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Stat Phys Lectures
Oxford MT 2011

§2. Classical Ideal gas.

We now construct the simplest model of gas we can get away with — and find its pdf.

Assumptions:

- Particles do not interact (e.g. don't attract each other) except for having (elastic) binary collisions during which they conserve total momentum and energy.
- They are point particles, i.e. do not occupy a significant volume (particle's ability to be anywhere is not compromised by being crowded out by other particles)
- They are classical particles, so there are no quantum correlations (e.g. jeopardising a particle's ability to have a particular energy state if it is already occupied by another particle) and we need not worry about the uncertainty principle in discussing particle's position and velocity.
- They are non-relativistic, so don't travel too fast.

In practice, this is all satisfied if the gas is sufficiently dilute (low enough n) and/or sufficiently hot (we'll learn in a moment what is meant by its temperature) — but not hot enough to be relativistic.

2.1 Maxwell's Distribution

[Pauli §25]

Consider the gas in a container of volume V and assume that there are no changes to external conditions.

We wait long enough so a few collisions have occurred and the memory of initial conditions is ~~forgotten~~ gone.

We now want to know what is the pdf for the gas in this state of equilibrium (NB: collisions are essential, otherwise initial conditions determine everything).

— If there are no special direction in the system, the pdf is isotropic:

equiv.!

$$f(\vec{V}) = f(V) \equiv G(V^2), \quad V^2 = V_x^2 + V_y^2 + V_z^2$$

— Maxwell (1859) argued (or conjectured) that the distributions of all three components of the velocity must be idependent [it is possible to prove this for classical ideal gas, but here we will simple assume this to be true — we'll prove it later from Stat. Mech., although it is also possible to prove it by analysing elastic collisions — Boltzmann]:

$$f(\vec{V}) = f(V_x) f(V_y) f(V_z) = h(V_x^2)\, h(V_y^2)\, h(V_z^2)$$

all the same because of isotropy

depend on squares because $f(V_x) = f(-V_x)$ (mirror symmetry, no flows)

$$h(v_x^2)\,h(v_y^2)\,h(v_z^2) = f(\vec{v}) = G(v^2) = G(v_x^2+v_y^2+v_z^2)$$

Let $\varphi(v_x^2) = \ln h(v_x^2)$

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

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

This can only be satisfied if φ and ψ are linear functions:

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

some undetermined constants

and so $\psi(v^2) = -\alpha v^2 + 3\beta$

Ex. Prove this! (hint: differentiate both sides of $(*)$ wrt v_x^2, then v_y^2)

Therefore

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

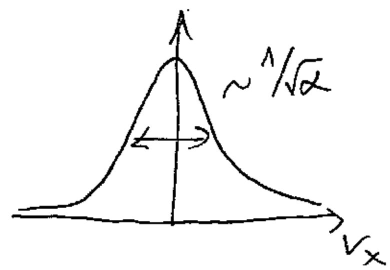
and

$$f(\vec{v}) = e^{-\alpha(v_x^2+v_y^2+v_z^2)+3\beta} \equiv \overset{e^{3\beta}}{\overset{\parallel}{C}}\, e^{-\alpha v^2} \quad (\&)$$

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

$$C\int d^3\vec{v}\, e^{-\alpha(v_x^2+v_y^2+v_z^2)} = C\left(\sqrt{\frac{\pi}{\alpha}}\right)^3 = 1 \Rightarrow C = \left(\frac{\alpha}{\pi}\right)^{3/2}$$

What is α? It tells us about the width of the distribution. Dim-lly, $\frac{1}{\sqrt{\alpha}}$ is some characteristic speed. We call it thermal speed:



$$v_{th} \equiv \frac{1}{\sqrt{\alpha}} \Rightarrow \boxed{f(\vec{v}) = \frac{e^{-v^2/v_{th}^2}}{(\pi v_{th}^2)^{3/2}}}$$

(Note $v_{th}^2/2$ is variance of the distribution of v_x: $\langle v_x^2\rangle = \frac{v_{th}^2}{2}$)

Proof that φ and ψ are linear functions.

1) Diff. wrt v_x^2 at const v_y^2, v_z^2:

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

Diff. wrt v_y^2 at const v_x^2, v_z^2:

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

some consts

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

2) Let $v_y^2 = v_z^2 = 0$. Then

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

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

$$\varphi(0) = 3\beta - 2\varphi(0) \Rightarrow \varphi(0) = \beta$$

So $\boxed{\varphi(v_x^2) = -\alpha v_x^2 + \beta}$

What is the physical significance of v_{th} (or α)?
We can write our distr. fn. in terms of particle energy $E = \frac{mv^2}{2}$

$$f \propto e^{-\frac{E}{mv_{th}^2/2}} \quad \text{and define} \quad \frac{mv_{th}^2}{2} \equiv k_B T$$

temperature (measured in K)

When we study Stat. Mech., we'll see that this formal definition of temperature indeed makes sense and coincides with the thermodynamical one.

Boltzmann constant $k_B = 1.3807 \cdot 10^{-23}\, JK^{-1}$ (this is just a dimensional conversion constant to do with historical units of **T** – really, temp. is energy!)

So, in terms of T,

$$f \propto e^{-\frac{E}{k_B T}}$$ Boltzmann distribution (very generic thing!)

$$\boxed{f = \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{mv^2}{2k_B T}}}$$ Maxwell's distribution

Another way to introduce T formally is calculate mean kinetic energy per degree of freedom (spatial dimension):

$$\langle v_x^2 \rangle = \int d^3\vec{v}\, v_x^2 \frac{e^{-(v_x^2+v_y^2+v_z^2)/v_{th}^2}}{(\pi v_{th}^2)^{3/2}} =$$

$$= \int dv_x\, v_x^2\, e^{-\alpha v_x^2} \left(\frac{\alpha}{\pi}\right)^{1/2} = \sqrt{\frac{\alpha}{\pi}} \left(-\frac{\partial}{\partial\alpha}\right) \int dv_x\, e^{-\alpha v_x^2} =$$

$$= \sqrt{\frac{\alpha}{\cancel{\pi}}} \left(-\frac{\partial}{\partial\alpha}\right) \sqrt{\frac{\cancel{\pi}}{\alpha}} = \frac{1}{2\alpha} = \frac{v_{th}^2}{2} = \frac{k_B T}{m}$$

(see p.14)

So we can define

$$\boxed{\frac{1}{2} k_B T \equiv \frac{m\langle v_x^2\rangle}{2}}$$ mean ~~en~~ energy per particle per degree of freedom

or $$\frac{3}{2} k_B T = \frac{m\langle v^2\rangle}{2}$$ total mean ~~en~~ energy per particle.

Thus temperature measures how energetic, on average, the particles are (gas hot $\equiv$ means particles are moving around fast).

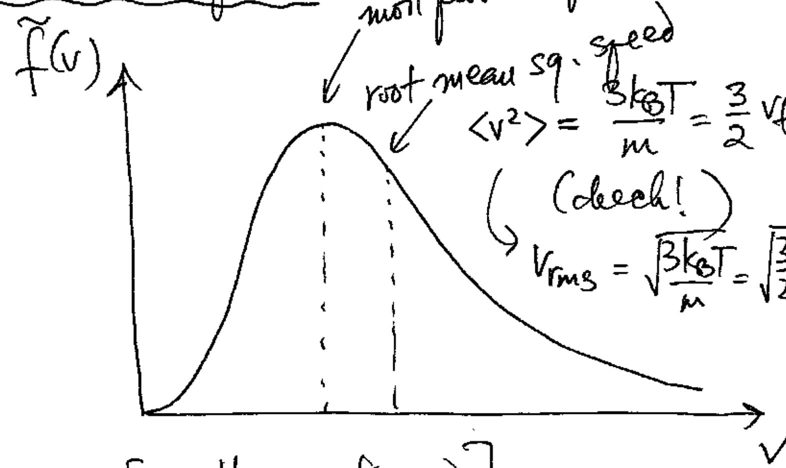
Note. This is actually quite generic. If we say that gas is in a container held at some temp. T, that means ~~the~~ atoms in the walls of the container are vibrating with some energy measured on average by T — and impart that to gas via collisions.

[We will prove later that in eq., if we bring together 2 bodies at different temperatures, these temperatures will equalise — but we'll need S.M. and Thermodynamics for this] [Note that we essentially already know this for say two subvolumes of gas - if they start with diff. T's, those will equalise in eq., via collisions]

Finally, note that since our pdf is isotropic, we can introduce the pdf of particle speeds:

From §1,

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



$\langle v^2\rangle = \frac{3k_BT}{m} = \frac{3}{2} v_{th}^2$ (check!)

$v_{rms} = \sqrt{\frac{3k_BT}{m}} = \sqrt{\frac{3}{2}}\, v_{th}$

[exp-lly confirmed]

Ex. Check

$$\int_0^\infty dv\, \tilde{f}(v) = 1$$

Ex.

We can now estimate what dilute, hot, non-relativistic limit meant.

Uncertainty principle: in order for quantum effects not to enter, we must have

$$\Delta X p \gg h \leftarrow \text{Planck constant } 6.6261 \cdot 10^{-34}\,\mathrm{Js}$$

ΔX: size of volume containing ~1 particle

p: particle momentum $p = mv$

$$\Delta x \sim 1/n^{1/3}$$

$$n\left(\frac{h}{mv}\right)^3 \ll 1$$

$\frac{h}{mv} = \lambda$ de Broglie wavelength

Estimate $v \sim v_{rms} \sim \sqrt{k_B T/m}$

$$n\left(\frac{h}{mv}\right)^3 \sim n\left(\frac{h}{\sqrt{m k_B T}}\right)^3 \ll 1$$

$$\boxed{T \gg \frac{h^2}{m k_B} n^{2/3}} \sim T_{deg.} \text{ degeneracy temperature.}$$

~a few K for air (check)
(will liquefy by then)

Nonrelativistic:

$$k_B T \ll mc^2$$

$$\boxed{T \ll \frac{mc^2}{k_B} \sim T_{relat}}$$

(~10^{14}K for air, but it'll be plasma by then)

2.2. Ideal gas Equation of State

Recall from §1:

$$p = mn\langle v_x^2\rangle = \frac{1}{3}mn\langle v^2\rangle = nk_BT$$

$$\boxed{p = nk_BT} = \frac{2}{3}\left(\frac{mn\langle v^2\rangle}{2}\right) = \frac{2}{3}\varepsilon$$ kin. energy density

Other forms of this equation:

$$\boxed{pV = Nk_BT}$$

or, if we let $N = n_m N_A$, (n_m: # moles; N_A: Avogadro #)

$$\boxed{pV = n_m RT} \qquad R = 8.31447\ \mathrm{J\,K^{-1}\,mol^{-1}}$$ gas constant.

We could in fact define temperature via $\frac{mn\langle v^2\rangle}{2} = \frac{3}{2}k_BT$ (avg. energy of particle motion).

$\frac{1}{2}k_BT$ = energy per particle per degree of freedom

This equation has been known for much longer than kinetic theory — dot's experimentally

$p \propto \frac{1}{V}$ @ const T — Robert Boyle - Edmé Marriotte Law 1662 1676

$V \propto T$ @ const p — Jacques Charles Law 1787

$p \propto T$ @ const V — Joseph Gay-Lussac law 1809

in fact, Guillaume Amontons 1699

[We could actually define ideal gas as satisfying this equ of state - which is more general than Maxwell's distribution]

Also $V \propto N$ @ const p, T Amedeo Avogadro 1811

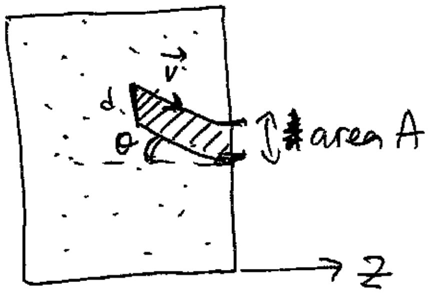
2.3. Effusion

How do we ~~sample~~ take a sample of particles w/o disturbing the macroscopic distribution?

Make a hole in the container $d \ll \lambda_{mfp}$ ← distance particle travels (on avg) between collisions. We'll calculate it in the next section

Then macroscopically the gas (as a collective) does not know about it, so we abduct particles w/o changing their distribution

[if the hole was $d \gg \lambda_{mfp}$, we'd set up a mean flow, the situation would become inhomogeneous etc.]



It is interesting to analyse what happens — let's practice our newly acquired knowledge of particle distributions.

1) How many particles per unit time (flux) will be emerging from the hole?

2) What will be their velocity distribution?
[something an experimentalist might measure]

This is analogous (somewhat) to our calculation of pressure:
# of particles (with given $\vec{v}$) per unit time per unit area that hit the wall of the container: but $f(\vec{v}) = \mathfrak{f}(v)$ isotropic

$$dN(\vec{v}) = v_z \cdot n f(\vec{v})\, d^3\vec{v} = v\cos\theta\, n\, \mathfrak{f}(v)\, v^2 dv \sin\theta\, d\theta\, d\varphi$$

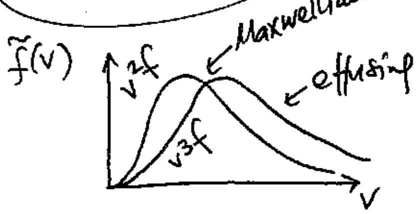
$$= n v^3 \mathfrak{f}(v) \cos\theta \sin\theta\, dv\, d\theta\, d\varphi \qquad \text{provided } v_z > 0$$

Distribution is neither isotropic nor Maxwellian

Answer to Q2

particles travelling at $\sim 90°$ to the wall get through with greater probability

faster particles get out with greater probability (Like smarter students into Oxford, through the very narrow admissions filter)



If we just want distribution of speeds, integrate out angles:

$$d\tilde{N}(v) = n v^3 f(v)\, dv \int_0^{\pi/2 \leftarrow NB!!!} d\theta \cos\theta \sin\theta \int_0^{2\pi} d\varphi = \pi n \underbrace{v^3 f(v)}_{\text{distribution of speeds for effusing particles}} dv$$

$$\left(= \frac{n}{4} v \tilde{f}(v)\, dv\right)$$

Note that for all particles we had

V-ties $\quad d N_{all}(\vec{v}) = n v^2 f(v) \sin\theta \, dv\, d\theta\, d\varphi$

Speeds $\quad d\tilde{N}_{all}(v) = n v^2 f(v)\, dv \int_0^{\pi} d\theta \sin\theta \int_0^{2\pi} d\varphi = \underbrace{4\pi n v^2 f(v)}_{\text{distr. of speeds for all particles}} dv$

$$\left(= n \tilde{f}(v)\, dv\right)$$

Flux of effusing particles:

$$\Phi = \int d\tilde{N}(v) = \int_0^{\infty} \pi n v^3 f(v)\, dv =$$

$$= \frac{1}{4} n \int_0^{\infty} dv\, v \tilde{f}(v) = \frac{1}{4} n \langle v \rangle$$

$$\langle v \rangle = \int_0^{\infty} dv\, v^3\, 4\pi\, e^{-\alpha v^2} \left(\frac{\alpha}{\pi}\right)^{3/2} =$$

Ex. $$= 2\pi \left(\frac{\alpha}{\pi}\right)^{3/2} \int_0^{\infty} dv^2\, v^2 e^{-\alpha v^2} = 2\pi \left(\frac{\alpha}{\pi}\right)^{3/2} \left(-\frac{\partial}{\partial \alpha}\right) \int_0^{\infty} dv^2 e^{-\alpha v^2}$$

$$= 2\pi \left(\frac{\alpha}{\pi}\right)^{3/2} \frac{1}{\alpha^2} = \frac{2}{\sqrt{\pi \alpha}} = \frac{2}{\sqrt{\pi}} v_{th} = \frac{2}{\sqrt{\pi}} \sqrt{\frac{2 k_B T}{m}} = \sqrt{\frac{8 k_B T}{\pi m}}$$

$$\boxed{\Phi = \frac{1}{4}\, n \sqrt{\frac{8 k_B T}{\pi m}}} = \boxed{\frac{p}{\sqrt{2\pi m k_B T}}}$$

$$n \to \frac{p}{k_B T}$$ eq. of state

Note that to calculate pressure we would do this:

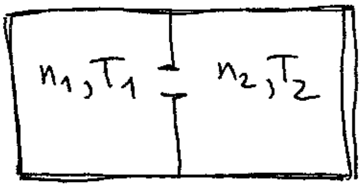
$$p = \int 2 m v_z \, dN(\vec{v}) = \int_0^\infty 2mn\, v^4 f(v)\, dv \int_0^{\pi/2} \cos^2\theta \sin\theta \, d\theta \int_0^{2\pi} d\varphi$$

$$= \frac{4\pi}{3} mn \int_0^\infty v^4 f(v)\, dv = \frac{1}{3} mn \langle v^2 \rangle \quad \text{as calculated before.}$$

Answer to Q1: # of particles escaping per unit time is ΦA.

Interesting consequence: Condition for no mass current between two containers connected by an effusion hole:

Ex.



$$\boxed{n_1 \sqrt{T_1} = n_2 \sqrt{T_2}} \quad \text{or} \quad \frac{p_1}{\sqrt{T_1}} = \frac{p_2}{\sqrt{T_2}}$$

End of L2