3/19/02. **Due:** Tuesday, April 2, 2002 (in class).

Physics 540: Statistical Mechanics I

Read: LL 41-51, 101-104
Problems to study: K.3 ex 3

"**LL** 1" means section 1 from Landau and Lifshitz book
"**K**.1 ex 2" means example 2 from section 1 of Kubo's book.

Homework 7

Exercise 1

Consider the free rotation of a diatomic molecule consisting of two atoms of mass m_1 and m_2, respectively, separated by a distance a. Assume that the molecule is rigid with center of mass fixed.

a) Starting from the kinetic energy ϵ_k, where

$$\epsilon_k = \frac{1}{2} \sum_{i=1}^{2} m_i(\dot{x}_i^2 + \dot{y}_i^2 + \dot{z}_i^2)$$

derive the kinetic energy of this system in spherical coordinates and show that

$$\epsilon_{rot} = \frac{1}{2} I(\dot{\theta}^2 + \dot{\phi}^2 \sin^2 \theta),$$

where I is the moment of inertia. Express I in terms of m_1, m_2, and a.

b) Derive the canonical conjugate momenta p_θ and p_ϕ. Express the Hamiltonian of this system in terms of p_θ, p_ϕ, θ, ϕ, and I.

c) The classical partition function is defined as

$$Z_{cl} = \frac{1}{h^2} \int_0^\pi \int_0^{2\pi} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} e^{-H/T} \, d\theta \, d\phi \, dp_\theta \, dp_\phi.$$

Calculate Z_{cl}. Calculate the energy, the entropy, and the heat capacity per particle.

Exercise 2

Quantum energy levels for the diatomic molecule from the exercise 1 are given by $\epsilon_{rot} = J(J+1)\Theta_{rot}$, where $\Theta_{rot} = \frac{\hbar^2}{2I}$ is a characteristic "rotational temperature" and $J = 0, 1, 2, \ldots$ is a rotational quantum number (quantized angular momentum of the molecule). Each rotational energy level is $2J + 1$ degenerate.

a) In the limit of high temperature $\Theta_{rot}/T \ll 1$ calculate the energy, the entropy, and the heat capacity per particle. Show that in this limit the results of the exercise 1 are reproduced.

b) In the limit of low temperature $\Theta_{rot}/T \gg 1$ the discreteness of the spectrum is important. Calculate the energy, the entropy, and the heat capacity per particle in this limit.

c) Plot the dependencies of rotational energy and specific heats as functions of temperature at all temperatures. Plots should be at least qualitatively correct.

Exercise 3

For some molecules there is an additional contribution to theromodynamic properties coming from two low-lying electronic energy levels. The oxygen molecule has two such energy levels at the distance $\epsilon = 11300K$ from each other and at high temperatures the first (lowest) and the second energy levels are three and two times degenerate, respectively. Estimate the temperature at which the electronic contribution to specific heat has a maximum and calculate the corresponding contribution to specific heat at that temperature.

Exercise 4

a) For the chemical reaction between ideal gases $\sum_{i=1}^{m} b_i B_i = 0$ the total pressure is given by the sum of partial pressures $P = \sum P_i$. Show that the law of mass action can be put into the form

$$P_1^{b_1} P_2^{b_2} \ldots P_m^{b_m} = K_p(T),$$

where the constant $K_p(T)$ depends only on T.

b) Show that under conditions of constant total pressure the heat of reaction per mole (i.e., the heat which must be supplied to transform $|b_i|$ moles of each of the reactants to $|b_i|$ moles of each of the reaction products) is given by the enthalpy change

$$\Delta H = \sum b_i h_i,$$

where h_i is the enthalpy per mole of the i-th gas at the given temperature and pressure.

c) ν_0 moles of H_2O are introduced into a container of fixed volume V at low temperature (no dissociation). For the reaction of dissociation $2H_2O \rightarrow 2H_2 + O_2$ write an equation relating ξ (the fraction of H_2O molecules which are dissociated at given temperature and pressure) to pressure P and constant $K_p(T)$.

d) It is known experimentally that at atmospheric pressure $\xi(T = 1500K) = 1.97 \times 10^{-4}$, $\xi(T = 1705K) = 1.2 \times 10^{-3}$, $\xi(T = 2155K) = 1.2 \times 10^{-2}$. What is the heat required to dissociate one mole of water vapor at 1 atmosphere into O_2 and H_2 at a temperature of $1700K$.