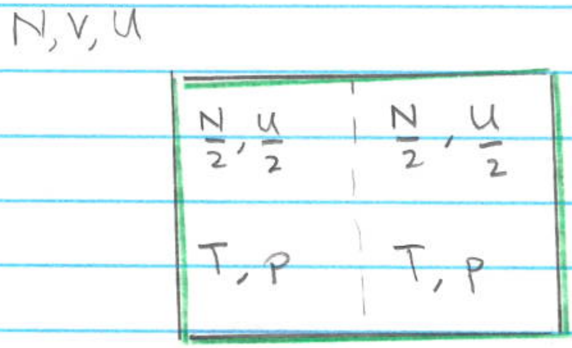
Ideal Gas and Estimates

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



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

$$PV = n_{me} R T$$

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

- $n_{m\ell}$ counts the number of particles

$N = n_{m\ell} N_A$ where $N_A = 6.02214076 \times 10^{23}$

↖ is fixed by definition these days

Thus

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

$PV = N k_B T$, where we defined the Boltzman constant

Thus we have $k_B \equiv R/N_A = 1.38 \times 10^{-23}$ J/°K

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

Here I have defined the number density

$n = \frac{N}{V}$ 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 ↗ $273^\circ K \longleftrightarrow k_B T \simeq 1/44\ \text{eV}$

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

↑ surface temperature of sun!

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

What is Temperature? Equipartion 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

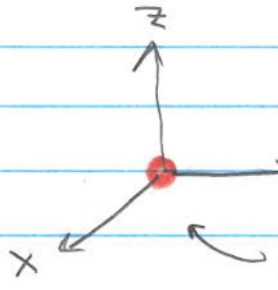
$$k_B T \sim \text{energy per "degree of freedom" (dof)}$$

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

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



atom can move in three directions

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

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

So

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

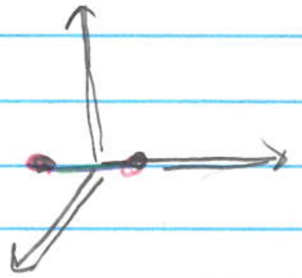
So the typical energy at room temperature is of order ~ 1/40 eV.

- So with the two equations

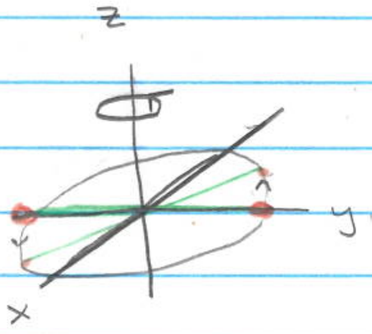
$$P = \left(\frac{N}{V}\right) k_B T \qquad k_B T = \frac{2}{3}\left(\frac{U}{N}\right)$$

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.

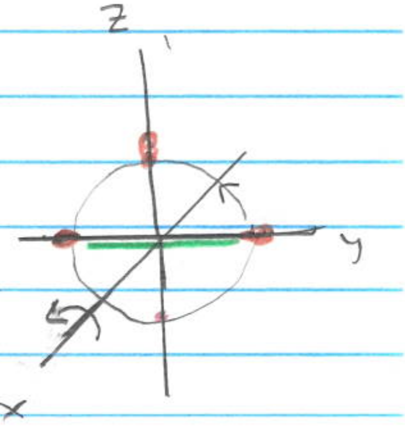
- For a diatomic gas there are 5N dof. Each molecule such as N_2, H_2, O_2 can translate in three directions and rotate around two axes



Translations ix x, y, z

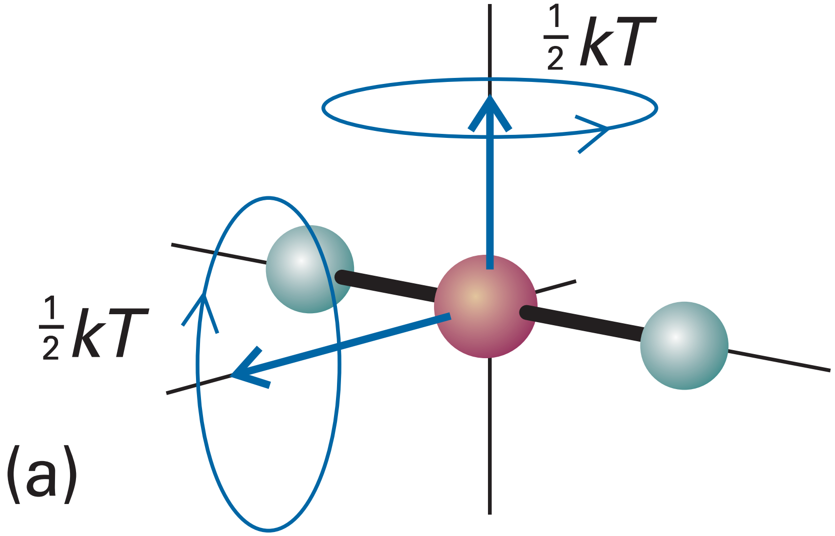


Rotation in xy plane



Rotation in yz plane

Two rotational degrees of freedom per particle



So for a diatomic atomic ideal gas (DAIG)

$$\boxed{\frac{E}{N} = \underset{\substack{\uparrow \\ \text{dof per particle}}}{5} \times \frac{1}{2} k_B T = \frac{5}{2} k_B T}$$

for DAIG

In general the energy (hamiltonian = H) of a particle is

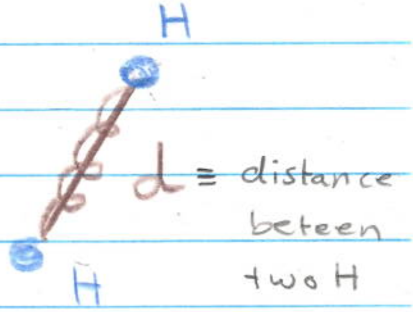
$$H = \underbrace{\frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}}_{\text{3 translations}} + \underbrace{\frac{1}{2} I \omega_z^2 + \frac{1}{2} I \omega_x^2}_{\text{2 rotations}}$$

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

- In general the energy of an ideal gas is a function of temperature, but not volume.

$$U = N\, e_0(T) \quad \leftarrow \text{this fcn can be complicated}$$

- For diatomic hydrogen the energy is



$$E = \underbrace{\frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2}_{\text{3 translations}}$$

$$+ \underbrace{\frac{1}{2}I\omega_x^2 + \frac{1}{2}I\omega_y^2}_{\text{2 rotations}}$$

vibrational PE

$$+ \underbrace{\frac{1}{2}m\dot{d}^2 + \frac{1}{2}kd^2}_{\text{two quadratic forms for vibrations KE+PE}}$$

- So at the highest temperature

$(N_A k_B = R!)$

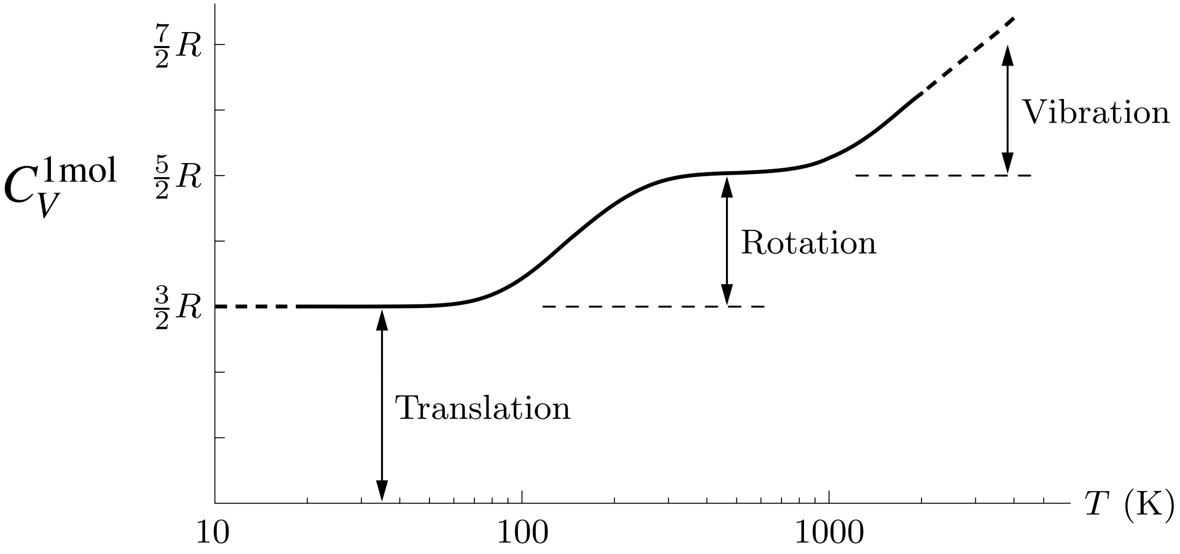
$$U^{1mol} = N_A \frac{7}{2} k_B T = \frac{7}{2} RT$$

So

$$C_V^{1mol} \equiv \frac{\partial U^{1mol}}{\partial T} = \frac{7}{2} R$$

Energy of one mole of diatomic hydrogen H_2

$$C_V^{1\text{mol}} \equiv \frac{\partial U^{1\text{mol}}}{\partial T}$$



The figure shows c_V for H_2.

At low temperatures the rotations are frozen. But the translations can be treated classically ; $U = \frac{3}{2} NkT$. At intermediate temperatures the molecule is rotating classically , $U = \frac{5}{2} NkT$. At the highest temperatures the molecule vibrates classically and U approaches $\frac{7}{2} NkT$. Most molecules dissociate before vibrations become very important. In much of the temperature range including translations and rotations classically is a good approximation