So far we've derived q_{atomic}

$\varepsilon_{atom} = \varepsilon_{translation} + \varepsilon_{electronic}$

$q_{atom} = q_{trans} * q_{electronic}$

$\varepsilon_{trans} = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right)$ ← particle in a box

$$q_{trans} = \sum_{n_x=1}^{\infty}\sum_{n_y=1}^{\infty}\sum_{n_z=1}^{\infty} e^{-\frac{\beta h^2}{8ma^2}\left(n_x^2+n_y^2+n_z^2\right)}$$

Big Box assumption

$$\approx \left(\int_0^{\infty} e^{-\beta h^2 n^2/8ma^2}\, dn\right)^3$$

$$\boxed{q_{trans}(V,T) = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V \quad \Rightarrow \quad \varepsilon_{trans} = \frac{3}{2} k_B T}$$

Also: $q_{elect} = g_1 + g_2 e^{-\beta(E_2-E_1)} + g_3 e^{-\beta(E_3-E_1)}$

g_1, g_2, g_3: Degeneracies

E_1: setting 0 of energy to ground electronic state

Now, for collective properties:

$$Q(N,V,T) = \frac{\left[q_{trans}(V,T)\, q_{elect}(T)\right]^N}{N!}$$

$$U = \langle E \rangle = -\left(\frac{\partial \ln Q}{\partial \beta}\right)$$

U: thermodynamic symbol for internal energy

to do this, we need $\ln Q$:

$$\ln Q = N\left[\ln q_{trans} + \ln q_{elect}\right] - \ln N!$$

$$= N\left[\frac{3}{2}\ln\left(\frac{2\pi m}{\beta h^2}\right) + \ln V + \ln q_{elect}\right] - \ln N!$$

$$\left(\frac{\partial \ln Q}{\partial \beta}\right) = \frac{3N}{2}\left(\frac{\beta h^2}{2\pi m}\right)\left(\frac{2\pi m}{h^2}\right)\left(\frac{-1}{\beta^2}\right) + \frac{N\left(\frac{\partial q_{elect}}{\partial \beta}\right)}{q_{elect}}$$

← mostly very small

$$U = \frac{3Nk_BT}{2} + \frac{N\left(g_2 e^{-\beta(\varepsilon_2-\varepsilon_1)} + \cdots\right)}{q_{elect}}$$

$$U \simeq \frac{3}{2}RT$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} = \frac{3}{2}R$$

One other interesting feature Pressure $= k_BT\left(\frac{\partial \ln Q}{\partial V}\right)_{N,T}$

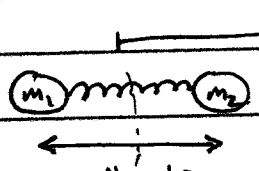
$$P = k_BT\,\frac{\partial}{\partial V}\left\{\left[\frac{3}{2}\ln\left(\frac{2\pi m}{\beta h^2}\right) + \ln V + \ln q_{elec}\right] - \ln N!\right\}$$

$$\boxed{P = k_BT \cdot \frac{1}{V}}$$

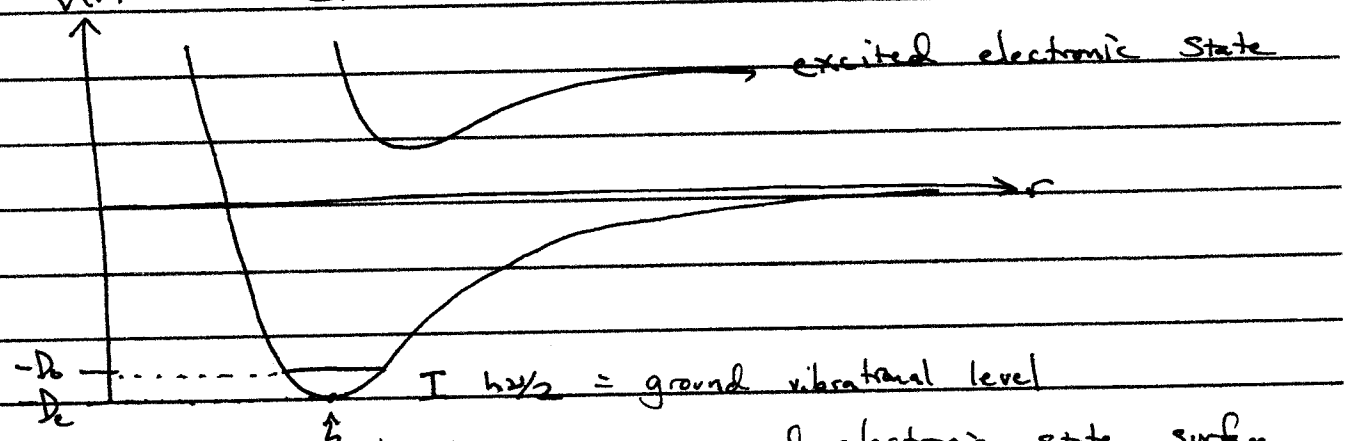
← ideal gas law is a result of particle in a box energy levels!

Diatomic Molecules

4 kinds of motion:



+ electronic excitation



D_e = dissociation energy from bottom of electronic state

D_0 = dissociation energy from lowest vibrational state

We'll leave: $q_{elect} = \sum_i g_i e^{-\beta \varepsilon_i}$

ε_i = energy of level i

g_i = degeneracy of level

Note that for molecules the 0 of energy is taken to be the dissociated atoms, not 0 for ground state

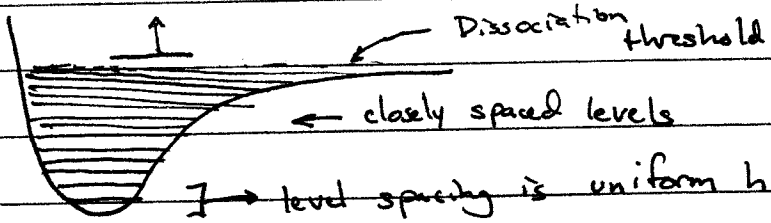
Translation is identical to atoms:

$$q_{trans} = \left(\frac{2\pi (m_1+m_2) k_B T}{h^2}\right)^{3/2} V$$

(m_1+m_2 = total mass)

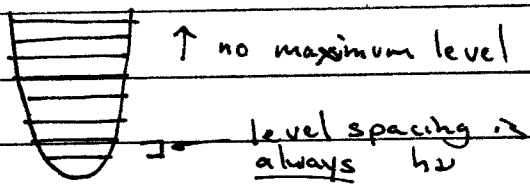
Rotation & Translation are new.

Vibrational Motion



$$E_v = (v+\tfrac{1}{2})h\nu - h\nu x_e (v+\tfrac{1}{2})^2$$ ← levels for a Morse oscillator

The Harmonic model



$$E_v = (v+\tfrac{1}{2})h\nu$$

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

$$q_{vib} = \sum_{v=0}^{\infty} e^{-\beta h\nu(v+\frac{1}{2})}$$

$e^{-\beta h\nu(v+\frac{1}{2})}$ ← Boltzmann factor for that state

↑ sum over states

$$= \sum_{v=0}^{\infty} e^{-\beta h\nu/2} e^{-\beta h\nu v}$$ ← first factor does not depend on v

$$= e^{-\beta h\nu/2} \sum_{v=0}^{\infty} e^{-\beta h\nu v}$$ Let $X = e^{-\beta h\nu}$

$$= \sqrt{X} \sum_{v=0}^{\infty} X^v$$ ← This is a geometric series!

$$= \sqrt{X}\,\frac{1}{1-X}$$

$$q_{vib} = \frac{e^{-\beta h\nu/2}}{1-e^{-\beta h\nu}} = \frac{e^{-h\nu/2k_BT}}{1-e^{-h\nu/k_BT}}$$

$\frac{h\nu}{k_B}$ has units of temperature

$\Theta_{vib} = \frac{h\nu}{k_B}$ ← constant; ← property of molecule

= "vibrational" temperature ← constant

$q_{vib} = \frac{e^{-\Theta_{vib}/2T}}{1 - e^{-\Theta_{vib}/T}}$ ← functional form is independent of molecular species!

Also: $h\nu = \hbar\omega = \hbar\sqrt{\frac{k}{\mu}}$ ← spring constant; ← reduced mass

$\mu = \frac{m_1 m_2}{m_1 + m_2}$

Average vibrational energy:

$$\langle E_{vib} \rangle = -N\left(\frac{\partial \ln q_{vib}}{\partial \beta}\right) = N k_B T^2 \left(\frac{\partial \ln q_{vib}}{\partial T}\right)$$

$$= N k_B \left(\frac{\Theta_{vib}}{2} + \frac{\Theta_{vib}}{e^{\Theta_{vib}/T} - 1}\right)$$

$$C_V = \frac{\partial \langle E_{vib} \rangle}{\partial T} = R \left(\frac{\Theta_{vib}}{T}\right)^2 \frac{e^{-\Theta_{vib}/T}}{\left(1 - e^{-\Theta_{vib}/T}\right)^2}$$