Non Eq Pt 1

What is Non-Equilibrium Stat Mech?

Real & modern non-eq stat mech:
Systems w/ dissipation, which means heat/entropy flows in or out of system [doing or having work done on system, non adiabatically]

- In many cases, this means time reversibility in dynamics is broken
- Sometimes we can reach a "non-equilibrium steady state" where there is constant driving but basically at equilibrium

Examples: Self assembly by drying / in a field
self driven / externally driven particles
molecular motors (consume ATP to do work)
folding / unfolding protein under force...

Some theories have developed to treat these "real" non-equilibrium systems

- All of that is built on understanding dynamics of systems "near" equilibrium first.
- Additionally, we have to understand/learn about dynamics, especially systems in contact w/ a bath & how to study them

[time dependent processes]

Back to Brownian motion & origin of Langevin equation

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

Physics observations say that the particle has drag:

$$m\frac{dv}{dt} = -\xi v, \qquad \xi = 6\pi\eta a$$

viscosity (η), radius (a)

Stokes law, 3d sphere

If this were whole story then

$$v(t) = v(0)\, e^{-\xi t/m}$$ [more drag, lighter particle stops faster]

This would mean that the particle stops moving over time

But we know (from before, also xpts) that

$$\langle v_x^2 \rangle = \frac{k_B T}{m}$$ so this must come from collisions w/ the solvent

$$\left[\langle \tfrac{1}{2} m v_x^2 \rangle = \langle KE \rangle = k_B T/2 \right] \Rightarrow \langle v^2 \rangle = kT/M$$

So this is where we get Langevin's idea of

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

fluctuating force in each direction

Assert collisions uncorrelated in time & mean zero

$$\langle \delta F(t) \rangle = 0 \qquad \langle \delta F(t)\, \delta F(t') \rangle = 2B\,\delta(t-t')$$

So how do we solve this equation? Have to do once by a "trick" for diff eq

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

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

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

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

integrate from 0 to τ

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

switching back to x,

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

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

$s = \tau - t$

$ds = -dt$

$$+ \int_\tau^0 e^{as} b(\tau - s)\,(-ds$$

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

going back to Langevin eqn

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

$$\Rightarrow v(t) = \underbrace{e^{-\xi/m\, t} v(0)}_{\text{If no random force, correct solution}} + \int_0^t dt' \, e^{-\xi/m(t-t')} \frac{\delta F(t')}{m}$$

Now we want to predict $\langle v_{(t)}^2 \rangle$

So what is $(v(t))^2$?

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

$$+ \int_0^t \int_0^t dt' dt'' \, e^{-\xi/m[(t-t')+(t-t'')]} \frac{\delta F(t') \, \delta F(t'')}{m^2}$$

So now take avg [over many start times, ind particles ...]

$\langle \delta F \rangle = 0$

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

$$+ \int_0^t dt' e^{-2\xi/m[t-t']} 2B/m^2$$

$$= e^{-2\xi/m\, t} v(0)^2 + \frac{B}{\xi m}\left[e^{-2\xi/m(t-t')}\right]_{t'=0}^{t'=t}$$

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

so starts w/ same velocity $v(0)$, but as $t \to \infty$, goes to the average velocity of any particular particle

$$\langle v(t)\rangle^2 \xrightarrow[t\to\infty]{} B/m\xi$$

And so $\boxed{B = k_B T \xi}$

The fluctuation-dissipation theorem (FDT)

Relates the strength of the random noise on an observable to the friction

Time correlation functions

Only one Eq state, but many non-equilibrium states. Hence there is no (probably) unique partition function. What we compute instead are time correlation functions (more like $g(r)$, but in time)

These will connect to:

viscosity, thermal cond, diffusion & scattering spectroscopy & NMR

Measurements are still averages, but now back to time averages

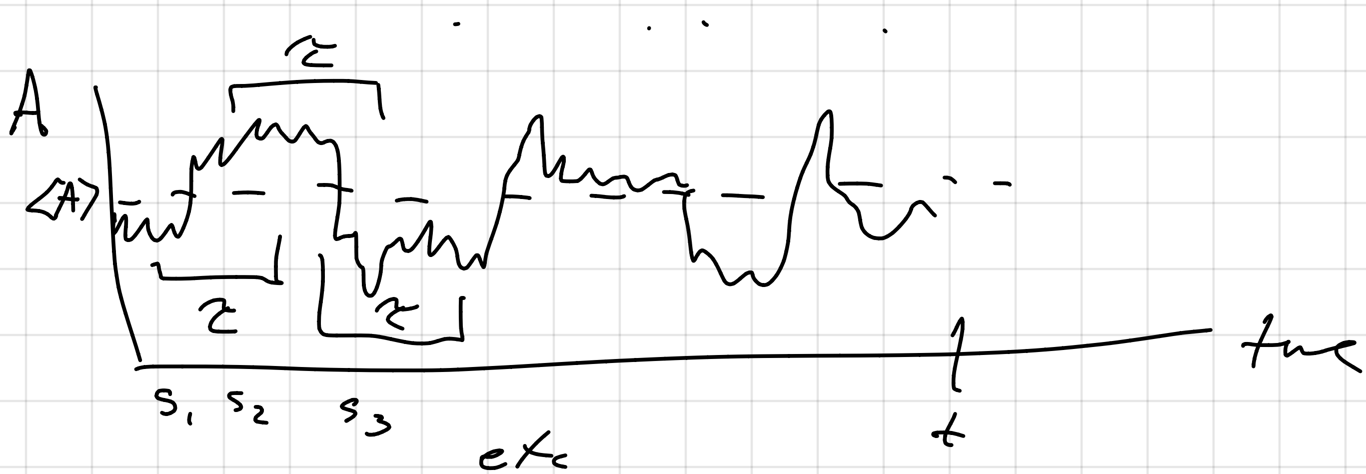
$$\langle A \rangle = \frac{1}{\tau}\int_0^{\tau} dt\, A(t)$$

Fluctuations from mean $\delta A(t) = A(t) - \langle A \rangle$

Fluctuations <u>are</u> correlated in time, so like $\langle \delta s_i \, \delta s_j \rangle$ in lattice model &

$\langle \delta\rho(r) \, \delta\rho(r') \rangle$ we need to compute

$$C(\tau) = \frac{1}{t} \int_0^t ds \, A(s) A(s+\tau)$$



If @ equilibrium or @ Neq steady state initial time doesn't matter and $C(t)$ only depends on observation window

Many experiments measure $C_\omega = \int_{-\infty}^{\infty} dt \, e^{-i\omega t} \, C(t)$

Fourier transform, called the "spectral density"

Eg optical absorption related to FT of dipole-dipole correlation func

Example — the correlations in velocity are related to the diffusion const

We showed / discussed Diffusion of a particle in 1d, Macrosopically Diffusion is defined by a diff Eq called the diffusion eq

$\rho(x,t)$ is conc at x at time t

$$\frac{\partial}{\partial t}\rho(x,t) = D\frac{\partial^2}{\partial x^2}\rho(x,t)$$

if $\rho(x,0) = \delta(x)$, spreads out as a gaussian w/ time, w/ $\langle \rho(x)\rangle = 0$

what is the MSD (also, the variance of this gaussian?

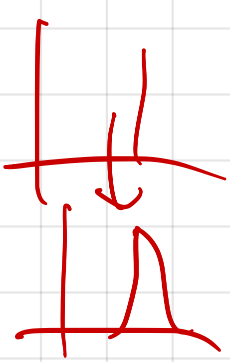
Start w/ $\langle x^2\rangle_t = \int_{-\infty}^{\infty} dx\, x^2 \rho(x,t)$

$$\frac{\partial}{\partial t}\langle x^2\rangle_t = \int_{-\infty}^{\infty} dx\, x^2\, \partial/\partial t\, \rho(x,t) = \int_{-\infty}^{\infty} dx\, D x^2 \frac{d^2}{dx^2}\rho(x,t)$$

$u = x^2 \qquad dv = \frac{d^2}{dx^2}\rho(x,t)$

$$= D\Big[\underbrace{\Big(x^2 \frac{d}{dx}\rho(x,t)\Big)\Big|_{-\infty}^{\infty}}_{0} - \int_{-\infty}^{\infty} \underbrace{2x}_{u}\, \underbrace{\frac{d}{dx}\rho(x,t)\, dx}_{dv}\Big]$$

$$= D\Big[\underbrace{(2x\rho(x))\Big|_{-\infty}^{\infty}}_{0} + 2\int_{-\infty}^{\infty} \rho(x,t)\, dx\Big] = 2D$$



$$\Rightarrow \langle x^2 \rangle = 2Dt$$

(showed for discrete random walk before)

But now, $\delta x(t) = \int_0^t v(s)\,ds$

$$\langle \delta x(t)\,\delta x(t) \rangle = \left\langle \left(\int_0^t v(s)\,ds \right)^2 \right\rangle$$

$$\frac{d}{dt} \langle (\delta x(t))^2 \rangle = \left\langle 2 \int_0^t v(s)\, v(t)\, ds \right\rangle$$

$$= 2 \int_0^t \langle v(s)\, v(t) \rangle\, ds$$

@ equilibrium, only $t-s$ matters

$$= 2 \int_0^t \langle v(s-s)\, v(t-s) \rangle\, ds$$

$$= 2 \int_0^t \langle v(t-s)\, v(0) \rangle\, ds$$

$$u = t - s \qquad du = -ds$$

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

but this equals $2D$

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