

Let us define characteristic temperatures

$$\Theta_1 = \frac{h^2}{2I} \quad \text{and} \quad \Theta_2 = h\nu$$

The partition function for a single molecule is:

$$Z_1 = Z_{\text{trans}} \sum_{l=0}^{\infty} \sum_{n=0}^{\infty} (2l+1) e^{-l(l+1)\Theta_1/T} e^{-(n+1/2)\Theta_2/T} \times e^{-(n+1/2)l(l+1)h/T}$$

$$\text{where } Z_{\text{trans}} = V \left( \frac{mT}{2\pi h^2} \right)^{3/2}$$

For temperatures  $T \gg \Theta_1$ , the sum(l) can be replaced by an integral.

$$\therefore Z_1 = Z_{\text{trans}} \sum_{l=0}^{\infty} \int_0^{\infty} dl (2l+1) e^{-l(l+1)[\Theta_1/T + (n+1/2)h/T]} e^{-(n+1/2)\Theta_2/T}$$

$$= Z_{\text{trans}} \sum_{n=0}^{\infty} \left( \frac{\Theta_1}{T} + \frac{h}{T} \left( n + \frac{1}{2} \right) \right)^{-1} e^{-(n+1/2)\Theta_2/T} =$$

$$= Z_{\text{trans}} \frac{T}{\Theta_1} \left( 1 + \frac{h}{\Theta_1} \frac{\partial}{\partial (\Theta_2/T)} + \dots \right) Z_{\text{vib}} =$$

$$= Z_{\text{trans}} \frac{T}{\Theta_1} Z_{\text{vib}} \left( 1 - \frac{\alpha \epsilon_{\text{vib}}}{\Theta_1 \Theta_2} + \dots \right),$$

$$\text{where } Z_{\text{vib}} = \sum_{n=0}^{\infty} e^{-(n+1/2)\Theta_2/T} = e^{-\frac{\Theta_2}{2T}} (1 - e^{-\frac{\Theta_2}{T}})^{-1}$$

$$\text{and } \epsilon_{\text{vib}} = - \frac{\partial \ln Z_{\text{vib}}}{\partial \beta} = \frac{h\nu}{2} \coth\left(\frac{h\nu}{2T}\right)$$

Here we have used the approximation that  $\frac{h}{\Theta_1}$  is small, while  $\frac{\epsilon_{\text{vib}}}{\Theta_2}$  is not large in

the temperature range considered

Finally, for a gas of  $N$  molecules, we obtain

$$E = -N \frac{\partial \ln Z_1}{\partial \beta} = \frac{5}{2} N T + \frac{N h \omega}{2} \coth\left(\frac{h \omega}{2 T}\right) - \frac{N d I \omega}{2 h} \operatorname{csch}^2\left(\frac{h \omega}{2 T}\right) + \dots$$

For this range of temperatures, translations and rotations contribute classically, giving rise to the first term, while the second is the quantum-mechanical contribution of vibrations. The last term is, of course, the leading correction due to interaction between the vibrational and rotational degrees of freedom.