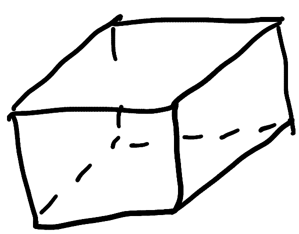
Classical ideal gas

In a gas with low density the average distance between particles (molecules) is very small. Then during most of the time each molecule is far from the other molecules and weakly interacts with them.

Ideal gas = gas without interactions

We will consider a classical gas



In principle, we could have integrated the equations of motion for each molecule

In reality, independence of initial conditions

Equilibrium - in this state it doesn't matter how the system arrived there

3N degrees of freedom

$\rho_0(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N, \vec{p}_1, \vec{p}_2, \ldots, \vec{p}_N)$

Distinguishable particles - we may trace each particle (wouldn't be possible, e.g. for electrons) but identical

$\rho_0(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N, \vec{p}_1, \vec{p}_2, \ldots, \vec{p}_N) =$

$= \rho(\vec{r}_1, \vec{p}_1)\, \rho(\vec{r}_2, \vec{p}_2) \cdots \rho(\vec{r}_N, \vec{p}_N)$,

because different molecules are independent systems.

Then how do they equilibrate?

We do need to assume that there is weak interaction. However, it won't affect the equilibrium distribution.

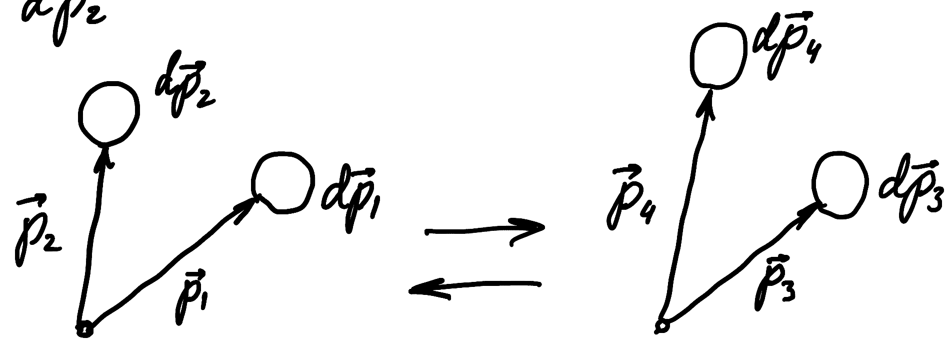
<u>Uniformity</u> (holds also for non-ideal gases with <u>short-range</u> <u>interactions</u>)

$$\rho(\vec{r}_i, \vec{p}_i) \equiv \rho(\vec{r}, \vec{p}) = \rho(\vec{p})$$

$\rho(\vec{p})$ must be a function of $|\vec{p}|$

– <u>isotropic</u> distribution

Consider two molecules with momenta near $\vec{p}_1$ and $\vec{p}_2$ in momentum volumes $d\vec{p}_1$ and $d\vec{p}_2$



$\rho(p_1)\,dp_1\,\rho(p_2)\,dp_2 = \rho(p_3)\,dp_3\,\rho(p_4)\,dp_4$

Now $dp_1\,dp_2 = dp_3\,dp_4$ due to Liouville's theorem.

Consider particles with quadratic dispersion

$$p_1^2 + p_2^2 = p_3^2 + p_4^2$$

We will write $\rho(\vec{p}_i) = \rho(p_i^2)$

$$\rho(p_1^2)\,\rho(p_2^2) = \rho(p_3^2)\,\rho(p_1^2 + p_2^2 - p_3^2)$$

– should hold for all p_1, p_2 and p_3

$$\ln\rho(p_1^2) + \ln\rho(p_2^2) = \ln\rho(p_3^2) + \ln\rho(p_1^2 + p_2^2 - p_3^2)$$

Differentiate wrt p_1^2

$$\frac{\rho'(p_1^2)}{\rho(p_1^2)} = \frac{\rho'(p_1^2 + p_2^2 - p_3^2)}{\rho(p_1^2 + p_2^2 - p_3^2)}$$

ρ' – derivative wrt the argument of the function

Differentiate wrt p_2^2

$$\frac{\rho'(p_2^2)}{\rho(p_2^2)} = \frac{\rho'(p_1^2 + p_2^2 - p_3^2)}{\rho(p_1^2 + p_2^2 - p_3^2)}$$

$$\rightarrow \quad \frac{\rho'(p_1^2)}{\rho(p_1^2)} = \frac{\rho'(p_2^2)}{\rho(p_2^2)}$$

That should hold for arbitrary p_1 and p_2

$$\frac{\rho'(p^2)}{\rho(p^2)} = -\alpha$$

$\rho(p^2)$

$$\rightarrow \boxed{\rho(\vec{p}) = A\, e^{-\alpha p^2}}$$

Normalisation : $V \int \rho(\vec{p})\, d\vec{p} = 1$

$$V \cdot A \int 4\pi p^2 e^{-\alpha p^2} dp = 1$$

Important integral $I(\alpha) = \int_0^\infty e^{-\alpha p^2} dp = \frac{1}{2}\sqrt{\frac{\pi}{\alpha}}$

$$\int p^2 e^{-\alpha p^2} dp = -I'(\alpha) = \frac{1}{4}\frac{\sqrt{\pi}}{\alpha^{\frac{3}{2}}}$$

$$V \cdot A \left(\frac{\pi}{\alpha}\right)^{\frac{3}{2}} = 1 \rightarrow A = \frac{1}{V}\left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}}$$

$$\rho(\vec{p}) = \frac{1}{V}\left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}} e^{-\alpha p^2}$$

The concentration of molecules in the volume element $d\vec{p}$ near momentum $\vec{p}$

$$dn = n \left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}} e^{-\alpha p^2} d\vec{p}$$

$$= n \underbrace{\left(\sqrt{\frac{\alpha}{\pi}}\, e^{-\alpha p_x^2} dp_x\right)}_{\text{The probability that the x-momentum lies between } p_x \text{ and } p_x + dp_x} \left(\sqrt{\frac{\alpha}{\pi}}\, e^{-\alpha p_y^2} dp_y\right)\left(\sqrt{\frac{\alpha}{\pi}}\, e^{-\alpha p_z^2} dp_z\right)$$

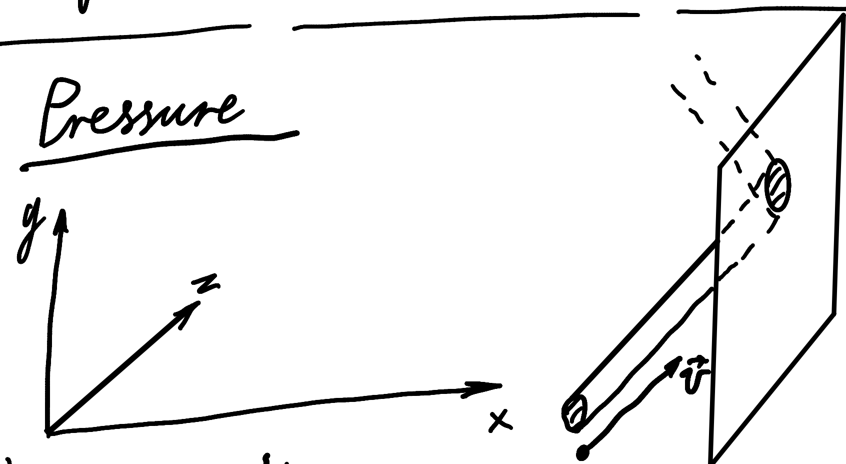
the prob... lies between p_x and $p_x + dp_x$

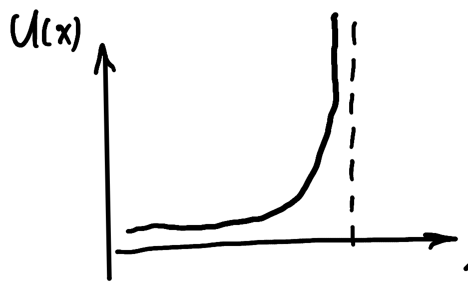
An alternative way to derive the distribution using that different degrees of freedom are independent of each other

$$w(p_x^2)\, w(p_y^2)\, w(p_z^2)\, d\vec{p} = w(p_x^2 + p_y^2 + p_z^2)\, w(0) w(0)\, d\vec{p}$$

$w(p_i^2) \sim e^{-\alpha p_i^2}$ – the only possible solution

Pressure





$$v_x, v_y, v_z \to -v_x, v_y, v_z$$

Let's compute the pressure

$2m v_x = 2p_x$ – momentum change during each collision

$dn_x = n \left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}} e^{-\alpha p_x^2}\, dp_x$ – the concentration of molecules with momenta $\in (p_x, p_x + dp_x)$

$$P = \int 2p_x \cdot \frac{p_x}{m}\, dn_x = \frac{2}{m} n \left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}} \int p_x^2 e^{-\alpha p_x^2}\, dp_x =$$

$$= \dots \left(\ \right)^{\frac{1}{2}} \dots \pi^{\frac{1}{2}} \dots = \frac{1}{\dots} n$$

$$= \frac{2}{m} n \left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}} \frac{1}{4} \frac{\pi^{\frac{1}{2}}}{\alpha^{\frac{3}{2}}} = \frac{1}{2m\alpha} n$$

$$P = \frac{1}{2m\alpha} \frac{N}{V}$$

Equation of state: $PV = NT$

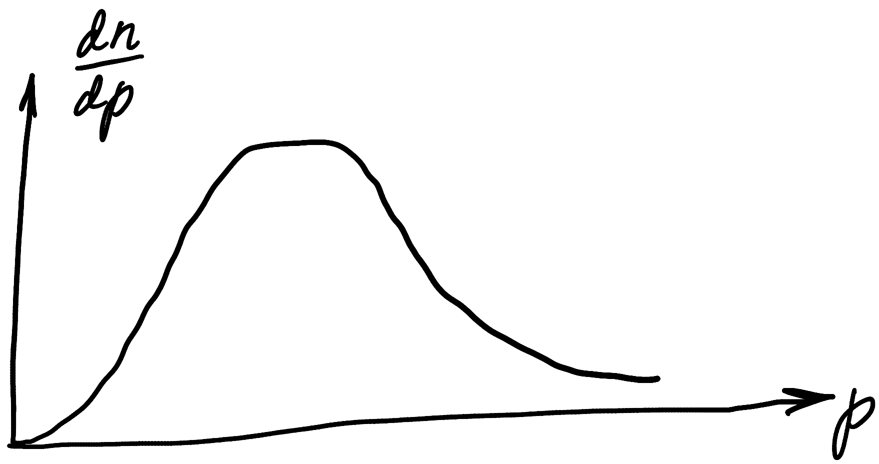
$(PV = k_B N T)$

$$T = \frac{1}{2m\alpha} \longrightarrow \alpha = \frac{1}{2mT}$$

$$\boxed{dn = n \frac{1}{(2\pi mT)^{\frac{3}{2}}} e^{-\frac{p^2}{2mT}} dp_x \, dp_y \, dp_z}$$

If we consider a spherical layer of thickness dp

$$dn_{dp} = \frac{4\pi n}{(2\pi mT)^{\frac{3}{2}}} p^2 e^{-\frac{p^2}{2mT}} d\vec{p}$$



The average energy

$$\left\langle \frac{p_x^2}{2m} \right\rangle = \int \frac{1}{\sqrt{2\pi m T}} e^{-\frac{p_x^2}{2mT}} dp_x = \frac{T}{2}$$

$$\left\langle \frac{p^2}{2m} \right\rangle = 3 \left\langle \frac{p_x^2}{2m} \right\rangle = \frac{3T}{2}$$