Problem 1:

Given that the entropy of a isolated system can only increase, show that, for a multicomponent fluid at equilibrium,

(a) The temperature is the same everywhere.

[This problem is solved in Chapt. 7 in the notes.] Consider two neighboring volumes within the material, and let them exchange an infinitesimal amount of energy without changing the volume or chemical content of either. This exchange describes a thermal interaction. Since energy is conserved the energy gained by subsystem 1 must be lost by subsystem 2. Hence

\[ dE_2 = -dE_1 \]  

The total entropy change in the process is

\[ dS = dS_1 + dS_2 = \frac{dE_1}{T_1} + \frac{dE_2}{T_2} \]

\[ = dE_1 \left[ \frac{1}{T_1} - \frac{1}{T_2} \right] \]  

where \( T_1 \) and \( T_2 \) are the temperatures of the two subsystems. Equation 1.2 shows that the system can only be in equilibrium if \( T_1 = T_2 \). If this is not the case then \( dS \) is positive for a transfer of energy from the high-temperature subsystem to the low-temperature one. Hence the two subvolumes are not in equilibrium with one another unless their temperatures are the same.

The same reasoning applies to any choice of subvolumes within the system. It also applies when the system is not isolated, since a system cannot be in equilibrium if it is out of equilibrium with respect to internal changes that do not affect its environment. We are therefore led to the condition of thermal equilibrium, which holds in general: a system in equilibrium has a uniform temperature.

\[ T = \text{const.} \]  

(b) The pressure is the same everywhere.

Assuming fluid-like deformation and neglecting external fields, the mechanical interaction displaces the boundary between the two subvolumes so that
\[ dV_2 = - dV_1 \]  

1.4

Since energy is conserved \( dE_2 = - dE_1 \) and temperature is constant (thermal equilibrium), the associated change in the entropy is

\[ dS = \frac{1}{T} \left[ P_1 dV_1 + P_2 dV_2 \right] = \frac{dV_1}{T} \left[ P_1 - P_2 \right] \]  

1.5

If \( P_1 \neq P_2 \), \( dS \) is positive when the volume of the high-pressure subsystem increases at the expense of that of the low-pressure one. We are hence led to the condition of mechanical equilibrium in the absence of external fields: a system in mechanical equilibrium in the absence of external fields has a uniform pressure.

\[ P = \text{const.} \]  

1.6

(c) The chemical potential of every species is the same everywhere.

Consider two neighboring volumes within the material and let them exchange a small amount of one component, which we arbitrarily label the \( k \)th component. We assume that external fields can be neglected. Since the total amount of the \( k \)th component is conserved, the quantity added to \( V_2 \) is equal to that lost from \( V_1 \),

\[ dN_k^2 = - dN_k^1 \]  

1.7

The entropy change at constant total energy and uniform temperature is

\[ dS = - \frac{1}{T} \left[ \mu_k^1 dN_k^1 + \mu_k^2 dN_k^2 \right] = - \frac{1}{T} \left[ \mu_k^1 - \mu_k^2 \right] dN_k^1 \]  

1.8

where \( \mu_k^i \) is the chemical potential of the \( k \)th component in the \( i \)th subsystem. If \( \mu_k^1 \neq \mu_k^2 \) the entropy increases if a quantity of the \( k \)th component is transferred from the system of higher chemical potential to that in which the potential is lower. We are therefore led to the condition of chemical equilibrium: a system in chemical equilibrium in the absence of external fields has a uniform value of the chemical potential of each of its components.

\[ \mu_k = \text{const.} \]  

1.9

Problem 2:

(a) Consider a system that has an open boundary, and is in thermal and mechanical contact with a reservoir that fixes its temperature and chemical potentials. Show that the thermodynamic potential that governs the behavior of this system is the work function,
\[ \Omega = E - TS + \sum_{i} \mu_i N_i \]  

in the sense that no spontaneous change in the internal state of the system can decrease \( \Omega \).

[This problem is solved in Chapt. 7 of the notes.] The system and the reservoir form an isolated system when they are taken together. The local condition of equilibrium for this composite system is that its entropy must be a maximum for infinitesimal changes in its state at constant values of the energy, volume and mole number. If this is true then any infinitesimal change of state satisfies the condition,

\[ (\delta S^T)_{E,V,\{N\}} \leq 0 \]  

that is, if the entropy is a maximum then any possible, infinitesimal change of state must cause the entropy to decrease or remain the same. The change in entropy is the sum of the change in the system \( (\delta S) \) and that in the reservoir \( (\delta S_R) \). Assuming that the reservoir is internally in equilibrium, its entropy change is due to its interaction with the system. It can exchange energy and matter, so

\[ \delta S_R = \frac{1}{T}(\delta E_R + \sum_i \mu_i \delta N_{iR}) \]  

Since the energy and volume of the composite, system plus reservoir, are constant, \( \delta E_R = -\delta E \), and \( \delta N_{iR} = -\delta N_i \). Moreover, the condition of thermal equilibrium requires that the system and the reservoir have the same temperature, \( T \), and the condition of chemical equilibrium requires that they have the same chemical potentials, \( \{\mu\} \). Hence

\[ \delta S^T = \delta S + \delta S_R = \delta S - \frac{1}{T}(\delta E + \sum_i \mu_i \delta N_i) \]

It follows that the condition, 1.2, is equivalent to the condition

\[ (T\delta S - \delta E - \sum_i \mu_i \delta N_i)_{E,V,\{\mu\}} \leq 0 \]  

where we have used the fact that \( T \) is positive and that the values of \( T \) and the \( \mu_i \) in the system are fixed by the reservoir. The quantity is parentheses on the left hand side of 1.5 contains only quantities that pertain to the system. The condition 1.2 can be written in the equivalent form

\[ \delta(E - TS - \sum_i \mu_i N_i)_{E,V,\{\mu\}} \geq 0 \]  

The quantity in parentheses is the work function
\[ \Omega = E - TS - \sum_i \mu_i N_i = -PV \]  

and the condition 1.6 states that a system in the situation described here is in equilibrium only if its work function has a minimum value with respect to infinitesimal changes of state at fixed values of T, P and \{N\}.

(b) Show that the differential of the work function is

\[ d\Omega = -SdT - PdV - \sum_k N_k d\mu_k \]

Infer that if \( \Omega \) is written as a function of \( T, V \) and the set of chemical potentials, \( \{\mu\} \), the first partial derivatives of this function give the entropy, pressure and chemical composition.

From the definition of the work function, its differential is

\[
d\Omega = d(E - TS - \sum_i \mu_i N_i)
= dE - TdS - SdT - \sum_i \mu_i dN_i - \sum_i N_i d\mu_i
= -SdT - PdV - \sum_i N_i d\mu_i
\]

If \( \Omega \) is written as a function of \( T, V \) and \( \{\mu\} \), then its differential is

\[
d\Omega = d\tilde{\Omega}(T,V,\{\mu\})
= \left[ \frac{\partial \tilde{\Omega}}{\partial T} \right] dT + \left[ \frac{\partial \tilde{\Omega}}{\partial V} \right] dV + \sum_k \left[ \frac{\partial \tilde{\Omega}}{\partial \mu_k} \right] d\mu_k
\]

Comparing 1.9 and 1.10,

\[
\left[ \frac{\partial \tilde{\Omega}}{\partial T} \right] = -S
\]

\[
\left[ \frac{\partial \tilde{\Omega}}{\partial V} \right] = -P
\]
\[
\left[ \frac{\partial \Omega}{\partial \mu_k} \right] = -N_k
\] 2.12

(c) From the results of part (a) and (b), show that the pressure, \( P \), can be written as a function of the temperature and chemical potentials:

\[
P = \tilde{P}(T, \{\mu\})
\] 2.13

Find the derivatives of this function, and show that the pressure of an open system at equilibrium has the highest value consistent with its temperature and chemical potentials.

Given

\[
\Omega = E - TS - \sum_i \mu_i N_i = -PV
\] 2.1

we have, for fixed volume,

\[
d\Omega = -VdP = -SdT - \sum_i N_i d\mu_i
\] 2.14

and, hence, that

\[
dP = S_VdT + \sum_i n_i d\mu_i
\] 2.15

where \( n_i = N_i/V \) is the molar density. It follows from eq. 1.15 that

\[
P = \tilde{P}(T, \{\mu\})
\] 2.13

with

\[
\left[ \frac{\partial \tilde{P}}{\partial T} \right] = S_V
\] 2.14

\[
\left[ \frac{\partial \tilde{P}}{\partial \mu_k} \right] = n_k
\] 2.15

The fact that \( P \) is maximum at equilibrium for given \( T, \{\mu\} \) then follows from eq. 2.1 and the fact that \( \Omega \) is minimum at equilibrium for given \( T, V, \{\mu\} \).

**Problem 3:**

The equilibrium phase diagram of a two-component material shows the phases present at equilibrium as a function of temperature \( T \) and solute content \( x \). It is possible to obtain three pieces of information from the binary phase diagram:

1. the phases present at equilibrium at any given composition and temperature;
2: the compositions of the phases;
3: the fractions of the phases.

Using a simple eutectic phase diagram as an example, describe how each of these three pieces of information can be found.

Fig. 3.1: Simple eutectic phase diagram for a binary system.

The binary phase diagram is a map of the equilibrium phases that appear in the system as a function of its temperature and composition. It contains three pieces of information for each temperature and composition. First, the phases present at equilibrium at (T,x) are given by the phase field in which the point (T,x) appears. In the example given in Fig. 3.1 the equilibrium state is a two-phase mixture of α and β solid solutions. Second, the phase diagram gives the compositions of the phases present. If the system has only a single phase then its composition is, of course, the overall composition, x. If the system contains two phases, however, their compositions differ. The two compositions can be found by drawing an isothermal line through the point (T,x), as shown in the figure. The compositions of the two phases are given by the intersections of the isothermal line with the boundaries of the single-phase fields on either side of it, as shown in the figure. Third, the fractions of the phase present can be found from the "lever rule". In the example below, the fraction of α, fα, at (T,x) is

\[ f_\alpha = \frac{x_\beta - x}{x_\beta - x_\alpha} \]

\[ f_\beta = 1 - f_\alpha = \frac{x - x_\alpha}{x_\beta - x_\alpha} \]

Problem 4:

The phase diagram of the Pb-Sn binary system is drawn below.
Fig. 3.2: Pb-Sn phase diagram with 60Sn-40Pb and 95Pb-5Sn compositions indicated.

(a) Pb and Sn do not form solid solutions at all compositions. Why would you expect this?

Solid Pb has an FCC crystal structure. At normal temperatures, solid Sn has a tetragonal crystal structure. Since the Sn crystal structure cannot be created by simply replacing Pb by Sn on the FCC lattice, the two elements cannot form a continuous range of solid solutions.

(b) Let an alloy of composition 63Sn-37Pb be solidified by relatively slow cooling. Describe the microstructure you would expect and explain why it should form.

63Sn-37Pb is almost precisely the eutectic composition. If a liquid of this composition is slowly cooled, it transforms at the eutectic temperature to a mixture of $\alpha$ (Pb-rich solid solution) and $\beta$ (Sn-rich solid solution). The expected microstructure is the classic eutectic microstructure that is discussed in the notes and that was observed in the Pb-Sb system you studied in the laboratory. For kinetic reasons, the $\alpha$ and $\beta$ phases grow as parallel lamellae, as shown in Fig. 3.3, to give the eutectic microstructure shown in Fig. 3.4, in which parallel lamellae are gathered into eutectic colonies.

![Illustration of a growing eutectic colony.](image-url)
Fig. 3.4: Schematic drawing of a eutectic microstructure. The grain-like features are eutectic colonies containing aligned plates or rods.

There is, however, a final (subtle) change that occurs in this microstructure as it is cooled to room temperature. As indicated by the phase diagram, the solubility of Sn in Pb decreases significantly as the temperature is lowered. This has the consequence that Sn-rich precipitates form within the lamellae of Pb-rich phase to achieve equilibrium concentration. (The solubility of Pb in Sn also decreases with temperature, but the solubility at the eutectic composition is so low that Pb-rich precipitates are not normally found in the Sn-rich phase.)

(c) Let an alloy of composition 95Pb-5Sn be solidified by slow cooling. What microstructure would you expect and why?

The 95Pb-5Sn composition is indicated in the phase diagram. If the material is cooled slowly enough that equilibrium is maintained then it will solidify into an $\alpha$ solid solution. The microstructure should consist of relatively equiaxed grains to minimize the interfacial energy. On further cooling the alloy penetrates the $\alpha+\beta$ region at lower temperature. Small particles of Sn-rich $\beta$ solid solution should then precipitate out of the $\alpha$ grains.

Problem 5:

Give qualitative explanations for the following observations concerning thermal conductivity in solids.

(a) At ordinary temperature the thermal conductivity of a metal is proportional to its electrical conductivity.

In most materials at ordinary temperature (greater than one-half the Debye temperature) the principal mechanism of thermal conductivity is energy transport by conduction electrons. Hence thermal conductivity is proportional to electrical conductivity.

(b) The thermal conductivity of diamond at room temperature may be even larger than the thermal conductivity of copper.
The thermal conductivity of an insulator is primarily due to lattice vibrations (phonons). Phonons are highly mobile in pure materials at low temperature, but are strongly scattered by the lattice at temperature greater than about $\Theta_D/2$, where $\Theta_D$ is the Debye temperature, for reasons discussed in the text. In ordinary metals and insulators, including copper ($\Theta_D \approx 315$K), room temperature is more than half the Debye temperature, so phonons are not efficient conductors of heat. However, the Debye temperature of diamond is $\Theta_D \approx 2000$K. Room temperature is a very low temperature for diamond, and the phonon conductivity is very high.

(c) Silica glass has low thermal conductivity at room temperature.

Since silica glass is an insulator, its thermal conductivity at room temperature is due primarily to conduction by phonons. Phonons are scattered by disordered or distorted regions of the lattice. Since the lattice of silica glass is disordered, the phonon mean free path is very short and the thermal conductivity is correspondingly small.

(d) The thermal conductivity of diamond films is very sensitive to the method of preparation.

Since diamond is an electrical insulator, it conducts heat primarily with phonons. Since phonons are strongly scattered by defects in the material, its thermal conductivity is proportional; to the density of defects and, hence, to the method of preparation.

Problem 6:

(a) Why is the activation energy for diffusion of a typical substitutional solute roughly twice as that of a typical interstitial solute?

An interstitial atom diffuses (moves through the crystal lattice) by performing discrete jumps from one interstitial site to another. The frequency of jumping, $\nu$ (number of jumps per unit time), is hence governed by an equation of the Arrhenius form:

$$\nu = A \exp\left(-\frac{Q_m}{kT}\right)$$  \hspace{1cm} 5.1

where $Q_m$ is the activation energy opposing an atom jump, $k$ is Boltzmann's constant, and $A$ is a pre-exponential factor. Since the diffusivity, $D$, is proportional to the jump frequency, it is given by an equation of the form

$$D_i = D_0 \exp\left(-\frac{Q_m}{kT}\right)$$  \hspace{1cm} 5.2

For a substitutional specie to perform a jump a neighboring site must be vacant. Vacancies are high-energy intrinsic defects in a crystal whose equilibrium concentration, $x_V$ (the fraction of vacant sites), is governed by the Arrhenius equation
\[ x_V = B \exp\left[ -\left( \frac{Q_V}{kT} \right) \right] \]  

where \( B \) is a pre-exponential factor and \( Q_V \) is the energy to form a vacancy. The probability that an substitutional atom jumps is the product of the probability that a neighboring site is vacant (\( x_V \) if the vacancies are randomly distributed) and the probability that the atom jumps to the vacant site (whose frequency is governed by an equation of the form 5.1). Hence

\[ \nu = C \exp\left[ -\left( \frac{\{Q_m+Q_V\}}{kT} \right) \right] \]  

where \( Q_m \) is the activation energy opposing the jump of a substitutional atom into a neighboring vacancy and \( C \) is a pre-exponential factor. The diffusivity is proportional to \( \nu \), and hence has the form

\[ D_s = D_0 \exp\left[ -\left( \frac{Q}{kT} \right) \right] \]  

where

\[ Q = Q_m + Q_V \]  

Since \( Q_m \approx 1 \) eV for most materials of interest, and \( Q_V \approx (1-4)Q_m \), the diffusivity of a substitutional component is typically much lower than that of an interstitial.

(b) Plot the expected form of the variation of diffusivity vs. temperature (the simplest plot is ln(D) vs. (1/T)) for a substitutional specie in a single crystal and in a polycrystal. Why do the two curves differ significantly only at low temperature?

In a polycrystal the substitutional species can diffuse along the grain boundaries (which form a continuous network) as well as through the bulk of the crystal. To a first approximation we can imagine that the grain boundary is like the crystal, but contains a high density of vacant sites. Hence the grain boundary diffusivity obeys an equation that is of the form

\[ D_B = D_0^B \exp\left[ -\left( \frac{QB}{kT} \right) \right] \]  

where \( QB < Q_m \) is much less than \( Q \), the activation energy for diffusion through the bulk, and reflects the fact that it is not necessary to form a vacancy to accomplish an atom jump. But the pre-exponential factor, \( D_0^B \), is also changed. The diffusivity is related to the flux of material through the solid (by Fick's law). The flux is the amount of material that flows across a fixed plane per unit time. The flux due to grain boundary diffusion is
restricted by the small fraction of grain boundary material per unit area on a cross-section through the material. The fractional area of grain boundary in a cross-section is proportional to \( (\delta/d) \), where \( \delta \) is the effective thickness of the grain boundary and \( d \) is the mean grain diameter. Hence

\[
D_0^B \approx D_0 \left[ \frac{\delta}{d} \right]
\]

Since \( \delta \) is of the order of a few Å, while \( d \) is typically of the order \( 10^4-10^6 \) Å,

\[
D_0^B \ll D_0
\]

Since it is possible for atoms to diffuse either through the solid or through the grain boundary, these diffusion paths are in parallel, and the net diffusion is the sum of the diffusion accomplished by each. The ratio of the two diffusivities is

\[
\frac{D_B}{D} = \left[ \frac{D_0^B}{D_0} \right] \exp \left[ \frac{(Q - Q_B)}{kT} \right]
\]

When the temperature is very large the exponential term approaches 1 and \( D_B \ll D \). Hence at high temperature diffusion is almost entirely through the bulk. As the temperature approaches zero, however, the exponential term becomes arbitrarily large since \( Q > Q_B \). It follows that at sufficiently low temperature \( D_B \gg D \) and the diffusion is almost exclusively through the grain boundaries.

The aggregate behavior is sketched qualitatively in Figure 3.5. Since

\[
\ln(D) = \ln(D_0) - \frac{Q}{kT}
\]

a plot of \( \ln(D) \) against \( (1/kT) \) is a straight line with slope \(-Q\) that approaches \( \ln(D_0) \) in the limit \( T \to \infty \) (\( T^{-1} \to 0 \)). Since the processes of bulk and grain boundary diffusion occur in parallel, the overall diffusivity is determined by the greater of the two. The net diffusivity is given by two straight lines that join at the temperature at which the dominant mechanism of diffusion changes, as shown in the figure.
Fig. 3.5: Semi-logarithmic plot of diffusivity against reciprocal temperature for a polygranular material.

(c) Explain the mechanism of the "Kirkendall effect". Would you expect to find a Kirkendall effect in a situation where diffusion was dominated by interstitial species?

When two substitutional species diffuse on the same lattice, they move by exchanging with vacancies rather than with one another. The consequence is that the two species ordinarily diffuse at different rates. There is, hence, a net transport of matter in the direction of diffusion of the faster-moving specie, and a net counterflow of vacancies in the opposite direction. This is the Kirkendall effect.

Problem 7:

Give qualitative explanations for the following phenomena:

(a) A sample of a metal is quenched rapidly from a relatively high temperature. A plot of the self-diffusion coefficient as a function of time after the quench shows that its value is initially high, but decreases with time to asymptote at the value appropriate to the final temperature.

The self-diffusion coefficient is the diffusivity of the atoms of the primary metal constituent itself, which necessarily diffuses by a substitutional mechanism. Hence diffusion requires the participation of vacancies. The equilibrium vacancy concentration increases exponentially with the temperature. If the sample is quenched rapidly from high temperature the vacancy concentration immediately after the quench is high, since it takes some time for the excess vacancies to diffuse to sites, such as interfaces and dislocations, where they can be annihilated. The diffusivity of a substitutional species can be written

\[ D = D_0 x \exp \left( -\frac{Q_m}{kT} \right) \]  \hspace{1cm} \text{(7.1)}
where $x_v$ is the atom fraction of vacancies. While the concentration of vacancies is high, the diffusivity is anomalously high. It decreases to its equilibrium value as the vacancy concentration equilibrates.

(b) NaCl is an ionic conductor in which charge is transported primarily by the diffusion of Na$^+$ ions. It is found experimentally that ionic conductivity increases dramatically is a small quantity of Mg is added to NaCl.

Mg is divalent, and hence tends to enter NaCl as an Mg$^{++}$ ion. When Mg$^{++}$ substitutes for Na$^+$ charge neutrality is achieved by increasing the atom fraction of vacancies on the Na sublattice. The increased concentration of vacancies raises the diffusivity of Na$^+$, hence increasing the ionic conductivity.

(c) A sample of Al is supersaturated with a solute that would precipitate if equilibrium were reached. The Al remains supersaturated until it is deformed, at which point the solute precipitates rapidly.

Deformation introduces defects into the material, including vacancies, that raise the diffusivity and promote precipitation. The process is called strain aging.