

Problem 1

Alternative expressions for chemical potential: 2 points

Starting from the generalized thermodynamic identity $dU = \tau d\sigma - p dV + \mu dN$, derive the following two expressions for the chemical potential:

$$\mu = \left(\frac{\partial U}{\partial N} \right)_{\sigma, V}$$

$$\mu = -\tau \left(\frac{\partial \sigma}{\partial N} \right)_{U, V}$$

Problem 2

Kittel & Kroemer, Chapter 5, problem 2 [Molecules in the Earth's atmosphere]: 3 points

If n is the concentration of molecules at the surface of the Earth, M the mass of a molecule, and g the gravitational acceleration at the surface, show that at constant temperature the total number of molecules in the atmosphere is

$$N = 4\pi n(R) e^{-MgR/\tau} \int_R^\infty dr r^2 e^{MgR^2/r\tau},$$

where r is measured from the center of the Earth; here R is the radius of the Earth. The integral diverges at the upper limit, so that N cannot be bounded and the atmosphere cannot be in equilibrium. Molecules, particularly light molecules, are always escaping from the atmosphere.

Problem 3

Kittel & Kroemer, Chapter 5, problem 3 [Potential energy of gas in gravitational field.]: 3 points

Consider a column of atoms each of mass M at temperature τ in a uniform gravitational field g . find the thermal average potential energy per atom. The thermal average kinetic energy density is independent of height. Find the total heat capacity per atom. The total heat capacity is the sum of contributions from the kinetic energy and from the potential energy. Take the zero of the gravitational energy at the bottom $h = 0$ of the column. Integrate from $h = 0$ to $h = \infty$.

Problem 4

Kittel & Kroemer, Chapter 5, problem 4 [Active transport.]: 3 points

The concentration of potassium K^+ ions in the internal sap of a plant cell (for example, a fresh water alga) may exceed by a factor of 10^4 the concentration of K^+ ions in the pond water in which the cell is growing. The chemical potential of the K^+ ions is higher in the sap because their concentration n is higher there. Estimate the difference in chemical potential at 300 K and show that it is equivalent to a voltage of 0.24 V across the cell wall. Take μ as for an ideal gas. Because the values of the chemical potentials are different, the ions in the cell and in the pond are not in diffusive equilibrium. The plant cell membrane is highly impermeable to the passive leakage of ions through it. Important questions in cell physics include these: How is the high concentration of ions built up within the cell? How is metabolic energy applied to energize the active ion transport?

Problem 5

Kittel & Kroemer, Chapter 5, problem 6 [Gibbs sum for a two level system.]: 5 points

(a): 1 point

Consider a system that may be unoccupied with energy zero or occupied by one particle in either of two states, one of energy zero and one of energy ϵ . Show that the Gibbs sum for this system is

$$\zeta = 1 + \lambda + \lambda e^{-\epsilon/\tau}$$

Our assumption excludes the possibility of one particle in each state at the same time. Notice that we include in the sum a term for $N = 0$ as a particular state of a system of a variable number of particles.

(b): 1 point

Show that the thermal average occupancy of the system is

$$\langle N \rangle = \frac{\lambda + \lambda e^{-\epsilon/\tau}}{\zeta}.$$

(c): 1 point

Show that the thermal average occupancy of the state at energy ϵ is

$$\langle N(\epsilon) \rangle = \frac{\lambda e^{-\epsilon/\tau}}{\zeta}.$$

(d): 1 point

Find an expression for the thermal average energy of the system.

(e): 1 point

Allow the possibility that the orbital at 0 and at ϵ may be occupied each by one particle at the same time; show that

$$\begin{aligned}\zeta &= 1 + \lambda + \lambda e^{-\epsilon/\tau} + \lambda^2 e^{-\epsilon/\tau} \\ &= (1 + \lambda)[1 + \lambda e^{-\epsilon/\tau}].\end{aligned}$$

Because ζ can be factored as shown, we have in effect two independent systems.

Problem 6**Kittel & Kroemer, Chapter 5, problem 10 [Concentration fluctuations.]: 2 points**

The number of particles is not constant in a system in diffusive contact with a reservoir. We have seen that

$$\langle N \rangle = \frac{\tau}{\zeta} \left(\frac{\partial \zeta}{\partial \mu} \right)_{\tau, V},$$

from Eq. 5.59.

(a): 1 point

Show that

$$\langle N^2 \rangle = \frac{\tau^2}{\zeta} \frac{\partial^2 \zeta}{\partial \mu^2}.$$

(b): 1 point

The mean-square deviation $\langle (\Delta N)^2 \rangle$ of N from $\langle N \rangle$ is defined by

$$\langle (\Delta N)^2 \rangle = \langle N^2 \rangle - \langle N \rangle^2 = \tau^2 \left[\frac{1}{\zeta} \frac{\partial^2 \zeta}{\partial \mu^2} - \frac{1}{\zeta^2} \left(\frac{\partial \zeta}{\partial \mu} \right)^2 \right].$$

Show that this may be written as

$$\langle (\Delta N)^2 \rangle = \tau \frac{\partial \langle N \rangle}{\partial \mu}.$$

In Chapter 6 we apply this result to the ideal gas to find that

$$\frac{\langle (\Delta N)^2 \rangle}{\langle N \rangle^2} = \frac{1}{\langle N \rangle}$$

is the mean square fractional fluctuation in the population of an ideal gas in diffusive contact with a reservoir. If $\langle N \rangle$ is of the order of 10^{20} atoms, then the fractional fluctuation is exceedingly small. In such a system the number of particles is well defined even though it cannot be rigorously constant because diffusive contact is allowed with the reservoir. When $\langle N \rangle$ is low, this relation can be used in the experimental determination of the molecular weight of large molecules such as DNA of MW 10^8 to 10^{10} .