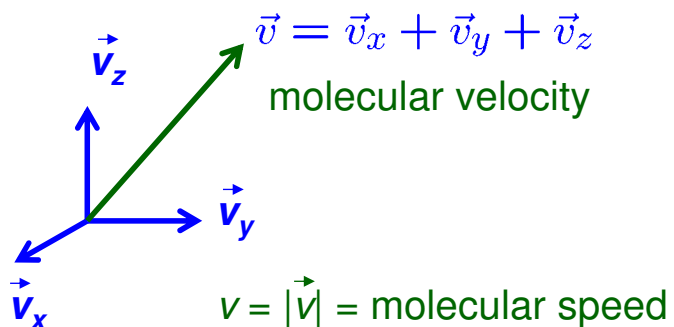# Chapter 8

Kinetic gas theory

8.1   Maxwell-Boltzmann distribution of speeds & velocities

8.2   Pressure

8.3   Effusion & Flux

8.4   Mean free path & elastic collisions

8.1 Maxwell-Boltzmann distribution

$$\vec{v} = \vec{v}_x + \vec{v}_y + \vec{v}_z$$

molecular velocity

$v = |\vec{v}|$ = molecular speed

Consider:

- A dilute monoatomic gas (size of the particles << average distance between them).

- Assume that the gas atoms are non-interacting, and neglect rotational and internal vibrational contributions to the total energy.

- In this case the only energy term present is the kinetic energy:

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

Velocity distribution

Further assumption:

- Particles can only exchange energy with each other due to collisions, but everything remains in equilibrium.

- This means every particle behaves like a small system connected to a heat reservoir at temperature ***T***, where the heat reservoir constitutes all other particles in the gas.

- The relative probability of a particle being in a particular microstate is therefore given by a Boltzmann factor.

$\vec{v}_x$
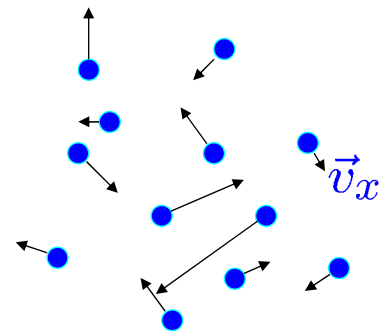
1-D velocity distribution

- We are considering what is the distribution of the x component (v_x) of the velocities of molecules in an ideal gas. Why?

  - The 3D expression can be derived from the 1D one

  - There are cases when all you need is the 1D distribution – for example to work out the pressure on a wall what matters is the component of velocity of the gas molecules directed towards the wall – if you assume elastic collisions with a flat wall, the components parallel to the wall are not affected by the collision. Another example if you are doing spectroscopy on a moving molecule, you will see a Doppler shift in the measured frequencies that are determined by the velocity of the atom in the direction of the beam of light that is probing the molecule.

- Define the velocity distribution function $f_{1D}(v_x)$ such that $f_{1D}(v_x)\delta v_x$ is the fraction of molecules with velocity components along the x – direction, that fall in the interval v_x to $v_x + \delta v_x$.

1-D velocity distribution

- Propose an infinitesimally small velocity state width ε_v, then the number of microstates in a velocity interval δv_x is $\delta N = \delta v_x / \varepsilon_v$ and the relative probability, δP_r of being the velocity being found in the interval v_x to $v_x + \delta v_x$ is:

$$\delta P_r = e^{-\frac{1}{2}mv_x^2/kT} \delta v_x / \varepsilon_v \propto f_{1D}(v_x)\delta v_x$$
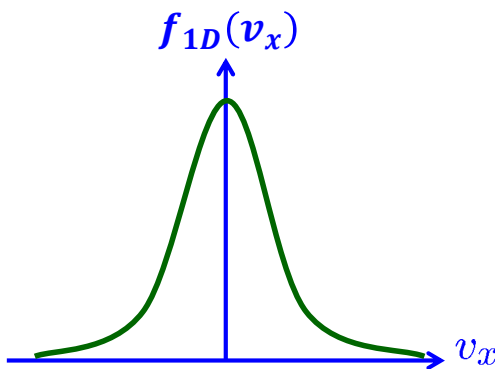
$f_{1D}(v_x)$

hence: $\quad f_{1D}(v_x) \propto e^{-\frac{1}{2}mv_x^2/kT}$

v_x

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1-D velocity distribution

- Normalizing $f_{1D}(v_x)$:

$$\int_{-\infty}^{\infty} f_{1D}(v_x)dv_x = 1$$

$$\int_{-\infty}^{\infty} e^{-mv_x^2 /2k_BT}dv_x = \sqrt{\frac{2\pi k_BT}{m}}$$

Hence, $\quad f_{1D}(v_x) = \sqrt{\frac{m}{2\pi k_BT}} e^{-mv_x^2 /2k_BT}$

- In order to find the expectation or average value $\langle v_x \rangle$ for the velocities of atoms we need to multiply v_x with the distribution function and integrate over all v_x.

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$\langle v_x^2 \rangle$ for 1-D velocity distribution

- Hence, since $f_{1D}(v_x)$ is an even function:

$$\langle v_x \rangle = \int_{-\infty}^{\infty} v_x f_{1D}(v_x) dv_x = 0$$

- To obtain the average magnitude we need to integrate over half of velocity space (the factor of 2 arises because $f_{1D}(v_x)$ is normalised on the interval $-\infty < v_x < \infty$:

$$\langle |v_x| \rangle = 2 \int_0^{\infty} v_x f_{1D}(v_x) dv_x$$

$$= 2 \int_0^{\infty} v_x \sqrt{\frac{m}{2\pi k_B T}} e^{-mv_x^2 /2k_B T} dv_x = \sqrt{\frac{2k_B T}{\pi m}}$$

- And

$$\langle v_x^2 \rangle = \int_{-\infty}^{+\infty} dv_x \, v_x^2 \frac{e^{-mv_x^2/2k_B T}}{\sqrt{2\pi k_B T/m}} = \frac{k_B T}{m}$$

(One can do this integral by parts, or more simply just use equipartition: $\langle KE \rangle = \frac{1}{2} m \langle v_x^2 \rangle = \frac{1}{2} k_B T \Rightarrow \langle v_x^2 \rangle = k_B T/m$)

3-D velocity distribution

- Because the three coordinates are independent of each other we can write for the 3D case:

$$f_{1D}(v_x) dv_x \, f_{1D}(v_y) dv_y \, f_{1D}(v_z) dv_z$$

$$= \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} e^{-mv_x^2 /2k_B T} dv_x \, e^{-mv_y^2 /2k_B T} dv_y \, e^{-mv_z^2 /2k_B T} dv_z$$

$$= \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} e^{-m\underline{v}^2 /2k_B T} dv_x dv_y dv_z$$

- The 3-D velocity distribution is a '3-D Gaussian' centred at $\underline{v} = (0,0,0)$ - ie the most likely **VELOCITY** is at the origin

- The most likely **SPEED**, however, has to take account of how much volume in 'v-space' lies between $|\underline{v}| = v$ and $|\underline{v}| = v + \delta v$.

Speed distribution

- In order to obtain the distribution of particle (molecular) SPEEDS in a gas, we first compute the fraction of particles that travel with speeds between $|\underline{v}| = v$ and $|\underline{v}| = v + \delta v$.

- Using spherical symmetry in the velocity space, the volume of a shell of thickness δv radius v is then $4\pi v^2 \delta v$.
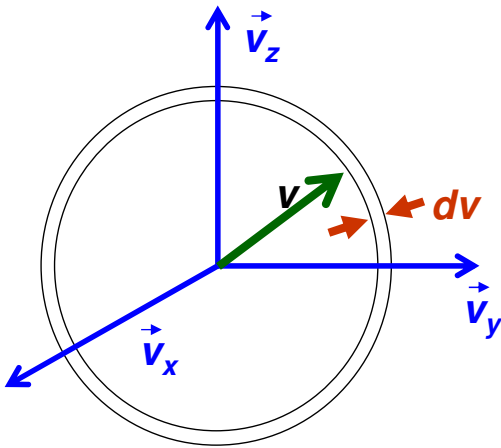
- Therefore, the fraction of molecules speeds between $|\underline{v}| = v$ and $|\underline{v}| = v + \delta v$ is

$$f(v)\mathrm{d}v \propto v^2 \mathrm{d}v \ e^{-mv^2/2k_BT}$$

with $f(v)$ = probability that a particle has the speed v.

Speed distribution

- Normalizing this function such that $\displaystyle\int_0^\infty f(v)dv = 1$

- We obtain $\displaystyle\int_0^\infty v^2 \ e^{-mv^2/2k_BT} \ \mathrm{d}v = \frac{1}{4}\sqrt{\frac{\pi}{(m/2k_BT)^3}}$

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

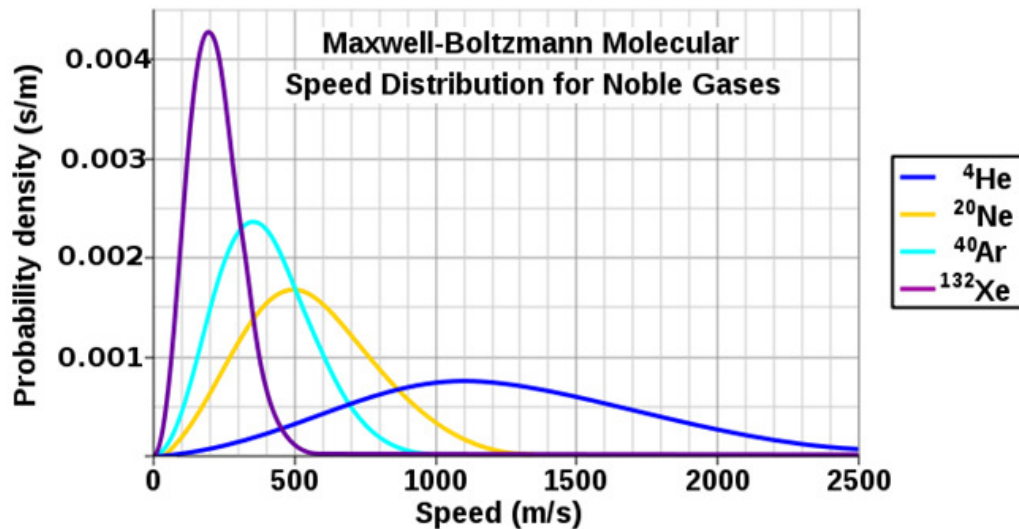***Maxwell-Boltzmann distribution***

of speeds in an ideal gas

Maxwell-Boltzmann distribution

● In 1D, the velocity distribution in an ideal gas is then:

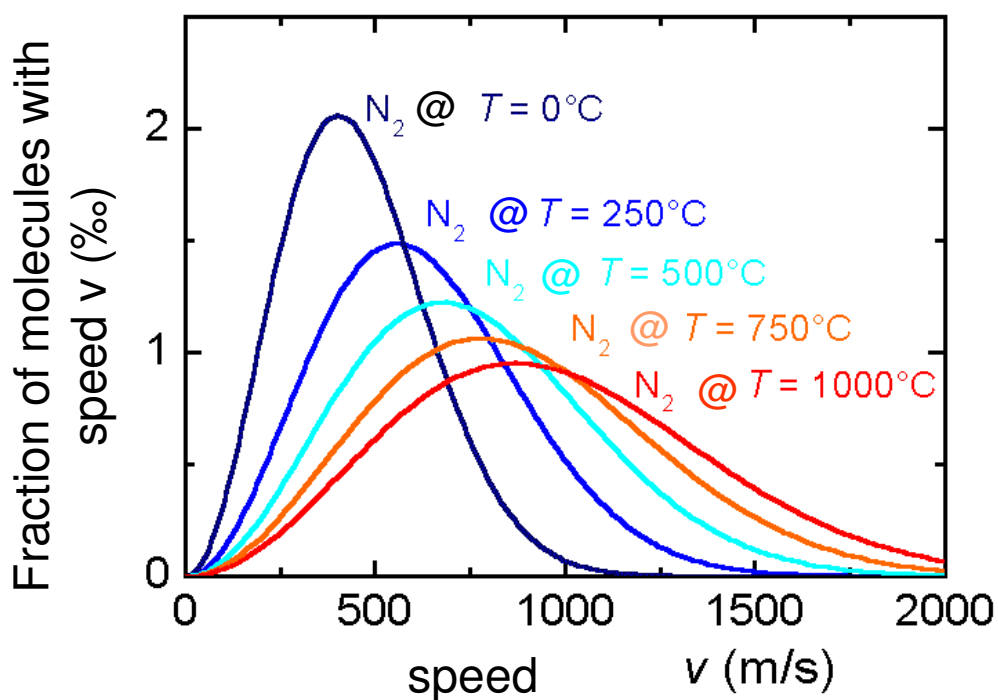$$f(v_x) = \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} e^{-mv_x^2/2kT}$$

And for 3D the speed distribution is:

$$f(v) = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \cdot 4\pi v^2 \cdot e^{-mv^2/2kT}$$

Maxwell-Boltzmann Molecular Speed Distribution for Noble Gases

- ^{4}He
- ^{20}Ne
- ^{40}Ar
- ^{132}Xe

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T-dependence of the MB-distribution

N_2 @ $T = 0°C$
N_2 @ $T = 250°C$
N_2 @ $T = 500°C$
N_2 @ $T = 750°C$
N_2 @ $T = 1000°C$

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Average speed & mean square speed of an ideal gas

$$f(v) = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \cdot 4\pi v^2 \cdot e^{-mv^2/2kT}$$

- By integrating $\overline{v} = \langle v \rangle = \int_0^\infty f(v)v\,\mathrm{d}v = \sqrt{\frac{8kT}{\pi m}}$

and $\overline{v^2} = \langle v^2 \rangle = \int_0^\infty f(v)v^2\,\mathrm{d}v = \frac{3kT}{m}$

or $\langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle =$

$$= \frac{k_B T}{m} + \frac{k_B T}{m} + \frac{k_B T}{m} = \frac{3k_B T}{m}$$
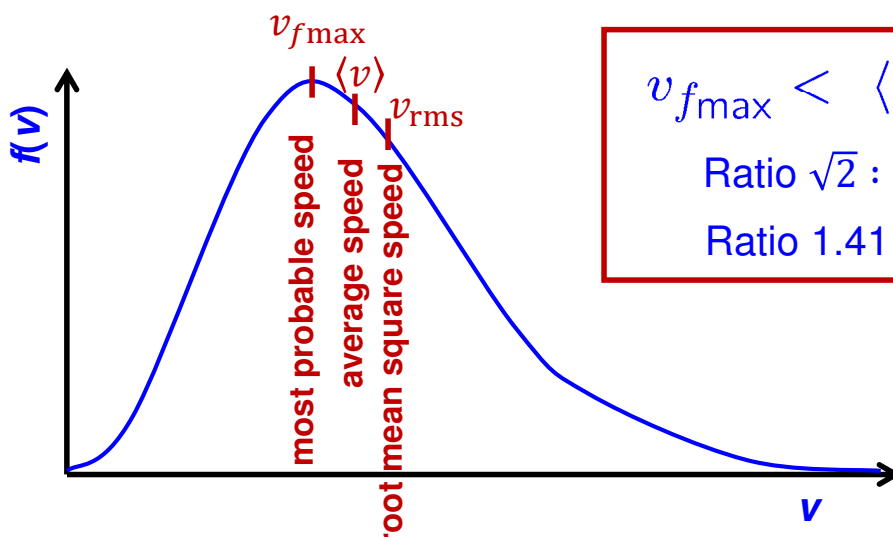
(as expected from equipartition)

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Maximum of the MB-distribution

- The maximum value of the Maxwell-Boltzmann distribution is obtained by setting

$$\frac{\mathrm{d}f(v)}{\mathrm{d}v} = 0 \quad \blacktriangleright \quad v_{f\max} = \sqrt{\frac{2k_B T}{m}}$$

$$v_{f\max} < \langle v \rangle < v_{\mathrm{rms}}$$

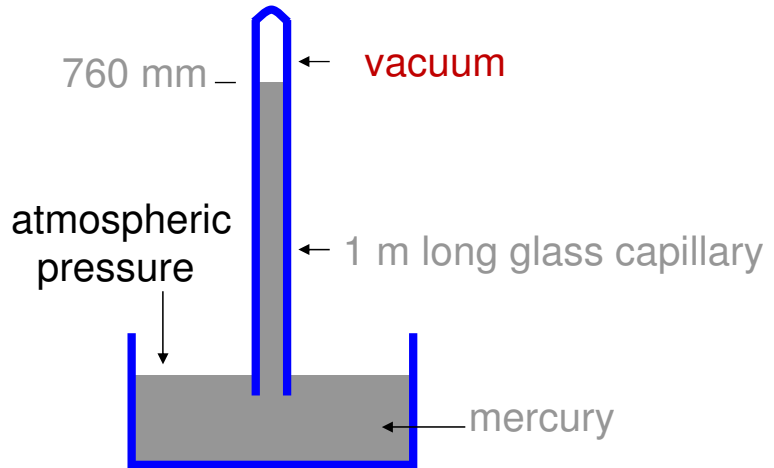Ratio $\sqrt{2} : \sqrt{8/\pi} : \sqrt{3}$

Ratio $1.41 : 1.60 : 1.73$

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8.2 Pressure

Inventor of the mercury barometer.

760 mm — ← vacuum

atmospheric pressure ↓ ← 1 m long glass capillary

← mercury

Evangelista Torricelli (1608–1647)

Pressure

Robert Boyle (1627–1692)

- Together with Robert Hooke, Boyle improved the air-pump and was able to generate "vacuum".

- He also discovered that pressure is inversely proportional to the volume at constant temperature

$$pV = \text{constant} \qquad (@\ \textbf{T} = \text{const.})$$

Boyle-Mariotte law

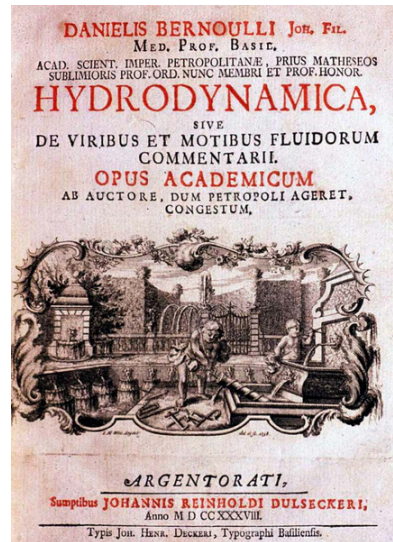- Mariotte discovered the same relationship independently.

Edme Mariotte (~1620–1684)

Pressure & molecular motion

● Attempted to explain Boyle-Mariotte's law by assuming that gases were composed of a vast number of tiny particles – this was only confirmed in the 20th century.

Daniel Bernoulli
(1700–1782)

DANIELIS BERNOULLI Joh. Fil.
MED. PROF. BASIL.
ACAD. SCIENT. IMPER. PETROPOLITANÆ, PRIUS MATHESEOS
SUBLIMIORIS PROF. ORD. NUNC MEMBRI ET PROF. HONOR.

HYDRODYNAMICA,
SIVE
DE VIRIBUS ET MOTIBUS FLUIDORUM
COMMENTARII.
OPUS ACADEMICUM
AB AUCTORE, DUM PETROPOLI AGERET,
CONGESTUM,

ARGENTORATI,
Sumptibus JOHANNIS REINHOLDI DULSECKERI,
Anno M D CC XXXVIII.
Typis Joh. Henr. Deckeri, Typographi Basiliensis.

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Ideal gases: revision

● Ideal gas equation derived experimentally from Boyle's law (pV constant) and Charles Law ($V \propto T$) but does not give the internal energy – which will depend on the nature of the gas.

● Classical thermodynamics cannot give you the internal energy – you have to measure, for example, a heat capacity, so we will have to use some simple statistical thermodynamics.

● Consider **N** gas molecules, mass **m**, in a box of volume V moving with speeds u_x towards one of the walls and velocity (u_y, u_z) parallel to a piece of wall area **A** – and consider an elastic collision with the wall.
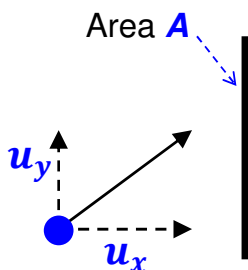
Impulse when molecule hits wall = $2mu_x$

Average force on wall = impulse x collision rate

Area **A**

u_y

u_x

We have N/V molecules per unit volume, of which half will be moving towards the wall. In 1 second molecules a distance u_x away from the wall will hit the wall, so the no of collisions per second is half of the molecules in a volume Au_x so:

Collision rate $= \frac{1}{2}Au_x N/V$

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Pressure and internal Energy

Area **A**

u_y

u_x
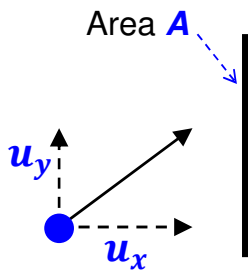
Average force on wall $= mu_x^2 A \dfrac{N}{V}$

Average pressure on wall $p = mu_x^2 \dfrac{N}{V}$

But we need to average over u_x so $p = m\overline{u_x^2} \dfrac{N}{V}$

But since on average $\overline{u_x^2} = \overline{u_y^2} = \overline{u_z^2} = \dfrac{1}{3}\overline{u^2}$

We have $pV = \dfrac{1}{3} Nm\overline{u^2} = nRT$ (n is the number of moles of gas)

For a monatomic gas, the internal energy is stored as translational kinetic energy, so:

$U = \dfrac{1}{2} Nm\overline{u^2} = \dfrac{3}{2} nRT$

For gases made of molecules energy can be stored in rotations and vibrations so U is higher and temperature dependent.

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## Pressure derived from detailed distributions

- Let *n* be the total number of molecules per unit volume & $f(v)$ the MB speed distribution.

- In order to get an expression for the **pressure** we need to compute the number of molecules per unit volume having a speed between v and $v + dv$: this number is given by

$$nf(v)dv$$

r

θ

s

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

- Assuming that the gas particles can travel in all directions with equal probability, the fraction whose trajectories lie in an elemental solid angle **dΩ** is
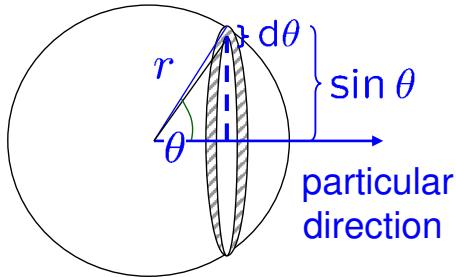
$$\dfrac{d\Omega}{4\pi}$$

r

A

Ω
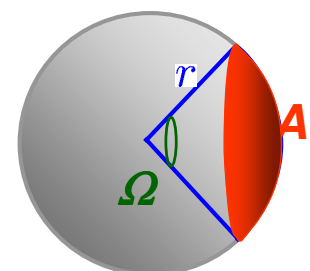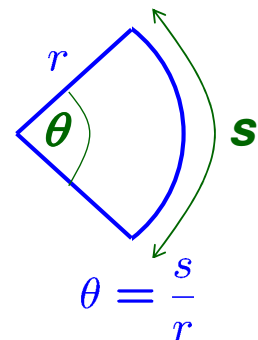
$$\Omega = \dfrac{A}{r^2}$$ 415

- Choosing a particular direction, then **dΩ** corresponding to the molecules travelling at angles between θ and $\theta + d\theta$ to that direction is equal to the area of an annular region given by

$$d\Omega = 2\pi \sin\theta d\theta$$, so that

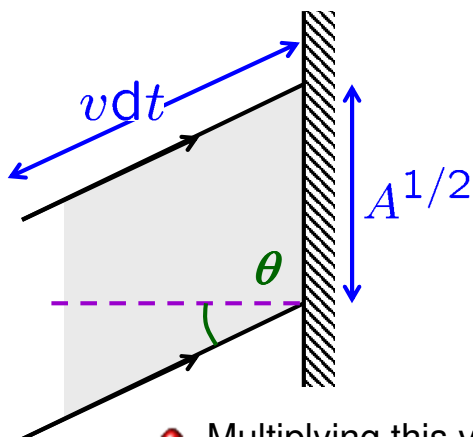$$\frac{d\Omega}{4\pi} = \frac{1}{2}\sin\theta d\theta$$

- Therefore, the number of particles per unit volume given by

$$nf(v)dv \; \frac{1}{2}\sin\theta d\theta$$

have a speed between v and $v + dv$ and are travelling at angles between θ and $\theta + d\theta$ to the chosen direction.

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Pressure – number of particles hitting a wall

- Let our particular direction be perpendicular to a wall of area **A**.

- In a small time interval **dt**, particles travelling at angle θ to the normal to the wall sweep a volume

$$Avdt\cos\theta$$

- Multiplying this volume by $$nf(v)dv \; \frac{1}{2}\sin\theta d\theta$$

… we obtain the number of particles hitting a wall of area **A** in time **dt** with a speed between **v** and **v + dv** and travelling at angles between θ and $\theta + d\theta$ to the normal to the wall:

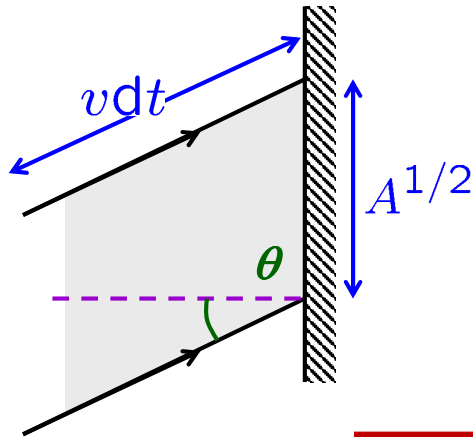**No of candidate molecules/unit area in dt**

Fraction within range v to v+dv

Fraction within range θ to $\theta + d\theta$

$$dN = nAv\cos\theta \, dt \, f(v)dv \; \frac{1}{2}\sin\theta \, d\theta$$

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Pressure – number of particles hitting a wall

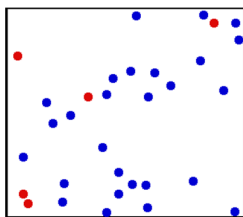$v\mathrm{d}t$

$A^{1/2}$

θ

- Therefore, the number of particles hitting a unit area of wall in unit time and having speeds between **v** and **v + dv** travelling at angles between θ and $\theta + \mathrm{d}\theta$ is

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

This expression allows us to compute the pressure a gas exerts on its container walls.
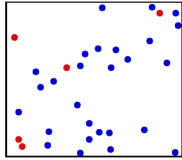
Pressure – the ideal gas law

- Assuming the wall is flat and that the collisions are elastic, each molecule hitting the wall of the container has a **momentum change** of $2mv\cos\theta$ perpendicular to the wall.

- If we multiply this momentum change by the number of molecules hitting unit area per unit time, and having speed between **v + dv** and angels between θ and $\theta + \mathrm{d}\theta$, and then integrate over **v** and θ, we get an expression for the pressure:

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

$$= mn\int_0^\infty \mathrm{d}v \ v^2 f(v)\int_0^{\pi/2}\cos^2\theta\sin\theta\mathrm{d}\theta$$

● Using the fact that $\int_0^{\pi/2} cos^2\theta \, sin\theta \, d\theta = \frac{1}{3}$

… we get $\quad p = \frac{1}{3}mn \underbrace{\int_0^\infty dv \, v^2 f(v)}_{\langle v^2 \rangle} = \frac{1}{3}mn < v^2 >$

● As **n** was the total number of particles per unit volume, the total number of particles in the container is **N = nV**.

➡ $\quad pV = \frac{1}{3}Nm < v^2 >$

● As previously, relating $\langle v^2 \rangle$ to T using equipartition, $(\frac{1}{2}m\langle v^2 \rangle = \frac{1}{2}m\langle v_x^2 \rangle + \frac{1}{2}m\langle v_y^2 \rangle + \frac{1}{2}m\langle v_z^2 \rangle = 3 \times \frac{1}{2}k_B T)$ gives the ideal gas equation:

$$pV = Nk_B T$$

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● In mixtures of gases such as air (nitrogen and oxygen) the total pressure is given by the sum of the pressures caused by the separate components and since the ideal gas equation is independent of the mass of the particles, the combined pressure has a very simple form.

$$p = nk_B T$$

Where for mixtures: $\quad n = \sum_i n_i$
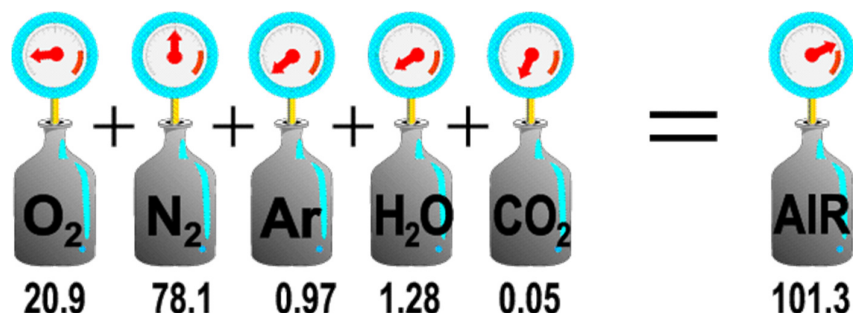
n_i = number density of the ith species.

➡ $$p = k_B T \sum_i n_i = \sum_i p_i$$

p_i = partial pressure of the **i^{th}** species.

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Dalton's law

For example:

$$O_2 \quad N_2 \quad Ar \quad H_2O \quad CO_2 \qquad AIR$$

$$20.9 \quad 78.1 \quad 0.97 \quad 1.28 \quad 0.05 \qquad 101.3$$

At standard air pressure and temperature (STP, 101.3kPa and 0°C) and 50% relative humidity, air is composed of the gases as shown above.

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http://resources.yesican-science.ca/plp/csa/aquanauts.html
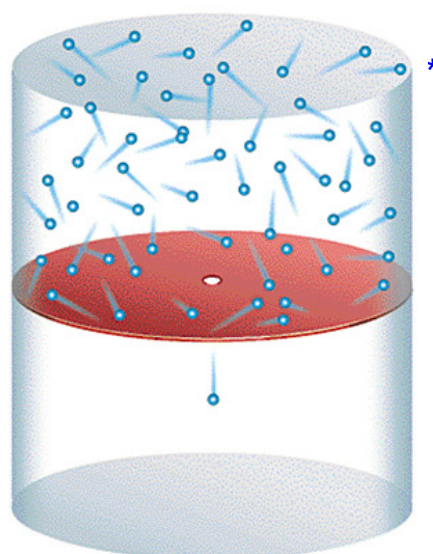

8.3 Effusion & flux

● Effusion is the process by which a gas escapes from a hole so small that a molecule or atom can pass without colliding with another.

● The root-mean-square (RMS) speed is:

$$v_{rms} = \sqrt{\frac{3RT}{M}}$$

(M =mass/mol)

● The rate of effusion will therefore be

proportional to $nAv_{rms} \propto nA\sqrt{\frac{T}{M}}$

(n=number density and A= hole area)

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Flux

The flux is a very important quantity in thermal physics.

- It can describe the flow of various quantities: e.g. particles, energy, photons, momentum, …

- Define the molecular flux Φ as the number of molecules striking a unit area per second:

$$\Phi = \frac{\text{number of molecules}}{\text{area} \times \text{time}}$$

- Similarly, the flux of heat can be defined as

$$\Phi_{\text{heat}} = \frac{\text{amount of heat}}{\text{area} \times \text{time}}$$

The units are $m^{-2}s^{-1}$.

Graham's law

- In 1833 **Thomas Graham** discovered that at equal pressure the effusion speed of different gases is inversely proportional to the square root of their densities.

- In this way isotopes in gases can be separated, which is chemically not possible.

- Example: in the separation of $^{235}UF_6$ and $^{238}UF_6$ the ratio of the effusion rates of the two gases is

$$\sqrt{\frac{\text{mass of } ^{238}UF_6}{\text{mass of } ^{235}UF_6}} = \sqrt{\frac{352.0412}{348.0343}} = 1.00574$$
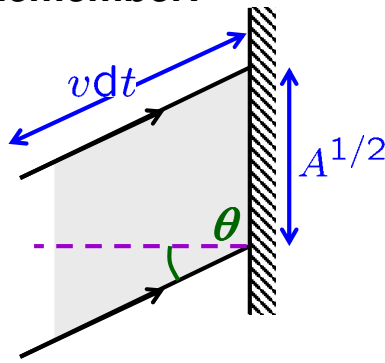
Flux

Remember:

- The number of particles hitting a unit area of wall in unit time and having speeds between **v** and **v + dv** travelling at angles between θ and $\theta + d\theta$:

$$dN = nv \cos\theta \ f(v)dv \ \frac{1}{2}\sin\theta \ d\theta$$

- The flux of molecules in a gas can be computed by integrating dN over v and θ:

$$\Phi = \int_0^\infty \int_0^{\pi/2} v \cos\theta \ nf(v)\mathrm{d}v \ \frac{1}{2}\sin\theta\mathrm{d}\theta$$

$$= \frac{n}{2}\int_0^\infty vf(v)\mathrm{d}v \underbrace{\int_0^{\pi/2} \cos\theta\sin\theta\mathrm{d}\theta}_{= \frac{1}{2}}$$

$$\boxed{\Phi = \frac{1}{4}n\langle v\rangle}$$

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Flux

- To obtain an explicit expression for the flux we use the ideal gas equation

$$p = nk_BT$$

and the average speed of molecules $\quad \langle v\rangle = \sqrt{\dfrac{8k_BT}{\pi m}}$

- to substitute **n** and **<v>** in the expression for the flux

$$\boxed{\Phi = \frac{1}{4}n\langle v\rangle = \frac{p}{\sqrt{2\pi mk_BT}}}$$

Note: $\Phi \propto 1/\sqrt{m}$, which is in agreement with Graham's law

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Effusion rate

- Consider a container filled with gas. A small hole of area **A** allows the gas to leak out.

- The hole is so small that the equilibrium of the gas is not disturbed.

- The number of molecules hitting a hole with cross-section **A** is equal to the flux **Φ** times the cross-sectional area **A**.

- **ΦA** is called the **effusion rate**.
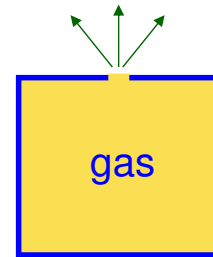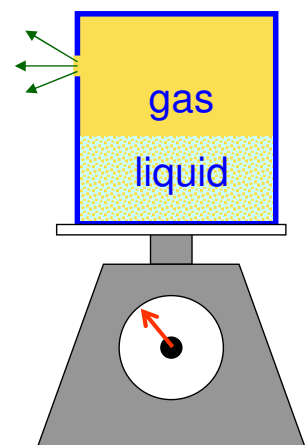
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Vapour pressure – Knudsen method

- Knudsen method for measuring the vapour pressure **p** from a liquid containing molecules of mass **m** at temperature **T**:

- The weight of the container **Mg** is measure as a function of time.

- In equilibrium, the effusion rate is

$$\Phi A = \frac{pA}{\sqrt{2\pi m k_B T}}$$

- Hence the rate of change of mass, **dM/dt**, is given by **-mΦA**.

$$p = \sqrt{\frac{2\pi k_B T}{m}} \frac{1}{A}\left(\frac{\mathrm{d}M}{\mathrm{d}t}\right)$$

vapour pressure

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Effusion – final remarks

● Effusion preferentially selects faster molecules $\Rightarrow$ **effusing molecules do not have a Maxwellian speed distribution**.

● The number of molecules hitting a wall or the hole of area **A** in time *dt* is given by

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

where: $\quad f(v)\mathrm{d}v \propto v^2\mathrm{d}v \ \mathrm{e}^{-mv^2/2k_BT}$

● Therefore, the distribution of molecules effusing through a hole during a given time interval is proportional to

$$v^3 \ \mathrm{e}^{-mv^2/2k_BT}$$

notice the extra factor of **v**

8.4 Mean free path & collisions

● The rms speed of air molecules (O_2 & N_2) is about 500 ms^{-1}.

$$v_{\mathrm{rms}} = \sqrt{3k_BT/m}$$

● Mixing of two gases would be almost instantaneous, if there were not **collisions** between the gas molecules.

● Strictly speaking these collisions are quantum mechanical events, but in a dilute gas we can treat them just like the collisions between billiard balls, hence using classical mechanics.

● A reasonable approximation as that after a collision the molecular velocities are randomized.

● Based on these assumption, we can derive an expression for the **mean free path.**

Mean collision time: stationary background gas

● Consider a gas in which all particles are stationary with the exception of one that is moving at a speed **v**.

● If each particle has a collision cross-section σ, then in a time δt, a particle will sweep out a volume $\sigma v \delta t$.

● If another molecule happens to lie inside this volume, there will be a collision.

● With **n** molecules per unit volume the number of collisions in time δt is then $n\sigma v \delta t$. If δt is small this will be a small number – say 0.1. What does hitting 0.1 molecules mean – it means there is a 1 in 10 chance of hitting one, so $n\sigma v \delta t$ is the chance of hitting a molecule in time δt.

v

Volume swept out in $\delta t = \sigma v \delta t$

Area σ

v

432
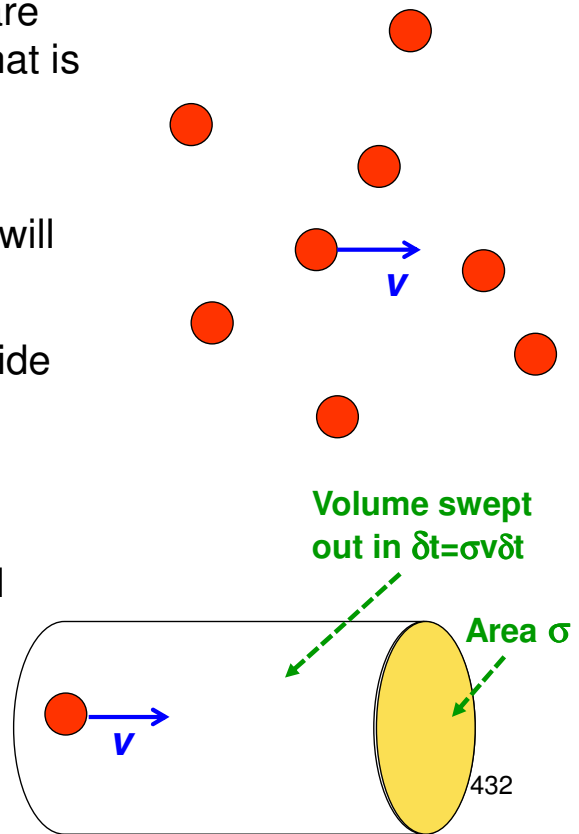
Mean collision time: stationary background gas

● Define **P(t)** as the probability that a molecule survives without colliding up to a time **t**.

This implies that $\quad P(t + \delta t) = P(t) + \dfrac{dP}{dt}\delta t$

● But, **P(t + δt)** is simply the probability that a molecule survives without collisions until time **t + δt.** The fraction **P(t + δt) / P(t)** is then the probability that the molecule survives without collisions until time **t + δt** given that it survived until time **t.**

$$\frac{P(t + \delta t)}{P(t)} = 1 - nv\sigma\delta t$$

$$1 + \frac{1}{P(t)}\frac{dP}{dt}\delta t = 1 - nv\sigma\delta t$$

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- Hence
$$\frac{1}{P}\frac{dP}{dt} = -nv\sigma$$

- Integrating and using **P(0) = 1**, we get

$$P(t) = e^{-nv\sigma t}$$

- The probability of a molecule surviving without collision up to time **t** and then colliding in the next **dt** is

$$e^{-nv\sigma t} n\sigma v dt$$

- This probability is already normalized:

$$\int_0^\infty e^{-nv\sigma t} n\sigma v\, dt = 1 \quad \left(\int_0^\infty e^{-x} dx = 1 \right)$$ 434

- Now if we set $t=0$ at the time of the last collision, we can compute the mean collision or scattering time τ, which is the average time between two collisions of a molecule as

$$\tau = \int_0^\infty t e^{-nv\sigma t} n\sigma v\, dt$$

$$= \frac{1}{n\sigma v} \int_0^\infty (n\sigma v t) e^{-nv\sigma t}\, d(n\sigma v t)$$

$$= \frac{1}{n\sigma v} \underbrace{\int_0^\infty x e^{-x}\, dx}_{= 1}$$

$$\boxed{\tau = \frac{1}{n\sigma v}}$$ 435

$$\tau = \frac{1}{n\sigma v}$$

🔴 Why go to all this trouble? Why not use the perfectly correct derivation that says if that the particle sweeps out a volume σv per second it will hit other particles at an average rate of $n\sigma v$ a second, giving a mean time between collisions of $\tau=1/ n\sigma v$?

(1) It is instructive derive P(t) and to see how it gives an exponentially decaying chance of survival without a collision.

(2) Statistics is a subject where you are always worrying about what you have forgotten to think about/allow for – going through the full derivation is reassuring that you have got the right answer. (For example, if this τ is the mean time to the next collision, is it not also the mean time since the last one? So why is the time between collisions not 2τ??)

🔴 How can we understand the cross-section σ?

🔴 Consider two spherical particles of radii a_1 and a_2, both having a hard-sphere potential $V(R)$, where R is the separation between the centres of the two spheres.

$$V(R) = \begin{cases} 0 & R > a_1 + a_2 \\ \infty & R \le a_1 + a_2 \end{cases}$$
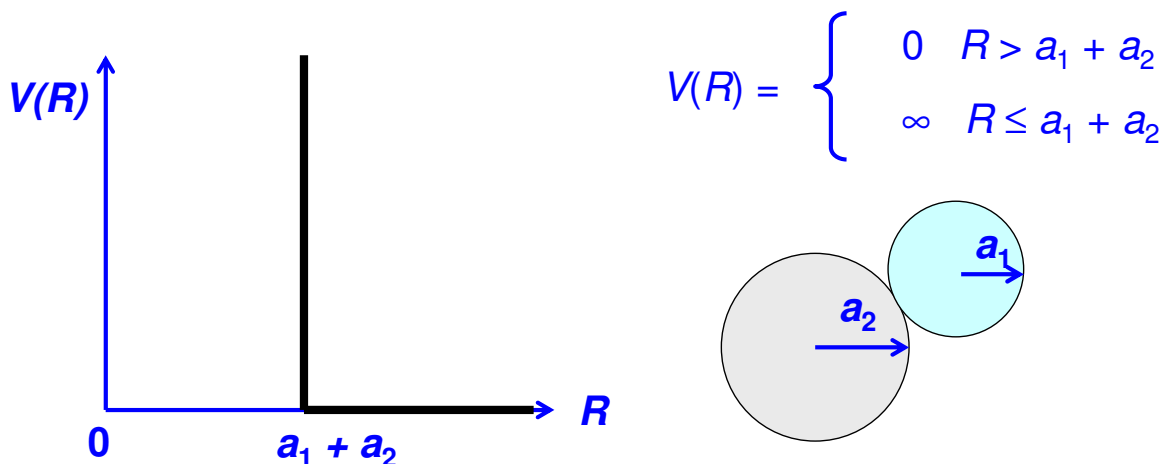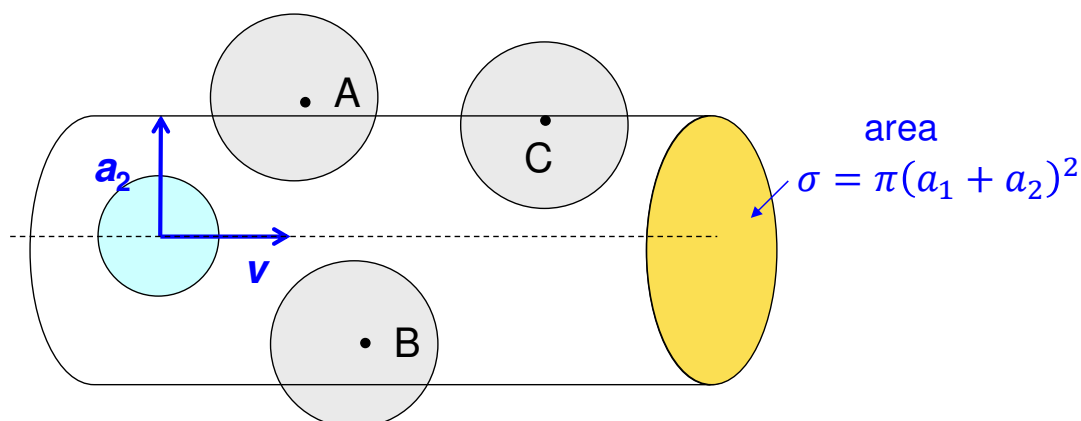
Collision cross-section

- Define **b** the impact parameter between two moving molecules as the distance of closest approach that would result if the molecular trajectories were **undeflected** by the collision.

- For hard-sphere potentials, a collision can only take place if $b < a_1 + a_2$.
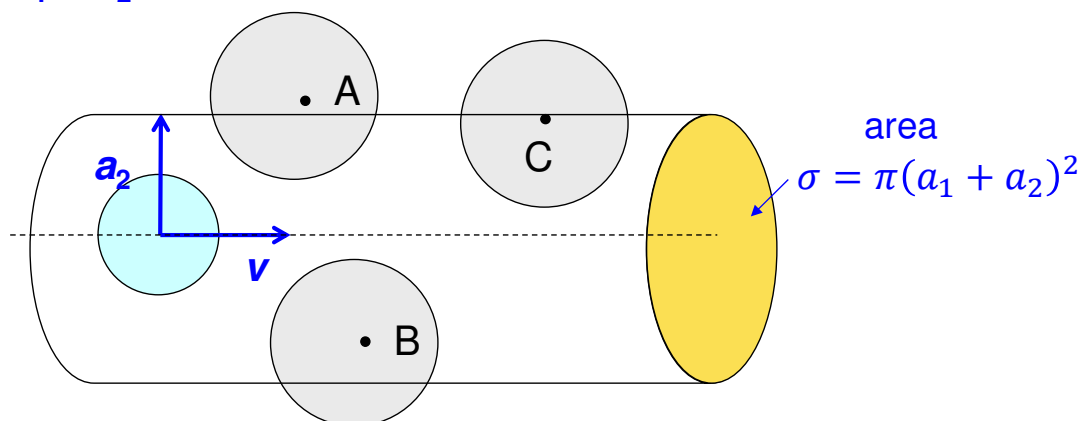
- A collision will take place when the centres of the larger molecules fall within a tube of radius $a_1 + a_2$.

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Collision cross-section

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

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

For identical molecules of diameter **d = 2a**

$$\sigma = \pi(2a)^2 = \pi d^2$$

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Mean free path

- We now can also derive an expression for the mean free path λ.

  It is $\qquad \lambda \approx \langle v \rangle \tau \approx \dfrac{\langle v \rangle}{n\sigma\langle v_r \rangle}$ $\qquad$ ($\langle v_r \rangle$ is the mean relative speed of the molecules in the gas)

- Careful! Until now we looked at a single moving particle in an array of fixed particles. In reality all the other particles move around as well.

- Consider first a single particle moving with velocity $\underline{v}_1$ in a cloud of particles all moving with velocity $\underline{v}_2$. Their relative velocity (the one we want) is:

$$\underline{v}_r = \underline{v}_1 - \underline{v}_2$$

$$\Longrightarrow \quad v_r^2 = v_1^2 + v_2^2 - 2\underline{v}_1.\underline{v}_2$$

averaging over all $\underline{v}_2$: $\quad \langle v_r^2 \rangle = v_1^2 + \langle v_2^2 \rangle = 2\langle v^2 \rangle$

$$\langle \underline{v}_1.\underline{v}_2 \rangle = 0 \quad \text{because} \quad \langle \cos(\theta) \rangle = 0 \qquad \text{440}$$

Mean free path

- Since the probability distribution describing the molecular speed is a Maxwell-Boltzmann distribution, then we only make a small error when writing

$$\langle v_r \rangle \; \approx \; \sqrt{\langle v_r^2 \rangle} \approx \sqrt{2}\langle v \rangle$$

  Thus we can write $\qquad \lambda = \dfrac{\langle v \rangle}{n\sigma\langle v_r \rangle} = \dfrac{1}{\sqrt{2}n\sigma}$

- Using the ideal gas law we then obtain for the **mean free-path**

$$\boxed{\lambda = \frac{k_B T}{\sqrt{2}p\sigma}}$$

- For a particular pressure, λ is inversely proportional to the pressure.

- Mean free path in air at atmospheric pressure (101325Pa) is 68nm.