Lecture 22:

Non-equilibrium Pt 2

Time correlation functions

Last time: talked about how we want to study time dep processes to understand Non-eq systems. Even at eq, microscopic dynamics will result in quantities being correlated in time

This is what we usually measure w/ Spectroscopy [frequencies / relaxation times]

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

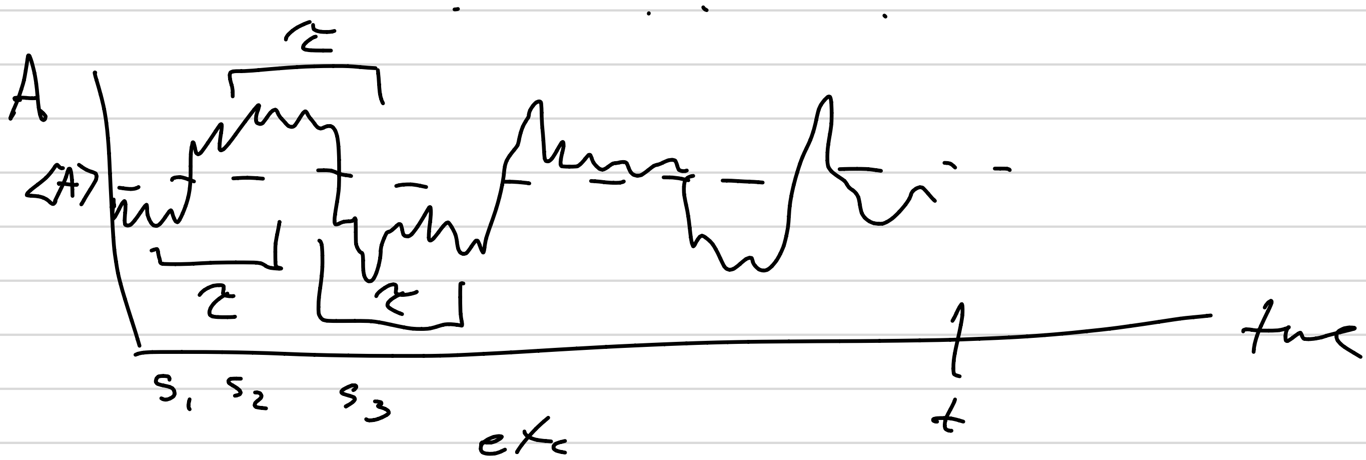
Fluctuations from mean $\delta A(t) = A(t) - \langle A \rangle$

Fluctuations <u>are</u> correlated in time, so can measure by

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

initial time

for flucts can look at $C_{\delta A \delta A}$



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

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

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

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

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

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

(showed for discrete random walk before)

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

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

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

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

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

Now we can look at how velocities are correlated in time & how this connects to diffusion:

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

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

if the initial time is in the infinite past, then all that matters is the history of the noise

$$v(t) = \frac{1}{m}\int_0^{\infty} e^{-\xi/m\, u}\, \delta F(t-u)\, du$$

So then we have the triple integral:

$$\langle v(t) v(t')\rangle_{time} = \int_0^{\infty} du_1 \int_0^{\infty} du_2\, e^{-\xi/m(u_1+u_2)}\, \frac{1}{\tau}\int_0^{\tau} ds\, \frac{1}{m^2}\, \delta F(t-u_1+s)\, \delta F(t'-u_2+s)$$

replace product by avg

$$\underbrace{\frac{1}{\tau}\int_0^{\tau} ds}_{=1}\, \frac{1}{m^2}\, 2B\,\delta(t-u_1-t'+u_2)$$

← no more s-dep

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

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

physically has to decay

$$= k_B T/m \, e^{-\xi/m|t-t'|}$$

time avg is same as eq avg, but why do we care? This will connect time integral w/ friction

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

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

$$\langle v(u)v(0)\rangle = \underbrace{\langle v(0)^2 \rangle}_{kT/m} e^{-\xi u/m} + C\cancel{\langle \delta F v \rangle}^{0}$$

$$= \int_0^\tau dt \, \frac{2k_BT}{m} \cdot \frac{m}{\xi}\left[-e^{-\xi u/m}\right]_0^t$$

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

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

at large $\tau = \frac{2k_BT}{\xi}$

and $MSD(t) = 2Dt$

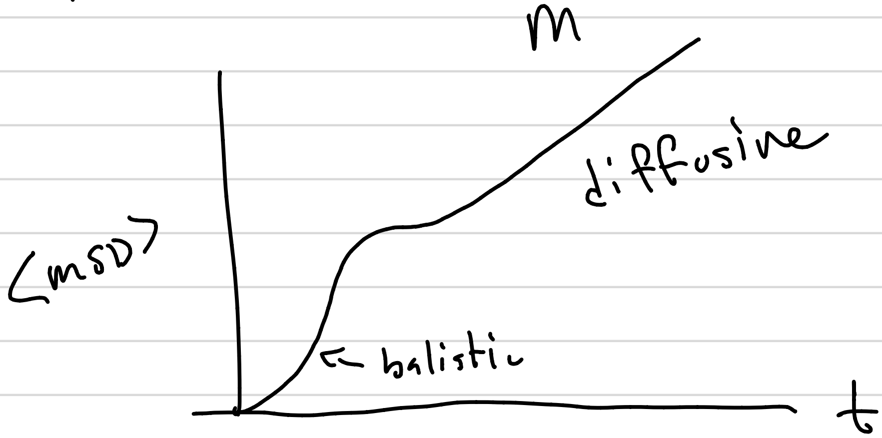
$$\boxed{D = k_B T / \xi}$$ Einstein Self Diffusion

At small τ,

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

So at small order

$$\langle \Delta x(\tau)^2 \rangle \approx \frac{k_B T}{m}\tau^2$$



We have sofar assumed that the dynamics are Markovian,

which here means that the force noise is "white noise" and that the friction only depends on the current velocity. However this is often not the case

The friction can depend on the velocities at previous times too [has "memory"]

Can write $\zeta v(t) \to -\int_{-\infty}^{t} K(t-s)\, v(s)$ or $-\int_0^{\infty} ds\, K(s) v(t-s)$ $[s \to t-s]$ (K is "memory kernel")

How would this arise? Simple example:

$$\frac{dx}{dt} = p/m$$

$$\frac{dp}{dt} = -m\omega^2 x - \zeta \frac{p}{m} + F_p(t) \qquad (H.O.)$$

lets say $p(-\infty) = 0$ — see last time

$$p(t) = \int_{-\infty}^{t} ds\, e^{-\zeta(t-s)/m} \left[-m\omega^2 x(s) + F_p(s)\right]$$

$$= \int_{-\infty}^{t} ds\, e^{-\zeta s/m} \left(-m\omega^2 x(t-s) + F_p(t-s)\right)$$

So
$$\frac{dx(t)}{dt} = \int_{-\infty}^{t} ds\, e^{-\zeta s/m} \left(-\omega^2 x(t-s) + \frac{F_p}{m}(t-s)\right)$$

$$\text{So } K(t) \equiv \omega^2 e^{-\zeta |t|/m}$$

$$F_x = \frac{1}{m} \int_0^{\infty} ds\, e^{-\zeta s/m} F_p(t-s)$$

$$\Rightarrow \frac{dx(t)}{dt} = -\int_0^\infty ds\, K(s)\, x(t-s) + F_x(t)$$

Same procedure as before gives $\quad$ Ex?

$$\langle F_x(t) F_x(t') \rangle = \langle x^2 \rangle_{eq}\, K(|t-t'|)$$

Non markovian FDT

and we knew before $\langle x^2 \rangle_{eq} = \frac{kT}{m\omega^2}$

Lagetime
Area of $K(t) = \int_{-\infty}^{\infty} dt\, \omega^2 e^{-\gamma|t|/m} = 2\frac{m\omega^2}{\gamma}$

can approx $K(t)$ w/ deltafunc same area $\quad K(s) \approx 2\frac{m\omega^2}{\gamma}\delta(s)$

And approx markovian

When variables removed from Markovian...

System, this makes a Non Markovian Sys

If memory decays exponentially in time, Non-Markovian → Markovian by adding a variable [adding back in?]

In general, prep @ time 0 and

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

& $\langle \vec{F}(t)\,\vec{F}(t')\rangle = \underline{\underline{K}}(t-t')\,\langle aa\rangle_{eq}$

[G.L.E.]