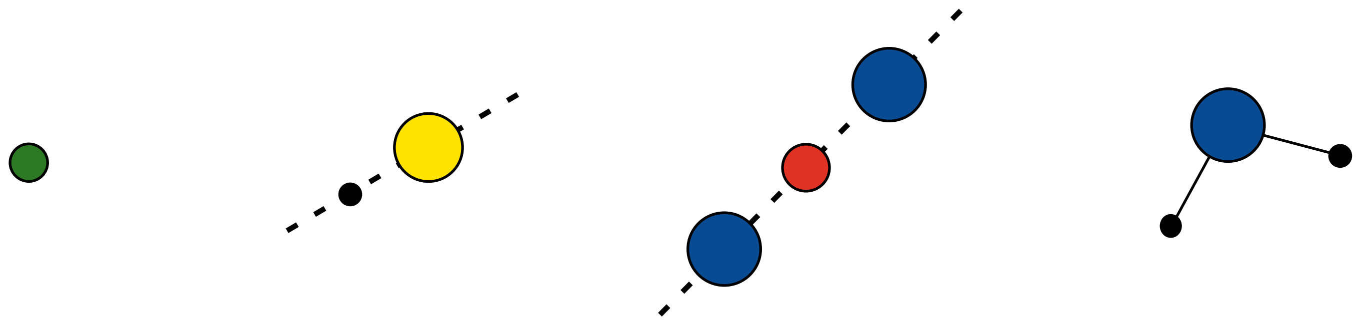
Polyatomic Gases

Non-interacting, identical $\Rightarrow Z = \frac{1}{N!} Z_1^N$ Find Z_1

Each molecule has # atoms $\Rightarrow$ 3# position coordinates

$$3\# = \underbrace{3}_{\text{C.M.}} + \underbrace{n_r}_{\text{rotation}} + \underbrace{(3\# - 3 - n_r)}_{n_v,\ \text{vibration}}$$

MONATOMIC	DIATOMIC	LINEAR TRI.	NON-LINEAR TRI.
Xe	HS	CO_2	H_2O



3	3	3	3
0	2	2	3
0	1	4	3
3	6	9	9

C.M. Motion:

Particle in a box ΔEs $\ll kT \Rightarrow$ classical

Rotation:

(H_2 $\nu_{\text{rot}} = 3.65 \times 10^{12}$ Hz $\rightarrow$ 175 K) $\Rightarrow$ Q.M.

Vibration:

(H_2 $\nu_{\text{vib}} = 1.32 \times 10^{14}$ Hz $\rightarrow 6,320$ K) $\Rightarrow$ Q.M.

$\mathcal{H} = \mathcal{H}_{\text{CM}} + \mathcal{H}_{\text{vib}} + \mathcal{H}_{\text{rot}} \Rightarrow$ problem separates

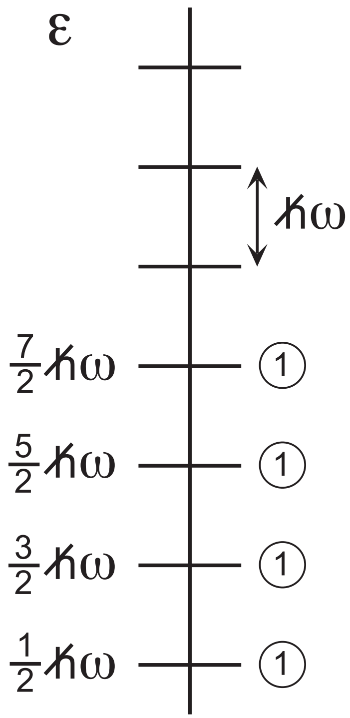
Vibration

$$\mathcal{H}_{\text{vib}} = \sum_{i=1}^{n_v} \left(\frac{1}{2} K_i \, a_i^2 + \frac{1}{2} \frac{K_i}{\omega_i^2} \, \dot{a}_i^2 \right)$$

n_v 1 dimensional harmonic oscillators, use Q.M.

$$\widehat{\mathcal{H}} \psi_n = \epsilon_n \psi_n \qquad \epsilon_n = (n + \tfrac{1}{2}) \hbar\omega \quad n = 0, 1, 2, \cdots$$

The energy levels are non-degenerate.



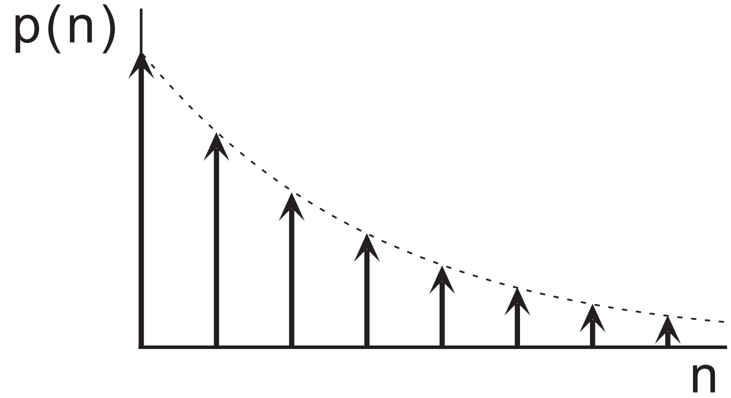
$$p(n) = e^{-(n+\frac{1}{2})\hbar\omega/kT} \Big/ \sum_{n=0}^{\infty} e^{-\epsilon_n/kT}$$

$$\sum_{n=0}^{\infty} e^{-(n+\frac{1}{2})\hbar\omega/kT} = e^{-\frac{1}{2}\hbar\omega/kT} \sum_{n=0}^{\infty} \left(e^{-\hbar\omega/kT}\right)^n$$

$$= e^{-\frac{1}{2}\hbar\omega/kT} \Big/ \left(1 - e^{-\hbar\omega/kT}\right)$$

$$p(n) = \left(1 - e^{-\hbar\omega/kT}\right)\left(e^{-\hbar\omega/kT}\right)^n = (1-b)b^n$$

Geometric or Bose-Einstein



$$< n > \;=\; \frac{b}{1-b} = \frac{1}{e^{\hbar\omega/kT} - 1}$$

$$\rightarrow \; e^{-\hbar\omega/kT} \quad \text{when} \quad kT \ll \hbar\omega$$

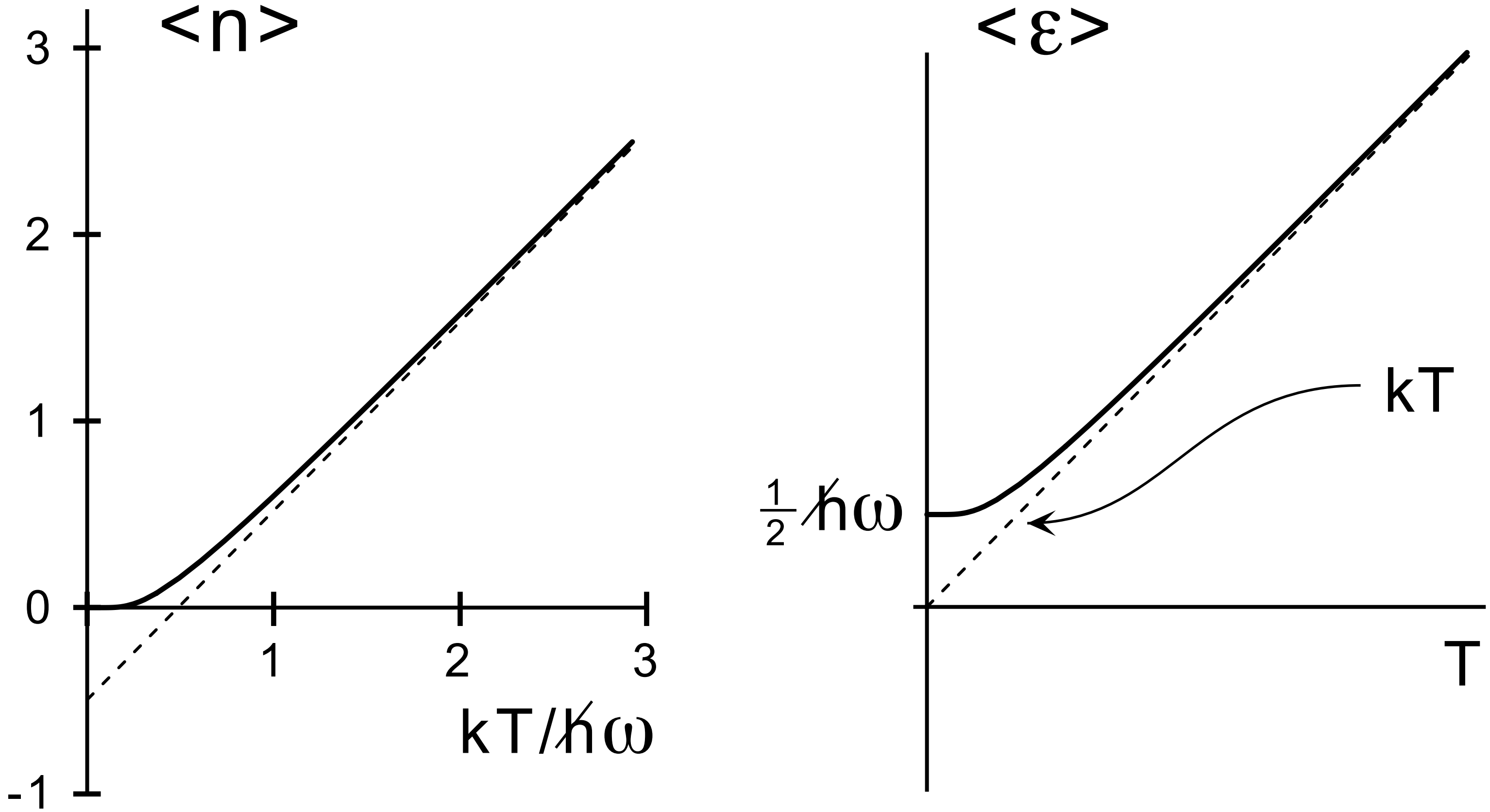
For $kT \gg \hbar\omega$ $\quad < n > \; \rightarrow \; \dfrac{1}{1 + \frac{\hbar\omega}{kT} + \frac{1}{2}\left(\frac{\hbar\omega}{kT}\right)^2 \cdots - 1}$

$$= \frac{kT}{\hbar\omega} \frac{1}{1 + \frac{1}{2}\left(\frac{\hbar\omega}{kT}\right)} \approx \frac{kT}{\hbar\omega}\left(1 - \frac{1}{2}\left(\frac{\hbar\omega}{kT}\right)\right)$$

$$= \frac{kT}{\hbar\omega} - \frac{1}{2}$$

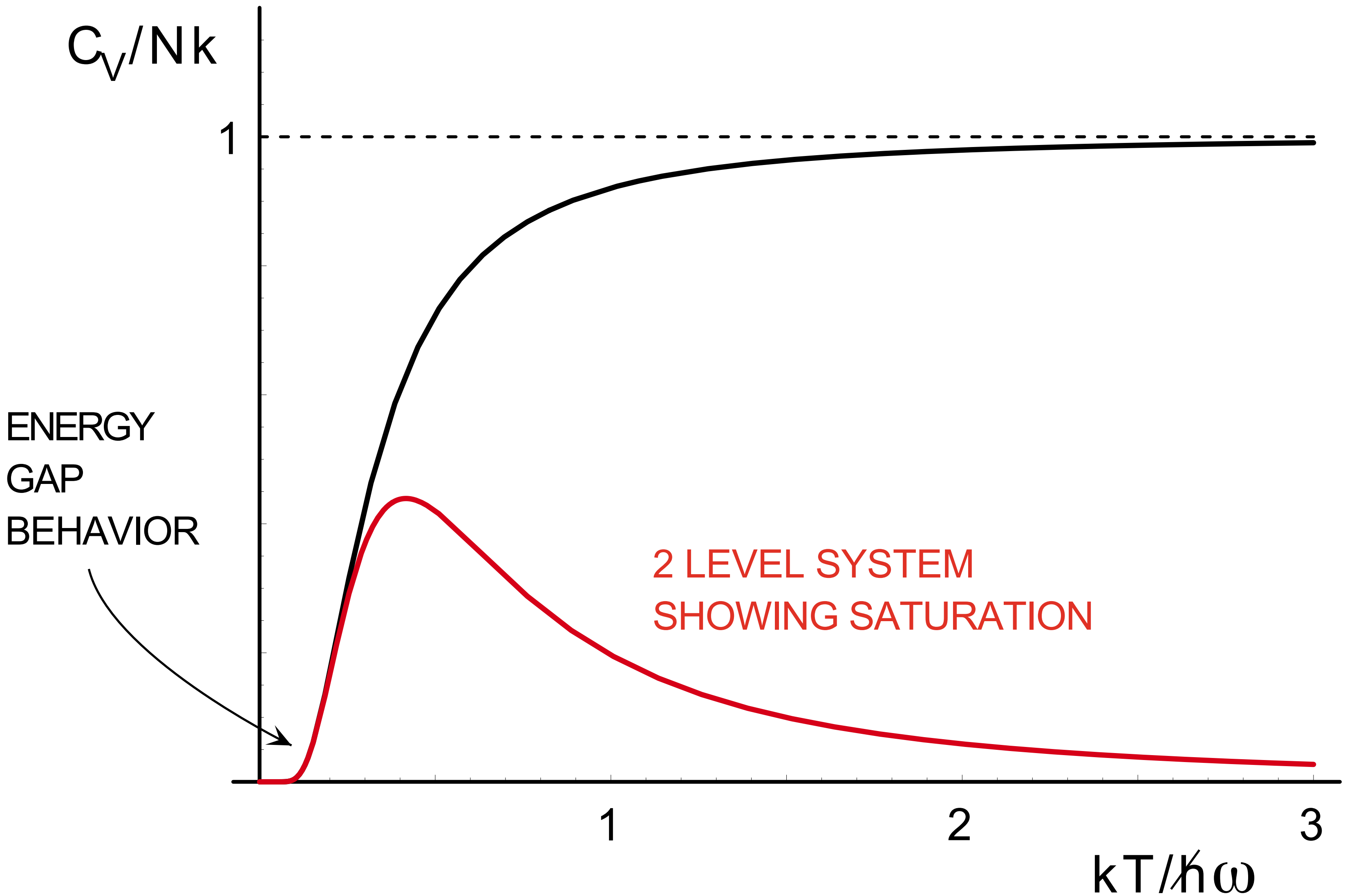
$< \epsilon >= (< n > + \frac{1}{2})\hbar\omega \;\rightarrow\; kT \quad kT \gg \hbar\omega$ (Classical)

$\rightarrow \; \frac{1}{2}\hbar\omega \quad kT \ll \hbar\omega$ (Ground state)



<n>
3
2
1
0
-1
1
2
3
kT/ħω
<ε>
kT
½ ħω
T

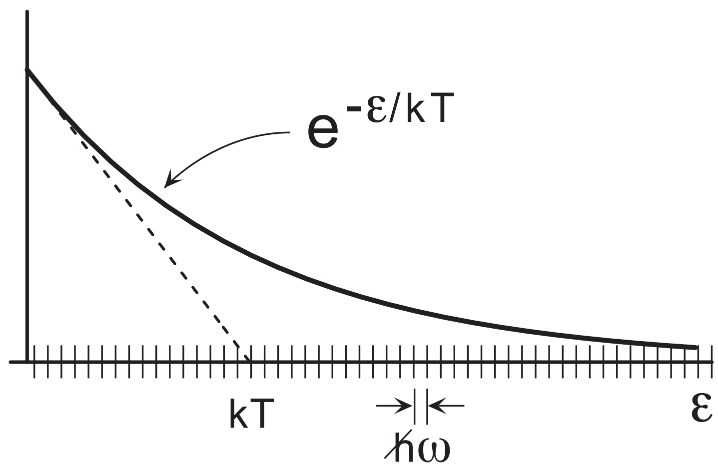
$$
\begin{aligned}
C_V &= N\left(\frac{\partial < \epsilon >}{\partial T}\right)_V = N\hbar\omega\frac{d < n >}{dT} \\
&= Nk\left(\frac{\hbar\omega}{kT}\right)^2 \frac{e^{\hbar\omega/kT}}{\left(e^{\hbar\omega/kT}-1\right)^2} \\
&\to Nk\left(\frac{\hbar\omega}{kT}\right)^2 e^{-\hbar\omega/kT} \quad kT \ll \hbar\omega \qquad (\text{energy gap behavior}) \\
&\to Nk \qquad kT \gg \hbar\omega
\end{aligned}
$$



C_V/Nk
1
ENERGY
GAP
BEHAVIOR
2 LEVEL SYSTEM
SHOWING SATURATION
1
2
3
$kT/\hbar\omega$

8.044 L14B9b

High and low temperature behavior without solving the complete problem Consider first the high T limit.



$\Delta\epsilon$ contains $\frac{\Delta\epsilon}{\hbar\omega}$ states

$$Z_1 = \sum_{n=0}^{\infty} e^{-\epsilon_n/kT}$$

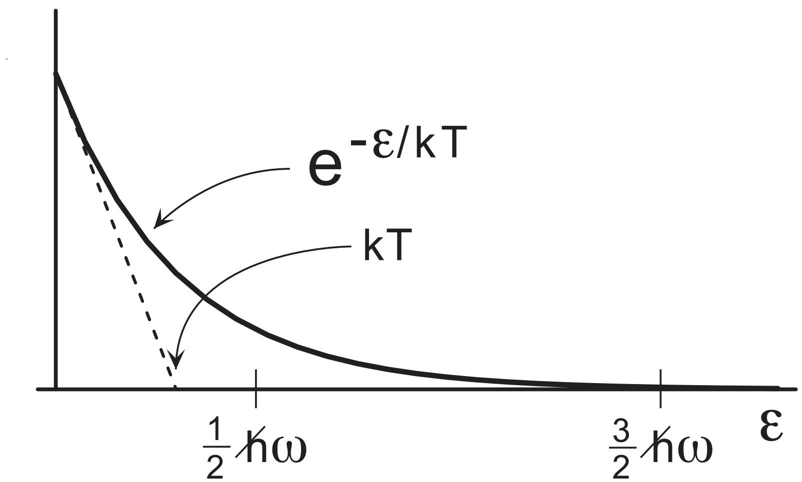
$$\approx \int_0^\infty \frac{1}{\hbar\omega} e^{-E/kT}\, dE = \frac{kT}{\hbar\omega}\int_0^\infty e^{-y}\, dy = \frac{kT}{\hbar\omega} \propto \beta^{-1}$$

$$Z_{\text{vib}} = Z_1^N \propto \beta^{-N}$$

$$U_{\text{vib}} = -\frac{1}{Z}\left(\frac{\partial Z}{\partial \beta}\right)_N = -\beta^N(-N)\beta^{-N-1} = \underline{NkT}$$

$$C_{\text{vib}} = \underline{Nk}$$

Next, consider the low T limit.



$\Rightarrow$ consider only 2 states

$$p(n=1) \approx \frac{e^{-\frac{3}{2}\hbar\omega/kT}}{e^{-\frac{1}{2}\hbar\omega/kT} + e^{-\frac{3}{2}\hbar\omega/kT}} = \frac{1}{e^{\hbar\omega/kT} + 1} \approx e^{-\hbar\omega/kT}$$

$$p(n=0) \approx 1 - e^{-\hbar\omega/kT}$$

$$< E >= \tfrac{1}{2}N\hbar\omega\left(1 - e^{-\hbar\omega/kT}\right) + \tfrac{3}{2}N\hbar\omega e^{-\hbar\omega/kT}$$

$$= \tfrac{1}{2}N\hbar\omega + N\hbar\omega e^{-\hbar\omega/kT}$$

$$C_V = \frac{\partial < E >}{\partial T} = N\hbar\omega\left(\frac{\hbar\omega}{kT^2}\right)e^{-\hbar\omega/kT} = \underline{Nk\left(\frac{\hbar\omega}{kT}\right)^2 e^{-\hbar\omega/kT}}$$

Angular Momentum in 3 Dimensions

CLASSICAL, 3 numbers: $(L_x,\ L_y,\ L_z)$; $(|\vec{L}|,\ \theta,\ \phi)$

QUANTUM, 2 numbers: magnitude and 1 component

$$\hat{\vec{L}} \cdot \hat{\vec{L}}\, \psi_{l,m} \equiv \widehat{L^2}\, \psi_{l,m} \ = \ l(l+1)\hbar^2\, \psi_{l,m} \quad l = 0, 1, 2 \cdots$$

$$\hat{L_z}\, \psi_{l,m} \ = \ m\hbar\, \psi_{l,m} \qquad m = \underbrace{l, l-1, \cdots - l}_{2l+1 \text{ values}}$$

Specification: 2 numbers l & m $\rightarrow$ $\psi_{l,m}$ or $|l, m>$

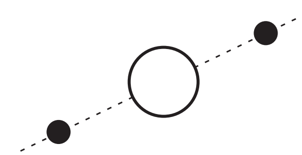
<u>Molecular rotation</u>

In general

$$\mathcal{H}_{\text{rot}} = \frac{1}{2I_1}L_1^2 + \frac{1}{2I_2}L_2^2 + \frac{1}{2I_3}L_3^2$$

For a linear molecule

$$\mathcal{H}_{\text{rot}} = \frac{1}{2I_\perp}(L_1^2 + L_2^2) = \frac{1}{2I_\perp}\vec{L}\cdot\vec{L}$$

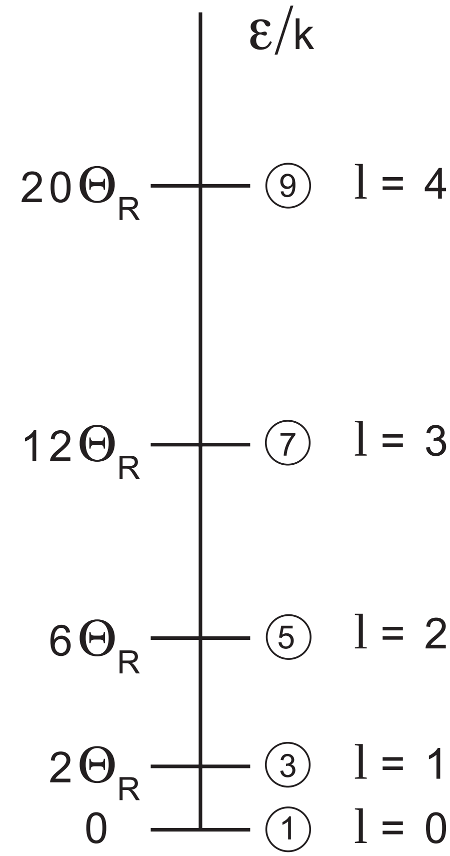


$$\begin{aligned} I_3 &= 0 \\ L_3 &= I_3\,\dot{\theta}_3 \\ &= 0 \\ I_1 &= I_2 \equiv I_\perp \end{aligned}$$

$$\hat{\mathcal{H}}_{\text{rot}} = \frac{1}{2I_\perp}\hat{L}^2$$

$$\hat{\mathcal{H}}_{\text{rot}}\,|l,m> \;=\; \epsilon_l|l,m>$$

$$=\; \frac{\hbar^2}{2I_\perp}l(l+1)|l,m>$$



ϵ_l depends on l only;

it is $2l+1$ fold degenerate.

$$\epsilon_l = k\Theta_R\, l(l+1)$$

$$\Theta_R \equiv \frac{\hbar^2}{2I_\perp k}$$ (rotational temp.)

$$p(l,m) = \frac{1}{Z_R} e^{-l(l+1)\Theta_R/T}$$

$$Z_R = \sum_{l,m} e^{-l(l+1)\Theta_R/T} = \sum_l (2l+1) e^{-l(l+1)\Theta_R/T}$$

For $T \ll \Theta_R$ $\quad Z_R \approx 1 + 3e^{-2\Theta_R/T} = 1 + 3e^{-2\Theta_R k\beta}$

$$< \epsilon >= -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = \frac{6\Theta_R\, k\, e^{-2\Theta_R k\beta}}{1 + 3e^{-2\Theta_R k\beta}} \approx 6\Theta_R\, k\, e^{-2\Theta_R/T}$$

$$C_V|_{\text{rot}} = N\frac{\partial < \epsilon >}{\partial T} = 6\Theta_R Nk \left(\frac{2\Theta_R}{T^2}\right) e^{-2\Theta_R/T}$$

$$= \underline{3Nk \left(\frac{2\Theta_R}{T}\right)^2 e^{-2\Theta_R/T}} \qquad \text{(energy gap behavior)}$$

For $T \gg \Theta_R$, convert the sum to an integral.

$$Z_R \approx \int_0^\infty (2l+1)e^{-l(l+1)\Theta_R/T}\,dl$$

$$x \equiv (l^2 + l)\Theta_R/T \qquad dx = (2l+1)\Theta_R/T\, dl$$

$$Z_R \approx \frac{T}{\Theta_R} \int_0^\infty e^{-x}\, dx = \frac{T}{\Theta_R} = \frac{1}{k\Theta_R}\beta^{-1}$$

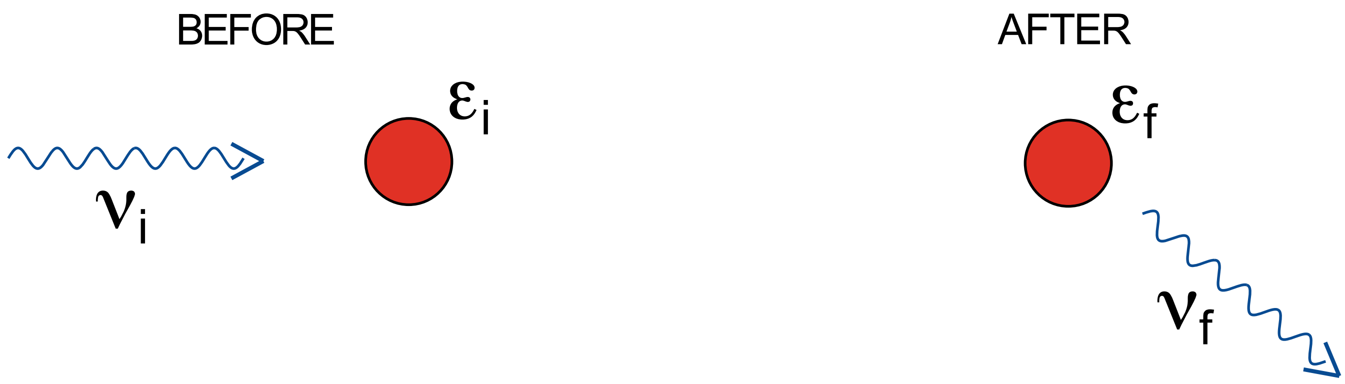
$$< \epsilon >= -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = \frac{(-1)(-1)Z/\beta}{Z} = \beta^{-1} = kT$$

$$C_V|_{\text{rot}} = N\frac{\partial < \epsilon >}{\partial T} \to Nk \qquad \text{(classical result)}$$

$$\mathcal{H} = \mathcal{H}_{\text{CM}} + \mathcal{H}_{\text{rot}} + \mathcal{H}_{\text{vib}}$$

$$C_V(T) = \underbrace{C_V|_{\text{CM}}}_{\text{all } T} + \underbrace{C_V|_{\text{rot}}}_{\text{appears at modest } T} + \underbrace{C_V|_{\text{vib}}}_{\text{only at highest } T}$$

Raman Scattering



$$\Delta\varepsilon = \varepsilon_f - \varepsilon_i = h(\nu_i - \nu_f)$$

FREQUENCY CHANGES IN THE SCATTERED LIGHT CORRESPOND TO ENERGY LEVEL DIFFERENCES IN THE SCATTERER.

WHICH ENERGY LEVEL CHANGES OCCUR DEPEND ON SELECTION RULES GOVERNED BY SYMMETRY AND QUANTUM MECHANICS

Example Rotational Raman Scattering

Selection rule: $\Delta l = \pm 2$

$$\Delta\nu_{l\uparrow} = -(k\Theta_R/h)[(l+2)(l+3) - l(l+1)]$$
$$= -(4l+6)(k\Theta_R/h)$$

$\Rightarrow$ uniform spacing between lines of $4(k\Theta_R/h)$

$I_{l\uparrow} \propto$ number of molecules with angular momentum l

$$\propto (2l+1)e^{-l(l+1)\Theta_R/T}$$

ROTATIONAL RAMAN SPECTRUM OF A DIATOMIC MOLECULE