Group Problems #1
Reciation 3.091
Fall 2003

From McQuarrie:

Highly Advised

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Problem 1

A system consists of N non-interacting atoms. Each atom may be in two states, a low energy state with energy, $E = 0$ and an 'excited' state, with energy E.

a) How many atoms are in the excited state?

b) What is the total energy U of this system as a function of N, E, k (the Boltzmann constant) and T?

Problem 2

Consider a system of N distinguishable non-interacting spins in a magnetic field H. Each spin has a magnetic moment of size μ, and each can point either parallel or anti-parallel to the field. The magnetic moment is given by $n_i\mu$ where $n_i = +/-1$. Note that since the system is made of non-interacting particles, the total energy of the system does not depend on the arrangements of the spins, i.e. the energy is constant.

(a) Determine the internal energy of this system as a function of β, H, and N by employing an ensemble characterized by these variables.

(b) Determine the entropy of this system as a function of β, H, and N.

(c) Determine the behavior of the energy and entropy for this system as $T \to 0$.

Problem 3

(a) For the system described in the previous problem, derive the average total magnetization,

$$\langle M \rangle = \left\langle \sum_{i=1}^{N} \mu n_i \right\rangle$$

as a function of β, H, and N.

(b) Similarly determine $\left\langle (\delta M)^2 \right\rangle$, where

$$\delta M = M - \langle M \rangle$$

and compare your result with the susceptibility

$$\left(\frac{\partial \langle M \rangle}{\partial H} \right)_{\beta, N}$$

(c) Derive the behavior of $\langle M \rangle$ and $\left\langle (\delta M)^2 \right\rangle$ in the limit $T \to 0$.

(Note: $\langle M \rangle$ denotes the average, so $\langle M \rangle = \overline{M}$)

Problem 4

Consider the system studied in Problems 2 and 3 above. Use an ensemble in which the total magnetization is fixed, and determine the magnetic field over temperature, βH, as a function of the natural variables for that ensemble. Show that in the limit of large N, the result obtained in this way is equivlent to that obtained in Problem 3.

Problem 5

Consider a one-component gas of non-interacting classical structureless particles of mass m at a temperature T.

(a) Calculate exactly the grand canonical partition function, Ξ, for this system as a function of volume, V, temperature, and chemical potential, μ. Your result should look like

$$\Xi = \exp(zV)$$

where z is a function of T and μ.

(b) From the result of part (a), determine the pressure, p, as a function of T and the average particle density, ρ.

(c) For 1 cc of gas at STP, compute the relative root mean square of the density fluctuations,
$$\left[\frac{\langle(\delta\rho)^2\rangle}{\rho^2}\right]^{\frac{1}{2}}.$$

(d) Calculate the probability of observing a spontaneous fluctuation in 1 cc of gas at STP for which the instantaneous density differs from the mean by one part in 10^6.

Problem 6

(a) Prove that if the energy eigenvalues of a system can be expressed as a sum of independent contributions $E = E_A + E_B + E_C$ (eg, electronic energy, vibrational energy, rotational energy) that the heat capacity can be written $C_v = C_v^{(A)} + C_v^{(B)} + C_v^{(C)}$. In addition, show that the heat capacity is independent of zero point energy.

(b) Derive an expression for the electronic heat capacity assuming that there are only three significant electronic states and that they have energies and degeneracies given by $\varepsilon_0, g_0; \varepsilon_1, g_1; \varepsilon_2, g_2$.

(c) Given that the energies required for electronic transitions correspond roughly to u.v. light ($\sim 50,000°C$), show how the calculated room temperature heat capacity of a diatomic molecule will change if the electronic degrees of freedome are totally neglected. What if the ground electronic state degeneracy is included but all excited electronic states are neglected?

(d) Show how the room temperature entropy of the same molecule will change in these two cases.