Physics 5524

Statistical Mechanics

Problem Set 5

Due: Friday, Feb. 13

5.1 Ideal Diatomic Gas — In Problem 4.2 you considered a model of a diatomic ideal gas in which the molecules were treated as classical harmonic oscillators with equilibrium length zero. For real diatomic molecules this is not a good approximation both because there is a *finite* equilibrium length (i.e. the length of the chemical bond), and because the splitting between quantized vibrational energy levels of the molecule is large (on the order of room temperature).

A better approximation for a diatomic gas is to assume the quantized vibrations are essentially "frozen out" so that the molecules can be treated as "rigid rotors." For real diatomic gases the splitting of the quantized rotational levels is much smaller than $k_B T$ at room temperature, so it is a good approximation to treat the rotor classically in this case (see next problem).

The Hamiltonian describing a single "rigid rotor" diatomic molecule is

$$H = \frac{\vec{p}^2}{2m} + \frac{p_\theta^2}{2I} + \frac{p_\phi^2}{2I\sin^2\theta},$$

where I is the moment of inertia of the molecule. Here $\vec{p} = (p_x, p_y, p_z)$ is the translational momentum of the center of mass of the molecule, θ and ϕ are the Euler angles describing the orientation of the molecule, and p_θ and p_ϕ are the momenta canonically conjugate to θ and ϕ.

(a) Show that the partition function for a single molecule confined to a volume V is

$$Q_1(T, V) = V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\left(\frac{8\pi^2 I k_B T}{h}\right).$$

(b) Determine the partition function for a gas of N noninteracting molecules and obtain the Helmholtz free energy for this gas.

(c) Find expressions for the pressure, entropy and internal energy of this gas. For the latter, show that your result agrees with the equipartition theorem.

(d) Determine the specific heat at constant volume, C_v, and the specific heat at constant pressure, C_p, for this gas. What is the value of the ratio $\gamma = C_p/C_v$?

(e) Using the expression for the entropy found in (b) verify that for adiabatic ($S =$ constant) processes, PV^γ is constant.

5.2 (From the Spring 1999 Comprehensive Exam. In this problem you will show that if the rigid rotor model from Problem 5.1 is treated quantum mechanically, in the high temperature limit the classical result is recovered.)

The energy levels of a three-dimensional quantum rigid rotor of moment of inertia I are given by

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

where $j = 0, 1, 2, \cdots$ and $m = -j, -j+1, \cdots, j$ for a given j. Consider a system of N such rotors. Assume that the rotors do not interact, and that the center of mass of each rotor is fixed at a specific point in space so that the system has only rotational degrees of freedom.

(a) Find expressions for the partition function $Q_N(T)$ and the internal energy $E(T)$ of this system. Do not attempt to evaluate these expressions.

(b) Show that at high temperatures the expressions you found in (a) can be approximated by integrals.

(c) Evaluate the high-temperature value of E and obtain the heat capacity C_v. How does your result compare with the classical result?

(d) Find approximate expressions for Q_N, E and C_v valid in the low-temperature limit.

5.3 A system consists of N clusters. Each cluster is made up of two spin-1/2 particles, each having a magnetic moment $\boldsymbol{\mu} = 2\mu \mathbf{S}/\hbar$. The system is placed in an external magnetic field $\mathbf{H} = H\hat{\mathbf{z}}$ and is in thermal equilibrium at temperature T. The Hamiltonian for each cluster is

$$\mathcal{H} = \frac{J}{\hbar^2} S_z(1) S_z(2) - \frac{2\mu}{\hbar} H (S_z(1) + S_z(2)),$$

where J and μ are positive constants.

(a) List all possible microscopic states (corresponding to $S_Z = \pm\frac{1}{2}\hbar$ for each spin, so there should be a total of four) of each cluster and give their energies. Sketch the energy level diagram as a function of H. Indicate any degeneracies.

(b) Obtain the partition function for this system $Q_N(T, H)$ and determine the Helmholtz free energy.

(c) Obtain an expression for the magnetization $M(T, H)$ for this system and determine the spin susceptibility

$$\chi(T) = \lim_{H\to 0} \frac{\partial M}{\partial H}. \tag{1}$$

(d) Show that at high temperatures

$$\chi(T)^{-1} \simeq \frac{T - \Theta}{C} \tag{2}$$

where $C \propto \mu^2$ is the Curie constant we would expect for noninteracting spins and $\Theta \propto J$. This result shows that measuring $\chi(T)$ for a material at high temperatures, and plotting its inverse vs. temperature, can reveal both the presence of local moments in that material and, by determining Θ, the energy scale characterizing interactions between these moments.