

OVERVIEW

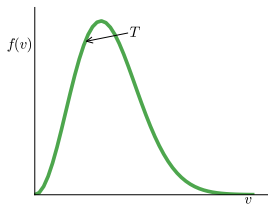
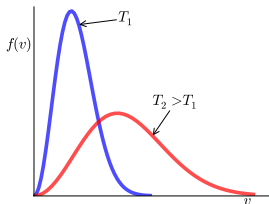
Kinetic theory of gases:

- Molecular collisions
- Brownian motion

A THOUGHT EXPERIMENT

Consider a vessel separated into two compartments — which contain a certain gas at temperatures T_1 and $T_2 > T_1$. Break the separator, the gases mix and (after a while) equilibrate at the final temperature

$$T = \frac{\nu_1 T_1 + \nu_2 T_2}{\nu_1 + \nu_2}$$



MOLECULAR COLLISIONS

Q: How exactly does this re-equilibration happen?

A: The key word is *collisions between molecules*

Notice that in the original ideal gas model we neglected them altogether. Now we need to take them into account.

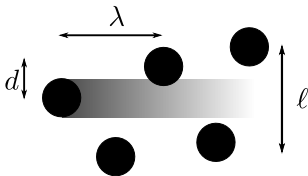
Q: What is a typical *rate of collisions*? Or a mean time between them? Or a *mean free path*?

A first idea (last week): N molecules in the volume V , hence concentration $n = N/V$, a typical length scale is $\ell \sim n^{-1/3}$.

In fact, need to be a bit more accurate.

MOLECULAR COLLISIONS: MEAN FREE PATH

Treating molecules as hard spheres, we can define a *mean free path*: a typical distance a molecule travels between collisions.

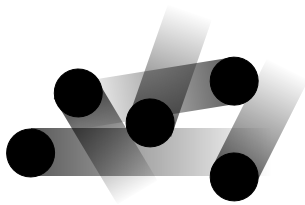


For point-like molecules:

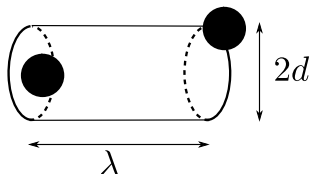
- ℓ is well defined
- λ would be infinite

For gases expect $\lambda \gg \ell$, for liquids expect $\lambda \sim \ell$

A more realistic cartoon: all the molecules are moving. (makes analysis more complicated, does not alter results much)



MEAN FREE PATH



Mean free path: there's exactly one molecule in the cylinder of length λ .

$$\pi d^2 \lambda \cdot \frac{N}{V} = 1$$

Therefore,

$$\lambda = \frac{1}{\pi d^2 \cdot N/V}$$

If we take into account that all molecules are in motion,

$$\lambda = \frac{1}{\pi \sqrt{2} d^2 \cdot N/V}$$

NB: λ does not depend on the speed of the molecules!

MEAN FREE PATH AND MEAN FREE TIME

Using the ideal gas law, $pV = Nk_B T$, hence

$$\lambda = \frac{1}{\pi\sqrt{2}d^2} \frac{k_B T}{p}$$

Mean free time, i.e. typical time between collisions:

$$\text{length} = \text{speed} \times \text{time}$$

hence estimate

$$\tau = \frac{\lambda}{v_{\text{rms}}}$$

Using $v_{\text{rms}} \propto (k_B T/m)^{1/2}$,

$$\tau \propto \frac{m^{1/2}(k_B T)^{1/2}}{d^2 p}$$

MEAN FREE PATH AND MEAN FREE TIME

Q: What is d ?

A: It's a diameter of an imaginary hard sphere, which we use to model a molecule.

This is sometimes called (twice the) *Van der Waals radius*

For N_2 , $d \approx 4.5 \text{ \AA} = 4.5 \cdot 10^{-10} \text{ m}$

For $p = 1 \text{ atm}$ and $T = 300 \text{ K}$, the mean free path of diatomic nitrogen is

$$\lambda = \frac{1}{\pi\sqrt{2}d^2} \frac{k_B T}{p} \approx 3.6 \cdot 10^{-8} \text{ m} = 36 \text{ nm}$$

(NB: values quoted in the literature are 40–70 nm)

The rms speed is $v_{\text{rms}} = \sqrt{3RT/\mu} \approx 5 \cdot 10^2 \text{ m/s}$, therefore the mean free time

$$\tau \sim 7 \cdot 10^{-11} \text{ s}$$

BROWNIAN MOTION

Consider a “large” object suspended in a liquid. Molecules strike it with random velocities and in random directions \Rightarrow random force. The motion of the object is irregular and jittery.

Usually credited to Robert Brown (1827), observing the motion of pollen in water. Was probably observed as early as 1785 — see wikipedia for details.

Theoretical explanations by Einstein (1905) and Smoluchowski (1906) — one of the first (indirect) confirmations of molecular-kinetic theory.

Is relevant in various contexts, from stock markets to swimming of bacteria.

HOW BACTERIA SWIM

Caulobacter crescentus:

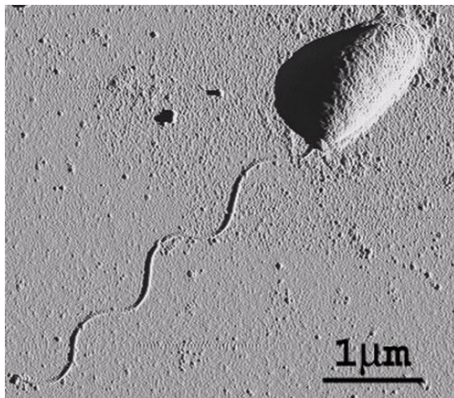


image: Guanglai Li/Brown University, Science daily, 19 Nov 2008

RANDOM WALK

We cannot take into account all the microscopic details of how molecules strike the object.

Hence, the simplest model of a Brownian motion: a random walk.

The simplest of random walks, the so-called “drunken sailor” model:

- A succession of steps \mathbf{r}_i
- Each step has the same length, $|\mathbf{r}_j| = \ell$
- The direction of each step is completely random. Or, more precisely, all directions are equally probable.
- The successive steps are not correlated with each other.

RANDOM WALK

Q: If a sailor starts at the origin, how far is he from the origin after N steps?

A: Can't really tell, it's random.

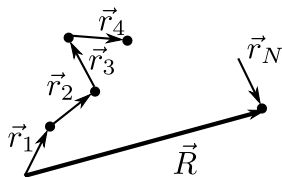
Q: If a sailor starts at the origin, how far is he from the origin after N steps *on average*?

- *Time average:* Follow the evolution of a sailor for $N \gg 1$ steps
- *Ensemble average:* Send a large number of sailors, see how far they moved after a fixed number of steps

Ergodic hypothesis: These two ways are equivalent.

RANDOM WALK

Q: If a sailor starts at the origin, how far is he from the origin after N steps *on average*?



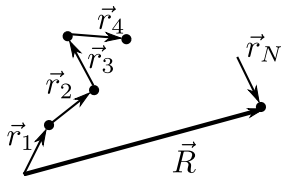
$$\mathbf{R} = \mathbf{r}_1 + \mathbf{r}_2 + \cdots + \mathbf{r}_N = \sum_{j=1}^N \mathbf{r}_j$$

Since the direction of each step is completely random, $\langle \mathbf{r}_j \rangle = 0$, thus

$$\langle \mathbf{R} \rangle = 0$$

Q: What about $\langle \mathbf{R}^2 \rangle$?

RANDOM WALK



$$\mathbf{R} = \mathbf{r}_1 + \mathbf{r}_2 + \cdots + \mathbf{r}_N = \sum_{j=1}^N \mathbf{r}_j$$

Each $|\mathbf{r}_j| = \ell$, the direction of each step is completely random: $\langle \mathbf{r}_j \rangle = 0$, and the direction of each step is independent of any other one.

$$\langle \mathbf{R}^2 \rangle = \left\langle \left(\sum_{j=1}^N \mathbf{r}_j \right)^2 \right\rangle = \sum_{j=1}^N \mathbf{r}_j^2 + 2 \sum_{j=1}^{N-1} \sum_{s=j+1}^N \langle \mathbf{r}_j \cdot \mathbf{r}_s \rangle$$

Since all the steps are independent, $\langle \mathbf{r}_j \cdot \mathbf{r}_s \rangle = \langle \mathbf{r}_j \rangle \cdot \langle \mathbf{r}_s \rangle = 0$, and

$$\langle \mathbf{R}^2 \rangle = \sum_{j=1}^N \ell^2 = N\ell^2$$