

## Classical ideal gas with internal degrees of freedom

assume  $m\lambda^3 \ll 1$  so molecules are classical as far as their translational motion is concerned

$$\Rightarrow Q_N = \frac{1}{N!} [Q_1]^N$$

$Q_1$  is single molecule partition function

Suppose molecule has internal degrees of freedom, so that its energy is

$$\frac{p^2}{2m} + \epsilon_i \quad \text{where } \epsilon_i \text{ are the internal energy levels}$$

Then

$$Q_1 = \int \frac{d^3r}{h^3} \int d^3p \sum_i e^{-\beta(\frac{p^2}{2m} + \epsilon_i)}$$

$$= \frac{V}{\lambda^3} \sum_i e^{-\beta \epsilon_i}$$

$$\lambda = \left( \frac{h^2}{2\pi m k_B T} \right)^{1/2}$$

sum over all internal states of molecule

$$\text{let } g = \sum_i e^{-\beta \epsilon_i}$$

$$\text{then } Q_1 = \frac{V}{\lambda^3} g$$

$$Q_N = \frac{1}{N!} \left[ \frac{V}{\lambda^3} g \right]^N$$

$$= Q_N^{(0)} g^N$$

$$Q_N^{(0)} = \frac{1}{N!} \left[ \frac{V}{\lambda^3} \right]^N$$

↑ partition function for point particle

## Helmholtz free energy

$$A(T, V, N) = -k_B T \ln Q_N$$

$$= -k_B T \ln Q_N^{(0)} - k_B T \ln q^N$$

$$= A^{(0)} - k_B T N \ln q$$

↑ free energy for point particles  
↖ free energy of internal degrees of freedom

effect of internal degrees of freedom are additive to free energy

$$A = A^{(0)} + A_{\text{int}}$$

$$A_{\text{int}} = -k_B T N \ln q$$

Note:  $q$  has no dependence on  $N$  or  $V$ ; only depends on  $T$ .

$$\Rightarrow \text{pressure } p = -\frac{\partial A}{\partial V} = \frac{\partial A^{(0)}}{\partial V} \quad \text{unaffected by internal degrees of freedom}$$

## chemical potential

$$\mu = +\frac{\partial A}{\partial N} = \frac{\partial A^{(0)}}{\partial N} - k_B T \ln q$$

$$= \mu^{(0)} + \mu_{\text{int}}$$

$$\mu_{\text{int}} = -k_B T \ln q$$

internal degrees of freedom add  $T$ -dependent constant to  $\mu$

## entropy

$$S = -\frac{\partial A}{\partial T} = -\frac{\partial A^{(0)}}{\partial T} + \frac{\partial}{\partial T} (k_B T N \ln q)$$

$$S = S^{(0)} + N k_B \ln q + N k_B T \frac{\partial}{\partial T} \ln q$$
$$= S^{(0)} + S_{\text{int}}$$

energy

$$\begin{aligned} A &= E - TS \\ \rightarrow E &= A + TS \\ &= E^{(0)} + A_{int} + TS_{int} \\ &= E^{(0)} + E_{int} \end{aligned}$$

$$\begin{aligned} E_{int} &= -k_B T N \ln q + T N k_B \ln q + N k_B T^2 \frac{\partial \ln q}{\partial T} \\ &= N k_B T^2 \frac{\partial \ln q}{\partial T} \end{aligned}$$

specific heat

$$C_V = \left( \frac{\partial E}{\partial T} \right)_{V, N} = C_V^{(0)} + C_{V, int}$$

$$\begin{aligned} C_{V, int} &= \frac{\partial}{\partial T} \left( N k_B T^2 \frac{\partial \ln q}{\partial T} \right) \\ &= 2 N k_B T \frac{\partial \ln q}{\partial T} + N k_B T^2 \frac{\partial^2 \ln q}{\partial T^2} \end{aligned}$$

The internal degrees of freedom can often be separated into different physical sources

- 1) electronic excitation
  - 2) vibrational excitation of bonds
  - 3) rotational motion of ~~some~~ molecule
- In many cases these different modes of excitation are only weakly interacting so one can write

$$E_i = E_{elec} + E_{vib} + E_{rot}$$

$$\begin{aligned} \Omega &= \sum_i e^{-\beta(E_{elec} + E_{vib} + E_{rot})} = \left( \sum_{i_{elec}} e^{-\beta E_{elec}} \right) \left( \sum_{i_{vib}} e^{-\beta E_{vib}} \right) \\ &\quad \times \left( \sum_{i_{rot}} e^{-\beta E_{rot}} \right) \end{aligned}$$

where  $i_{elec}$ ,  $i_{vib}$ ,  $i_{rot}$  stand for the quantum numbers associated with the electronic, vibrational, and rotational degrees of freedom

$$Q = Q_{elec} Q_{vib} Q_{rot}$$

$$A_{int} = A_{elec} + A_{vib} + A_{rot}$$

example

A monoatomic gas - particles are single atoms. internal degrees of freedom are excitations to higher electron levels. Electronic excitation energies are  $\sim 1 \text{ eV} \sim 10^4 \text{ K}$  so at room temperatures, only the lowest excited states can be populated.

$$Q \approx g_0 e^{-\beta \epsilon_0} + g_1 e^{-\beta \epsilon_1}$$

where  $\epsilon_0$  and  $\epsilon_1$  are energies of ground + 1st excited states, and  $g_0$  and  $g_1$  are their degeneracies

$$Q = g_0 e^{-\beta \epsilon_0} \left( 1 + \frac{g_1}{g_0} e^{-\beta \Delta \epsilon} \right) \quad \Delta \epsilon = \epsilon_1 - \epsilon_0$$

$$A_{int} = -k_B T N \ln \left( 1 + \frac{g_1}{g_0} e^{-\beta \Delta \epsilon} \right) + N \epsilon_0 - k_B T N \ln g_0$$

$$C_{v \text{ int}} = \frac{\partial}{\partial T} (N k_B T^2 \frac{\partial}{\partial T} \ln Z)$$

$$= \frac{\partial}{\partial T} (N k_B T^2 \frac{\partial}{\partial T} (\ln g_0 - \frac{\epsilon_0}{k_B T} + \ln(1 + \frac{g_1}{g_0} e^{-\beta \Delta \epsilon})))$$

$$= \frac{\partial}{\partial T} (N k_B T^2 \left[ \frac{\epsilon_0}{k_B T^2} + \frac{\frac{g_1}{g_0} e^{-\beta \Delta \epsilon} (\frac{\Delta \epsilon}{k_B T^2})}{1 + \frac{g_1}{g_0} e^{-\beta \Delta \epsilon}} \right])$$

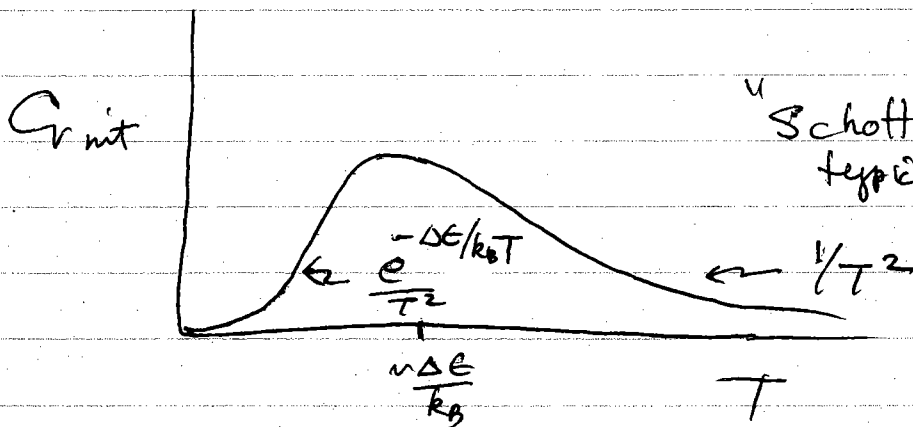
$$= N \frac{\partial}{\partial T} \left[ \epsilon_0 + \frac{\Delta \epsilon (\frac{g_1}{g_0}) e^{-\beta \Delta \epsilon}}{1 + \frac{g_1}{g_0} e^{-\beta \Delta \epsilon}} \right]$$

$$= N \Delta \epsilon (\frac{g_1}{g_0}) \frac{[1 + \frac{g_1}{g_0} e^{-\beta \Delta \epsilon}] e^{-\beta \Delta \epsilon} (\frac{\Delta \epsilon}{k_B T^2}) - e^{-\beta \Delta \epsilon}}{[1 + \frac{g_1}{g_0} e^{-\beta \Delta \epsilon}]^2}$$

$\times (\frac{g_1}{g_0}) e^{-\beta \Delta \epsilon} \frac{\Delta \epsilon}{k_B T^2}$

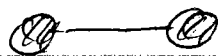
~~is not~~

$$C_{v \text{ int}} = N k_B \left( \frac{\Delta \epsilon}{k_B T} \right)^2 \left( \frac{g_1}{g_0} \right) \frac{e^{-\beta \Delta \epsilon}}{[1 + \frac{g_1}{g_0} e^{-\beta \Delta \epsilon}]^2}$$



"Schottky anomaly"  
typical of excitation of one energy level

## Diatonic molecules



vibrational excitations

$$E_{\text{vib}} = (n + 1/2) \hbar \omega_0$$

$\omega_0$  is vibrational frequency related to stiffness of bond + mass of atoms.  $\omega_0 = \sqrt{k/m}$

$$q_{\text{vib}} = \sum_{n=0}^{\infty} e^{-\beta(n+1/2)\hbar\omega_0} = e^{-\beta\hbar\omega_0/2} \sum_{n=0}^{\infty} \left[ e^{-\beta\hbar\omega_0} \right]^n$$

$$q_{\text{vib}} = \frac{e^{-\beta\hbar\omega_0/2}}{1 - e^{-\beta\hbar\omega_0}} = \frac{1}{e^{\beta\hbar\omega_0/2} - e^{-\beta\hbar\omega_0/2}}$$
$$= \frac{1}{2 \sinh(\beta\hbar\omega_0/2)}$$

$$C_{\text{vib}} = \frac{\partial}{\partial T} \left( N k_B T^2 \frac{\partial}{\partial T} \ln q_{\text{vib}} \right)$$

$$= \frac{\partial}{\partial T} \left( N k_B T^2 \frac{\partial}{\partial T} \left[ -\ln \left( \frac{e^{\beta\hbar\omega_0/2} - e^{-\beta\hbar\omega_0/2}}{2} \right) \right] \right)$$

$$= \frac{\partial}{\partial T} \left( N k_B T^2 (-1) \frac{\left( -\frac{\hbar\omega_0}{2k_B T^2} \right) e^{\beta\hbar\omega_0/2} - \left( \frac{\hbar\omega_0}{2k_B T^2} \right) e^{-\beta\hbar\omega_0/2}}{e^{\beta\hbar\omega_0/2} - e^{-\beta\hbar\omega_0/2}} \right)$$

$$= \frac{\partial}{\partial T} \left( N k_B T^2 \frac{\hbar\omega_0}{2k_B T^2} \frac{e^{\beta\hbar\omega_0/2} + e^{-\beta\hbar\omega_0/2}}{e^{\beta\hbar\omega_0/2} - e^{-\beta\hbar\omega_0/2}} \right)$$

$$= \frac{N \hbar \omega_0}{2} \frac{\partial}{\partial T} \left( \coth \left( \frac{\beta \hbar \omega_0}{2} \right) \right)$$

$$C_{vib} = \frac{N\hbar\omega_0}{2} \frac{[\sinh^2(\frac{\beta\hbar\omega_0}{2}) - \cosh^2(\frac{\beta\hbar\omega_0}{2})]}{\sinh^2(\frac{\beta\hbar\omega_0}{2})} \left(-\frac{\hbar\omega_0}{2k_B T^2}\right)$$

$$= Nk_B \left(\frac{\hbar\omega_0}{k_B T}\right)^2 \frac{1}{4} \frac{1}{\sinh^2(\frac{\beta\hbar\omega_0}{2})}$$

$$C_{vib} = Nk_B \left(\frac{\hbar\omega_0}{k_B T}\right)^2 \frac{e^{\beta\hbar\omega_0}}{[e^{\beta\hbar\omega_0} - 1]^2}$$

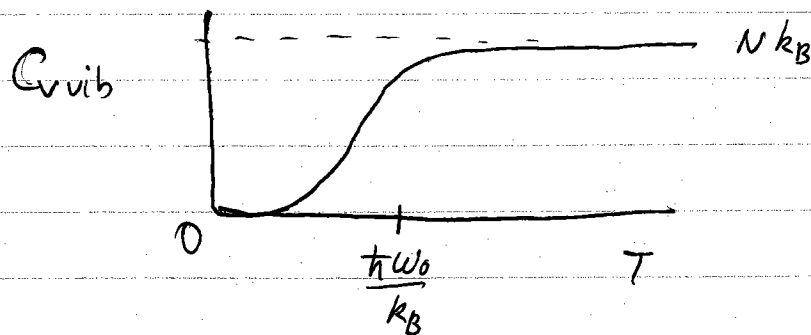
For ~~high~~  $\beta\hbar\omega_0 = \frac{\hbar\omega_0}{k_B T} \ll 1$  at high temp

$$C_{vib} \approx Nk_B \left(\frac{\hbar\omega_0}{k_B T}\right)^2 \frac{1}{\left(\frac{\hbar\omega_0}{k_B T}\right)^2} = Nk_B$$

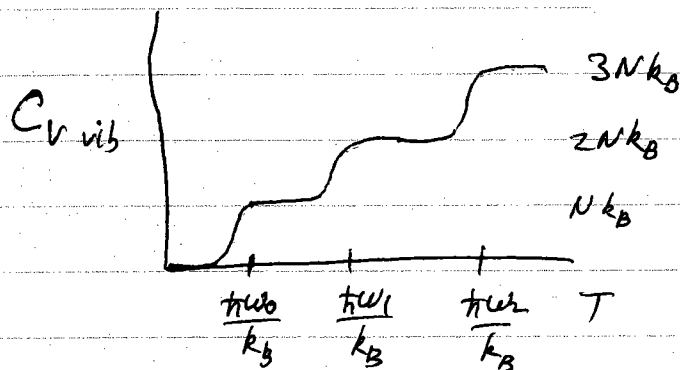
classical equipartition result

At low T,  $\beta\hbar\omega_0 \gg 1$

$$C_{vib} \approx Nk_B \left(\frac{\hbar\omega_0}{k_B T}\right)^2 e^{-\hbar\omega_0/k_B T}$$



for a polyatomic molecule with many bonds of freq  $\omega_0 < \omega_1 < \omega_2$ ,  $C_{vib}$  is just sum of terms for each bond



### Rotational degree of freedom

$$H_{rot} = \frac{\hbar^2 L^2}{2I}$$

$L$  = angular momentum  
 $I$  = moment of inertia  
 for diatomic molecule

$$I = \mu R^2 \quad \mu = \frac{m_1 m_2}{m_1 + m_2} \text{ reduced mass}$$

$$E_{rot} = \frac{l(l+1)\hbar^2}{2I}$$

$$g_{rot} = \sum_{l=0}^{\infty} (2l+1) e^{-\beta l(l+1)\hbar^2/2I}$$

↑  
 degeneracy of angular momentum eigenvalue  $l$

$$\approx \int_0^{\infty} dl (2l+1) e^{-\beta l(l+1)\hbar^2/2I}$$

↑  
 good when

$$\text{let } x = l(l+1)$$

$$dx = (2l+1) dl$$

$$\frac{\beta \hbar^2}{2I} \ll 1 \quad \text{i.e. } k_B T \text{ larger than level spacing}$$



$$g_{\text{rot}} = \int_0^{\infty} dx e^{-\beta \hbar^2 x^2 / 2I} = \frac{2I}{\beta \hbar^2} = \frac{2I k_B T}{\hbar^2} = \frac{T}{\Theta_R}$$

$$\text{where } \Theta_R = \frac{\hbar^2}{2I k_B}$$

$$C_{V, \text{rot}} = \frac{\partial}{\partial T} (N k_B T^2 \frac{\partial}{\partial T} \ln g_{\text{rot}})$$

$$= \frac{\partial}{\partial T} (N k_B T^2 \frac{\partial}{\partial T} \ln (T/\Theta_R))$$

$$= \frac{\partial}{\partial T} (N k_B T^2 \frac{1}{T}) = N k_B \quad \text{classical equipartition result.}$$

To do better than approx sum by integral use Euler-Maclaurin series

$$\sum_{n=0}^{\infty} f(n) = \int_0^{\infty} f(x) dx + \frac{1}{2} f(0) - \frac{1}{12} f'(0) + \frac{1}{720} f'''(0) + \dots$$

$$\text{using } f(x) = (2x+1) \exp(-x(x+1) \Theta_R/T)$$

$$\Rightarrow g_{\text{rot}} = \frac{T}{\Theta_R} + \frac{1}{3} + \frac{1}{15} \frac{\Theta_R}{T} + \frac{4}{315} \left(\frac{\Theta_R}{T}\right)^2 + \dots$$

↑  
used a version of this when did Landau diamagnetism

$$C_{V, \text{rot}} = N k_B \left\{ 1 + \frac{1}{45} \left(\frac{\Theta_R}{T}\right)^2 + \frac{16}{945} \left(\frac{\Theta_R}{T}\right)^3 + \dots \right\}$$

For low T, then  $\frac{\beta \hbar^2}{2I} \gg k_B T$  or  $\Theta_R \gg T$   
the first few terms of  $\sum \frac{e^{-\beta \hbar^2 x^2 / 2I}}$  give

$$g_{\text{rot}} \approx 1 + 3 e^{-2\Theta_R/T} + 5 e^{-6\Theta_R/T} + \dots$$

$$C_{v, \text{rot}} \approx 12 N k_B \left( \frac{\theta_R}{T} \right)^2 e^{-2\theta_R/T}$$

