Statistical Mechanics

February 7, 2007

Work 2 of the 3 problems. Please put each problem solution on a separate sheet of paper and put your name on each sheet.

Problem 1

Consider a classical monatomic ideal gas composed of particles of mass m. The gas is enclosed in a rigid container and kept at a constant temperature T and a pressure P. Find the total kinetic energy of the gas molecules striking a *unit area* of the container wall per *unit time*.

Problem 2

The three lowest energy levels of a certain molecule are $E_1 = 0$, $E_2 = \epsilon$ and $E_3 = 10\epsilon$. For a system of N molecules in the thermodynamic limit, $N \to \infty$, show that there is a temperature T_c, which we will call the critical temperature, such that for temperatures $T < T_c$ only the first two levels will be populated. Estimate this critical temperature T_c.

HINT: You don't need to consider levels higher than these three at very low temperatures. Thus, the total number of molecules N is the sum of the three populations N_i, where $i \in \{1, 2, 3\}$. Write the expressions for the relative populations with respect to level 1. You may want to exploit the fact that these occupancies must be natural numbers. Notice that even though $N_3 = 0$ does mean there are no particles on level 3, it doesn't quite define the critical temperature T_c, which is the temperature for which the last particle remaining at level 3 has *just* migrated down.

Problem 3

For an ideal gas molecule, AB, undergoing dissociation into its component parts via the reaction

$$AB \Longleftrightarrow A + B$$

the equilibrium constant $K(T)$ is defined as

$$K(T) = \frac{n_{AB}}{n_A n_B}$$

where n_A, n_B and n_{AB} represent the amounts (in numbers of molecules per unit volume) of each species.
Consider the following gas-phase reaction for two of the Isotopomers of Hydrogen. Use statistical mechanics to derive an expression for the equilibrium constant for the reaction

$$D_2 + H_2 \Longleftrightarrow 2HD$$

where D and H represent Deuterium and Hydrogen, respectively, at temperatures high enough to allow the use of the classical approximation for rotational motion. Evaluate your expression to determine the concrete value of the equilibrium constant.