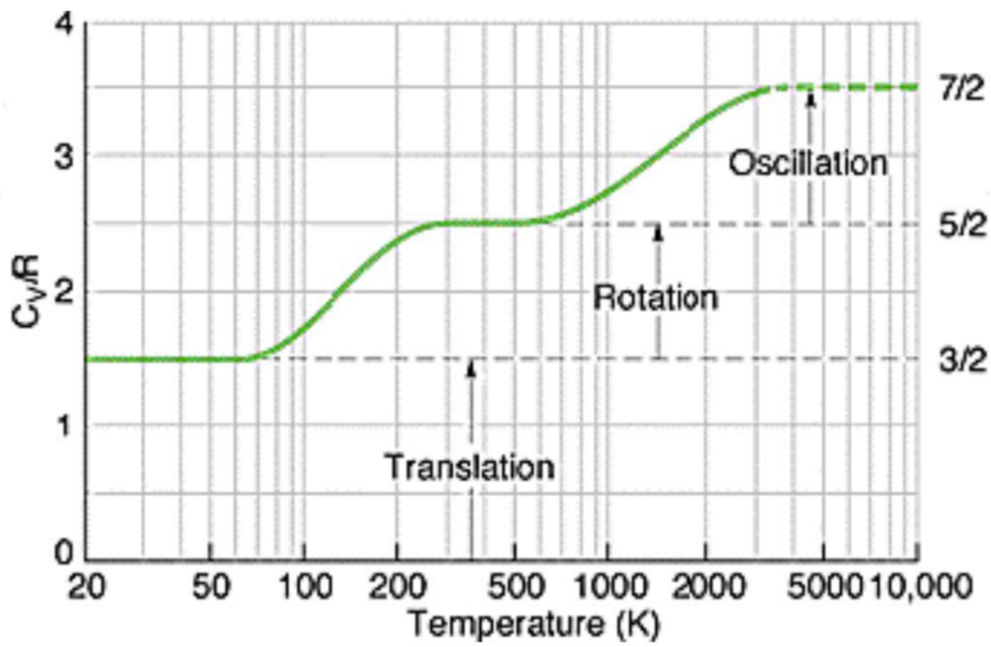
Previously, we derived that the heat capacity of the diatomic gas is $\frac{7}{2} N k_B$. However, experimentally, we observe that this result has a temperature-dependence (taken from Tong lecture notes).



We explain this result using quantum mechanical considerations.

Our previous derivation computed the heat capacity using $Z = Z_{trans} \cdot Z_{rot} \cdot Z_{vib}$.

Z_{trans} is unchanged by QM, and gives us

$$Z_{trans} = \left(\frac{1}{8\pi^3 \hbar^3} \cdot V \cdot \sqrt{\frac{2m\pi}{\beta}} \right)^{3N} \Rightarrow \langle E \rangle = -\frac{\partial}{\partial \beta} \log Z =$$

$$-\frac{\partial}{\partial \beta} -\frac{3N}{2} \log \beta = \frac{3N}{2\beta} \Rightarrow C_V = \frac{3}{2} N k_B.$$

This explains the first plateau on our plot.

The rotational quantum Hamiltonian

$$\hat{H} = \frac{\hat{p}_\theta^{\,2}}{2I} + \frac{\hat{p}_\phi^{\,2}}{2I\sin^2\theta}$$

*I cannot derive this at present.

has a spectrum given by $E_j = \hbar^2 j(j+1)/2I$, $j \in \mathbb{N}$.* Each E_j has $2j+1$ degeneracy. It follows that the partition function is given by

$$Z_{rot} = \sum_{j=0}^{\infty} (2j+1) e^{-\beta\hbar^2 j(j+1)/2I}$$

High temp limit: $\beta\hbar^2/2I \ll 1 \longrightarrow$

$$Z_{rot} \approx \int_0^\infty (2x+1) e^{-\beta\hbar^2 x(x+1)/2I} dx = \frac{2I}{\beta\hbar^2},$$

which agrees with the classical result. It follows that

$$\langle E \rangle = -\frac{\partial}{\partial\beta} N \log \frac{2I}{\beta\hbar^2} = \frac{N}{\beta} \Rightarrow C_V = Nk_B \Rightarrow$$

$C_{v,tot} = 5/2 \cdot Nk_B$. This explains the height of the second plateau.

Low temp limit: $\beta\hbar^2/2I \gg 1 \Rightarrow e^{-\beta\hbar^2/2I} \approx 0 \Rightarrow$

$Z_{rot} \approx 1$, as only the $j=0$ term will not vanish.

Thus, at low temperatures, the rotational degrees of freedom are "frozen out" and do not contribute to the heat capacity.

Finally, the vibrational degrees of freedom can be modeled as a quantum harmonic oscillator.

$$E_n = \hbar\omega(n+1/2) \Rightarrow Z_{vib} = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+1/2)} =$$

$$e^{-\beta\hbar\omega/2} \sum_{n=0}^{\infty} e^{-\beta\hbar\omega n} = e^{-\beta\hbar\omega/2} / 1-e^{-\beta\hbar\omega} =$$

$$\frac{1}{e^{\beta\hbar\omega/2} - e^{-\beta\hbar\omega/2}} = \frac{1}{2\sinh\beta\hbar\omega/2}.$$

High temp limit: $\beta\hbar\omega \ll 1 \rightarrow Z_{vib} \approx \frac{1}{\beta\hbar\omega} \rightarrow$

$$\langle E \rangle = \frac{-\partial}{\partial\beta} \log(\beta\hbar\omega)^{-N} = N\log\beta \Rightarrow C_v = Nk_B \Rightarrow$$

$C_{v,tot} = \frac{7}{2} N k_B$. This explains the final plateau of the plot.

Low temperature limit: $\beta\hbar\omega \gg 1 \Rightarrow Z_{vib} \approx e^{-\beta\hbar\omega/2}$

$\Rightarrow \langle E \rangle = \frac{\hbar\omega}{2} \Rightarrow C_v = 0$. Thus, the vibrational degrees of freedom are <u>also</u> frozen out at low temperatures. In this way, quantum mechanical considerations allow our model of the diatomic gas to agree with experimental observations.