What is Statistical Mechanics

Chemists $\Leftarrow$ atoms, molecules
materials

Compute properties of molecules
w/ QM (small molecules)

Chemistry expts $\Leftarrow 10^{23}$ atoms
or more

Most properties of a system [heat capacity, T_m, density] don't depend on the arrangement of the atoms

Guess: all of these properties are <u>averages</u> over molecular arrangements [no reactions]

In this class - how measurable properties arise from averages over molecular configur...

Connect Classical Mechanics

→ how atoms move

to:

① Thermodynamics (entropy free energy, heat capacity...)

(2) Kinetics - rates of going between states

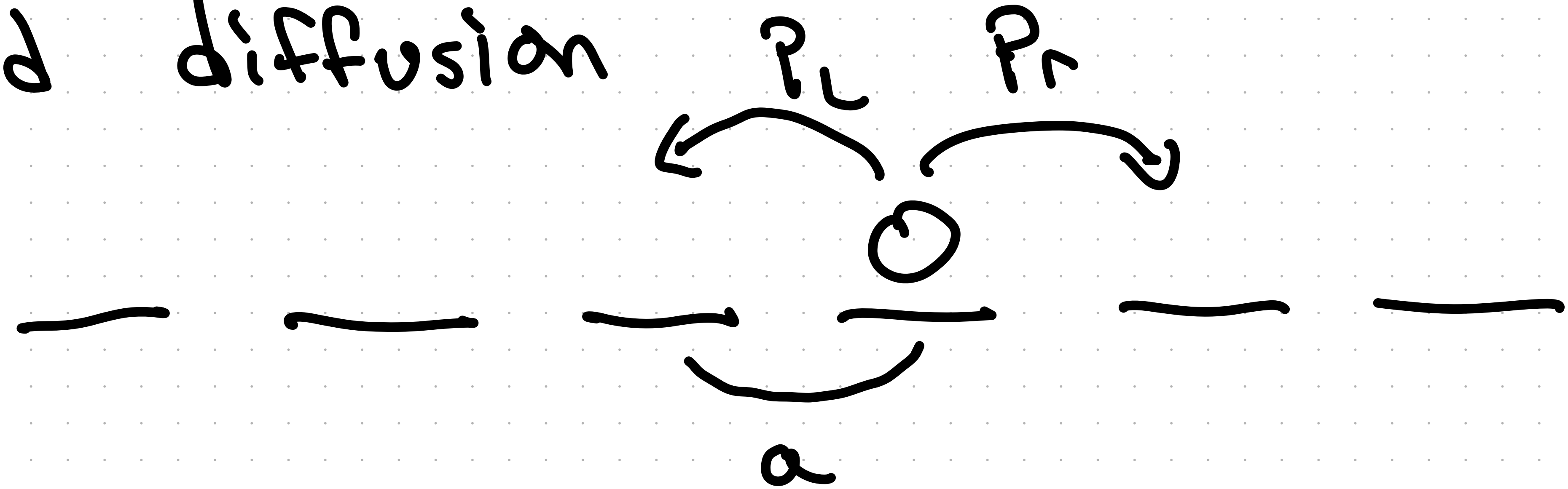
(3) Computer simulations can solve problems w/ no exact solution

Statistical mechanics

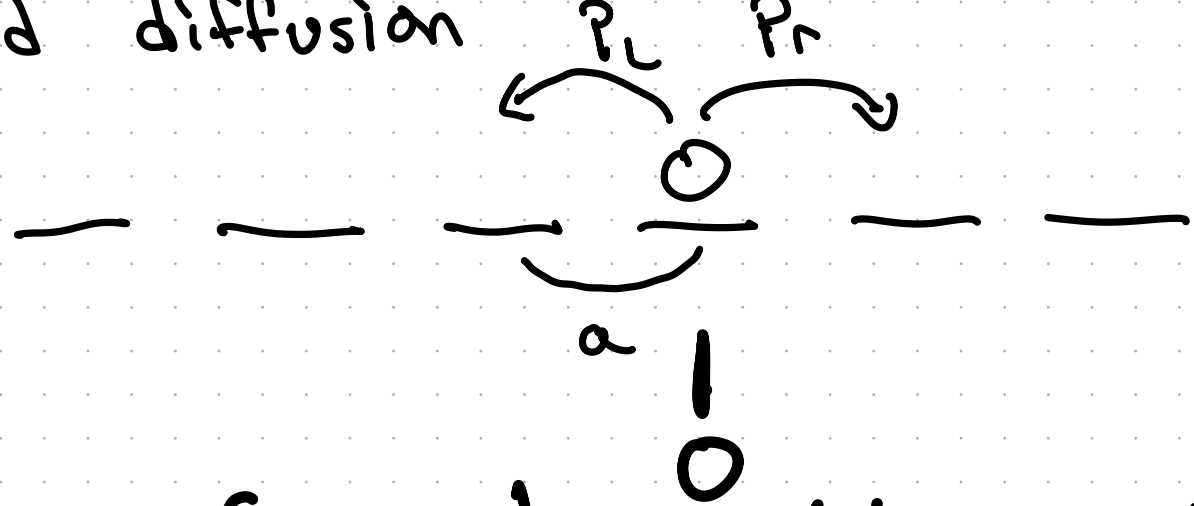
Eg: Diffusion in 1 dimension on a lattice

Later: 3D diffusion & brownian motion, Einstein 1905

1-d diffusion



1-d diffusion



imagine $P_L = P_r = 0.5$

How far does it go in N steps

"dynamics", flipping a coin N times

$$\text{mover: } \{m_i\} = \{\overset{m_1}{L}, \overset{m_2}{R}, R, R, L, L, \ldots\}$$

$$\text{trajectory: } \{x_i\} = \{\overset{x_0}{0}, \overset{x_1}{-a}, \overset{x_2}{0}, a, 2a, a, 0, \ldots\}$$

How do we analize it:

Time averages; for observable A, $A(x_i)$

$$\langle A \rangle_{time} = \lim_{M \to \infty} \frac{1}{M} \sum_{i=1}^{M} A(x_i)$$

$$\text{displacement}_i = x_i - x_0 \equiv d_i$$

$$\langle d \rangle = \frac{1}{M} \sum_{j=1}^{M} d_j = -x_0 + \left(\frac{1}{M} \sum_{j=1}^{M} x_j \right)$$

large M $\quad = \langle x \rangle - x_0$

$$x_j = x_0 + \sum_{i=1}^{j} a m_i = x_0 + a N_R(j) - a N_L(j)$$

$$\langle x \rangle = \frac{1}{M} \sum_{j=1}^{M} x_i = \frac{1}{M} \sum_{j=1}^{M} \left[x_0 + a N_R(j) - a N_L(j) \right]$$

$$= x_0 + \frac{a}{M} \sum_{j=1}^{M} \left(\frac{N_R(j)}{j} - \frac{N_L(j)}{j} \right) j$$

$$\approx x_0 + a/M \sum_{j=1}^{M} (P_R - P_L) j = \frac{2a}{M} \sum_{j=1}^{M} (P_R - 1/2) j$$

$P_R + P_L = 1$

$P_L = 1 - P_R$

$$= x_0 + \frac{2a}{M} \cdot \frac{M(M-1)}{2} \left(P_R - \frac{1}{2} \right)$$

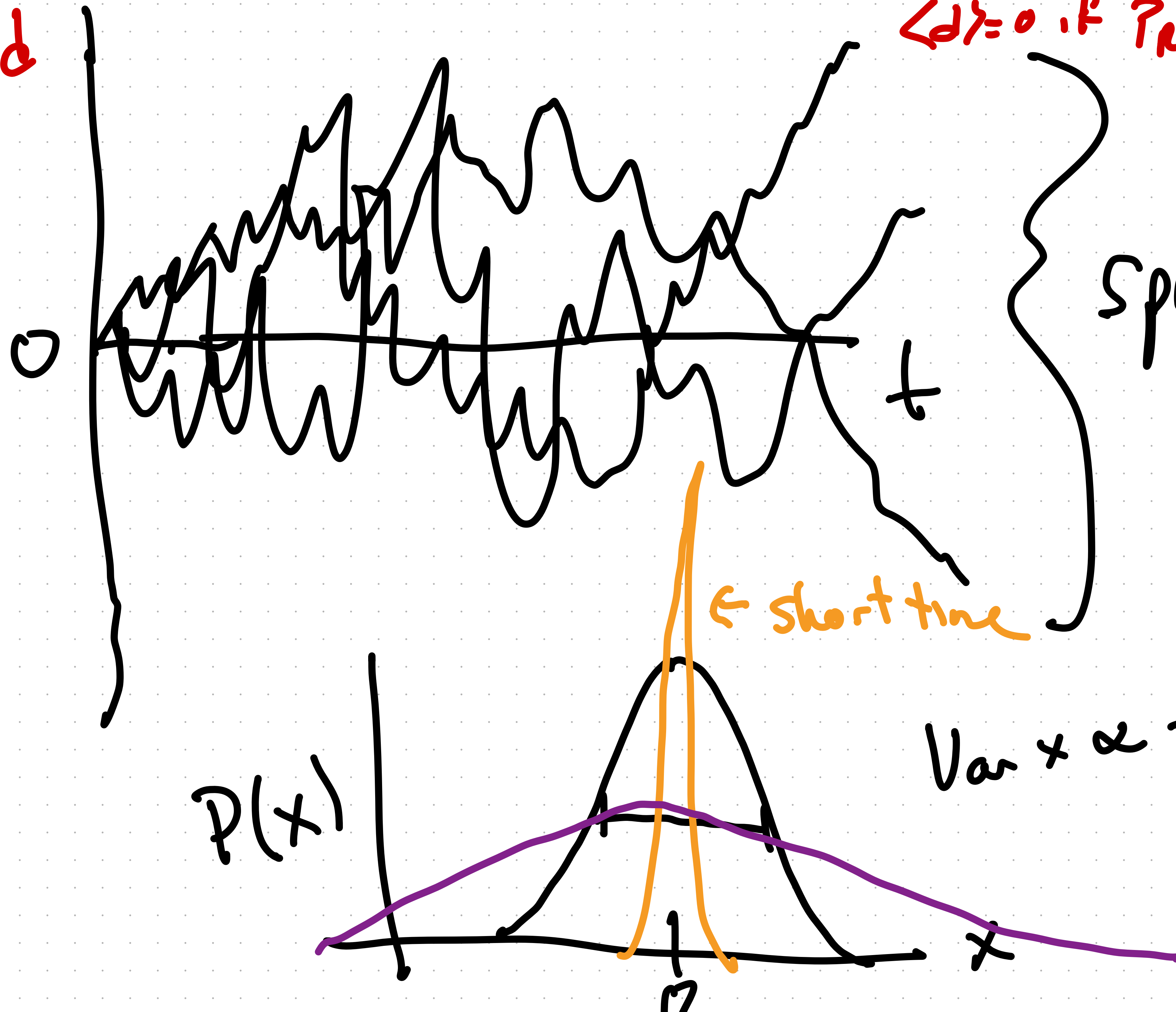
$$\approx x_0 + a M \left(P_R - \frac{1}{2} \right)$$

$$\langle d \rangle \approx a M \left(P_R - 1/2 \right)$$

if $P_R > 1/2$

"drifts"

$\langle d \rangle = 0$ if $P_R = 1/2$



Spreads out

$\mathrm{Var}\, x \propto t$