

## §2. Classical Ideal Gas in Equilibrium.

We now construct the simplest possible model of a gas - and compute its pof.

### Assumptions:

- Particles do not interact (e.g. don't attract or repel each other) except for hard elastic binary collisions during which they conserve total momentum and energy (and don't split or stick)
- They are point particles, i.e. do not occupy a significant fraction of the system's volume (a particle's ability to be anywhere <sup>in space</sup> is not restricted by being crowded out by other particles)
- They are classical particles, so there are no quantum correlations (which would jeopardize a particle's ability to have a particular energy if the corresponding quantum state(s) are already occupied by other particles)
- They are non-relativistic, so  $v \ll c$ .

will be relaxed for "real gases"

will be relaxed for "quantum gases"

In practice, all this is satisfied if the gas is sufficiently dilute (low enough  $n$ )

and hot (high enough  $T$  to avoid QM)

but not hot enough to be relativistic

[I will work out what this means after I define  $T$ .]

## 2.1 Maxwell's Distribution

[see, e.g., Pauli §25]

- Consider our gas in a container of volume  $V$  and assume there are no changes to external conditions / fields — everything is homogeneous in time and space.
- Wait long enough for a few collisions to occur, so memory of initial conditions is lost.

We'll refer to the resulting state as equilibrium in the sense that it will be statistically stationary, i.e. particles will have some <sup>velocity</sup> distribution ~~that~~ independent of time or position or the initial state

[we'll study in subsequent lectures how the system gets into such a state]

↑ collisions are essential for this!

Since it doesn't depend on anything, we must be able to figure out what this distribution is:  $f(\vec{v}) = ?$

- If there are no special directions in the system, the pdf is isotropic:  $f(\vec{v}) = f(\underset{\uparrow}{v}) = \underset{\uparrow}{g}(v^2)$   
speed equivalent

Ex. Well, there might be special directions. E.g. gravity! (particles have mass!)  
 After I am done with the derivation, think under what conditions gravity can be ignored.

Also Earth is rotating in a definite direction. Under what conditions can this be ignored?

- Maxwell (1859) argued (or conjectured) that the distributions of the three components of the velocity must be independent random variables

[it is possible to prove this for classical ideal gas

- we'll do it later from Stat. Mechanics

- it is also possible to prove it by analysing elastic binary collisions (Boltzmann),

but for now we will simply assume that this is true]

Therefore

all the same because of isotropy

$$f(\vec{v}) = f(v_x) f(v_y) f(v_z) = g(v^2)$$

$$\underbrace{\begin{matrix} \text{"} & \text{"} & \text{"} \\ h(v_x^2) & h(v_y^2) & h(v_z^2) \end{matrix}}$$

They depend only on squares if we assume that distributions are even,  $f(v_x) = f(-v_x)$  (mirror symmetry, no flows or fluxes)

Thus,  $h(v_x^2) h(v_y^2) h(v_z^2) = g(v^2)$

Now let  $\varphi(v_x^2) = \ln h(v_x^2)$

and  $\psi(v^2) = \ln g(v^2)$ . Then

$$\boxed{\varphi(v_x^2) + \varphi(v_y^2) + \varphi(v_z^2) = \psi(v^2) = \psi(v_x^2 + v_y^2 + v_z^2)} \quad (1)$$

This can only be satisfied if  $\varphi$  and  $\psi$  are linear functions:

$$\varphi(v_x^2) = -\alpha v_x^2 + \beta$$

some as yet undetermined constants

and so  $\psi(v^2) = -\alpha v^2 + 3\beta$  (- sign purely a matter of convention) (2)

Proof. Differentiate (1) wrt  $v_x^2$  at const.  $v_y^2$  and  $v_z^2$ :

$$\psi'(v_x^2 + v_y^2 + v_z^2) = \varphi'(v_x^2)$$

Differentiate again wrt  $v_y^2$  at const  $v_x^2$  and  $v_z^2$ :

$$\psi''(v_x^2 + v_y^2 + v_z^2) = 0$$

$$\text{or } \psi''(v^2) = 0 \Rightarrow \psi(v^2) = \underset{-\alpha}{C_1} v^2 + \underset{3\beta}{C_2}$$

Now sub. this into (1) and let  $v_y^2 = v_z^2 = 0$ :

$$\varphi(v_x^2) + 2\varphi(0) = \psi(v_x^2) = -\alpha v_x^2 + 3\beta$$

$$\varphi(v_x^2) = -\alpha v_x^2 + 3\beta - 2\varphi(0)$$

$$\text{let } v_x^2 = 0 \Rightarrow \varphi(0) = 3\beta - 2\varphi(0) \Rightarrow \varphi(0) = \beta$$

$$\text{So } \varphi(v_x^2) = -\alpha v_x^2 + \beta, \text{ q.e.d.}$$

$$\text{So, } h(v_x^2) = e^{\varphi(v_x^2)} = e^{-\alpha v_x^2 + \beta}$$

$$\text{and } f(\vec{v}) = h(v_x^2) h(v_y^2) h(v_z^2) = e^{-\alpha(v_x^2 + v_y^2 + v_z^2) + 3\beta}$$

$$\boxed{f(\vec{v}) = C e^{-\alpha v^2}} \quad \text{where } C = e^{3\beta} \quad (3)$$

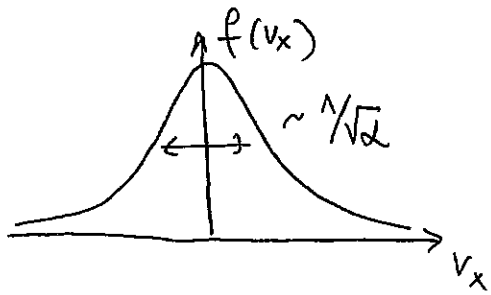
What are the constants  $C$  and  $\alpha$ ?

We know that  $\int d^3\vec{v} f(\vec{v}) = 1$ , so

$$C \int d^3\vec{v} e^{-\alpha v^2} = C \left(\sqrt{\frac{\pi}{\alpha}}\right)^3 = 1 \Rightarrow \boxed{C = \left(\frac{\alpha}{\pi}\right)^{3/2}} \quad (4)$$

NB: We have expressed  $f(\vec{v})$  in terms of only one scalar quantity  $\alpha$ ! Something out of nothing? No, functional form ~~was~~ followed from assumptions about symmetries.

What is  $\alpha$ ?



It tells us about the width of the velocity distribution in any given direction.

Dimensionally,

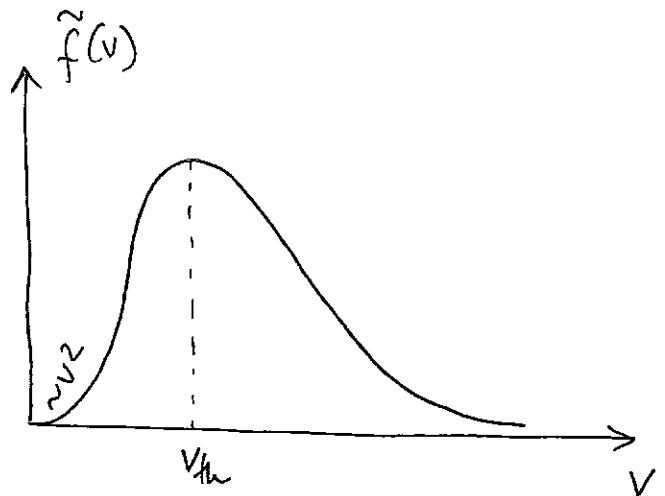
$\frac{1}{\sqrt{\alpha}}$  is some characteristic speed:

$$v_{th} \equiv \frac{1}{\sqrt{\alpha}} \quad \text{"Thermal speed"}$$

So, 
$$f(\vec{v}) = \frac{e^{-v^2/v_{th}^2}}{(\pi v_{th}^2)^{3/2}} \quad (5)$$

Alternatively, think in terms of the distribution of speeds: from eq. (15) of §1,

$$\tilde{f}(v) = 4\pi v^2 \frac{e^{-v^2/v_{th}^2}}{(\pi v_{th}^2)^{3/2}} \quad (6)$$



↳ Most probable speed (max. of  $\tilde{f}$ ) is  $v = v_{th}$  (Ex.)

However, this is just a reaming of ~~some~~ a constant.

To relate  $v_{th}$  to something physical, we need to relate it to something measurable.

What is measurable?

- pressure (measure force on the wall or piston)

- temperature (stick in a thermometer as defined in thermodynamics)

↳ clearly  $v_{th}$  will be related to  $T$  because  $v_{th}$  (or const  $\alpha$ ) is what has to end up being the same across the system in equilibrium. But how to relate it?

2.2 Equation of State & Temperature

We know how to compute pressure: eq. (13) §1:

$$p = \frac{1}{3} mn \langle v^2 \rangle = \frac{1}{3} mn \int d^3\vec{v} v^2 \frac{e^{-v^2/v_{th}^2}}{(\pi v_{th}^2)^{3/2}} = \frac{nmv_{th}^2}{2}$$

||  
 $\frac{3}{2} v_{th}^2$  (exercise)

or  $pV = N \frac{mv_{th}^2}{2}$  (7)

But we know empirically (from thermodynamic experiments of Boyle, Mariotte, Charles, Gay-Lussac and Amontons)

1662	1676	1787	1809	1699
$p \propto \frac{1}{V}$	$V \propto T$	$p \propto T$		
@ const T	@ const p	@ const V		

↗

that

$pV = RT$  for  $N = N_A$ , where  $R = 8.31447 \frac{J}{K \cdot mol}$  (8)

gas constant

So, from (7) & (8),

$\frac{mv_{th}^2}{2} = \frac{R}{N_A} T = k_B T$ , where  $k_B = 1.3807 \cdot 10^{-23} \frac{J}{K}$  (9)

Boltzmann constant

and so  $p = nk_B T$  equation of state (10)

NB:  $k_B$  is just a dimensional conversion constant to do with historical unit of T. Really, temperature

is energy:  $p = \frac{2}{3} \frac{U}{V} = \frac{2E}{3}$  (eq. (13) §1), so

[ $U = U(T)$  for ideal gas established exply by Joule]

$\frac{U}{N} = \frac{3}{2} k_B T \Rightarrow$  heat capacity  
 $C_V = \frac{3}{2} k_B N$  (11)

(1.2 ended here)

... or  $k_B T = \frac{1}{3} m \langle v^2 \rangle = m \langle v_x^2 \rangle$  (12)

So  $\frac{1}{2} k_B T$  is mean energy per particle per degree of freedom.

This gives Maxwell's distribution ("the Maxwellian")

$$f(\vec{v}) = \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{mv^2}{2k_B T}} \quad (13)$$

NB:  $f \propto e^{-\frac{\epsilon}{k_B T}}$  particular case of the much more general "Boltzmann distribution" (comp up in SM)

( $\epsilon = \frac{mv^2}{2}$  energy of particle)

Temperature turns out to measure how energetic, on average, particles are — this in progress over thermodynamics, where it was a rather mysterious (if indispensable) quantity.

The key property of T is that it is equalised across the system in equilibrium — and will equalise if two systems ~~was~~ at different temperatures are brought together.

~~It's~~ It's clear how that happens for two volumes of gas (particles collide, global Maxwellian with a single  $\alpha$ ,  $v_{th}$ , or T, is established)

or for gas touching hot (or cold) wall (particles of gas collide with vibrating molecules of wall).

↑ that's also T — see S.M.

OK, so, to summarize, we now have the full thermodynamics of the classical ideal gas:

- { Energy:  $U = \frac{3}{2} k_B T N$
- { Heat capacity:  $C_V = \frac{3}{2} k_B N$
- { Equation of state:  $p = nk_B T$  etc.

... but in addition we know its velocity distribution:

$$f(\vec{v}) = \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{mv^2}{2k_B T}}$$

and so can calculate other interesting things, which thermodynamics is ignorant of.

Ex. Obtain the exact formula for the energy fluctuations  $\langle (E-U)^2 \rangle^{1/2} / U = ?$  for a Maxwellian gas. (see §1).

**2.3 Validity of classical limit**

No quantum correlations:  $\Delta r \cdot p \gg h$  ← Plank constant  
 ↑ size of volume containing ~ 1 particle  
 $\Delta r \sim 1/n^{1/3}$

So  $\frac{mv_{th}}{n^{1/3}} \gg h$

or  $n \left( \frac{h}{mv_{th}} \right)^3 \sim n \left( \frac{h}{\sqrt{mk_B T}} \right)^3 \ll 1 \Rightarrow \boxed{T \gg \frac{h^2 n^{2/3}}{mk_B} \sim T_{deg.}}$  (14)

"  $\lambda$  de-Broglie's wavelength

Degeneracy temperature  
 (~ a few K for air at 1atm)  
 ↑  
 will liquefy by then!

Non-relativistic:

$\frac{mv_{th}^2}{2} = k_B T \ll mc^2 \Rightarrow \boxed{T \ll \frac{mc^2}{k_B} \sim T_{relat.}}$  (15)

(~  $10^{14}$  K for air, but it will be plasma by then!)