Brownian motion, Langevin Equation

$$F_{total} = ma = m\frac{dv}{dt}$$

Drag from solvent on particle

$$m\frac{dv}{dt} = -\xi v$$

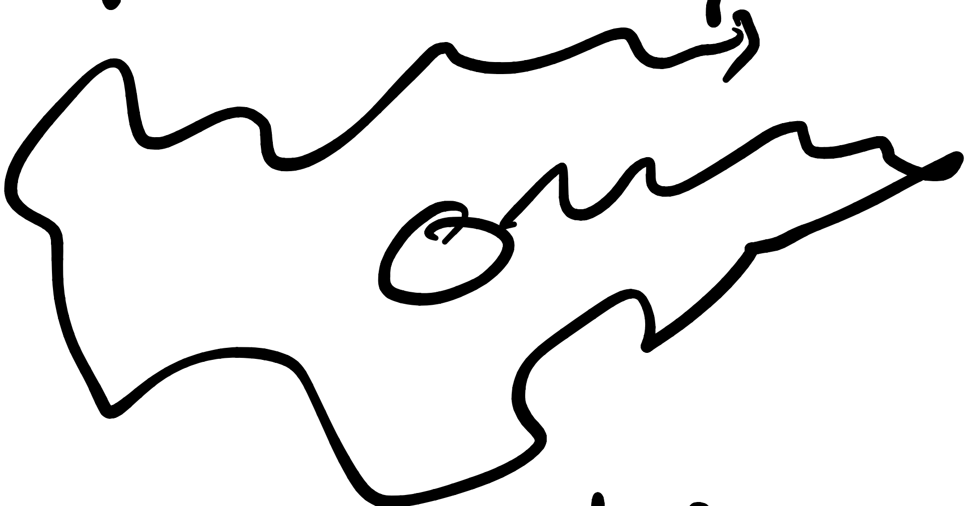
[Stokes law
spherical particle
$\xi = 6\pi\eta a$
viscosity
radius

$$\rightarrow$$

$$\frac{1}{v}\frac{dv}{dt} = -\xi/m$$

$$\Rightarrow \quad v(t) = v(0)\, e^{-\xi/m\, t}$$

Particles keep moving



$$\langle v_x^2 \rangle = \frac{k_B T}{m}$$

Langevin

all force

External force, pair forces $-\nabla U$

random force

$$m\frac{dv}{dt} = -\xi v + \delta F(t)$$

$$\langle \delta F(t) \rangle = 0$$

if $t \neq t'$ independent $\langle \delta F(t) \rangle \cdot \langle \delta F(t') \rangle = 0$

$$\langle \delta F(t)\, \delta F(t') \rangle = \underbrace{2B}_{\text{variance}}\, \delta(t-t')$$

$$m\frac{dv}{dt} = -\frac{\xi}{m}v + \delta F(t)$$

[appendix Zwanzig]

$$\frac{dx(t)}{dt} = a\,x(t) + b(t)$$

$\leftarrow x(t) = e^{at}y(t)$

$$e^{at}\frac{dy(t)}{dt} + \cancel{a e^{at} y(t)} = \cancel{a e^{at} y(t)} + b(t)$$

$$\frac{dy(t)}{dt} = e^{-at}b(t)$$

$$\int_0^{\tau} \frac{dy(t)}{dt}\,dt = \int_0^{\tau} e^{-at}\, b(t)\, dt$$

$$y(\tau) - y(0) = \int_0^{\tau} e^{-at}\, b(t)\, dt$$

$$y(t) = e^{-at} x(t)$$

$$e^{-a\tau} x(\tau) - x(0) = \int_0^{\tau} e^{-at}\, b(t)\, dt$$

$$x(\tau) = e^{a\tau} x(0) + \int_0^{\tau} e^{-a(t-\tau)}\, b(t)\, dt$$

$$= e^{a\tau} x(0) + \int_0^{\tau} e^{as}\, b(\tau - s)\, ds$$

$$s = \tau - t$$

$$ds = -dt$$

$$\star \quad X(\tau) = e^{a\tau} x(0) + \int_0^\tau e^{as} b(\tau - s)\, ds$$

$$\frac{dx(t)}{dt} = a\, x(t) + b(t)$$

$$\frac{dv(t)}{dt} = \underbrace{-\xi/m}_{a}\, v(t) + \underbrace{\frac{1}{m} \delta F(t)}_{b}$$

$$\Rightarrow V(\tau) = \underbrace{v(0) e^{-\xi/m\,\tau}}_{\text{no random force}} + \frac{1}{m} \int_0^\tau \underbrace{e^{-\xi/m\, s}}_{\text{memory}} \cdot \delta F(\tau - s)\, ds$$

$$V(\tau) = v(0)e^{-\xi/m\,\tau} + \frac{1}{m}\int_0^\tau e^{-\xi/m\, s}\cdot \delta F(\tau - s)\,ds$$

$$+ \frac{1}{m}\int_0^\tau e^{-\xi/m(\tau - t)}\,\delta F(t)\,dt$$

"want" connect "B" to the fact

that $\langle V^2 \rangle = k_B T/m$

$$\langle V(\tau)^2\rangle = \langle V(0)^2\rangle e^{-2\xi/m\,\tau} + \frac{2}{m}\int_0^\tau \langle v(0) e^{-\xi/m(\tau - t)}\cdot \delta F(t)\rangle$$

0

$\frac{k_B T}{m}$ if equilibrim

$$+ \frac{1}{m^2}\int_0^\tau\int_0^\tau dt_1\,dt_2 \langle \delta F(t)\,\delta F(t')\rangle\, e^{-\xi/m[\tau - t_1 + \tau - t_2]}$$

$2B\delta(t-t')$

$$\langle v(\tau)^2\rangle = \langle v(0)^2\rangle e^{-2\xi/m\,\tau}$$

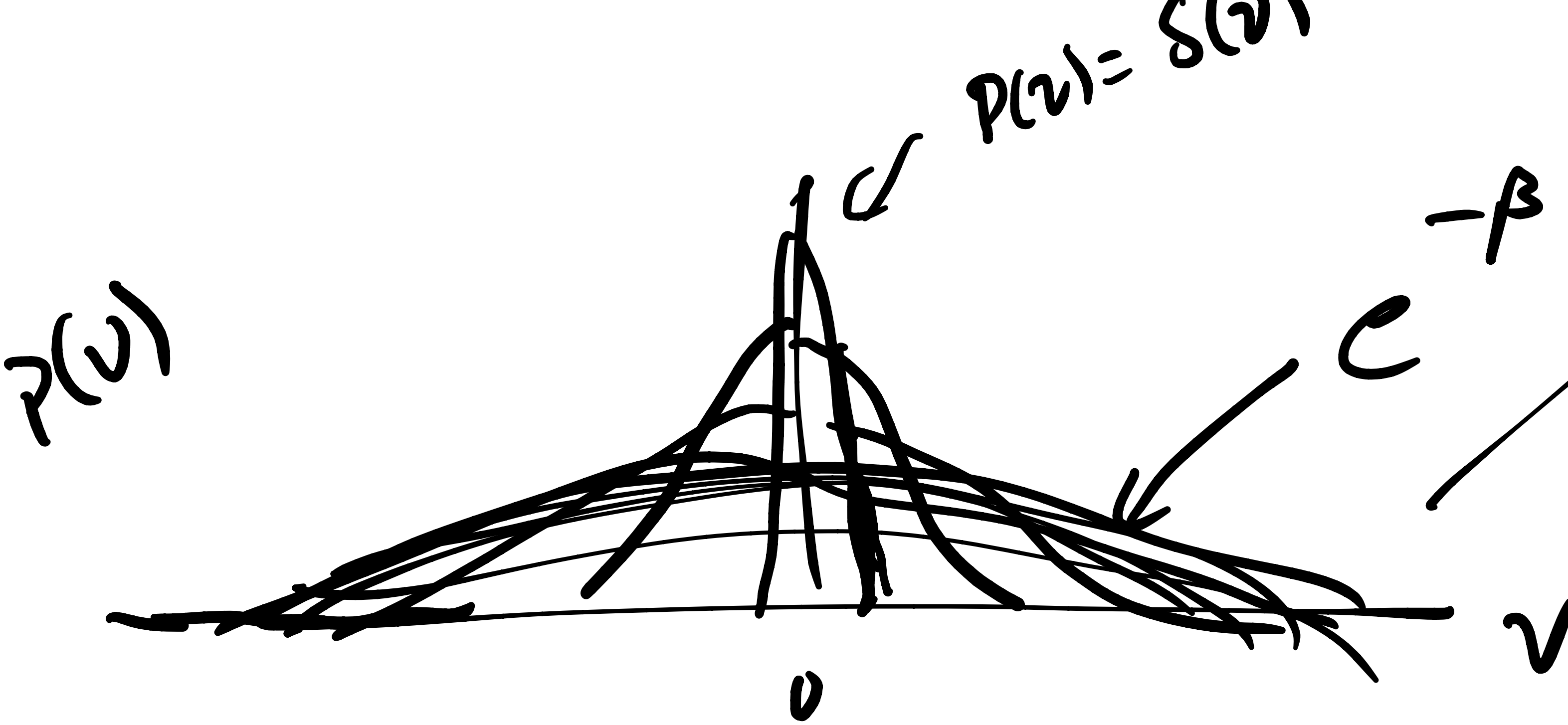
$$+ \frac{2B}{m^2}\underbrace{\int_0^\tau\int_0^\tau dt_1\,dt_2\, e^{-\xi/m(2\tau - t_1 - t_2)}\,\delta(t_1 - t_2)}_{\int_0^\tau e^{-2\xi/m(\tau - t_1)}\,dt_1}$$

Fluctuation dissipation theorem

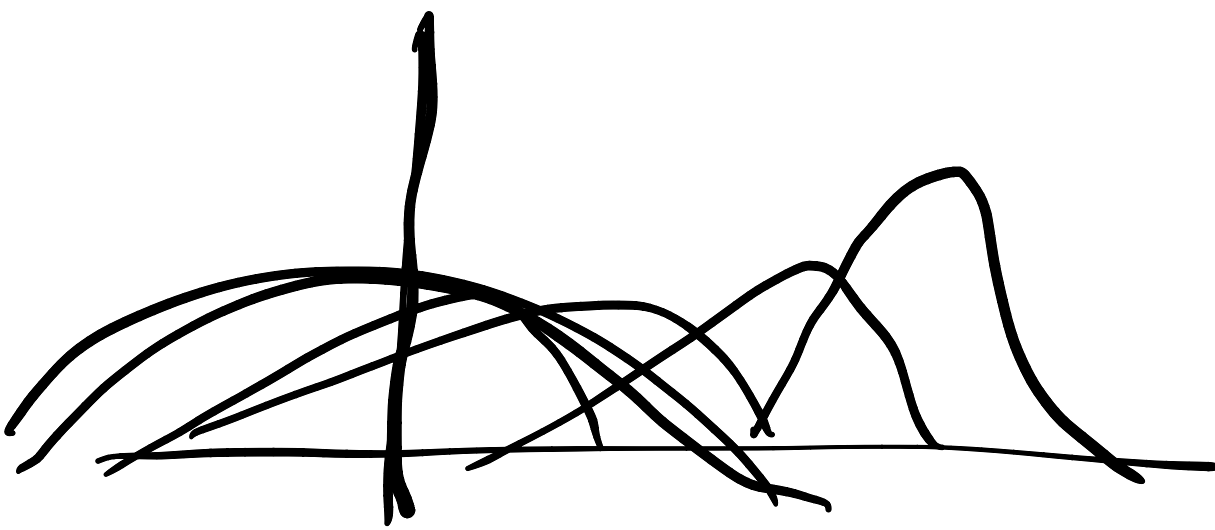
$$= \langle v(0)^2\rangle e^{-\xi/m\,\tau}_{\tau} + \frac{B}{\xi m}\left[1 - e^{-2\xi/m\,\tau}\right]$$

Start w/ initial velocity distribution

$$\langle v(\tau)^2\rangle \xrightarrow[t\to\infty]{} B/\xi m = \frac{k_B T}{m} \Rightarrow \boxed{B = k_B T \xi}$$



$$\frac{e^{-\beta \frac{1}{2} m v^2}}{\sqrt{2\pi k_B T / m}}$$



compute exactly from eqn?

Time Correlation Functions (TCF)

No equivalent of a partition func for Non Eq b/c

To get Z, need to know $P(X)$

$$Z = \int dx \, P(x)$$

in non eq $P(X)$ depends on how the system was prepared

Instead consider TCFs

$\langle a(t_1)\, b(t_2) \rangle$ $\leftarrow$ 2 point
2 quantity
TCF

$\langle v(t)\, v(0) \rangle$ or $\langle x(t)\, x(0) \rangle$

TCFs $\longleftrightarrow$ thermodynamic quantities
viscosity, diffusion constant
thermal conductivity
spectroscopic signals

Measurements now correspond to time averages

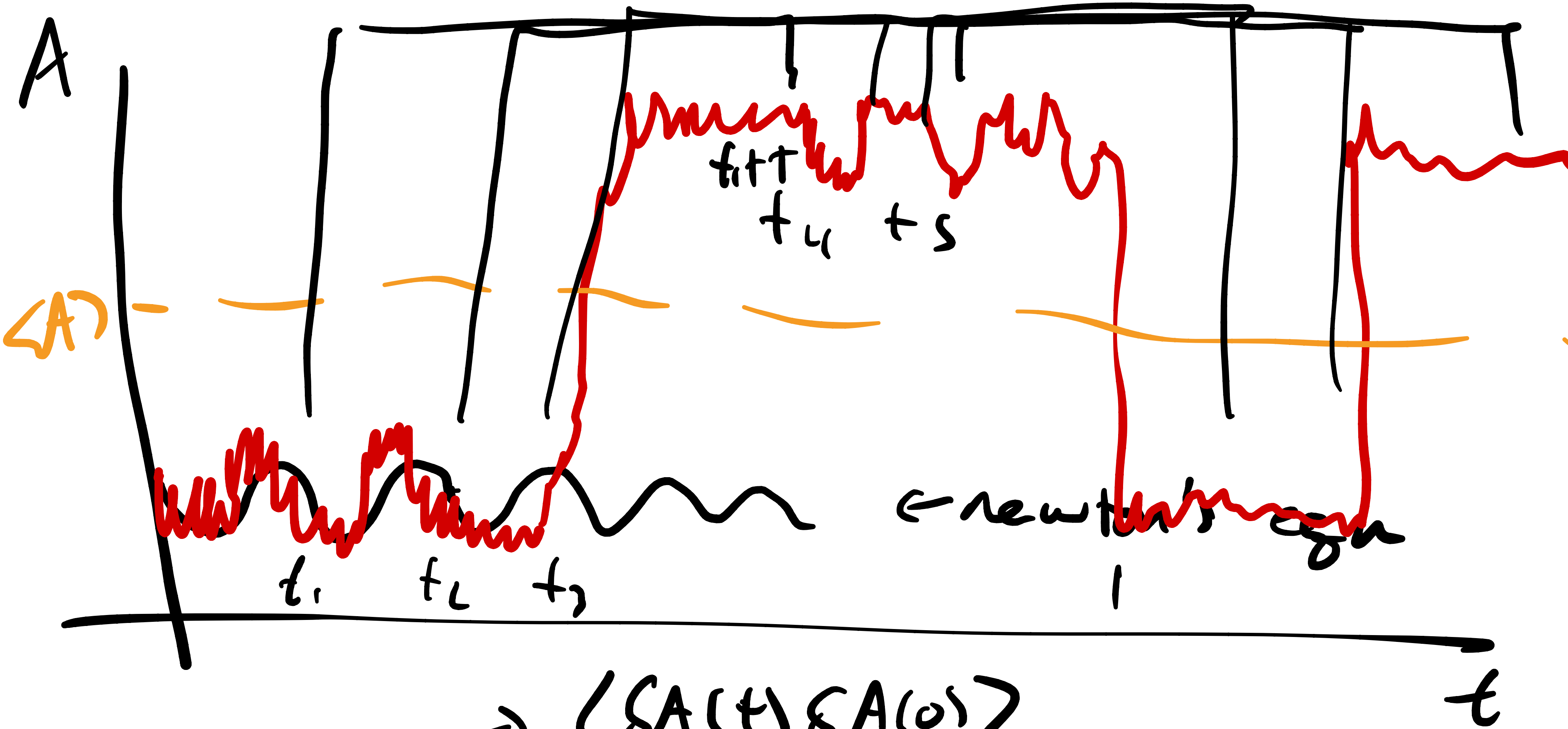
$$\langle A \rangle = \frac{1}{\tau}\int_0^{\tau} A(t)\,dt$$

$$\langle \delta v(\tau)\delta v(0)\rangle$$

$$\underbrace{\langle \overbrace{\langle v(\tau)\, v(0)\rangle}^{\text{time average}} \rangle}_{\text{ensemble}} = \frac{1}{\tau}\int_0^{\tau} \langle v(\tau) v(0)\rangle\,dt$$

Fluctuation from average

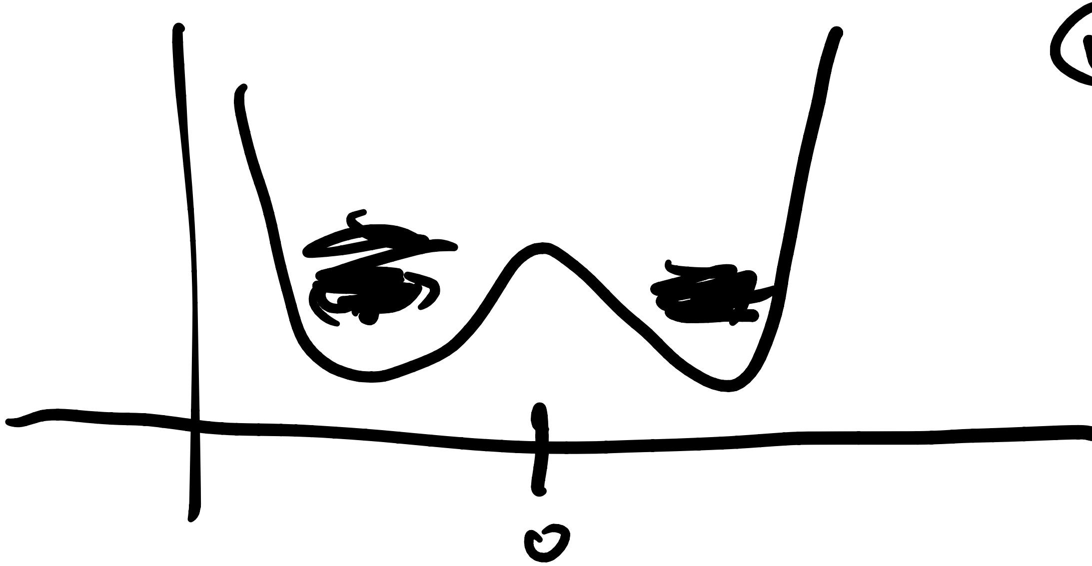
$$\delta A(t) = A(t) - \langle A \rangle$$

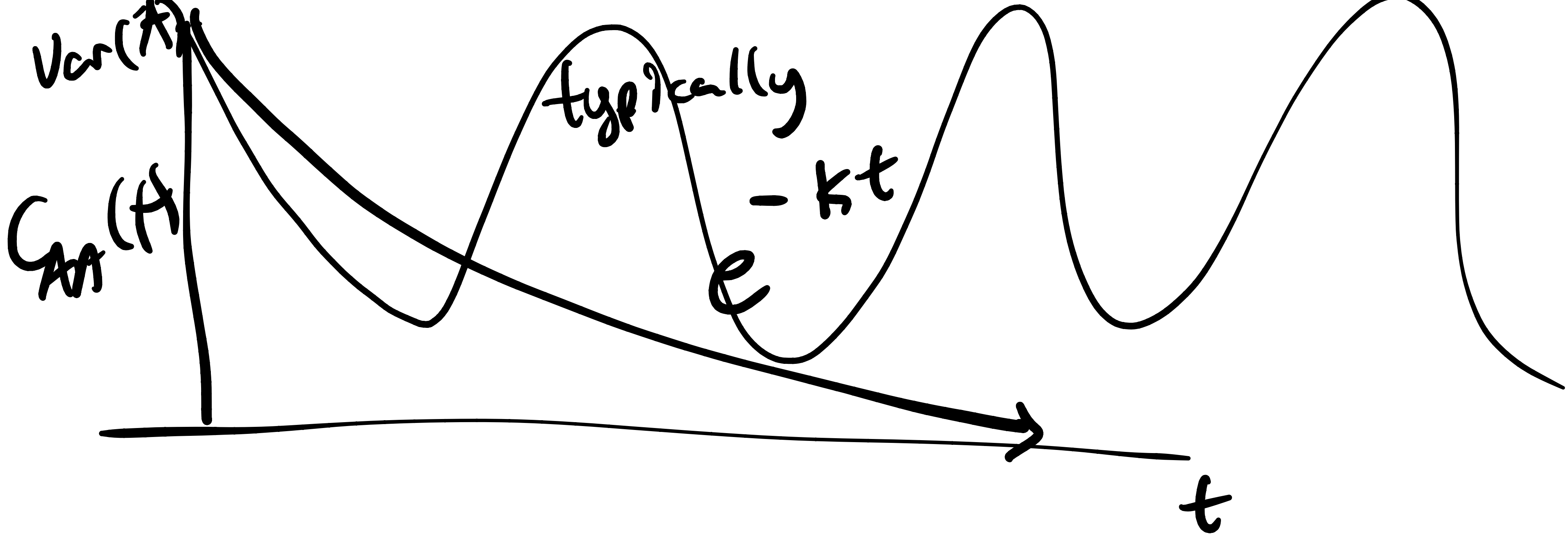


$\rightarrow \langle \delta A(t)\, \underbrace{\delta A(0)}\rangle$

@ eq, only difference matters

$A = x$

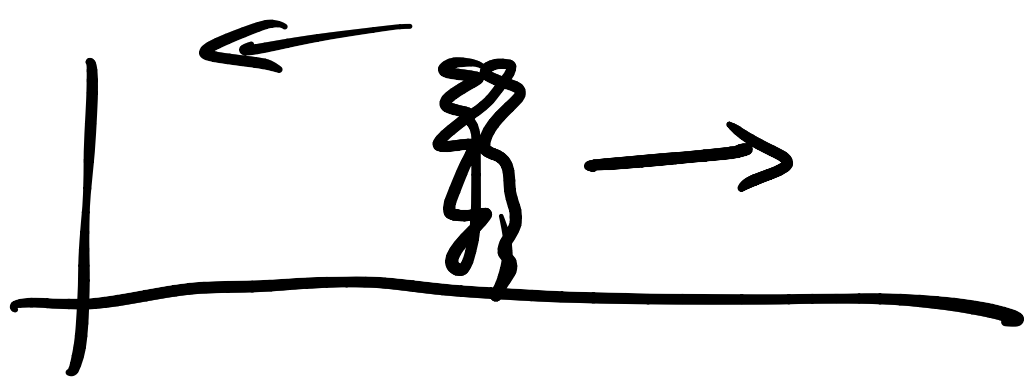




$$\langle \delta A(0)\delta A(0)\rangle = C_{AA}(0)$$

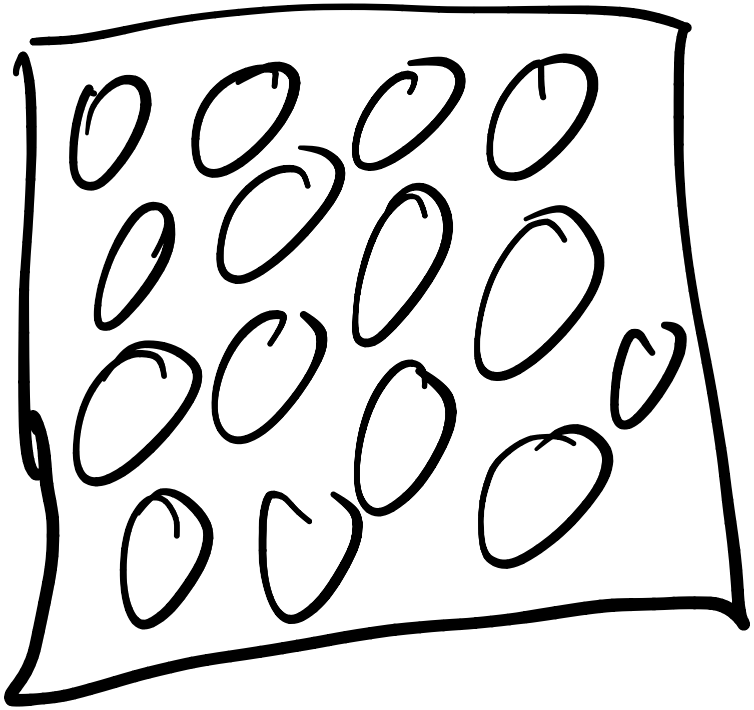
at $t \to \infty$ $\langle \delta A(t)\delta A(0)\rangle \to \langle \delta A(t)\rangle\langle \delta A(0)\rangle$

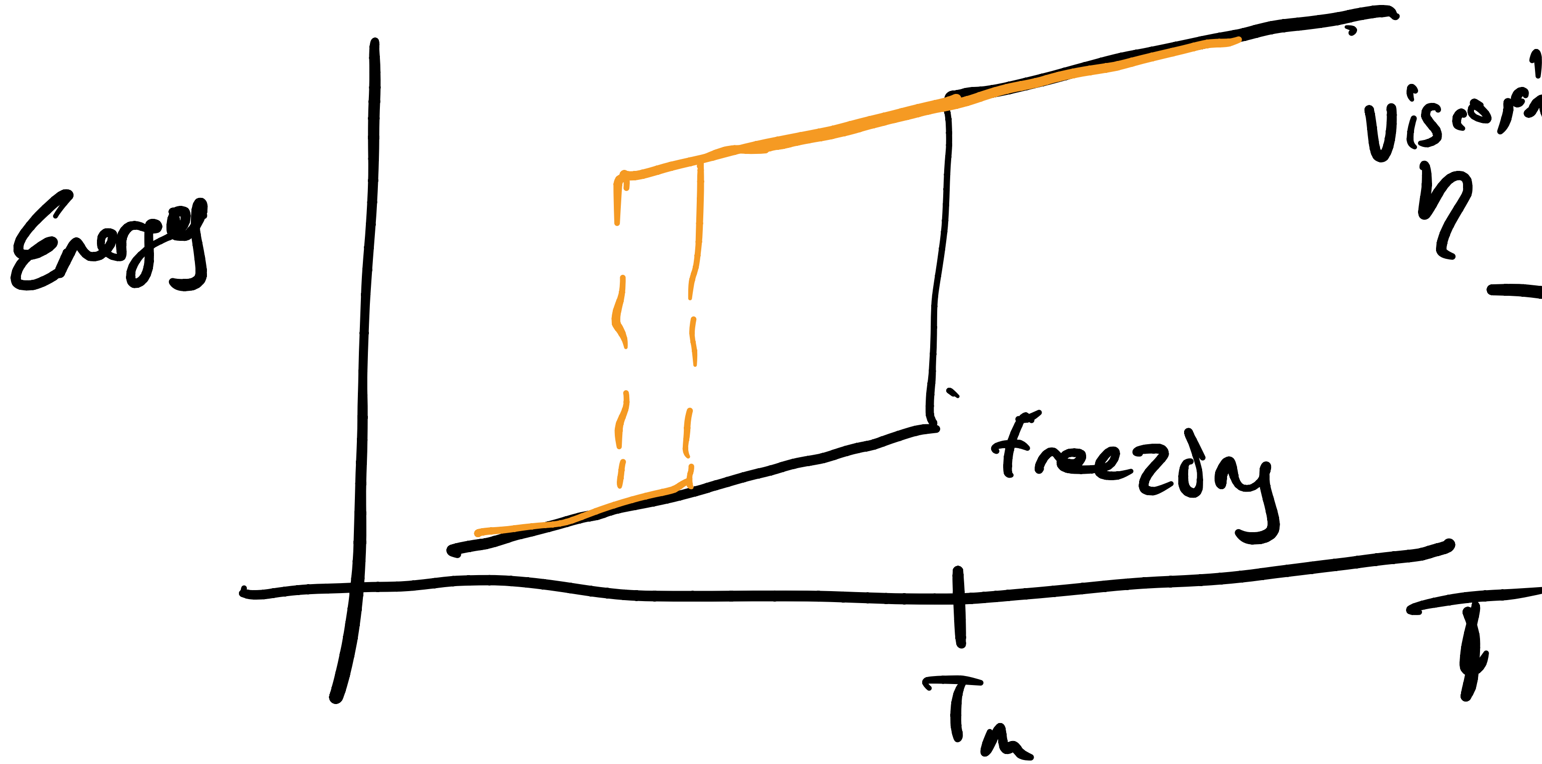
$= 0$

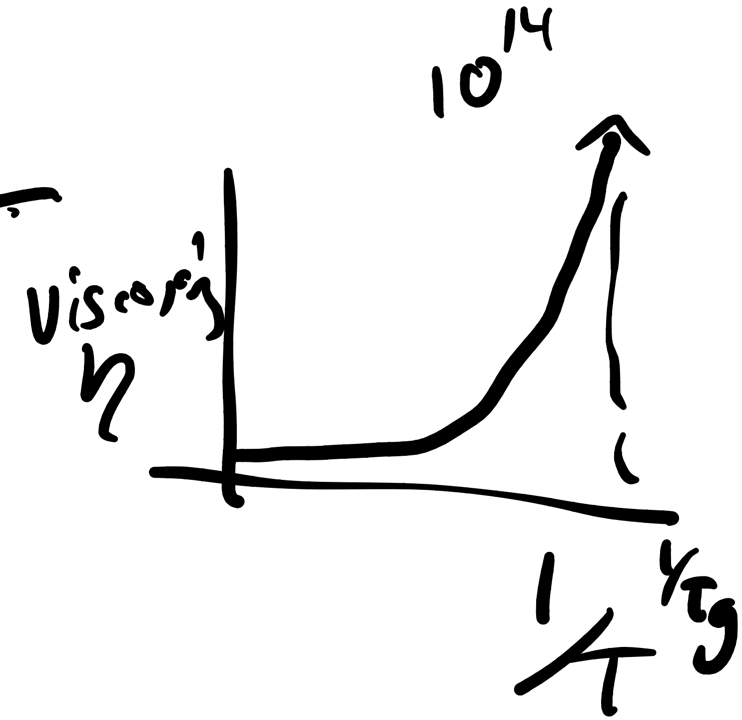


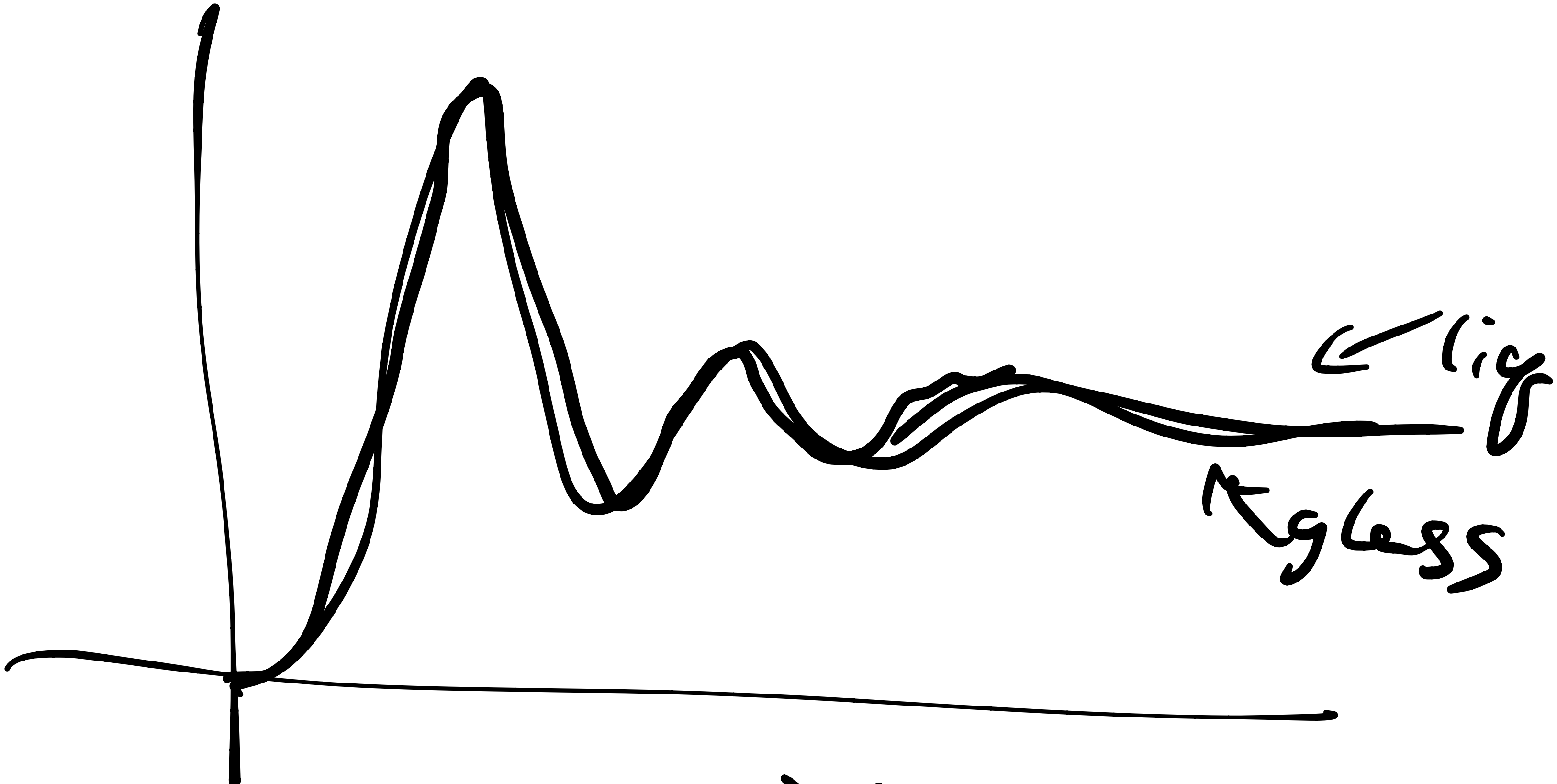
Glasses & Supercooled liquids

Jamming









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