On the menu today
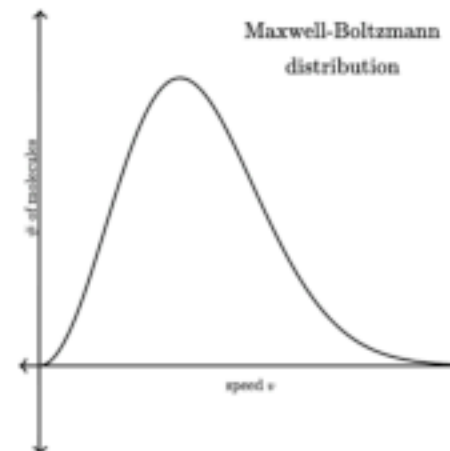
09/10/2021

Lecture 3: chapters 5, 6, and 8

Lecture 5. *The Maxwell-Boltzmann distribution*

- In this unit we will learn about

  - Motion of gas molecule

Next few lectures will be on kinetic theory of gas

Setting the stage

- Gas is monoatomic (we ignore rotational and vibrational degrees of freedom)

- There is no interacting force between molecules

- Molecules can exchange energy and momentum through collisions

- We consider only linear motion

- The energy is thus, simply:

$$\frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 = \frac{1}{2}mv^2$$
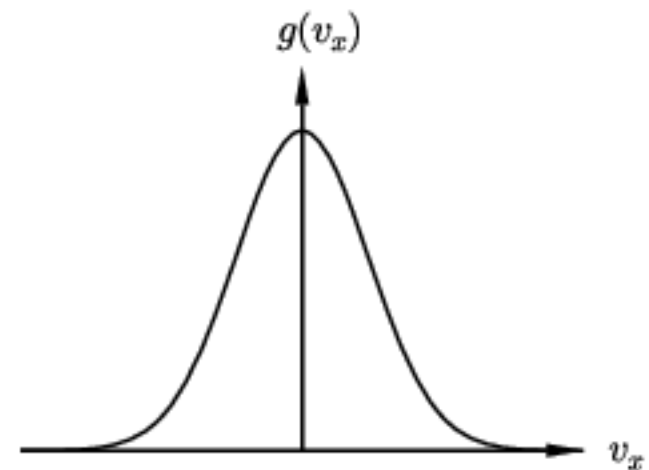
Velocity distribution

- Each molecule can be considered as a system connected to a bath of the other molecules and the Boltzmann distribution applies

- In one dimension, the velocity distribution function is the probability density of finding the particle with velocity between v_x and $v_x + dx$

$$g\left(v_x\right) \propto \mathrm{e}^{-mv_x^2/2k_{\mathrm{B}}T}$$

Normalisation

$$\int_{-\infty}^{\infty} g\left(v_x\right) \mathrm{d}v_x = 1$$

Statistical properties

$$\langle v_x \rangle = \int_{-\infty}^{\infty} v_x g(v_x) \, \mathrm{d}v_x = 0$$

$$\langle |v_x| \rangle = 2 \int_{0}^{\infty} v_x g(v_x) \, \mathrm{d}v_x = \sqrt{\frac{2 k_{\mathrm{B}} T}{\pi m}}$$

$$\langle v_x^2 \rangle = \int_{-\infty}^{\infty} v_x^2 g(v_x) \, \mathrm{d}v_x = \frac{k_{\mathrm{B}} T}{m}$$

Total probability (3D)

$$g\left(v_x\right)\mathrm{d}v_x\, g\left(v_y\right)\mathrm{d}v_y\, g\left(v_z\right)\mathrm{d}v_z$$

This is the fraction of molecules with velocities between $\left(v_x, v_y, v_z\right)$ and $\left(v_x + \mathrm{d}v_x, v_y + \mathrm{d}v_y, v_z + \mathrm{d}v_z\right)$

Speed distribution

- **Question:** number of molecules with velocity between v and $v + dv$

- This is different from what we calculated before (shell *vs.* cube)

- Volume in velocity space is $4\pi v^2 dv$

- Fraction of molecules that have velocity between v and $v + dv$:

$$f(v)\mathrm{d}v \propto v^2 \mathrm{d}v e^{-mv^2/2k_{\mathrm{B}}T}$$
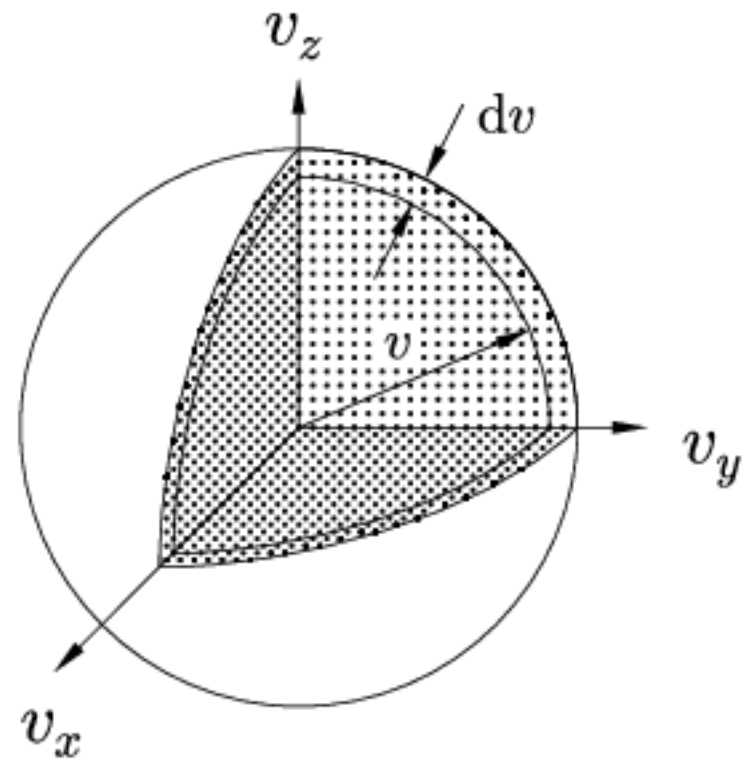
Normalization

$$\int_0^\infty f(v)\mathrm{d}v = 1$$

Expectation values $\langle v \rangle$ and $\langle v^2 \rangle$

$$\langle v \rangle = \int_0^\infty v f(v)\mathrm{d}v = \sqrt{\frac{8k_\mathrm{B}T}{\pi m}}$$

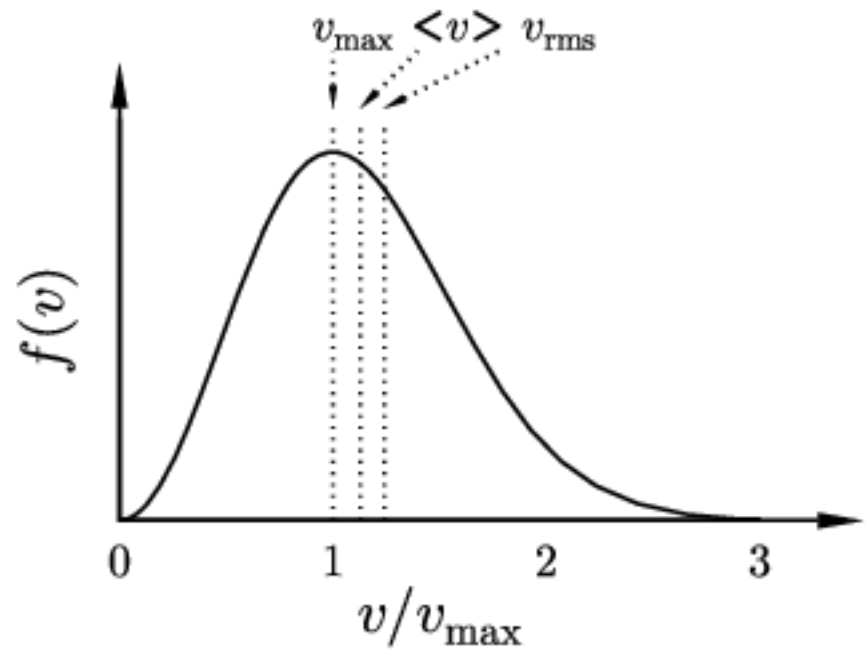$$\langle v^2 \rangle = \int_0^\infty v^2 f(v)\mathrm{d}v = \frac{3k_\mathrm{B}T}{m}$$

- Root mean square of velocity:

Mean kinetic energy of a gas <u>molecule</u>

$$\langle E_{\mathrm{KE}} \rangle = \frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} k_{\mathrm{B}} T$$

More information on the distribution

$$v_{\text{rms}} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3k_{\text{B}}T}{m}}$$

Example: rms speed of N$_2$ molecules at RT?

$$v_{\mathrm{rms}} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3k_{\mathrm{B}}T}{m}}$$

For nitrogen at room temperature, $m = (0.028\mathrm{kg})/(6.022 \times 10^{23})$ and so $v_{\mathrm{rms}} \approx 500\mathrm{ms}^{-1}$. This is about 1100 miles per hour, and is the same order of magnitude as the speed of sound.

Summary

We have shown that the corresponding expression for the probability distribution of molecular speeds is given by

$$f(v) \propto v^2 e^{-mv^2/2k_\mathrm{B}T}$$

This is known as a Maxwell-Boltzmann distribution, or sometimes as a Maxwellian distribution.

Two important average values of the Maxwell-Boltzmann distribution are:
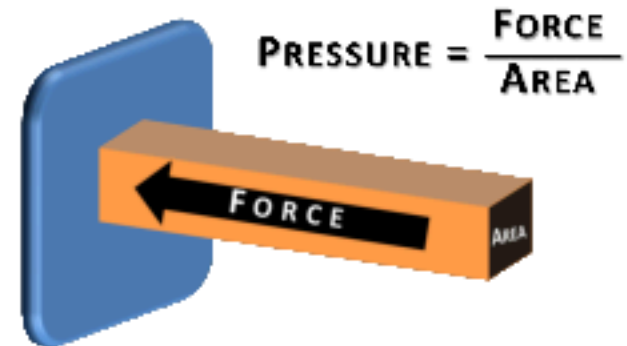
Lecture 6. *Pressure*

- In this unit we will learn about

  - Pressure of a gas

  - The origins of the ideal gas law

  - Connection between pressure and kinetic energy density

https://taaublog.wordpress.com/2017/12/11/pressure/

Definition

$$\text{PRESSURE} = \frac{\text{FORCE}}{\text{AREA}}$$

The pressure p due to a gas (or any fluid) is defined as the **ratio of the perpendicular contact force to the area of contact**.

The unit is that of force (N) divided by that of area $\left(m^2\right)$ and is called the pascal $(Pa = Nm^{-2})$.

The direction in which pressure acts is normal to the surface upon which it is acting.

Illustration: estimation of atmosphere height

Air has a density of about 1.29 kg m^{-3}

Atmospheric pressure $p \approx 10^5$ Pa is due to the weight of air $\rho g h$ in the atmosphere (**with assumed height h and uniform density ρ**) pressing down on each square meter.

Hence $h = p/\rho g \approx 10^4$ m (which is about the cruising altitude of planes).

Of course, in reality the density of the atmosphere falls off with increasing height.
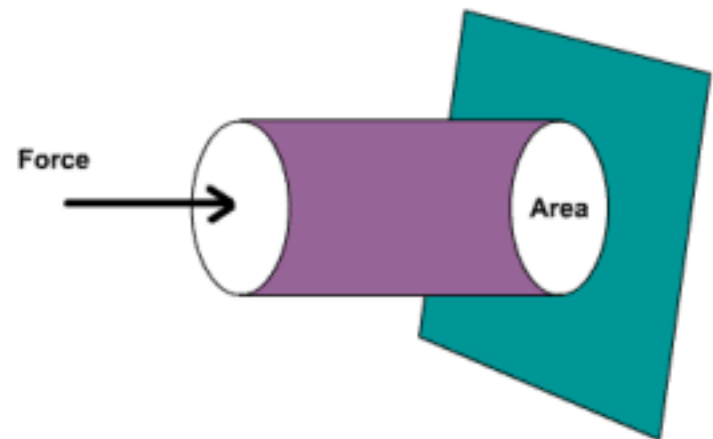
Equation of state

The pressure p of a volume V of gas (comprising N molecules) depends on its temperature T via an **equation of state**, which is an expression of the form

$$p = f(T, V, N)$$

where   is some function.

One example of an equation of state is that for an ideal gas

Kinetic theory of gas

Daniel Bernoulli (1700-1782) attempted an explanation of Boyle's law ($p \propto 1/V$) by assuming (controversially!) that gases were composed of a vast number of tiny particles.

This was the first serious attempt at a **kinetic theory of gases** of the sort that we will describe in this lecture to derive the ideal gas equation.
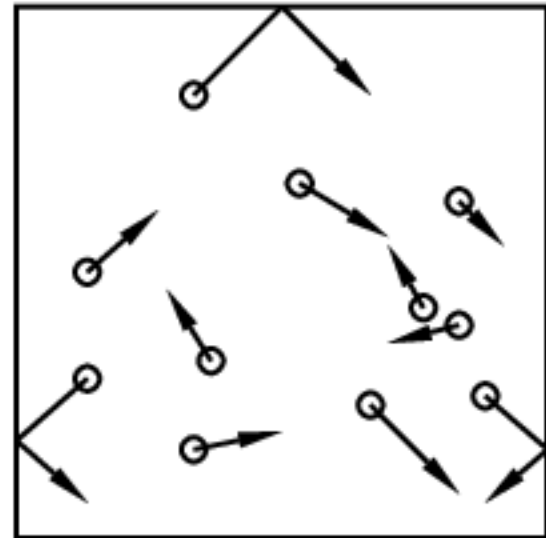
In the KTG a gas is modeled as a number of individual tiny particles, which can bounce off the walls of the container and each other.

pressure: force per unit area $\qquad p = \dfrac{F_\perp}{A}$

force: change in momentum with time $\qquad F = \dfrac{dmv_\perp}{dt}$

We need to calculate the total impulse on a surface area per unit time

How many particles have speed v?

Molecular distribution

$$f(v) = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2k_{\mathrm{B}}T} \right)^{3/2} v^2 \mathrm{e}^{-mv^2/2k_{\mathrm{B}}T}$$

In the previous chapter we derived the Maxwell-Boltzmann speed distribution function $f(v)$.

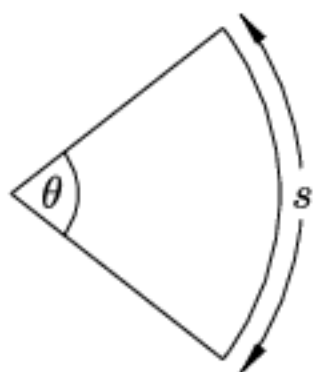We denote the total number of molecules per unit volume by the symbol n.

The number of molecules per unit volume traveling with speeds between v and $v + dv$ is then given by $nf(v)dv$.

We now seek to determine the distribution function of molecules traveling in different directions.
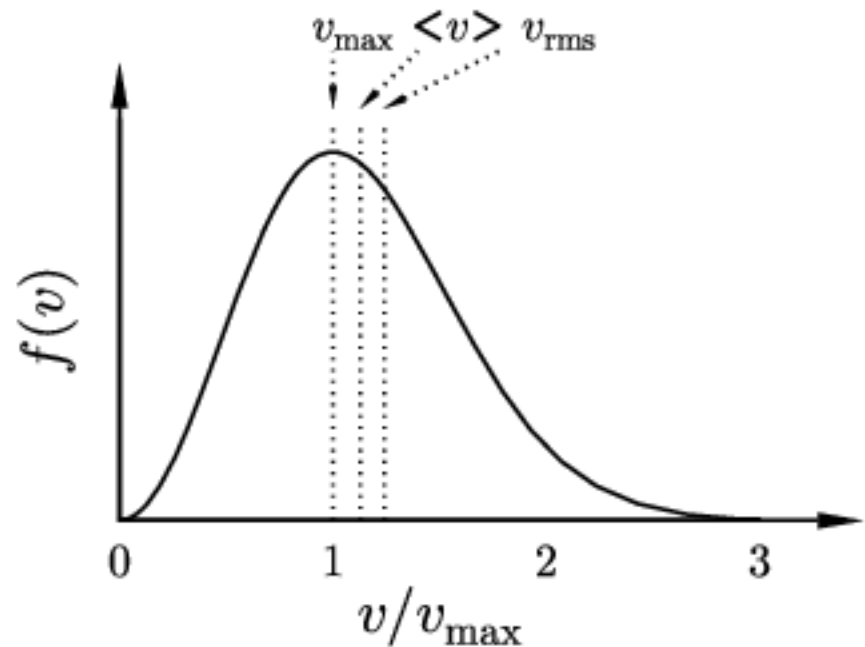
Solid Angle

$$\theta = \frac{s}{r}$$

If we have an isotropic system, the fraction of particles that are in a $d\Omega$ solid angle is

$$\frac{d\Omega}{4\pi}$$

Number of molecules hitting a wall

In a small time dt, the molecules traveling at angle θ to the normal to the wall sweep out a volume $Avdt\cos\theta$.

Multiplying this volume by the number of particles described in the previous slide implies that in time dt, the number of molecules hitting a wall of area A is

$$Avdt\cos\theta nf(v)\mathrm{d}v\frac{1}{2}\sin\theta\mathrm{d}\theta$$

The number of molecules hitting a unit area of wall in unit time, and having speeds between   and   and traveling at angles between   and   is given by
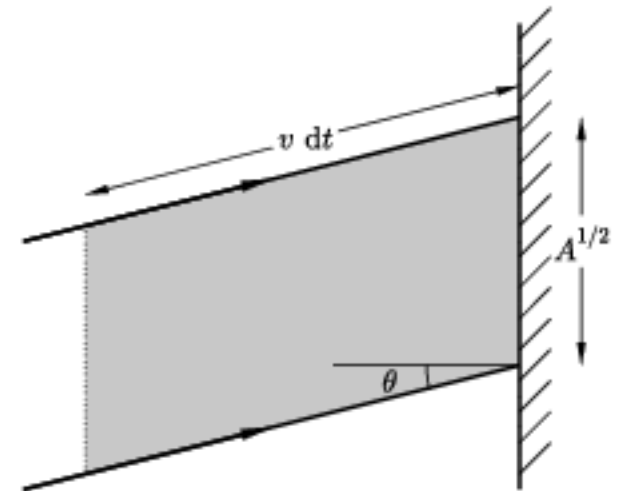
The ideal gas law

Each molecule hitting the wall of the container has a momentum change of $2mv\cos\theta$.

Hence, if we multiply $2mv\cos\theta$ by the number of molecules hitting unit area per unit time, and "having speeds between v and $v + \mathrm{d}v$ and angles between θ and $\theta + \mathrm{d}\theta$" and then integrating over θ and v, we get

MOMENTUM TRANSFER **NUMBER OF MOLECULES HITTING SURFACE**

$$p = \int_0^\infty \int_0^{\pi/2} (2mv\cos\theta)\left(v\cos\theta n f(v)\mathrm{d}v\frac{1}{2}\sin\theta\mathrm{d}\theta\right)$$

Total number of molecules N in volume V as $N = nV$

$$pV = \frac{1}{3}Nm\left\langle v^2 \right\rangle$$

Connection between pressure and kinetic energy

The kinetic energy of a gas molecule moving with speed v is

$$\frac{1}{2}mv^2$$

The total kinetic energy of the molecules of a gas per unit volume, *i.e.* the kinetic energy density, which we will call   , is therefore given by

so that we have that

Dalton's law

If one has a mixture of gases in thermal equilibrium, then the total pressure $p = nk_{\mathrm{B}}T$ is simply the sum of the pressures due to each component of the mixture. We can write n as

$$n = \sum_i n_i$$

where   is the number density of the   th species. Therefore

where   is known as the partial pressure of the   th species.

The observation that   is known as Dalton's law, after the British chemist John Dalton (1766-1844), who was a pioneer of the atomic theory.

Example of Dalton's law

$$p_{\mathrm{CO_2}} = \frac{\frac{0.05}{44} \times 1\mathrm{atm}}{\frac{75.5}{28} + \frac{23.2}{32} + \frac{1.3}{40} + \frac{0.05}{44}} = 0.00033\mathrm{atm}$$

Summary

1) The pressure, p, is given by

$$p = \frac{1}{3} nm \left\langle v^2 \right\rangle$$

where   is the number of molecules per unit volume and   is the molecular mass.

2) This expression agrees with the ideal gas equation

where   is the volume,   is the temperature and   is the Boltzmann constant.

Lecture 8. *Mean free path and collisions*

- In this unit we will learn about

  - Mean free path

  - Collision cross-section

In this lecture we will model the effect of collisions in a gas and develop the concepts of a mean **collision time**, the **collision cross-section** and the **mean free path**.

Setting the stage

At room temperature, the rms speed of O_2 or N_2 is about 500 ms^{-1} .

Processes such as the diffusion of one gas into another would therefore be almost **instantaneous**, were it not for the occurrence of **collisions** between molecules.

Collisions are fundamentally quantum mechanical events, but in a dilute gas, molecules spend most of their time between collisions and so we can consider them as classical billiard balls and ignore the details of what actually happens during a collision.

After collisions the molecules' velocities become essentially randomized.

Mean collision time

- Suppose a molecule travels at speed v among other, stationary, molecules.

- Suppose a molecule as *section ("cross-section")* σ . *("molecule personal space")*

- During time $\mathrm{d}t$, the molecule will "sweep" volume $\sigma v \mathrm{d}t$

- If a molecule happened to be in that volume a that time, there will be a collision

- If we suppose that the density of molecule is n, the probability of a collision is thus $n\sigma v \mathrm{d}t$

σ

$v\mathrm{d}t$
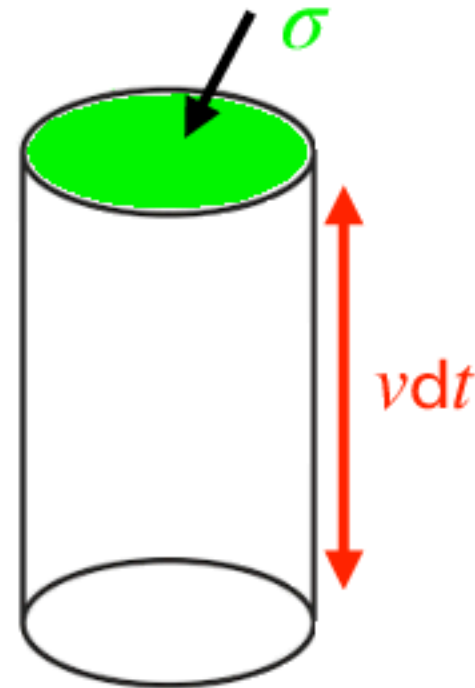
Probability that we do *not* have a collision up to time *t*

$$P(t + dt) = P(t) + \frac{dP}{dt} dt$$

- $P(t + dt)$ is the probability of no collision up to time t and from t+dt.

Probability of no collision up to t and then collision in the next dt

$$e^{-n\sigma vt} n\sigma v \mathrm{d}t$$

- Of course integrates to 1 as a probability should

- Mean scattering time τ: average time elapsed between collisions for a given molecule

Collision cross-section

- Consider two spherical molecules with a **hard-sphere potential**

- **Impact parameter:** distance of closest approach that would result if the molecular trajectories were undeflected by the collision

  - e.g., for the HSP, there is only collision if $b < a_1 + a_2$.
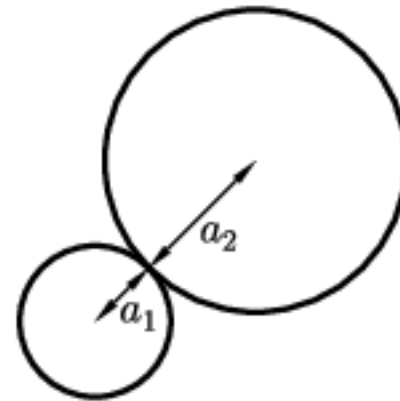
$$V(R) = \begin{cases} 0 & R > a_1 + a_2 \\ \infty & R \le a_1 + a_2 \end{cases}$$
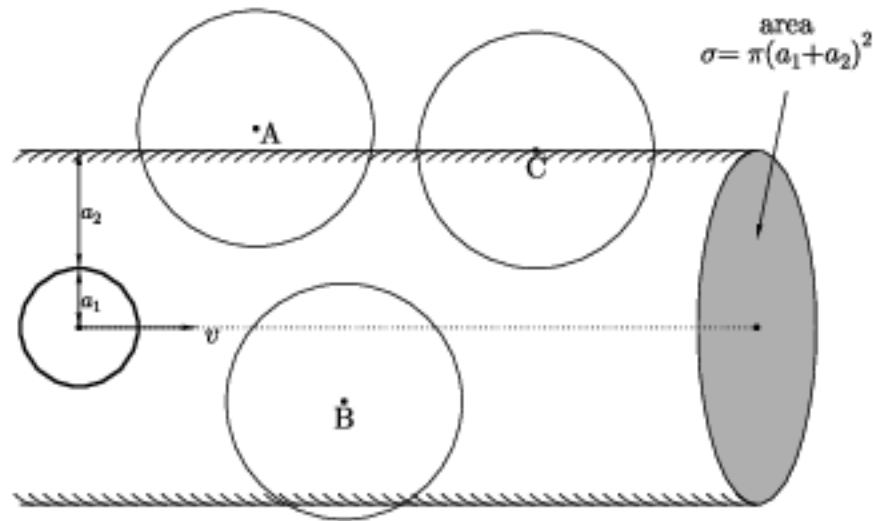
A collision will only take place if the centre of these other molecules comes inside a tube of radius $a_1 + a_2$ (i.e., A would not collide, B and C would)

Thus our first molecule can be considered to sweep out an imaginary tube of space of **cross-sectional area** $\pi(a_1 + a_2)/2$ that defines its "personal space".

The area of this tube is called the collision cross-section σ and is then given by

$$\sigma = \pi \left(a_1 + a_2 \right)^2$$

Note: Is the hard-sphere potential correct?

It is a good approximation at lower temperatures, but progressively worsens as the temperature increases.

Molecules are not really hard spheres but slightly squashy objects, and when they move at higher speeds and plough into each other with more momentum, you need more of a direct hit to cause a collision. **Thus as the gas is warmed, the molecules may appear to have a smaller cross-sectional area.**
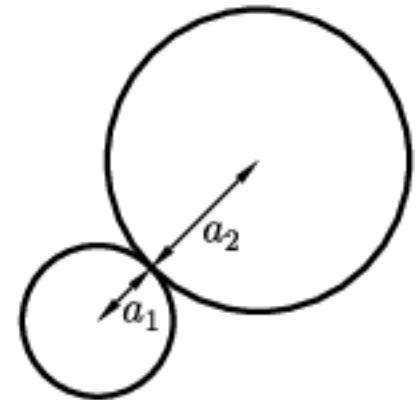
$$V(R) = \begin{cases} 0 & R > a_1 + a_2 \\ \infty & R \leq a_1 + a_2 \end{cases}$$

The mean free path

Having derived the mean collision time, it is tempting to derive the mean free path as

$$\lambda = \langle v \rangle \tau = \frac{\langle v \rangle}{n\sigma v}$$

but what should we take as

A first guess is to use   but that turns out to be not quite right. **What has gone wrong?**

Our approach to molecular scattering has been to focus on one molecule as the moving one, and think of all of the others as sitting ducks, fixed in space waiting patiently for a collision to occur.

We should therefore take v as the average relative velocity, i.e., $\langle v_r \rangle$, where

$v_r = v_1 - v_2$ and   and   are the velocities of two molecules labelled 1 and 2 .

, so that

because   (which follows because   ).

The quantity which we want is   but what we have an expression for is   If the probability distribution describing molecular speed is a Maxwell-Boltzmann distribution, then the error in writing   is small, so to a reasonable degree of approximation we can write

$$\langle v_{\rm r} \rangle \approx \sqrt{\langle v_{\rm r}^2 \rangle} \approx \sqrt{2}\langle v \rangle$$

and hence we obtain an expression for   as follows:

To increase the mean free path by a certain factor, the pressure needs to be decreased by the same factor.

1) The mean scattering time is given by

$$\tau = \frac{1}{n\sigma \langle v_{\mathrm{r}} \rangle}$$

where the collision cross-section is   is the molecular diameter and

2) The mean free path is