rho(+q)\, \delta\rho(-q) \rangle$.

Dynamic :

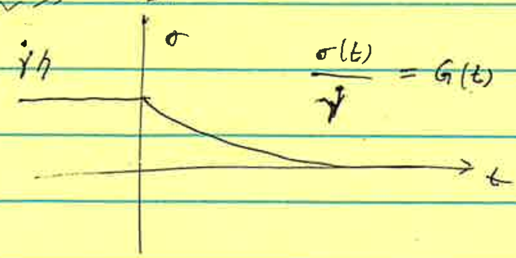
①. $D = \frac{1}{3} \int_0^\infty dt\, \langle v(0)\, v(t) \rangle = \mu k_B T$.

② $\eta = \frac{1}{V k_B T} \int_0^\infty dt\, \langle J(0)\, J(t) \rangle$.

③. $\lambda = \frac{1}{3 V k_B T} \int_0^\infty dt\, \langle s(0)\, s(t) \rangle$. thermal conductivity.

④ Stress relaxation modulus.

$\underset{\sim}{G(t)} = \frac{V}{k_B T} \langle \sigma_{\alpha\beta}(0)\, \sigma_{\alpha\beta}(t) \rangle$.



$\frac{\sigma(t)}{\dot{\gamma}} = G(t)$

$\dot{\gamma}(t)$: strain rate.

$$\sigma(t) = \underbrace{\int_{-\infty}^{0}}_{\text{history.}} dt'\, G(t-t')\, \dot{\gamma}(t')$$

- Light absorption.

electrical dipole moment

$$I(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{-j\omega t} \langle \mu(0)\mu(t) \rangle$$

Raman : $\langle \beta(0)\,\beta(t) \rangle$

- Dynamic light scattering

$$I(q,t) = \langle \delta\rho(q,t)\,\delta\rho(-q,0) \rangle$$

Fluctuation response to $G(t) \leftrightarrow \sigma = \frac{1}{2\pi d} \sim$ (R.N. model).

$$= F^{-1}\{ X(j\omega) H(j\omega) \}$$

- Fluctuation : $\langle A(0)\, B(t) \rangle$ $\boxed{\text{Perturbation}}$.

Response Function : $\underbrace{H_0 - A\,h(t)}$. conjugate to $h(t)$ $\rightarrow$ $B(t) = \underset{eq.}{B_0} + \int_{-\infty}^{t} dt'\, \chi_{B,A}(t-t')\, h(t')$

$\boxed{\text{Response function}}$

$$\boxed{\text{Key : } \chi_{BA}(t) = -\frac{1}{k_B T}\cdot\frac{d}{dt}\cdot\underbrace{\langle A(0)\, B(t)\rangle}_{= C_{BA}(t)}}$$

Q) Do we need noise for F-R. theorem ?

Or is it sufficient with "Large" systems ?

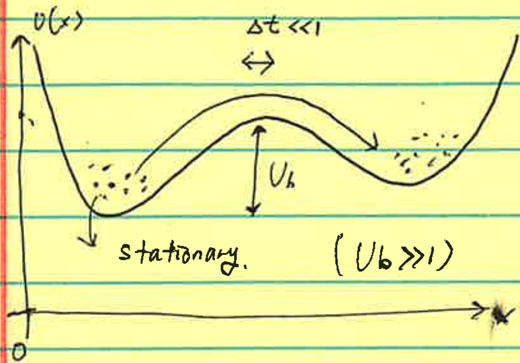
A) Discrete objects. & Many (large)

Langevin is just an example — discrete quantum objects ?

$D(\Delta t) \sim \langle(\Delta x)^2\rangle$

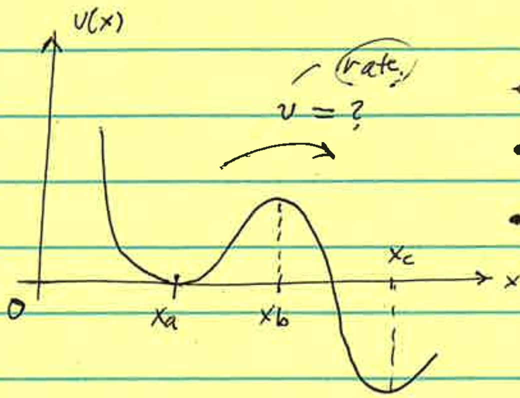
$1/N^a$

11/12/2024

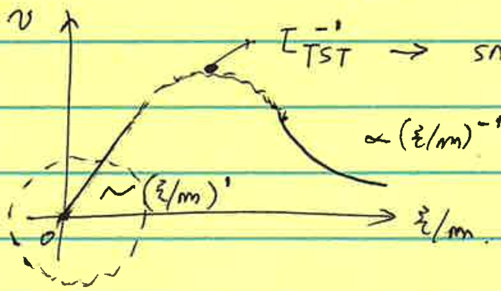


+ Friction ($\xi = 1/\mu$) + ?

Kramers → Marcus? (Quantum)



- $[j] = [\nu] = 1/s$ (only for 1D).
- $\Delta U \gg k_BT$ (activated process).
- Kramer's eq. $\begin{cases} \text{overdamped} & \xi/m \gg 1 \Rightarrow \underline{\text{Smoluchowski}} \\ \text{under-damped} & \xi/m \ll 1 \\ \text{intermediate} & \xi/m \approx 1 \end{cases}$



→ small friction dependence. (≡ Kramer's turnover).

↳ Always cross at the peak of the barrier

↳ why TST works.

$\frac{\xi}{m} = 0$ → No fluctuation / dissipation.

→ Newtonian mechanics.

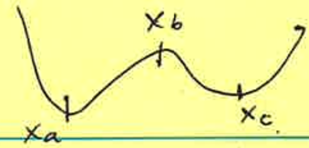
- High Friction. $\rho = \rho(x, \cancel{v}, t) = \rho(x, t)$

Conservation of probability : $\frac{\partial}{\partial t}\rho = -\frac{\partial}{\partial x} j$ where $j = -\frac{1}{\xi}\left(\frac{\partial U}{\partial x}\rho + k_BT\frac{\partial \rho}{\partial x}\right)$

⇒ Stationary flux : j = constant.

$$j = -\underbrace{\frac{k_BT}{\xi}}_{=D} \cdot e^{-U/(k_BT)} \cdot \frac{\partial}{\partial x}\left(e^{-U/(k_BT)} \cdot \rho\right) = \text{const.}$$

$$\Rightarrow j\,\frac{\xi}{k_BT} \cdot e^{U/(k_BT)} = -\frac{\partial}{\partial x}\left(e^{-U/(k_BT)} \cdot \rho\right) \rightarrow \text{integrate!}$$



$p(x_c) = 0$

Integrating from $x_a \sim x_c$

$$\Rightarrow j \cdot 1/D \cdot \int_{x_a}^{x_c} dx\, e^{-\frac{U(x)}{k_BT}} = - e^{U(x)/k_BT} \cdot p(x) \Big|_{x_a}^{x_c}$$

$p(x_a) \sim \frac{1}{Z} e^{-U(x_a)/(k_BT)}$

$$= \frac{1}{\int_{-\infty}^{x_b} dx\, e^{-\frac{U(x)}{k_BT}}} \quad = N$$

$\Rightarrow$ Approximate $U(x) \approx U_b + \frac{U_b''}{2}(x - x_b)^2 \quad (\because U_b' = 0)$

where $\omega_b^2 = -\frac{1}{m} U_b''$

$$\Rightarrow e^{U_b/k_BT} \int_{x_a}^{x_c} dx\, e^{-\frac{m\omega_b^2}{2k_BT}(x-x_b)^2} = e^{U_b/k_BT} \left(\frac{2\pi k_BT}{m\omega_b^2}\right)^{1/2} \quad \text{—— ①}$$

Similarly, $-\infty \le x \le x_b$. $\rightarrow U(x) = U(a) + \frac{U''(a)}{2}(x-a)^2$

$$\Rightarrow N = e^{-U_a/k_BT} \cdot \left(\frac{2\pi k_BT}{m\omega_a^2}\right)^{1/2} \quad \text{—— ②}$$

$$①, ② \Rightarrow j = \frac{\cancel{k_BT}}{\zeta} \cdot \frac{1}{2\pi \cancel{k_BT}} \| U''(a)\, U''(b) \| \cdot e^{-\frac{U_b - U_a}{k_BT}}$$

$$\Rightarrow r = \boxed{\frac{1}{2\pi\zeta} \cdot \| U''(a) \cdot U''(b) \| \cdot e^{-\frac{\Delta U}{k_BT}}} \quad //$$

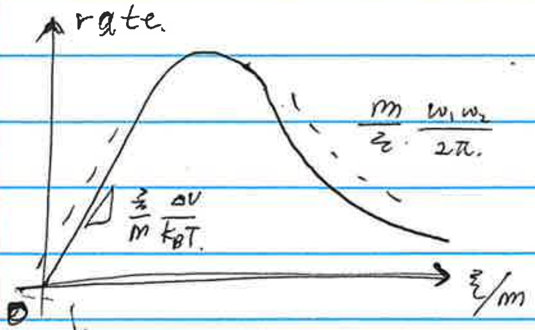
$$= \frac{m}{\zeta} \cdot \frac{\omega_a \omega_b}{2\pi} e^{-\frac{\Delta U}{k_BT}} \quad //$$

$V_0, V_1, \cdots V_d, V_{d+1}$ $\left\{ \sum_{i=0}^{d} \left(\frac{V_{i+1} - V_i}{\Delta x}\right)^2 \cdot \frac{\lambda}{2} + \sum_{i=0}^{d} (1 - V_i^2)^2 \cdot \frac{1}{4\lambda} \right\} \Delta x \rightarrow$ min/max

$V_0 = 0$, $V_{d+1} = 0$

11/14/2024

$$V(u) = \int_0^1 \frac{\lambda}{2}(u')^2 + \frac{1}{4\lambda}(1-u^2)^2 \, dx. \qquad u(0) = u(1) = 0.$$

- 

Low friction. (~ Newtonian)

$\because$ Less fluctuation. ↓

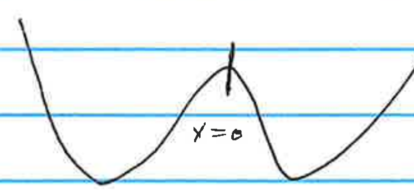
- Transition State Theory. (1D)

→ Assumption : equilibrium statistics is adequate. — (*)

Ex) overdamped : velocity is equilibrated, position is NOT equilibrated) $\neq$ (*) assumption.

$$P(x, v) \propto \exp\left(-\frac{U(x) + mv^2/2}{k_B T}\right)$$

$$dx\, P(0, v) = \exp\left(-\frac{U(0) + mv^2/2}{k_B T}\right)$$



→ Assumption : only $\boxed{v>0}$ will cross at $x=0$,

$$\Rightarrow \underbrace{\int_0^\infty dv \cdot P(0, v)\, dx}_{\text{population to RHS.} \rightarrow} \propto \int_0^\infty dv \cdot \exp\left(-\frac{U(0) + mv^2/2}{k_B T}\right).$$

$$= \frac{\left(e^{-\frac{U(0)}{k_B T}} \int_0^\infty dv \cdot e^{-\frac{mv^2}{2k_B T}}\right) dx}{\int_{-\infty}^{\infty} dv \int_{-\infty}^{0} dx \cdot e^{-\frac{U(x) + mv^2/2}{k_B T}}} \Rightarrow j = \frac{\partial P}{\partial t} \Rightarrow$$

$$\therefore j = \frac{e^{-\frac{U(0)}{k_B T}} \int_0^\infty dv\, e^{-\frac{mv^2}{2k_B T}} \cdot \overset{dx/dt}{\overset{\|}{v}}}{\int_{-\infty}^{\infty} \int_{-\infty}^{0} dx \cdot e^{-\frac{U(x) + mv^2}{k_B T}}}$$

eig. value of [4.]

Evaluate integral, $j = e^{-\frac{\Delta V}{k_B T}} \cdot \frac{\omega_a}{2\pi}$

$\left(U(x) \sim U(a) + \frac{m\omega_a^2}{2} \cdot (x - x_a)^2 \right)$

- Underdamped Regime $P(x, v)$.

$$\frac{\partial P}{\partial t} = \underbrace{\left(- v \frac{\partial P}{\partial x} + \frac{1}{m} \frac{\partial U}{\partial x} \frac{\partial P}{\partial v} \right)}_{\text{deterministic}} + \underbrace{\frac{\zeta}{m} \cdot \frac{\partial}{\partial v} \left(vP + \frac{k_B T}{m} \cdot \frac{\partial P}{\partial v} \right)}_{\text{random}} \quad \text{--- (1)}$$

proposal : $P(v, x) = \underbrace{Q(v, x)}_{\text{correction}} \cdot P_{eq}(v, x)$

$\hookrightarrow \propto \exp\left(- \frac{U(x) + mv^2/2}{k_B T} \right)$.

$$\rightarrow v \frac{\partial}{\partial x} (Q P_0) = v \cdot Q \frac{\partial P_0}{\partial x} + v P \cdot \frac{\partial Q}{\partial x}$$

(1) $\Rightarrow \frac{\zeta}{m} \cdot v \frac{\partial Q}{\partial v} + v \frac{\partial Q}{\partial x} + \omega_b^2 x \cdot \frac{\partial Q}{\partial v} = \frac{\zeta k_B T}{m^2} \frac{\partial^2 Q}{\partial v^2}$ (after algebra ...) --- (2)

$\hookrightarrow$ Linear equation in Q (transport equation).

$\Rightarrow$ "Method of characteristics"

$\Rightarrow$ " Self similar solutions "

$Q = f(z)$, $z = v - \alpha x$. $\Rightarrow \left(\frac{\partial f}{\partial v} = f', \quad \frac{\partial f}{\partial x} = -\alpha f' \right)$

$$\Rightarrow \underbrace{\left(\frac{\zeta}{m} v - \alpha v + \omega_b^2 x \right)}_{\text{must be lin. func. of } 'z' . = -\lambda z} \cdot f'(z) = \frac{\zeta k_B T}{m^2} f''(z).$$

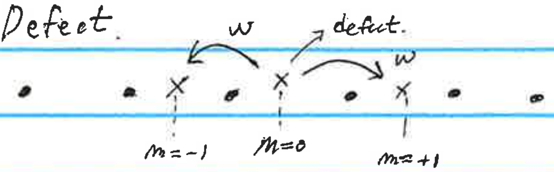
$\Rightarrow \lambda_{\pm} = - \alpha_{\mp}$, $\alpha_{\pm} = \frac{1}{2m} \left(\zeta \pm \sqrt{\zeta^2 + 4m^2 \omega_b^2} \right)$ --- (3)

(2) & (3) $\Rightarrow -\lambda \cdot z \, f'(z) = \frac{\zeta k_B T}{m} \cdot f''(z)$.

$\Rightarrow \frac{-\lambda m^2}{\zeta k_B T} z = f''(z) / f'(z) \Rightarrow \boxed{f}$ #

12/03/2024.

- Defect.



$\rightsquigarrow$ Hopping of a defect.

$P_m(t)$ for $m = 0, \pm 1, \pm 2, \dots$: probability at site m time t

$dP_m(t)/dt = \dot{P}_m(t) = w P_{m+1} + w P_{m-1} - 2w \cdot P_m$ ($\because$ prob. cons.).

$$\Rightarrow [\dot{P}] = \begin{pmatrix} -2w & +w & 0 & - & 0 & +w \\ w & -2w & w & 0 & - & 0 \\ & & \vdots & & & \\ +w & 0 & - & 0 & +w & \underbrace{-2w}_{\text{for periodic}} \end{pmatrix} [P] \quad \text{for } m. \text{ states.} \quad \text{—— ①}$$

Fourier transform of $P_m(t) \to \hat{P}_k(t)$

$$\Rightarrow \hat{P}_k(t) = \sum_{m=-\infty}^{\infty} P_m(t) \cdot e^{-jkm} \quad \text{and} \quad P_m(t) = \frac{1}{2\pi}\int_{-\pi}^{\pi} dk \cdot \hat{P}_k(t)\, e^{jkm}.$$

Apply to ①,

$$① \Rightarrow \underbrace{\frac{d}{dt}\left(\sum_{m=-\infty}^{\infty} P_m(t)\, e^{-jkm}\right)}_{=\hat{P}_k'(t)} = w \cdot \left[\sum_{m=-\infty}^{\infty} \underbrace{P_{m-1}(t)\, e^{-jkm}}_{=P_{m-1}\cdot e^{-jk(m-1)} \cdot e^{-jk}} + \sum \underbrace{P_{m+1}\, e^{-jkm}}_{\| \; P_{m+1}\, e^{-jk(m+1)} \cdot e^{jk}}\right] - 2w \cdot \underbrace{\sum P_m \cdot e^{-jkm}}_{=\hat{P}_k(t)}$$

$$\Rightarrow \hat{P}_k(t)' = w\left[\underbrace{e^{-jk} + e^{+jk}}_{=2\cos(k)}\right] \cdot \hat{P}_k(t) - 2w \cdot \hat{P}_k(t).$$

$$= 2w\, \hat{P}_k(t) \{\cos(k) - 1\}.$$

$$\Rightarrow \hat{P}_k(t)' / \hat{P}_k(t) = 2w\{\cos k - 1\} \Rightarrow \ln \hat{P}_k(t) = 2w\{\cos k - 1\} \cdot t + A.$$

Using $\hat{P}_k(t) = 1$ at $t = 0$, (assumption : $P_m(0) = \delta_{m,0}$).

$$\Rightarrow \boxed{\hat{P}_k(t) = \exp\left(-2w(1-\cos k) \cdot t\right)}$$

$$\Rightarrow \boxed{P_m(t) = \frac{e^{-2wt}}{2\pi}\int_{-\pi}^{+\pi} dk\, e^{2wt \cdot \cos k + jkm}}$$

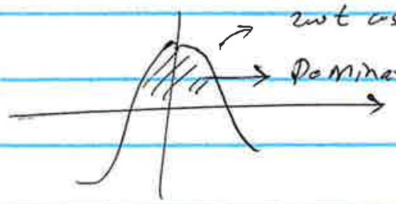
$$P_m(t) = \frac{e^{-2wt}}{2\pi}\int_{-\pi}^{\pi} dk\, e^{2wt\cos k + ikm}$$

- Limits of $P_m(t)$.

① $t \to 0$

$$P_m(t) \cong \frac{e^{-2wt}}{2\pi} \cdot \frac{2\sin(m\pi)}{m} = \begin{cases} 0 & (m \neq 0) \\ e^{-2wt}\delta_{m,0} & (m = 0) \end{cases}$$

② $t \to \infty$



$\Rightarrow 2wt\cos k$ near $k \doteqdot 0$

$\doteqdot \underline{2wt\cdot(1 - k^2/2!)}$

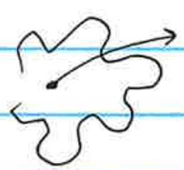
$$\Rightarrow P_m(t) = \frac{e^{-2wt}}{2\pi}\int_{-\infty}^{\infty} dk \cdot e^{-wtk^2} e^{ikm} = \underbrace{\frac{1}{\sqrt{4\pi wt}} \cdot e^{-\frac{m^2}{4wt}}}_{\text{smear out Gaussian}}$$

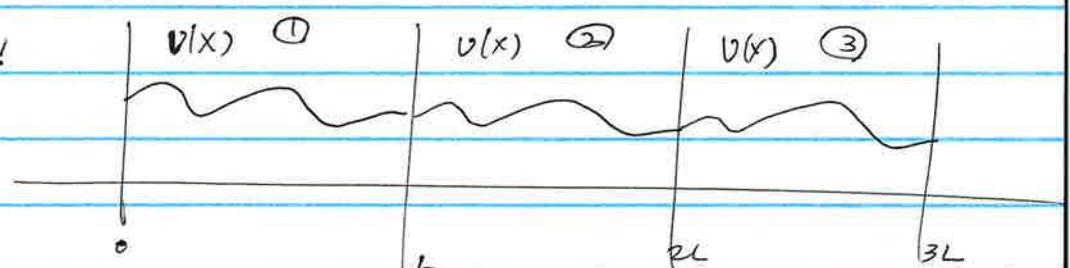
- Statistics

$$\langle m^2 \rangle = 2wt \Rightarrow a^2\langle m^2\rangle = 2\underbrace{(wa^2)}_{=D}t$$

$$\Rightarrow a^2 \cdot 1 = 2D\,\Delta t \Rightarrow \Delta t = \frac{a^2}{2D}$$

- 1962, Lifson – Jackson





$\rightarrow$ repeating boundaries.

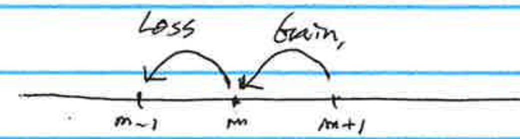
$r_{①\to②}$, $r_{②\to③}$ can be considered...

$$D = \underbrace{\frac{D_0}{\langle e^{U(x)/k_BT}\rangle\langle e^{-U(x)/k_BT}\rangle}}_{(*)} \qquad \begin{cases} \langle e^{U(x)/k_BT}\rangle = \frac{1}{L}\int_0^L dx\, e^{U(x)/k_BT} \\ \langle e^{-U(x)/k_BT}\rangle = \frac{1}{L}\int_0^L dx\, e^{-U(x)/k_BT} \end{cases}.$$

We can prove that $D < D_0$. since $(*) > 1$ $\rightsquigarrow$ Kramers' "overdamped".

Q) $0 < x < L$ underdamped $\Rightarrow$ ① → ② → ③ overdamped?

- Master equation. (simple)



$A \xrightarrow{k_{AB}} B$. (only forward!)

A : m mol
B : n mol

$m + n = N$

$n = N - m$, $\Rightarrow$ only need $P_m(t)$

$$\frac{d}{dt} P_m(t) = k_{AB} \cdot m, = P_{m+1} \cdot k \cdot (m+1). \quad (\because \text{only forward})$$
$$- P_m \cdot k \cdot (m)$$

rate of single molecule.

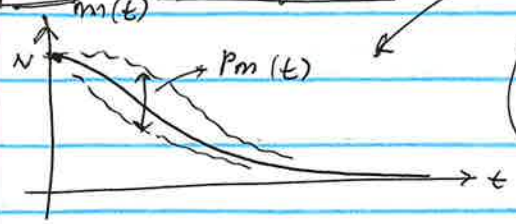
$$\Rightarrow \frac{d}{dt} P_m(t) = k \left\{ P_{m+1} \cdot (m+1) - P_m \cdot m \right\}.$$

$A \xrightarrow{k} B$ [Microscopic]

$$\frac{dP_m(t)}{dt} = k\left[(m+1)P_{m+1} - m P_m\right]$$

12/05/2024.

$\boxed{\text{Transport Equation}}$



$\boxed{\text{Method of generating function}}$

$$\Rightarrow F(s,t) = \sum_{m=0} P_m(t)\cdot s^m$$

$$\partial F/\partial s\Big|_{s=1} = \sum m P_m(t).$$

$$\partial^2 F/\partial s^2\Big|_{s=1} = \sum m^2 P_m(t) - \sum m P_m(t)$$

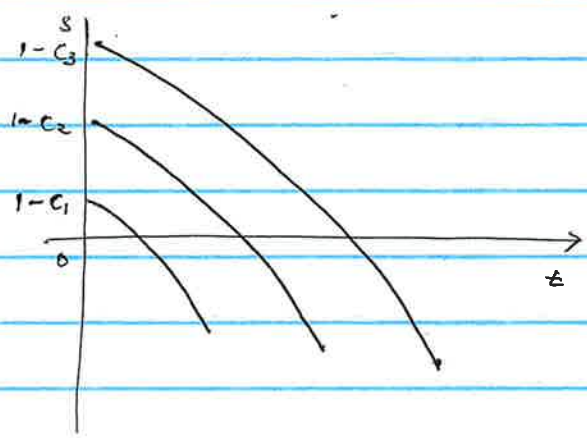
$$= \langle m^2\rangle - \langle m\rangle$$

LHS: $\frac{d}{dt}\left(\sum_m P_m(t)\, s^m\right)$

RHS: $k\left[\sum (m+1) P_{m+1}\, s^m - \sum m P_m \cdot s^m\right]$

$$\Rightarrow \frac{\partial}{\partial t} F(s,t) = k(1-s)\cdot\frac{\partial F(s,t)}{\partial s} \quad (\text{Linear!})$$

$\boxed{\text{Method of characteristic}}$ line : $dt = -\frac{ds}{k(1-s)} \Rightarrow s = 1 - c e^{kt}$



Initial condition $P_m(0) = \delta_{m,N}$

$$\Rightarrow F(s,0) = \sum_m \delta_{m,N}\, s^m = s^N$$

$$= (1-c)^N$$

$$F(s,t) = (1-c)^N.$$

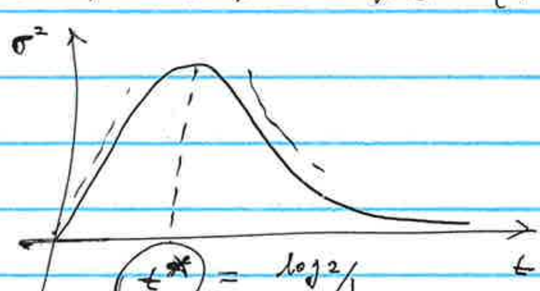
$$= \left(1-(1-s)e^{-kt}\right)^N \quad \text{①}$$

- Using $\langle m\rangle = \partial F/\partial s\Big|_{s=1}$ and $\langle m^2\rangle = \partial^2 F/\partial s^2\Big|_{s=1} + \partial F/\partial s\Big|_{s=1}$ to ①,

$$\Rightarrow \langle m(t)\rangle = N\left(1-\cancel{(1-s)}^{\,0}e^{-kt}\right)^{N-1} e^{-kt} = N e^{-kt} \quad [\text{Macroscopic}]$$

by Mc.Quarrie

$$\sigma^2(t) = \langle m^2\rangle - \langle m\rangle^2 = N e^{-kt}\left(1-e^{-kt}\right).$$



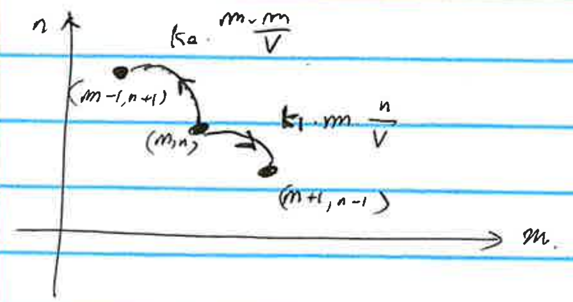
$t^* = \log 2/k.$

peak.

.pkl → GAEncoder → $\tilde{z}$ → Decoder → .pkl.

- $A + B \underset{k_2}{\overset{k_1}{\rightleftarrows}} A + A$ $\qquad N = A + B,\ A = m,\ B = n$

$\ \ m \quad\ n$ $\qquad\qquad n = N - m$ (single variable)



$$\Rightarrow \frac{d}{dt} P_m(t) = \underbrace{\frac{k_1}{V}\left[(m-1)(N-m+1)P_{m-1} - m(N-m)P_m\right]}_{\text{forward}}$$

$$+ \underbrace{\frac{k_2}{V}\left[(m+1)^2 P_{m+1} - m^2 P_m\right]}_{\text{backward}}$$

As $V \to \infty$,

$C = m/V \to m+1/V = c + 1/V \Rightarrow$ continuum $\rho(c,t) \Leftrightarrow P_m(t)$.

$$\Rightarrow \underbrace{\partial\rho/\partial t = -\frac{\partial}{\partial c}\cdot(\dot{c}\rho)}_{\text{Liouville Equation}} \quad \text{where} \quad \dot{c} = dc/dt = k_1 \cdot c(c_0 - c) - k_2 c^2$$

↳ elementary equation.