Diatomic Molecule as a Rigid Rotor

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6.2 Diatomic Molecule as Rigid Rotor

Consider a molecule, such as Carbon Monoxide, which consists of two different atoms, one Carbon and one Oxygen, separated by a distance d. Such a molecule can exist in quantum states of different orbital angular momentum. Each state has the energy

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

where $I = \mu d^2$ is the moment of inertia of the molecule about an axis through its centre of mass and μ is the reduced mass defined by $\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$. $l = 0, 1, 2, \ldots$ is the quantum number associated with the orbital angular momentum. Each energy level of the rotating molecule has the degeneracy $g_l = 2l + 1$.

1. Find the general expression for the canonical partition function Z.
2. Show that for high temperatures, Z can be approximated by an integral and calculate this integral.
3. Evaluate the high temperature mean energy E and the heat capacity C_V.
4. Find the low-temperature approximations to the canonical partition function, the mean energy E and the heat capacity C_V.

Solution

1. The generic partition function is given by

$$\begin{aligned} Z &= \sum_{j=0}^{\infty} g_j e^{-E_j \beta} \\ &= \sum_{l=0}^{\infty} (2l+1) e^{-l(l+1)\frac{\hbar^2}{2I}\beta} \end{aligned}$$

2. For high temperatures, the energy spacing between the energy levels is small compared to $k_B T$, so the summation can be replaced by the integral

$$\begin{aligned} Z &= \int_0^{\infty} (2l+1) e^{-l(l+1)\frac{\hbar^2}{2I}\beta} dl \\ &= \int_0^{\infty} e^{\frac{-\beta\hbar^2 l(l+1)}{2I}} d(l(l+1)) \\ &= \frac{2I}{\beta\hbar^2} \end{aligned}$$

3. Finding the energy in the high-temperature limit.

$$\begin{aligned} <E> &= -\frac{\partial}{\partial\beta}\ln Z \\ &= -\frac{\partial}{\partial\beta}\ln\frac{2I}{\beta\hbar^2} \\ &= \frac{1}{\beta} = k_B T \end{aligned}$$

And the heat capacity:

$$C_V = \frac{\partial <E>}{\partial T} = k_B$$

4. For the low-temperature approximation, most of the particles will be in the ground state, so we can approximation the partition function by simply the first two terms like so:

$$\begin{aligned} Z &= \sum_{l=0}^{\infty}(2l+1)e^{-l(l+1)\frac{\hbar^2}{2I}\beta} \\ &= 1+3e^{-\beta\hbar^2/I} \end{aligned}$$

So the average energy again is

$$\begin{aligned} <E> &= -\frac{\partial}{\partial\beta}\ln Z \\ &= -\frac{\partial}{\partial\beta}\ln\left(1+3e^{-\frac{\hbar^2}{I}\beta}\right) \\ &= -\frac{3\frac{-\hbar^2}{I}e^{-\frac{\hbar^2}{I}\beta}}{1+3e^{-\frac{\hbar^2}{I}\beta}} \\ &= \frac{3\hbar^2/I}{e^{\beta\hbar^2/I}+3} \end{aligned}$$

For the heat capacity,

$$\begin{aligned} C_V &= \frac{\partial\beta}{\partial T}\frac{\partial}{\partial\beta} <E> \\ &= -\frac{1}{k_B T^2}\frac{\partial}{\partial\beta}\left(\frac{3\hbar^2/I}{e^{\beta\hbar^2/I}+3}\right) \\ &= \frac{3\hbar^4}{k_B T^2 I^2}\frac{e^{\hbar^2\beta/I}}{\left(e^{\beta\hbar^2/I}+3\right)^2} \\ &\approx 3k_B\left(\frac{\hbar^2}{Ik_BT}\right)^2\exp\left(-\hbar^2/Ik_BT\right) \end{aligned}$$