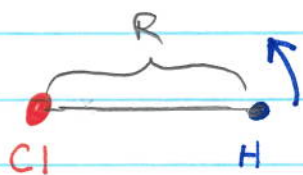# Rotational Partition Functions

- Consider a Molecule such as HCl. The molecule can move as a whole (translate) and rotate:

Chlorine is 35 times heavier than hydrogen

- The center of mass is essentially on the Chlorine atom. The rotational energy is:

$$K = \frac{1}{2} I \omega^2 = \frac{L^2}{2I}$$

where $I = M_H R^2$. $L = I\omega$

moment of inertia

- We have assumed that the Chlorine is infinitely heavy, so the hydrogen rotates around it. Taking L^2 as the quantum operator the energy levels of the system are:

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

$$\Delta \equiv \hbar^2/2I$$

Spherical Harmonics

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

$$L_z Y_{\ell m} = m\hbar Y_{\ell m}(\theta,\phi)$$

- The allowed quantum numbers are

$$\ell = 0, 1, 2, \ldots \ldots \infty$$

and $m = -\ell, -\ell+1, \ldots \ell-1, \ell$, making $2\ell+1$ states for each ℓ.

the angles and wave fcns describe how the molecule is oriented for given quantum numbers ℓ, m

For example: for $\ell = 2$ $m = -2, -1, 0, 1, 2$

- Following the book we will label each energy level by J

$$\mathcal{E}_J = J(J+1)\,\hbar^2/2I$$

- Each energy level consists of $(2J+1)$ states with $m = -J, -J+1, \ldots, J-1, J$. The angular-momentum around the z-axis is $m\hbar$, while the total angular momentum squared is $J(J+1)\hbar^2$

- The symbol J usually means we are considering spin, and the total angular momentum is then either integral or half-integral. We will not consider spin here.

So

$$Z_{rot} = \sum_{J=0}^{\infty} \sum_{m=-J}^{J} e^{-\beta E_J}$$

$$Z_{rot} = \sum_{J=0}^{\infty} (2J+1) \, e^{-\beta \Delta J(J+1)} \qquad\qquad \Delta \equiv \frac{\hbar^2}{2I}$$

- Now this sum cant be done in closed form, But can be done numerically. Then the probability of finding the molecule with given J (and m = -J, ... , +J)

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

see slide
for graph
versus J

Then

$$\langle E_{rot} \rangle = \sum_{\ell} P_J \, E_J$$

And

$$C_V = \frac{\partial \langle E_{rot} \rangle}{\partial T}$$

these need to be done numerically

see slide

- Lets try to estimate the rotational energy:

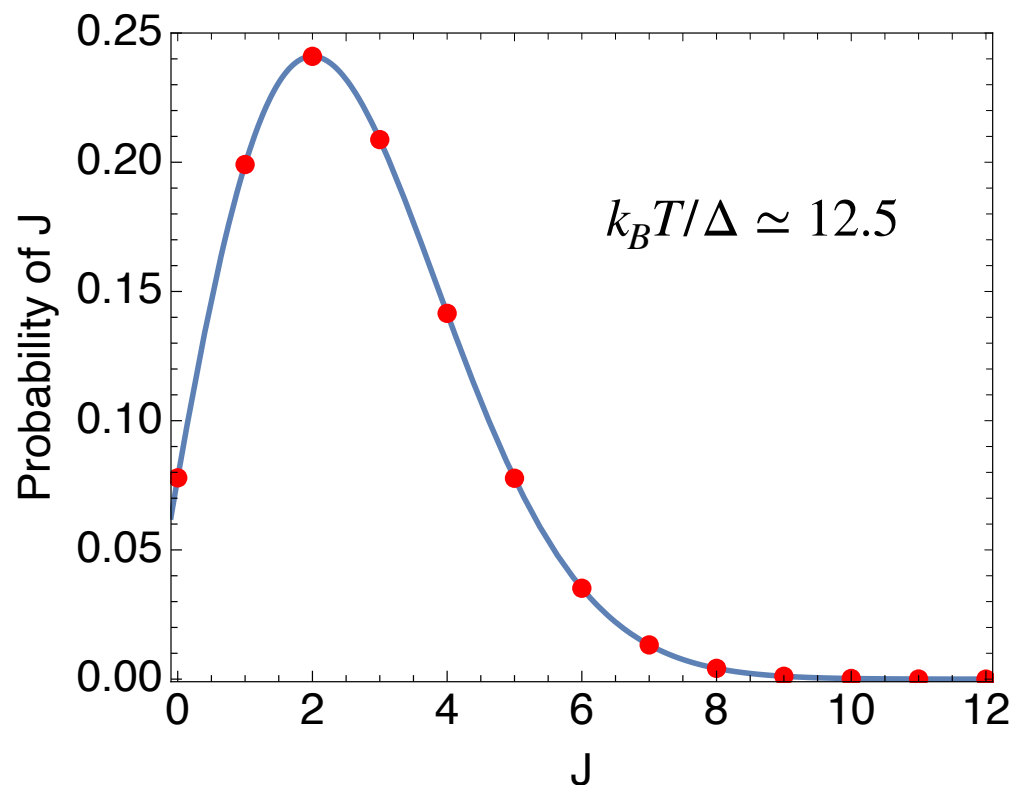$$\Delta = \frac{\hbar^2}{2I} = \frac{\hbar^2}{2 m_p R^2} \qquad \text{where} \quad R \simeq 1 \, \overset{\circ}{A}$$

← typical radius

← proton mass

Find $\Delta = 0.004$ eV

Rotational Partition Function

$k_B T/\Delta \simeq 12.5$

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

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, $m = -J \ldots J$.

So with $k_B T \simeq 1/40 eV$

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

The probability for $\frac{k_B T}{\Delta} \simeq 12.5$ is shown on the slide.

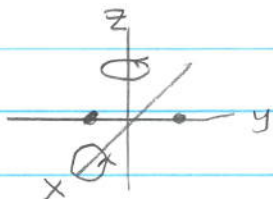- Since we are populating many energy levels we can approximate the sum by an integral:

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

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

Then

$$\langle \varepsilon_{rot} \rangle \simeq \frac{1}{Z} \frac{-\partial Z}{\partial \beta} = \frac{1}{\beta} = kT$$

And $C_V^{rot} = \frac{\partial \langle E_{rot} \rangle}{\partial T} = k_B$

This is what we would expect from the equipartition theorem! There are two rotational dof here. Rotations around X and around Z
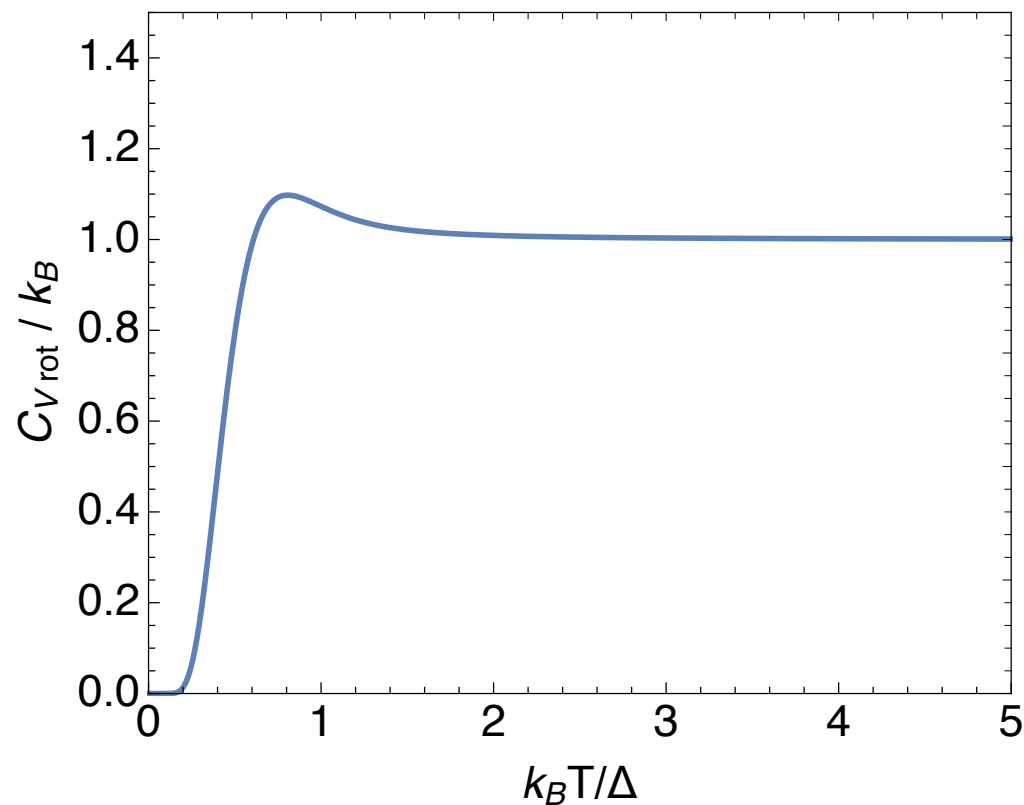

$$\langle E_{rot} \rangle = 2 \times \frac{1}{2} k_B T = k_B T$$
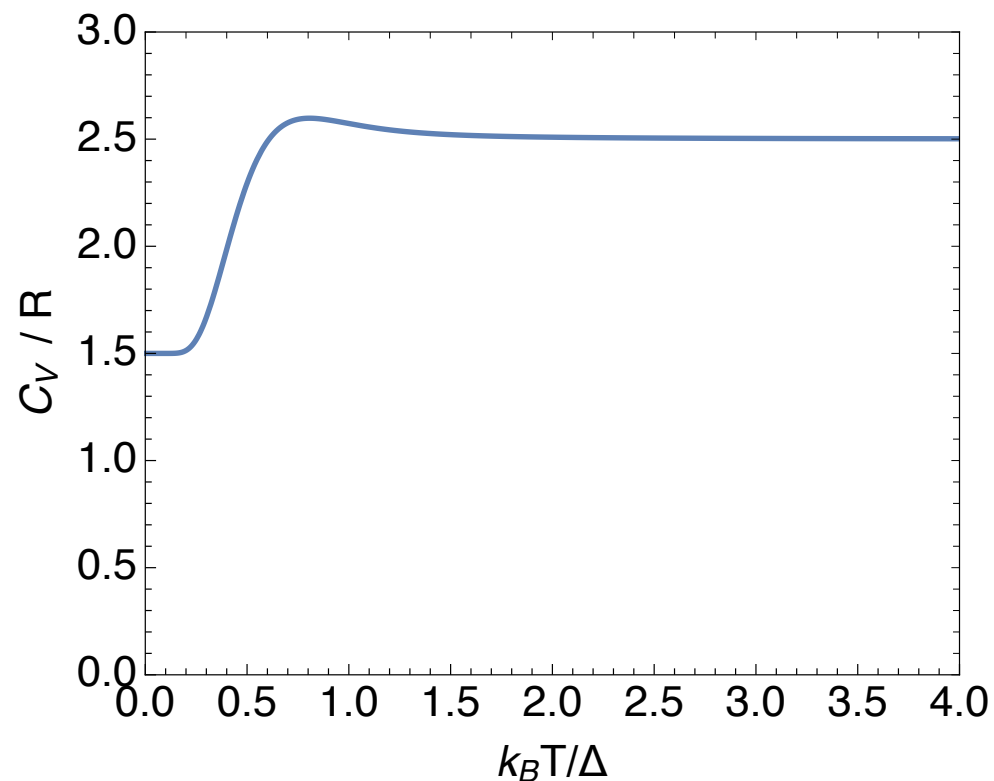
Specific Heat From Rotational Partition Function

The constant value at high temperature $C_{V\,rot}$ is k_B. This is consistent with the equipartition theorem. There are two rotational degrees of freedom per particle – so the energy per particle is $2 \times \frac{1}{2}k_B T$ in the classical limit (high temperature). In the high temperature limit, we replaced the sum over J by an integral to evaluate the partition function

Total Partition Function: Translations + Rotations

You will do this in homework. In general the full partition function is the translational one, times the rotational one. Specific heat (for one mole) has a contribution from translations $C_V = 3/2R$, and a contributions from rotations. In the high temperature limit the specific heat for N_A particles rotating is $C_{V,rot} = N_A k_B = R$. So the full partition function is $C_V = 3/2R + R = 5/2R$ at high temperatures