Non Equilibrium - Pt 1 (R. Zwanzig)

"Real" Nonequilibrium Stat Mech

Systems with Dissipation

↳ heat flows in/out of system
changes amount of work you can do

↳ $dS = \delta q / T$ (entropy production)

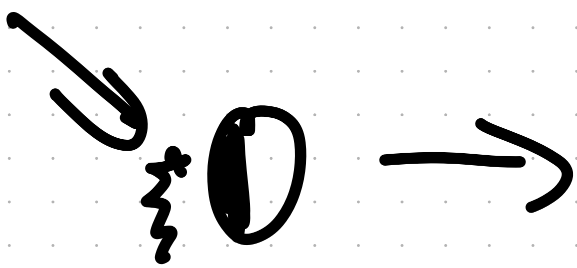
Adiabatic process - $dS = 0$

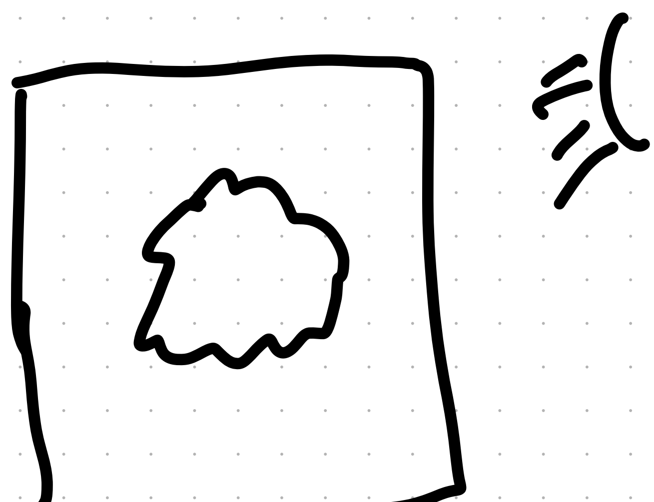
Non-equilibrium steady state

Examples:

Self assembly - dry system

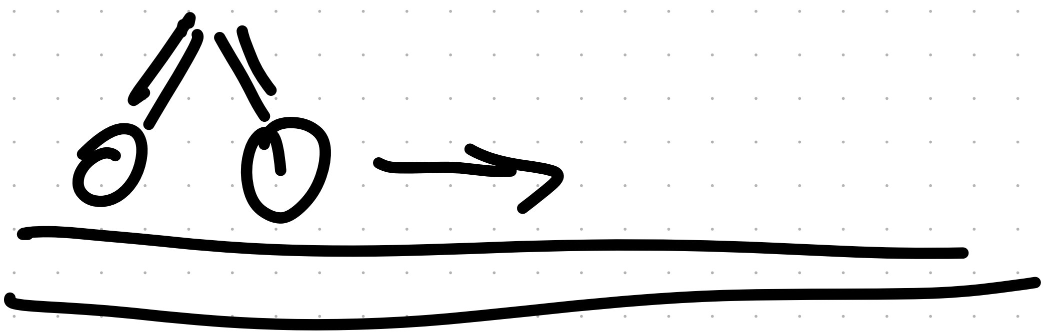
driven particles / self driven



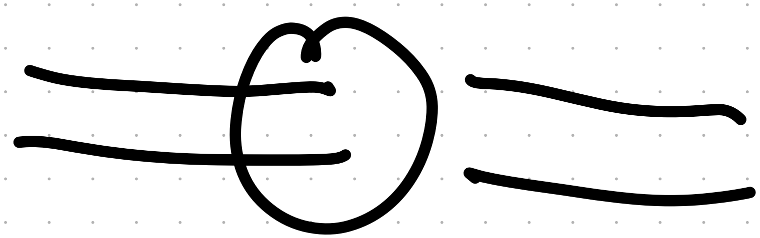


motility induced phase separation (MIPs) molecular motors:

consume ATP to do work



myosin/
kinesin/dynein



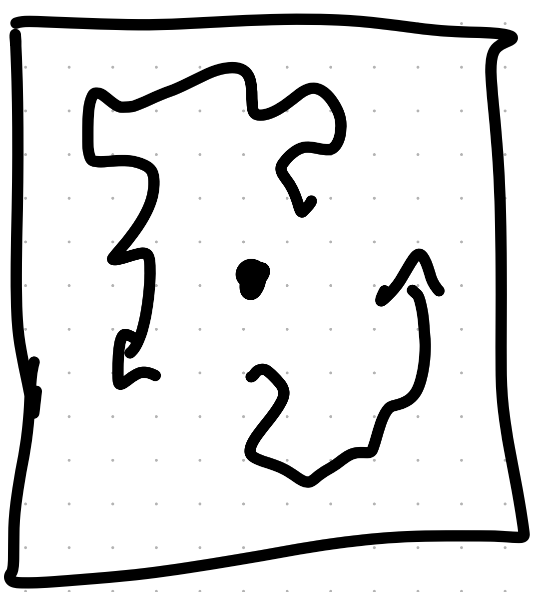
Ribosome

Folding/unfolding

molecules under force

Dynamics <-> Equilibrium

Brownian Motion



$$\vec{F}_{total} = m\vec{a} = m\frac{d\vec{v}}{dt}$$

drag, $F_{drag} = -\xi \vec{v}$

no random forces

$$m\frac{d\vec{v}}{dt} = \xi \vec{v}$$

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

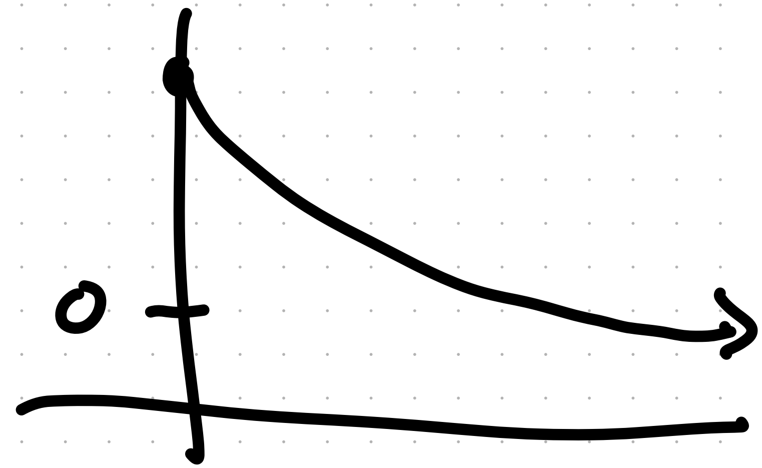
viscosity

radius

stokes law, 3d sphere

$$m \frac{d\vec{v}}{dt} = -\xi \vec{v}$$ ← from this equation

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



bigger mass,
more viscosity,
bigger radius

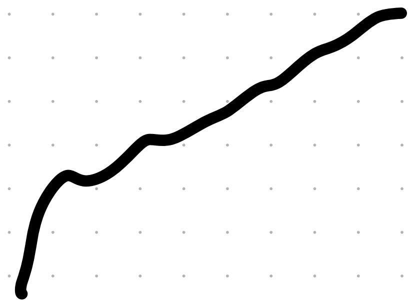
} Stops faster

$\langle v \rangle = 0$ by symmetry @ equilib.

$\langle v^2 \rangle$ $\qquad$ $\langle KE \rangle = \frac{3}{2} N k_B T$ 3d

$$Z_p = \int dp_x \, dp_y \, dp_z \; e^{-\frac{1}{2}m\left(p_x^2+p_y^2+p_z^2\right)/k_BT}$$

$$\left\langle \frac{1}{2} m v^2 \right\rangle = \frac{1}{2} k_B T$$



$$\langle v^2 \rangle = k_BT/m$$

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

random force

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

$$\langle \delta F(t) \delta F(t') \rangle = 2B\, \delta(t-t')$$

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

what $v(t)$

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

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

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

$$(a+b)^2 = a^2 + 2ab + b^2$$

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

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

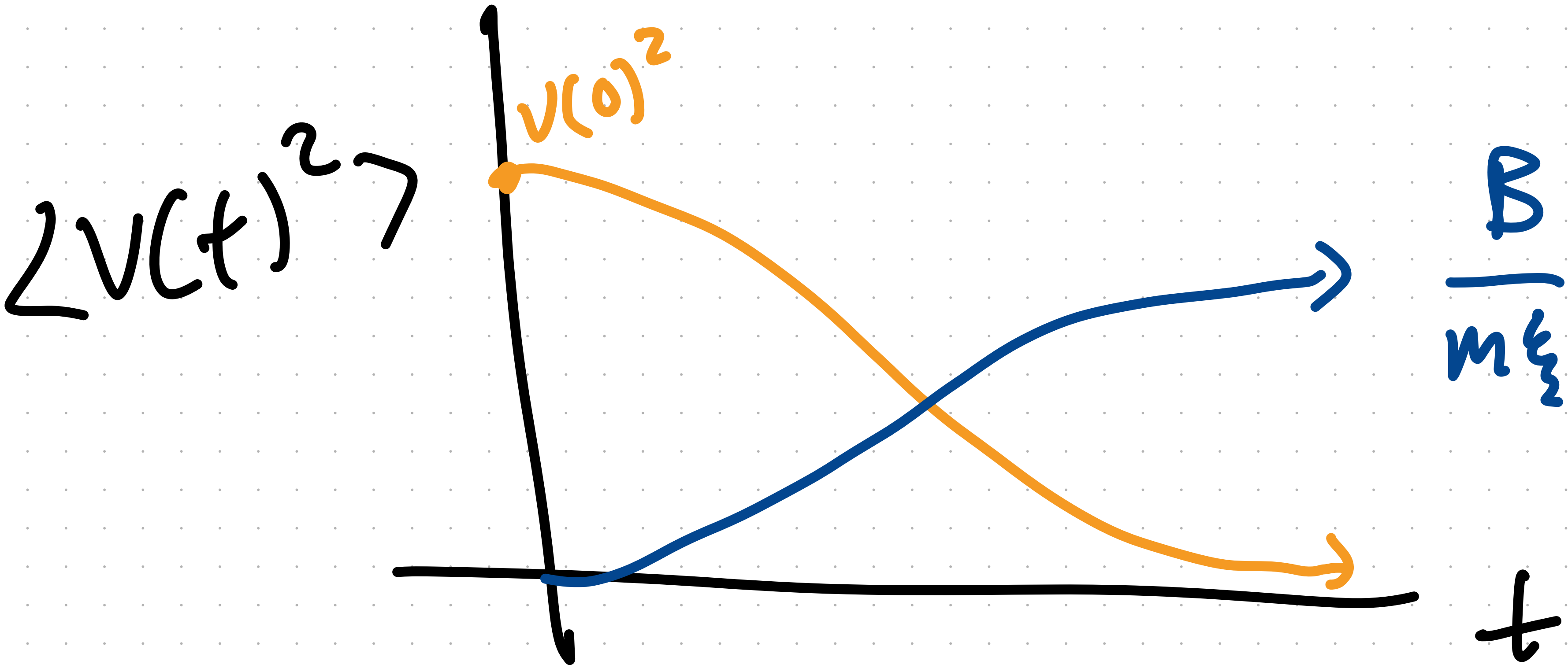
$$+ \, 2 e^{-\xi/m\, t} \int_0^t dt\, e^{-\xi/m\,(t-t')} \overbrace{\left\langle v(0)\, \frac{\delta F(t')}{m} \right\rangle}^{0}$$

$$+ \frac{1}{m^2} \int_0^t dt' \int_0^t dt''\, e^{-\xi/m\left[(t-t') + (t-t'')\right]} \underbrace{\langle \delta F(t')\, \delta F(t'') \rangle}_{2B\, \delta(t'-t'')}$$

$$\langle v(t)^2 \rangle = e^{-2\xi t/m} \langle v(0)^2 \rangle + \int_0^t dt' \, e^{-2\xi/m[t-t']} \cdot \frac{2B}{m^2}$$

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

@ $t=0$ $\quad \langle v(\overset{t=0}{t})^2 \rangle = \langle v(0)^2 \rangle$



$$\langle v^2 \rangle = k_B T / m$$

$$\underline{B} = m\xi \cdot \left(\frac{k_B T}{m}\right) = \underline{k_B T \, \xi}$$

$$\boxed{B = k_B T \, \xi}$$

$$\left[\frac{\partial A}{\partial x} \propto \mathrm{var}(x) \right.$$

- Fluctuation Dissipation Theorem

Size fluctuations (B)

$\propto$ strength of dissipation (ξ)

Time Correlation function

Before: $g(r) \sim \langle \delta(r)\, \delta(r') \rangle$

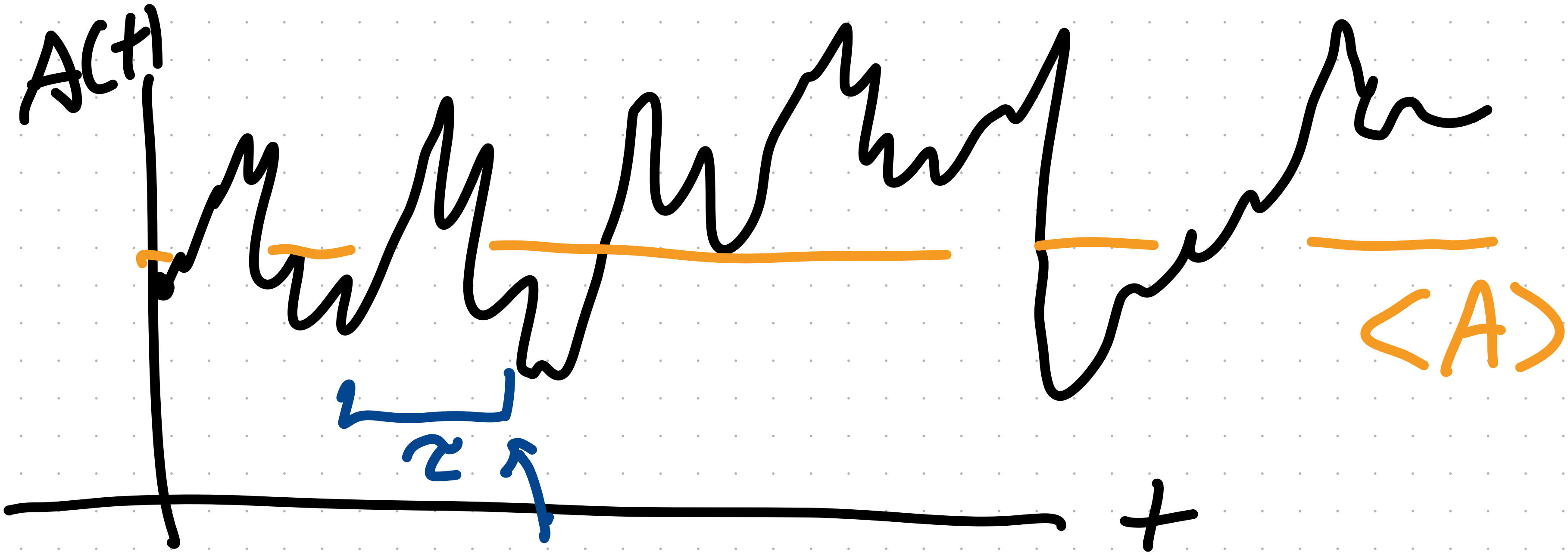
$C_{ij} \sim \langle \sigma(r)\, \sigma(r') \rangle$

Observable A

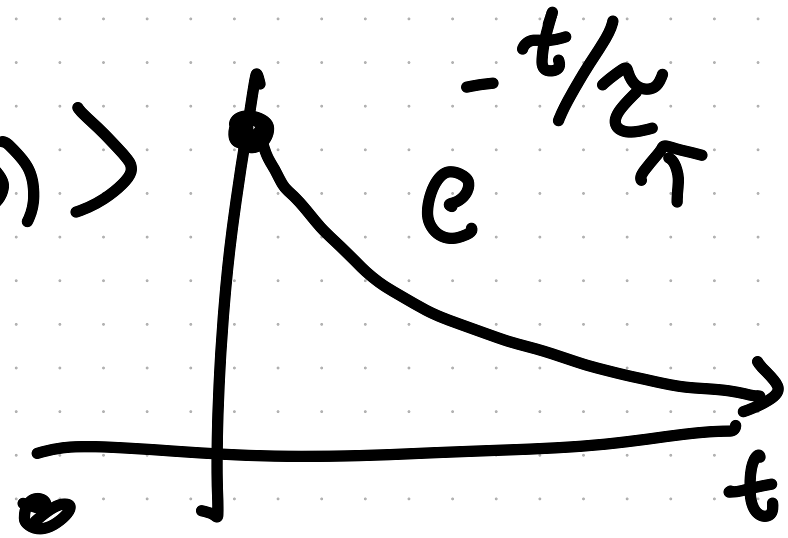
$A(t)\, A(t')$

$\delta A(t)\, \delta A(t')$ $\quad \delta A = A - \langle A \rangle$

$$\langle A \rangle_{time} = \frac{1}{T}\int_0^T dt\, A(t)$$

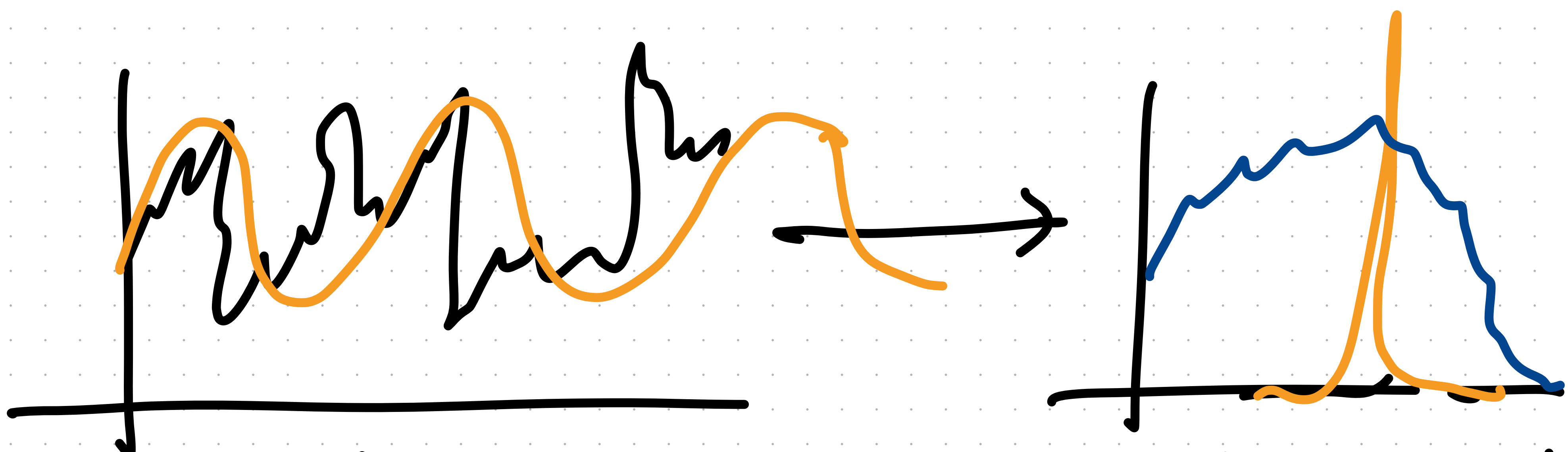


$$C(t) = \langle \delta A(t)\, \delta A(0) \rangle$$



Spectral Density

$$C_\omega \propto \int_{-\infty}^{\infty} dt\, e^{-i\omega t}\, C(t)$$



Eg: optical obstion - FT dipole-dipole C(t)

Connection btwn material properties
time correlation functions

[Green-Kubo relations]

$$\langle \delta\vec{x}(t)^2 \rangle \propto \underbrace{2dDt}$$

$$\langle \delta x(t)^2 \rangle = 2Dt$$

1d

$$\frac{d}{dt}\langle \delta x(t)^2 \rangle = 2D$$

$$\delta x(t) = x(t) - x(0) = \int_0^t \frac{dx}{dt}\, dt$$

$$= \int_0^t v(t)\, dt$$

$$\frac{d}{dt}\left\langle \left[\int_0^t v(t')\,dt'\right]^2 \right\rangle = 2D$$

F.T.C.

$$\frac{d}{dt}\int_0^t A(t')\,dt' = A(t)$$

$$2\int_0^t \langle v(s)\,v(t')\rangle\,dt'$$

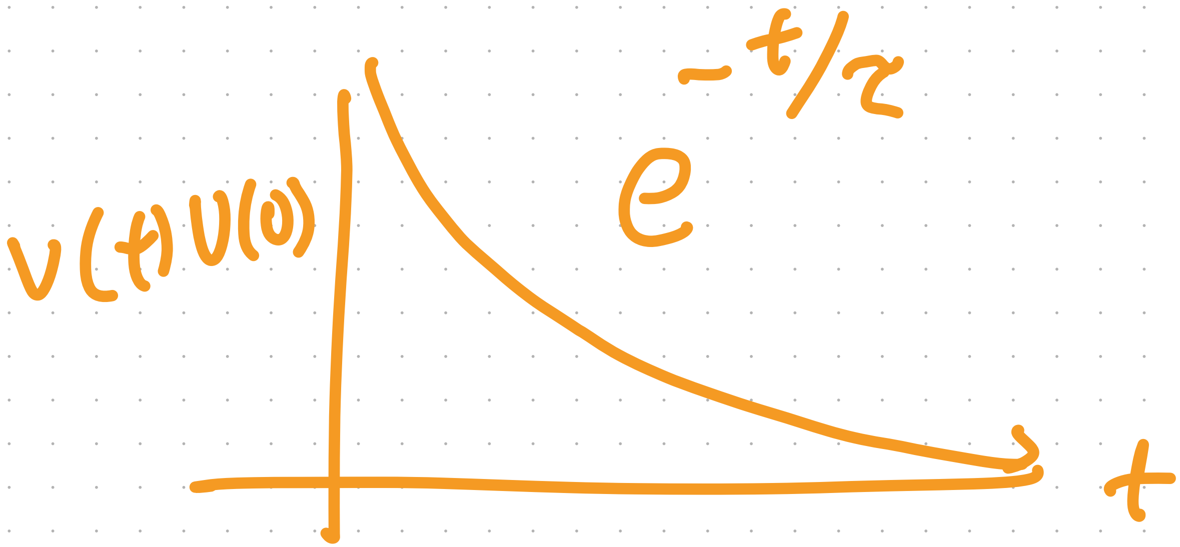
v – v correlation function

$$u = s - t'$$

$$= 2\int_0^t \langle v(u)\,v(0)\rangle\,du \leftarrow = 2D$$

$$D_{1d} = \int_0^t \langle v(u) v(0) \rangle \, du \quad \Big\} \lim_{t \to \infty}$$

$$D_{3d} = \frac{1}{3} \int_0^t \langle \vec{v}(u) \, \vec{v}(0) \rangle \, du$$



Dynamic Light Scattering

Berne & Pecora

Time Correlation functions and transport coefficients

Annual Reviews Physical Chemistry 1965

R. Zwanzig