20: Brownian motion & Langevin eqn

Observation: pollen particles jiggle randomly
predictable behavior on average (Brown)

Einstein postulated, maybe due to random collisions w/ solvent

$$F_{total} = m a = m \frac{dv}{dt}$$

physical observations / Stokes - has drag

$$m \frac{dv}{dt} = -\xi v$$

$\xi = 6\pi \eta a$ for sphere
viscosity
radius

if this is whole story

$$m \frac{dv}{dt} = -\xi v \Rightarrow v(t) = v(0)\, e^{-\xi/m\, t}$$

more drag, lighter particle stops faster

But, we know particles keep moving, &

in particular, recall

$$P\left(\sum \tfrac{1}{2} m \vec{v}^2\right) = e^{-\beta \sum \frac{1}{2} m v^2} \Big/ \int dv^{3N}\, e^{-\beta \sum \frac{1}{2} m v^2}$$

st $\langle \tfrac{1}{2} m \vec{v}^2 \rangle = \langle KE \rangle = 3k_BT/2 \Rightarrow$

$$\langle v_x^2 \rangle = k_BT/m\ !$$

$\uparrow$ & y, & z

Langevin/Einstein

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

Assert: collisions uncorrelated in time

& mean zero st

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

How do we solve? Diff eq trick

If $\frac{dx(t)}{dt} = a x(t) + b(t)$, insert
$x(t) = e^{at} y(t)$

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

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

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

but now $y(t) = e^{-at} x(t)$

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

$s = \tau - t$

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

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

Therefore since

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

$$v(\tau) = \underbrace{e^{-\xi/m\,\tau}\ v(0)}_{\text{if no random force}} + \int_0^\tau dt\, \underbrace{e^{-\xi/m(\tau - t)}}_{\substack{\text{add up history}\\ \text{of forces, old}\\ \text{matter least}}} \frac{\delta F(t)}{m}$$

Want to solve for

$$\langle v(t)^2 \rangle = \underset{\text{should be as } t \to \infty}{k_B T/m}$$

$$v(\tau) = e^{-\xi/m\,\tau} v(0) + \int_0^\tau dt\, e^{-\xi/m(\tau-t)} \frac{\delta F(t)}{m}$$

$$v^2(\tau) = e^{-2\xi/m\,\tau} v(0)^2 + 2e^{-\xi/m\,\tau} v(0) \int_0^\tau dt\, e^{-\xi/m(\tau-t)} \frac{\delta F(t)}{m}$$

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

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

over particles, start times, indep'ts

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

$$\langle v(\tilde{\tau})^2 \rangle = \langle v(0)^2 \rangle e^{-2\xi/m \tilde{\tau}} + \frac{2B}{m^2} \int_0^{\tilde{\tau}} dt \, e^{-2\xi/m[\tilde{\tau}-t]}$$

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

so, starts w/ some initial v dist at $\tau = 0$

but as $\tau \to \infty$

$$\langle v(\tau)^2 \rangle \to B/\xi m = \frac{k_B T}{m}$$

$$\Rightarrow B = k_B T \xi \; !$$

F.D.T. : size of flucts proportional to dissp strength

Time correlation functions (TCF)

No partition function in general in non eq stat mech b/c no way to say what is $P(X)$ since it depends on how the system got to X

Instead, we study TCFs, to see how long certain quantities are correlated in time

TCFs can be used to compute things like Diffusion, viscosity thermal conductivity and spectroscopic signals

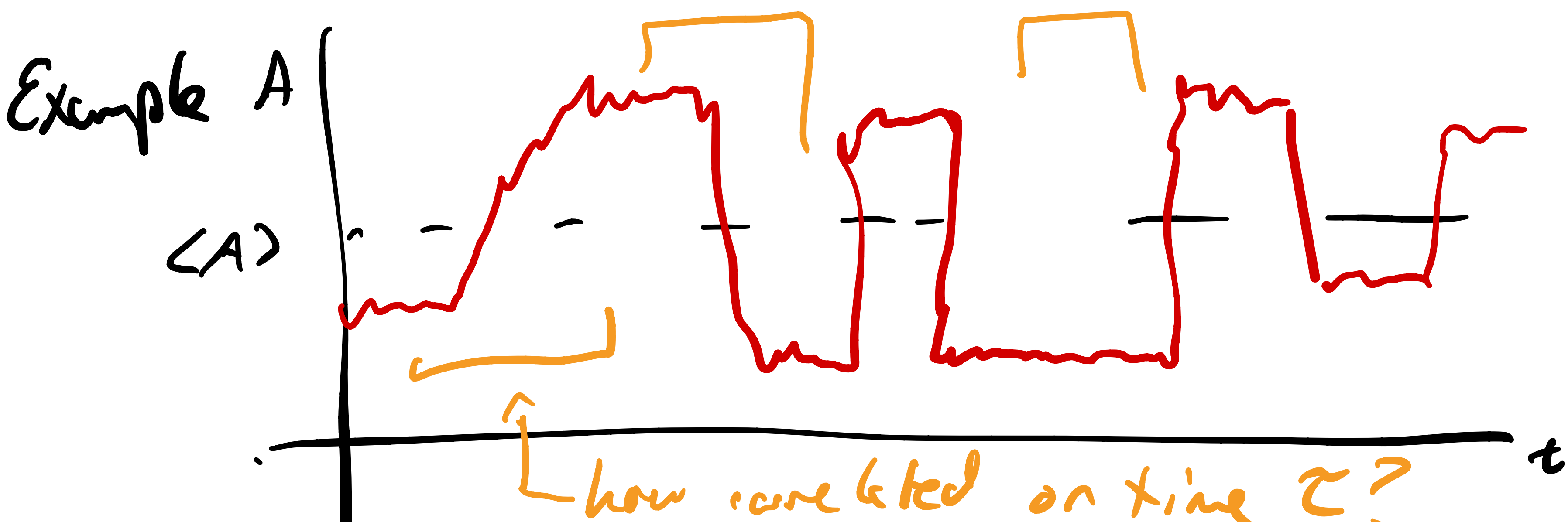
Measurements are now time averages of observables

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

<u>Fluctuations</u> are diff from mean,

$$\delta A \equiv A(t) - \langle A \rangle$$

Fluctuations are correlated in time, and we want to know for how long

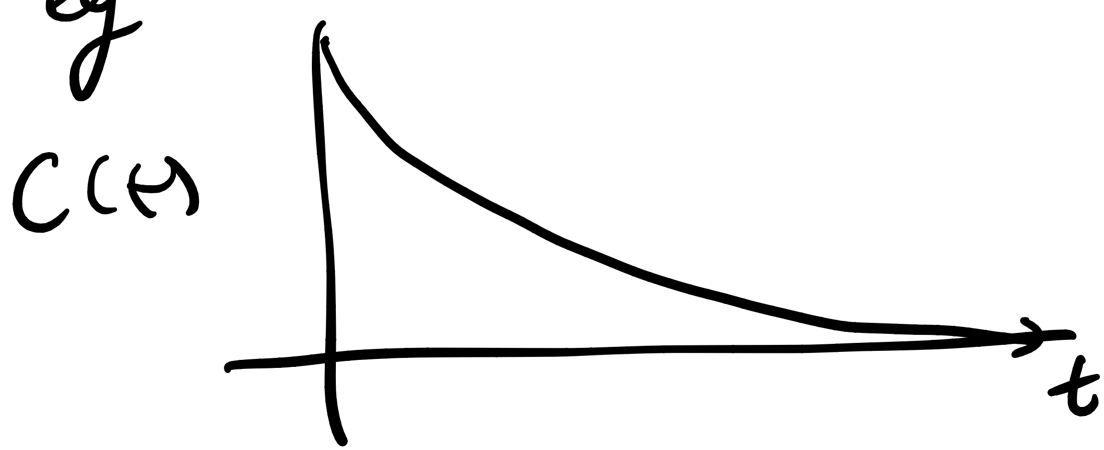


Define $C_{AA}(\tau) = \frac{1}{\tau}\int_0^t dt\, A(s)\, A(s+\tau)$

or $[C_{\delta A \delta A}] = \frac{1}{\tau}\int_0^t dt\, \delta A(s)\,\delta A(s+\tau)$

If at equilibrium or non eq steady state, doesn't depend on initial time, only observation window on average

eg



Many experiments measure "spectral density"

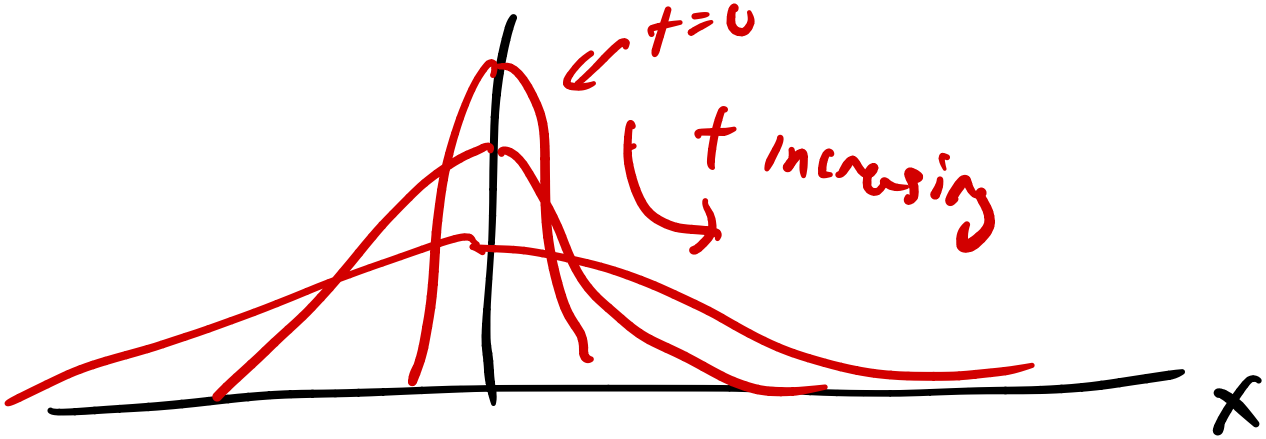
$$C_\omega = \int_{-\infty}^{\infty} dt \, e^{-i\omega t} \, C(t)$$

Eg: optical absorption <-> FT of dipole-dipole correlation function

Eg 2: velocity correlations related to diffusion constant! To see, have to know real def'n of diffusion

Diffusion equation (will do in 1d)

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



consider, what does this mean, when go up or down?

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

$\rho(x,0) = \delta(x) \rightarrow$ gaussian w/ $\langle\rho\rangle = 0$ &

Mean squared displacement = variance of this gaussian

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

static average

$$\parallel$$

$$\langle x^2 \rangle_t = \int_{-\infty}^{\infty} dx\, x^2 \rho(x,t) \qquad \text{(mean zero)}$$

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

if diffusion

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

$$= \underbrace{\left[x^2 \frac{d}{dx}\rho(x,t)\right]_{-\infty}^{\infty}}_{0} - \int_{-\infty}^{\infty} dx\, 2Dx \frac{d}{dx}\rho(x,t)$$

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

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

$$\langle x^2+y^2+z^2 \rangle = 3\langle x^2 \rangle = 6Dt$$

Now how does this connect to velocity?

Well, $\delta x(t) = \int_0^t v(s)\,ds$ so

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

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

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

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

at eq, only time origin doesn't matter

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

$$\frac{d}{dt}\langle \delta x^2(t)\rangle = 2\int_0^t \langle v(t-s)\, v(0)\rangle\, ds$$

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

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

$$= 2D \quad \text{from before!}$$

so $$D = \int_0^t \langle v(u) v(0)\rangle\, du \quad !$$

Now, what does v-v correlation function look like for Langevin process?

$$v(\tau) = \underbrace{e^{-\xi/m\,\tau}\, v(0)} + \int_0^{\tau} dt\, \underbrace{e^{-\xi/m\,(\tau - t)}}\, \frac{\delta F(t)}{m}$$

if $T = 0$ in infinite past,

$$V(\tau) = \int_{-\infty}^{\tau} dt\, e^{-\xi/m\,(\tau - t)}\, \delta F(t)/m$$

$\leftarrow$ infinite past

$$u = \tau - t$$

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

$u_2 - (u_1 + \tau_2 - \tau_1)$

$$\langle v(\tau_1)\, v(\tau_2)\rangle = \frac{1}{m^2}\int_0^{\infty} du_1 \int_0^{\infty} du_2\, e^{-\xi/m(u_1 + u_2)}\, \langle \delta F(\tau_1 - u_1)\, \delta F(\tau_2 - u_2)\rangle$$

$$= \frac{1}{m^2}\int_0^{\infty} du_1 \int_0^{\infty} du_2\, e^{-\xi/m(u_1 + u_2)}\, 2B\,\delta\big((\tau_1 - u_1) - (\tau_2 - u_2)\big)$$

$$= \frac{1}{m^2} 2B \int du_1 \, e^{-\xi/m(2u_1 + \tau_2 - \tau_1)}$$

$$= \frac{2B}{m^2} e^{-\xi/m(\tau_2 - \tau_1)} \cdot m/(\xi 2)$$

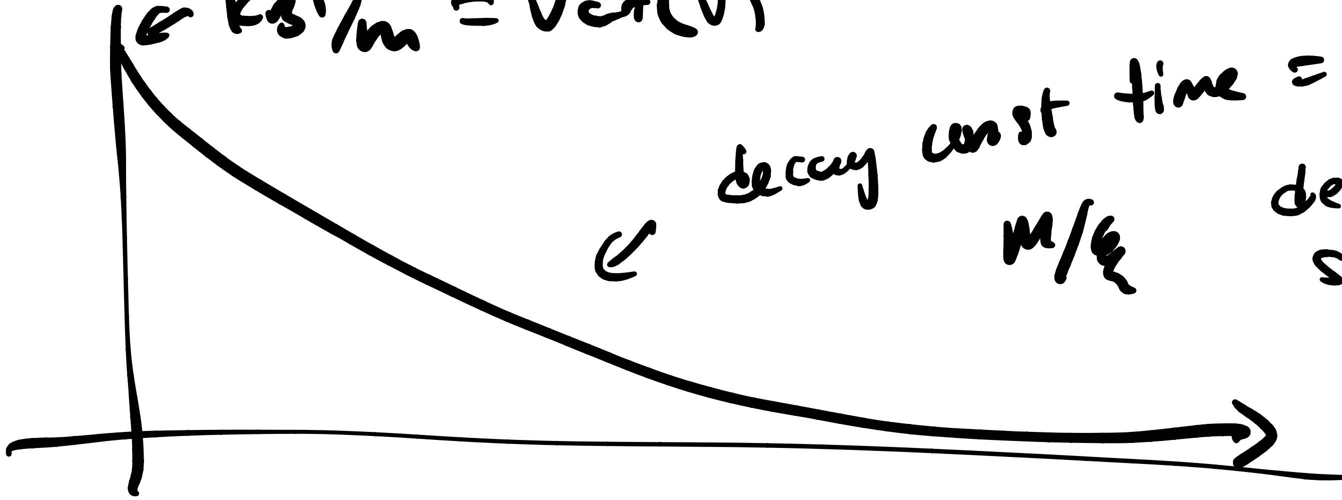
$$= \frac{B}{m\xi} e^{-\xi/m(\tau_2 - \tau_1)}$$

can only decay, depend on diff

$$B = k_B T \xi$$

$$\langle v(\tau_2) v(\tau_1) \rangle = \frac{k_B T}{m} e^{-\xi/m |\tau_2 - \tau_1|}$$

$\Rightarrow$



Now

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

$$= 2\int_0^\tau dt \int_0^t \frac{k_BT}{m} e^{-\xi/m \, u} du$$

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

$$= \frac{2k_BT}{\xi} \int_0^\tau dt \left[1 - e^{-\xi/m \, t} \right] = \frac{2k_BT}{\xi} \left[\tau + \frac{m}{\xi} \left[e^{-\xi/m \, t} \right]_0^\tau \right]$$

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

at large τ, first term dominates

and

$$MSD(t) = \frac{2k_BT}{\xi}\tau = 2D\tau$$

$$\Rightarrow D = k_BT/\xi \quad !$$

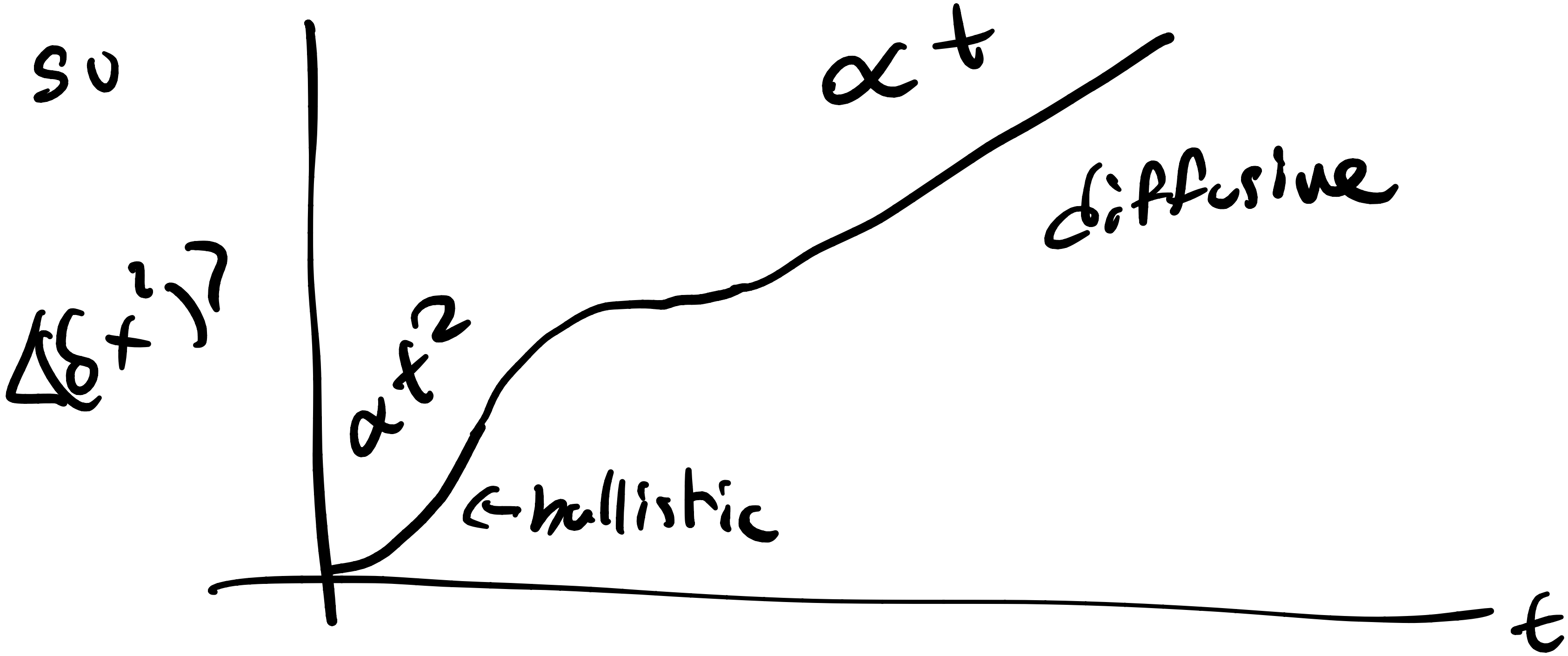
Einstein self diffusion formula

[if $\xi = 6\pi\eta a$, Stokes einstein relation]

at small τ, $e^{-\xi/m\,\tau} \simeq 1 - \tau + \frac{m}{\xi}\cdot\left(\frac{\xi}{m}\right)^2\cdot\frac{1}{2}\tau^2$

$\approx \underbrace{k_BT/m}_{\leftarrow \langle v^2 \rangle}\,\tau^2$ or $d = \sqrt{\langle v^2 \rangle}\,t =$ "vt"

so


$\langle (\delta x)^2 \rangle$
$\propto t^2$
$\propto t$
diffusive
← ballistic
t