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 the dynamics, especially systems in contact w/a bath & how to study then. [time dependent processes]

Back to Brownian motion & origin of Langevin equation

\[ F_{\text{total}} = ma = m \frac{dv}{dt} \]

Physics observations say that the particle has drag: \( \frac{1}{2} \pi r^2 \)

\[ m \frac{dv}{dt} = -\zeta v, \quad \zeta = 6\pi \eta a \]

Stokes law, 3d sphere
If this were whole story then
\[ v(t) = v(0) e^{-\frac{kt}{m}} \]

This would mean that the particle stops moving over time.

But we know (from before, also xpts) that

\[ \langle v^2 \rangle = \frac{kT}{m} \]

So this most one from collisions with the solvent

\[ \left[ \langle \frac{1}{2} m v^2 \rangle = \langle kT \rangle = \frac{kT}{2} \right] \Rightarrow \langle v^2 \rangle = kT/m \]

So this is where we get Langevin’s idea of

\[ \frac{mdv}{dt} = -\frac{v}{\tau} + SF(t) \]

Random force

Fluctuating force in each direction

Assert collisions uncorrelated in time & near zero

\[ \langle SF(t) \rangle = 0 \]

\[ \langle SF(t) SF(t') \rangle = 2\delta(t-t') \]

So how do we solve this equation? Have to do once by a "trick" for diff eq
\[ \frac{dx(t)}{dt} = -\alpha x(t) + b(t) \]

Insert \( x(t) = e^{\alpha t} y(t) \)

Then \[ e^{\alpha t} \frac{dy(t)}{dt} + \alpha e^{\alpha t} y(t) = a e^{\alpha t} y(t) + b(t) \]

\[ \Rightarrow \frac{dy(t)}{dt} = e^{-\alpha t} b(t) \]

Integrate from \( 0 \) to \( T \)

\[ y(T) - y(0) = \int_0^T e^{-\alpha t} b(t) \, dt \]

Switching back to \( x \),

\[ e^{-\alpha t} x(t) = x(0) + \int_0^T e^{-\alpha t} b(t) \, dt \]

\[ x(t) = e^{\alpha t} x(0) + \int_0^T e^{\alpha t} - \alpha(t - \tau) \, b(t) \, dt \]

\[ s = \tau - t \]

\[ ds = -dt \]

\[ + \int_0^\tau e^{\alpha s} b(\tau - s) \, (-ds) \]

\[ x(T) = e^{\alpha T} x(0) + \int_0^\tau e^{\alpha s} b(\tau - s) \, ds \]
Going back to Langevin and

\[ \frac{dv(t)}{dt} = -\frac{e}{m} v(t) + \frac{SF(t)}{m} \]

\[ v(t) = e^{-\frac{e}{m} t} v(0) + \int_0^t dt' e^{-\frac{e}{m} (t-t')} \frac{SF(t')}{m} \]

If no random force, correct solution

Now we want to predict \( \langle v(t)^2 \rangle \)

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

\[ v(t)^2 = e^{-2\frac{e}{m} t} v(0)^2 + 2e^{-\frac{e}{m} t} v(0) \int_0^t dt' e^{-\frac{e}{m} (t-t')} \frac{SF(t')}{m} \]

\[ + \int_0^t \int_0^t dt' dt'' e^{-\frac{e}{m} [t-t'] + (t''-t')} \frac{SF(t') SF(t'')}{m^2} \]

So now take avg \( \langle \text{over many start times, ind particles...} \rangle \)

\[ \langle v(t)^2 \rangle = e^{-2\frac{e}{m} t} v(0)^2 + \int_0^t \int_0^t dt' dt'' e^{-\frac{e}{m} [t-t'] + (t''-t')} \frac{2BS(t''-t')}{m^2} \]

\[ + \int_0^t dt e^{-\frac{e}{m} [t-t]} 2B / m^2 \]
\[
\begin{align*}
&= e^{-2\sigma / \Lambda t} V(0)^2 + \frac{B}{\epsilon m} \left[ e^{-2\sigma / \Lambda (t + \tau)} \right]_{t = 0}^{t = +} \\
&= e^{-2\sigma / \Lambda t} V(0)^2 + \frac{B}{\epsilon m} \left[ 1 - e^{-2\sigma / \Lambda t} \right]
\end{align*}
\]

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

\[
\langle \Delta U(t)^2 \rangle \quad \to \quad \frac{B}{m \epsilon^2}
\]

And so \( B = k_B T \frac{\epsilon}{\xi} \)

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 and, diffusion & scattering, spectroscopy & NMR

Measurements are still averages, but now back to time averages

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

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

Fluctuations are correlated in time, so
Like \( \langle S_1 S_2 \rangle \) in lattice model \&
\[ \langle S_p(t) S_p(t') \rangle \] we need to compute
\[
C(t) = \frac{1}{t} \int_0^t ds \ A(s)A(s+t).
\]

If at equilibrium or at early stage, initial time doesn't matter and \( C(t) \) only depends on observation window

Many experiments measure
\[
C_0 = \int_{-\infty}^{\infty} dt e^{-i\omega t} C(t)
\]
Fourier transform, called the 'spectral density'.

E.g. optical absorption related to FT of dipole-dipole correlation function.
Example - the correlations in velocity are related to the diffusion cost

We showed (discussed) diffusion of a particle in 1d. Macroscopically, diffusion is defined by a drift Eq called the diffusion Eq

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

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

What is the MSD? (also, the variance of this gaussian?)

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

\[ \frac{\partial}{\partial t} \langle x^2 \rangle_t = 2 \int_{-\infty}^{\infty} dx x^2 \left[ \frac{d}{dx} \rho(x,t) \right] = \int_{-\infty}^{\infty} dx \left[ x^2 \frac{d^2}{dx^2} \rho(x,t) \right] \]

\[ = D \left[ (x^2 \frac{d}{dx} \rho(x,t)) \right]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} dx x \frac{d}{dx} \rho(x,t) \]

\[ = D \left[ (2x \rho(x)) \right]_{-\infty}^{\infty} + 2 \int_{-\infty}^{\infty} dx \rho(x,t) dx \]

\[ = 2 D \]
\[ \langle x^2 \rangle = 2D t \] (showed for discrete random walks before)

Now, \[ SX(t) = \int_0^t U(s) \, ds \]

\[ \langle SX(t) \cdot SX(t) \rangle = \langle \left( \int_0^t U(s) \, ds \right)^2 \rangle \]

\[ \frac{d}{dt} \langle (SX(t))^2 \rangle = \langle 2 \int_0^t U(s) \cdot U(t) \, ds \rangle \]

\[ = 2 \int_0^t \langle U(s) \cdot U(t) \rangle \, ds \]

At equilibrium, only \( t-s \) matters

\[ = 2 \int_0^t \langle U(t-s) \cdot U(t-s) \rangle \, ds \]

\[ = 2 \int_0^t \langle U(t-s) \cdot U(0) \rangle \, ds \]

\[ u = t-s \quad du = -ds \]

\[ = 2 \int_0^t \langle U(u) \cdot U(0) \rangle \, du \]

but this equals \( 2D \)

So \[ D = \int_0^t \langle U(u) \cdot U(0) \rangle \, du \]

\[ \text{and} \quad D_{\text{ed}} = \frac{1}{3} \int_0^t \langle U(u) \cdot U(0) \rangle \, du \]