

Ideal Gas and Estimates

- Take a dilute gas in a volume V , with N particles, and total energy U ,

N, V, U

$\frac{N}{2}, \frac{U}{2}$	$\frac{N}{2}, \frac{U}{2}$
T, P	T, P

N, V, U are extensive

and grow with the system size. If I halve the system size N, V, U all decrease by a factor 2.

- Also note that N, U are constants of motion, which explains their importance in characterizing the gas.
- Other quantities such as the temperature and pressure T, P , are intensive and are constant throughout. Halving the volume leaves these unchanged.
- Now take the ideal gas Law

$$PV = n_{me} RT$$

where P is the pressure, V is the volume
 $R = 8.31 \text{ J/mol}^\circ\text{K}$, n_{me} is the number of moles
and T is the temperature in Kelvins

• n_{me} counts the number of particles

$$N = n_{me} N_A \quad \text{where} \quad N_A = 6.02214076 \times 10^{23}$$

↑ is fixed by definition
these days

Thus

$$PV = n_{me} N_A \left(\frac{R}{N_A} \right) T$$

$$PV = N k_B T, \quad \text{where we defined the Boltzmann constant}$$

Thus we have

$$k_B \equiv R/N_A = 1.38 \times 10^{-23} \text{ J/K}$$

$$P = \left(\frac{N}{V} \right) k_B T \equiv n k_B T$$

Here I have defined the number density

$$n = \frac{N}{V} \quad \text{which is intensive}$$

Also we will use the specific volume (volume per particle), V/N , which is also intensive

$$P \left(\frac{V}{N} \right) = k_B T$$

• $k_B T$ has units of energy. And often

people will quote temperatures as energy

e.g. $k_B T = 1/44 \text{ eV}$ at standard temperature

ice $\rightarrow 273^\circ \text{K} \longleftrightarrow k_B T \approx 1/44 \text{ eV}$

$6000^\circ \text{K} \longleftrightarrow k_B T \approx 0.5 \text{ eV}$

\uparrow
surface temperature of sun!

Often people just write T for $k_B T$, but I will not do this.

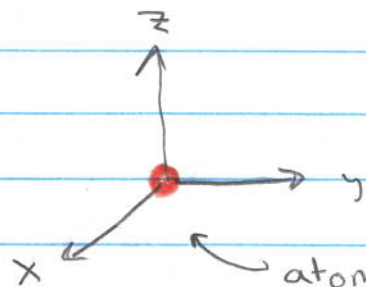
What is Temperature? Equipartition Theorem

- Hard to define precisely. That is a goal of the course. It is a parameter that describes how the energy is shared amongst the degrees of freedom

$$k_B T \sim \text{energy per "degree of freedom" (dof)}$$

We need to define what we mean by "dof"

- We will give an operational definition of temperature later
- For the moment consider a mono-atomic ideal gas (MAIG) such as He, Ar. Each atom can move in three ways. The number of dof



is

$$3N = \text{dof for MAIG}$$

The equipartition theorem (which we will derive later) says that the energy per dof is $\frac{1}{2} k_B T$

$$\frac{\mathcal{U}}{\text{dof}} = \frac{1}{2} k_B T$$

So

$$U = \frac{3}{2} N k_B T \quad \text{for a MAIG}$$

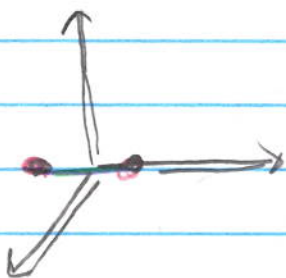
So the typical energy at room temperature is of order $\sim 1/40$ eV.

• So with the two equations

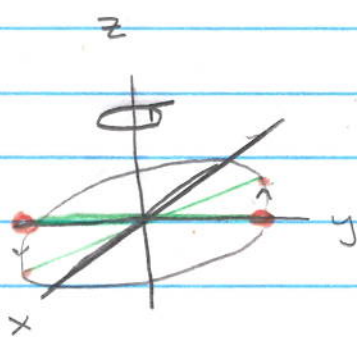
$$P = \left(\frac{N}{V}\right) k_B T \quad k_B T = \frac{2}{3} \left(\frac{U}{N}\right)$$

we have expressed the intensive variables in terms of the extensive ones N/V , and U/N , which will always be one of our goals.

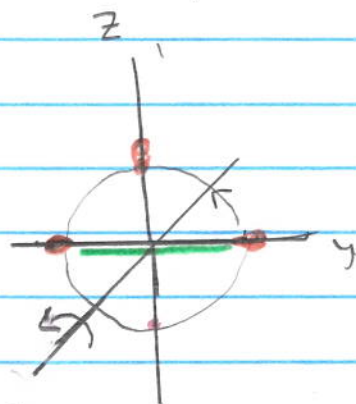
• For a diatomic gas there are $5N$ dof. Each molecule such as N_2 , H_2 , O_2 can translate in three directions and rotate around two axes



Translations in
 x, y, z



Rotation in
 xy plane



Rotation in
 yz plane

So for a diatomic atomic ideal gas (DAIG)

$$\frac{E}{N} = 5 \times \frac{1}{2} k_B T = \frac{5}{2} k_B T$$



dof per particle

for DAIG

In general the energy (hamiltonian) of a particle is

$$H = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} + \frac{1}{2} I \omega_z^2 + \frac{1}{2} I \omega_x^2$$



3 translations



2 rotations

More formally, the equipartition theorem says that for classical systems, the energy is $\frac{1}{2} k_B T$ per "quadratic form" in the hamiltonian. In this case there are five quadratic forms in the Hamiltonian

Some estimates:

- spacing between atoms/molecules
- typical size of atoms/molecules
- typical speed of atoms/molecules
- typical de Broglie wavelength

Later can discuss typical distance between collisions l_{mfp} and typical time between collisions τ_R .

① Typical Spacing:

- We have $PV = n_m RT$ so we can find the volume per particle, V/N , and the typical spacing is $l_0 = (V/N)^{1/3}$. The volume is

$$V = \left(\frac{n_m RT}{P} \right) \approx 22 \text{ Liters}$$

$$1 \text{ Liter} = 1000 \text{ cm}^3$$

★ For one mole at, at standard temperature $T \equiv 273^\circ \text{K}$,
at standard pressure, $P_{STP} \equiv 1 \text{ bar} \equiv 10^5 \frac{\text{N}}{\text{m}^2} \approx 1 \text{ atm}$.

$$\text{So } l_0 \equiv \left(\frac{V}{N_A} \right)^{1/3} \equiv \text{typical distance}$$

$$l_0 \approx 3.33 \text{ nm}$$

★ STP is "Standard Temperature Pressure", $T = 273^\circ \text{K}$, $P = 1 \text{ bar} = 10^5 \frac{\text{N}}{\text{m}^2} \approx 1 \text{ atm}$

② The typical size of an atom is the Bohr Radius

$a_0 = 0.5 \text{ \AA}$ or slightly larger for

Larger atoms. For molecules the typical bond length is $1 \sim 2 \text{ \AA}$. $1 \text{ \AA} = 0.1 \text{ nm}$

So you should have the picture (which is roughly to scale) in your head:



Spacing

$$l_0 \approx 3.3 \text{ nm}$$

electron cloud

$$2-3a_0$$



③ Typical Speeds.

- Take a mono-atomic ideal gas (MAIG). All of the energy is a result of the translational KE of ideal gas:

$$\frac{U}{N} = \frac{3}{2} k_B T = \left\langle \frac{1}{2} m \vec{v}^2 \right\rangle = \frac{1}{2} m \langle v^2 \rangle = \frac{1}{2} m \overline{v^2}$$

means average, the bar also means average

$$\vec{v}^2 = v_x^2 + v_y^2 + v_z^2 \quad \text{is the square of the velocity}$$

The brackets denotes an average over the atoms of the gas, i.e. molecule 1 has \vec{v}_1 , molecule 2 has \vec{v}_2 etc

$$\langle \vec{v}^2 \rangle = \frac{1}{N} \sum_i \vec{v}_i^2 \equiv \overline{v^2}$$

Thus

$$\langle \vec{v}^2 \rangle = \left(\frac{3}{2} \frac{k_B T}{m} \right)$$

$$\langle v_x^2 + v_y^2 + v_z^2 \rangle = \underbrace{\langle v_x^2 \rangle}_{\text{these are equal}} + \underbrace{\langle v_y^2 \rangle}_{\text{these are equal}} + \langle v_z^2 \rangle = 3 \frac{k_B T}{m}$$

these are equal

$$\text{i.e.} \quad \overline{v_x^2} = \frac{k_B T}{m}$$

the "root-mean-square" velocity is the square root of this

$$V_{\text{rms}} \equiv \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3 k_B T}{m}}$$

Take He which has 2 protons + 2 neutrons.

Take STP, so $T = 273^\circ \text{K}$. Find V_{rms} without looking up the numbers

$$V_{\text{rms}} = \sqrt{\frac{3 N_A k_B T}{m N_A}} = \left(\frac{3 \cdot 8.32 \text{ J} (273)}{4 \text{ g}} \right)^{1/2} = \underline{\underline{1300 \text{ m/s}}}$$

we used

$$m N_A = 4 \text{ g}, \quad N_A k_B = R = 8.32 \text{ J}.$$

Notice that this is of order of the speed of sound in air, $c_s = 330 \text{ m/s}$. It is somewhat higher than this, reflecting the fact that He is a light atom.

④ Debroglie Wavelength

$$\lambda_{th} \sim \frac{h}{p} \quad \text{now} \quad p \sim mv \sim m \sqrt{\frac{k_B T}{m}} \sim \sqrt{m k_B T}$$

So

$$\lambda_{th} \sim \frac{h}{(m k_B T)^{1/2}}$$

• The book defines (based on calculations)

$$\lambda_{th} \equiv \frac{h}{(2\pi m k_B T)^{1/2}}, \quad \text{but the } \sqrt{2\pi} \text{ here}$$

is completely arbitrary at this time. To substitute numbers it helps to know a few numbers:

$$m_p c^2 = 938 \text{ MeV} \approx 1 \text{ GeV}$$

↑ mass of proton times c^2

Note also the electron mass $m_e/m_p \approx 1/2000$ so $m_e c^2 \approx 0.511 \text{ MeV}$. Protons and neutrons have approx the same mass. Note also the conversion factors

$$\hbar c = 197 \text{ eV nm}$$

$$hc = 1240 \text{ eV nm}$$

So

$$\lambda_{th} = \frac{hc}{(2\pi m_{He} c^2 k_B T)^{1/2}} = \frac{1240 \text{ eV nm}}{(2\pi \cdot 4 \cdot 1 \text{ GeV} \cdot \frac{1}{44} \text{ eV})^{1/2}}$$

At STP, we have $k_B T = \frac{1}{44} \text{ eV}$, finally

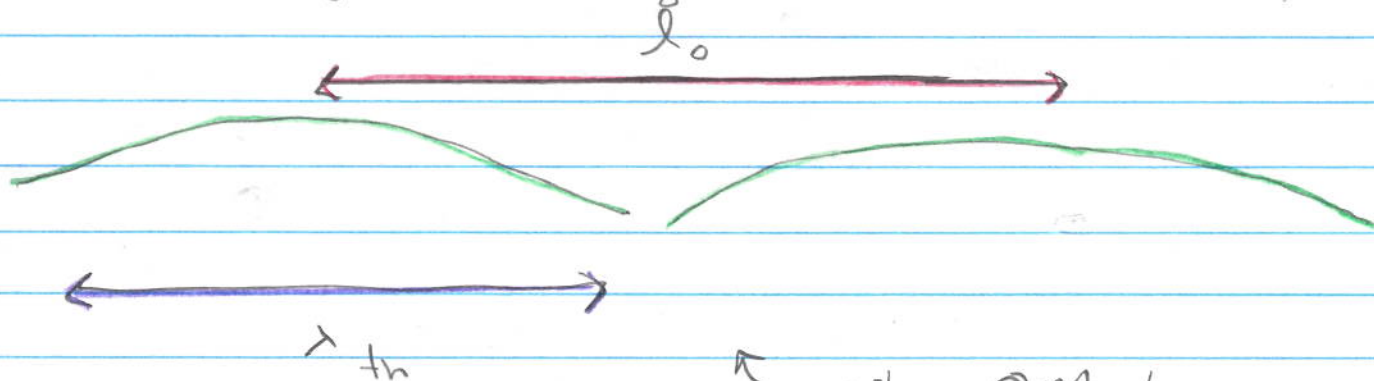
$$\lambda_{th} \approx 1.0 \text{ \AA}$$

- So this is really quite short. One might be able to cool to say 10°K which

$$\lambda \sim \frac{h}{\sqrt{m k_B T}} \propto \frac{1}{\sqrt{T}} \quad \frac{\lambda_{10}}{\lambda_{273}} = \sqrt{\frac{273^\circ \text{K}}{10^\circ \text{K}}}$$

So the wavelength gets longer by $\sqrt{\frac{273}{10}} \approx 5$ increasing

the de Broglie wavelength to $\lambda_{th} = 5 \text{ \AA}$. By increasing the density of atoms and cooling further one could hope to reach an interesting regime where the spacings between the atoms is comparable to their De Broglie wavelength



When QM becomes important

In this regime the quantum mechanical character of the particles becomes important. We will deal with this at the end of the course, when we discuss Bose Condensates.