

Dilute polyatomic Gases (continued)

We're well on our way to understanding the behavior of the heat capacities of polyatomic gases.

We've considered the quanta of vibrational modes, and we've seen that they asymptotically contribute the classical value of

$$\frac{C_{\text{vib}}}{(\# \text{ vibrational modes})} = k_B T \quad \text{as } T \rightarrow \infty$$

But for $T \ll \Theta_{\text{vib}} = \frac{h\nu}{k_B}$, ← vibrational frequency

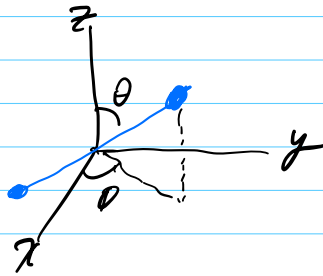
$$C_{\text{vib}} \xrightarrow{T \rightarrow 0} 0.$$

We can understand this because at low T very few particles will have enough energy to be able to excite the lowest quantum of vibrational energy (through collisions or other interactions).

To understand the behavior of the heat capacity at still lower energy we need to examine the rotational modes.

Rotational Modes

Diatom molecule $L = \frac{I}{2} (\dot{\theta}^2 + \sin^2 \theta \dot{\phi}^2)$ ← Moment of Inertia



Conjugate Momenta

$$P_{\theta} = \frac{\partial L}{\partial \dot{\theta}} = I \dot{\theta}, \quad P_{\phi} = \frac{\partial L}{\partial \dot{\phi}} = I \sin^2 \theta \dot{\phi}$$

Hamiltonian for rotations:

$$\begin{aligned} \mathcal{H}_{\text{rot}} &= \frac{1}{2I} \left(P_{\theta}^2 + \frac{P_{\phi}^2}{\sin^2 \theta} \right) \\ &= \frac{1}{2I} \left(I^2 \dot{\theta}^2 + I^2 \sin^2 \theta \dot{\phi}^2 \right) \end{aligned}$$

I^2 squared angular momentum

Classical partition function:

$$\begin{aligned} Z_{\text{rot}}^{\text{classical}} &= \frac{1}{h^2} \int_0^{\pi} d\theta \int_0^{2\pi} d\phi \int_{-\infty}^{\infty} dP_{\theta} \int_{-\infty}^{\infty} dP_{\phi} \exp \left[-\frac{\beta}{2I} \left(P_{\theta}^2 + \frac{P_{\phi}^2}{\sin^2 \theta} \right) \right] \\ &= \frac{2\pi}{h^2} \left(\frac{2\pi I}{\beta} \right) \int_0^{\pi} d\theta \left(\frac{2\pi I \sin^2 \theta}{\beta} \right)^{1/2} \\ &= \frac{2\pi}{h^2} \left(\frac{2\pi I}{\beta} \right) \cdot 2 = \frac{2I k_B T}{h^2} \end{aligned}$$

Internal energy

$$E_{\text{rot}}^{\text{classical}} = - \frac{\partial \ln Z_{\text{rot}}^{\text{classical}}}{\partial \beta} = k_B T$$

Quantum: $L^2 = \hbar^2 l(l+1)$, $l = 0, 1, 2, \dots$

Degeneracy $2l+1$ ($L_z = -l, -l+1, \dots, l-1, l$)

\uparrow arbitrary direction

$$Z_{\text{rot}}^{\text{quantum}} = \sum_{l=0}^{\infty} \exp\left[-\frac{\beta \hbar^2 l(l+1)}{2I}\right] (2l+1)$$

$$= \sum_{l=0}^{\infty} \exp\left[-\frac{\theta_{\text{rot}} l(l+1)}{T}\right] (2l+1)$$

where $\theta_{\text{rot}} = \frac{\hbar^2}{2Ik_B}$

a) $T \gg \theta_{\text{rot}}$ regime:

$$\lim_{T \rightarrow \infty} Z_{\text{rot}}^{\text{quantum}} \approx \int_0^{\infty} dl (2l+1) \exp\left[-\frac{\theta_{\text{rot}} l(l+1)}{T}\right]$$

$l \approx l(l+1)$
 $\approx \int_0^{\infty} dy \exp\left[-\theta_{\text{rot}} y/k\right]$

$$= T/\theta_{\text{rot}}$$

$$= Z_{\text{rot}}^{\text{classical}}$$

b) $T \ll \Theta_{rot}$:

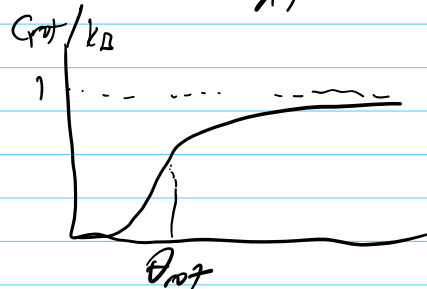
$$\lim_{T \rightarrow 0} Z_{rot}^{quantum} = 1 + 3 e^{-2\Theta_{rot}/T} + \mathcal{O}(e^{-6\Theta_{rot}/T})$$

↑
↑
↑
from $l=0$
from $l=1$
from $l=2$

$$E_{rot}^{quantum} = -\frac{\partial \ln Z}{\partial \beta} \approx 6k_B \Theta_{rot} e^{-2\Theta_{rot}/T}$$

Heat capacity

$$C_{rot}^{quantum} = \frac{dE_{rot}}{dT} \approx 6k_B \Theta_{rot} \left(\frac{2\Theta_{rot}}{T^2} \right) e^{-2\Theta_{rot}/T}$$



Typical values: $\Theta_{rot} \sim 1-10 \text{ K}$

Combining contributors to C from translations ($\frac{3}{2} k_B$), vibrations, and rotators:

