Non Eq Pt 2

Reminders:

for $\frac{dx}{dt} = ax + b$

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

so from Langevin Eq -

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

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

can integrate to get MSD

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

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

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

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

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-dependence

Int over u_2

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

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

physically has to decay

$[B = k_B T\xi]$

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

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 τ, $\ldots = \frac{2k_BT}{\xi}\tau$

and $MSD(t) = 2Dt$

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

Einstein
Self Diffusion

$\xi = 6\pi\eta a \Rightarrow D\eta = k_BT/6\pi a$ Stokes-Einstein

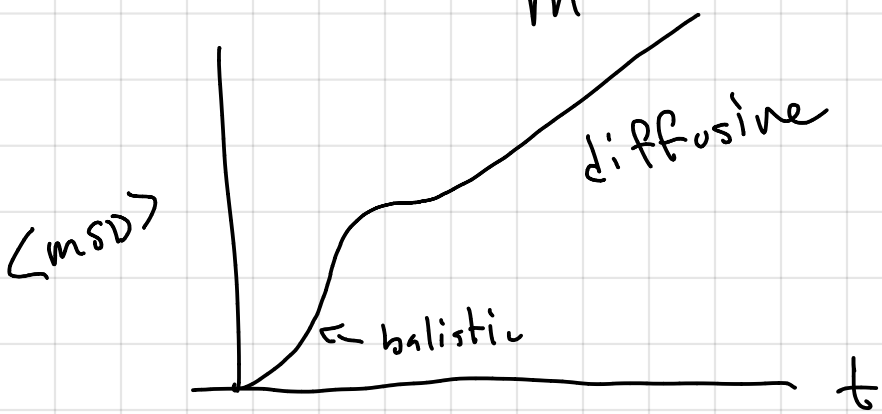
* Note violation in glasses

At small τ,

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

So at small order

$$\langle \Delta x(\tau)^2 \rangle \approx \frac{k_B T}{m} \tau^2 \quad \Longleftrightarrow \quad d = vt$$



We have so far 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 non markovian behavior arise? Simple example:

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

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

(H.O.), combine to eq for dx/dt only

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

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

$$=\int_0^{\infty} ds\, e^{-\xi s/m}\left(-m\omega^2 x(t-s)+F_p(t-s)\right)$$

so $$\frac{dx(t)}{dt}=\int_0^{\infty} ds\, e^{-\xi s/m}\left(-\omega^2 x(t-s)+\frac{F_p}{m}(t-s)\right)$$

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

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

(Removed P)

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

Same procedure as before gives (long calc)

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

Non markovian FDT

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

Area of $K(t)$ = $$\int_{-\infty}^{\infty} dt\, \omega^2 e^{-\xi|t|/m}=2\frac{m\omega^2}{\xi}$$ Longtime can approx $K(t)$ w/ deltafunc same area $K(s) \approx \delta(s)$

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 $t=0$, not eq w/ $t=-\infty$ start

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

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

sometimes written for $a = \dot{q}$ &

[Ω "frequency", related to deriv of potential, like HO]