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

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

Q_1 is single molecule partition function

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

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

Then

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

$$= \frac{V}{\lambda^3} \sum_i e^{-\beta \epsilon_i} \qquad \lambda = \left(\frac{h^2}{2\pi m k_B T}\right)^{1/2}$$

sum over all
internal states
of molecule

let $\quad q = \sum_i e^{-\beta \epsilon_i}$

then $\quad Q_1 = \frac{V}{\lambda^3} q$

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

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

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

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

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

chemical potential

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

$$= \mu^{(0)} + \mu_{int} \qquad \mu_{int} = -k_B T \ln q$$

internal degrees of freedom add T-dependent constant to μ

entropy

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

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

$$= S^{(0)} + S_{int}$$

energy

$$A = E - TS$$

$$\Rightarrow \quad E = A + TS$$

$$= E^{(0)} + A_{int} + T S_{int}$$

$$= E^{(0)} + E_{int}$$

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

$$= N k_B T^2 \frac{\partial}{\partial T} \ln q$$

specific heat

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

independent of V

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

$$= 2 N k_B T \frac{\partial}{\partial T} \ln q + N k_B T^2 \frac{\partial^2}{\partial T^2} \ln q$$

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 ~~mom~~ molecule

In many cases these different modes of excitation are only weakly interacting so one can write

$$\epsilon_i = \epsilon_{elec} + \epsilon_{vib} + \epsilon_{rot}$$

$$q = \sum_i e^{-\beta (\epsilon_{elec} + \epsilon_{vib} + \epsilon_{rot})} = \left(\sum_{i\,elec} e^{-\beta \epsilon_{elec}} \right) \left(\sum_{i\,vib} e^{-\beta \epsilon_{vib}} \right)$$

$$\times \left(\sum_{i\,rot} e^{-\beta \epsilon_{rot}} \right)$$

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 $O(1 ev) \sim O(10^4 \, ^\circ K)$ so at room temperatures, only the lowest excited states can be populated.

$$q \simeq g_0 \, e^{-\beta \epsilon_0} + g_1 \, e^{-\beta \epsilon_1}$$

where ϵ_0 and ϵ_1 are energies of ground + 1st excited states, and g_0 and g_1 are their degeneracies

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

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

$$C_{V \, int} = \frac{\partial}{\partial T}\left(N k_B T^2 \frac{\partial}{\partial T} \ln \xi\right)$$

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

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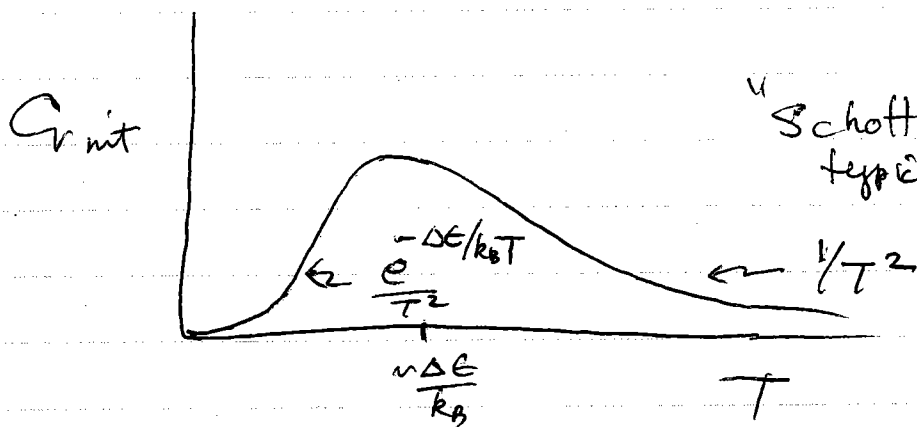
$$= N \frac{\partial}{\partial T}\left[\epsilon_0 + \frac{\Delta \epsilon \, (g_1/g_0) e^{-\beta \Delta \epsilon}}{1 + g_1/g_0 \, e^{-\beta \Delta \epsilon}}\right]$$

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

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

$$= N \Delta \epsilon$$

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

$C_{V \, int}$

$\leftarrow \frac{e^{-\Delta \epsilon/k_B T}}{T^2}$

$\leftarrow 1/T^2$

$\sim \frac{\Delta \epsilon}{k_B}$

T

"Schottky anomaly" typical of excitation of one energy level

Diatomic molecules $\bigcirc\!-\!\bigcirc$

vibrational excitations

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

ω_0 is vibrational frequency related to stiffness of bond + mass of atoms. $\omega_0 = \sqrt{K/_{2m}}$

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

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

$$= \frac{1}{2\sinh(\beta\hbar\omega_0/2)}$$

$$C_{V\,vib} = \frac{\partial}{\partial T}\left(Nk_BT^2 \frac{\partial}{\partial T}\ln q_{vib}\right)$$

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

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

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

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

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

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

$$C_{v \cdot vib} = N k_B \left(\frac{\hbar\omega_0}{k_BT}\right)^2 \frac{e^{\beta\hbar\omega_0}}{\left[e^{\beta\hbar\omega_0}-1\right]^2}$$

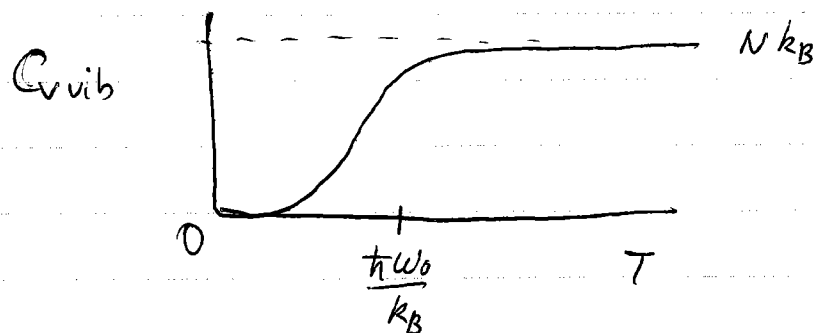For ~~that~~ $\beta\hbar\omega_0 = \frac{\hbar\omega_0}{k_BT} \ll 1$ ie high temp

$$C_{v \cdot vib} \simeq N k_B \left(\frac{\hbar\omega_0}{k_BT}\right)^2 \frac{1}{\left(\frac{\hbar\omega_0}{k_BT}\right)^2} = N k_B$$
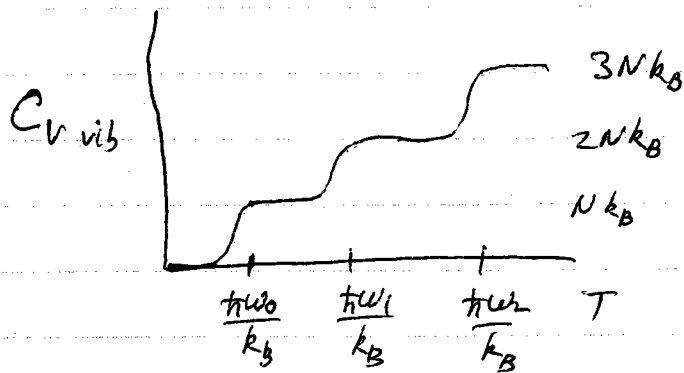
classical equipartition result
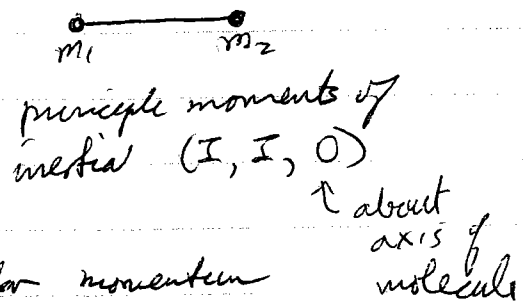
At low T, $\beta\hbar\omega_0 \gg 1$

$$C_{v \cdot vib} \simeq N k_B \left(\frac{\hbar\omega_0}{k_BT}\right)^2 e^{-\hbar\omega_0/k_BT}$$

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

Rotational degree of freedom

principle moments of
inertia $(I, I, 0)$

$\uparrow$ about
axis of
molecule

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

L = angular momentum

I = moment of inertia

for diatomic molecule

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

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

$$\mathcal{Z}_{rot} = \sum_{\ell=0}^{\infty} (2\ell+1) e^{-\beta \ell(\ell+1)\hbar^2/2I}$$

$\uparrow$
degeneracy of angular momentum
eigenvalue ℓ

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

$\nearrow$
good when

let $x = \ell(\ell+1)$

$dx = (2\ell+1) d\ell$

$\beta \frac{\hbar^2}{2I} \ll 1$ ie $k_B T$ larger then level spacing

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

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

$$C_{v\,rot} = \frac{\partial}{\partial T} \left(N k_B T^2 \frac{\partial}{\partial T} \ln q_{rot} \right)$$

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

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

(2 rotational degrees of freedom)

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

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

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

used a version of this when did Landau diamagnetism

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

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

For low T, therefore $\frac{\beta \hbar^2}{2I} \gg k_B T$ or $\Theta_R \gg T$

the first few terms of $\sum_e$ give

$$q_{rot} = 1 + 3 e^{-2\Theta_R/T} + 5 e^{-6\Theta_R/T} + \cdots$$

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

$C_{v\,rot}$

θ_R T

1