Molecules diffusing in a volume $\rightsquigarrow$ collide + react: "chemistry" $\rightsquigarrow$ networks of reactions

$\rightsquigarrow$ add fuel $\rightsquigarrow$ living systems $\rightsquigarrow$ populations + evolution

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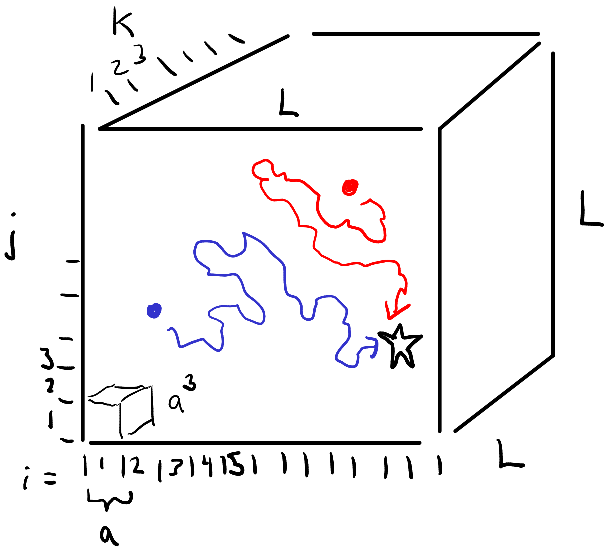

Question: 2 molecules diffusing in a volume

$\Rightarrow$ how long before they meet on average?

volume $L^3 = V$

broken up into small boxes of size a^3

assumption: above some time scale δt we assume enough collisions w/ environ. have occurred $\Rightarrow$ random motion of two molecules

influences: density, temperature, viscosity, etc.

1) state of particle: $\vec{n} = (i, j, k)$ = labels box where particle currently is

$i = 1, \ldots\ldots, N = \frac{L}{a}$

2) define dynamics; focus on one dimension of box (for example x dim.)

time t: particle is at i

where is it at time $t + \delta t$?

possibilities	probability
$i \to i-1$	$w\,\delta t$
$i \to i+1$	$w\,\delta t$
$i \to i$	$1 - 2w\,\delta t$

$\left.\begin{matrix} w\,\delta t \\ w\,\delta t \end{matrix}\right\}$ same by symmetry

sum to 1

assume δt small enough that other cases ($i \to i+2$) not likely

$$w = \frac{\text{probability}}{\text{time}} = \text{prob. rate} = \text{transition rate}$$

$\Rightarrow$ units: $[\text{time}]^{-1}$

$\downarrow$

this could depend: δt, temp., a, density, viscosity, ...

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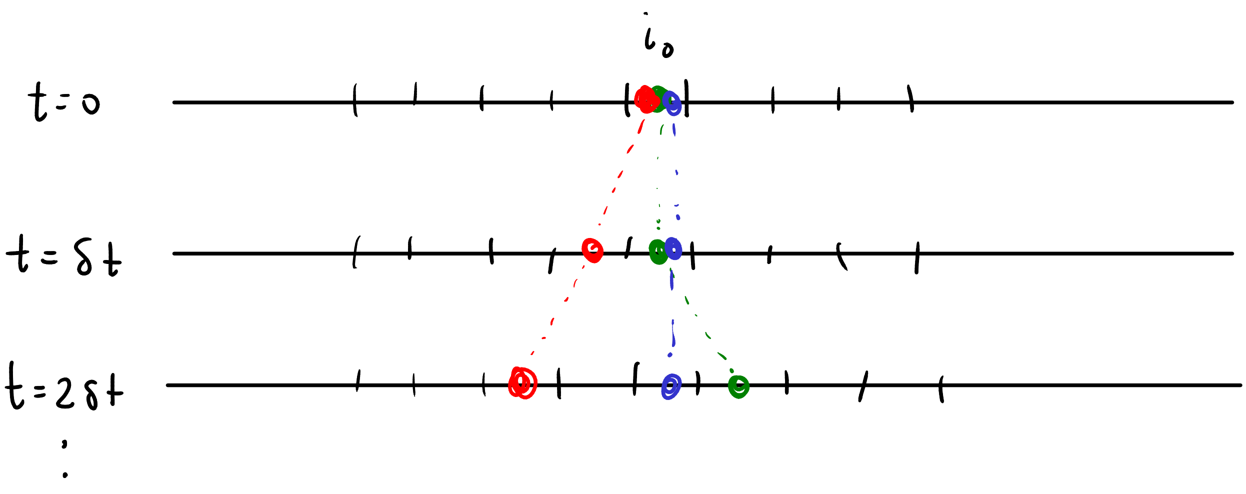
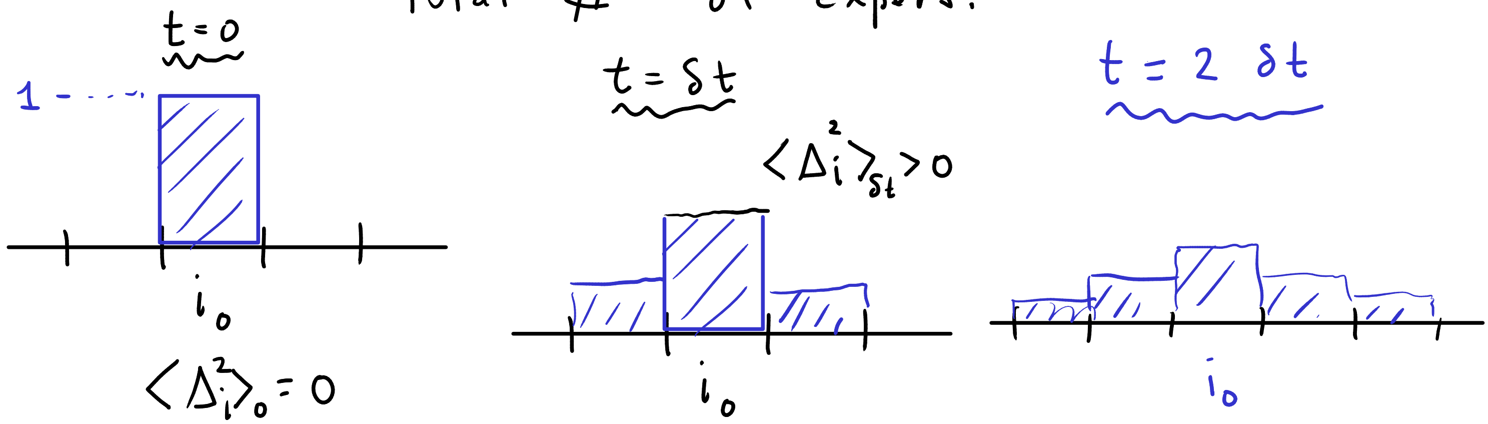
imagine running many "experiments" all starting w/ molecule at position i_0 at $t=0$



$p_i(t)$ = prob. to observe i at time t

$$= \frac{\#\text{ expers. w/ molecule at } i \text{ at time } t}{\text{total } \# \text{ of expers.}}$$



normalized: $\sum_{i=1}^{N} p_i(t) = 1$ at all times

properties: avg. position at time t $\quad \langle i \rangle_t \equiv \sum_{i=1}^{N} i \, p_i(t)$ "1st moment"

avg. of func $f(i)$ $\quad \langle f(i) \rangle_t = \sum_{i=1}^{N} f(i) \, p_i(t)$

$f(i) = i^2 \quad \langle i^2 \rangle_t = \sum_{i=1}^{N} i^2 \, p_i(t)$ "2nd moment"

define displacement: $f(i) = \Delta_i \equiv a(i - i_0)$ distance moved

$\langle \Delta_i \rangle_t = 0$ by symmetry

$\langle \Delta_i^2 \rangle_t \equiv$ mean squared displacement (MSD)

length^2

$\Rightarrow$ how to calculate?

$\sqrt{\langle \Delta_i^2 \rangle_t} = \text{RMSD}$ ~ units: length

$\sim$ typical distance (in any dir.) moved in time t

$$\langle \Delta_i^2 \rangle_t = \sum_{i=1}^{N} a^2 (i - i_0)^2 \, p_i(t)$$

$$= a^2 \left[\sum_i i^2 p_i(t) - 2 i_0 \sum_i i \, p_i(t) + i_0^2 \sum_i p_i(t) \right]$$

$$= a^2 \left[\langle i^2 \rangle_t - 2 i_0 \langle i \rangle_t + i_0^2 \right]$$

need to calc. these moments

$\Rightarrow$ need an equ. for $p_i(t)$ as a func. of time

$$p_i(t+\delta t) = p_i(t) - \left[\begin{array}{l} \text{loss in prob.} \\ \text{due to leaving } i \end{array} \right] + \left[\begin{array}{l} \text{gain in prob.} \\ \text{due to entering } i \end{array} \right]$$

$$= p_i(t) \underbrace{- \underbrace{2 w \delta t}_{\text{prob. you leave } i} \; \underbrace{p_i(t)}_{\text{prob. of being in } i \text{ at previous time}}}_{\text{loss}} \; \underbrace{+ \, w \delta t \, p_{i+1}(t) + w \delta t \, p_{i-1}(t)}_{\text{gain}}$$

$$\frac{p_i(t+\delta t) - p_i(t)}{\delta t} = -2 w \, p_i(t) + w \left(p_{i-1}(t) + p_{i+1}(t) \right)$$

at timescales $t \gg \delta t$, we can approx. LHS as a continuum time quantity:

$$\boxed{\frac{dp_i(t)}{dt} = -2w\, p_i(t) + w\left(p_{i-1}(t) + p_{i+1}(t)\right)}$$

example of master equation: how prob. changes in time