Non eq - pt 2

Langevin equation

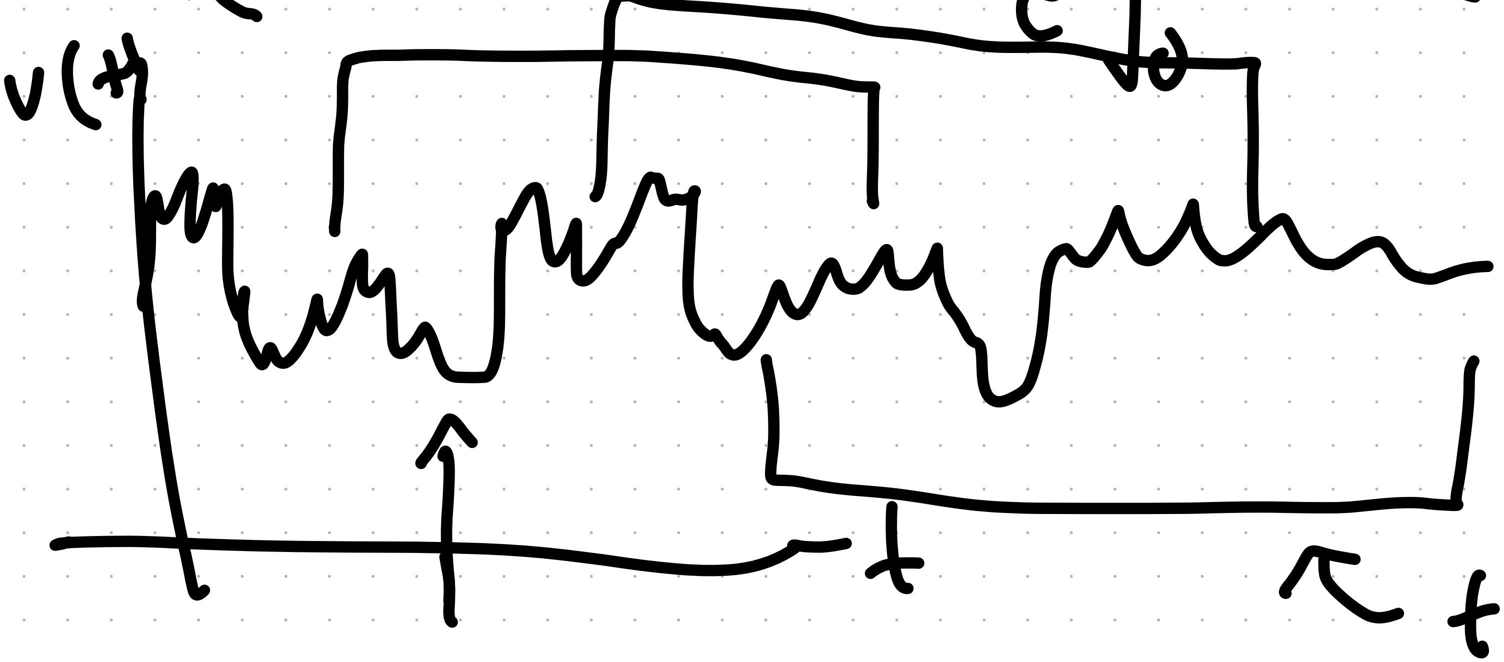
$$m\frac{dv}{dt} = -\xi v - \nabla U + \delta F(t)$$

$$v(t) = v(0)\, e^{-\xi t/m} + \frac{1}{m}\int_0^t dt'\, e^{-\xi(t-t')/m}\, \delta F(t')$$

$$\frac{d}{dt}\langle \delta x(t)^2 \rangle = 2\int_0^t \langle v(u)\, v(0)\rangle\, du = 2D$$

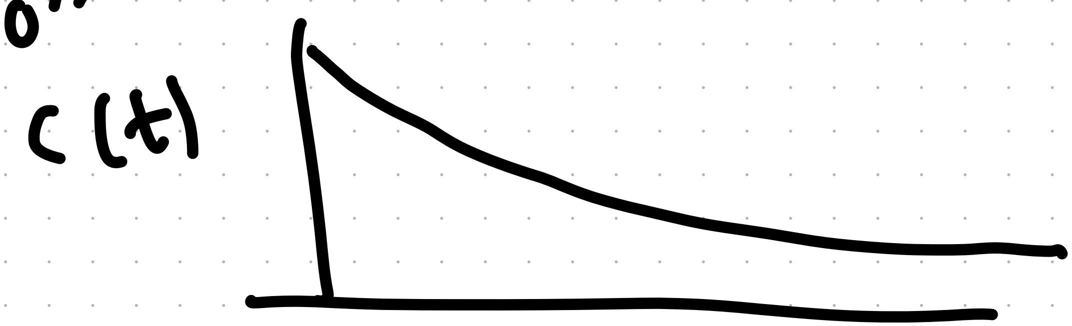
MSD $\propto t$ (at long times)

$$\langle v(t)\, v(t') \rangle_{time} = \frac{1}{\tau}\int_0^{\tau} ds\, v(t+s)\, v(t'+s)$$



$$\langle v(t)\, v(0) \rangle = C(t)$$

"t" "0"



want $v(t)\, v(0)$

want $\int_0^t \langle v(u) v(0) \rangle \, du$

$$v(t) = \cancel{v(0)\, e^{-\xi t/m}} + \frac{1}{m} \int_0^t dt' \, e^{-\xi (t-t')/m} \, \delta F(t')$$

assumption that $t =$ "0" is in infinite past ...

in equilibrium

$$\langle v(t)\,v(t')\rangle = \frac{1}{\tau}\int_0^\tau ds \int_0^\infty du_1 \int_0^\infty du_2 \; \underline{\qquad}$$

$$1$$

$$v(t) = \int_0^t \frac{\delta F(u_1)}{m} e^{-u_1 \xi/m} du_1$$

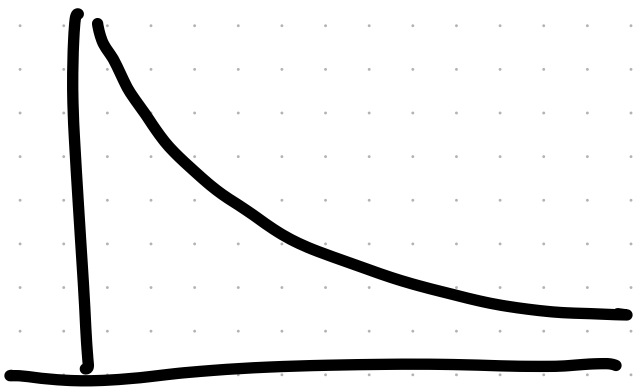
$$\frac{1}{m^2}\, \underbrace{\delta F(t-u+s)\,\delta F(t'-u_2+s)}$$

replace w/ average $\quad 2B\delta(t-u_1-t'+u_2)$

$$\langle v(t)\, v(t')\rangle = \int_0^{\infty} du_1\, e^{-\xi/m[u_1 - (t - u_1 - t')]} \cdot \frac{2B}{m^2}$$

$$= \underbrace{\frac{2B}{m^2} \cdot \frac{m}{2\xi}}\; e^{\xi/m(t-t')}$$

$$'' \quad \frac{B}{m\xi}\, e^{-\frac{\xi}{m}|t-t'|}$$



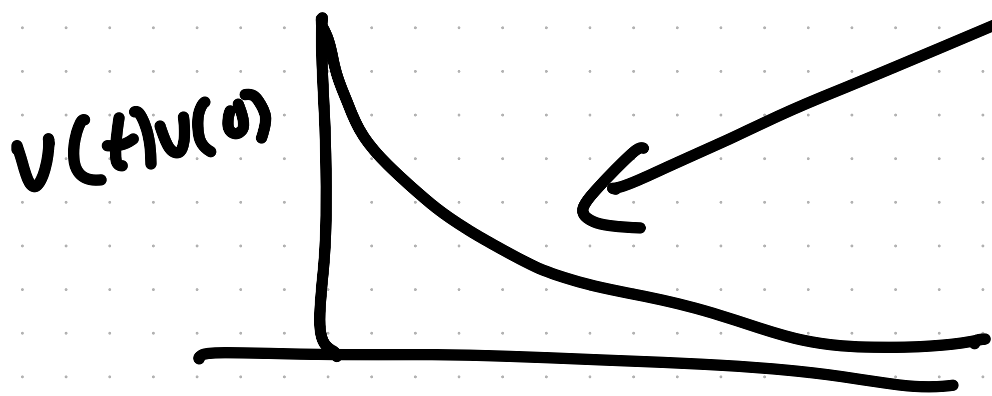
$$B = k_B T \xi$$

$$\langle v(t) v(t')\rangle = \frac{k_B T}{m}\, e^{-\xi/m|t-t'|}$$

Time average <-> Equilibrium Average

$$\langle v(t)v(t')\rangle = \frac{k_B T}{m} e^{-\xi/m|t-t'|}$$

$$\langle \Delta x(\tau)^2\rangle = \int_0^\tau dt\, 2\int_0^t \langle v(u)v(0)\rangle du$$



$$\langle \Delta x(\tau)|^2 \rangle = \int_0^{\tau} dt \; 2\int_0^{t} \frac{k_B T}{m} e^{-\xi/m \, u} \, du$$

$$= \int_0^{\tau} dt \; \frac{2k_B T}{m} \frac{m}{\xi} \left[-e^{-\xi u/m} \right]_0^{t}$$

$$= \int_0^{\tau} dt \; \frac{2k_B T}{m} \frac{m}{\xi} \left[1 - e^{-\xi t/m} \right]$$

$$= \frac{2k_B T}{\xi} \left[\tau - \frac{m}{\xi} + \frac{m}{\xi} e^{-\xi \tau/m} \right]$$

at large $\tau \rightarrow \frac{2k_B T}{\xi} \tau$

at large τ

$$MSD(\tau) \approx \frac{2k_BT}{\xi} \cdot \tau$$

$$\approx \underline{2D \cdot \tau}$$ ← before

Einstein relation

$$\boxed{D = \frac{k_BT}{\xi}}$$

energy

force/vel

Einstein self diffusion

units of $D = \frac{m^2}{s}$

ℓ^2/t

$\xi = 6\pi \eta a$ stokes formula

viscosity radius

$$D = \frac{k_B T}{6\pi \eta a} \Rightarrow \boxed{D \cdot \eta = \frac{k_B T}{6\pi a}}$$

Stokes-Einstein relation

* Note: violated in "Glasses"

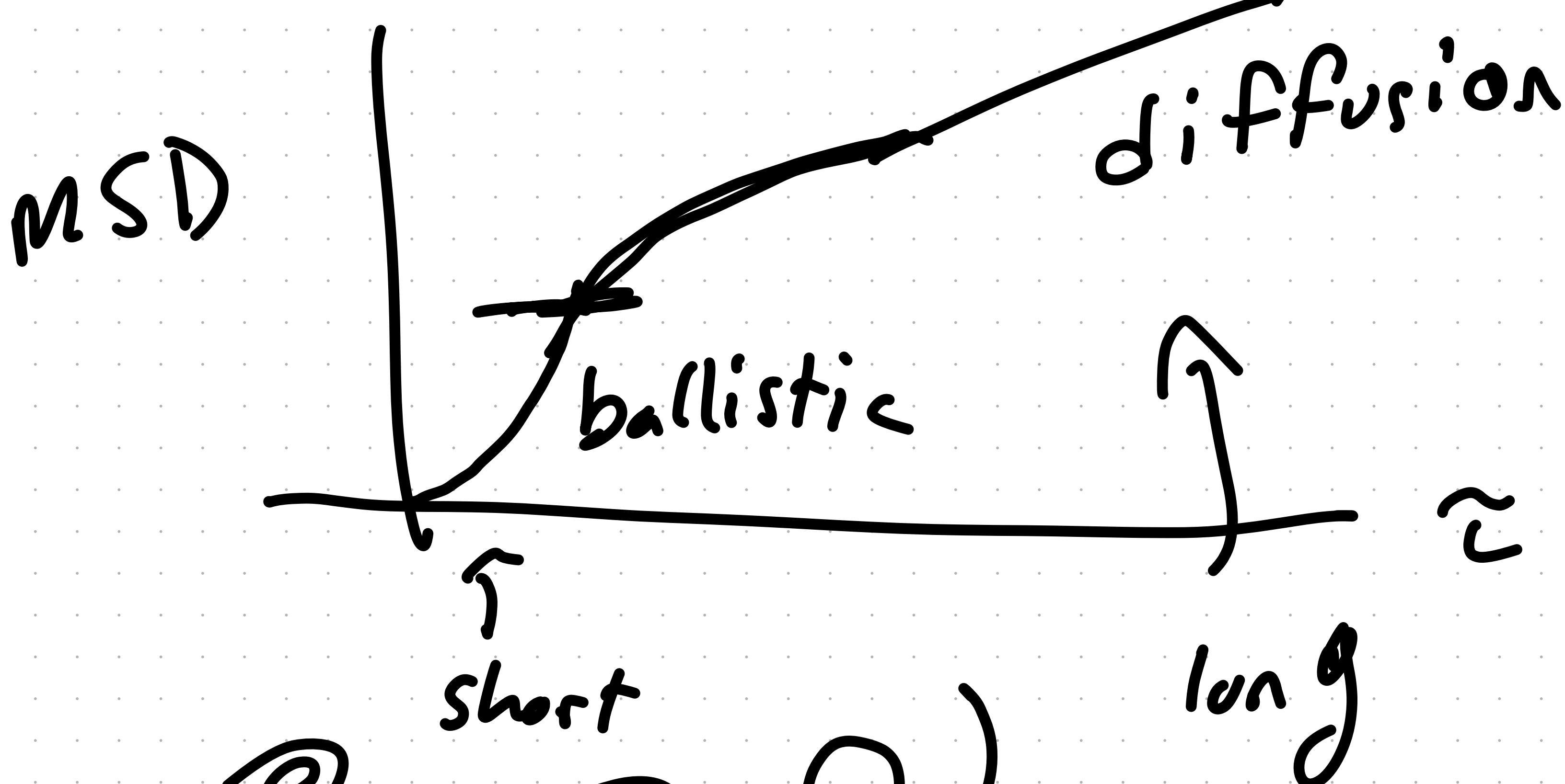
$$\langle \Delta x(\tau)^2 \rangle = \frac{2k_BT}{\xi}\left[\tau - \frac{m}{\xi} + \frac{m}{\xi} e^{-\xi\tau/m}\right]$$

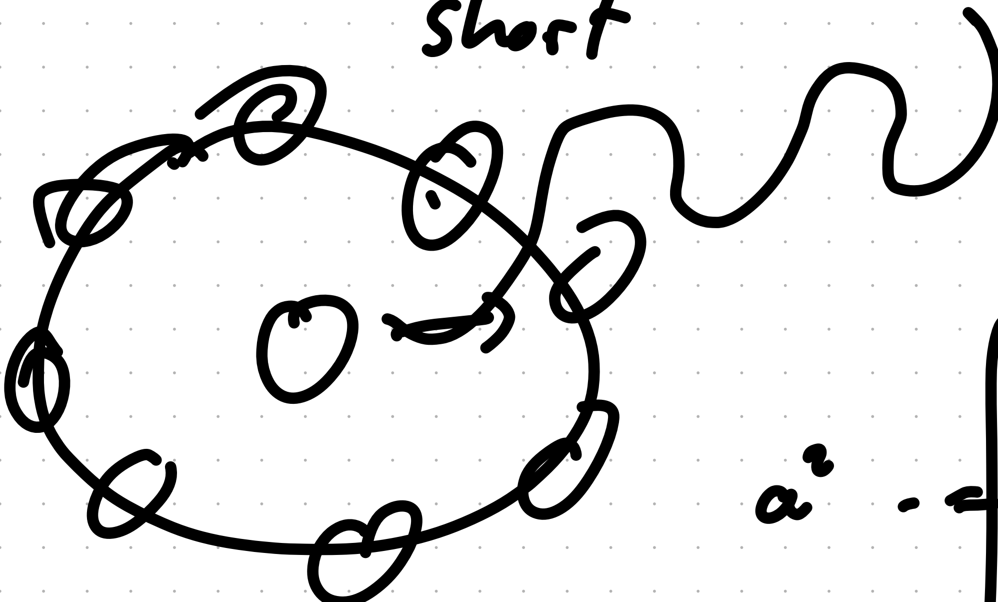
at small τ

$$\exp(-\xi\tau/m) \approx 1 - \frac{\xi\tau}{m} + \frac{\xi^2}{2m^2}\tau^2 + \dots$$

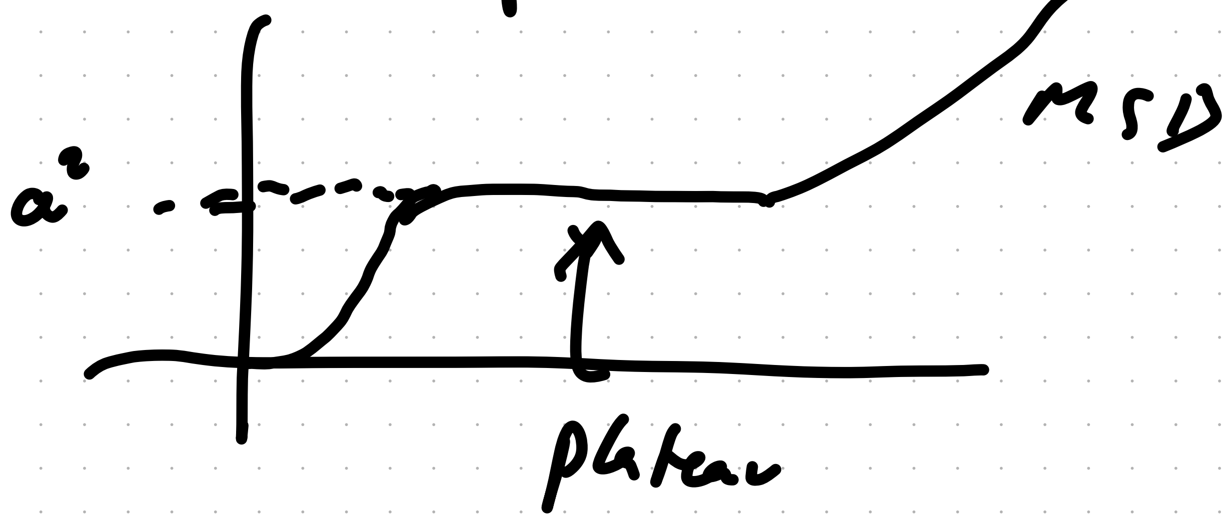
$$\propto \frac{k_BT}{m}\tau^2 + \text{higher order}$$

[$d = vt$, ballistic motion]





Supercooled



Non-Markovian

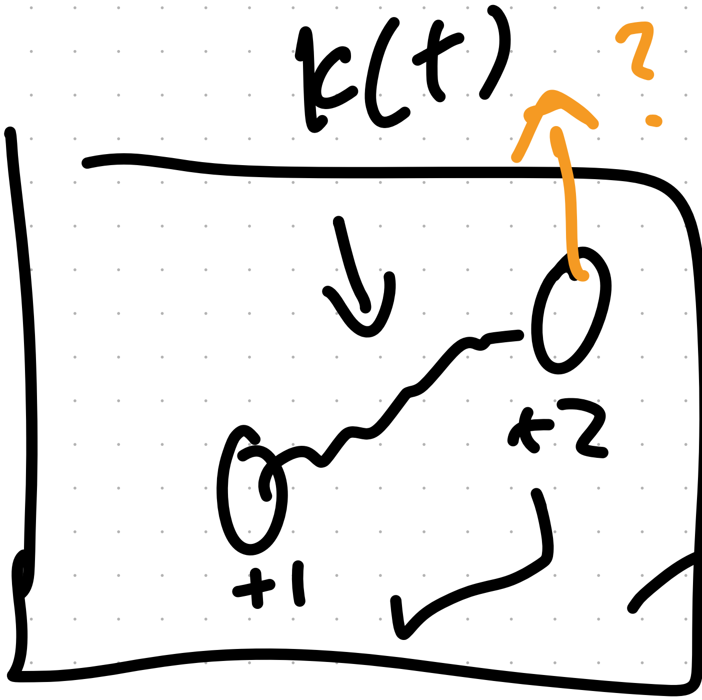
Markovian means, dynamics only depend on $\underline{X} = (\vec{q}, \vec{p})$, $\mathcal{H}$

N.M- dependence on "history"

$$-\xi v(t) \to -\int_{-\infty}^{t} k(t-s)\, v(s)\, ds$$

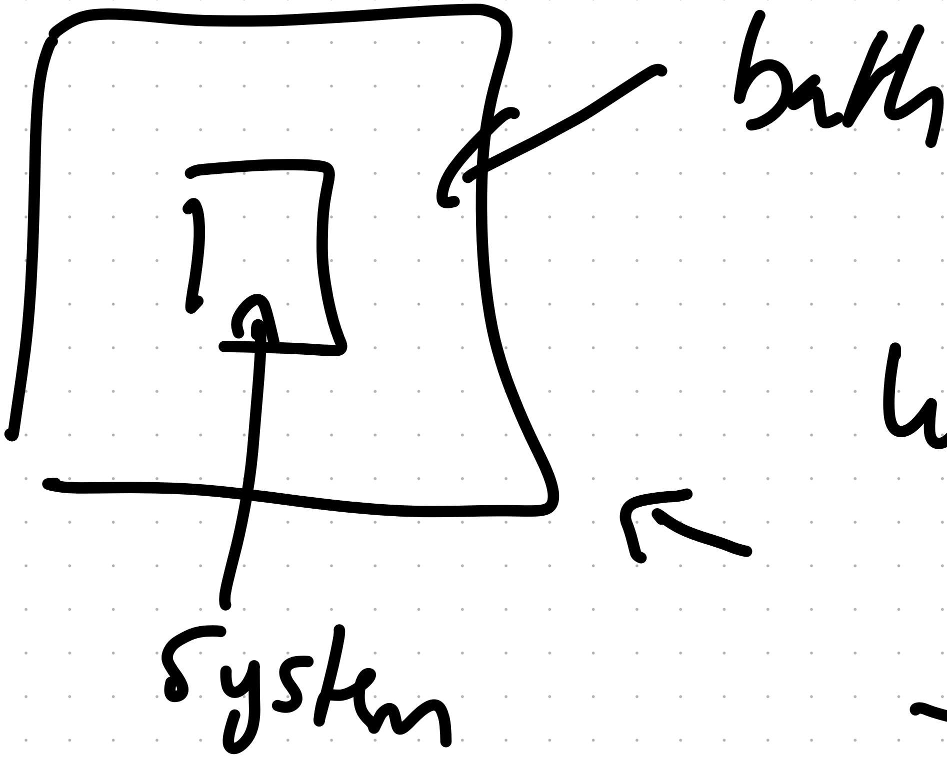
"Memory kernel"

$$\text{or} \quad -\int_{0}^{\infty} ds\, k(s)\, v(t-s)$$



$t = t_2 - t_1$

- Can be non-equilibrium
- Can be from "coarse graining"



Whole "universe"

system + bath

Hamiltonian dynamics

follows N, V, E

"Integrate out" bath

N, V, T heat in and out

$K(s)$

if memory is exponential

$$K(s) \propto e^{-as}$$

make system markovian by putting back in degrees of freedom

$$m\frac{d\vec{v}}{dt} = -\xi\vec{v} - \nabla u + \delta\vec{F}(t)$$

$$= -\int_0^t ds\, K(s)\,\vec{v}(t-s) - \nabla u + \delta\vec{F}(t)$$

Generalized langevin equation

$$\frac{d\vec{a}(t)}{dt} = i\underline{\underline{\Omega}}\cdot a(t) - \int_0^t ds\, K(s)\,\vec{a}(t-s) + \delta\vec{F}(t)$$

$$\langle \delta\vec{F}(t)\delta F(t') \rangle = \underline{\underline{K}}(t-t')\langle \delta a \delta a \rangle_{eq}$$

$i\,\Omega$ related to the derivative(s) of the "potential"

$= \Omega$ matrix

Harmonic oscilator

$$U(x) = \frac{1}{2} m\omega^2 x^2$$

$$U' = \omega^2 x$$