



General Physics I

Lect17. Maxwell-Boltzmann Distribution

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Boltzmann & Maxwell distributions

- Boltzmann's distribution:** the probability of finding molecules in a given spatial arrangement varies exponentially with the negative of the potential energy of that arrangement, divided by kT .

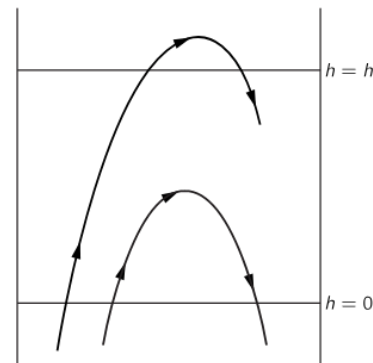
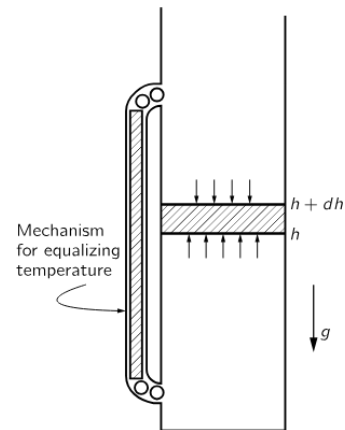
$$n = n_0 e^{-mgh/kT} \quad (\text{specific})$$

$$n = (\text{constant}) e^{-\text{P.E.}/kT} \quad (\text{generalize})$$

- Maxwell's distribution:** the probability of finding molecules in a given spatial arrangement varies exponentially with the negative of the potential energy of that arrangement, divided by kT .

$$\boxed{mu^2/2 = mgh} \quad \frac{n_{>u}(0)}{n_{>0}(0)} = e^{-mgh/kT} = e^{-mu^2/2kT} \quad (\text{specific})$$

$$f(p) dp = C e^{-\text{K.E.}/kT} dp. \quad (\text{generalize})$$



Unitarity of probability density

To calculate the unknown $f(u) du = C e^{-mu^2/2kT} du$, such that $\int_{-\infty}^{\infty} f(u) du = 1$, we first calculate I :

Let $x = \sqrt{2kT/mu}$ $I = \int_{-\infty}^{\infty} e^{-x^2} dx.$

Then

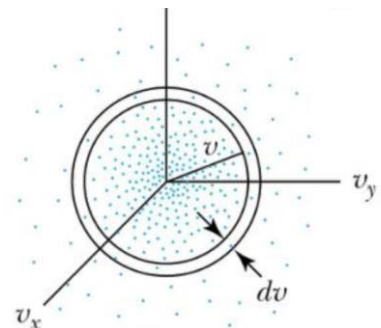
$$\begin{aligned} I^2 &= \int_{-\infty}^{\infty} e^{-x^2} dx \cdot \int_{-\infty}^{\infty} e^{-y^2} dy \\ &= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-(x^2+y^2)} dy dx, \end{aligned}$$

which is a double integral over the whole xy -plane. But this can also be written in polar coordinates as

$$\begin{aligned} I^2 &= \int_0^{\infty} e^{-r^2} \cdot 2\pi r dr \\ &= \pi \int_0^{\infty} e^{-t} dt = \pi. \implies C = \sqrt{m/2\pi kT} \end{aligned}$$

Maxwell distribution in 3D

$$\left\{ \begin{array}{l} f(v_x)dv_x = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-\frac{mv_x^2}{2kT}} dv_x \\ f(v_y)dv_y = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-\frac{mv_y^2}{2kT}} dv_y \\ f(v_z)dv_z = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-\frac{mv_z^2}{2kT}} dv_z \end{array} \right. \Rightarrow \iiint f(v_x, v_y, v_z) dv_x dv_y dv_z = \iiint \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{m(v_x^2+v_y^2+v_z^2)}{2kT}} dv_x dv_y dv_z$$

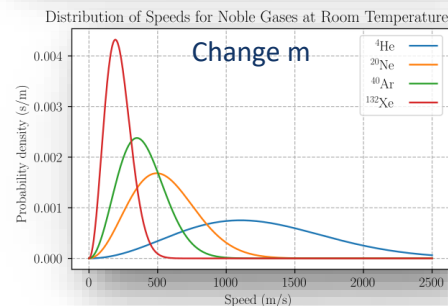
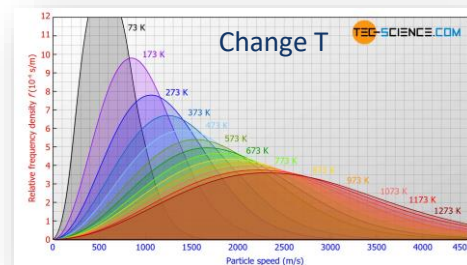


Velocity (momentum) distribution in 3D, v is the speed.

Write as $f(v, \theta, \varphi)$:

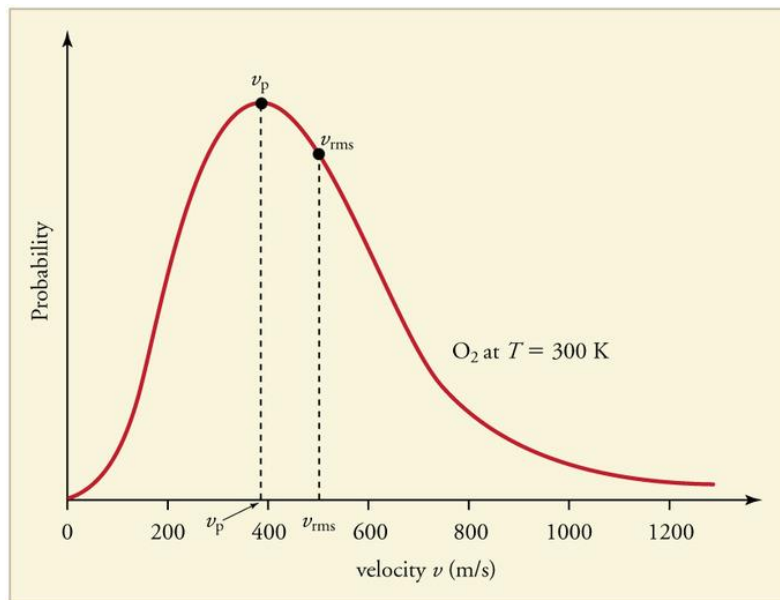
$$\left(\frac{m}{2\pi kT}\right)^{3/2} \int v^2 e^{-\frac{m(v_x^2+v_y^2+v_z^2)}{2kT}} dv \int \sin\theta d\theta \int d\varphi$$

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



Properties of Maxwell distribution

$$\text{In 3D: } f(v) = 4\pi \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} v^2 e^{-\frac{mv^2}{2kT}}$$



$$\text{By solving } \frac{df(v)}{dv} = -8\pi \left[\frac{m}{2\pi kT} \right]^{\frac{3}{2}} v \left[\frac{mv^2}{2kT} - 1 \right] \exp\left(-\frac{mv^2}{2kT}\right) = 0$$

$$\Rightarrow v_p = \sqrt{\frac{2kT}{m}} \quad (\text{most probable speed})$$

$$\langle v \rangle = \int_0^{\infty} v f(v) dv = \sqrt{\frac{8kT}{\pi m}} \quad (\text{average speed})$$

$$v_{\text{rms}} = \sqrt{\langle v^2 \rangle} = \left[\int_0^{\infty} v^2 f(v) dv \right]^{\frac{1}{2}} \quad (\text{root-mean-square speed})$$

$$= \sqrt{\frac{3kT}{m}} \quad \text{Observe } \langle mv^2/2 \rangle = \mathbf{3kT/2!}$$

$$v_p \approx 88.6\% \langle v \rangle < \langle v \rangle < 108.5\% \langle v \rangle \approx v_{\text{rms}}$$

Maxwell distribution in n-dimensional space

In n -dimensional space, Maxwell–Boltzmann distribution:

$$f(v)d^n v = \left[\frac{m}{2\pi kT}\right]^{\frac{n}{2}} \exp\left(-\frac{m|v|^2}{2kT}\right) d^n v$$

Velocity distribution:

$$C \times \exp\left(-\frac{mv^2}{2kT}\right) \times v^{n-1} dv$$

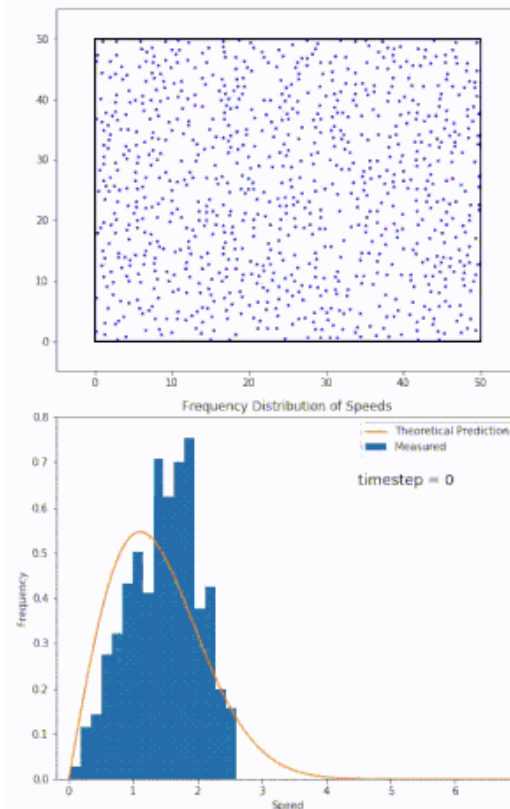
Mean squared velocity:

$$\langle v^2 \rangle = \frac{\int_0^{+\infty} v^2 \cdot v^{n-1} \exp\left(-\frac{mv^2}{2kT}\right) dv}{\int_0^{+\infty} v^{n-1} \exp\left(-\frac{mv^2}{2kT}\right) dv}$$

$$\Gamma(x) = \int_0^{\infty} t^{x-1} e^{-t} dt$$

$$= \left[\frac{2kT}{m}\right] \frac{\Gamma\left(\frac{n+2}{2}\right)}{\Gamma\left(\frac{n}{2}\right)}$$

$$= \left[\frac{2kT}{m}\right] \frac{n}{2} = \frac{nkT}{m}$$



Simulation of a 2D gas relaxing towards a Maxwell–Boltzmann speed distribution (wiki)

Example: velocity profile of dark matter (DM) halo

The Boltzmann equation describes the evolution of the phase-space density $f(\mathbf{x}, \mathbf{v})$ of a DM particle. Conservation of probability:

$$\int f(\mathbf{x}, \mathbf{v}) d^3\mathbf{x} d^3\mathbf{v} = 1$$

While solving the position-dependent Boltzmann equation is beyond the scope of this lecture (c.f. [1603.03797](#)), we can use the nice conclusion from Jeans Theorem that the phase-space distribution is solely a function of energy E for a halo in steady state:

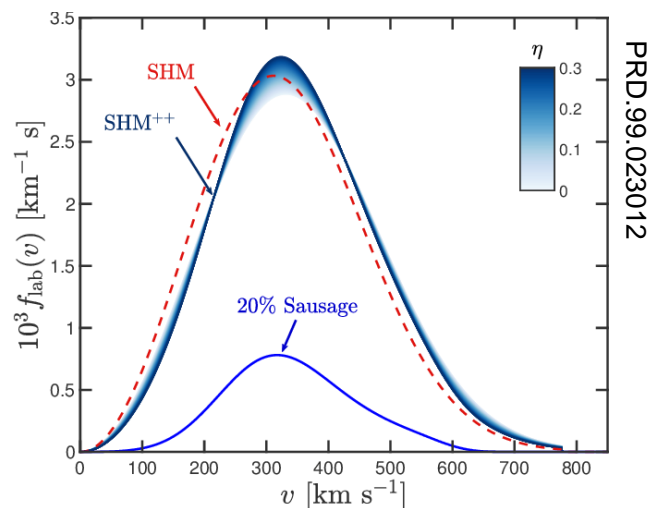
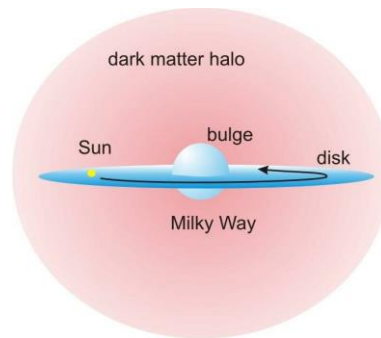
$$f(\mathbf{x}, \mathbf{v}) = f(\mathcal{E}) \quad \text{where} \quad \mathcal{E} = \Psi - \frac{1}{2}v^2$$

Phase-space distribution for a spherical isotropic halo in a steady state is well-modeled by

$$\rho(r) \propto 1/r^2 \quad \text{and} \quad f(v) \propto e^{-v^2/\sigma^2}$$

$$f_{\text{Galaxy}}(\mathbf{v}) = \frac{1}{N(v_0)} \exp\left(-\frac{\mathbf{v}^2}{v_0^2}\right) \Theta(v_{\text{esc}} - |\mathbf{v}|)$$

where $v_0 \approx 220 \text{ km/s}$, $v_{\text{esc}} \approx 500\text{-}600 \text{ km/s}$



A self-gravitating isothermal gas sphere!

The specific heats of gases

From the 1st law of thermal dynamics*:

$$dU = -PdV + dQ$$

$$C_V = (dQ/dT)_V = dU/dT = U/T$$

$$C_P = (dQ/dT)_P = dU/dT + PdV/dT$$

$$\text{Given } (PdV = NkdT)_P \Rightarrow C_P = U/T + Nk$$

$$C_P / C_V = (U + NkT)/U = 1 + NkT/U$$

From the total internal energy:

$$PV = (\gamma-1)U \Rightarrow 1/U = (\gamma-1)/PV$$

$$\text{Hence, } C_P / C_V = 1 + NKT(\gamma-1)/PV = \gamma$$

This suggest that, by measuring the $\gamma = C_P / C_V$ of different gases, we can infer the total energy U for each of them.

Indeed, for monatomic gas, it has three degrees of freedom, thus $U=3NkT/2$ and we expect γ to be $5/3 \approx 1.666\dots$ We found exactly the case from He, Kr, Ar and so on!

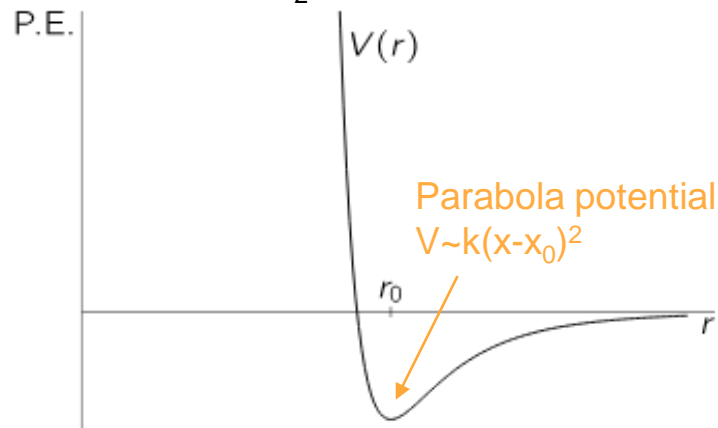
Gas	$T(^{\circ}\text{C})$	γ
He	-180	1.660
Kr	19	1.68
Ar	15	1.668

The total energy of diatomic molecule (classical)

In L16, we said that the total *kinetic* energy of a diatomic molecule is $3kT$. This can be seen as each atom carries $3kT/2$ energy, or $3kT/2$ from C.O.M motion, kT from rotational motion (2 axis) and $kT/2$ from vibrational kinetic energy.

There is, however, another $kT/2$ from the potential energy, coming from the fact that the bottom of $V(r)$ is close to a parabolic potential, i.e, the harmonic oscillator. Thus, we have $\langle K.E. \rangle = \langle P.E. \rangle$ from *Virial Theorem*, or simply based on our experience.

Potential of an O_2 molecule:



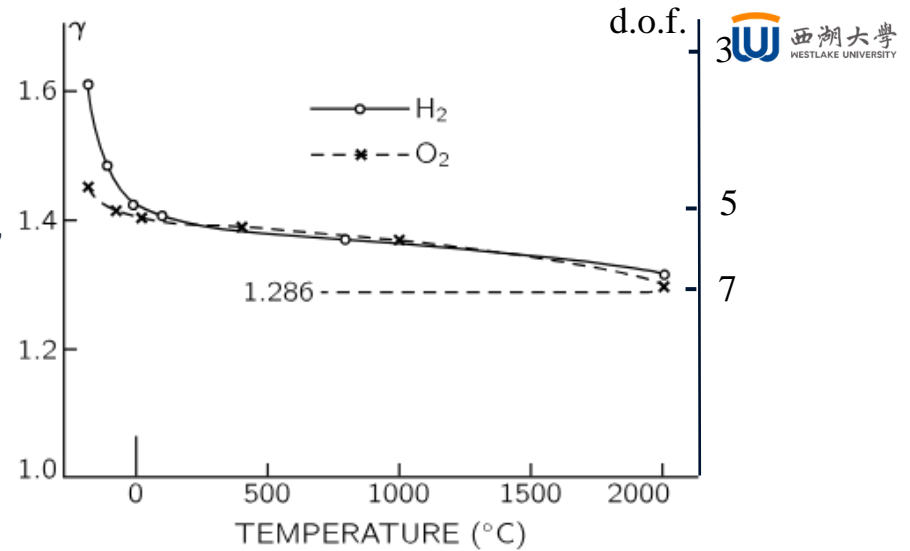
Therefore, the *total energy* of a diatomic molecule is $7kT/2$.

We can also see that, classically, the total energy of a molecule with N atoms keeps increasing, $U = (6N-6)kT/2$ for $N \geq 3$

Failure of classical physics

With the total energy of a diatomic molecule being $7kT/2$, we expect $\gamma = 9/7 \approx 1.286$ independent of its temperature.

Gas	$T(^{\circ}\text{C})$	γ
He	-180	1.660
Kr	19	1.68
Ar	15	1.668
H ₂	100	1.404
O ₂	100	1.399
HI	100	1.40
Br ₂	300	1.32
I ₂	185	1.30
NH ₃	15	1.310
C ₂ H ₆	15	1.22



In experiment, we saw a strong dependence of γ with temperature. Seems that the effective d.o.f. decreases to 3 ($\gamma = 5/3$) with $T \rightarrow 0$. And this effect is stronger for H_2 than O_2 .

“I have now put before you what I consider to be the greatest difficulty yet encountered by the molecular theory.” -- Maxwell in 1869

Need for quantum mechanics

Now 150 years later, we know that this problem can be solved beautifully by quantum mechanics, as a solution to a next difficulty in statistical mechanics that we will cover soon.

Without proof, let's assume the molecule takes discrete energy states, $E_0, E_1, E_2 \dots$. The number of particles in state E_1 compared of that of E_0 follows the Maxwellian relation ($E \sim mv^2$):

$$n_1 = n_0 e^{-(E_1 - E_0)/kT}$$

$$\begin{array}{lll} \frac{N_4}{\quad} & E_4 = 4\hbar\omega & P_4 = A \exp(-4\hbar\omega/kT) \\ \frac{N_3}{\quad} & E_3 = 3\hbar\omega & P_3 = A \exp(-3\hbar\omega/kT) \\ \frac{N_2}{\quad} & E_2 = 2\hbar\omega & P_2 = A \exp(-2\hbar\omega/kT) \\ \frac{N_1}{\quad} & E_1 = \hbar\omega & P_1 = A \exp(-\hbar\omega/kT) \\ \frac{N_0}{\quad} & E_0 = 0 & P_0 = A \end{array}$$

In fact, the energy levels are equipartition, and each level adds a suppression factor of $e^{-\hbar\omega/kT}$ for the distribution.

At $\hbar\omega \gg kT$, almost all molecule is at E_0 , effectively “frozen” ---no contribution to the specific heat. At $\hbar\omega \ll kT$, the behavior of the gas approaches classical physics (quantization \rightarrow continuum)