Exercises in Statistical Mechanics

Based on course by Doron Cohen, has to be proofed
Department of Physics, Ben-Gurion University, Beer-Sheva 84105, Israel

This exercises pool is intended for a graduate course in "statistical mechanics". Some of the problems are original, while other were assembled from various undocumented sources. In particular some problems originate from exams that were written by B. Horovitz (BGU), S. Fishman (Technion), and D. Cohen (BGU).

[Exercise 4211]

The law of mass action for diatomic molecules

Consider a diatomic AB molecule, where A and B are different spin 0 atoms, each having a 1-unit atomic mass m_0. The length of the molecule is a, the binding energy is $-\varepsilon_0$, and the vibration frequency of the bond is ω_0. The vibration amplitude is much smaller compared with a. The temperatures are not low, namely $T \gg 1/(\mathsf{m}_0 a^2)$, such that the rotation-spectrum can be treated as a continuum. For higher temperatures ($T \gg \omega_0$) also the vibration-spectrum can be treated using a classical approximation.

In item (3) below we consider Hydrogen H_2, Deuterium D_2, and HD molecules. The respective masses of the atoms are $\mathsf{m}_H, \mathsf{m}_D$. Note that the Deuterium nucleus has spin 1. Assume that neither the energy nor the "spring constant" of the binding are affected by the $H \mapsto D$ replacement.

(1) Find the one molecule partition function Z^{AB} for an AB molecule that is held in a container that has volume L^3. Assume that the temperature is not low, but not necessarily high.

(2) Write the law of mass action for the reaction $A + B \leftrightarrow AB$. Find an explicit expression for the equilibrium constant $K(T)$ in the high temperature regime.

(3) Write the law of mass action for the reaction $H_2 + D_2 \leftrightarrow 2HD$. Express the equilibrium constant $K(T)$ in terms of one-particle partition functions Z^C, were C stands for H_2, and D_2, and HD.

(4) Find expressions for the ratio Z^C/Z^{AB} in the high temperature regime, where A and B are distinct spinless atoms that have the same masses as that of the C constituents. Explain why the high temperature assumpation is essential in order to get a simple result.

(5) What is the explicit result for $K(T)$ of item (3) in the high temperature regime?

Tip: The Hamiltonian of a diatomic molecule consist of center of mass degrees of freedom, and of a relative motion degrees of freedom. The latter involves the reduced mass $\mathsf{m}_A\mathsf{m}_B/(\mathsf{m}_A + \mathsf{m}_B)$. For intermediate calculations you can use the notation α for spring constant.