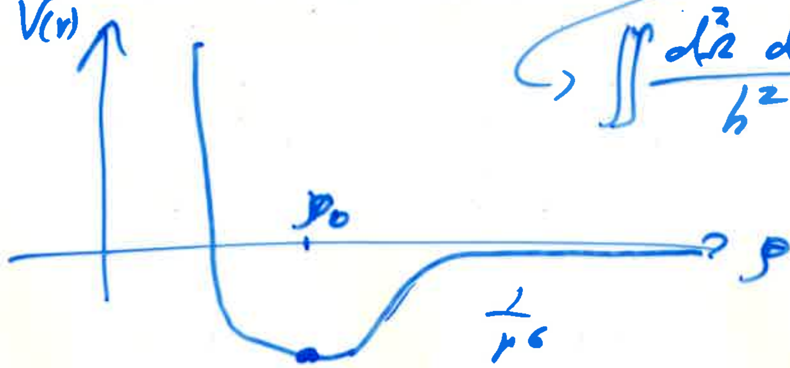
$$z_1 = \underbrace{\frac{V}{\lambda_Q^3}} \cdot \underbrace{\int \frac{d\pi\, d\rho}{h}\, e^{-\frac{\beta \pi^2}{2\mu}}\, e^{-\beta \frac{1}{2}\mu\omega^2\rho^2}}_{\text{vibrations}} \cdot \iint \frac{d^2\Omega\, d^2\vec{L}}{h^2}\, e^{-\frac{\beta \vec{L}^2}{2I}}$$

$$\lambda_Q = \frac{h}{\sqrt{2\pi M k_B T}}$$



$$V(\rho) = V(\rho_0) + \underbrace{V''(\rho)\Big|_{\rho_0} \frac{(\rho-\rho_0)^2}{2!}}_{\frac{1}{2}\mu\omega^2\rho^2} + \cdots$$

$$d^2\Omega = \sin\theta\, d\theta\, d\phi$$

$$z = \underbrace{\frac{V}{\lambda_0^3}}_{\text{trans.}} \cdot \underbrace{\frac{1}{h}\sqrt{\frac{2\pi\mu}{\beta}}\sqrt{\frac{2\pi}{\mu\beta}}}_{\text{vib}} \cdot \frac{4\pi}{h^2} \cdot \left(\sqrt{\frac{2\pi I}{\beta}}\right)^2$$

$$V\left(\frac{2\pi M}{\beta h^2}\right)^{3/2}$$

$$\epsilon = -\frac{\partial \ln(z)}{\partial \beta} = \underbrace{\frac{3}{2}\frac{1}{\beta}}_{\text{trans}} + \underbrace{\frac{1}{2}\frac{1}{\beta} + \frac{1}{2}\frac{1}{\beta}}_{\text{vib.}} + \underbrace{\frac{1}{\beta}}_{\text{rot}} = \frac{7}{2} k_B T$$

$$C_V = \frac{d\epsilon}{dT} = \frac{7}{2} k_B$$ per molecule

Quantum Mechanics for vibrations (1905)

$$E_j^{vib} = \left(j+\tfrac{1}{2}\right)\hbar\omega \qquad \text{Quantum S.H.O.}$$

$$z_{QM}^{vib} = \sum_{j=0}^{\infty} e^{-\beta E_j} = \sum_{j=0}^{\infty} e^{-\beta\left(j+\frac{1}{2}\right)\hbar\omega}$$

$$= e^{-\beta\frac{\hbar\omega}{2}} \sum_{j=0}^{\infty} e^{-\beta j\hbar\omega} = e^{-\beta\frac{\hbar\omega}{2}} \frac{1}{1-\underbrace{e^{-\beta\hbar\omega}}_{1-\beta\hbar\omega}}$$

z_{QM}^{vib} high T low β $\rightarrow$ $\cancel{e^{-\frac{\beta\hbar\omega}{2}}}^{\to 1}\left[\frac{1}{\beta\hbar\omega}\right] = \frac{1}{\beta\hbar\omega}$

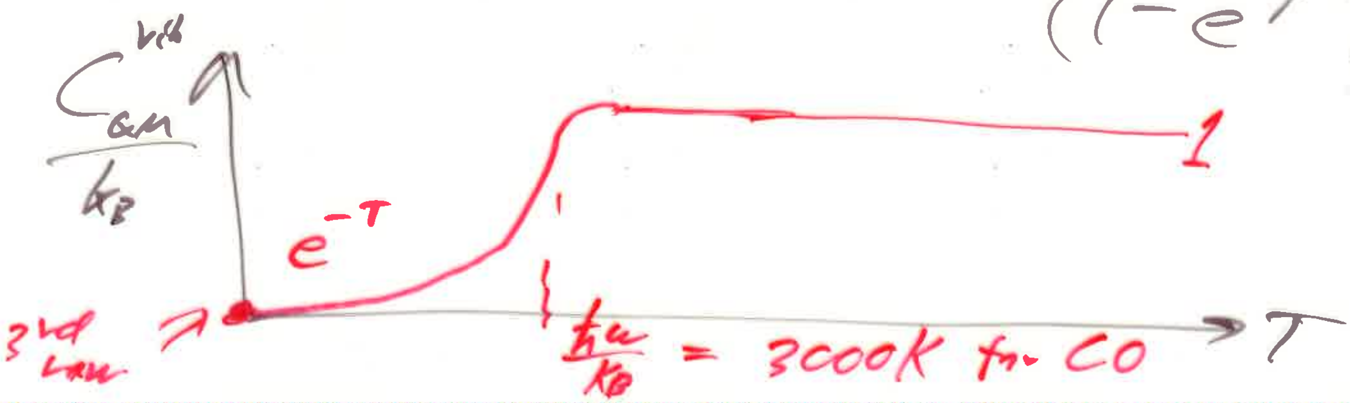
z_{QM}^{vib} low T high β $\rightarrow$ $e^{-\frac{\beta\hbar\omega}{2}}\left[1 + e^{-\beta\hbar\omega} + \dots\right]$

$$\epsilon_{QM}^{vib} = -\frac{\partial(z_{QM}^{vib})}{\partial\beta} = \frac{\hbar\omega}{2} + \frac{\hbar\omega\, e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}$$

high T $\rightarrow$ $\frac{1}{\beta} = k_B T$

low T $\rightarrow$ $\frac{\hbar\omega}{2} + \hbar\omega e^{-\beta\hbar\omega}$

$$C_{QM}^{vib} = \frac{d\epsilon_{QM}^{vib}}{dT} = 0 + k_B\left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{e^{-\beta\hbar\omega}}{\left(1-e^{-\beta\hbar\omega}\right)^2}$$



QM for rotations (1920s)

$$-\ell \le m_\ell \le +\ell$$

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

$\ell = 0, 1, 2, \ldots$
s p d f ...

$$Z_{QM}^{rot} = \sum_{\ell=0}^{\infty} (2\ell+1)\, e^{-\beta E_{\ell}^{rot,QM}} = \sum_{\ell=0}^{\infty} (2\ell+1)\, e^{-\beta \frac{\hbar^2}{2I}\ell(\ell+1)}$$

All micro states

+2 +1 0 −1 −2

+1 0 −1

$\ell = 0$ $\ell = 1$ $\ell = 2$