

1 Boltzmann probabilities

Consider a three-state system with energies $(-\epsilon, 0, \epsilon)$.

- At infinite temperature, what are the probabilities of the three states being occupied? What is the internal energy U ? What is the entropy S ?
- At very low temperature, what are the three probabilities?
- What are the three probabilities at zero temperature? What is the internal energy U ? What is the entropy S ?
- What happens to the probabilities if you allow the temperature to be negative?

2 Diatomic hydrogen

At low temperatures, a diatomic molecule can be well described as a *rigid rotor*. The Hamiltonian of such a system is simply proportional to the square of the angular momentum

$$H = \frac{1}{2I}L^2 \quad (1)$$

and the energy eigenvalues are

$$E_{\ell m} = \hbar^2 \frac{\ell(\ell + 1)}{2I} \quad (2)$$

- What is the energy of the ground state and the first and second excited states of the H_2 molecule? i.e. the lowest three distinct energy eigenvalues.
- At room temperature, what is the relative probability of finding a hydrogen molecule in the $\ell = 0$ state versus finding it in any one of the $\ell = 1$ states?
i.e. what is $P_{\ell=0,m=0} / (P_{\ell=1,m=-1} + P_{\ell=1,m=0} + P_{\ell=1,m=1})$
- At what temperature is the value of this ratio 1?
- At room temperature, what is the probability of finding a hydrogen molecule in any one of the $\ell = 2$ states versus that of finding it in the ground state?
i.e. what is $P_{\ell=0,m=0} / (P_{\ell=2,m=-2} + P_{\ell=2,m=-1} + \dots + P_{\ell=2,m=2})$

3 Gas in the atmosphere

Let's consider our atmosphere. In this problem we will make an inaccurate assumption that the entire atmosphere is at room temperature.

- (a) What is the relative probability of a nitrogen molecule of being in a particular eigenstate outside the influence of the Earth's gravity, relative to being in an eigenstate at the Earth's surface. You may assume the energy difference of the two states is the gravitational potential energy difference? How about an oxygen molecule?
- (b) How does your answer change if you consider a helium atom?

4 Nucleus in a Magnetic Field

Nuclei of a particular isotope species contained in a crystal have spin $I = 1$, and thus, $m = \{+1, 0, -1\}$. The interaction between the nuclear quadrupole moment and the gradient of the crystalline electric field produces a situation where the nucleus has the same energy, $E = \varepsilon$, in the state $m = +1$ and the state $m = -1$, compared with an energy $E = 0$ in the state $m = 0$, i.e. each nucleus can be in one of 3 states, two of which have energy $E = \varepsilon$ and one has energy $E = 0$.

- (a) Find the Helmholtz free energy $F = U - TS$ for a crystal containing N nuclei which do not interact with each other.
- (b) Find an expression for the entropy as a function of temperature for this system. (Hint: use results of part a.)
- (c) Indicate what your results predict for the entropy at the extremes of very high temperature and very low temperature.

5 Heat capacity for particle in a box

Consider a particle in a box. The energy eigenvalues are given by

$$E_n = E_1 n^2 \quad \text{where } n = 1, 2, 3, \dots \quad (3)$$

- (a) Solve for the entropy of this system at temperature T where $k_B T \gg E_1$. Your analytic solution should not involve a summation or an integral.
- (b) When $kT \gg E_1$, solve for the heat capacity C_V of this system, given by

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V \quad (4)$$

$$= T \left(\frac{\partial S}{\partial T} \right)_V \quad (5)$$

Hint: You will need to approximate a sum as an integral in this problem. You will also need to explain in words why this approximation is justified.