PHY 5524: Statistical Mechanics

February 1^{st}, 2012
Assignment # 5
(We will solve these problems next Monday, February 6^{th}, in preparation for the first Midterm Exam, to be held on Wednesday, February 8^{th}, 2012.)

Problem 1

Consider a *classical* system of N non-interacting diatomic molecules enclosed in a box of volume V at temperature T. The Hamiltonian for a *single* molecule is,

$$H(\mathbf{p}_1, \mathbf{p}_2, \mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2m}(\mathbf{p}_1^2 + \mathbf{p}_2^2) + \frac{1}{2}K|\mathbf{r}_1 - \mathbf{r}_2|^2 \ ,$$

where $\mathbf{p}_1$, $\mathbf{p}_2$, $\mathbf{r}_1$, and $\mathbf{r}_2$ are the momenta and coordinates of the two atoms in a molecule.

1.a) Find the partition function and the Helmholtz free energy of the system (*Hint*: the integration over phase space is easier if, in the integration over $d\mathbf{r}_1 d\mathbf{r}_2\,(= d^3r_1 d^3r_2)$ one changes variables from the coordinates of the individual atoms, $(\mathbf{r}_1, \mathbf{r}_2)$, to the coordinates of the *reduced system*, $(\mathbf{R}, \mathbf{r})$, where $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$ is the position vector of the center of mass of the two atoms, and $\mathbf{r} = (\mathbf{r}_1 - \mathbf{r}_2)$ is the relative distance between the two. In other words, apply what you know about the classical mechanics solution of a two-body problem!).

1.b) Find the specific heat at constant volume.

1.c) Find the mean square molecular diameter, $\langle|\mathbf{r}_1 - \mathbf{r}_2|^2\rangle$.

Problem 2

A simple anti-ferromagnetic system consists of a chain of N non-interacting and identical localized spin-1/2 *dimers*. The system is placed in an external magnetic field $\mathbf{B} = B\hat{\mathbf{Z}}$ and is in contact with a heat reservoir at a fixed temperature T. The Hamiltonian for an individual dimer is given by the following expression,

$$H = J\mathbf{S}(1) \cdot \mathbf{S}(2) - \mu B\,(S_z(1) + S_z(2)) \ ,$$

where J and μ are positive constants.

2.a) Obtain the eigenvalues and the eigenvectors of H.

2.b) Determine the partition function for the system (i.e. N non-interacting and localized dimers) correct to second order in B, but correct to all orders in T.

2.c) Evaluate the expectation value of the magnetization $M = \mu\langle S_z(1) + S_z(2)\rangle$ to leading order in B. Justify your result in the limit $T \to 0$.

2.d) Obtain the magnetic susceptibility defined as follows,

$$\chi = \left(\frac{\partial \langle M \rangle}{\partial B} \right)_{T,B=0} .$$

You are told that the magnetic susceptibility is proportional to the variance in the magnetization. Is your answer consistent with this statement? Explain.

Problem 3

Consider a diluted gas of diatomic molecules. For most such systems, at temperatures above the normal boiling point of the fluid, the rotational energies are so closely spaced that they approximate a continuum, and *classical* statistical mechanics can be used. Let the mass of a molecule be M and the moment of inertia I.

3.a) Express the rotational kinetic energy in terms of the two Euler angles ϕ and θ, and show that in terms of the corresponding canonical momenta P_ϕ and P_θ, it takes the form,

$$K_{\text{rot}} = \frac{1}{2I} \left(P_\theta^2 + \frac{P_\phi^2}{\sin^2 \theta} \right) .$$

(*Hint*: as in Problem 1, here too you are dealing with a diatomic molecule, i.e. a two-body system. Consider the suggestions given in **Problem 1**).

3.b) Ignoring the vibrations, write down the partition function.

3.c) Evaluate the partition function and show that the result is of the form,

$$Z = \frac{V^N}{N!} \left(\frac{2\pi M k_B T}{h^2} \right)^{3N/2} \left(\frac{8\pi^2 I k_B T}{h^2} \right)^N .$$

3.d) Compute the internal energy and the entropy of this gas.

3.e) Using the expressions from **(3.d)**, examine the behavior of the entropy at low temperatures. Does the obtained result agree with the third law of thermodynamics? Explain what happens at low temperatures.