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## Polyatomic Molecules.

For each molecule the hamiltonian will involve several degrees of freedom.

$$\tilde{H}_B = \tilde{H}_t + \tilde{H}_e + \tilde{H}_r + \tilde{H}_v$$

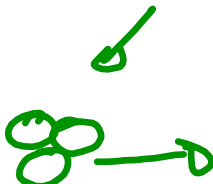
translations      electrons      vibrations

rotations

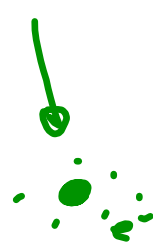
already in monatomic molecules.

The above degrees of freedom interact weakly with each other so:

$$\mathcal{E}(s) = \mathcal{E}_t(s_t) + \mathcal{E}_e(s_e) + \mathcal{E}_r(s_r) + \mathcal{E}_v(s_v)$$

  
translational

$$\mathcal{E}_t = \frac{3}{2} kT$$







relevant

$\Delta E \sim 1 \text{ eV} \Rightarrow T = 10000 \text{ K}$   
then only the ground state is relevant here.

$kT$  has units of energy and it is important to compare  $\Delta E$  (separation between quantum levels) with  $kT$ .  $1 \text{ eV} \equiv 10000 \text{ K} \Leftarrow k \cdot 10000 \text{ K} = 1 \text{ eV}$   
Boltzmann's constant.

Then for one molecule:

$$z = \sum_{s_t, s_e, s_r, s_v} e^{-\beta [\epsilon_t + \epsilon_e + \epsilon_r + \epsilon_v]} =$$

$$= z_t z_e z_r z_v$$

i) Translational:

$$z_t = \frac{V}{h^3} [2\pi \sum_i m_i kT]^{3/2}$$

For diatomic  
 $\sum_i m_i = m_1 + m_2$

Corresponds to the center of mass translation.

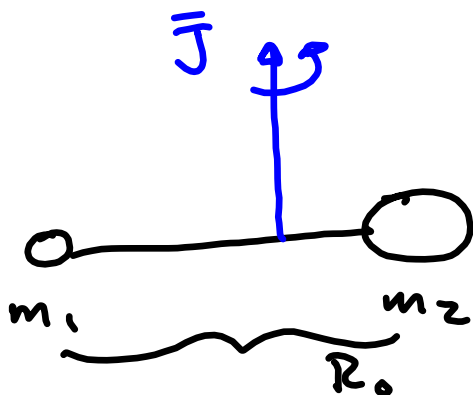
2) Electronic:

Since  $\Delta E \sim 1 \text{ eV} \sim 10,000 \text{ K}$   
 at room temperature or below only the  
 ground state matters then:

$$Z_e = \Omega_0 e^{-\beta \epsilon_{cs}}$$

constant in the sense  
 that no new  $\epsilon_r$   
 terms contribute to  $Z_e$ .

3) Rotational:



$$I = \frac{1}{2} \mu R_0^2$$

moment of inertia.

$$\vec{L} = I \vec{\omega}$$

$$L = h \bar{J}$$

We will consider the contributions of rotations about axis  $\perp$  to the molecule axis.

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad \text{reduced mass}$$

$$E_{\text{rot}} = \frac{1}{2} I \omega^2 = \frac{L^2}{2I} = \frac{(h \bar{J})^2}{2I}$$

Equation will be valid at high  $T$   
 $E_{\text{rot}} = kT$  (because there are 2  $\perp$  axes).

In quantum mechanics  $J^2 \propto J(J+1)$  with

$$J = 0, 1, 2, 3, \dots$$

$$\epsilon_r = \frac{\hbar^2}{2I} J(J+1)$$

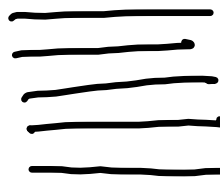
Degeneracy is given by

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

$2J+1$  possible values.

Then

$$Z_r = \sum_{J=0}^{\infty} (2J+1) e^{-\beta \frac{\hbar^2 J(J+1)}{2I}} \quad (1)$$



$$\Delta \epsilon_r \sim 10^{-4} \text{ eV} \sim 1 \text{ K}$$

then at  $T = 300 \text{ K}$   
many levels will be active.

Then the separation between levels is small and  $J$  can be considered a continuous variable.

$$u = J(J+1)$$

(1) beams

$$Z_r \approx \int_0^{\infty} du e^{-\frac{\beta \hbar^2 u}{2I}} = \frac{2I}{\beta \hbar^2}$$

If  $u_1 = u_2$  (same molecules) then

$$Z_r = \frac{I}{\beta \hbar^2} \quad (\text{we need to divide by 2 to avoid double counting}).$$

Now  $\ln Z_r = -\ln \beta + \text{constant}$

$$\bar{E}_r = -\frac{\partial \ln Z_r}{\partial \beta} = \frac{1}{\beta} = kT$$

result obtained from equipartition.

Vibration:

$$\Sigma_D(R) = -\epsilon'_0 + \frac{1}{2} b \xi^2$$

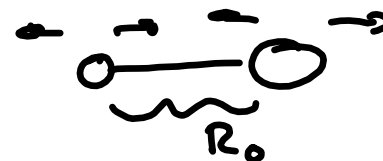
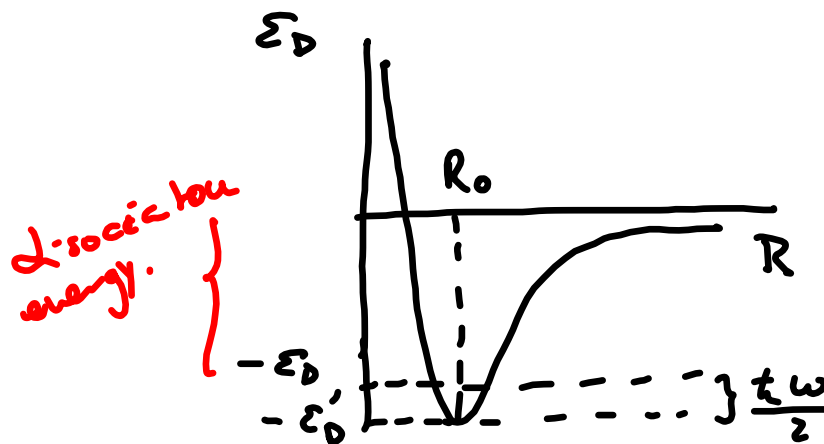
$$\xi = (R - R_0)$$

$$b = \left. \frac{\partial^2 \Sigma_D}{\partial R^2} \right|_{R_0}$$

$$K_{\text{vib}} = \frac{1}{2} \mu \dot{R}^2 = \frac{1}{2} \mu \dot{\xi}^2$$

$$\omega = \sqrt{\frac{b}{\mu}}$$

classical frequency of vibration.





The energy levels  $\epsilon_v$  will be obtained by quantizing this classical oscillator.

$$\epsilon_v = \hbar \omega \left( v + \frac{1}{2} \right) \quad v = 0, 1, 2, \dots$$

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

$\hbar \omega \sim 0.1 \text{ eV}$  for most molecules  $\sim 10^3 \text{ K}$

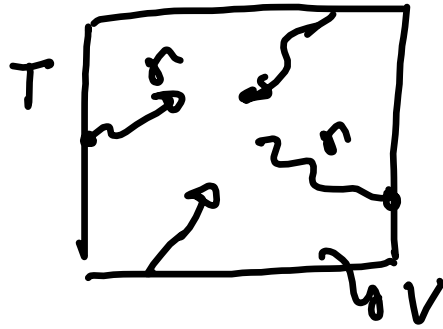
Then  $\beta \hbar \omega \gg 1$  if  $\beta \sim$  room temperature.

So as for the electrons only the ground state matters for  $Z_v$ .

$Z_0 \sim e^{-\frac{\beta \hbar \omega}{2}}$  (ground state) No classical treatment can be used.

Now you have all the ingredients to calculate properties of polyatomic molecules.

## Black-body radiation:



Photons are continuously emitted and absorbed from and by the walls in order to keep  $T$  constant.  $N$  is not well defined. The amount of radiation inside  $V$  depends on  $T$ ,

$$dE = -\bar{p} dV + T dS + \cancel{\mu dN}$$

$S=1$  for photons so they are bosons.

We found that

$$\bar{n}_s = \frac{1}{e^{\beta \epsilon_s} - 1} \quad \textcircled{1} \quad \text{B-E with } \mu=0.$$

The radiation inside the cavity consists of electromagnetic plane waves that obey the wave equation.

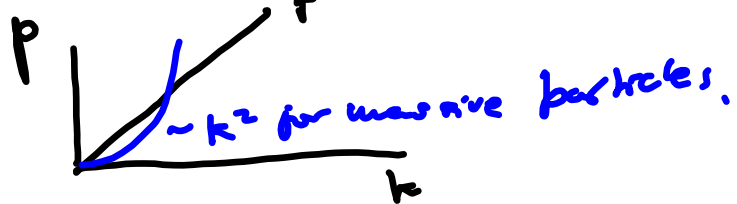
$$\nabla^2 \bar{\mathbf{E}} = \frac{1}{c^2} \frac{\partial^2 \bar{\mathbf{E}}}{\partial t^2} \quad \Rightarrow \quad \bar{\mathbf{E}} = \bar{\mathbf{A}} e^{i(\bar{\mathbf{k}} \cdot \bar{\mathbf{r}} - \omega t)} = \epsilon_0 c(\bar{\mathbf{r}}) e^{-i\omega t} \quad (2)$$

$$(3) \quad \nabla^2 \bar{\mathbf{E}} = -\frac{\omega^2}{c^2} \bar{\mathbf{E}} \quad \text{Helmholtz equation.}$$

$\underbrace{\hspace{1.5cm}}_{k^2}$

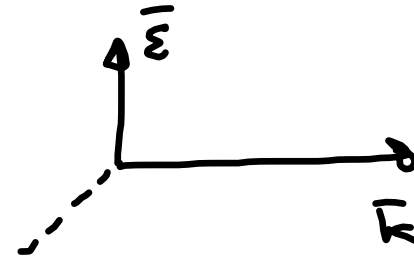
For a photon  $\epsilon = \hbar \omega$  and  $\bar{\mathbf{p}} = \hbar \bar{\mathbf{k}}$

$$|\bar{\mathbf{p}}| = \hbar |\bar{\mathbf{k}}| = \frac{\hbar \omega}{c}$$



$$\nabla \cdot \bar{\epsilon} = 0 \quad \text{Maxwell}$$

$$0 = \nabla \cdot \bar{\epsilon} = \bar{k} \cdot \bar{\epsilon} \Rightarrow \bar{k} \perp \bar{\epsilon}$$



$$\bar{n}_s \equiv \bar{n}_k = \frac{1}{e^{\beta \hbar \omega_k} - 1} = \frac{1}{e^{\beta \hbar k c} - 1} \quad \omega_k = kc$$

Let's

$f(\bar{k}) d^3k$  be the mean number of photons per unit volume with  $\bar{k}$  between  $\bar{k}$  and  $\bar{k} + d^3k$  with one specific polarization,

To find the quantized values of  $k$  we need to solve Helmholtz equation in a volume  $V$ .

$$\nabla^2 \epsilon_0 + k^2 \epsilon_0 = 0$$

Assume PBC to obtain plane wave solutions:

$$\epsilon(\vec{r}) = \epsilon(\vec{r} + L_i \hat{i})$$

$$\epsilon = \bar{A} e^{i\vec{k} \cdot \vec{r}}$$

$$e^{i k_i L_i} = 1$$

I want  $k_i L_i = 2\pi m_i$        $m_i = 0, \pm 1, \pm 2, \dots$

$$k_i = \frac{2\pi m_i}{L_i}$$

$$dk_i = \frac{2\pi \Delta m_i}{L_i}$$

$(m_x, m_y, m_z)$  characterize the energy state.

Number of states  $(n_x, n_y, n_z)$  in  $d^3k =$

$$= \frac{L_x}{2\pi} \frac{L_y}{2\pi} \frac{L_z}{2\pi} d^3k = \frac{V}{(2\pi)^3} d^3k$$

Per unit volume the number of states is just

$$\frac{d^3k}{(2\pi)^3}$$

Then

$$f(k) d^3k = \underbrace{\frac{1}{e^{\beta \hbar k c} - 1}}_{\substack{\# \text{ of photons} \\ \text{per value of } k \\ \hline \bar{n}_k}} \underbrace{\frac{d^3k}{(2\pi)^3}}_{\substack{\# \text{ degeneracy } (n_i) \text{ of} \\ \text{this value of } k.}} \quad (1)$$

The # of photons with both polarizations and  $\omega$  between  $\omega$  and  $\omega + d\omega$  is then

$$2 \int f(k) k^2 dk \underset{\substack{\text{integration} \\ \text{over } d\Omega}}{4\pi} \stackrel{\textcircled{1}}{=} \frac{2 \cdot 4\pi k^2 dk}{(e^{\beta \hbar \omega} - 1) (2\pi)^3} =$$

$$k = \omega/c$$

$$dk = \frac{d\omega}{c}$$

$$= \frac{4\pi \omega^2}{c^2 (e^{\beta \hbar \omega} - 1)} \frac{d\omega}{c} = \frac{8\pi}{(2\pi c)^3} \frac{\omega^2 d\omega}{e^{\beta \hbar \omega} - 1}$$

Average energy per unit volume  $\bar{u}$ :

$$\bar{u}(\omega, T) = \hbar \omega \cdot \frac{2 \int f(k) k^2 dk \cdot 4\pi}{(2\pi c)^3 (e^{\beta \hbar \omega} - 1)} \stackrel{\textcircled{2}}{=} \frac{8\pi \hbar \omega^3 d\omega}{(2\pi c)^3 (e^{\beta \hbar \omega} - 1)}$$

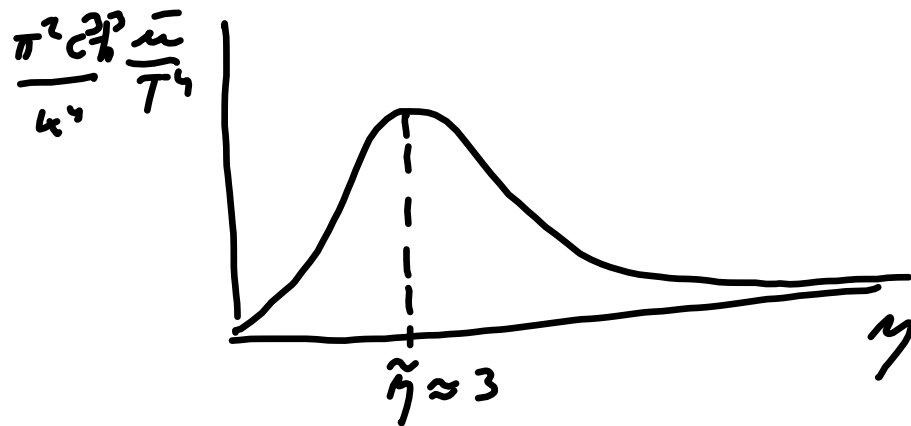


Let's define  $\eta = \beta \hbar \omega = \frac{\hbar \omega}{kT}$

$$d\eta = \beta \hbar d\omega$$

Replacing in (2):

$$\bar{u}(\eta, T) = \frac{8\pi \hbar \eta^3 d\eta}{(\beta \hbar)^4 (2\pi c)^3 (e^\eta - 1)} = \frac{\hbar}{\pi^2 c^3} \left(\frac{kT}{\hbar}\right)^4 \frac{\eta^3 d\eta}{(e^\eta - 1)}$$



Planck's distribution

$$\tilde{\eta} = \frac{\hbar \tilde{\omega}_1}{kT_1} = \frac{\hbar \tilde{\omega}_2}{kT_2}$$

$$\frac{\tilde{\omega}_1}{T_1} = \frac{\tilde{\omega}_2}{T_2} \quad \text{Wien's displacement law.}$$

$$\bar{u}_0(T) = \int_0^\infty \bar{u}(T, \omega) d\omega = \frac{\hbar}{\pi^2 c^3} \left(\frac{kT}{\hbar}\right)^4 \underbrace{\int_0^\infty \frac{\gamma^3 d\gamma}{e^\gamma - 1}}_{\frac{\pi^4}{15}}$$

$$= \frac{\pi^2}{15} \frac{(kT)^4}{(c\hbar)^3} \propto T^4 \quad \text{Stefan-Boltzmann's law.}$$

Radiation pressure:  $p_s = -\frac{\partial \mathcal{E}_s}{\partial V}$

$$\bar{p} = \sum_s \bar{u}_s \left(-\frac{\partial \mathcal{E}_s}{\partial V}\right)$$

$$\begin{aligned}\mathcal{E}_s &= \hbar \omega = \hbar c k = \hbar c (k_x^2 + k_y^2 + k_z^2)^{1/2} = \\ &= \frac{\hbar c}{L} (n_x^2 + n_y^2 + n_z^2)^{1/2}\end{aligned}$$

$$\mathcal{E}_s \propto V^{-1/3} \quad L^3 = V$$

$$\frac{\partial \mathcal{E}_s}{\partial V} = -\frac{c}{3} V^{-4/3} = -\frac{c V^{-1/3}}{3 V^{2/3}} = -\frac{\mathcal{E}_s}{3V}$$

$$\bar{p} = \sum_s \bar{n}_s \frac{\mathcal{E}_s}{3V} = \frac{\bar{E}}{3V} = \frac{\bar{u}_0}{3}$$