
Problem Set 4

Due: 27 Sept 2006

Please staple problems 1+2 and 3+4.

1. **Harmonic Oscillator** (based on Callen, 16.5-5)

(a) Calculate the probability that a harmonic oscillator with energy levels $n\epsilon$, where $n = 0, 1, 2, \dots$, is in a state with an odd quantum number ($n = 1, 3, 5, \dots$) at temperature τ . Your answer should not involve sums. (Hint: Recall that for $x < 1$ we have

$$\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}.) \quad (1)$$

(b) To what values do you expect this probability to reduce in the limits of zero and infinite temperature? Explain your reasoning. Show that your result conforms to these limiting values.

(c) Compute the average energy of a harmonic oscillator in equilibrium at temperature τ . Compare your answer to the one for an Einstein solid in the low- and high-temperature limits. Explain how these results are related to each other.

(d) Calculate the entropy of a harmonic oscillator in equilibrium at temperature τ .

2. **Energy Fluctuations** (based on Schroeder, 6.16 and 6.18)

(a) Prove that, for any system in equilibrium with a reservoir at temperature τ , the average value of the energy is

$$U = \bar{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta} \ln Z, \quad (2)$$

if $\beta = 1/\tau$. You will find that this expression might be easier to use than the one we derived in class.

(b) Show that the variance in the energy of the system is

$$\sigma_E^2 = \overline{(E - \bar{E})^2} = \overline{E^2} - (\bar{E})^2 = -\frac{\partial U}{\partial \beta} = \tau^2 \frac{\partial U}{\partial \tau}, \quad (3)$$

where $U = \bar{E}$. (Hint: Start by showing that

$$\overline{E^2} = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2}.) \quad (4)$$

(c) Show that

$$\sigma_E^2 = \tau^2 C_V, \quad (5)$$

where C_V is the heat capacity at constant volume of the system. Calculate σ_E/U , the fractional fluctuation in the energy of an Einstein solid in the low- and high-temperature limits (see HW#2, problem 1). Comment on your result.

3. A Binary Alloy

A binary alloy is composed of N_A atoms of type A and N_B atoms of type B . Each A -type atom can exist in its ground state or in an excited state of energy ϵ (all other states are of such high energy that they can be neglected at the temperatures of interest). Each B -type atom can similarly exist in its ground state of energy zero or in an excited state of energy 2ϵ . The system is in equilibrium at temperature τ .

(a) Assuming that each atom has a fixed physical location, calculate the Helmholtz free energy of the system. (*Hint*: It is easiest to start with a single-particle partition function.)

(b) Calculate the average internal energy U and the entropy of the system.

(c) Now assume that atoms are free to move around. Show that there is an extra contribution to the entropy of this system, called entropy of mixing, given by the following expression:

$$\sigma_{mix} = -(N_A + N_B)[x \ln x + (1 - x) \ln (1 - x)], \quad (6)$$

where $x = N_A/(N_A + N_B)$.

(d) Explain why the new expression for the Helmholtz free energy is just

$$F' = F - \tau \sigma_{mix}, \quad (7)$$

where F is your result from (a). Does this change the partition function of this system? What about its equilibrium energy?

4. Additivity of the Canonical Entropy (based on Reif, 6.13)

Consider a composite system in thermal equilibrium with a reservoir which consists of subsystems A and B . Let the probability that A is found in a microstate i be P_i^A , and the probability that B is found in a microstate k be P_k^B . Use the expression for the entropy of a system at constant temperature that we derived in lecture, to prove that $\sigma_{A+B} = \sigma_A + \sigma_B$.