

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:

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

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

For the energy $U(\sigma, V, \tau)$, the total differential is written generally as

$$dU = \left(\frac{\partial U}{\partial \sigma} \right)_{V, N} d\sigma + \left(\frac{\partial U}{\partial V} \right)_{\sigma, N} dV + \left(\frac{\partial U}{\partial N} \right)_{V, \sigma} dN.$$

We can compare this to the generalized thermodynamic identity above to see that

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

To see the other relation, we can rearrange the thermodynamic identity to solve for $d\sigma$:

$$d\sigma = dU/\tau + (p/\tau) dV - (\mu/\tau) dN.$$

This total differential is generally

$$d\sigma = \left(\frac{\partial \sigma}{\partial U} \right)_{V, N} dU + \left(\frac{\partial \sigma}{\partial V} \right)_{U, N} dV + \left(\frac{\partial \sigma}{\partial N} \right)_{U, V} dN.$$

Comparing this with the line above, we see

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

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.

In this chapter, an example is done in which the concentration is calculated as a function of height h above ground: $n(h) \propto e^{-Mgh/\tau}$. This derivation assumed we were close enough to the ground that the gravitational potential energy of a particle was Mgh . In order to extend this to greater altitudes, we must use a more accurate form of the gravitational potential energy: $U_G = -GM_e M/r$, where G is Newton's gravitational constant, M_e is the mass of the Earth, and r is the distance from the center of the Earth. Using the fact that $g = GM_e/R^2$, where R is the Earth's radius, we can write $U_G = -MgR^2/r$. Then the result for the concentration of particles at a distance r from the center of the earth is $n(r) \propto e^{MgR^2/r\tau}$. With this result, we can see that

$$\frac{n(r)}{n(R)} = \frac{e^{MgR^2/r\tau}}{e^{MgR/\tau}},$$

or

$$n(r) = n(R) e^{-MgR/\tau} e^{MgR^2/r\tau}.$$

This result should be valid everywhere. To get the total number of particles in the atmosphere, we can integrate the concentration $n(r)$ over the entire atmosphere, which is a spherical shell of inner radius R and outer radius ∞ . Since the integrand is spherically symmetric, the angular integrals evaluate to 4π , and we have

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

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 $h = \infty$.

Let our column be a square column of side length L . If we slice this column into small slices of height dh , each slice will have a volume of $dV = L^2 dh$, and the total number of particles dN in a slice at height h will be $dN = n(h)dV = L^2 n(h)dh$, where $n(h)$ is the concentration of particles at height h . We know from the text that this is given by $n(h) = n(0)e^{-Mgh/\tau}$, so $dN = L^2 n(0)e^{-Mgh/\tau} dh$. The total number of particles in this column will be

$$\begin{aligned} N &= \int dN = \int_0^\infty dh L^2 n(0) e^{-Mgh/\tau} \\ &= -\frac{\tau L^2 n(0)}{Mg} [e^{-Mgh/\tau}]_0^\infty \\ &= \frac{\tau L^2 n(0)}{Mg}. \end{aligned}$$

We can then see that the number of particles in a slice is

$$dN = \frac{MgN}{\tau} e^{-Mgh/\tau} dh.$$

Now, each particle in that slice should have a potential energy of Mgh , so the total potential energy du in that slice is

$$du = (Mgh)dN = \frac{M^2 g^2 h N}{\tau} e^{-Mgh/\tau} dh.$$

We can integrate this over the whole column to get the total potential energy u of the particles in the column:

$$u = \int du = \frac{M^2 g^2 N}{\tau} \int_0^\infty dh h e^{-Mgh/\tau} = \frac{M^2 g^2 N}{\tau} \left(\frac{\tau}{Mg} \right)^2 \int_0^\infty dx x e^{-x}.$$

You can look up the value of this integral; it equals 1. Thus the total potential energy per particle is

$$\frac{u}{N} = \tau.$$

We know from earlier results that the thermal average kinetic energy per particle for free particles is $K/N = \frac{3}{2}\tau$. Thus the total heat capacity per atom is

$$\frac{C_V}{N} = \frac{\partial}{\partial \tau} (u/N + K/N)_V = \frac{5}{2}.$$

The heat capacity tells us: if we heat up our system, how much will the temperature change? A larger heat capacity corresponds to less change in temperature when heated. In this case, some of the energy from heating goes to increasing the potential energy of the particles, instead of only increasing the kinetic energy.

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?

If we treat the ions like an ideal gas, the chemical potential is related to the concentration as $\mu = \tau \ln(n/n_Q)$. If n_c is the concentration of the potassium ions in the cell and $n_p = 10^{-4}n_c$ is their concentration in the pond, the difference in chemical potentials in the pond and cell will be

$$\begin{aligned}\mu_c - \mu_p &= \tau \ln(n_c/n_Q) - \tau \ln(n_p/n_Q) \\ &= \tau \ln(n_c/n_p) \\ &= \tau \ln(10^4).\end{aligned}$$

At $T = 300$ K, $\tau = k_B T = 0.0259$ eV. Thus at 300 K,

$$\mu_c - \mu_p = (0.0259 \text{ eV}) \ln(10^4) = 0.24 \text{ eV}.$$

The ions are singly-charged, and so an energy difference of 0.24 eV across the membrane corresponds to a voltage of 0.24 V.

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.

We can calculate:

$$\begin{aligned}\zeta &= \sum_{ASN} \lambda^N e^{-\epsilon_s/\tau} = \lambda^0 e^0 + \lambda e^0 + \lambda e^{-\epsilon/\tau} \\ &= 1 + \lambda + \lambda e^{-\epsilon/\tau}.\end{aligned}$$

(a): 1 point

(b): 1 point

Show that the thermal average occupancy of the system is

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

We can directly calculate based on the definition of averages:

$$\begin{aligned}\langle N \rangle &= \frac{\sum_{ASN} N \lambda^N e^{-\epsilon_s/\tau}}{\zeta} = \frac{(0)\lambda^0 e^0 + (1)\lambda e^0 + (1)\lambda e^{-\epsilon/\tau}}{\zeta} \\ &= \frac{\lambda + \lambda e^{-\epsilon/\tau}}{\zeta}.\end{aligned}$$

(b): 1 point

(c): 1 point

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

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

We can directly calculate based on the definition of averages:

$$\begin{aligned}\langle N(\epsilon) \rangle &= \frac{\sum_{ASN} N(\epsilon) \lambda^N e^{-\epsilon_s/\tau}}{\zeta} = \frac{(0)\lambda^0 e^0 + (0)\lambda e^0 + (1)\lambda e^{-\epsilon/\tau}}{\zeta} \\ &= \frac{\lambda e^{-\epsilon/\tau}}{\zeta}.\end{aligned}$$

(c): 1 point

In the second term in the numerator on the first line, the total number of particles in the *system* is 1, but the total number of particles in the state of energy ϵ is zero.

(d): 1 point

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

We can directly calculate based on the definition of averages, denoting by U the total energy of the system:

$$\begin{aligned}\langle U \rangle &= \frac{\sum_{ASN} U \lambda^N e^{-\epsilon_s/\tau}}{\zeta} = \frac{(0)\lambda^0 e^0 + (0)\lambda e^0 + (\epsilon)\lambda e^{-\epsilon/\tau}}{\zeta} \\ &= \frac{\epsilon \lambda e^{-\epsilon/\tau}}{\zeta}.\end{aligned}$$

(d): 1 point

This makes sense, since with this result we have $\langle U \rangle = \epsilon \langle N(\epsilon) \rangle$.

(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.

Now we can have $N = 0$, $N = 1$, and $N = 2$, and for the $N = 2$ case there is only one possible state, with one particle occupying each of the two energy states, so the total system energy will be $0 + \epsilon = \epsilon$ in that case. We can calculate:

$$\begin{aligned}\zeta &= \sum_{ASN} \lambda^N e^{-\epsilon_s/\tau} = (\lambda^0 e^0) + (\lambda e^0 + \lambda e^{-\epsilon/\tau}) + (\lambda^2 e^{-\epsilon/\tau}) \\ &= 1 + \lambda + \lambda e^{-\epsilon/\tau} + \lambda^2 e^{-\epsilon/\tau} \\ &= (1 + \lambda)[1 + \lambda e^{-\epsilon/\tau}].\end{aligned}$$

(e): 1 point

The two systems that this factors into is one system that consists of a single energy level with zero energy that can be occupied or unoccupied; and another system that consists of a single energy level with energy ϵ that can be occupied or unoccupied.

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

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

Let's see:

$$\begin{aligned} \langle N^2 \rangle &= \frac{\sum_{ASN} N^2 e^{(N\mu - \epsilon_s)/\tau}}{\zeta} \\ &= \frac{\tau \frac{\partial}{\partial \mu} \sum_{ASN} N e^{(N\mu - \epsilon_s)/\tau}}{\zeta} \\ &= \frac{\tau^2 \frac{\partial^2}{\partial \mu^2} \sum_{ASN} e^{(N\mu - \epsilon_s)/\tau}}{\zeta} \\ &= \frac{\tau^2 \frac{\partial^2 \zeta}{\partial \mu^2}}{\zeta}. \end{aligned}$$

(a): 1 point

(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} .

Let's work backwards:

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

(b): 1 point