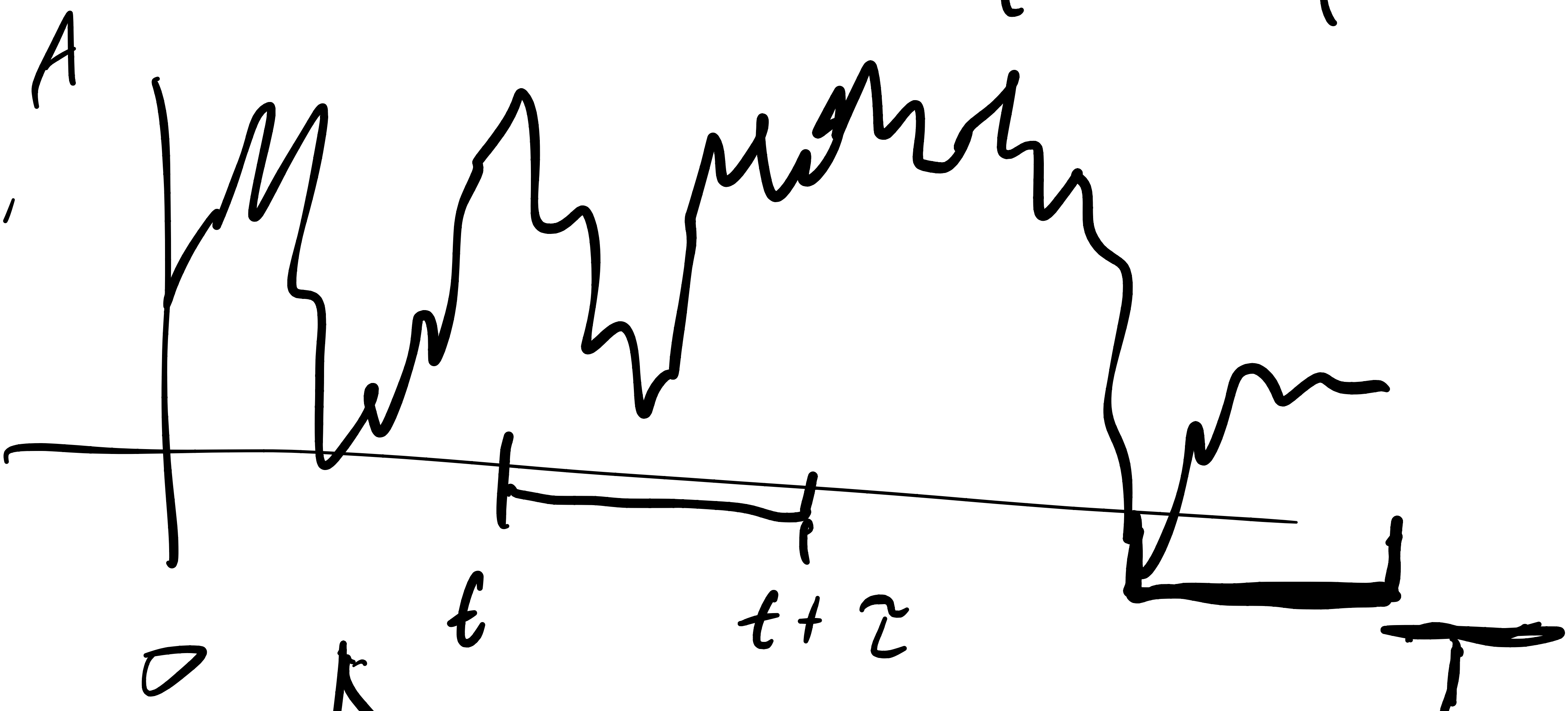
Lecture 21 - Diffusion

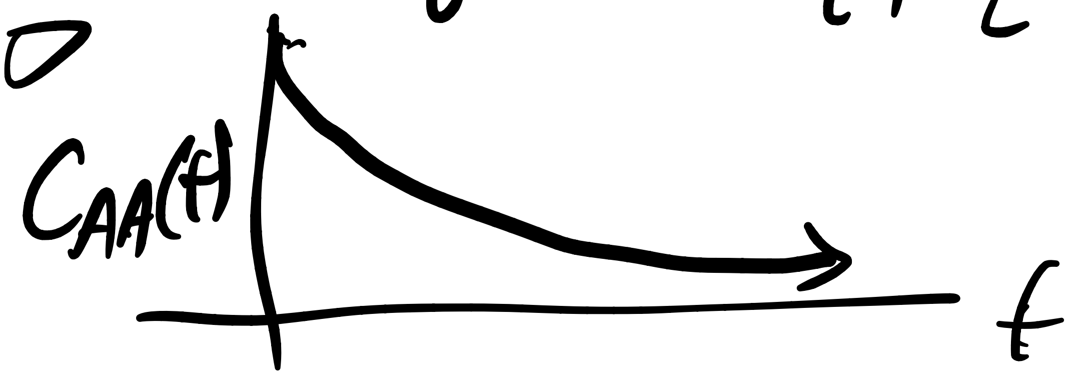
Showed that variance of random thermal forces is directly related to the macroscopic drag molecules feel

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

$$B = k_B T \xi \,, \quad F_{drag} = -\xi v \,, \quad \xi = 6\pi \eta a$$

$$C_{AA}(\tau) = \frac{1}{T}\int_0^{T-\tau} \delta A(\tau + t)\, \delta A(t)\, dt$$





Most experiments, measure "spectral density"

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

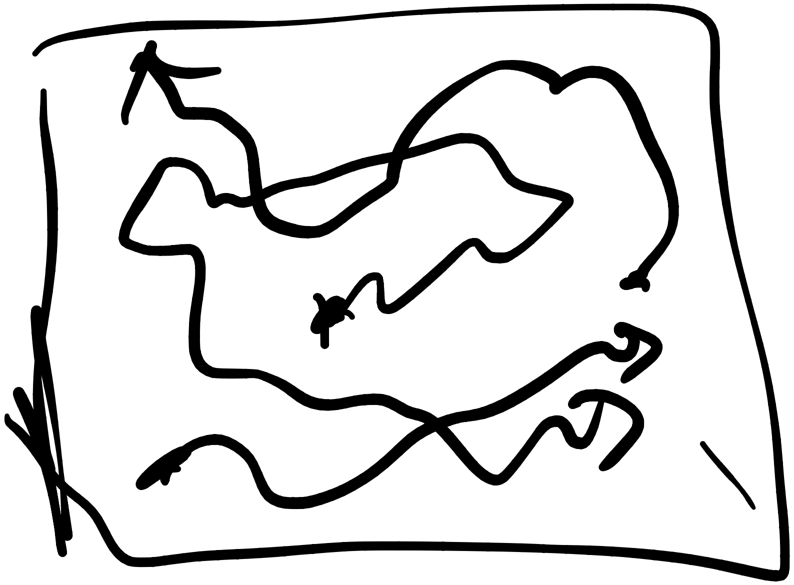
$FT[e^{-tk}]$

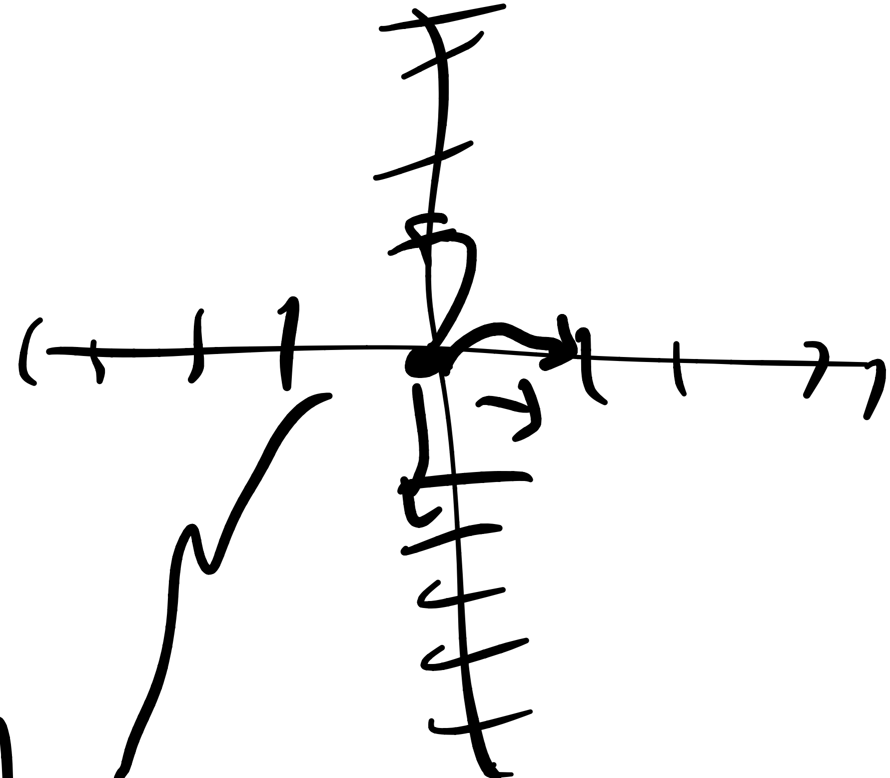
$$\int_{-\infty}^{\infty} e^{-it(\omega-\omega')} dt$$

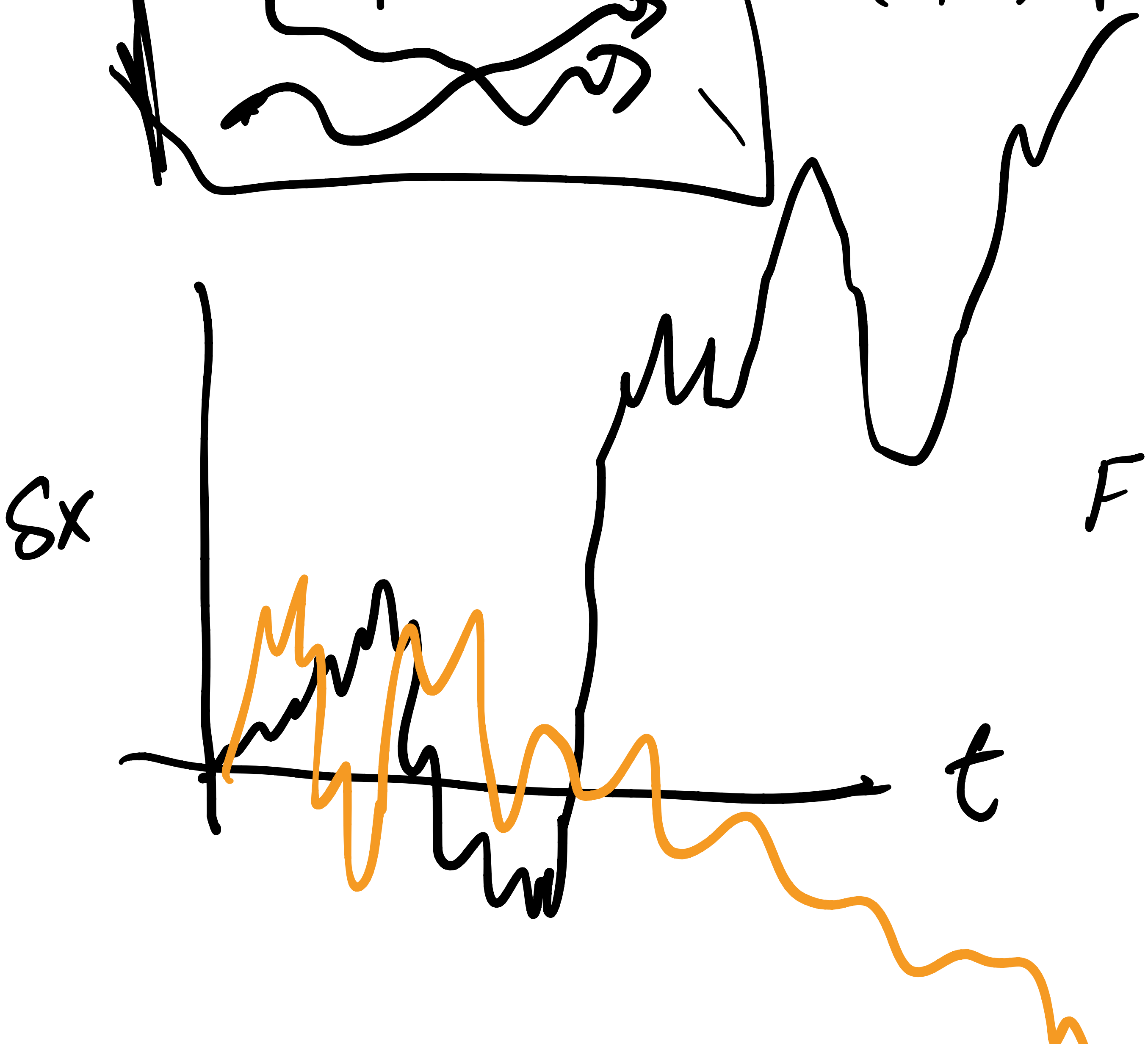
$$C(t) = A\cos(\omega' t)$$

$$= \frac{A}{2}\left[e^{i\omega' t} + e^{-i\omega' t}\right]$$

FT

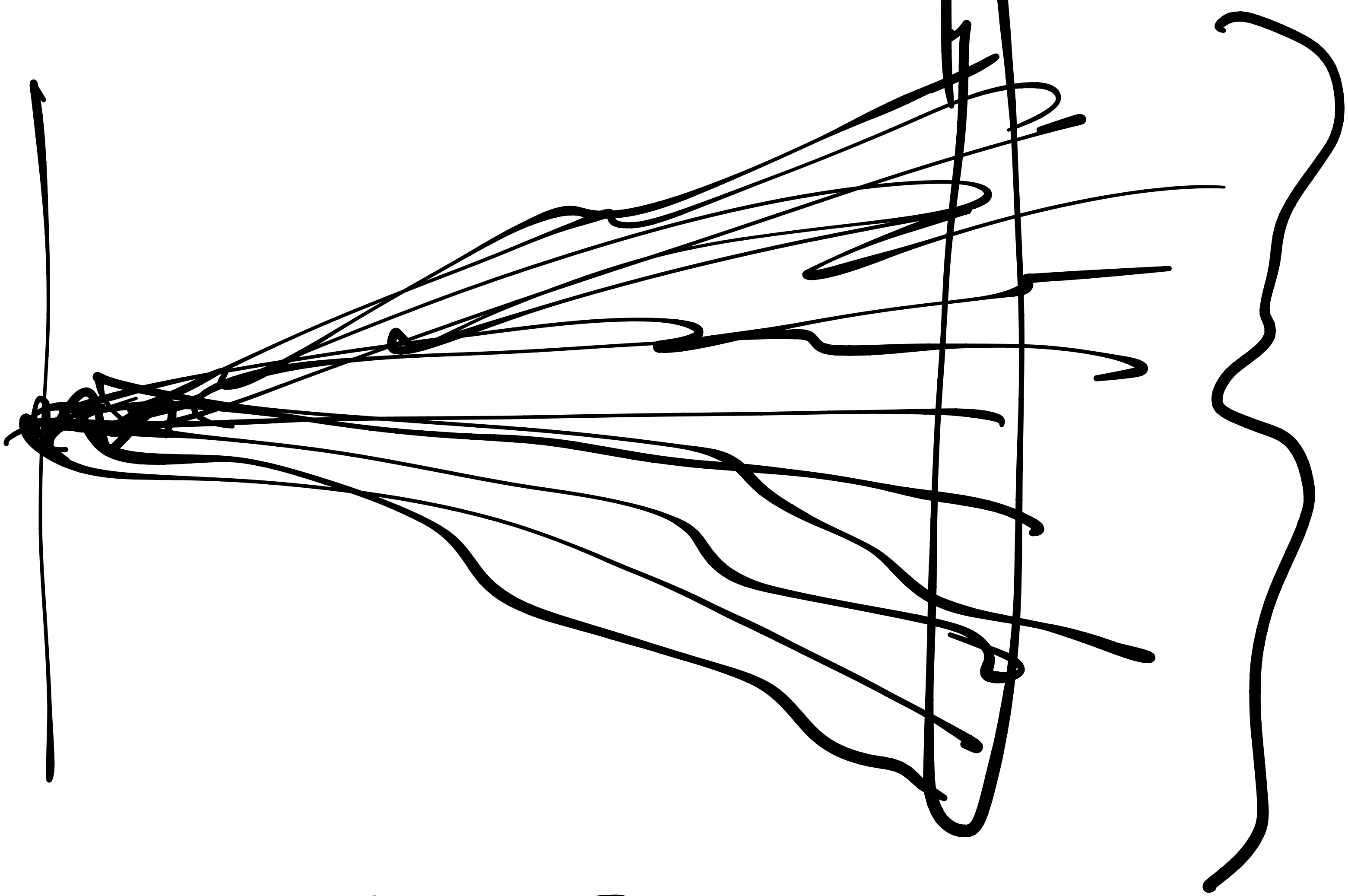






$$F = -\nu \xi + F_{rand}(t)$$

$$\langle \delta x \rangle = 0$$

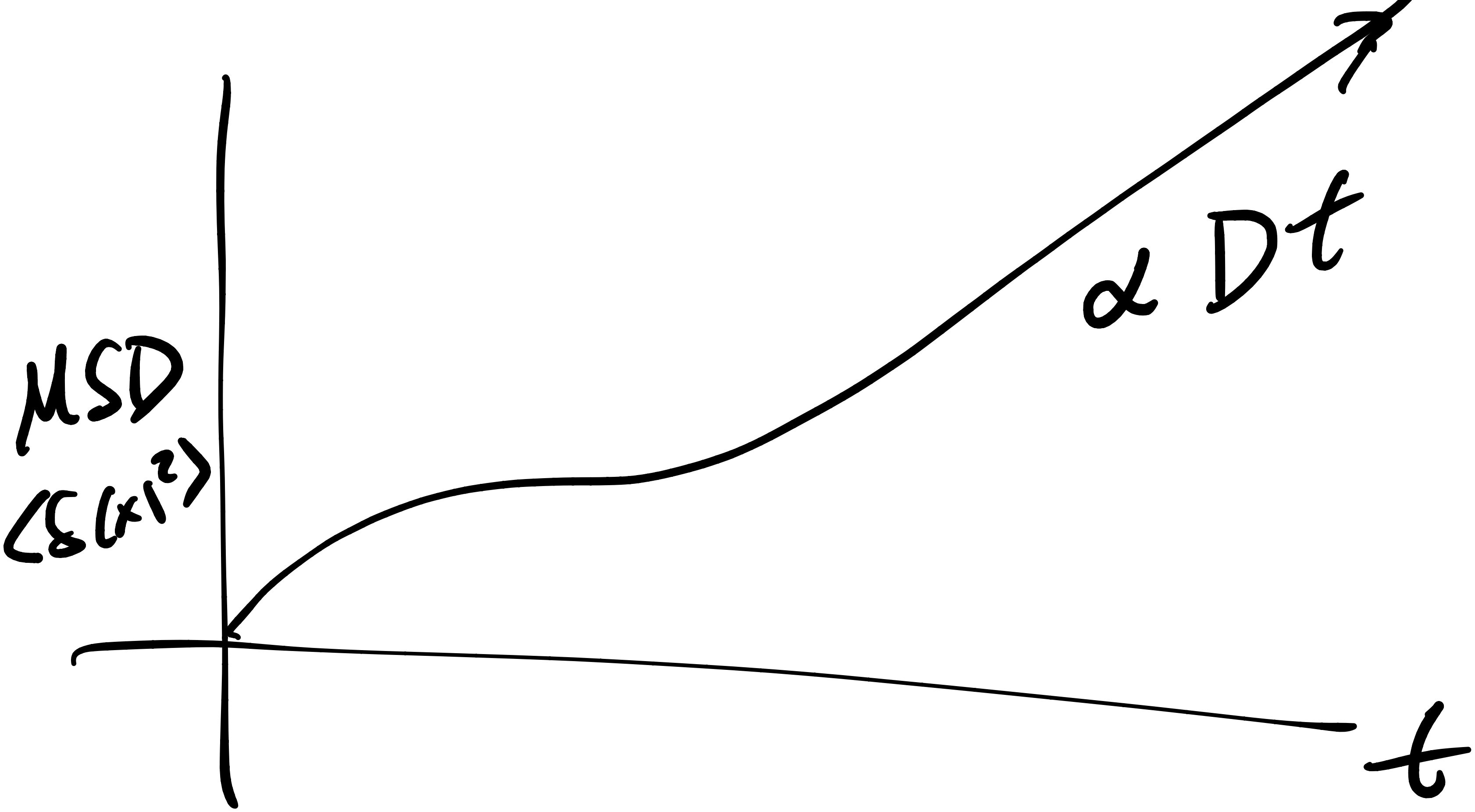


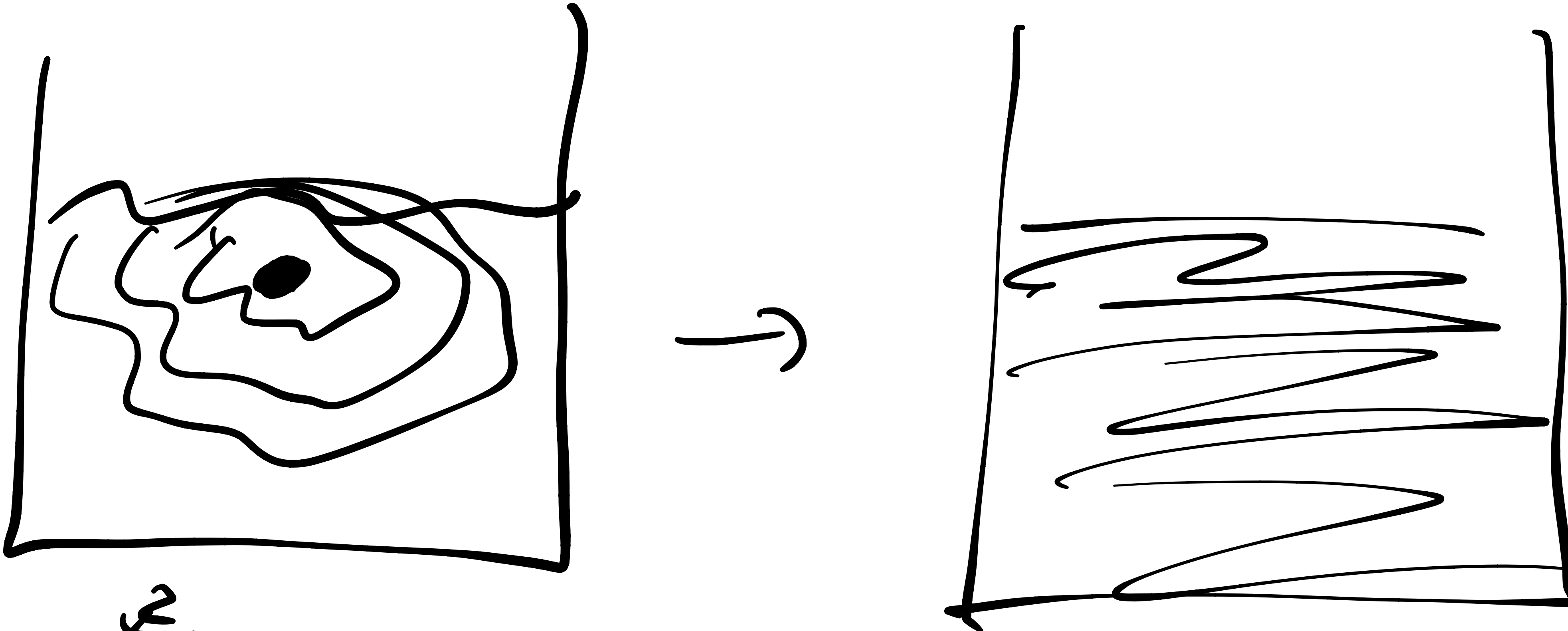
σ_x

$\sqrt{\langle \delta x\, \delta x \rangle}$

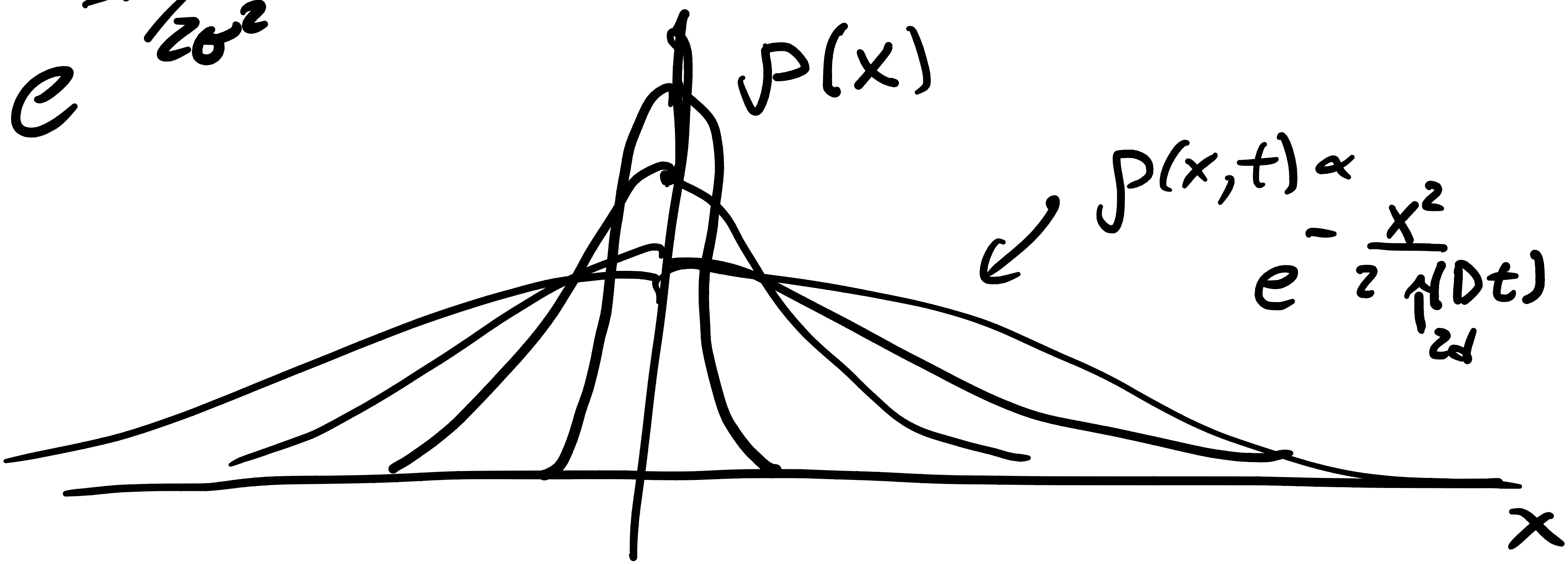
$$\langle (\delta x)^2 \rangle \propto t$$

$$\langle (\delta x)^2 \rangle = 2 d D t$$


MSD
$\langle \delta(x)^2 \rangle$
$\propto Dt$
t

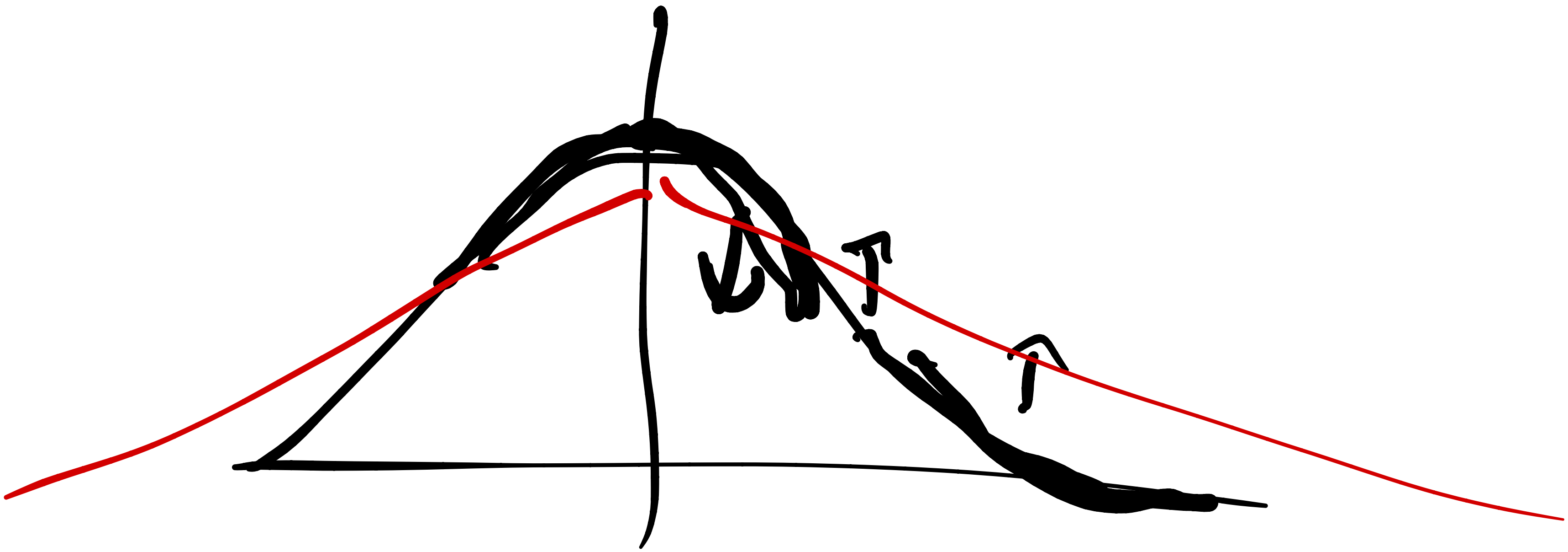


$$e^{-x^2/2\sigma^2}$$



$$\rho(x,t) \propto e^{-\frac{x^2}{2\underset{2d}{\uparrow}(Dt)}}$$

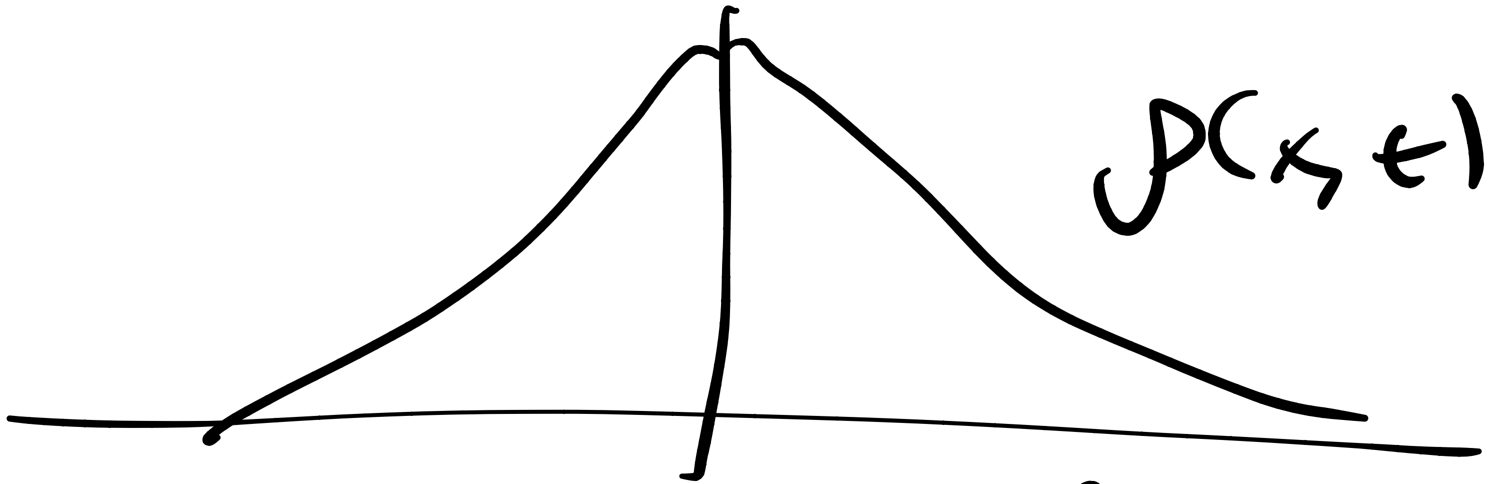
$$\frac{\partial \rho(x,t)}{\partial t} = D \frac{\partial^2}{\partial x^2} \rho(x,t)$$



$$\rho(x,0) = \delta(x)$$

$$\rho(x \to \pm\infty) = 0$$

$$d\rho/dx\,(x \to \pm\infty) = 0$$



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

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

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

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

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

$$= 2D$$

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

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

$$\vec{r} = (\delta x, \delta y, \delta z)$$

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

$$\frac{d}{dt}\langle(\delta x)^2\rangle = \frac{d}{dt}\left\langle\left(\int_0^t v(t')\,dt'\right)^2\right\rangle$$

$$\int_0^t v(t')\,dt'$$

$$= \left\langle 2\int_0^t v(t')\,dt' \cdot v(t)\right\rangle$$

$$= 2\int_0^t \underbrace{\langle v(t')v(t)\rangle}_{C_{vv}}\,dt'$$

$$s = t - t'$$

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

time translational inv.

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

$$= 2D$$

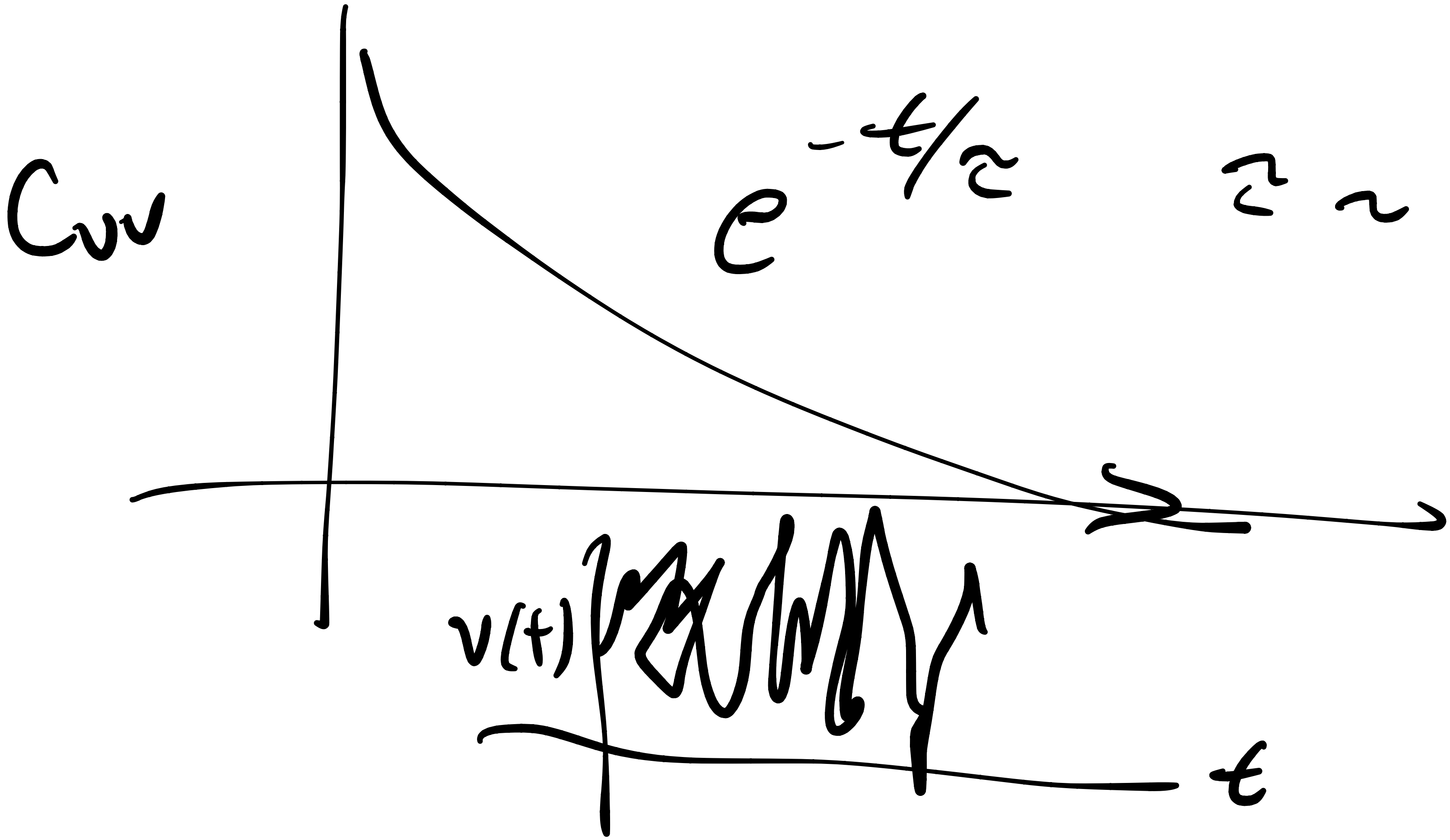
$$\Rightarrow D = \int_0^t \langle v(s)\,v(0)\rangle\, ds$$

$$[D] = \frac{[\text{distance}]^2}{[\text{time}]}$$

$D = \mu m^2/s$ $\qquad$ $R = \frac{1}{2}\,\mu m$

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

$$\rho(x,t) = 1$$



$$v(\tau) = e^{-\xi/m\,\tau}\, v(0) \qquad \xi/m \sim \tau^{-1}$$

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

imagine "$t=0$" is in infinite past

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

$$u = \tau - t$$

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

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

$$\langle V(\tau_1)\, V(\tau_2)\rangle = \frac{1}{m^2}\int_0^\infty du \int_0^\infty du'\; e^{-\xi/m\, u}\, e^{-\xi/m\, u'}\, \langle \delta F(\tau_1-u)\, \delta F(\tau_2-u')\rangle$$

$$2B\,\delta\left[\tau_1-u-(\tau_2-u')\right]$$

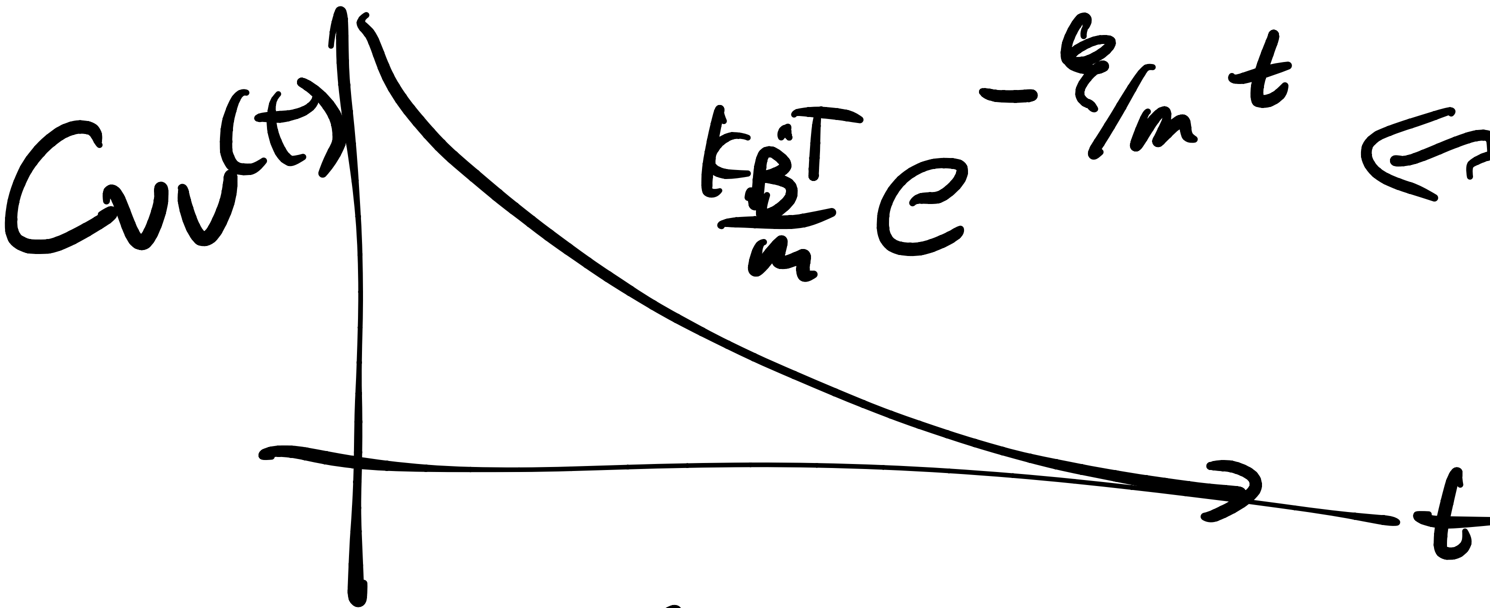
$$= \frac{1}{m^2}\, 2B \int du\, e^{-\xi/m\,(2u+\tau_2-\tau_1)}$$

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

$$= \frac{1}{m^2} 2B\, e^{-\xi/m(\tau_2 - \tau_1)} \int_0^{\infty} du\, e^{-\xi/m \cdot 2u}$$

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

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



$$\frac{k_B T}{m} e^{-\frac{\xi}{m} t}$$

ξ/m is an inverse time

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

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

$$MSD(\tau) = 2\int_0^{\tau} dt \int_0^{t} \frac{k_B T}{m} e^{-\xi/m\, s} ds$$

$$\Rightarrow \Rightarrow \Rightarrow$$

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

$$MSD \propto 2D\tau \quad \text{large } \tau$$

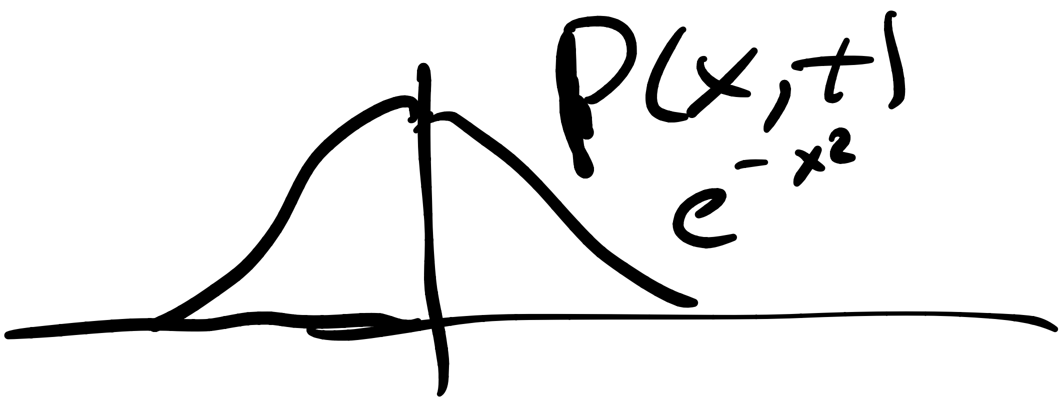
$$\boxed{D = \frac{k_BT}{\xi}}$$

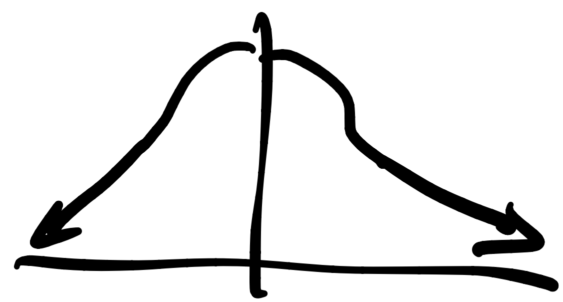
$\Uparrow$

as $\tau \to \infty$ $\quad MSD \to \frac{2k_BT}{\xi}\tau = 2D\tau$

$$\underbrace{D = \frac{k_B T}{\xi}}_{} = \frac{k_B T}{6\pi \eta a}$$

$$\underbrace{D \cdot \eta = \frac{k_B T}{6\pi a}}_{\text{Stokes-Einstein}} \propto T$$





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

Small time $\quad\tau$ smaller than m/ξ

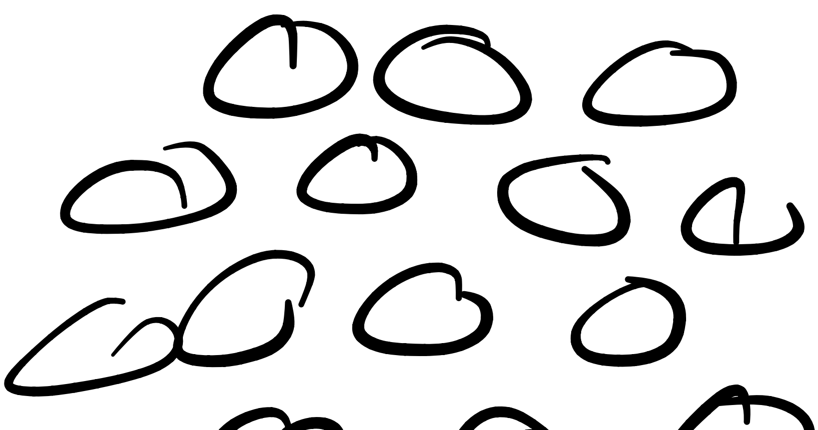
$$e^{-\xi/m\,\tau} \approx 1 - \frac{\xi}{m}\tau + \left(\frac{\xi}{m}\right)^2 \cdot \frac{1}{2}\tau^2 + \dots$$

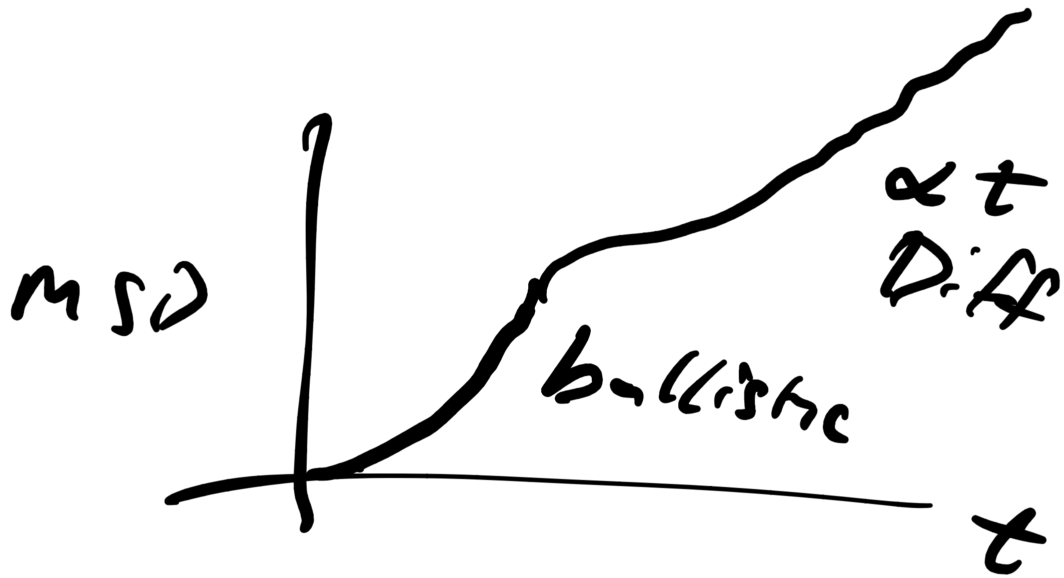
$$MSD(\tau) \approx \frac{k_BT}{\xi}\cdot\frac{m}{\xi}\left(\frac{\xi}{m}\right)^2\tau^2 = \frac{k_BT}{m}\tau^2$$

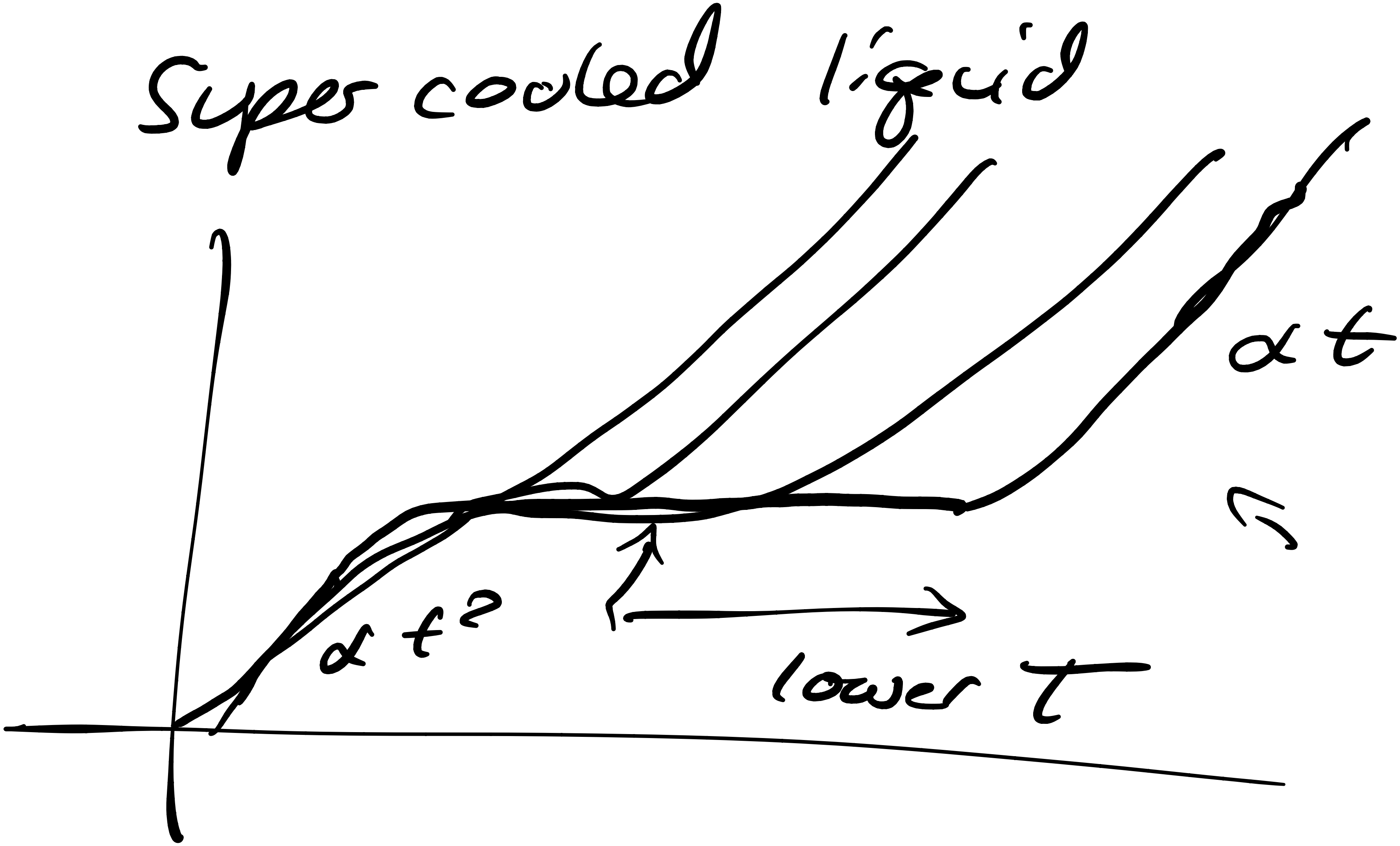
$$\langle \delta x^2 \rangle (t) \approx \underbrace{\frac{k_B T}{m}}_{\langle v^2 \rangle} t^2$$

$$= \langle v^2 \rangle t^2$$

$$\sim \delta x_{rms} = v_{rms}\, t \quad \leftarrow \text{ballistic motion}$$






Super cooled liquid
$\propto t$
$\propto t^2$
lower T