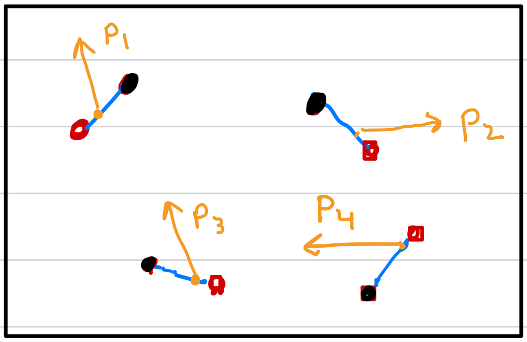
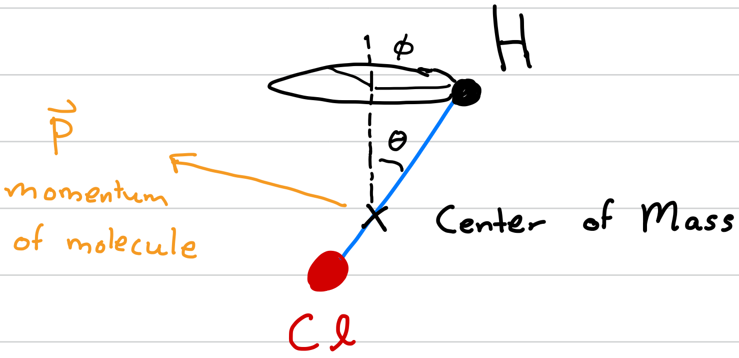
Diatomic Gas eg HCl





Each diatomic molecule can move with total momentum $\vec{p}$ and rotate around the center of mass. The angular momentum of the molecule around the center of mass is $\vec{L}$. The rotational kinetic energy is

$$K_{rot} = \frac{1}{2} I \omega^2 = \frac{L^2}{2I} \qquad (L = I\omega)$$

The total energy for a single particle is:

$$\mathcal{E}(p,\ell) = \frac{p^2}{2m} + \frac{\langle L^2 \rangle}{2I} = \frac{p^2}{2m} + \mathcal{E}_\ell$$

We will treat the internal rotations quantum mechanically. The energy levels of the quantized rotations are

$$\mathcal{E}_\ell = \frac{\hbar^2}{2I} \ell(\ell+1) \equiv \ell(\ell+1)\Delta \qquad \Delta \equiv \frac{\hbar^2}{2I}$$

$\langle L^2 \rangle = \ell(\ell+1)\hbar^2$ = average over $Y_{\ell m}$ wave function

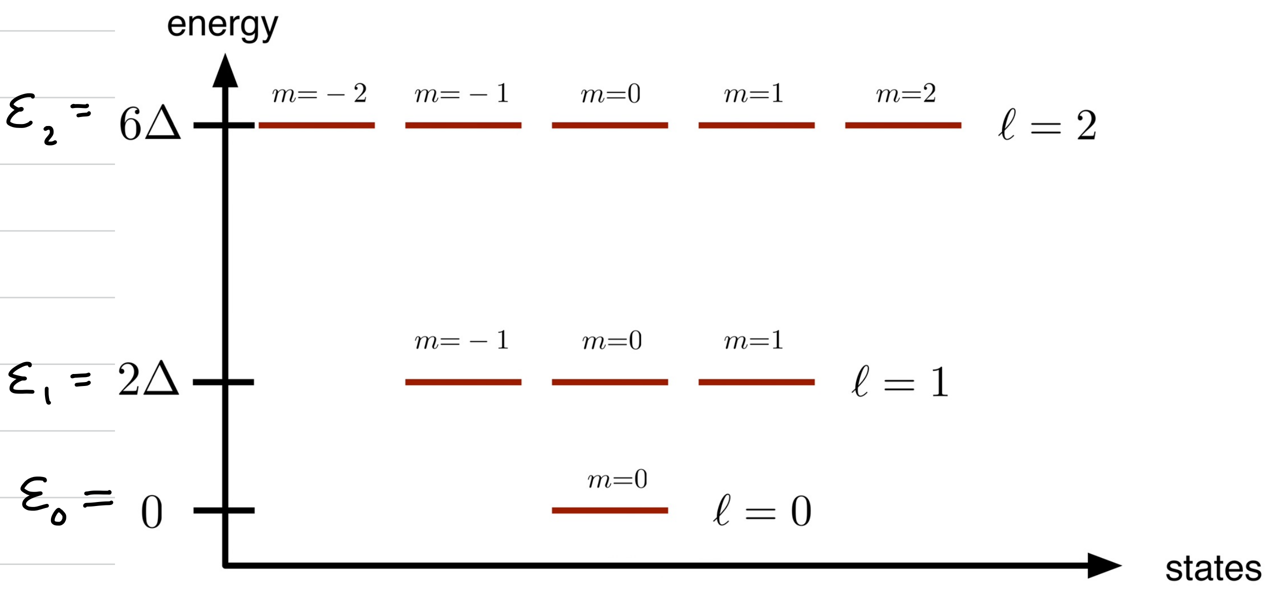
We are using that the states of the angular momentum are labelled by two integers ℓ and m

$$L^2 Y_{\ell m}(\theta,\phi) = \ell(\ell+1)\hbar^2 Y_{\ell m}(\theta,\phi) \qquad \ell = 0, 1, \ldots, \infty$$

these angular wave functions squared $|Y_{\ell m}(\theta,\phi)|^2$ determine the probability of finding the molecule with angles θ, ϕ.

$$L_z Y_{\ell m} = m\hbar Y_{\ell m} \qquad \underbrace{m = -\ell, -\ell+1, \ldots, \ell-1, \ell}_{2\ell+1 \text{ states}}$$

The energy levels are:



ℓ labels how fast the molecule is spinning $\langle L^2 \rangle = \ell(\ell+1)\hbar^2$

m determines the orientation of the spinning $\langle L_z \rangle = m\hbar$. The energy only depends on $\langle L^2 \rangle$, or ℓ

If ℓ is Large, the motion is nearly classical. The classical approximation is good here (as we will see).

- Following the book we will use J, and m instead of l, m

$$\mathcal{E}_J = J(J+1)\Delta \qquad J \equiv 0, 1, 2 \ldots \infty$$

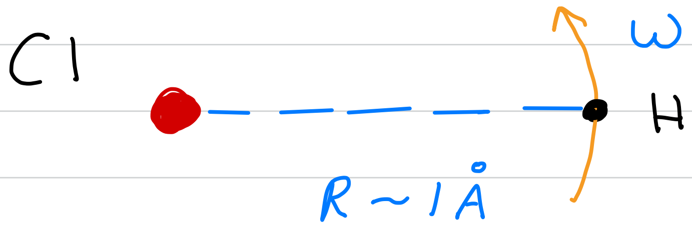
$$m_J = -J, -J+1, \ldots\ldots, J$$

Normally we use J to indicate the total angular momentum including spin. But let's ignore this complication here.

Statistical Mechanics of Diatomic Gasses

Lets estimate $\Delta = \hbar^2/2I$ = the energy gap between levels, for HCl

The Cl is 35 times heavier than the hydrogen So the Cl is essentially the center of mass. Thus the Hydrogen essentially just rotates around the Chlorine



typical bond length which you should know!

$$I = m_H R^2$$

So

$$\Delta = \frac{\hbar^2}{2 m_H R^2} \simeq 0.004\,\text{eV} \longleftarrow$$

You should be able to estimate this

proton mass approximately

So with $k_B T \simeq 0.025\,\text{eV} \simeq 1/40\ \text{eV}$ we find:

$$\frac{k_B T}{\Delta} \simeq 12.5 \Leftarrow$$

this is already pretty large. This means that the temperature will excite many quantum states. The quantum numbers will be almost continuous, and the dynamics will be almost classical.

The probability for the molecule to be in a rotational state labeled by J, m is:

$\varepsilon_J = J(J+1)\Delta$

$$P_{J,m} = \frac{e^{-\beta \varepsilon_J}}{Z_{rot}} \quad \text{with} \quad Z_{rot} = \sum_{J=0}^{\infty} \sum_{m=-J}^{J} e^{-\beta \varepsilon_J}$$

$$= \sum_{J=0}^{\infty} (2J+1)\, e^{-\beta \varepsilon_J}$$

Generally we dont care about m, we care only about the total angular momentum labelled by J.

$$P_J = \sum_{m=-J}^{J} P_{J,m} = \frac{(2J+1)\, e^{-\beta \varepsilon_J}}{Z_{rot}}$$

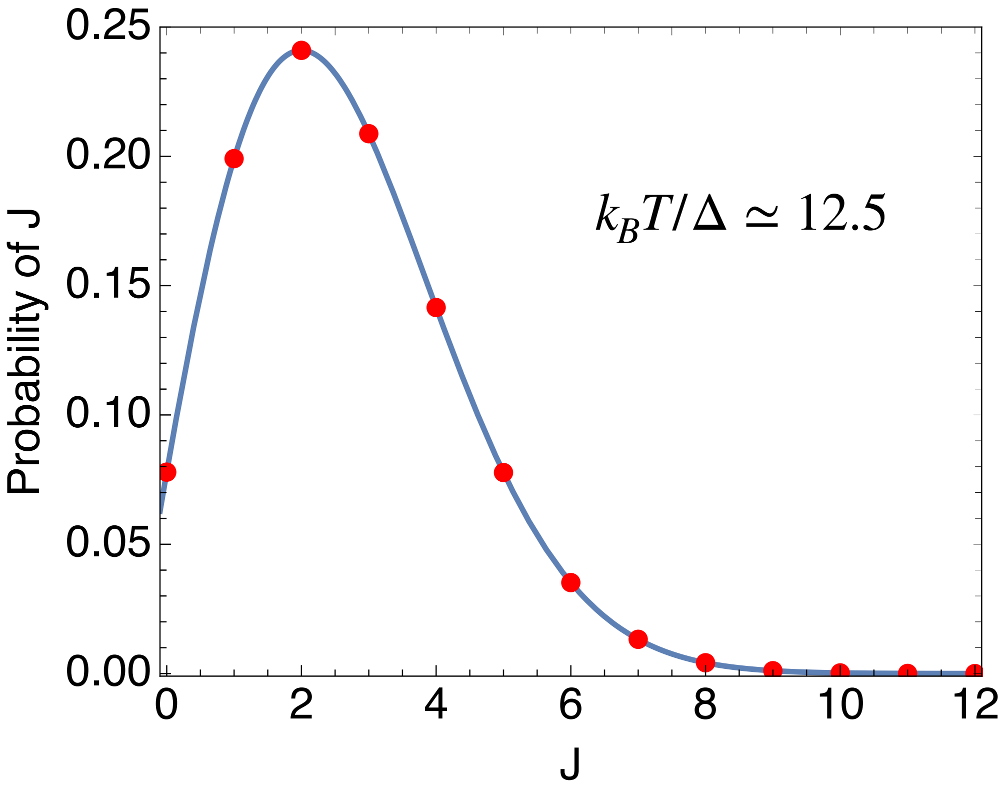
Now the partition function can't be evaluated in closed form. But, it can be evaluated numerically, and P_J is presented on the next page.

The energy is:

$$\langle \varepsilon_{rot} \rangle = \sum_{J=0}^{\infty} P_J \varepsilon_J$$

You will evaluate this in homework.

Rotational Partition Function



$$P_J = \frac{1}{Z_{\rm rot}} e^{-J(J+1)\beta\Delta} \times (2J+1)$$

This is the probability to find the atom with a give angular momentum quantum number J. We have $\sum_J P_J = 1$. The factor of $(2J+1)$ is because there for each J we have $(2J+1)$ states for the m quantum number, $m = -J \ldots J$.

We can find an approximate form for Z_{rot} by replacing the sum with an integral. This is a good approximation when kT/Δ is large, i.e. when the system is classical.

$$Z_{rot} \simeq \int_0^\infty dJ\, (2J+1)\, e^{-\beta\Delta J(J+1)}$$

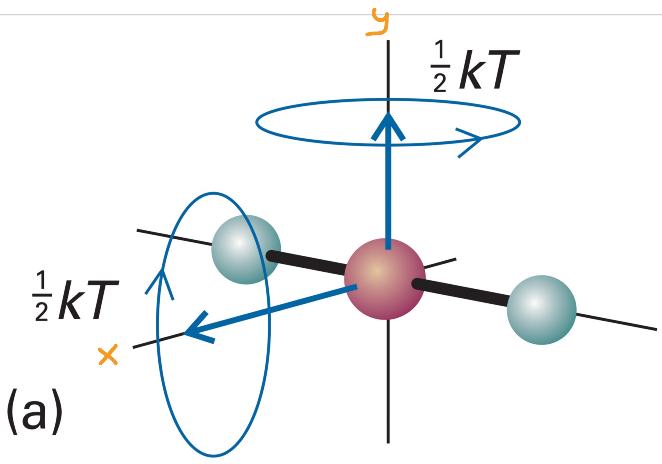
$$= -\frac{e^{-\beta\Delta J(J+1)}}{\beta\Delta}\Bigg|_0^\infty$$

$$= \frac{1}{\beta\Delta}$$

Then the rotational energy per particle is

$$\langle \varepsilon_{rot} \rangle = -\frac{\partial \ln Z_{rot}}{\partial \beta} = \frac{1}{\beta} = kT$$

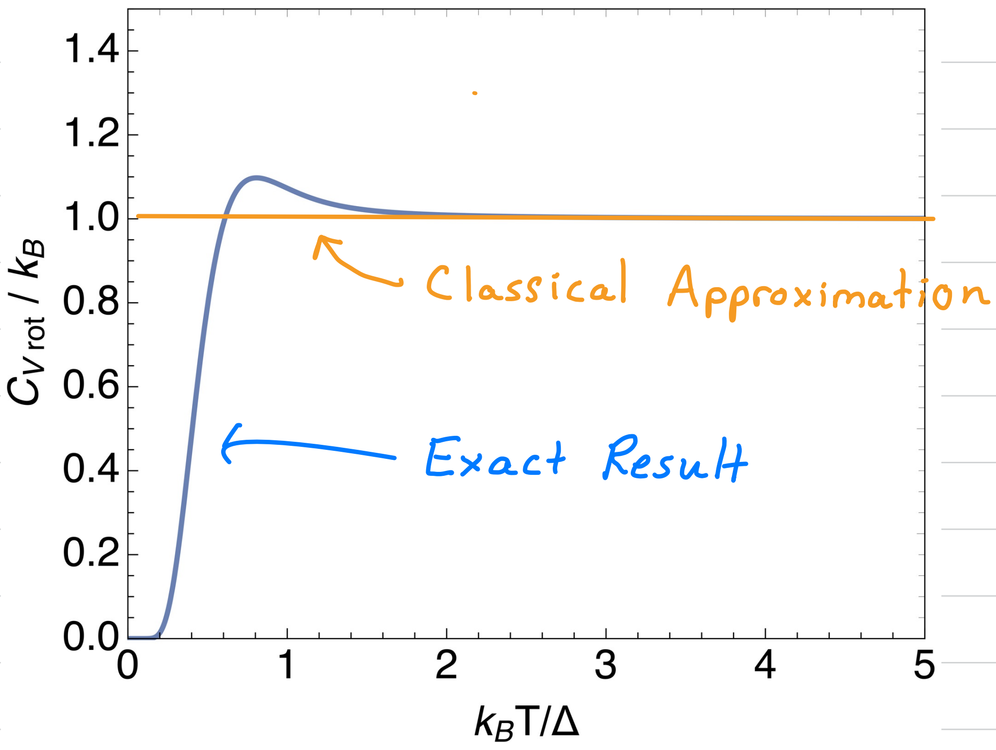
← this is what you get from the equipartition theorem. There are two rotational dof: around the two axes x and y



Replacing the sum with an integral is a classical approximation, which is why the equipartition theorem applies in this limit.

The specific heat per particle from rotations is

$$C_{V\,1\mathrm{rot}} \cong \frac{\partial\langle\varepsilon_{\mathrm{rot}}\rangle}{\partial T} = k_B$$



Translational Motion:

The partition function of the full system is

$$Z_N = \frac{1}{N!} Z_1^N \simeq \left(\frac{eZ_1}{N}\right)^N \Longleftarrow \text{See previous note}$$

Where

$$Z_1 = \overset{\text{same as MAIG}}{Z_{1\mathrm{trans}}} Z_{1\mathrm{rot}}$$

Where Z_{1rot} determines the rotational contribution to the free energy per particle of the system

$$U = -\frac{\partial \ln Z_N}{\partial \beta} = U_{trans} + U_{rot}$$

$$= N\left[-\frac{\partial \ln Z_{1trans}}{\partial \beta} + -\frac{\partial \ln Z_{1rot}}{\partial \beta}\right]$$

$$= N\frac{3}{2}kT + N\langle \varepsilon_{rot}\rangle \,]$$

see MAI6

new part ≃ NkT

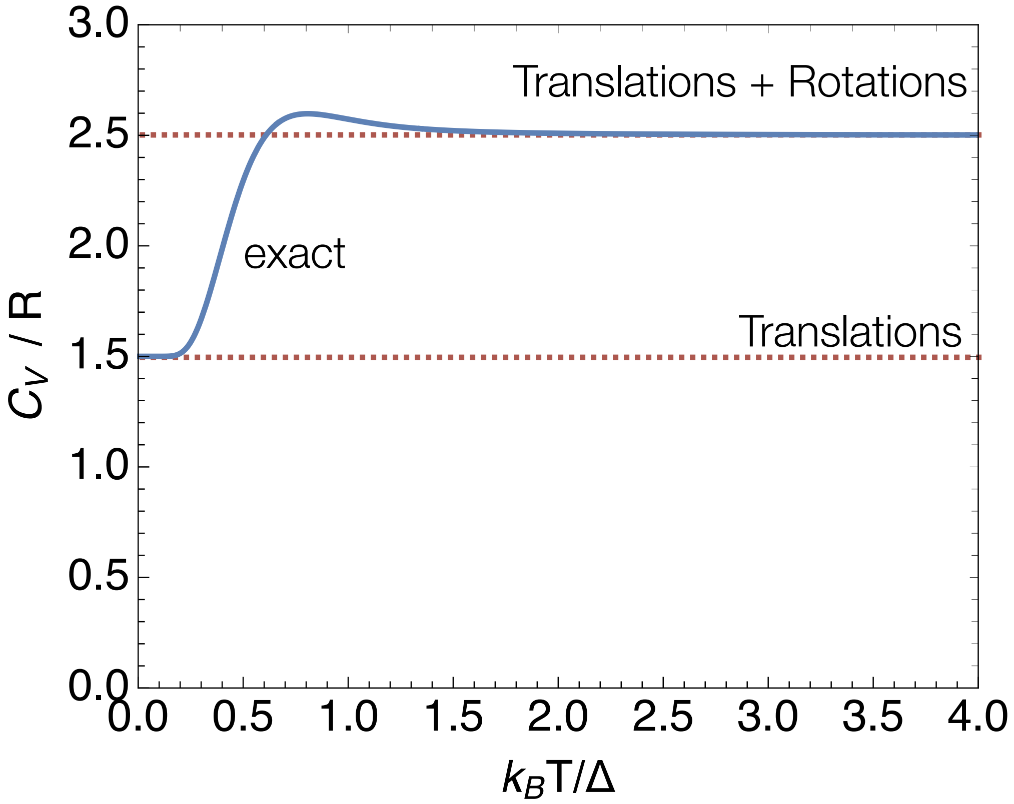
For 1mol of Substance, and using $C_v = \partial U/\partial T$

$$C_v = \frac{\partial U}{\partial T} = N_A \frac{3}{2}k_B + Nk_B\left(\frac{C_{v1rot}}{k_B}\right)$$

this is approx one, with the classical approximation

$$\simeq R\left[\frac{3}{2} + 1\right]$$

Total Partition Function: Translations + Rotations



$5/2 = \frac{3}{2} + 1$

$3/2$