PHYS 813: Statistical Mechanics, Assignment 6

Due 4/23/09

1. A surface with N_0 adsorption centers has $N < N_0$ gas molecules adsorbed on it, at most one molecule per center. Assume that the canonical partition function for a single adsorbed molecule is known and denote it by $a(T)$. Neglect interactions between adsorbed molecules. Find the chemical potential of the system:
   (a) using the canonical partition function;
   (b) using the grand canonical partition function. In this case N can vary from 0 to N_0.

2. As a continuation of the previous problem, consider the (ideal) gas which is in equilibrium with the surface. Find the pressure of the gas as a function of the fraction of average number of occupied sites and of temperature.

3. For a single electron in a magnetic field $\boldsymbol{B}$, the Hamiltonian is

$$\hat{H} = -\mu_B \hat{\boldsymbol{\sigma}} \cdot \boldsymbol{B}$$

   where μ_B is a constant and $\hat{\boldsymbol{\sigma}}$ is the spin operator. Choose the z axis to be directed along $\boldsymbol{B}$ and find the expression for the canonical density matrix elements ρ_{mn} in the representation in which
   (a) $\hat{\sigma}_z$ is diagonal;
   (b) $\hat{\sigma}_x$ is diagonal.

   Next, calculate the average value of $\hat{\sigma}_z$ in both representations.

4. A system with two energy levels is populated by N distinguishable noninteracting particles at temperature T with occupations determined by the canonical distribution.
   (a) Find the average energy per particle.
   (b) Find the behaviour of this energy as $T \to 0$ and $T \to \infty$.
   (c) Find the specific heat to the system.
   (d) Find the behaviour of the specific heat as $T \to 0$ and $T \to \infty$. Interpret the obtained results.

5. Consider a dilute, noninteracting gas of N distinguishable diatomic molecules of mass m. Each molecule is a rigid rotor with $(2J+1)$-degenerate energy levels $\epsilon_J = \hbar^2 J(J+1)/2I$, where I is the moment of inertia. Start from the general expression for the canonical partition function $Q_N(V,T) = \sum_n \mathrm{e}^{-E_n/kT}$ where E_n is the total energy of N-molecule system. Calculate then the average energy, the specific heat at constant volume, and the entropy of the system in the limit $kT \gg \hbar^2/2I$. You may use without proof the partition function for the ideal monoatomic gas $Q_N^{\text{ideal}}(V,T) = \left[V(2\pi mkT)^{3/2}/h^3\right]^N$. *Hint:* In the assumed limit, $\sum_n f(n) = \int_0^\infty f(x)dx$.

6. Use the Debye model to calculate the internal energy and heat capacity of a one-dimensional atomic solid with length L for both high and low temperature. Assume periodic boundary conditions. The Debye model treats the solid as a set of coupled harmonic oscillators and approximates the unknown normal modes of the system as plane waves propagating with the velocity of sound.

7. Consider a free particle in a box with periodic boundary conditions, in the momentum representation. The particle is in equilibrium with a heat bath and therefore is described by the canonical distribution. Denote the eigenfunctions of the Hamiltonian as

$$\phi_{\boldsymbol{k}}(\boldsymbol{r}) = \frac{1}{L^{3/2}} \mathrm{e}^{i\boldsymbol{k}\cdot\boldsymbol{r}}$$

   (a) Evaluate matrix elements of $\mathrm{e}^{-\beta\hat{H}}$ in the basis $\phi_{\boldsymbol{k}}(\boldsymbol{r})$.

   (b) Find the canonical partition function in terms of L and $\lambda = h/\sqrt{2\pi mkT}$.

   (c) Find the density operator $\hat{\rho}$ in the basis $\phi_{\boldsymbol{k}}(\boldsymbol{r})$.

   (d) Calculate the average value of $\hat{H}$ as $\mathrm{Tr}(\hat{\rho}\hat{H})$. Express your answer in terms of L, λ, and T.