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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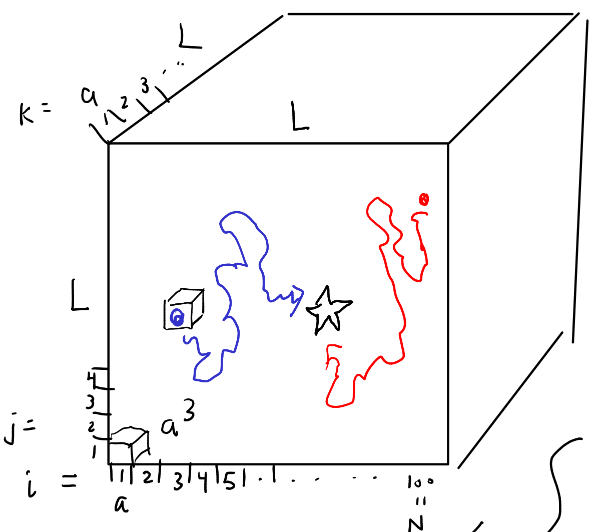
Question: 2 molecules diffusing in a crowded volume $\Rightarrow$ how long on avg. before they meet?



Volume $V = L^3$

$\Rightarrow$ break up into boxes of vol. a^3

assumption: above some time scale st we assume enough env. collisions have occurred $\Rightarrow$ get totally random motion of 2 molecules

physical influences: temperature, charges (dragging along water molecules), molecule size, density, viscosity

1) state of molecule:

$\vec{n} = (i, j, k)$ $\leftarrow$ labels of box where molec. is

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

2) define dynamics: focus on one molecule in one dim.

time t: particle is at i

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

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

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

assume δt small enough so we ignore $i \to i+2$, etc.

$w = \dfrac{\text{probability}}{\text{time}}$ = prob. rate = transition prob units: $[\text{time}]^{-1}$

↳ could depend on all physical influences

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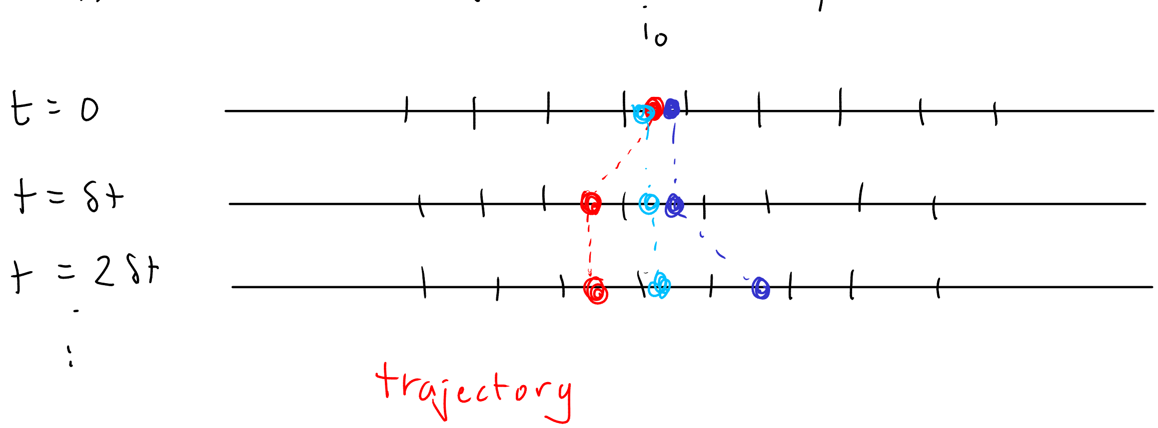
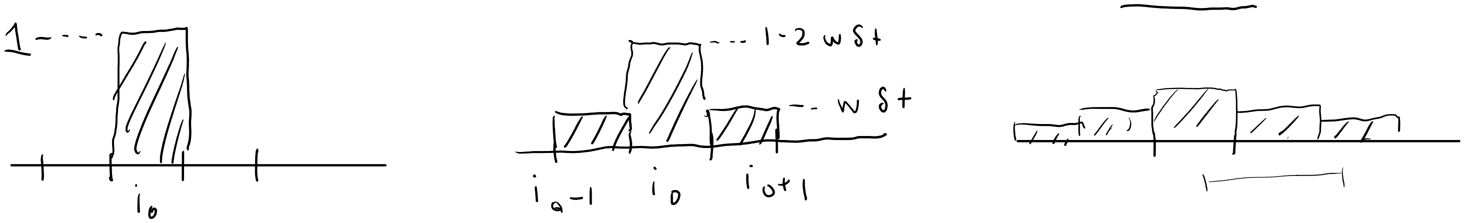
imagine running many "experiments" all starting w/ molec. at initial pos. i_0 at $t = 0$



$p_i(t)$ = probability to observe part. at i at time t $= \dfrac{\#\text{ expers w/ molec. at } i \text{ at time } t}{\text{total \# expers}}$

$t = 0$ $t = \delta t$ $t = 2\delta t$



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

properties:

avg. position at time t ("first moment") $\langle i \rangle_t = \sum_{i=1} i \, p_i(t)$

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

example: $f(i) = i^2$ $\langle i^2 \rangle_t = \sum_{i=1}^{N} i^2 \, p_i(t)$

2nd moment

nth moment $f(i) = i^n$ $\langle i^n \rangle_t = \sum_{i=1}^{N} i^n \, p_i(t)$

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

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

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

length^2

$\Rightarrow$ how to calculate?

$\sqrt{\langle \Delta_i^2 \rangle_t}$ = RMSD = root MSD units: length

$\rightarrow$ standard deviation: typical distance moved in any direction

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

$$= a^2 \left[\sum_i i^2 p_i(t) - 2 i_0 \sum_i i \, p_i(t) + i_0^2 \underbrace{\sum_i p_i(t)}_{1} \right]$$

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

need to calculate 1st + 2nd moments

Next time: need an equation for $p_i(t)$ as a func. of time