Materials Science and Engineering Problems

MSE Faculty

July 21, 2022

This document includes the assigned problems that have been included so far in the digitized portion of our course curriculum.

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1.1 Course Organization

1) Send an email to Prof. Shull (k-shull@northwestern.edu) and Alane (Alane.lim@k-shull@northwestern.eduu.northwestern.edu) with the following information:

1. Any background about yourself that you want to share.

2. What you have enjoyed most and have found the most frustrating about your major.

3. One particular aspect of materials science that you would like to learn more about this quarter.

1.2 Atomic Structure and Bonding

2) Classify each of the following materials as to whether it is a metal, ceramic, or polymer. Justify each choice. (a.) brass; (b.) magnesium oxide (MgO); (c.) Plexiglass®; (d.) polychloroprene; (e.) boron carbide (B_4C); and (f.) steel.

3) Site the difference between *atomic mass* and *atomic weight*.

4) Silicon has three naturally occurring isotopes: 92.23% of ^{28}Si, with an atomic weight of 27.9769 amu, 4.68% of ^{29}Si, with an atomic wight of 28.9738 amu, and 3.69% of ^{30}Si, with an atomic weight of 29.938 amu. On the basis of these data, confirm that the *average* atomic weight of Si is 28.09.

5) Indium has two naturally occurring isotopes: ^{113}In, with an atomic weight of 112.904 amu, and ^{115}In, with an atomic weight of 114.904 amu. If the average atomic weight for In is 114.818 amu, calculate the fraction-of-occurrences of these two isotopes.

6) Address the following concepts concerning atomic mass.

1. How many grams are there in one *amu* of material?

2. Mole, in the context of this book, is taken in units of gram-mole. On this basis, how many atoms are there in a pound-mole of a substance?

7) Relative to electrons and electronic states, what does each of the four quantum numbers specify?

8) Give the electron configurations for the following ions: P^{5+}, P^{3-}, Sn^{4+}, Se^{2-}, I^- and Ni^{2+}.

9) Potassium iodide (KI) exhibits predominately ionic bonding. The K^+ and I^- ion have electron structures that are identical to which two inert gases?

10) Without consulting Callister Figure 2.8 or Table 2.2, determine whether each of the following atomic electron configurations is an inert gas, a halogen, an alkali metal, an alkaline earth metal, or a transition metal. List the number of valence electrons for each atom (except for the transition metals). Justify your choices.

1. $1s^2 2s^2 2p^6 3s^2 3p^5$

2. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$

3. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$

4. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$

5. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^5 5s^2$

6. $1s^2 2s^2 2p^6 3s^2$

11) The atomic radii of Mg^{2+} and F^- ions are 0.072 and 0.133 nm respectively.

1. Calculate the force of attraction between the two ions at their equilibrium interionic separation (i.e., when the ions just touch one another).

2. What is the force of repulsion at this same separation distance?

12) The force of attraction between a divalent cation and a divalent anion is 1.67×10^{-8} N. If the ionic radius of the cation is 0.080 nm, what is the anion radius?

Here we're provided with the two pieces of information: the force of attraction between a cation/anion pair and the cation's atomic radius. With this information and an understanding of the Coulomb interaction we can calculate the anion radius.
The force of attraction between two isolated ions is defined by Callister Eq. 2.13:

13) The net potential energy between two adjacent ions, E_N, may be represented by the sum of Callister equations 2.9 and 2.11. That is:

$$E_N = -\frac{A}{r} + \frac{B}{r^n} \tag{1.1}$$

Determine the equilibrium ionic bond energy, E_0, in terms of the parameters A, B, and n. Note that equilibrium occurs when the net force on the ions is zero. Use the following procedure:

1. Differentiate E_N with respect to r to acquire the expression for the interatomic *force*.

2. Assume two adjacent ions a E_N versus r is minimum at E_0.

3. Solve for r in terms of A, B, and n, which yields r_0, the equilibrium interionic spacing.

4. Determine the expression for E_0 by substituting r_0 into the equation.

14) For an Na^+-Cl^- ion pair, attractive and repulsive energies (E_A and E_R, respectively), depends on the distance between ions:

$$E_A = -\frac{1.44\,\text{eV} \cdot \text{nm}}{r} \tag{1.2}$$

$$E_R = \frac{7.32 \times 10^{-6}\,\text{eV} \cdot \text{nm}^8}{r^8} \tag{1.3}$$

1. Superimpose on a single plot (by hand or using plotting software) E_A, E_R, and the net energy E_N up to $r = 1.0$ nm. **Hint:** You may have to truncate the plot on the y-axis for good visualization.

2. From this plot, derive the equilibrium spacing, r_0 and the magnitude of the bonding energy, E_0 at the equilibrium spacing.

3. Now consider instead a K^+-Cl^- bonding pair. The K^+ ion is larger, which changes the repulsive term E_R to be:

$$E_R = \frac{5.80 \times 10^{-6}\,\text{eV} - \text{nm}^9}{r^9} \tag{1.4}$$

Without plotting the new E_N, how do you expect E_0 and r_0 to change for the K^+-Cl^- ion pair?

15) Briefly discuss the main differences between 1.) ionic, 2.) covalent, and 3.) metallic bonding.

16) Plot the bonding energy vs melting temperature for the following metals.

Element	Bonding Energy (kJ/mol)	Melting Temperature (°C)
Hg	62	-39
Al	330	660
Ag	282	962
W	850	3414

Using this plot, approximate the bonding energy for molybdenum, which has a melting temperature of $T_M = 2617°C$.

17) Compute the percent ionicity (&IC) of the interatomic bonds for each of the following compounds: MgO, GaP, CsF, CdS, and FeO. Which would we consider primarily ionic, and which would we consider primary covalent? Semiconductors typically possess covalent bonds - which of the compounds above do you expect is (are) used as in semiconductor applications?

18) What are the predominant type(s) of bonding would be expected for each of the following materials: solid xenon, calcium fluoride (CaF_2), bronze (a copper alloy), cadmium telluride (CdTe), rubber, and tungsten?

1.3 Crystal Structure

19) The body-centered cubic (BCC) crystal structure is shown below in Fig. 1.1 Demonstrate the following:

1. The unit cell length (also referred to as a lattice parameter) is $a = 4r/\sqrt{3}$, where r is the atomic radius.

2. The atomic packing factor (APF) is 0.68.
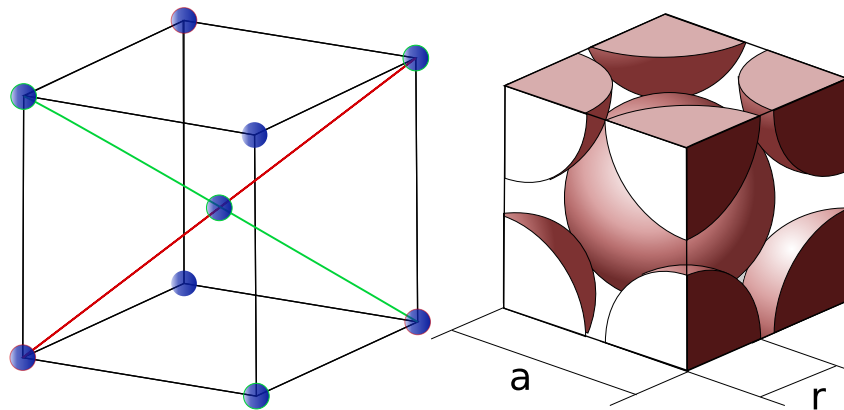
Figure 1.1: The BCC structure.

This is the first problem you have in navigating and performing calculations on basic unit cells. This process is identical for all single-element unit cells (practice more if you need, see suggested problems) and you should be able to perform it for any cubic unit cell. In this case, visualizing how the atoms stack in the close-packed (touching) {111} directions is critical as well as some simple geometry and vector calculations.

20) Molybdenum has a BCC crystal structure, an atomic radius of 0.1363 nm, and an atomic weight of 95.94 g/mol. Compute and compare its theoretical density with the experimental value found inside the front cover of the Callister book.

21) Strontium has an FCC crystal structure, an atomic radius of 0.215 nm, and an atomic weight of 87.62 g/mol. Calculate the theoretical density for Sr. Make sure to use intuitive units (not g/nm^3).

22) Calculate the radius of a palladium (Pd) atom, given that Pd has an FCC crystal structure, a density of $\rho_{Pd} = 12.0$ g/cm^3, and an atomic weight of $A_{Pd} = 106.4$ g/mol.

23) The atomic weight, density, and atomic radius for the three hypothetical alloys are listed in Table 1.1. For each, determine whether its crystal structure is FCC, BCC, or simple cubic (SC) and then justify your determination. *Only work on this problem until you understand the concepts. It can get tedious.*

Alloy	Atomic Weight (g/mol)	Density (g/cm^3)	Atomic radius (nm)
A	43.1	6.40	0.122
B	184.4	12.30	0.146
C	91.6	9.60	0.137

Table 1.1: Alloy Properties

24) Iron (Fe) undergoes an allotropic transformation at 912 °C. Upon heating it transitions from a BCC (α phase) to an FCC (γ phase). Accompanying this transformation is a change in the atomic radius of Fe – from $r_{BCC} = 0.12584$ nm to $r_{FCC} = 0.12894$ nm – and, in addition, a change in density (and volume). Compute the percentage volume change associated with this transformation. Does the volume increase or decrease?

25) For the tetragonal crystal system ($a = b \neq c$, $\alpha = \beta = \gamma = 90°$), identify the lattice directions that are equivalent to the (a) [011] and the (b) [100] directions, respectively.

26) Determine the indices for the directions shown in the following cubic unit cell (only do this problem until you understand the process):
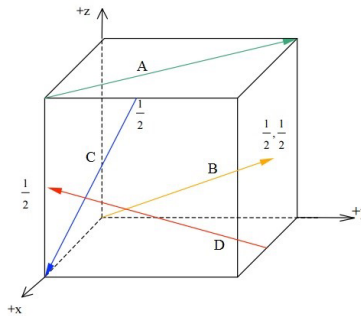
27) Determine the indices for the directions shown in the cubic unit cell below Fig. 1.2(a). Do as much of this problem as you need to understand the process.
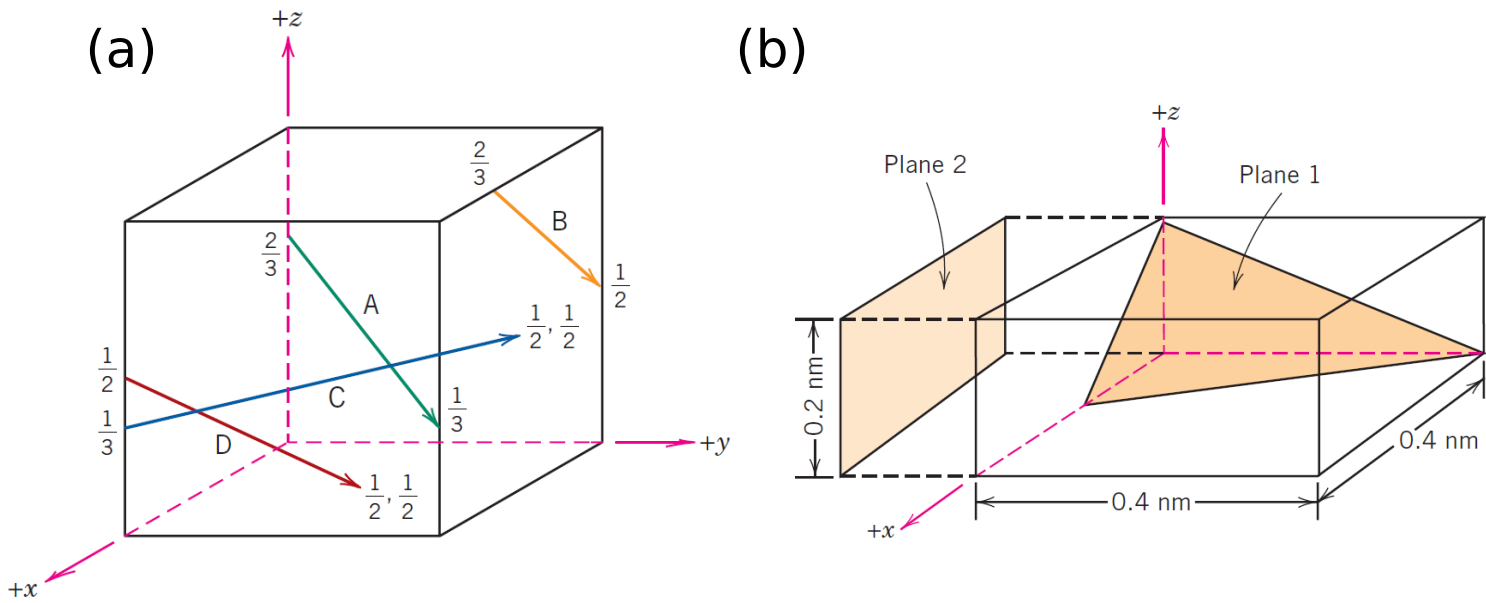
Figure 1.2: Some crystallographic directions (a) and planes (b)

28) For the tetragonal crystal system ($a = b \neq c$, $\alpha = \beta = \gamma = 90°$), identify the lattice directions that are equivalent to the (a) [011] and the (b) [100] directions, respectively.

29) Determine the Miller indices for the planes shown in the following unit cell:
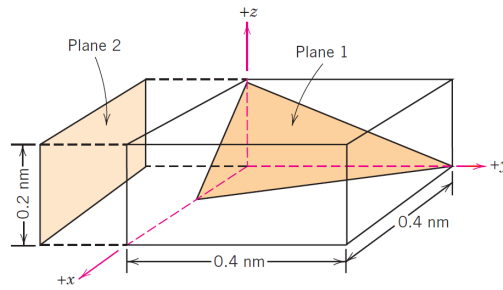
30) Determine the Miller indices for the planes shown in the following unit cell:
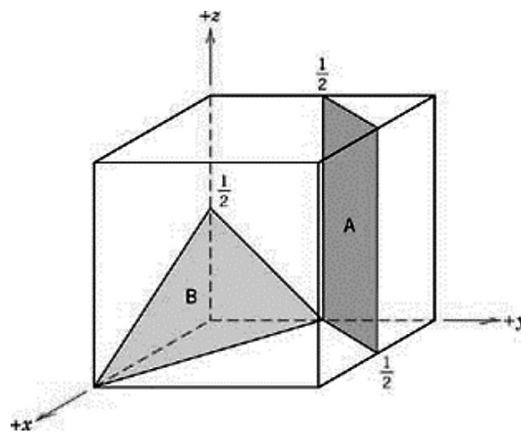
31) For the tetragonal crystal system ($a = b \neq c$, $\alpha = \beta = \gamma = 90°$), identify the lattice directions that are equivalent to the (a) [011] and the (b) [100] directions, respectively.

32) Would you expect a material in which the atomic bonding is predominantly ionic is in nature to be more likely or less likely to form a noncrystalline solid upon solidification than a covalent material? Why? (See Callister Section 2.6)

33) Fig. 1.3 shows two tiled patterns. In each, draw a 2D unit cell — the simplest repeat unit in these patterns. Note — there are more than one possible answers.
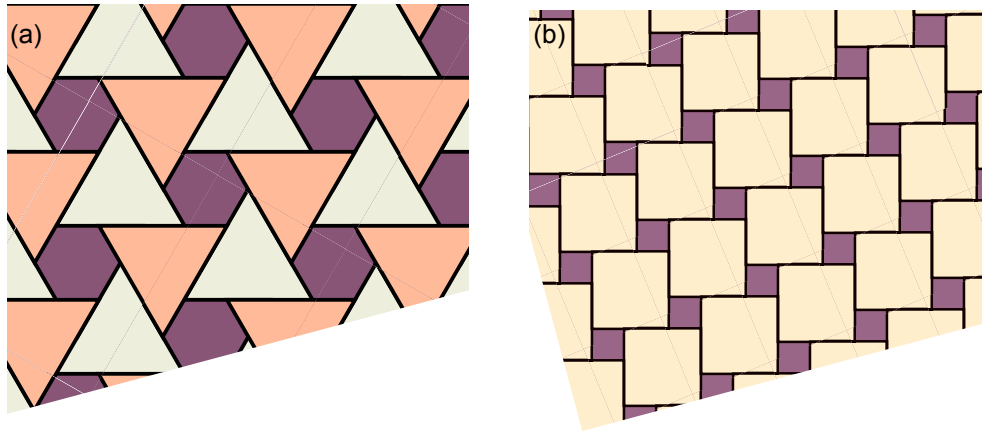

Figure 1.3: Periodic tiled patterns. From Baelde (Own work) [CC BY-SA 3.0 (https://creativecommons.org/licenses/by-sa/3.0) via Wikimedia Commons.

Similar problems: Google Image Search "Periodic Tessalation" and try some of those images. Warning — Google searches will not always yield a periodic tile... so be careful not to waste your time.

34) Describe the differences in short-range order (bonding, local geometry) and long-range order (crystallinity) between crystalline and non-crystalline materials.

1.4 Imperfections

35) For some hypothetical metal, the equilibrium number of vacancies at 900 °C is 2.3×10^{25} m^{-3}. If the density and atomic weight of this metal are 7.40 g/cm^3 and 85.5 g/mol, respectively, calculate the fraction of vacancies for this metal at 900 °C.

36) Calculate the activation energy for vacancy formation in aluminum given that the equilibrium number of vacancies at 500°C (773 K) is 7.57×10^{23} m^{-3}. The atomic weight and density (at 500°C) for aluminum are, respectively, 26.98 g/mol and 2.62 g/cm^3.

37) For both FCC and BCC crystal structures, there are two different types of interstitial sites. In each case, one site is larger than the other and is normally occupied by impurity atoms. For FCC, this larger one is located at the center of each edge of the unit cell; it is termed an *octahedral interstitial site*. On the other hand, with BCC the larger site type is found at $0 \frac{1}{2} \frac{1}{4}$ positions - that is, lying on {100} faces and situated midway between two unit cell edges on this face and one-quarter of the distance between the other two unit cell edges; it is termed a *tetrahedral interstitial site*. For both FCC and BCC crystal structures, compute the radius r of an impurity atom that will just fit into one of these sites in terms of the atomic radius R of the host atom.

38) Derive the following equations: (a) Equation 4.7a (b) Equation 4.9a (c) Equation 4.10a (d) Equation 4.11b

39) Atomic radius, crystal structure, electronegativity, and the most common valence are given in the following table for several elements; for those that are nonmetals, only atomic radii are indicated.

Element	Atomic Radius (nm)	Crystal Structure	Electronegativity	Valence
Ni	0.1246	FCC	1.8	+2
C	0.0710			
H	0.0460			
O	0.0600			
Ag	0.1445	FCC	1.9	+1
Al	0.1431	FCC	1.5	+3
Co	0.1253	HCP	1.8	+2
Cr	0.1249	BCC	1.6	+3
Fe	0.1241	BCC	1.8	+2
Pt	0.1387	FCC	2.2	+2
Zn	0.1332	HCP	1.6	+2

Which of these elements would you expect to form the following with nickel at room temperature?:

1. a substitutional solid solution having complete solubility

2. a substitutional solid solution of incomplete solubility

3. an interstitial solid solution

40) (a)Compute the radius r of an impurity atom that will just fit into an FCC octahedral site in terms of the atomic radius R of the host atom (without introducing lattice strains).
(b) Repeat part(a) for the FCC tetrahedral site. (*Note:* You may want to consult Callister Figure 4.3*a*.)

41) (a) For BCC iron, compute the radius of a tetrahedral interstitial site. (For this problem, you need the result of Problem 4.9, which is $r = 0.291R$, where R is the radius of the atoms in the FCC unit cell and r is the tetrahedron radius. You should do 4.9 if you don't understand how to find this.)

42) What is the composition, in weight percent, of an alloy that consists of 5 at% Cu and 95 at% Pt?

43) Molybdenum forms a substitutional solid solution with tungsten. Compute the number of molybdenum atoms per cubic centimeter for a molybdenum-tungsten alloy that contains 16.4 wt percent Mo and 83.6 wt percent W. The densities of pure molybdenum and tungsten are 10.22 and 19.30 g/cm3, respectively.

44) Calculate the number of atoms per cubic meter in Pb.

45) Cite the relative Burgers vector-dislocation line orientations for edge, screw, and mixed dislocations.

46) For an FCC single crystal, would you expect the surface energy for a (100) plane to be greater or less than that for a (111) plane? Why? (*Note:* You may want to consult the solution to Problem 3.60 at the end of Chapter 3.)

47) (a)For a given material, would you expect the surface energy to be greater than, the same as, or less than the grain boundary energy? Why?
(b) The grain boundary energy of a small angle grain boundary is less than for a high-angle one. Why is this so?

48) Aluminum-lithium (Al-Li) alloys have been developed by the aircraft industry to reduce the weight and improve the performance of its aircraft. A commercial aircraft skin material having a density of 2.47 g/cm^3 is desired. Compute the concentration of Li (in wt%) that is required.

1.5 Electrical Properties

49)   Consider a cylindrical silicon specimen 7.0 mm in diameter and 57 mm in length.

1. A current of 0.25 A passes along the specimen in the axial direction. A voltage of 24 V is measured across two probes that are separated by 45 mm. What is the electrical conductivity of the specimen?

2. Compute the resistance over the entire 57 mm of the specimen.

50)   A plain carbon steel wire 3 mm in diameter is to offer a resistance of no more than 20 Ω. Using Callister Table 18.1, compute the maximum wire length.

51)   Consider an aluminum wire 5 mm in diameter and 5 m in length.

1. Using the data in Callister Table 18.1, compute the resistance of the wire.

2. What would be the current flow if the potential drop across the ends of the wire is 0.04 volt?

3. What is the current density?

4. What is the magnitude of the electric field across the ends of the wire?

52)   Recall electronic band structure as discussed in the book and lecture.

1. How does the electron structure of an isolated atom differ from that in a solid?

2. In terms of electron energy band structure, discuss the reasons for the difference in electrical conductivity among metals, semiconductors, and insulators.

53)   Briefly state what is meant by the *drift velocity* and *mobility* of a free electron.

54)   Consider free electrons moving in silicon at room temperature.

1. Calculate the drift velocity of the electrons when the magnitude of the electric field is 500 V/m.

2. Under these circumstances, how long does it take an electron to traverse a 25-mm length of crystal?

55)   Silicon and germanium are two of the most technologically relevant semiconducting materials.

1. Using the data presented in Callister Fig. 18.16, determine the number of free electrons per atom for intrinsic germanium and silicon at room temperature (298 K). The densities for Ge and Si are 5.32 and 2.33 g/cm^3, respectively.

2. Now, explain the difference in these free-electron-per-atom values.

56)   For intrinsic semiconductors, the intrinsic carrier concentration n_i, depends on temperature as follows:

$$n_i \propto \exp\left(-\frac{E_g}{2k_B T}\right)$$

or, by taking the log of both sides of the equation:

$$\ln n_i \propto -\frac{E_g}{2k_B T}$$

1. A plot of $\ln n_i$ versus $1/T$ will therefore be linear and yield a slope of $-\frac{E_g}{2k_B}$. This is provided for you below for both Si and Ge. Using this information determine the band gap energies for silicon and germanium and compare these values with those in Callister Table 18.3.

2. Where does the factor of 2 in the denominator come from in these equations?
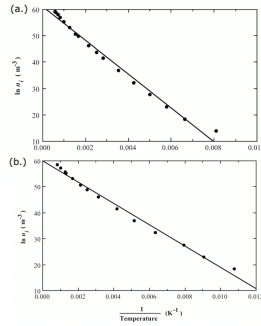
Figure 1.4: An Arrhenius plot relating n_i and T for (a.) Si and (b.) Ge.

57) Is it possible for compound semiconductors to exhibit intrinsic behavior? Explain your answer.

58) For each of the following pairs of semiconductors, decide which has the smallest band gap energy, E_g, and cite the reason for your choice.

1. C (diamond) and Ge

2. AlP and InAs

3. GaAs and ZnSe

4. ZnSe and CdTe

5. CdS and NaCl

59) For each impurity element in the following table , predict whether it will act as a donor or an acceptor when added to the indicated semiconducting material. Assume the that impurity elements are substitutional.

Impurity	Semiconductor
N	Si
B	Ge
S	InSb
In	CdS
As	ZnTe

Figure 1.5: Electronegativity values for the elements.

60) A concentration of 10^{24} As atoms per cubic meter have been added to germanium to form an extrinsic semiconductor. At room temperature, virtually all of the As atoms can be considered to be ionized (i.e., one charge carrier exists for each As atom).

1. Is this material n-type or p-type?

2. Calculate the electrical conductivity of this material, assuming electron and hole mobilities of 0.1 and 0.05 $m^2/V-s$, respectively.

61) Calculate the conductivity of intrinsic silicon at 80 °C.

62) Compare the temperature dependence of the conductivity for metals, intrinsic, and extrinsic semiconductors. Briefly explain the difference in behavior.

63) Calculate the room-temperature electrical conductivity of silicon that has been doped with 10^{23} m^{-3} carriers of arsenic atoms.

64) Briefly describe electron and hole motions in a p-n junction for forward and reverse biases. How do these lead to rectifying behavior?

65) Summarize Matthiessen's rules. That is, what are the factors that influence resistivity in metals?

1.6 Diffusion

66) Consider different diffusion mechanisms in solids:

1. Compare interstitial and vacancy atomic mechanisms for diffusion.

2. Cite two reasons why interstitial diffusion is normally more rapid than vacancy diffusion.

67) Consider the diffusion of carbon in BCC iron (α-Fe).

1. What diffusion mechanism to you expect for C in α-Fe: interstitial or substitutional? Why?

2. Assuming that diffusion occurs via adjacent tetrahedral sites in α-Fe, what family of crystallographic directions does this diffusion take place? Refer to the figure below to recall the locations f the interstitial sites in a BCC material.
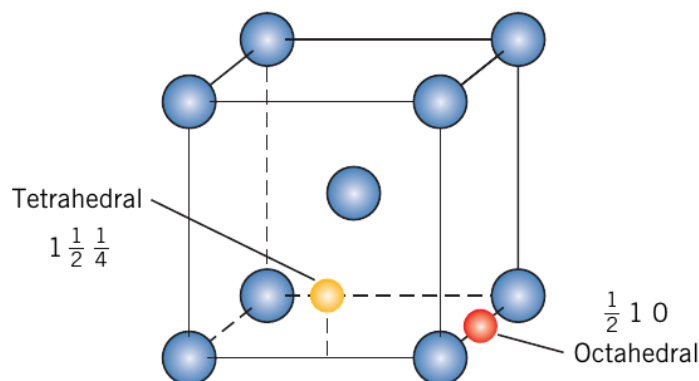
68) Consider the role of the driving force in diffusion:

1. Briefly explain the concept of a driving force.

2. What is the driving force for steady-state diffusion?

69) A sheet of steel 2.5-mm thick has nitrogen atmospheres on both sides at 900°C and is permitted to achieve a steady-state diffusion condition. The diffusion coefficient for nitrogen in steel at this temperature is $1.85 \times 10^{-10}\,\text{m}^2/\text{s}$, and the diffusion flux is found to be $1.0 \times 10^{-7}\,\text{kg}/\text{m}^2 \cdot \text{s}$. Also, it is known that the concentration of nitrogen in the steel at the high-pressure surface is $2\,\text{kg}/\text{m}^3$. How far into the sheet from this high-pressure side will the concentration be $0.5\,\text{kg}/\text{m}^3$? Assume a linear concentration profile.

70) A sheet of BCC iron 2 mm thick was heated to 675 °C exposed to a carburizing gas atmosphere on one side and a decarburizing atmosphere on the other. After reaching steady-state, the iron was then quickly cooled to room temperature and the carbon concentrations on the two surfaces were determined to be 1.18 kg/m^3 and 0.535 kg/m^3. Compute the diffusion coefficient if the diffusion flux is $7.36 \times 10^{-9}\,\text{kg}/(\text{m}^2 \cdot \text{s})$. (You will need to convert wt% to mass density (Callister Eq. 4.9). Assume that the density of carbon is 2.25 g/cm^3.)

71) Show that

$$C_x = \frac{B}{\sqrt{Dt}} \exp\left(-\frac{x^2}{4Dt}\right)$$

is a solution to the Fick's second law:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}.$$

Here, the parameters B and D are constant with respect to both x and t.

72) Determine the carburizing time necessary to achieve a carbon concentration of 0.30 wt% at a position 4 mm into an iron-carbon alloy that initially contains 0.10 wt% C. The surface concentration is to be maintained at 0.90 wt% C, and the treatment is to be conducted at 1100 °C. Use the diffusion data for γ-Fe in Table 5.2

73) Nitrogen from a gaseous phase is to be diffused into pure iron at 675 °C. If the surface concentration is maintained at 0.2 wt% N, what will be the concentration 2 mm from the surface after 25 h? The diffusion coefficient for nitrogen in iron at 675 °C is $2.8 \times 10^{-11}\,\text{m}^2/\text{s}$.

74) Cite the values of the diffusion coefficients for interdiffusion of carbon in both α-iron (BCC) and γ-iron (FCC) at 900 Â°C Which is larger and why?

75) The diffusion coefficients for nickel in iron are given at two temperatures, as follows:

T (K)	$D\,(\text{m}^2/\text{s})$
1473	2.2×10^{-15}
1673	4.98×10^{-14}

1. Determine the values of D_0 and the activation energy, Q_d.

2. What is the magnitude of D at 1300 °C (1573 K)?

76) The diffusion coefficients for carbon in nickel are given at two temperatures, as follows:

T °C	$D\,(\text{m}^2/\text{s})$
600	5.5×10^{-14}
700	3.9×10^{-13}

1. Determine the values of D_0 and Q_d.

2. What is the magnitude of D at 850 °C?

77) The figure below shows a plot of the base-10 logarithm of the diffusion coefficient vs reciprocal of the absolute temperature for the diffusion of gold in silver. Determine the values for the activation energy and the preexponential.

78) For the predeposition heat treatment of a semiconducting device, gallium atoms are to be diffused into silicon at a temperature of 1150 °C for 2.5 hrs. If the required concentration of Ga at a position 2 μm below the surface is 8×10^{23} atoms/m^3, compute the required surface concentration of Ga. Assume the following:

1. The surface concentration remains constant

2. The background concentration is 2×10^{19} Ga atoms/m^3

3. Preexponential and activation energies are 3.74×10^{-5} m^2/s and 3.39 eV/atom, respectively.

79) Suppose you are considering two carburization processes for steel. Assume that both processes give materials with identical performance characteristics, and that your goal is to minimize the processing time. Process A requires that the carbon diffuse twice as far into the iron as process B. The carbon diffusion coefficient for process A is 3 times as large as for process B. Which process do you choose, and why?

1.7 Phase Diagrams

80) At 100 °C, what is the maximum solubility of the following:

1. Pb in Sn

2. Sn in Pb
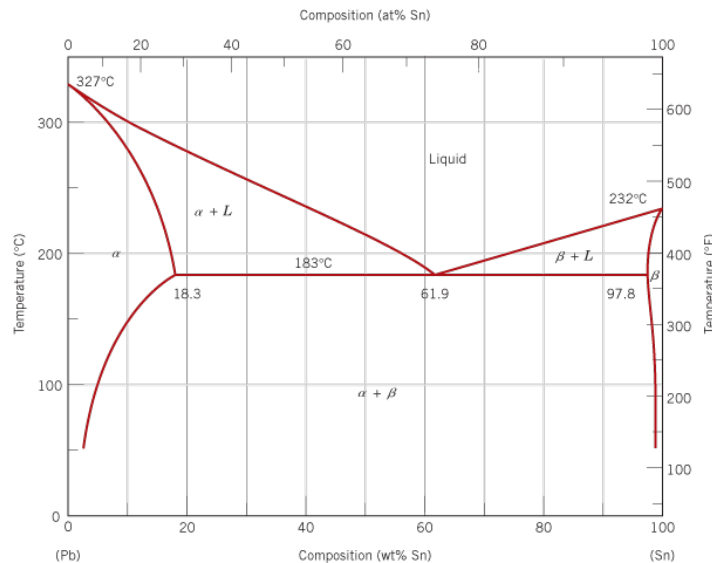
Figure 1.6: Pb-Sn Phase Diagram

81) What thermodynamic condition must be met for a state of equilibrium to exist?

82) A 50 wt% Ni-50 wt% Cu alloy is slowly cooled from 1400 °C to 1200 °C.

1. At what temperature does the first solid phase form?

2. What is the composition of this solid phase?

3. At what temperature does the liquid solidify?

4. What is the composition of this last remaining liquid phase?
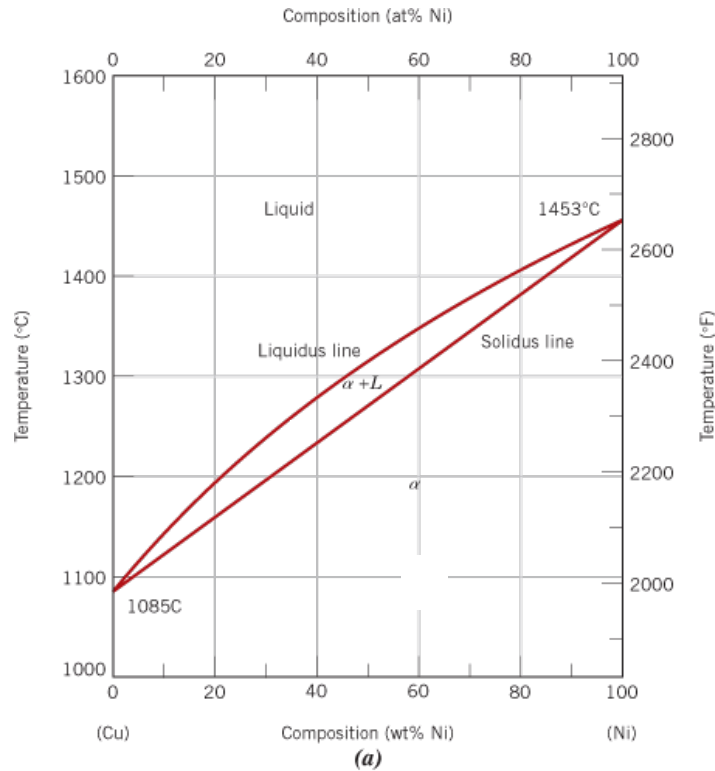
Figure 1.7: Cu-Ni Phase Diagram

83)   A 40 wt% Pb-60 wt% Mg alloy is heated to a temperature within the α+Liquid phase region. If the mass fraction of each phase is 0.5, then estimate:

1. The temperature of the alloy

2. The compositions of the two phases in weight percent
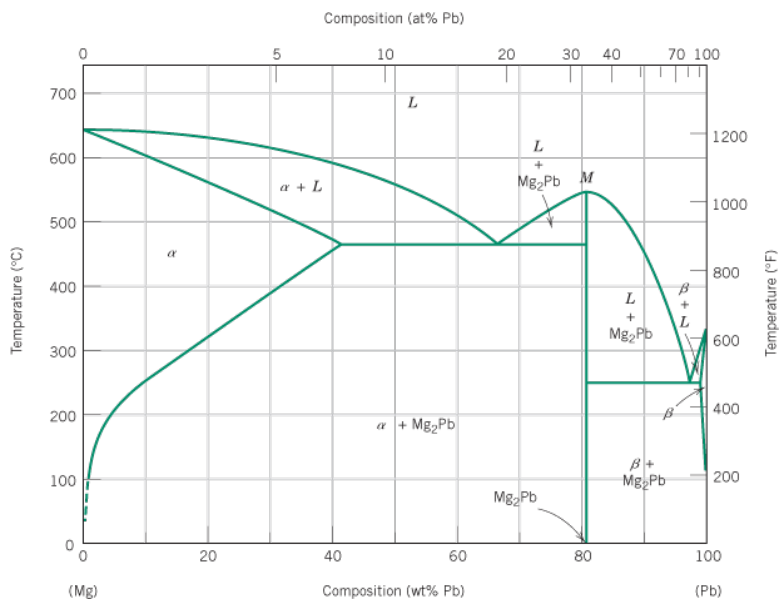
Figure 1.8: Mg-Pb phase diagram.

84)   A copper/silver alloy is heated to 900 °C and is found to consist of α and liquid phases. If the mass fraction of the liquid phase is 0.68, determine:

1. The composition of both phases, in both weight percent and atom percent.

2. The composition of the alloy, in both weight percent and atom percent.
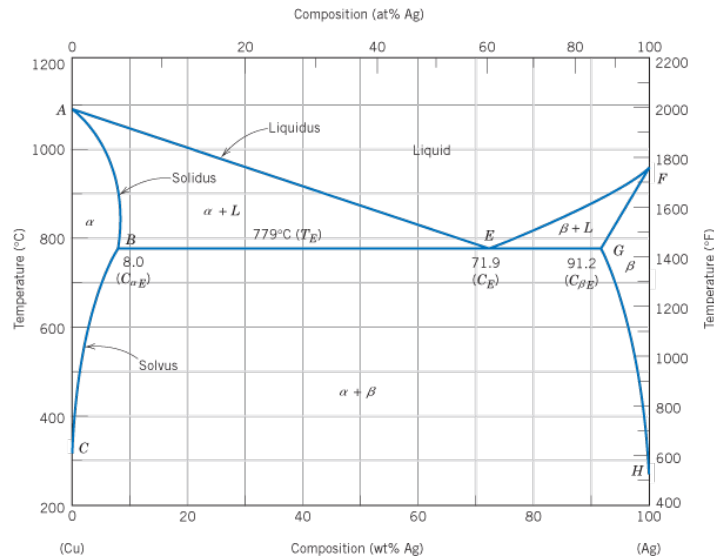
Figure 1.9: Cu/Ag Phase Diagram.

85) A 60 wt percent Pb-40 wt percent Mg alloy (see Fig. 1.8) is rapidly quenched to room temperature from an elevated temperature in such a way that the high-temperature microstructure is preserved. This microstructure is found to consist of the α phase and Mg_2Pb, having respective mass fractions of 0.42 and 0.58. Determine the approximate temperature from which the alloy was quenched.

86) For a 76 wt% Pb-24 wt% Mg alloy (see Fig. 1.8), make schematic sketches of the microstructure that would be observed for conditions of very slow cooling to the following temperatures: 575 °C, 500 °C, 450 °C, and 300 °C. Label all phases and indicate their approximate compositions.

87) For the tin/gold system, specify the temperature-composition points at which all eutectics, eutectoids, peritectics, and peritectoid phase transformations occur. Also, for each, write the reaction upon cooling. Note, β, γ, and δ are labeling the *intermetallic* phases which are indicated by vertical lines on the phase diagram.
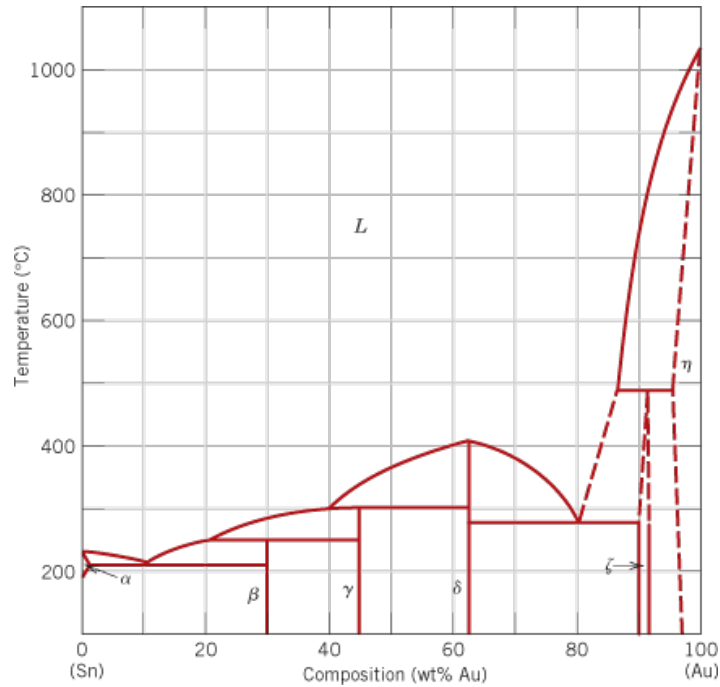
Figure 1.10: Sn/Au Phase Diagram

88) Compute the mass fractions of α-ferrite and cementite Fe_3C that in pearlite, formed by cooling steel with a composition equal to the eutectoid composition.
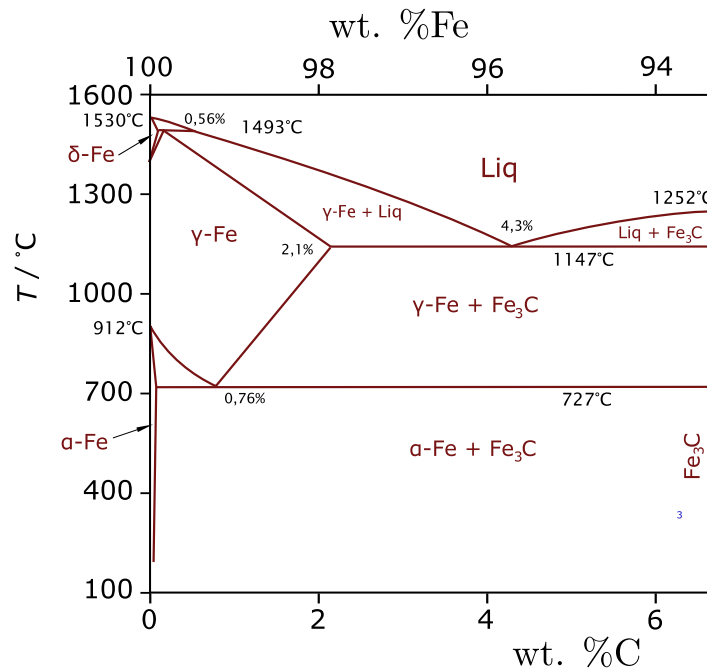
Figure 1.11: Fe-C Phase Diagram

89) 3.5 kg of austenite containing 0.95 wt% C is cooled below 727 °C.

1. What is the proeutectoid phase?

2. How many kilograms each of total ferrite and cementite form?

3. How many kilograms each of pearlite and proeutectoid phase form?

4. Schematically sketch and label the resulting microstructure.

1.8   Phase Transformations

90)   The kinetics of the austenite-to-pearlite transformation obeys the Avrami relationship. Using the fraction transformed-time data given below, determine the total time required for 95% of the austenite to transform to pearlite.

Fraction Transformed	Times (s)
0.2	280
0.6	425

91)   Using the isothermal transformation diagram for an iron-carbon alloy of eutectoid composition (Callister Figure 10.22), specify the nature of the final microstructure (in terms of microconstituents present and the approximate percentages of each) of a small specimen that has been subjected to the following time-temperature treatments. In each case, assume that the specimen begins at 760 °C and that it has been held at this temperature long enough to have achieved a complete and homogeneous austenitic structure. Do this problem until you feel that you understand the process.

1. Cool rapidly to 350 °C, hold for 10^3 s, and then quench to room temperature.

2. Rapidly cool to 625 °C, hold for 10 s, and then quench to room temperature.

3. Rapidly cool to 600 °C, hold for 4 s, rapidly cool to 450 °C, hold for 10 s, then quench to room temperature.

4. Reheat the specimen in part (c) to 700 ° for 20 h.

5. Rapidly cool to 300 °C, hold for 20 s, then quench to room temperature in water. Reheat to 425 °C for 10^3 s and slowly cool to room temperature.

6. Cool rapidly to 665 °C, hold for 10^3 s, then quench to room temperature.

7. Rapidly cool to 575 °C, hold for 20 s, rapidly cool to 350 °, hold for 100 s, then quench to room temperature.

8. Rapidly cool to 350 °C, hold for 150 s, then quench to room temperature.

92)   Callister Figure 10.40 shows the continuous-cooling transformation diagram for a 0.35 wt% C iron-carbon alloy. Make a copy of this figure and then sketch and label the continuous-cooling curves to yield the following microstructures:

1. Fine pearlite and proeutectoid ferrite

2. Martensite

3. Martensite and proeutectoid ferrite

4. Coarse pearlite and proeutectoid ferrite

5. Martinsite, fine pearlite, and proeutectoid ferrite.

1.9   Mechanical Properties

93)   The figure to the right below shows the tensile stress-strain curve for a plain-carbon steel. Extract the following:

1. The alloy's tensile strength.

2. The modulus of elasticity.

3. The yield strength.
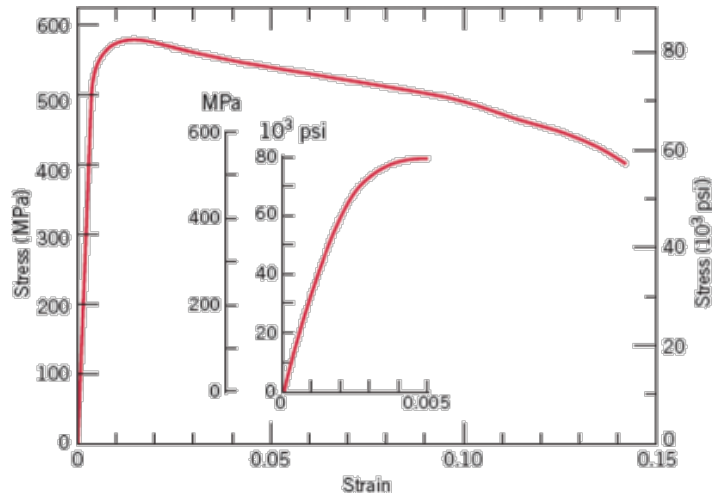
94) A specimen of copper having a rectangular cross section 15.2 mm × 19.1 mm is pulled in tension with 44,500 N force, producing only elastic deformation. Calculate the resulting strain.

95) Consider a cylindrical specimen of a steel alloy (Figure 6.22) 8.5 mm in diameter and 80 mm long that is pulled in tension. Determine its elongation when a load of 65,250 N is applied.

96) The net bonding energy E_N between two isolated positive and negative ions is a function of interionic distance r as follows:

$$E_N = -\frac{A}{r} + \frac{B}{r^n}$$

where A, B, and n are constants for the particular ion pair. Equation 6.31 is also valid for the bonding energy between adjacent ions in solid materials. The modulus of elasticity E is proportional to the slope of the interionic force-separation curve at the equilibrium interionic separation; that is,

$$E \propto \left(\frac{dF}{dr}\right)_{r_0}$$

Derive an expression for the dependence of the modulus of elasticity on these A, B, and n parameters (for the two-ion system), using the following procedure:

1. Establish a relationship for the force F as a function of r, realizing that:

$$F = -\frac{dE_n}{dr}$$

2. Now take the derivative dF/dr.

3. Develop an expression for r_0, the equilibrium separation. Because r_0 corresponds to the value of r at the minimum of the E_N-versus-r curve (Callister Figure 2.10b), take the derivative dE_N/dr, set it equal to zero, and solve for r, which corresponds to r_0.

4. Finally, substitute this expression for r_0 into the relationship obtained by taking dF/dr.

97) Consider the brass alloy for which the stress-strain behavior is shown below. A cylindrical specimen of this material 10.0 mm in diameter and 101.6 mm long is pulled in tension with a force of 10,000 N. If it is known that this alloy has a value for Poisson's ratio of 0.35, compute **(a)** the specimen elongation and **(b)** the reduction in specimen diameter.

19
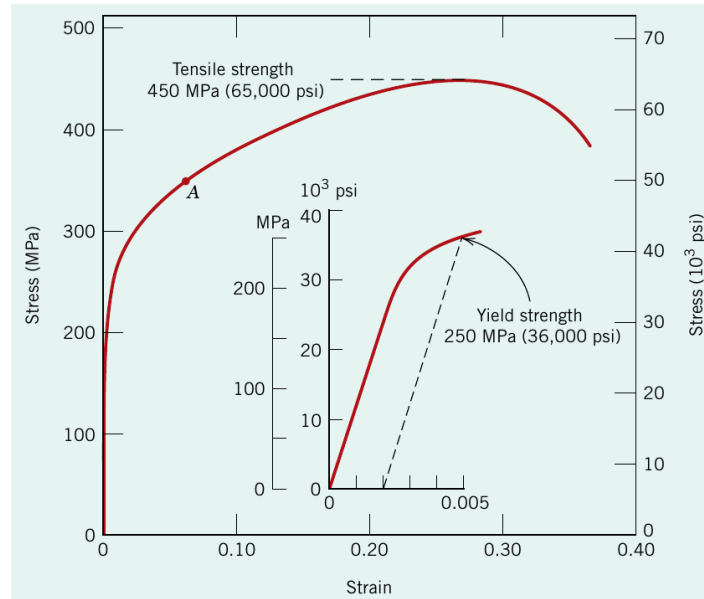
98) The figure below shows the tensile engineering stress-strain behavior for a steel alloy.

1. What is the modulus of elasticity?

2. What is the yield strength at a strain offset of 0.002?

3. What is the tensile strength?

4. What is the elongation-to-failure, or ductility?

5. What is the resilience, U_r, of the material?
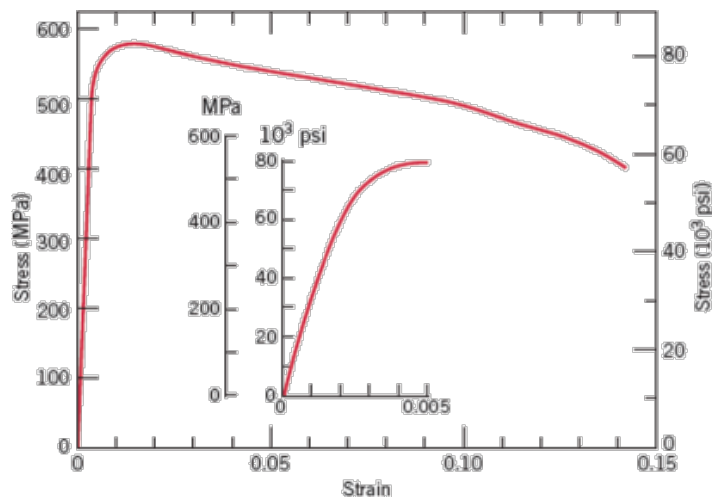
99) The figure below shows the tensile engineering stress-strain behavior fro a steel alloy.

1. What is the modulus of elasticity?

2. What is the proportional limit?

3. What is the yield strength at a strain offset of 0.002?

4. What is the tensile strength?
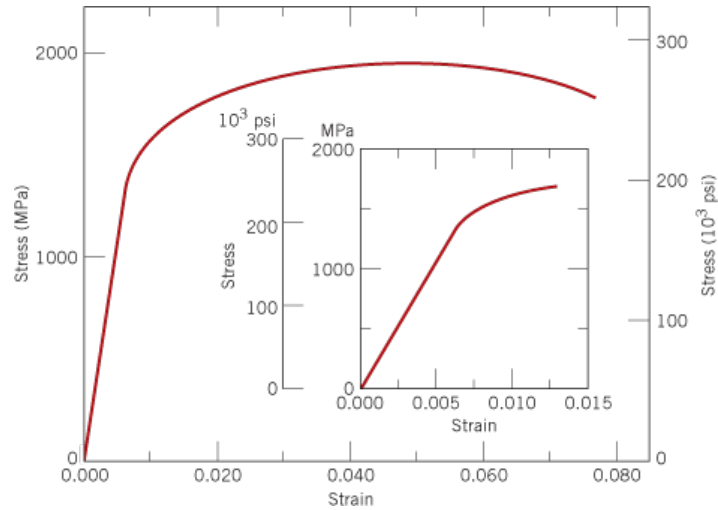
100) Calculate the modulus of resilience for the material having the stress-strain behavior shown in Fig. 6.12 and 6.22.

101) Determine the modulus of resilience for each of the following alloys.

Material	Yield Strength (GPa)	Young's Modulus (GPa)
Steel alloy	0.830	207
Brass alloy	0.380	97
Aluminum alloy	0.275	69
Titanium alloy	0.690	107

102) A steel alloy to be used for a spring application must have a modulus of resilience of at least 2.07 MPa. What must be its minimum yield strength?

103) Find the *toughness* (or energy to cause fracture) for a metal that experiences both elastic and plastic deformation. Assume Callister Eq. 6.5 for elastic deformation, that the modulus of elasticity is 103 GPa, and that the elastic deformation terminates at a strain of 0.007.
For plastic deformation, assume the relationship between stress and strain is described by Eq. 6.19, in which the values for K and n are 1520 MPa and 0.15, respectively. Furthermore, plastic deformation occurs between strain values of 0.007 and 0.60, at which point fracture occurs.

104) The motion of dislocations is influenced by a material's crystal structure.

1. Define a slip system.

2. Do all metals have the same slip system? Why or why not?

105) One of the slip systems in the BCC crystal structure is {110}⟨111⟩ Sketch a plane that is a member of the {110} family, representing atoms with circles. Using arrows, indicate two different ⟨111⟩ slip directions within this plane.

106) The expressions for the Burger's vectors for FCC and BCC crystal structures are both of the form

$$\mathbf{b} = \frac{a}{2}\langle uvw \rangle$$

.
Here, a is the unit cell length and uvw are the crystallographic direction indices. We can find the magnitudes of the Burger's vector using:

$$\mathbf{b} = \frac{a}{2}\left(u^2 + v^2 + w^2\right)^{1/2}$$

Determine the values of $|\mathbf{b}|$ for Cu and α-Fe.

107)   Consider a simple cubic (SC) crystal structure.

1. In the same manner as Callister Eqs. 7.1a-7.1c, specify the Burgers vector for the simple cubic crystal structure whose unit cell is shown in Callister Figure 3.3. You may find Figures 4.4 and 7.1 useful.

2. Formulate an expression for the magnitude of the Burgers vector for the simple cubic system in the same form as that in Callister Eq. 7.11.

108)   Consider a metal single crystal oriented such that the normal to the slip plane and the slip direction are at angles of $60°$ and $35°$, respectively, with the tensile axis. If the critical resolved shear stress is 6.2 MPa, will an applied stress of 12 MPa cause the single crystal to yield? If not, what stress would be necessary?

109)   Consider a single crystal of nickel oriented such that a tensile stress is applied along a [001] direction. If slip occurs on a (111) plane and in a $[\bar{1}01]$ direction and is initiated at an applied tensile stress of 13.9 MPa, compute the critical resolved shear stress.

110)   A single crystal of a metal that has the FCC crystal structure is oriented such that a tensile stress is applied parallel to the [001] direction.
If the critical resolved shear stress for this material is 0.5 MPa, calculate the magnitude(s) of applied stress(es) necessary to cause slip to occur on the (111) plane in each of the $[\bar{1}10]$, $[\bar{1}01]$, and $[0\bar{1}1]$ directions.

111)   Describe in your own words the following three strengthening mechanisms: grain size reduction, solid-solution strengthening, and strain hardening. Explain how dislocations are involved in each of the strengthening techniques.

112)   In the manner of Callister Figures 7.17b and 7.18b, indicate the location in the vicinity of an edge dislocation at which an interstitial impurity atom would be expected to be situated. Now briefly explain in terms of lattice strains why it would be situated at this position.

113)   A cylindrical specimen of cold-worked copper has a ductility (%EL) of 15%. If its cold-worked radius is 6.4 mm, what was its radius before deformation?

114)   Briefly cite the differences between recovery, recrystallization, and grain growth in terms of mechanism and influence on mechanical properties.

1.10   Fracture Mechanics

115)   What is the magnitude of the maximum stress that exists at the tip of an internal crack having a radius of curvature of 1.9×10^{-4} mm and a crack length of 3.8×10^{-2} mm when a tensile stress of 140 MPa is applied?

116)   An MgO component must not fail when a tensile stress of 13.5 MPa is applied. Determine the maximum allowable surface crack length if the surface energy of MgO is $1.0\,\text{J/m}^2$. Data found in Callister Table 12.5 may prove helpful.

117)   An aircraft component is fabricated from an aluminum alloy that has a plane-strain fracture toughness of $40\,\text{MPa}\sqrt{\text{m}}$. It has been determined that fracture results at a stress of 300 MPa when the maximum (or critical) internal crack length is 4.0 mm. For this same component and alloy, will fracture occur at a stress level of 260 MPa when the maximum internal crack length is 6.0 mm? Why or why not?

118)   A cylindrical bar of ductile cast iron is subjected to reversed and rotating-bending tests; test results (i.e. *S-N* behavior) are shown in Callister Figure 8.20. If the bar diameter is 9.5 mm, determine the maximum cyclic load that may be applied to ensure that fatigue failure will not occur. Assume a factor of safety of 2.25 and that the distance between loadbearing points is 55.5 mm.

119)   List four measures that may be taken to increase the resistance to fatigue of an alloy.

120) The creep data below were taken on an aluminum alloy at 480 °C and a constant stress of 2.75 MPa. Plot the data as strain *vs* time, then determine the steady-state or minimum creep rate. *Note:* The initial and instantaneous strain is not included.

121) For a cylindrical S-590 alloy specimen (Callister Figure 8.32) originally 14.5 mm in diameter and 400 mm long, what tensile load is necessary to produce a total elongation of 52.7 mm after 1150 hr at 650 °C? Assume that the sum of instantaneous and primary creep elongations is 4.3 mm.

122) The fracture toughness, K_{IC} for a brittle material can be approximated as $\sigma_{max}^f \sqrt{\rho_c}$, where σ_{max}^f is the maximum stress in that the material can support and ρ_c is the crack tip radius of curvature. In a very brittle material we can often approximate σ_{max}^f as $E/10$ where E is Young's modulus. Look up values for E and K_{IC} for window glass to obtain an estimate for ρ_c.

1.11   Corrosion

123)

1. Briefly explain the difference between oxidation and reduction electrochemical reactions.

2. Which reaction occurs at the anode and which at the cathode?

124)

1. Write down the reaction to form water from hydrogen and oxygen. Use the standard free energy of this reaction (-236 kJ/mole) to determine the energy content of hydrogen fuel in electron volts per hydrogen atom.

2. Write down the two half cell reactions for each of the following versions of the reaction from part a:

   (a) The version involving involving proton conduction through a polymer electrolyte membrane.

   (b) The version involving oxygen anion diffusion through a solid oxide electrolyte like ZrO_2.

3. Look up the standard electrode potentials for the two half reactions for the polymer electrolyte membrane calculation, and show that it the total energy obtained from the fuel cell is consistent with the energy per hydrogen atom calculated from part a.

125) For the following pairs of alloys that are electrically coupled in seawater, predict the possibility of corrosion for each. If corrosion is probable, identify the metal/alloy that will corrode.

1. Aluminum and cast iron

2. Inconel and nickel

3. Cadmium and zinc

4. Brass and Titanium

5. Low-carbon steel and copper.

126)

1. From the galvanic series (Table 17.2 in Callister), cite three metals/alloys that may be used to galvanically protect cast iron.

2. Galvanic corrosion at an interface between two metals can be prevented by making an electrical contact between the two metals in the couple and a third metal that is anodic to the other two. Using the galvanic series, name one metal that could be used to protect a nickel-steel galvanic couple.

127)

1. Describe how protection mechanisms at work in the following two cases:

   (a) Galvanized iron

   (b) Stainless steel

2. Provide an an application where you would choose to use galvanized iron, and one where you would choose to use stainless steel, and provide your reasoning.

128) A brine solution is used as a cooling medium in a steel heat exchanger. The brine is circulated within the heat exchanger and contains some dissolved oxygen. Suggest three methods (limit yourselves to those covered in class) other than cathodic protection that would reduce the corrosion of the the steel in the brine. Explain the rational for each suggestion.

1.12 Ceramics

129) Show that the minimum cation-to-anion radius ratio for a coordination number of 4 is 0.225.

130) Show that the minimum cation-to-anion radius ratio for a coordination number of 6 is 0.414. (*Hint:* Use the NaCl crystal structure in Figure 12.2, and assume that anions and cations are just touching along cube edges and across face diagonals.)

131) Demonstrate that the minimum cation-to-anion radius ratio for a coordination number of 8 is 0.732.

132) On the basis of ionic charge and ionic radius given in Callister Table 12.3, predict crystal structures for the following materials and justify your decision:

1. CaO

2. MnS

3. KBr

4. CsBr

133) The zinc blende crystal structure is on that can be derived from close-packed planes of anions. The sulfide anion sub-lattice will be FCC. *Don't just copy values from Table 12.4. You already know how to look things up in tables...*

1. Will cations fill tetrahedral or octahedral positions? Why?

2. What fraction of the positions will be occupied?

134) Compute the theoretical density of NiO, given that it has the rock salt crystal structure.

135) Compute the atomic packing factor for the rock salt crystal structure in which $\frac{r_C}{r_A} = 0.414$

136) A hypothetical AX type of ceramic material is known to have a density of 2.10 g/cm^3 and a unit cell of cubic symmetry with a cell edge length of 0.57 nm. The atomic weights of the A and X elements are 28.5 and 30.0 g/mol, respectively. On the basis of this information, which of the following crystal structures is (are) possible for this material: sodium chloride, cesium chloride, or zinc blende? Justify your choice(s).

137) What happens to the oxygen vacancy concentration in ZrO$_2$ if a small amount of Zr on the crystal lattice is replaced by Ca? How would this affect the performance of the ZrO$_2$ used as a solid electrolyte in a solid oxide fuel cell?

1.13 Polymers

138) Compute the repeat unit molecular weights for the following. Only do this problem until you are confident you understand the process:

1. polytetrafluoroethylene

2. poly(methyl methacrylate)

3. poly(ethylene terephthalate)

139) Consider the thermoplastic and thermoset nature of polymers: (a) Is it possible to grind up and reuse an epoxy? Why or why not? (b) Is it possible to grind up and reuse polypropylene? Why or why not?

140) An alternating copolymer is known to have a number-average molecular weight of 100,000 g/mol and a degree of polymerization of 2210. If one of the repeat units is ethylene, which of styrene, propylene, tetrafluoroethylene, and vinyl chloride is the other repeat unit? Why?

141) For each of the following pairs of polymers, state whether it is possible to determine whether one polymer is more likely to crystallize than the other, and give the reason for your answer.

1. Atactic poly(vinyl chloride); linear and isotactic polypropylene

2. A fully cured epoxy sample; linear and isotactic polystyrene

142) Calculate the repeat unit molecular weights for each of the polymers shown in the 'common polymers' section of the text.

143) Draw the chemical structure of the monomer(s) and the repeating unit for one polymer in each of the following classes:

1. A polymer polymerized by chain growth addition to a double bond.

2. A polymer polymerized by ring opening chain growth.

3. A linear stop growth polymer.

Note: you should be draw the chemical structures of the repeat unit, given the structure of the monomers, and vice versa, for all of the polymer structures in in the 'common polymers' portion of the online 301 text.

144) Draw Lewis diagrams illustrating the valence shell configurations for polystyrene, poly(methyl methacrylate).

145) Draw Lewis diagrams illustrating the valence shell configurations for amide, ester and urethane linkages.

146) Consider the following 5 monomers:

(1)
$$CH_2\text{-}CH\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH\text{-}CH_2$$
with epoxide O groups at (1) and (4)

(2)
$$O=C=NR_1N=C=0$$

(3)
$$H_2NCH_2CH_2NH_2$$

(4)
$$OH-\overset{O}{\underset{\|}{C}}-\underset{\text{(benzene ring)}}{}-\overset{O}{\underset{\|}{C}}-OH$$

(5)
$$HOCH2CH2OH$$
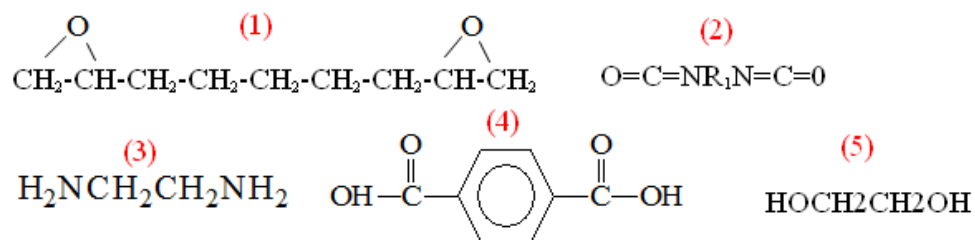
1. Draw the repeat units for two linear polymers that can be produced by reactions between the monomers in this list. Identify these polymers according to their type (polyamides, polyesters, etc.), and indicate whether each polymerization reaction is condensation reaction or not.

2. What combination of monomers from this list would you choose in order to produce a three-dimensional network?

147) Suppose you want to sell a set of cheap plastic mugs which are suitable for drinking coffee. Briefly discuss the potential applicability of the following materials for this purpose:

1. atactic polystyrene

2. atactic poly(vinyl chloride)

3. high density polyethylene

2 314 Problems

2.1 Phases and Components

1) (2014) For each of the following thermodynamic systems, indicate the number of components, the number of phases, and whether the system is open or closed.

1. An open jar of water at room temperature (assume that the jar defines the boundaries of the system). Assume that the water molecules do not dissociate.

2. A sealed jar of water at room temperature.

3. A sealed jar of water with ice.

4. An open jar of water with NaCl entirely dissolved within.

5. If the jar is left open, in what ways might your description change?

6. How would your answer to (a) change if you take into account equilibrium between water, protons, and hydroxyl ions?

2.2 Intensive and Extensive Properties

2) (2014) Classify the following thermodynamic properties are intensive or extensive:

1. The mass of an iron magnet.

2. The mass density of an iron magnet.

3. The concentration of phosphorous atoms in a piece of doped silicon.

4. The volume of the piece of silicon.

5. The fraction by weight of copper in a penny.

6. The temperature of the penny in your pocket.

7. The volume of gas in a hot air balloon.

2.3 Differential Quantities and State Functions

3) (2014) Consider the function $z = 6x^2y^3 \cos^2 u$.

1. Write down the total differential of z. Identify the coefficients of the three differentials in this expression as partial derivatives.

2. Demonstrate that three Maxwell relations (see section 2.3) hold between the coefficients identified under (a).

4) (2014) Why are state functions so useful in calculating the changes in a thermodynamic system?

5) (2014) Derive equation 4.41 starting from 4.34 and 4.31. Note that other equations listed in table 4.5 can be derived in a similar fashion.

2.4 Entropy

6) (2015) Following Section 3.6, compute the change in entropy in the formation of one mole of SiO_2 from Si and O at room temperature.

7)   (2015) Consider an isolated system consisting of three compartments A, B, and C. Each compartment has the same volume V, and they are separated by partitions that have about. Initially, the valves are closed and volume A is filled with an ideal gas to a pressure P_0 at 298 K. Volumes B and C are under vacuum.

1. Calculate the change in entropy when the valve between compartment A and B is opened.

2. Calculate the change in entropy when the valve between compartment B and compartment C is opened.

3. Without considering the calculations above, how would you know that the overall change in entropy is positive?

4. What would you need to do to the system to restore the initial condition?

2.5   Thermodynamic Data

8)   (2015) This problem requires you to find sources to look up the values of important materials parameters that will be used to compute thermodynamic functions.

1. Find values of the coefficient of thermal expansion for a metal, a semiconductor, an insulator, and a polymer. Provide the information below in your answer.

Material Type	Specific Material	α	Source (include page or link info)
Elemental Metal	*e.g.* Gold		
Semiconductor			
Insulator			
Polymer			

2. What is a common material with a negative α?

3. How is the coefficient of compressibility related to the bulk modulus?

4. Which metal has the highest bulk modulus at room temperature, and what is the value?

5. The heat capacity is an extensive quantity. Define the related intensive quantity.

6. What trend do you observe in elemental solids?

7. What is the smallest value you can find for a solid material? (Explain your search method, and cite your sources.)

9)   (2014) The density of silicon carbide at 298 K and 1 atm is ~3.2 g/cm^3. Estimate the molar volume at 800 K and a pressure of 1000 atm. See tables 4.1 and 4.2 on page 61 of DeHoff for useful materials parameters.

10)   (2015) The density of aluminum at 298 K and 1 atm (or "bar") is 2.7 g/cm3. Estimate the molar volume at 1000 K and a pressure of 1000 atm. See tables 4.1 and 4.2 on page 61 of DeHoff, and Appendix B, for useful materials parameters. Hint: break the problem into two steps, each corresponding to a path.

11)   (2015) Use the car mileage dataset provided to do the following:

1. Create a second order polynomial fit to determine the coefficients for the mileage dataset online. Use the systems of equations we developed during discussion to help you solve for the coefficients. Write your polynomial coefficients down in your submitted assignment.

2. Using your curve of best fit, determine the optimal speed for driving that maximizes your mileage.

3. Identify an obvious failure of your model and comment on it below.

12) (2015) Answer the following questions using the heat capacity dataset and the following model:

$$C_p = a + bT + c/T^2 + dT^2$$

1. Use the system of equations derived in class to determine the coefficients a, b, c, d.

2. Give a possible Gibbs free energy function for bulk silicon using your heat capacity fit. The Gibbs free energy is related to the heat capacity through the following equation:

$$C_p = -T \left(\frac{\partial^2 G}{\partial T^2} \right)_P$$

13) (2015) Compare the change in entropy for the specific examples below of isothermal compression and isobaric heating of gases and solids.

1. One mole of nitrogen (N_2) at 1000 K is compressed isothermally from 1 to 105 bar.

2. One mole of silicon at 300 K is compressed isothermally from 1 to 105 bar.

3. One mole of oxygen (O2) at 300 K is heated isobarically from 300 to 1200 K.

4. One mole of tungsten at 300 K is heated isobarically from 300 to 1200 K.

14) (2015) For each of the following processes carried out on one mole of a monatomic ideal gas, calculate the work done by the gas, the heat absorbed by the gas, and the changes in internal energy, enthalpy, and entropy (of the gas). The processes are carried out in the specified order.

1. Free expansion into the vacuum to twice the volume, starting from 300 K and 4 bar. Then,

2. Heating to 600 K reversibly with the volume held constant. Then,

3. Reversible expansion at constant temperature to twice the volume of the previous state. Then,

4. Reversible cooling to 300 K at constant pressure.

15) (2015) Consider one mole of a monatomic ideal gas that undergoes a reversible expansion one of two ways.

1. Under isobaric conditions, the gas absorbs 5000 J of heat in the entropy of the gas increases by 12.0 J/K. What are the initial and final temperatures of the gas?

2. Under isothermal conditions, 1600 J of work is performed, resulting in an entropy increase of 5.76 J/K and a doubling of the volume. At what temperature was this expansion performed?

16) (2015) In class we learned that the change in entropy of a material with temperature is given by:

$$S_2 - S_1 = \int_{T_1}^{T_2} \frac{C_p(T)}{T} dT \tag{2.1}$$

In a prior homework, we fit the heat capacity to a polynomial, which we could then integrate. Now, we will numerically integrate the data points using the Trapezoid Rule discussed in class:

$$\int_{T_1}^{T_2} f(x) \approx (T_2 - T_1) \left[\frac{f(T_1 + f(T_2))}{2} \right] \tag{2.2}$$

where the function $f(T)$ in our case is the right hand side of Equation , is simply the right hand side of Equation 2.1. Do this by creating a "FOR" loop in MATLAB that sums up all the trapezoids in the temperature range. Email your MATLAB script to the TA by the due date.

1. What is the difference in entropy at 300 K and 1300 K?

2. Previously, we determined that the heat capacity is given by:

   (a)

$$C_p = 22.83 + 3.826x10^{-3}T - \frac{3.533x10^5}{T^2} + 2.131x10^{-8}T^2 \tag{2.3}$$

   (b) Use Equation 2.1 to analytically solve for the change in entropy using Equation 2.3. Which method do you think is more accurate? Explain your reasoning.

2.6 Temperature Equilibration

17) (2015) 100 g of ice at 250 K is added to 100 g of water at 300 K, and the mixture is allowed to come to equilibrium in an isolated container at constant pressure. You may assume that C_p is constant for this problem (though it is not the same for water and ice) and that the melting point is 273 K.

1. What is the final temperature?

2. How much liquid is present?

3. How would your answer change if the initial liquid was 40% ethanol?

18) (2015) A square block of Al, initially at a uniform temperature of 300 K, is brought into contact with another block of aluminum, initially at a uniform temperature of 600K. Both blocks are of equal mass, and they are isolated at constant pressure while they come to equilibrium. The questions below assume equilibrium has been reached.

1. What do you know about the final temperatures of the Al blocks?

2. Will the final temperature(s) be 450 K? Justify your answer.

3. Find the final temperature.

2.7 Statistical Thermodynamics

19) (2015) DeHoff 6.3: Consider a system of two particles (A and B) that may each occupy any of the four energy levels ($\epsilon_1, \epsilon_2, \epsilon_3, \epsilon_4$).

1. How many distinct microstates are there for this system?

2. List each of the microstates and indicate which microstates have the same energy.

3. How many macrostates are there?

4. List the most probable macrostates.

20) (2015) DeHoff 6.5 Variant: Consider the system consisting of 9 identical but distinguishable particles, each of which can be in any of three states. The respective energy levels of the states are $\epsilon_0 = 0, \epsilon_1 = \epsilon, \epsilon_2 = 2\epsilon$. The system has a temperature T.

1. Write the partition function for a single particle.

2. Calculate the average number of particles in each state.

3. Determine the number of configurations that have the following occupation numbers for the three states: $n_0 = 4$, $n_1 = 3$, $n_2 = 2$.

4. Calculate the entropy of the macrostate described by the occupation numbers above.

5. Calculate the internal energy.

6. Choose a different set of occupation numbers to give the same internal energy (*e.g.* (3,5,1)) and repeat your calculation of the entropy. Which macrostate is more likely?

21) (2015) DeHoff 6.7 variant: A System containing 500 particles and 15 energy levels is in the following macrostate: {14, 18, 27, 38, 51, 78, 67, 54, 32, 27, 23, 20, 19, 17, 15}. Estimate the change in entropyu when the system undergoes a process leading to the following changes in occupation numbers: {0, 0, -1, -1, -2, 0, 1, 0, 3, 2, -1, 1, -1, 0, -1}.

2.8 Single Component Thermodynamics

22) (2015) DeHoff 6.10: Compute the change in entropy when one mole of a monatomic ideal gas is compressed from an initial condition at 273K and 1 bar to 500K at 3.5 bar.

1. Calculate using the phenomenological thermodynamics of Chapter 4.

2. Calculate using the results of statistical thermodynamics. Hint: first calculate the initial and final volumes.

23) (2015) DeHoff 7.5: Sketch $G(T)$ for an element that the pressure corresponding to the triple point. Repeat the sketch for a pressure slightly above and slightly below the triple point.
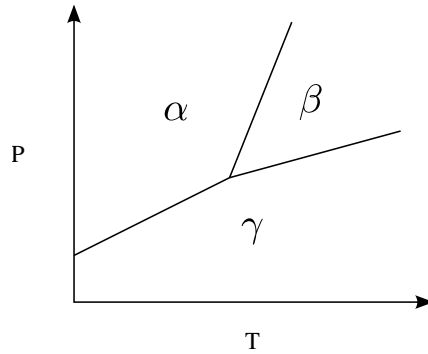
24) (2015) DeHoff 7.6 See Lecture 17, last page.

25) (2015) DeHoff 7.7 variant: At what pressure will ice melt at -2°C?

26) (2015) DeHoff 7.8: At 1 atm pressure and below 1155 K, the ε form of titanium is stable; above 1155 K, the β form is the stable phase (ε becomes metastable). Given the following data:

- $\Delta S^{\varepsilon \to \beta} = 3.43\,\text{J/mol} \cdot \text{K}$ (This is the difference in molar entropy 3 between the phases).

- The change in molar entropy upon melting is $9.02\,\text{J/mol} \cdot \text{K}$.

- $T_m^\beta = 1940$ K.

    1. Sketch G^ε, G^β and G^ℓ in the temperature range of interest.

    2. What is T_m^ε?

    3. There is a database of the Gibbs free energy of 78 pure elements as a function of temperature. The database can be found here: http://www.crct.polymtl.ca/sgte/unary50.tdb

      (a) Find the ε phase of titanium (labeled as GHSERTI), the β phase (labeled as GBCCTI), and the liquid phase (labeled as GLIQTI) and repeat a and b using the empirical formulas. Compare your answers and comment on the accuracy of your assumptions.

      NOTE: The formula is written so that a program called Thermocalc can read them. Each free energy curve is a piecewise formula. The ";" separates the parts of the function over different temperature ranges. In addition, a "**" is the same as an exponent or "^".

2.9 Mulitcomponent Thermodynamics

27) (2015) DeHoff 8.1: Titanium metal is capable of dissolving up to 30 atomic percent oxygen. Consider a solid solution in the system Ti–O containing an atom fraction, $X_0 = 0.12$. The molar volume of this alloy is 10.68 cc/mol. Calculate the following:

    1. The weight percent of O in the solution.

    2. The molar concentration (mol/cc) of O in the solution.

    3. The mass concentration (gm/cc) of O in the solution.

    4. Use these calculations to deduce general expressions for weight percent, molar, and mass concentrations of a component in a binary solution in terms of the atom fraction, X_2, the molar volume, V, and the molecular weights, MW_1 and MW_2, of the elements involved.

28) (2015) DeHoff 8.4: Use the partial molal volumes computed in Problem 8.3 (worked out in class) to demonstrate that the Gibbs – Duhem equation holds for these properties in this system.

29) (2015) DeHoff 8.6: For an ideal solution it is known that, for component 2, $\Delta G_2 = RT \ln X_2$. Use the Gibbs – Duhem integration to derive corresponding relation for component 1.

30) (2015) One mole of solid Cr_2O_3 at 2500 K is dissolved in a large volume of a liquid Raoultian solution (also at 2500 K) of Al_2O_3 and Cr_2O_3 with $X_{Cr_2O_3} = 0.2$. Calculate the resulting changes in the total enthalpy and entropy given the following:

$$T_{m,Cr_2O_3} = 2538\,\text{K}; \ \Delta H_{m,Al_2O_3} = 107,500\,\text{J/mol at } T_{m,Al_2O_3} = 2324\,\text{K}; \ \Delta S_{m,Al_2O_3} = \Delta S_{m,Cr_2O_3}$$

2.10 Computational Exercises

31) (2015) For this problem, you will be using MATLAB's symbolic solver (fzero) and function handles to find the zero of an equation. On last week's quiz we found that 89.1 grams of ice were necessary to cool a 1 kg block of Pb down to 300 K from 600 K. We will be plotting the change in temperature for both the Pb and ice. You will need the following parameters:

$$C_p^{Pb} = 0.1169 + 4.2x10^{-5}T \ \tfrac{\text{kg}}{\text{kg·K}}$$
$$C_p^{H_2O} = 4.2 \ \tfrac{\text{kJ}}{\text{kg·K}}$$
$$\Delta H_{fus}^{H_2O} = 344 \ \tfrac{\text{kJ}}{\text{kg}}$$
$$\tfrac{dH}{dt} = a\Delta T$$

Here a is a coefficient that controls the heat transfer in conduction, which we will assume to be $3.33x10^{-3}$ kJ/K · s, and ΔT is the temperature difference between the two materials.

32) Use the equations derived in class to plot the change in temperature for H2O and Pb. Assume dt=1 s and calculate the first 200 time steps. How do you know when the system is at equilibrium?

1. Create a plot that shows the amount of water in the system as a function of time. At what time is all the ice gone?

2. Create a plot that shows the total heat transfer occurring between the Pb and H2O. How can you tell when equilibrium is reached from this plot?

33) (2015) We will be putting together a program to help calculate phase diagrams of all sorts piece by piece. The first step is to create a MATLAB script that solves a system of two equations. The system is below:

$$G_s - X_s\frac{dG_s}{dX_s} = G_\ell - X_\ell\frac{dG_\ell}{dX_\ell} \tag{2.4}$$

$$\frac{dG_s}{dX_s} = \frac{dG_\ell}{dX_\ell} \tag{2.5}$$

where G_s and G_ℓ are given by the following expressions:

$$G_s(X_s) = \Omega_s X_s (1 - X_s) +$$
$$RT\left[X_s \ln X_s + (1 - X_s)\ln(1 - X_s) + 200X_s - 400(1 - X_s)\right].$$

$$G_\ell(X_\ell) = \Omega_\ell X_\ell (1 - X_\ell) + RT\left[X_\ell \ln X_\ell + (1 - X_\ell)\ln(1 - X_\ell)\right].$$

Here G_s is the Gibbs energy of the solid phase, G_ℓ the Gibbs free energy of the liquid phase, R the gas constant (8.314 J/K), T the absolute temperature, X_s and X_ℓ are the compositions of the solid and liquid phase respectively, and Ω_s, Ω_ℓ are parameters to be defined later. We can rewrite Eqs. 2.4 and 2.5 as follows:

$$G_s - X_s\frac{dG_s}{dX_s} - G_\ell + X_\ell\frac{dG_\ell}{dX_\ell} = 0 \tag{2.6}$$

$$\frac{dG_s}{dX_s} - \frac{dG_\ell}{dX_\ell} = 0 \tag{2.7}$$

Create a MATLAB function that takes X_s, X_ℓ, T, Ω_s and Ω_ℓ as inputs and then create a script that uses the MATLAB command fsolve to calculate X_s and X_ℓ for T=700K, $\Omega_\ell = 1500$ cal/mol and $\Omega_s = 3000$ cal/mol.

34) (2015) Now that we are able to solve for the composition of the solid and liquid at one point, we will improve our script to calculate it over a range of temperatures. Start with an initial guess for both the solid and liquid near zero and a temperature of 900 K. Determine the composition of the liquid and solid down to 1 K for each temperature using a for loop. Make sure to update your guess with the correct answer for the previous temperature to help your program converge. Repeat again starting from 600 down to 1 K, this time starting with an initial guess near 1, and plot your results. Use the following parameters to make the Gibbs energy more physical:

$$T_m^\alpha = 900\,\text{K}$$

$$T_m^\beta = 600\,\text{K}$$

$$\Delta H_f^\alpha = 2000\,\frac{\text{cal}}{\text{mol}}$$

$$\Delta H_f^\beta = 1300\,\frac{\text{cal}}{\text{mol}}$$

The liquid and solid free energies are given by the following expressions. (Note that the Gibbs energy for the solid phase has changed slightly and should be adjusted in your code. In these units $R = 1.987\,\text{cal}/\text{mol} \cdot \text{K}$

$$G_s(X_s) = \Omega_s X_s (1 - X_s) + RT +$$

$$\left[X_s \ln X_s + (1 - X_s) \ln (1 - X_s) + X_s \Delta G_\beta^{\ell \to s} + (1 - X_s) \Delta G_\alpha^{\ell \to s} \right].$$

$$G_\ell(X_\ell) = \Omega_\ell X_\ell (1 - X_\ell) + RT \left[X_\ell \ln X_\ell + (1 - X_\ell) \ln (1 - X_\ell) \right].$$

As a reminder, the free energy change for the melting transition can be written in terms of the enthalpic and entropic contributions to the free energy:

$$\Delta G^{s \to \ell} = \Delta H^{s \to \ell} - T\Delta S^{s \to \ell}$$

35) (2015) Our phase diagram calculation is almost complete! We only have to find the equilibrium between the two solid phases left. To do that, we simply take the derivative of the Gibbs free energy of the solid phase and set it equal to zero. The equation becomes:

$$RT \ln \left(\frac{X_s}{1 - X_s} \right) - \Omega_s (2X_s - 1)$$

Again, assume that Ω_s= 3000 cal/mol. This is easily done by creating a for loop that solves for the temperature at each composition between .01 and .99. Plot your results on the same figure from the previous homework and voila, your first phase diagram!

Now with your working code, replot the diagrams for the following interaction coefficients. You will have to change the range of temperatures for one of the sets below. You can figure out which one it is, if you think of the physical significance of the parameters.

1. $\Omega_s = 3000\,\text{cal}/\text{mol} : \Omega_\ell = 0$

2. $\Omega_s = 0 : \ \Omega_\ell = 3000\,\text{cal}/\text{mol}$

3. $\Omega_s = 0; \Omega_\ell = 0$

4. $\Omega_s = 3000\,\text{cal}/\text{mol} : \Omega_\ell = 3000\,\text{cal}/\text{mol}$

    For each phase diagram, plot your results and describe how the changing interaction parameters changed the shape of the plot.

3 315 Problems

1) Use the Ellingham Diagram (reproduced here as Figure 3.1) to answer the following.

1. Find the temperature and partial pressure of O_2 where Ni(s), Ni(l), and NiO(s) are in equilibrium.

2. Can the same equilibrium be achieved with H_2 and H_2O instead of oxygen? If so, what is the ratio of H_2/H_2O?

3. At 1245°C, H_2, and H_2O with a ratio of partial pressures of 10:1 is flowed through a tube furnace containing a crucible filled with MnO powder. Determine the driving force for the reaction

4. Can you safely melt aluminum in a magnesia (MgO) container? Why or why not? What is the resulting reaction and its driving force?

5. Establish the T-log P_{O_2} phase diagram between 1000°C and 1500°C fort he Mn-O system at 1 atm total pressure.

2) In the days before the industrial revolution the P_{CO_2} in the earth's atmosphere was 275 ppm. Use the data in Figure 3.2 to calculate how high one would need to heat $CaCO_3$ to decompose it at a P_{CO_2} for the preindustrial concentration of 275 ppm and for present day P_{CO_2} (You will have to look this up, please give your source). Also calculate how high one would need to heat $CaCO_3$ to decompose it if the CO_2 level in the atmosphere reaches 500 ppm.

3) Based on Raoultian liquid solution behavior, calculate the Sn-Bi eutectic phase diagram (using Excel, Mathematica, MATLAB, etc). Assume that there is negligible solid solubility of both Sn and Bi in the other component, and that $\Delta Cp \approx 0$ for both end members. Use the following melting points and enthalpies of fusion:

Material	Tm(K)	$\Delta H(s \rightarrow l)(J/mol)$
Sn	505.12	7030
Bi	544.59	11300

4) Use MATLAB or a spreadsheet to calculate liquidus and solidus lines for a "lens-type" T-X diagram for the A-B system, using the data below. You may assume both the liquid and solid solutions behave ideally.

Type	Tm(°C)	$\Delta Hm(J/mol)$
A	910	34700
B	1300	49800

1. Plot the T vs. X phase diagram. Label each region on the diagram with the phases present and the degrees of freedom.

2. For the temperatures 800°C, 1100°C, and 1500°C, draw plots of the activity of component A vs. composition. Include two plots for each: One with respect to liquid as the reference state and one with respect to solid as the reference state.

5) Based upon the temperature at the top of the miscibility gap in the Cr-W system (see Figure 3.3), do the following:

1. Predict the miscibility gap (solvus) and spinodals based upon the regular solution model. Use the spreadsheet and plot the results.

2. Compare your miscibility gap with the experimental one in the attached figure. Speculate about why there might be differences.

6) Consider the Pb-Sn phase diagram (see Figure 3.4).

1. Label each region on the diagram with the degrees of freedom.

2. Sketch free energy vs. composition curves for all phases at 150°C, 200°C, 250°C, and the eutectic temperature.

3. For each temperature from part (b), draw plots of the activity of Sn vs. composition. Include two plots for each: One with respect to liquid as the reference state and one with respect to solid as the reference state. You may assume the liquid solution to be Raoultia. At 150°C, only plot activity of Sn vs. composition with respect to the solid reference state. At 250°C, only plot activity of Sn vs. composition with respect to the liquid reference state.
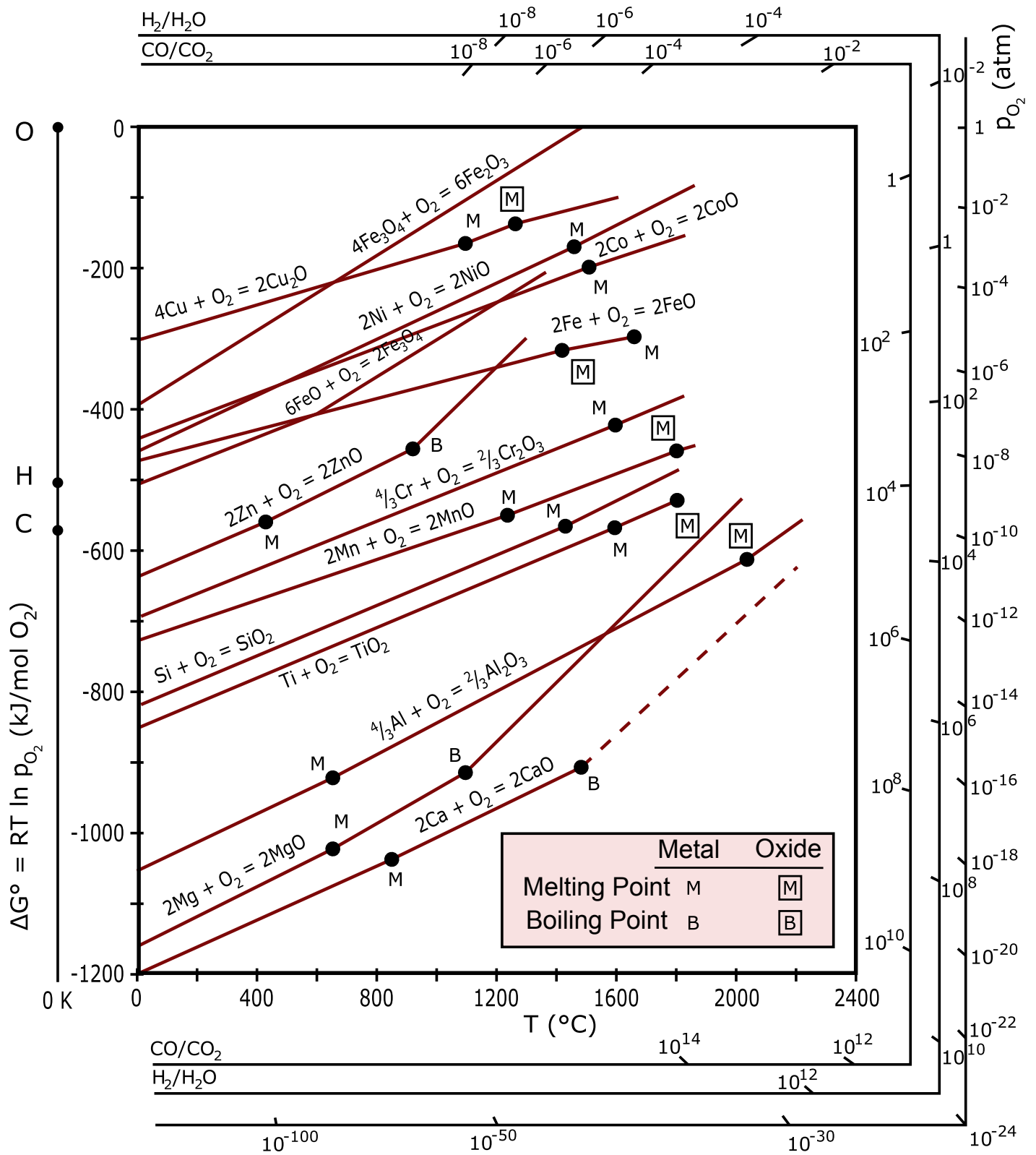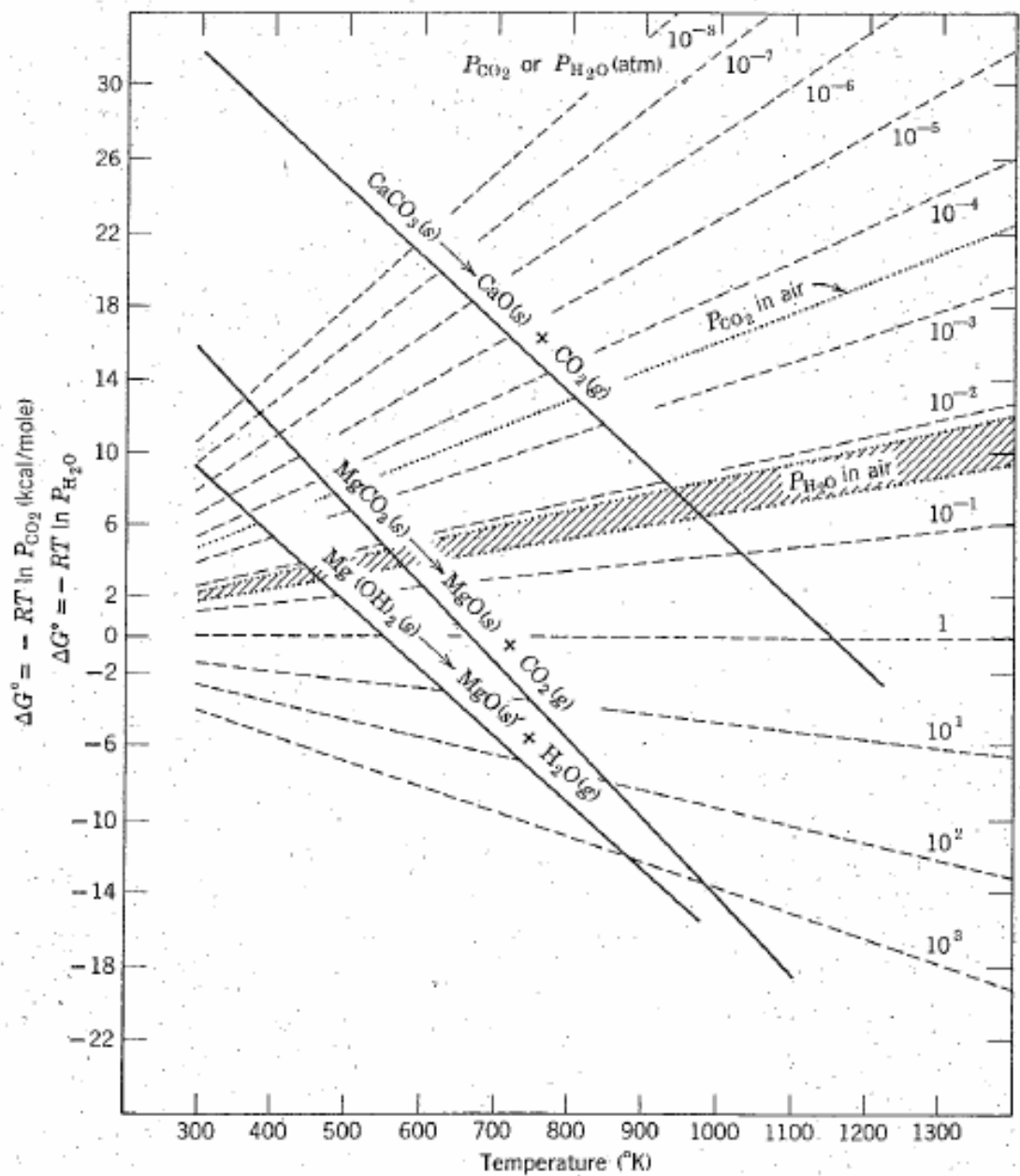
Figure 3.1: Ellingham diagram.

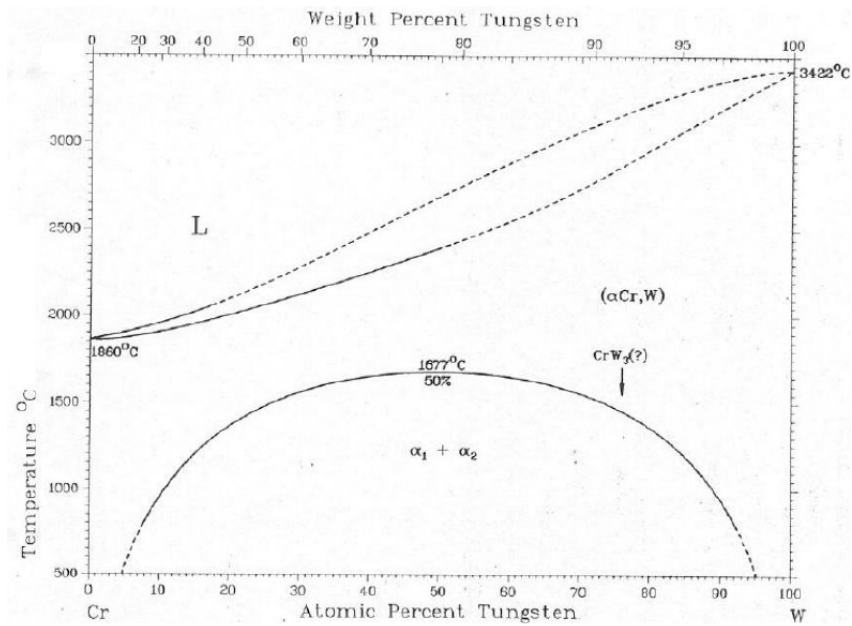**Figure 3.2:** Thermodynamic data for Mg and Ca oxides and carbonates.
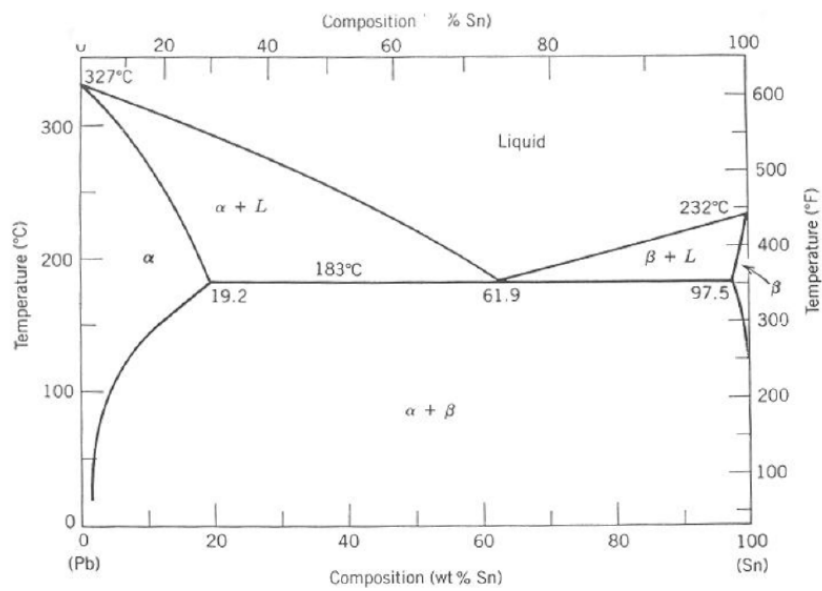
Figure 3.3: Cr-W Phase diagram.

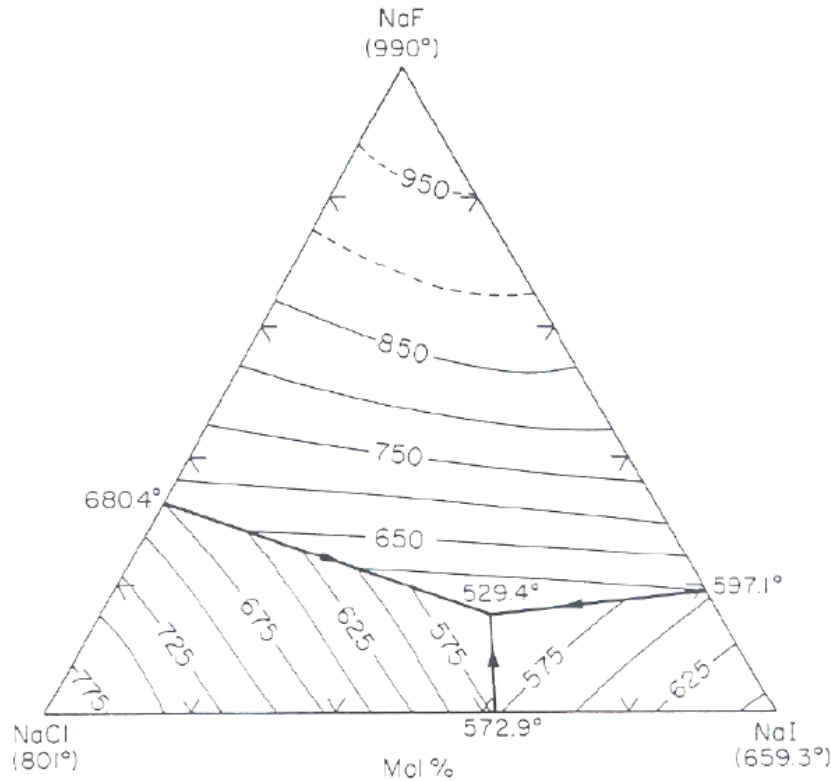
Figure 3.4: Pb-Sn phase diagram.

Figure 3.5: NaF-NaCl-NaI phase diagram. From ref. [1].

7) Calculate and plot the liquidus projection of the ternary phase diagram for the NaF-NaCl-NaI system. The melting temperatures and heats of fusion are as follows: NaF (990°C, 29,300 J/mol), NaCl (801°C, 30,200 J/mol) and NaI (659.3°C, 22,300 J/mol). Assume and ideal liquid solution and negligible solid solubility. Compare your result with the experimental diagram shown in Figure 3.5. Why might they be different?

8) On the liquidus projection diagram for the hypothetical system A-B-C shown in Figure 3.6), complete the following:

1. Label primary phase fields

2. Draw the subsolidus compatibility joins.

3. Label all the binary and ternary invariant points.

4. Indicate the directions of falling temperature (binaries and ternary).

5. Sketch all the binary phase diagrams (including those formed by subsolidus compatibility joins).

9) Using the attached liquidus projection diagram for the hypothetical system A-B-C shown in Figure 3.7, complete the following:

1. Determine the equilibrium crystallization path for the composition marked with the star.

2. Determine the microstructural constituents:

   (a) Just prior tot he liquid striking the phase boundary (liquid + solid 1 + solid 2).
   (b) At the eutectic but just prior to eutectic crystallization.
   (c) After crystallization is complete.
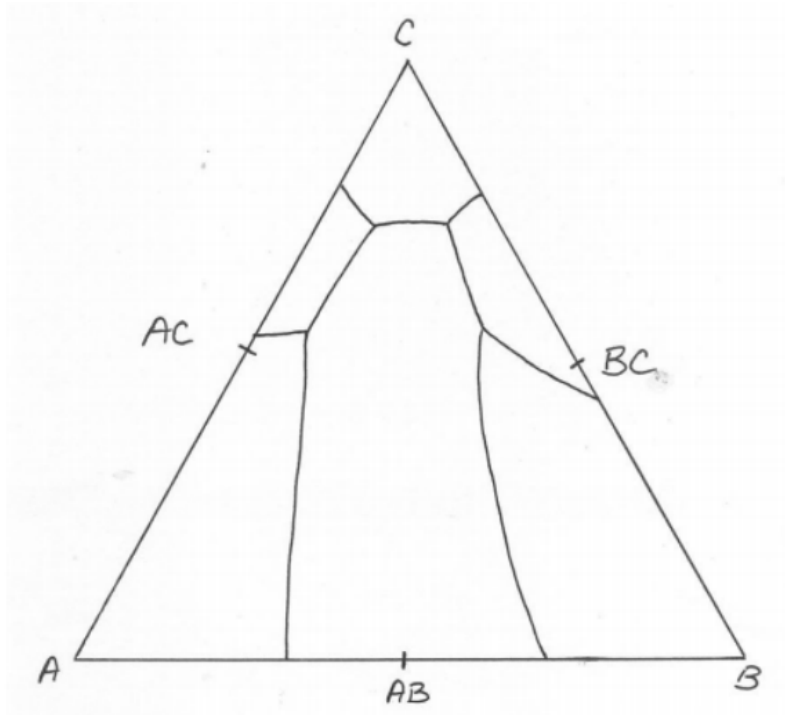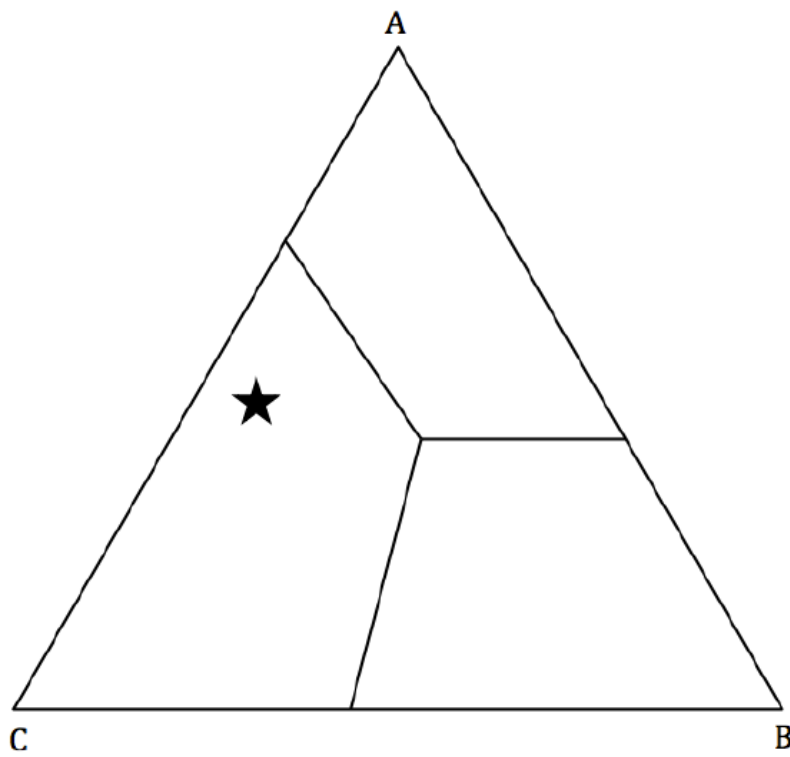
Figure 3.6: Liquidus projection diagram.

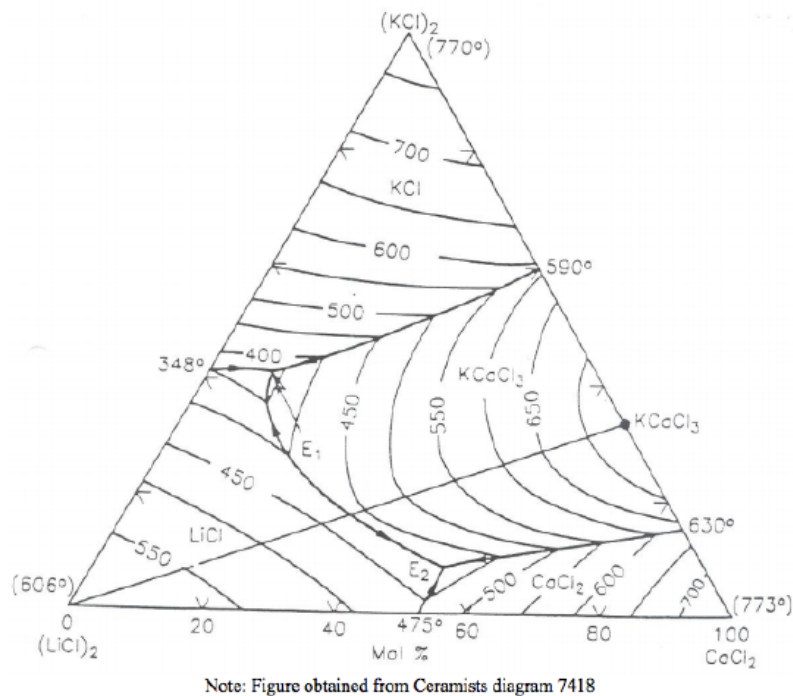**Figure 3.7:** Liquidus projection diagram.

Figure 3.8: $(LiCl)_2 - CaCl_2 - (KCl)_2$ phase diagram.

10) On the $(LiCl)_2 - CaCl_2 - (KCl)_2$ phase diagram shown in Figure 3.8, draw isothermal sections at the following temperatures: (note- Ternary eutectic E_1 is at 332°C and ternary eutectic E_2 is at 412°C)

1. 600°C

2. 450°C

3. 400°C

4. 300°C

5. Also determine the precise (not schematic!) $(LiCl)_2 - KCaCl_3$ phase diagram.

11) (Bonus question - 10% of problem set value) Starting with the regular solution model, prove that regardless of how positive the interaction parameter (or heat of mixing) might be, the inital slope on any free energy vs. composition curve must be infinitely negative on the left side ($X_B \rightarrow 0$) and infinitely positive on the right side ($X_B \rightarrow 1$).

12) A steel tank contains hydrogen at 15 atm pressure. If the solubility of hydrogen in steel is 1×10^{-2} g/cm^3 under 15 atm pressure, the diffusion coefficient is 8×10^{-5} cm^2/s at room temperature and the tank is placed in a vacuum, calculate the flux of hydrogen through a 3.5 mm thick wall.

13) Austenite ($\gamma-$Fe) with .85 wt% carbon has a diffusion coefficient of 1.9×10^{-11} m^2/s at 900°C.

1. Determine the jump distance in terms of the lattice parameter a_o and the coordination number for carbon diffusion in this structure.

2. How many jumps does a carbon interstitial make each second? Assuming a lattice vibration frequency of 10^{13}s^{-1}, what fraction of jumps is successful?

3. Calculate and compare the random walk distance with the total distance (back and forth) traveled by an interstitial carbon atom in one second.

14) Ferrite (α−Fe) (BCC structure) dissolves carbon to a lesser extent than austenite (FCC structure).

1. Determine the jump distance in terms of the lattice parameter a_o and the coordination number for carbon diffusion in this structure.

2. Given the data in Table 2.1 of Porter, Easterling & Sherif, make an Arrhenius plot of diffusion coefficients of carbon and nitrogen from room temperature to 800°C.

3. A different interstitial solute diffuses at a rate of 4.1×10^{-2}mm^2/s at 300°C and 7.3×10^{-2}mm^2/s at 600°C. Determine its activation energy and pre-exponential factor.

15) Write a MATLAB code to evaluate the composition as a function of distance for the draining plate problem.

1. For $t/\tau = 0.05$ how many terms in the series is necessary to obtain a composition that is converged to within 1% of the exact answer. The percent error is the maximum value of $|c(x) - c_{exact}(x)|/c_{exact}(c) \times 100$. To determine the exact answer evaluate the summation to $j = 200$. L=100um, C$_o$ = 0.1at. %

2. Plot the converged solution as a function of x for t/τ = 0.05, 0.5, 1.0, 2.0.

3. For what approximate value of t/τ does a single term in the summation with $j = 0$ provide an approximation to the exact solution within 10%?

16) (After Shewmon 2-13) We wish to consider the rate at which the vacancy concentration increases in a specimen after an increase in temperature. We assume that the vacancy concentration in the lattice near the free surface, grain boundaries and edge dislocations will rise to the new equilibrium value of the new temperature as soon as the temperature is raised. The vacancy concentration far from these vacancy sources rises only as fast as vacancies can diffuse to the region from the source.

1. Assume that vacancies come only from grain boundaries, and the grain diameter is approximately 1 mm. Calculate the relaxation time in two regimes, at high temperatures where the diffusion coefficient Dv is 10^{-5}cm^2/s.

2. Calculate the relaxation time (τ) given a dislocation line length (dislocation density) of 10^7cm/cm^3. (Hint: First, calculate the distance between dislocations, i.e, the vacancy sources.)

17) The diffusion coefficient of carbon in austenite can be approximated as:

$$D_c = 0.2 \exp \left(\frac{-136,000 \, \text{J/mol}}{RT} \right) \text{cm}^2/\text{s}$$

1. How long does it take for the composition $c_{0.5}$ during carburization to penetrate .45 mm at 900°C? How long for 5 mm?

2. What annealing temperature is required to double the penetration in a given time?

18) Consider two blocks initially one pure A and the other pure B that are welded together and annealed at 1100°C. Plot the diffusion profile as a function of distance after half an hour. Assume that the diffusion coefficient of both specie is $D = 4.5 \times 10^{-11}$m^2/s and that D is not a function of concentration.

19) Calculate the enthalpy and entropy of vacancy formation ($\Delta H_v, \Delta S_v$) for a system given the equilibrium concentration of vacancies (X_v^β) is 1.7×10^{-8} at 440 K and 1.5×10^{-5} at 650 K.

20) Given that $D = \frac{1}{6}\Gamma v \alpha^2$, consider the diffusion of vacancies in an FCC lattice:

1. Let $\frac{\Delta S_m}{R} = 2$ and $v = 10^{13}$s^{-1}. Calculate the pre-exponential factor D_o for vacancies (assume $a_o = 0.4$ nm.)

2. If $\Delta H_m = 6.5$ kJ/mol, calculate D_v for vacancies at 750°C

21) Below are the linear thermal expansion ($\Delta L/L_o$) and X-ray lattice parameter ($\Delta a/a_o$) results at different temperatures for aluminum. Calculate and plot $\ln X_v$ from this data versus T^{-1} and determine the enthalpy and entropy of vacancy formation in aluminum. Show all equations used.

22)   Below is a table of linear thermal expansion ($\Delta L/L$) and lattice parameter expansion ($\Delta a/a$) vs. temperature for aluminum. Calculate and plot $\ln X_v$ form this data versus $1/T$ and determine the enthalpy and entropy of vacancy formation in this material. Show all equations used.

23)   A gold specimen is quenched from 700°C to room temperature (25°C). An identical specimen is air cooled from 700°C to room temperature. The difference in their resistances is $\Delta \rho_o$. The quenched specimen is annealed at 40°C for 120 hours and then annealed at 60°C. Resistivity measurements were taken periodically by quenching the sample to room temperature. From the two slopes shown in attached Figure 2-16, find ΔH_{motion}.

24)   Write balanced Kröger-Vink reactions for the following reactions, assuming full ionic charge for all ionic species.

1. Schottky defect formation in Li_2O

2. Anion Frenkel defect formation in Nb_2O_5

3. Oxidation of CdO to yield $Cd/O < 1/1$ (write both possible reactions)

4. Doping Al_2O_3 with ZnO to produce oxygen vacancies.

25)   Pure ZnO is an n-type semiconductor dominated by oxygen vacancies, but it can be further donor-doped by substituting Al^{3+} for Zn^{2+} sites.

1. Draw a schematic Brouwer diagram as a function of pO_2 at fixed Al content.

2. Draw a schematic Brouwer diagram at fixed pO_2 as a function of Al content. Include all relevant point defect reactions and mass-action relationships.

26)   Given the following oxygen ion diffusivities for calcia-stabilized zirconia (CSZ) of composition $(ZrO_2)_{0.85}(CaO)_{0.15}$ and density 5.5 g/cm^3, calculate a) the ionic conductivity at each temperature, and b) the enthalpy of motion. Assume oxygen vacancies are the dominant defect.

4 316-1 Problems

Introduction

1)   Send an email to Prof. Shull (k-shull@northwestern.edu) and Kyoungdoc
(kyoungdockim2013@u.northwestern.edu) with the following information:

1. Anything about yourself (why you are interested in MSE, previous work experience, etc., outside interests apart from MSE) that will help me get to know you a bit (feel free to be brief - any info here is fine).

2. Your level of experience and comfort level with MATLAB. Be honest about your assessment (love it, hate it, don't understand it, etc.).

3. Let us know if you have NOT taken 314 or 315 for some reason.

Diffusion

2)   Consider a diffusion couple with composition C_1 as $z \to -\infty$ and C_2 as $z \to \infty$. The solution to the diffusion equation is:

$$C(z,t) = \frac{C_1 + C_2}{2} - \frac{C_1 - C_2}{2}\text{erf}\left(\frac{z}{2\sqrt{Dt}}\right)$$

where $\text{erf}(y) = \frac{2}{\pi}\int_0^y e^{-t^2}dt$. Note that in the definition of the error function t is a dummy variable of integration, thus the error function is a function of y. Also, erf(0)=0, and erf(∞)=1. You will determine if these boundary conditions are correct.

1. Show that the boundary conditions at $z = \pm\infty$ are satisfied by the solution.

2. Does the composition at $z = 0$ vary with time? If not, what is its value? Why do you think this is the case?

3. Write the solution in terms of $\eta = z/t^{1/2}$.

4. Show that the solution satisfies the following diffusion equation that is written in terms of η:

$$D\frac{d^2C}{d\eta^2} + \frac{\eta}{2}\frac{dC}{d\eta} = 0$$

   You will needed to take a derivative of the error function. Leibniz's formula for the differentiation of integrals will be helpful:

$$\frac{d}{dz}\int_{h(z)}^{g(z)} f(t)\,dt = \frac{dg(z)}{dz}f(g(z)) - \frac{dh(z)}{dz}f(h(z))$$

3)   A diffusion couple including inert wires was made by plating pure copper on to a block of α-brass with $X_{Zn} = 0.3$, as shown in Figure 4.1. After 56 days at 785 °C the marker velocity was 2.6x10^{-8} mm/s, with a composition at the markers of $X_{Zn} = 0.22$, and a composition gradient, $\partial X_{Zn}/\partial z$ of 0.089 mm^{-1}. A detailed analysis of the data gives $\tilde{D} = 4.5x10^{-13}$ m^2/s for $X_{Zn} = 0.22$. Use these data to calculate D_{Zn} and D_{Cu} for $X_{Zn} = 0.22$. How would you expect D_{Zn}, D_{Cu} and $\tilde{D}$ to vary as a function of composition?

4)   In class we developed an expressions for J'_a. Show that $J'_a = -J'_b$. (Recall that these primed fluxes correspond to fluxes in the laboratory frame of reference).
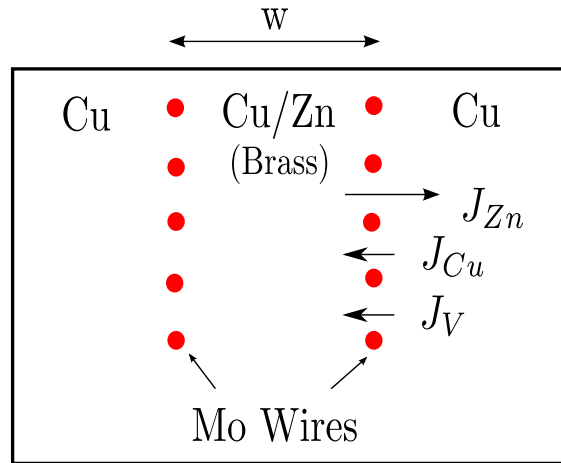
Figure 4.1: Experimental Geometry for the Kirkendall experiment.

5) Consider two binary alloys with compositions $X_b = X_1$ and $X_b = X_2$, shown in Figure 4.2 along with the free energy curves for α and β phases formed by this alloy. Draw the composition profile across the interface shortly after the two alloys are brought into contact with one another, assuming that the interface is in "local equilibrium", i.e. the interface compositions are given by the equilibrium phase diagram. Describe the direction in which you expect the B atoms to diffuse on each side of the interface.
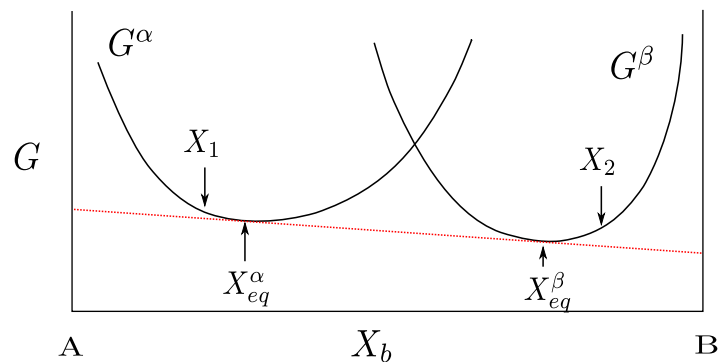

Figure 4.2: Free energy curves for a model A/B alloy.

6) The following MATLAB script runs the vacancy simulation shown in class. It saves the data into a 'structure' called output, which can be loaded into MATLAB later. The file can be downloaded from this link:
http://msecore.northwestern.edu/316-1/matlab/vacancydiffusion.m

```
1  tic % start a timer so that we can see how long the program takes to run
2  n=30;   % set the number of boxes across the square grid
3  vfrac=0.01;   % vacancy fraction
4  matrix=ones(n);
5  map=[1,1,1;1,0,0;0,0,1];  % define 3 colors:  white, red, blue
6  figure
7  colormap(map)  % set the mapping of values in 'matrix' to a specific color
8  caxis([0 2]) % range of values in matrix goes from 0 (vacancy) to 2
9  % the previous three commands set things up so a 0 will be white, a 1 will
10 % be red and a 2 sill be blue
11 matrix(:,n/2+1:n)=2;  % set the right half of the matrix to 'blue'
12 i=round(n/2);   % put one vacancy in the middle
13 j=round(n/2);
14 matrix(i,j)=0;
15 imagesc(matrix); % this is the command that takes the matrix and turns it into a plot
16 t=0;
17 times=[1e4,2e4,5e4,1e5];
18 showallimages=1; % set to zero if you want to speed things up by not showing images,  set to 1 if you
       want to show all the images during the simulation
19
```

```matlab
%% now we start to move things around
vacancydiff.matrices={};  % makea blank cell array
while t<max(times)
    t=t+1;
    dir=randi([1 4], 1, 1);
    if dir==1
        in=i+1;
        jn=j;
        if in==n+1; in=1; end
    elseif dir==2
        in=i-1;
        jn=j;
        if in==0; in=n; end
    elseif dir==3
        in=i;
        jn=j+1;
        if jn>n; jn=n; end
    elseif dir==4
        in=i;
        jn=j-1;
        if jn==0; jn=1; end
    end
    % now we need to make switch
    neighborix=sub2ind([n n],in,jn);
    vacix=sub2ind([n n],i,j);
    matrix([vacix neighborix])=matrix([neighborix vacix]);
    if showallimages
        imagesc(matrix);
        drawnow
    end
    if ismember(t,times)
        vacancydiff.matrices=[vacancydiff.matrices {matrix}]; % append matrix to output file
        imagesc(matrix);
        set(gcf,'paperposition',[0 0 5 5])
        set(gcf,'papersize',[5 5])
        print(gcf,['vacdiff' num2str(t) '.eps'],'-depsc2')
    end
    i=in;
    j=jn;
end
vacancydiff.times=times;
vacancydiff.n=n;
save('vacancydiff.mat','vacancydiff') % writes the vacancydiff structure to a .mat file that we can
  read in later
toc
```

1. Run the vacancy diffusion script, and include in your homework the .jpg files generated for time steps of 1e4, 2e4, 4e4 and 1e5.

2. For the longest time step, develop a plot of average composition along the horizontal direction.

   Here is the MATLAB script that I used to do this (available at http://msecore.northwestern.edu/316-1/matlab/vacancyplot.m):

```matlab
load vacancydiff % load the previously saved output.mat file
figure
figformat % not necessary, this is the standard initialization script I use to standardize what
  my plots look like
n=vacancydiff.n;
matrix=vacancydiff.matrices{4};
matrixsum=sum(matrix,1); % sum of each column in the matrix
plot(1:n,matrixsum/n,'+b')
xlabel ('z')
ylabel ('C')
print(gcf,'../figures/vacancyplot.eps','-depsc2') % this creates an .eps file, which I use for
  the coursenotes but which may not be as useful for many of you as the jpg file
% saveas(gcf,'vacancyplot.jpg') % this is what to do if you just want to save a .jpg file
```

   Note that 'figformat' is NOT a matlab command. This line calls another file called names figformat.m that includes a few commands to standardize plots that I am making for this class. Here's what it looks like:

```
1  set(0,'defaultaxesbox', 'on') % draw the axes box (including the top and right axes)
2  set(0,'defaultlinelinewidth',2)
3  set(0,'defaultaxesfontsize',16)
4  set(0,'defaultfigurepaperposition',[0,0,7,5])
5  set(0,'defaultfigurepapersize',[7,5]')
```

3. In the previous problem set we obtained concentration profiles from the MATLAB. Now we'll take these concentration profiles and see if they are consistent with the solution to the diffusion equation.

   (a) For each of the 4 time points used in the simulation, plot the concentration profile and fit it to the error function to the diffusion equation, using the interfacial width, w, $(w = 2\sqrt{Dt})$ as a fitting parameter:

   $$C(z,t) = \frac{C_1 + C_2}{2} - \frac{C_1 - C_2}{2}\mathrm{erf}\left(\frac{z}{w}\right)$$

   Note: This problem is a curve fitting exercise in MATLAB. The most frustrating part is getting all the syntax right, but once you know the proper format for the MATLAB code, it's pretty straightforward. Take a look at the section entitled 'Fitting a Function to a Data Set' in the MSE MATLAB help file:

   http://msecore.northwestern.edu/matlab.pdf

   This section includes a MATLAB script that you can download and modify as needed.

   (b) Plot w^2 as a function of the time (expressed here as the number of time steps in the simulation). Obtain the slope of a line drawn through the origin that best fits the data.

   (c) When diffusion occurs by a vacancy hopping mechanism in a 2-dimensional system like the one used in our simulation, the diffusion coefficient is given by the following expression:

   $$D = KX_v\Gamma a^2$$

   Here is the average hop frequency for any given vacancy and a is the hopping distance. From the the slope of the curve of w vs. the total number of jumps, extract an estimated value for K.

**7)** A region of material with a different composition is created in an infinitely long bar. The following plot shows the mole fraction of component A as a function of position. Assume that the intrinsic diffusion coefficient of the A atoms is twice as large as the intrinsic diffusion coefficient for the B atoms.
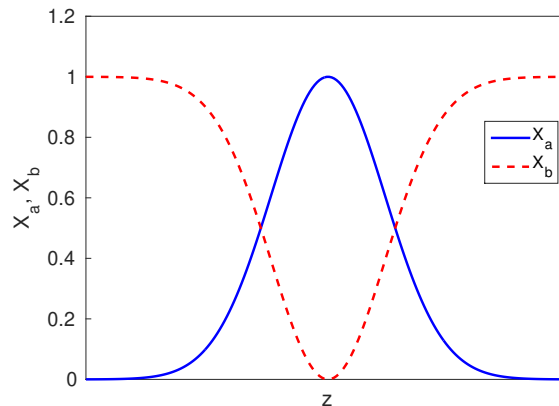

1. Plot the flux of A and the flux of B relative to the lattice as a function of position in the graph above.

2. Plot the vacancy creation rate as a function of position in the graph above.

3. Plot the flux of A and B in the lab frame as a function of position in the graph above.

4. Plot the lattice velocity as a function of position in the graph below. What are the physical implications of this plot?

8) The values for the intrinsic diffusion coefficients for Cu and Ni in a binary Cu/Ni alloy are shown below on the left (note that Cu and Ni are completely miscible in the solid state). A diffusion couple is made with the geometry shown below on the right.
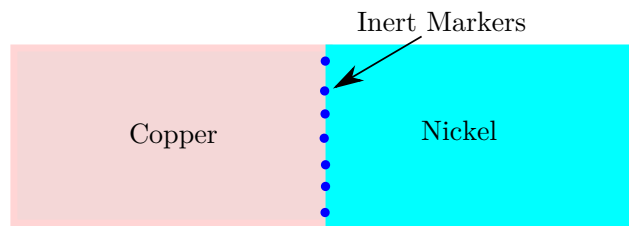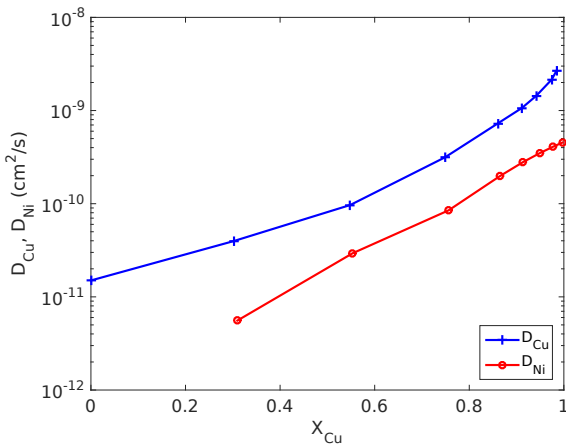
1. What is the value of the interdiffusion coefficient $\tilde{D}$, for an alloy consisting of nearly pure Nickel?

2. Will the markers placed initially at the Cu/Ni interface move toward the copper end of the sample, the nickel end of the sample, or stay at exactly the same location during the diffusion experiment.

3. The copper concentration across the sample is sketched below after diffusion has occurred for some time.
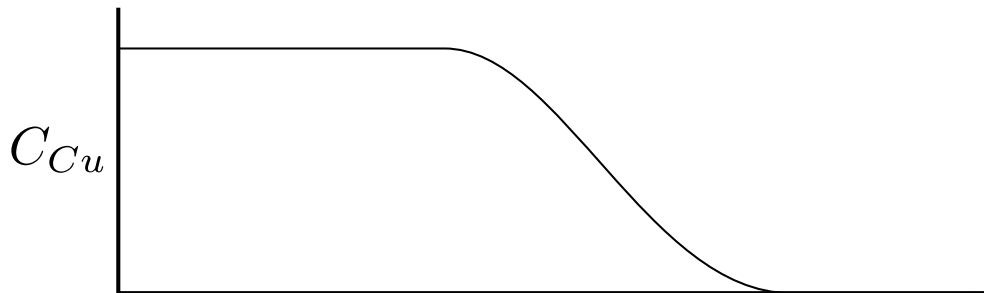
4. Sketch the fluxes of Copper, Nickel and vacancies, defining positive fluxes as those moving to the right.

5. Now sketch the rate at which vacancies are created or destroyed within the sample in order to maintain a constant overall vacancy concentration throughout.

9) An experiment is performed to determine the tracer diffusion coefficient of metal A in a matrix of metal B. This is done by depositing a very thin film of metal A onto the surface of metal B and measuring the concentration profile of metal A into the depth of the material at different times. The concentration profiles in the left figure below are obtained at two times, t_1 and t_2:
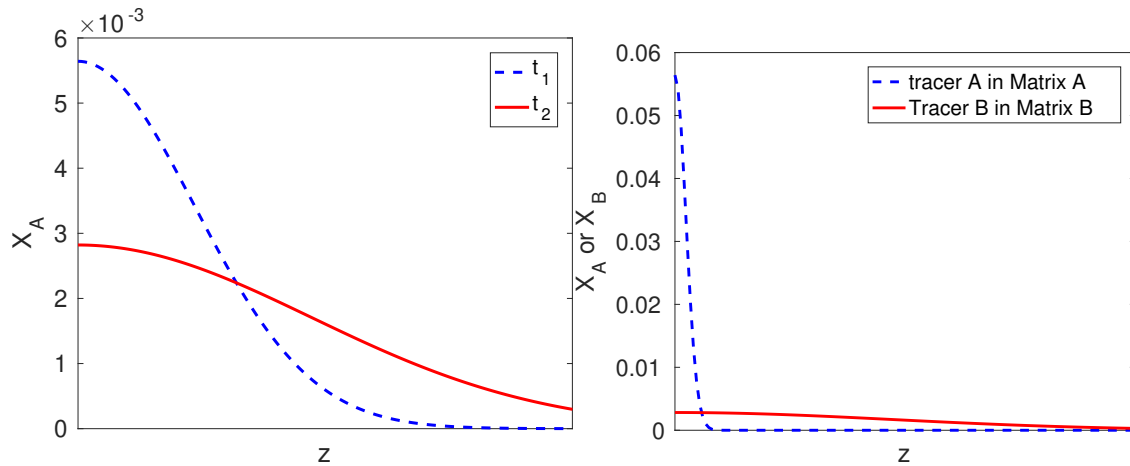

1. Estimate the ratio t_2/t_1

2. Now suppose we measure the self diffusion coefficients of A and B. Performing measurements at the same time and temperature gives the concentration profiles shown in the figure above to the right. Which element (A or B) do you expect has the highest melting temperature, and why?

3. Now we'll make a diffusion couple with element A on the right half and element B on the left half. Assume that A and B are miscible at the diffusion temperature, and form a one phase alloy. Mark up the following diagram as directed on the next page:
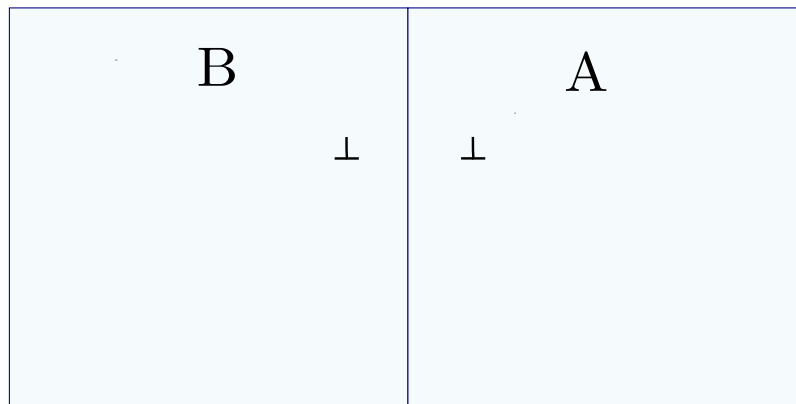
   (a) Put an arrow labeled 'M' on the diagram indicating the direction that inert markers placed originally at the interface will move.

   (b) Put an arrow labeled 'V' on the diagram indicating the the net vacancy flux due to diffusion in the sample.

   (c) Put a 'C' on the region of the sample where you expect vacancies to be created, and a 'D' on the sample where you expect vacancies to be destroyed, assuming that the total vacancy concentration must remain at equilibrium.

   (d) Two edge dislocations are also indicated in the diagram. Place arrows on top of each dislocation to illustrate he directions you expect these dislocations to move in order to create or destroy the vacancies from part iii.

Stress and Strain

10) A tensile stress, σ, is applied to a single crystal of zinc, which has an HCP structure. The close packed planes of atoms (the slip plane for an HCP material) is oriented with its surface normal in the plane of the paper, inclined to the tensile axis by an angle ϕ as shown below, with $\phi = 30°$. Assume that the critical resolved shear stress for motion of the dislocation is 50 MPa (5×10^7 Pa). The shear modulus of Zn is 43 GPa (4.3×10^{10} Pa) and its atomic radius is 0.13 nm.
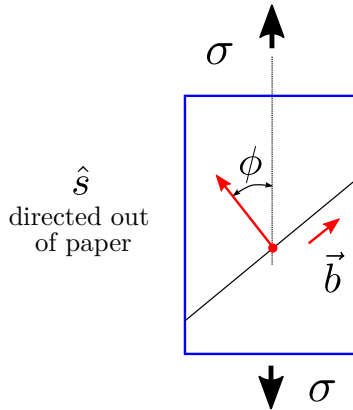
1. Is this an edge dislocation, a screw dislocation, or a mixed dislocation, and how do you know?

2. Put an arrow on the drawing above to indicate the direction in which the dislocation moves under an applied tensile stress.

3. Calculate the tensile yield stress for this sample.

4. Suppose that the slip plane is oriented so that $\vec{b}$ is still in the plane of the paper, but that ϕ is increased to $60°$. Will the yield stress increase, decrease or stay the same.

5. Suppose that the dislocation is impeded by pinning points (precipitates, for example), that are uniformly spaced and separated by 1 μm (10^{-6} m). The resolved shear stress is determined by the stress required to move the dislocation around these pinning points. Use the information given in this problem to determine the energy per length of the dislocation. Compare this to the expressions given for the energies of edge and screw dislocations to see if it makes sense.

Dislocation Structure

11)   A right handed screw dislocation initially located in the middle of the front face of the sample shown below moves toward the back of the sample in response to an applied shear stress on the sample.
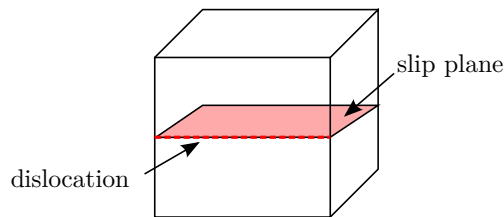
1. Sketch the shape of the sample after the dislocation has propagated halfway through the sample, and again when it has propagated all the way through the sample. Use arrows to specify the shear force that is being applied.

2. Repeat part a for a left-handed screw dislocation.

12)   Draw an edge dislocation and on the same figure dot in the positions of the atoms after the dislocation has shifted by $\vec{b}$.

13)   How can two edge dislocations with opposite Burgers vectors meet to form a row of vacancies? How can they meet to form a row of interstitials? Draw pictures of both situations.

14) Given a crystal containing a dislocation loop as shown in the following figure:

final location of dislocation loop
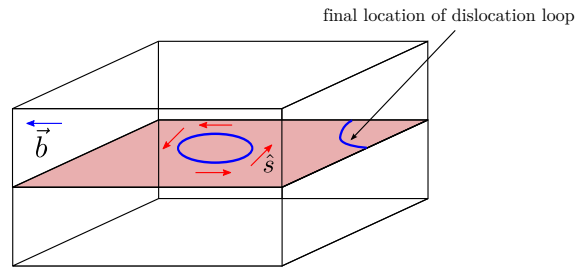
Let the loop be moved (at constant radius) toward a corner until three-fourths of the loop runs out of the crystal. This leaves a loop segment that goes in one face and comes out the orthogonal face. Sketch the resultant shape of the crystal, both above and below the slip plane.

15) Given a loop with a Burger's vector that is perpendicular everywhere to the dislocation line, determine the resulting surface morphology after the loop propagates out of the crystal. Assume that the loop moves only by glide.

16) Show that it is impossible to make a dislocation loop all of whose segments are pure screw dislocations, but that it is possible with edge dislocations. For the case of the pure edge dislocation loop, describe the orientation of the extra half plane with respect to the dislocation loop.

17) Draw the compressive and tensile regions surrounding an edge dislocation.

18) Consider the dislocation loop shown below:
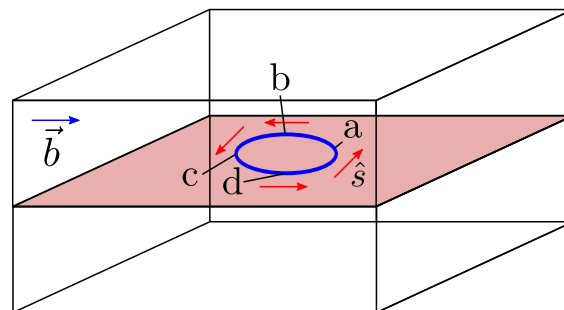
1. Circle the drawing below that corresponds to the shape of the material after the dislocation has expanded and moved out outside the crystal.
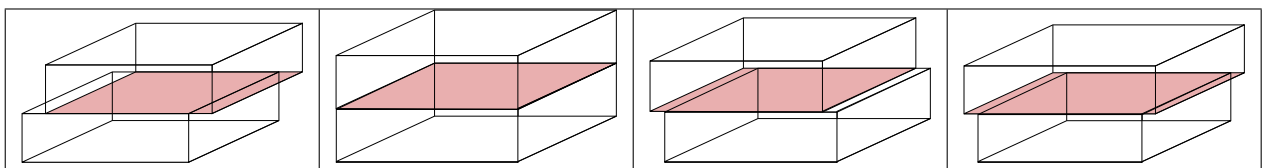
2. Indicate in the spaces below the locations (a, b, c, or d) where the dislocation has the following characteristics:

   (a) It is a right handed screw dislocation:_____

   (b) It is a left handed screw dislocation:_____

(c) It is an edge dislocation with the extra half plane above the plane of the loop:_____

(d) It is an edge dislocation with the extra half plane below the plane of the loop:_____

3. Add arrows to the illustration of the dislocation loop to show the orientation of the shear stress that will most efficiently cause the dislocation to loop to grow.

Dislocation Interactions

19)   If edge dislocations with opposite signs of the Burger's vectors meet, does the energy of the crystal increase or decrease? Defend your answer.

20)   A nanowire is grown such that it is free of dislocations. Why would the stress required to deform the nanowire be larger than a bulk material?

21)   If an anisotropic alloy system has a nearly zero dislocation line tension, would you expect the precipitate spacing to have a large effect on the yield stress of the alloy? Explain your reasoning

22)   Given an edge dislocation in a crystal, whose top two-thirds is under a compressive stress σ acting along the glide plane (see figure below):
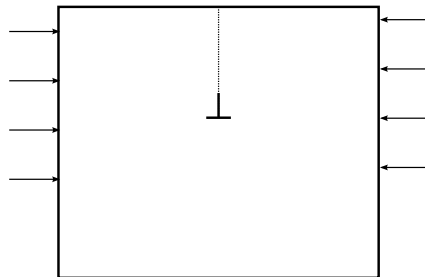
1. If diffusion occurs, which way will thee dislocation move? Explain why and tell where the atoms go that leave the dislocation.

2. Derive an equation relating the stress, σ to b and the force tending to make the dislocation move in the vertical plane.

3. If the edge dislocation is replaced by a screw dislocation, which which way will the dislocation tend to move?

23)   Construct a plot of the interaction energy vs. dislocation separation distance for two identical parallel edge dislocations that continue to lie one above the other as climb occurs. Justify your plot qualitatively by explaining how the strain energy changes with vertical separation.

24)   Repeat the previous problem for edge dislocations of opposite sign.

25) On the following sketch of a dislocation, indicate the direction that it must move in order for vacancies to be created.
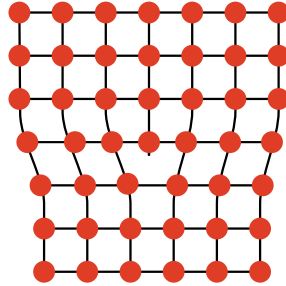
26) Consider an isolated right-handed screw dislocation. Suppose a shear force is applied parallel to the dislocation line, as illustrated below.

Stress into plane of paper on this surface

screw dislocation

Stress out of plane of paper on this surface

Front View

screw dislocation

direction of shear force

Stress out of plane of paper on this surface

Top View
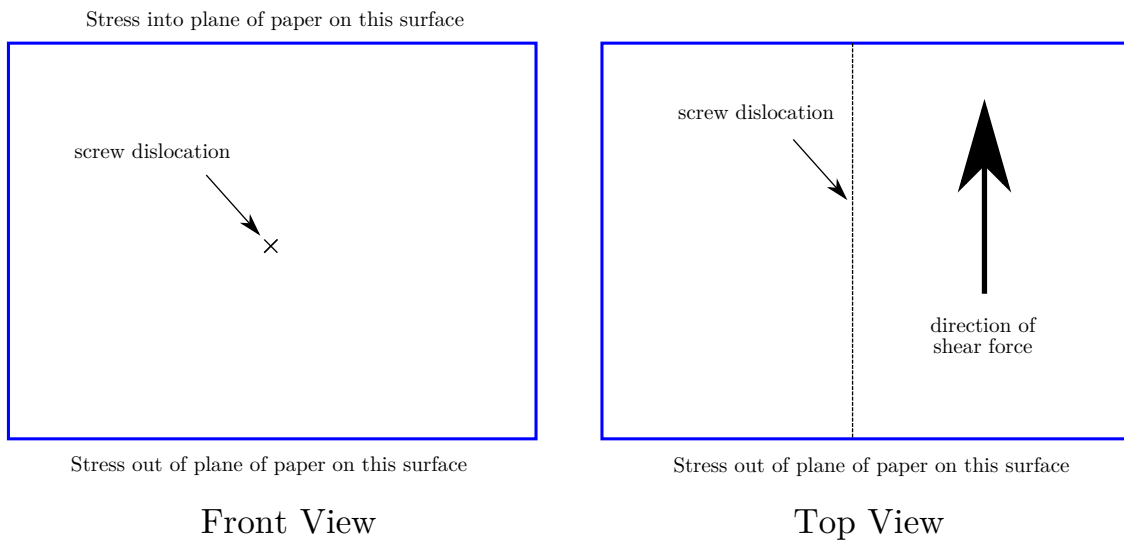
1. What is the direction of the force, F_s^{τ}, that is applied to the dislocation as a result of the applied stress.

2. Suppose the screw dislocation is replaced by a dislocation loop with the same Burgers vector as the dislocation from part a, as shown below. Use arrows to indicate the direction F_s^{τ} at different points along the dislocation loop. (The direction of F_s^{τ} has already been indicated at the right edge of the dislocation).

Stress into plane of paper on this surface

dislocation loop

Stress out of plane of paper on this surface

Front View

dislocation loop

F_s^{τ}

direction of shear force

Top View
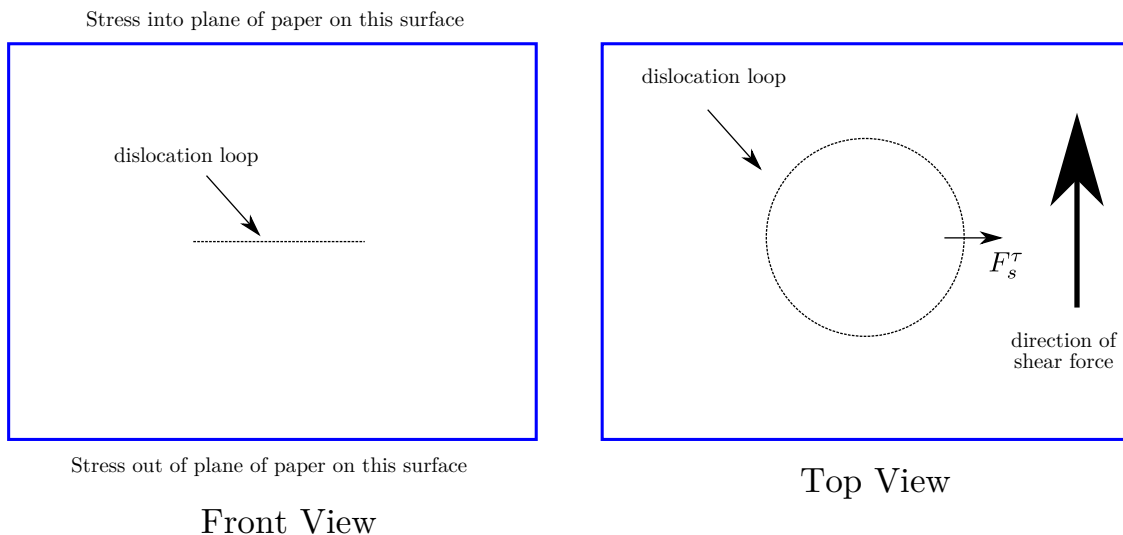
3. Describe how the magnitude of F_s^τ changes (if at all) for different locations along the dislocation loop.

4. What to you expect to happen to the dislocation loop if you remove the external applied stress (will the loop grow, shrink or stay the same size)?

5. Suppose the straight screw dislocation from is pinned by obstacles that are separated by a distance d, as illustrated in the following figure. Sketch the shape of the dislocation for an applied shear stress that is just large enough for dislocation to pass around the obstacles.

Stress into plane of paper on this surface   screw dislocation

direction of shear force

screw dislocation

Stress out of plane of paper on this surface   Stress out of plane of paper on this surface

Front View   Top View
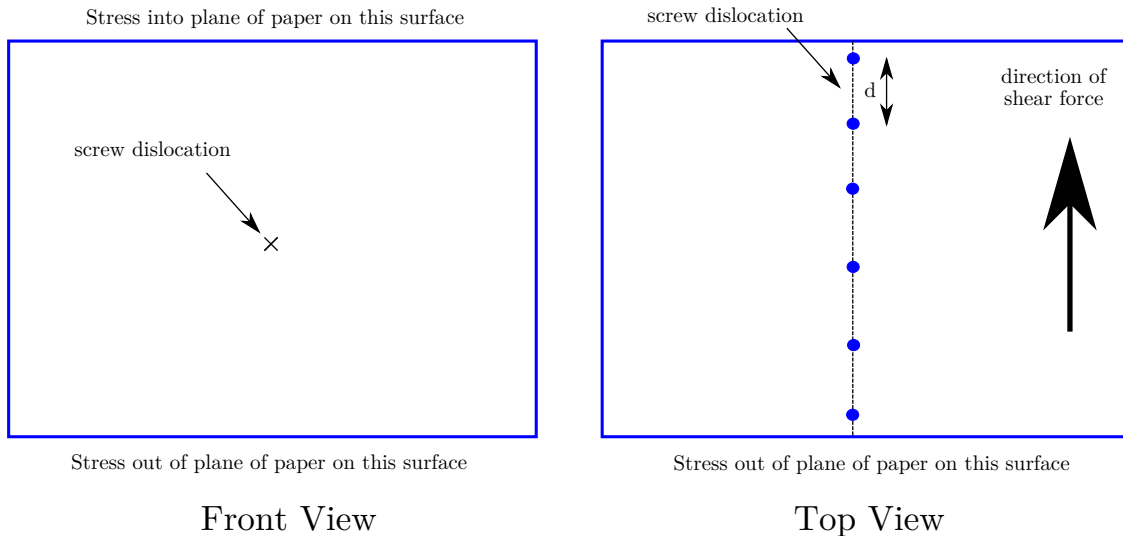
6. What do you expect to happen to the critical resolved shear stress of the material if d is decreased by a factor of 2. (Will the critical resolved shear stress increase, decrease or stay the same).

Interfacial Thermodynamics

27)   Consider the following:

1. Is the molar latent heat positive or negative?

2. Is the melting temperature , T , for a very small particle greater to or less than the equilibrium value of T_m for a bulk material?

3. Must this always be the case?

4. For metals, what is the typical value of r for which a change in melting temperature of 10K is observed. What about a change of 1K?

28)   The molar enthalpy of a phase varies with temperature as

$$H_m\left(T\right) - H_m\left(T_0\right) + \int_{T_0}^{T} C_p\left(T\right) dT$$

where C_p is the molar heat capacity. Given this, at what temperature is the latent heat appearing in expression for the melting point reduction evaluated?

29) Consider the case of a pure liquid spherical droplet embedded in a pure solid. Create a graphical construction plotting the temperature dependence of the free energy of the solid and liquid phases for this case, and use it to determine if the melting point above or below the bulk melting temperature.

30) Consider the Co-Cu phase diagram shown below:
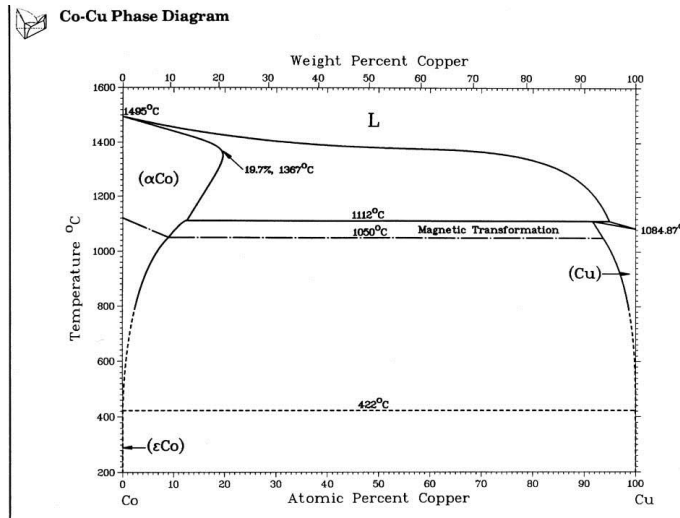
1. Plot the equilibrium activity of Cobalt as a function of composition across the entire phase diagram at 900°C.

2. From the phase diagram, estimate the solubility limit of Co in Cu at 900 °C. Suppose the interfacial free energy for the Cu/Co interface is $300\,\text{mJ/m}^2$. For what radius of a Co precipitate will this solubility limit be increased by 10%?

Surface and Interface Structure

31) Look up values for heats of sublimation for any of the materials in Table 6.1 that have close-packed crystal structures (FCC or HCP). Compare the estimated values of the surface free energy that you obtain from these heats of sublimation to the tabulated values in Table 6.1.

32) Determine the equilibrium shape of a crystal. This should be done using a computer and your favorite program or language (most likely MATLAB). The equation of a straight line in polar coordinates drawn from the origin of the polar coordinate system is $r\cos(\theta - \alpha) = d$, where (r, θ) locate the points on the line, d is the perpendicular distance from the origin to the line and α is the angle between the perpendicular to the line and the x-axis (see Figure 4.3).

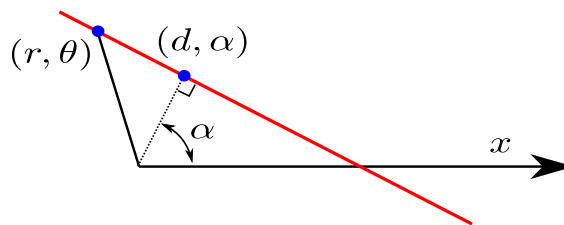**Figure 4.3:** Representation of a line drawn a distance d from the origin.

1. Determine the equilibrium shape of a crystal where the surface energy is given by $\gamma = 1\,\text{J/m}^2$ (independent of α).

2. Determine the equilibrium shape of a crystal where the surface energy is given by $\gamma = 1 + 0.05\cos(4\alpha)\,\text{J/m}^2$ (α in radians). Are there any corners on the equilibrium shape?

3. Determine the equilibrium shape of a crystal where the surface energy is given by $\gamma = 1 + 0.07 \cos(4\alpha)$ J/m^2. Are there any corners on the equilibrium shape?

4. Determine the equilibrium shape of a crystal where the surface energy is given by $\gamma = 1 + 0.6 \cos(4\alpha)$ J/m^2. Are there any corners on the equilibrium shape? How is the shape shown in (c) different from that in (d), and why (argue on the basis of the physics of the problem)?

As a headstart on this problem, here's a MATLAB script that generates polar plots of the γ as defined in the problem:

```
1  close all
2  A=[0,0.05,0.07,0.6];   % these are the 4 values of A defined in the problem
3  % define a function where the radius d is the surface energy and alpha
4  % is the angle
5  d=@(A,alpha) 1+A*cos(4*alpha);
6  figure
7  for k=1:4
8      alpha=linspace(0,2*pi,200);
9      subplot(2,2,k)  % this makes a 2 by 2 grid of plots
10     polar(alpha,d(A(k),alpha),'r-');  % poloar is the command to make a polar plot
11     title(['A=' num2str(A(k))],'fontsize',20)  % label each subplot
12 end
13 % adjust the print command as necessary to change the format, filename,
14 % etc.
15 print(gcf,'../figures/matlabwulffenergy.eps', '-depsc2') % save the eps file
```

This generates the following polar plots for the four different functions that are given (with A defined so that $\gamma = 1 + A \cos(4\alpha)$).
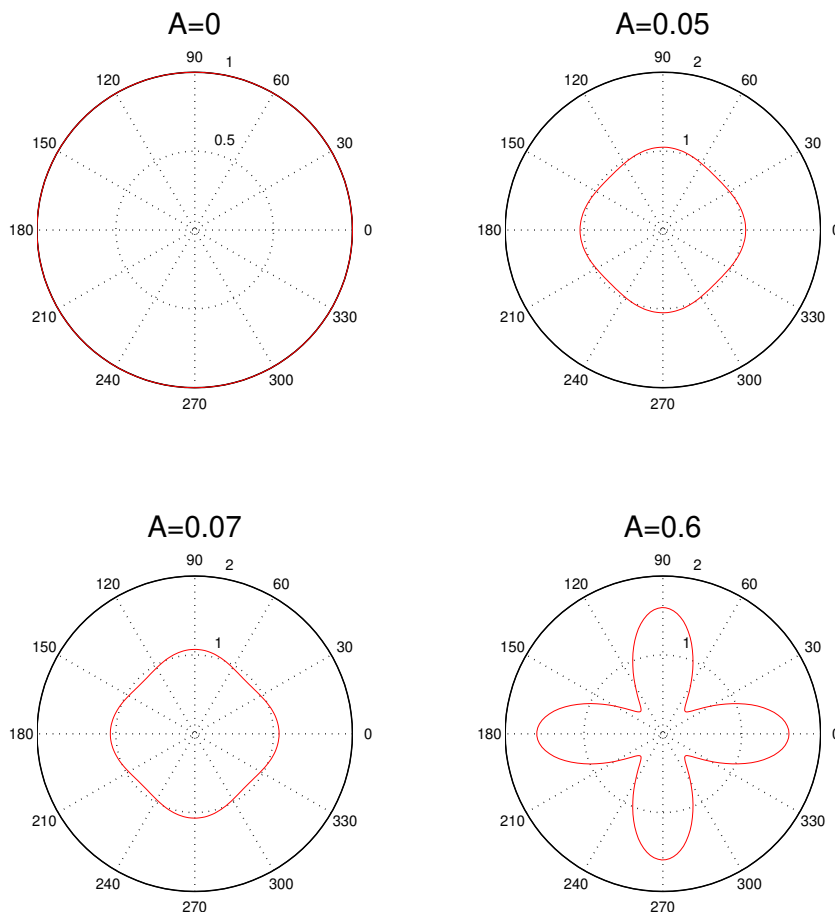
33) Assume a simple cubic crystal structure with nearest neighbor interactions. Calculate the ratio of the surface energies for the {110} and {100} surfaces.

34) The octahedral particles of FCC golds shown below were created by controlling the growth rates of the different crystal facets. For these crystals, were the growth rates fastest in the $\langle 100 \rangle$ directions or in the $\langle 111 \rangle$ directions? Provide a brief explanation of your answer.

35) The relationship between the the interfacial energy between α and β phases and the pressure difference across a curved interface is obtained from the following expression:
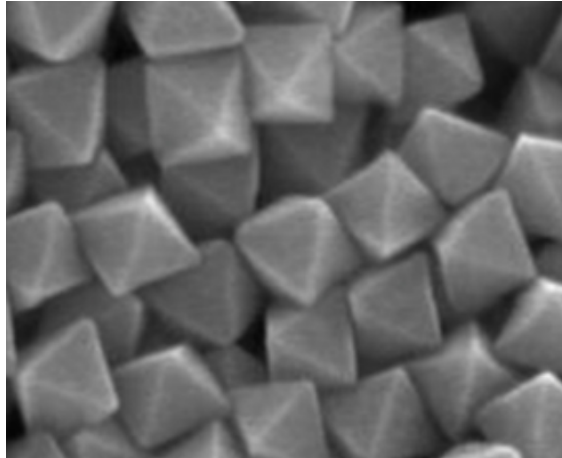
$$-P^\alpha \delta V^\alpha - P^\beta \delta V^\beta + \gamma_{\alpha\beta} \delta A^\Sigma = 0$$

1. Use this expression to obtain the pressure difference between a cylinder of β phase with a radius r and a surrounding α phase.

2. Repeat the calculation for a cube where the length of each side is a. Assume that the surface energy of each of the cube faces is the same.

Wetting and Contact Angles

36) Consider the an oil droplet that forms on the surface of water, as shown schematically in the following Figure:
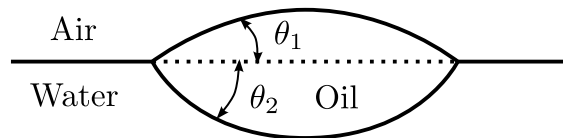
Determine θ_1 and θ_2 if the air/water interfacial free energy is 72 mJ/m^2, the air/oil interfacial free energy is 30 mJ/m^2 and the oil/water interfacial free energy is 50 mJ/m^2.

37) Suppose a, hemispherical liquid Au droplet with a radius of curvature of r is in contact with solid Si cylinder with the same radius as shown below. Derive a relationship between the three interfacial energies that must be valid in order for the equilibrium shape of the Au/Si interface to be flat, as drawn in the picture.
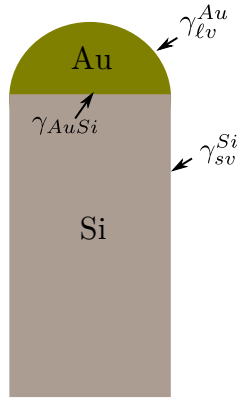
Grain Boundaries

38) The surface energy of the interface between nickel and its vapor is 1.580 J/m ^{2} at 1100K. The average dihedral angle measured for grain boundaries intersecting the free surface is 168 $°$. Thoria dispersed nickel alloys are made by dispersing fine particles of ThO $_2$ in nickel powder and consolidating the aggregate. The particles are left at the grain boundaries in the nickel matrix. Prolonged heating at elevated temperatures gives the particles their equilibrium shape. The average dihedral angle measured inside the particle is 145 $°$. Estimate the interfacial energy of the thoria-nickel interface. Assume the interfacial energies are isotropic.

39) Consider a gold line deposited on a silicon substrate. The grain boundaries run laterally completely across the line, giving a "bamboo" structure as shown in the figure below. The grain boundary energy of gold at 600K is 0.42 J/m ^{2} and the surface energy is 1.44 J/m ^{2}. Assume all the interfacial energies are isotropic.

1. Compute the dihedral angle (θ in the diagram above) where a grain boundary meets the external surface.

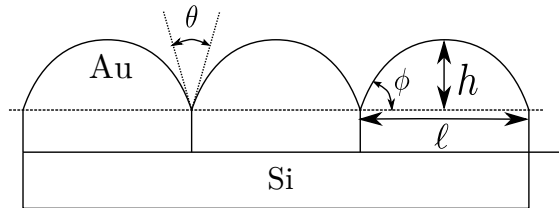2. Find the critical grain boundary spacing ℓ_c for which the equilibrium grain shape produces a hole in the film, assuming $h = 1\,\mu$m. Note that for a spherical cap, ℓ, h and ϕ are related to each other by the following expression: $\tan(\phi/2) = 2h/\ell$.

40) Why does the velocity of a grain boundary depend on temperature? Assume that the driving force for grain boundary motion is independent of temperature.

41) Consider the following junction between three grains. Suppose that the grain boundary free energy between grains 1 and 2, and between 1 and 3, is 0.5 J/m ^{2}. What is the grain boundary energy between grains 2 and 3?
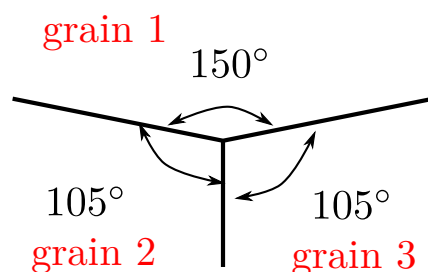
42)   Consider the following image from the grain growth simulation:
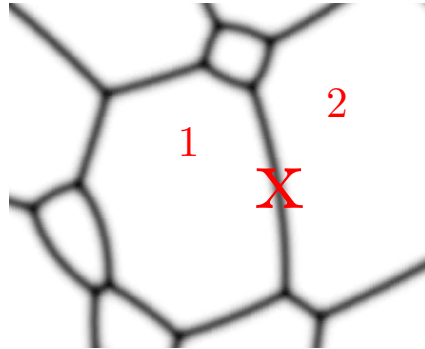
1. The boundary marked with an 'X' separates grains 1 and 2. Do you expect this boundary to move toward grain 1 or grain 2 during the process of grain growth?

2. Suppose that the interface marked above is the cross section through a grain boundary in aluminum, and that this section of the grain boundary has a spherical shape with a radius of curvature of 1 μm. Assuming a grain boundary energy of 0.25 J/m^2, calculate the chemical potential difference, $\Delta\mu$ between Al atoms on the '1' and '2' sides of the grain boundary.

3. On the schematic below, indicate which grain is grain 1 and which one is grain 2.
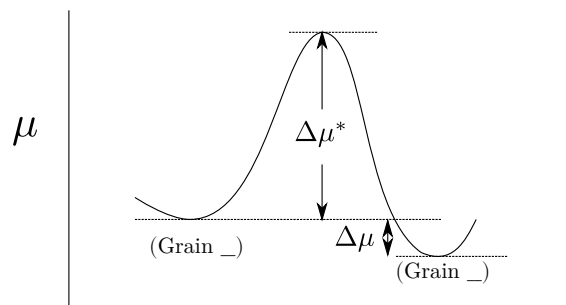
4. Suppose $J_{1\rightarrow 2}$ is the rate at which Al atoms hop from grain 1 to grain 2, and $J_{2\rightarrow 1}$ is the rate at which atoms hop from grain 2 to grain 1. Calculate the ratio, $J_{1\rightarrow 2}/J_{2\rightarrow 1}$ at $T = 500$K.

Transformation Kinetics

43)   Does the time to 50% transformed increase or decrease with an increase in nucleation rate? Defend your answer without using any equations.

Interphase Interfaces

44)   Consider a material with the orientational dependence of the surface energy shown in each of the 3 plots below. For each of these three materials, sketch the equilibrium shape that you would expect to obtain. On each drawing, indicate any interfaces that you expect to be coherent.
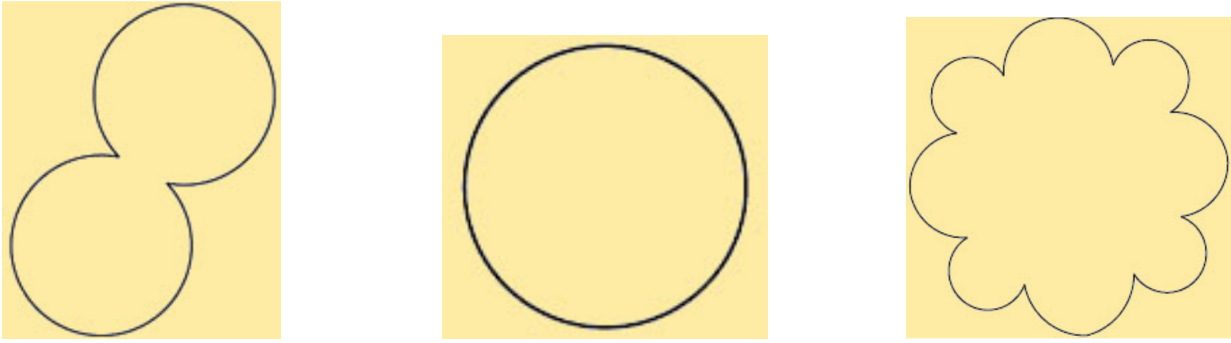
45)   Consider the shapes of the particles in the simulations below of misfitting particles in an elastically anisotropic system. The left column is the entire system, whereas the right column is a magnification of a small region of the figure in the left column. These are snapshots taken as function of time while the particles are growing. Are these cuboidal shapes due to elastic stress, an anisotropic interfacial energy, or both?
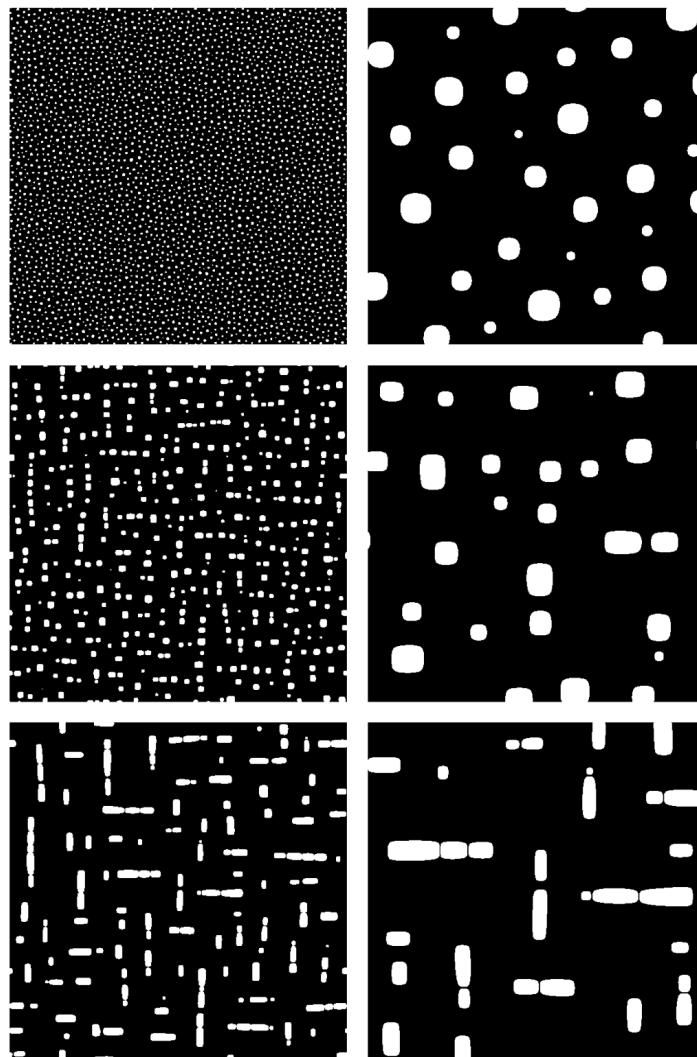
46)   Explain the structure and energies of coherent, semicoherent and incoherent interfaces, paying particular attention to the role of orientation relationships and misfit.

47)   Explain why fully coherent precipitates tend to lose coherency as they grow.

48)   Why do very small precipitates tend to have coherent interfaces?

49)   A thin film of Zn with an HCP crystal structure is deposited on a Ni FCC substrate with a {111} orientation. Which plane of the HCP crystal would you expect to contact the {111} Ni surface?

50)   Given an example of an interface between two crystals that that displays a very large change in free energy with a change in the orientation of the interface.

51)   Consider an FCC metal (metal A) with a surface energy of 1 J/m^2. An HCP metal (metal B) with a surface energy of 0.7 J/m^2 is deposited onto the {111} surface of metal A. Assume that the atomic diameter of the HCP metal is 3% larger than the atomic diameter of the FCC metal, and that the chemical component of the interfacial energy between the two metals is 0.2 J/m^2.

1. For B layers that are sufficiently thin, do you expect that a coherent interface will form between the A and B materials? Justify your answer.

2. How do you expect the interface between the A and B metals to change as the thickness of the B layer increases?

3. Do you expect thick films to remain continuous, or will isolated drops of B be formed on the surface. Describe any assumptions that you make.

52)   Consider the vacancy shown below, for a simulation of 'red' and 'blue' atoms that are undergoing phase separation. Is the vacancy more likely to move to the right or to the left? Justify your answer.
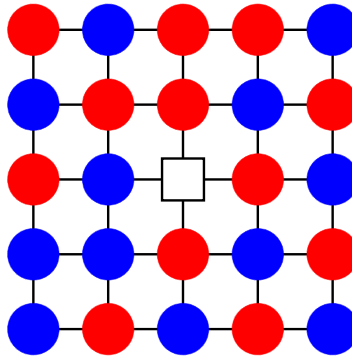
53)   Consider the tilt boundary shown in the image to the left. On the axes on the right, sketch the relationship between the grain boundary free energy and the tilt angle that you expect to observe for values of theta between 0 and 10 °.
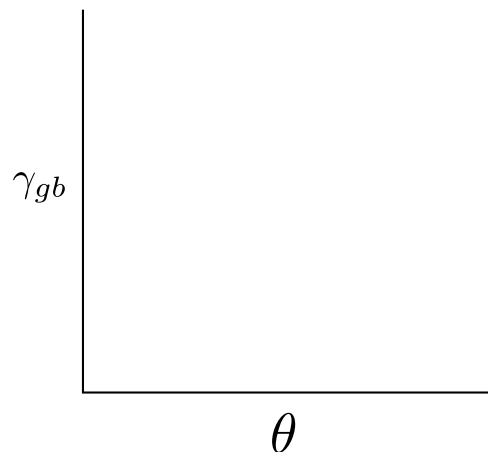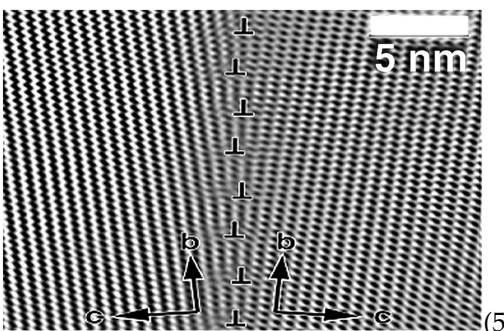
54)   Suppose you need to apply a coating to a surface, and you want the coating to spread as a smooth uniform film for all thicknesses. You have a choice of three different coatings, which have the thickness-dependent free energies shown below. Which material to you choose, and why?
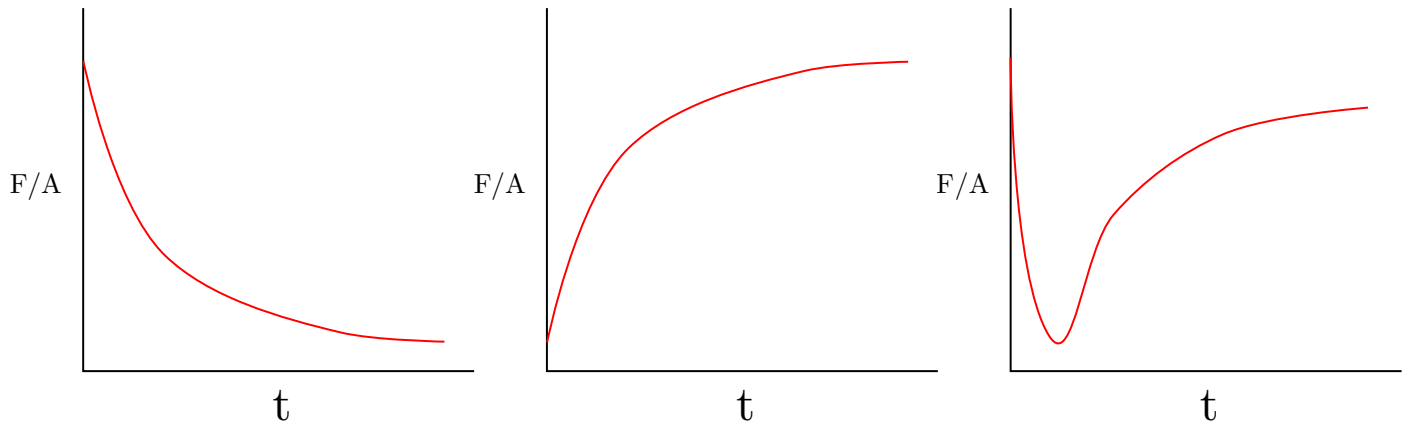
5 316-2 Problems

5.1 General

(1) Write a paragraph discussing the relevance of phase transformations in your daily life.

5.2 Laplace Pressure Derivation

(2) Derive the expression for the Laplace pressure inside a long cylinder of radius R.

5.3 Homogeneous Nucleation

(3) Consider the following data for nickel:

Melting point	1452 °C
Molar entropy of solid at T_m	56.07 J/K
Molar entropy of liquid at T_m	66.27 J/K
Solid density	8.9 g/cm^3
Molar mass	58.7

In their classic experiment Turnbull and Cech studied the undercooling of small droplets for a number of different metals . Assuming that nucleation in the droplets occurs homogeneously and using the data given below calculate the following at 1100 °C and 1200 °C:

a The molar volume of nickel.

b The work of nucleation (W_R^*).

c The dimensionless ratio, $W_R^*/k_B T$.

d The radius of the critical nucleus.

e The pressure of the critical nucleus in pascals (assume the surrounding liquid is at atmospheric pressure).

f The molar enthalpy of melting at T_m.

g Suppose a Ni droplet with a volume of about 100 μm^3 is solidified. Approximate the temperature to which the droplet must be cooled in order for solidification to occur by homogeneous nucleation.

(4) Import the file labeled ElementData.mat that includes the required data for various elements on the periodic table into Matlab and:

a Derive the expressions for ΔP, R^*, W_R^*, and $W_R^*/k_B T$ in terms of T_m, ΔT, V_m, ΔS_f, and γ.

b Plot V_m, ΔS_f, γ, ΔP, R^*, W_R^*, and $W_R^*/k_B T$ using $\Delta T = 100K$ versus atomic number (Z) and label all axes including units and each data point with the chemical symbol corresponding to the element. Hint: You should only consider those elements for which the values of γ are included in the ElementData.mat file. For both W_R^* and $W_R^*/k_B T$ plot the y axis on a log scale. Also, in order to label the data points with the chemical symbol you will need to use the text(x, y, 'string') function. You may want to use subplots.

The ElementData.mat file has the following format:

```
1   ElementData =
2   Name: {118x1 cell}
3   Symbol: {118x1 cell}
4   DeltaH0f: [118x1 double]
5   Tm: [118x1 double]
6   Z: [118x1 double]
7   Aw: [118x1 double]
8   rho: [118x1 double]
9   gamma: [118x1 double]
10  Vm: [118x1 double]
11  DeltaS0f: [118x1 double]
12  Structure: {118x1 cell}
13  Units: {1x8 cell}
```

c Discuss the plots from part (b) with respect to trends in the periodic table, which variables are really important, outliers, and rules of thumb i.e. typical range of values or average value. Does homogeneous nucleation ever really happen?

d Now replot the data for both $\Delta T = 352K$ and $\Delta T = 252K$ and compare the R^* and W_R^* values obtained for Ni to those you calculated in question (3).

(5) Derive expressions for R^* and W_R^* for a cuboidal nucleus.

(6) In the derivations for nucleation in this course we assume that the nucleus is incompressible. Show that this is a valid assumption for solidification of Ni with $\gamma = 2.38 J/m^2$ and $R^* = 1nm$. Hint: Assume that the material is linearly elastic and isotropic. Therefore, you can calculate the bulk modulus using a simple relationship which is a function of Young's modulus and Poisson's ratio. Please cite your source for the values of E and ν that you use.

5.4   Surface and Interface Effects

(7) The surface free energy of solid gold at its melting point (1063°C) is $1.400 J/m^2$. The surface energy of liquid gold at this temperature is $1.128 J/m^2$, and the interfacial energy for the gold solid/liquid interface is = $0.132 J/m^2$. The latent heat of fusion for gold is $1.2x10^9 J/m^3$.

a What is the contact angle for liquid gold on a solid gold surface at 1063°C ?

b Is there thermodynamic barrier for the melting of a gold surface?

c Suppose a thin liquid gold layer of thickness δ exists at the surface of gold at 1058 °C (5 ° below the equilibrium melting point). By comparing to the free energy of a gold surface that does not have this liquid layer, estimate the maximum thickness of the liquid layer that will be thermodynamically stable at this temperature.

d Very small gold particles have melting points that differ from the melting point of bulk gold. From the analysis given above, do you expect the melting point of a particle with a diameter of 2 nm to be higher or lower than the melting point of bulk gold? Give a brief explanation for your answer.

(8) Suppose precipitates form at grain boundaries within the matrix phase, with geometries that look like the following:

Precipitate

Grain boundary

140°
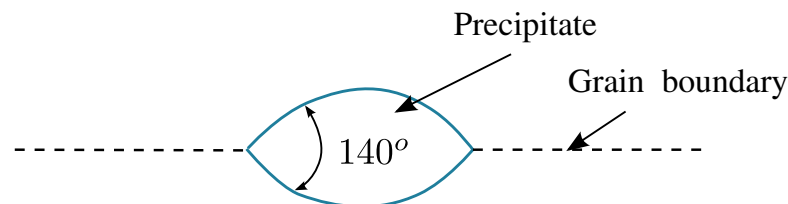
What is the ratio of the grain boundary free energy to the interfacial energy between the precipitate and the matrix phase?

(9) Water beads up on a freshly waxed car to form droplets with a contract angle of 80°. What is the interfacial free energy for the wax/water interface, if the surface energy of the wax is $0.025 J/m^2$? (Note: you'll need to look up the surface energy of water to do this problem).

(10) An oil droplet (δ phase) is placed on the water surface (phase β) in contact with air (phase α). The schematic of the cross section of the droplet is as describe in class (and repeated below). The surface free energy of water (against air) is $0.072 J/m^2$. If the measured values of θ_1 and θ_2 in the figure below are 37° and 23°, respectively, what are the values of the oil surface energy and the oil/water interfacial energy.
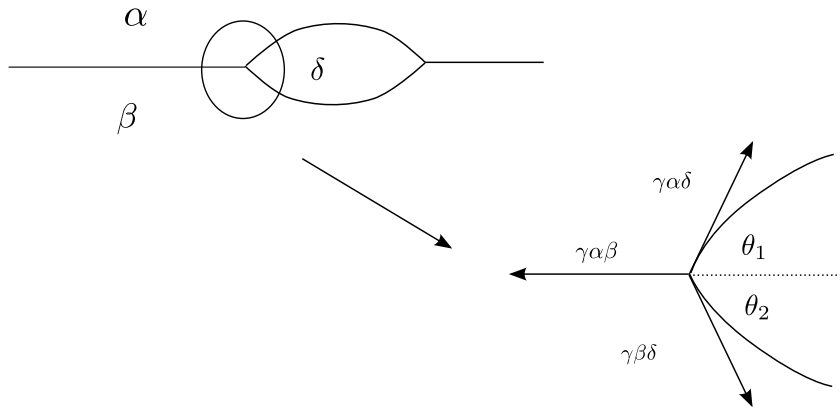
5.5 Heterogeneous Nucleation

(11) Derive the structure factor, $S(\theta)$.

(12) Suppose that nucleation of a solid, single component metal occurs heterogeneously at a wall. Based on the values given for Ni in problem (3), what contact angle for the critical nucleus must be obtained in order to increase the minimum temperature required for solidification by 50°C?

5.6 Nucleation in a Binary System

(13) 3. Consider the formation of a nucleus β^* with composition $X^{\beta*}$ from metastable α with composition X_0^α. At temperature T, the composition of stable α is X_{eq}^α, that of stable β is X_{eq}^β (all X refer to X_1). In class we derived an expression for the molar Gibbs free energy of formation for the nucleus:

$$\Delta G_m^{\alpha \to \beta*} = G_m^\beta(X^{\beta*}) - G_m^\alpha(X_0^\alpha) - \left.\frac{\partial G^\alpha}{\partial X}\right|_{X_0^\alpha} (X^{\beta*} - X_0^\alpha) \tag{5.1}$$

Show that for $X_0^\alpha - X_{eq}^\alpha \to 0$ and $X^{\beta*} - X_{eq}^\beta \to 0$, Eq. (1) can be rewritten in the following form:

$$\Delta G_m^{\alpha \to \beta*} = -\left.\frac{\delta^2 G^\alpha}{\delta X^2}\right|_{X_0^\alpha} (X_0^\alpha - X_{eq}^\alpha)(X_{eq}^\beta - X_{eq}^\alpha)$$

Hint: Express $G_m^\beta(X^{\beta*})$ in terms of G_m^α. Approximate all terms at non-equilibrium compositions as Taylor expansions around suitable equilibrium values.

(14) In class we used the definition of the misfit parameter for a β nucleus in an α matrix as

$$\varepsilon = \frac{1}{3}\left(\frac{V_m^\beta - V_m^\alpha}{V_m^\alpha}\right)$$

i.e. one third of the volume strain. Show that for cubic systems, the misfit parameter can be approximated as

$$\varepsilon_{cubic} = \frac{a^\beta - a^\alpha}{a^\alpha}$$

where a is the lattice parameter. Hint: Write ΔV in terms of ε_{cubic} and look at the behavior as $\varepsilon_{cubic} \to 0$.

(15) A coherent precipitate nucleates much more easily than does an incoherent particle of the same precipitate. To illustrate this:

a What is the ratio of W_R^* for the two types of precipitate if $\gamma_{coherent} = 30\,\text{ergs/cm}^2$ and $\gamma_{incoherent} = 300\,\text{ergs/cm}^2$? Assume that the precipitate is unstrained.

b If the chemical driving force (ΔG_v) is given by $-50\Delta T/T_e\,\text{cal/cm}^3$, $T_e = 1000\,\text{K}$, the misfit strain is 0.001 for the coherent precipitate and zero for the incoherent precipitate, at what ΔT are the W_R^*'s for the two equal? Assume a shear modulus of the matrix of $5.46x10^{10}\,\text{Pa}$ and bulk modulus of the precipitate of $15x10^{10}\,\text{Pa}$.

c Repeat the previous calculation using a misfit strains of 0.01 and 0.1.

d If the number of nuclei formed per cubic centimeter per second is given by $N = 10^{27}\exp(-W_R^*/kT)$, what is the rate of coherent nucleation at $\Delta T = 25K$ and $250K$ with a misfit of 0.01? What is it for incoherent nucleation at these same values of ΔT?

(16) Consider the following Al-Cu phase diagram:

Al-Cu
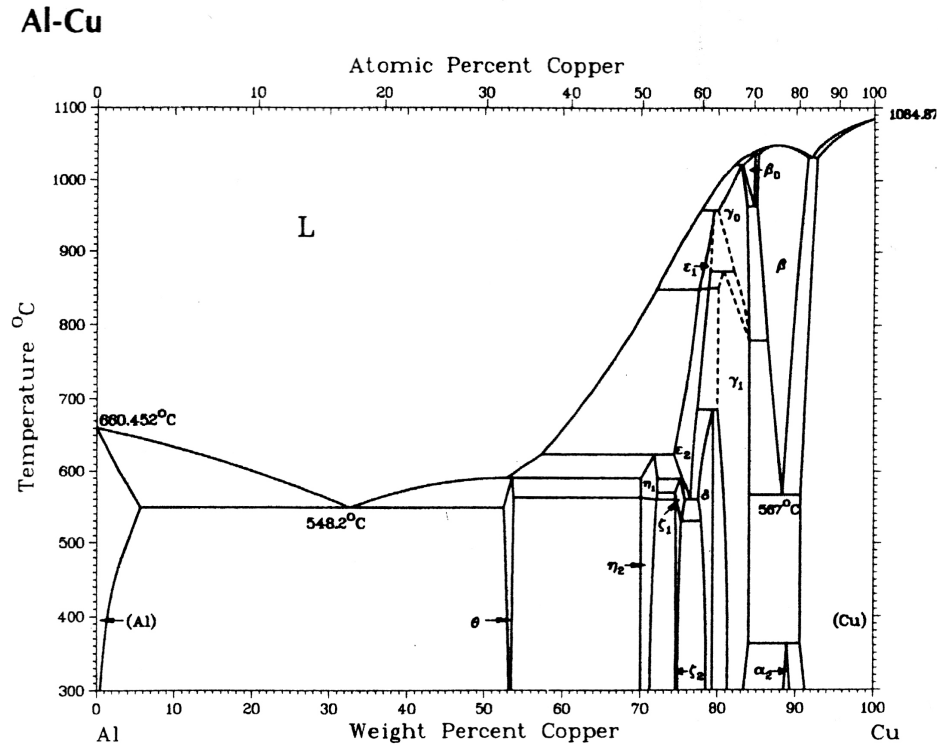
Suppose that a dispersion of roughly spherical θ precipitates is formed at 300 °C. Estimate the precipitate radius for which Cu solubility in the α phase (the Al-rich phase) will be increased by 25% in comparison to a flat α/θ interface. Assume an interfacial free energy for the α/θ interface of 0.3 J/m^2 and a molar volume for the α and β phases of 7 cm^3.

(17) Consider the Co-Cu phase diagram shown below:
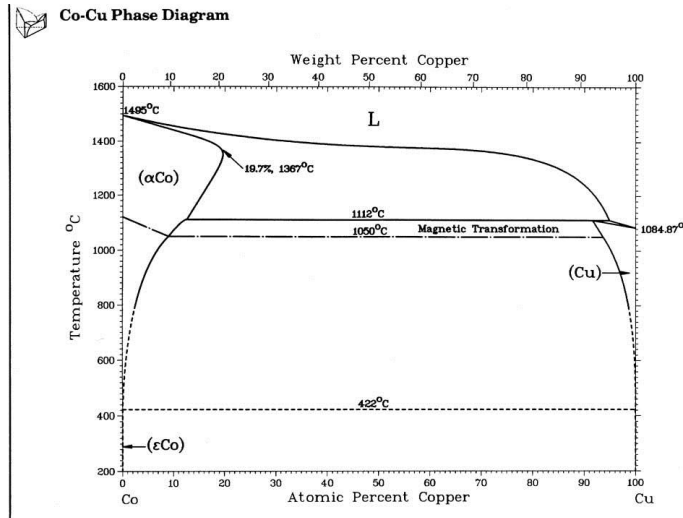
Co-Cu Phase Diagram

a Plot the equilibrium activity of Cobalt as a function of composition across the entire phase diagram at 900°C.

b Suppose the interfacial free energy for the Cu/Co interface is $300\,\text{mJ}/\text{m}^2$. Develop an expression for r^*, the critical radius for a cobalt precipitate, as function of the atomic % cobalt in the alloy.

c Calculate W_r^* for a Copper rich alloy at 900°C with a cobalt composition that exceeds the equilibrium composition by a factor of 1.15.

5.7 Spinodal Decomposition

(18) A and B form a regular solution with a positive heat of mixing so that the A-B phase diagram contains a miscibility gap.

a Starting from $G = X_A G_A + X_B G_B + \Omega X_A X_B + RT\left(X_A ln X_A + X_B ln X_B\right)$, derive an equation for $d^2 G/dX_B^2$, assuming $G_A = G_B = 0$.

b Use the above equation to calculate the temperature at the top of the miscibility gap T_c in terms of Ω.

c Using MATLAB plot the miscibility gap for this system.

d On the same diagram plot the chemical spinodal.

(19) For a homogeneous alloy of composition X_0 decomposes into two parts, one with composition $X_0 + \Delta X$ and the other with composition $X_0 - \Delta X$, show that the total chemical free energy will change by an amount ΔG_c given by

$$\Delta G_c = \frac{1}{2}\frac{d^2 G}{dX^2}(\Delta X)^2$$

Hint: Express $G(X_0 + \Delta X)$ and $G(X_0 - \Delta X)$ as Taylor series.

(20) Describe the effect of each of the following, and briefly explain your answer.

a The effect of coherent strains on the characteristic wavelength of the two-phase structure formed by spinodal decomposition.

b The effect of a reduction of the surface free energy on the nucleation rate.

c The effect of a decrease in the contact angle of a precipitate on its heterogeneous nucleation rate.

d Can a diffusion coefficient ever be negative? If so, when is this the case?

5.8 Constitutional Undercooling and the 'Mushy Zone'

(21) In our classroom discussion of interface stability, we considered the case where impurities decrease the melting point. Suppose that the impurities increase the melting point, so that the phase diagram looks like this:

66
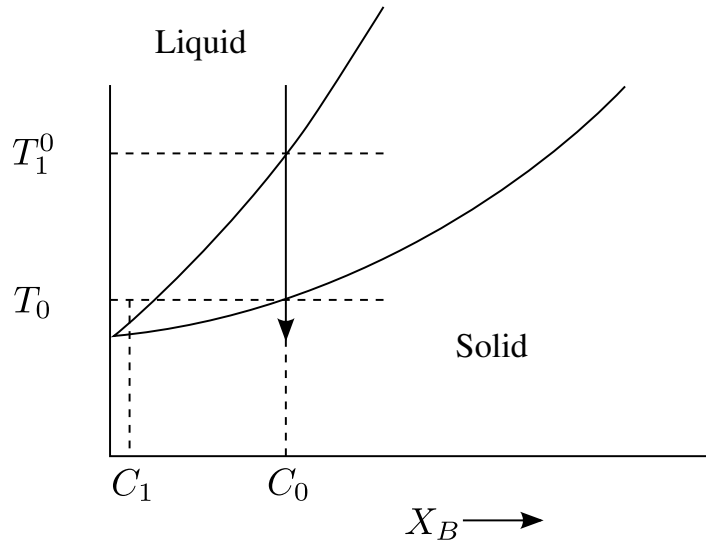
Suppose sample with the composition indicated by the arrow is solidified, so that the front moves forward with a certain velocity.

    a Sketch the behavior of the impurity concentration in the liquid phase just ahead of the solidification front. Reference any specific compositions to the corresponding compositions on the phase diagram.

    b On a separate figure, sketch the liquidus temperature in the liquid phase just ahead of the solidification front. Reference any specific temperatures to the corresponding temperatures on the phase diagram.

    c Comment on the types of temperature profiles that can lead to the formation of a dendritic microstructure for this type of phase diagram. Is the criterion for interface stability qualitatively different from the criterion discussed in class?

(22) Consider the Al/Si phase diagram shown below, along with the following thermodynamic and kinetic data:

Heat of fusion for Al: $10.790 \, \text{kJ/mol}$

Diffusion coefficient for impurities in liquid Al: $\sim 5x10^{-9} \, \text{m}^2/\text{s}$
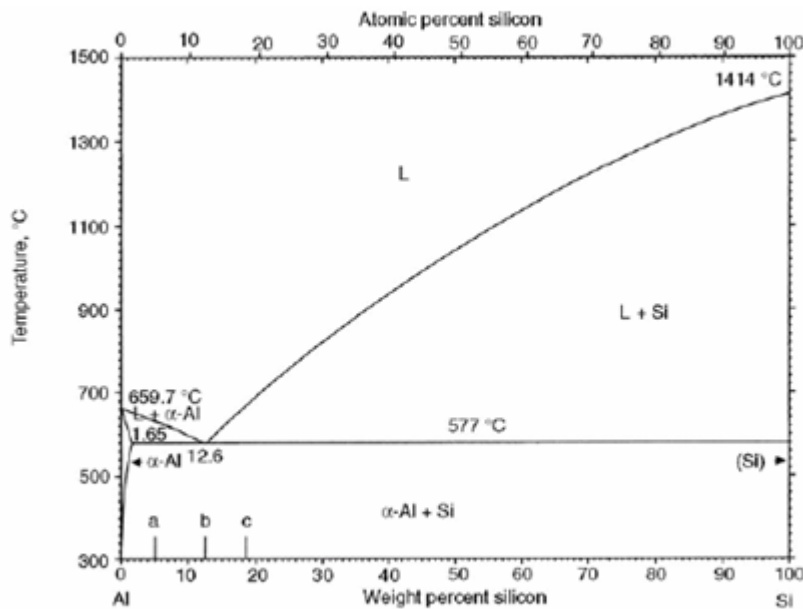
Suppose an alloy with 0.8 wt. % Si is solidified at a rate of $5\mu m/s$. (This is the velocity at which the solid/liquid interface is moving.)

a What is the interface temperature in the steady state?

b What is the thickness of the diffusion layer (*i.e.* the distance into the liquid phase, measured from the solid/liquid interface, over which the liquid composition differs from the average bulk composition far from the interface?

c Estimate the temperature gradient required to eliminate the appearance of a 'mushy zone'.

5.9 Coarsening

(23) The size of Co clusters in Cu vs. aging time at several temperatures was measured using a magnetic technique. At 600 °C the data indicate the following: 10 minute aging, average particle radius = 18 Å, 100 minutes, 35 Å, 1,000 minutes, 70 Å.

a Assuming that the coarsening kinetics are consistent with Lifshitz-Slyozov-Wagner theory that was discussed in class, estimate the size of particles at $t = 0$, the end of the precipitation stage, where the cobalt supersaturation was first in equilibrium with the average size of the cobalt clusters.

b Using the data for the Co/Cu system given in the previous homework, determine the difference in the average mole fraction of Co in the Cu phase at aging times of 100 minutes and 1,000 minutes.

c Use the data given to estimate the diffusion coefficient for Co in Cu at 600 °C.

(24) Assume the following "law" for the kinetics of precipitation:

$$X(t) = 1 - \exp\left[-(t/\tau)^m\right]$$

Consider the following experimental data for the formation of Gunier-Preston zones in Al-2 wt.% Cu at 0°C for $X(t)$ less than 0.25. .

Time in hours	$X(t)$
0.4	0.08
0.7	0.10
1	0.14
2	0.17
4	0.23
6	0.28

a Determine the value of the exponent m in the above equation by plotting this equation in an appropriate fashion. (Hint: you need to rearrange the equation and take logarithms so that m is the slope of the plot).

b Plot the qualitative temperature dependence that you would expect for the time constant, τ. Note that you cannot obtain this from the data provided – you need to make some assumptions about what you expect this to look like) Comment on the factors that cause τ to become very large at high and low temperatures. From Fig. 5.25 in Porter and Easterling, what can you say about the behavior of τ in the high temperature regime (i.e., at what temperature must τ diverge to infinity)?

5.10 Eutectic Solidification

(25) Refer to the Al/Si phase diagram and thermodynamic data below to answer the following questions.

Heat of fusion for Al: 395 J/g

Heat of fusion for Si: 1408 J/g
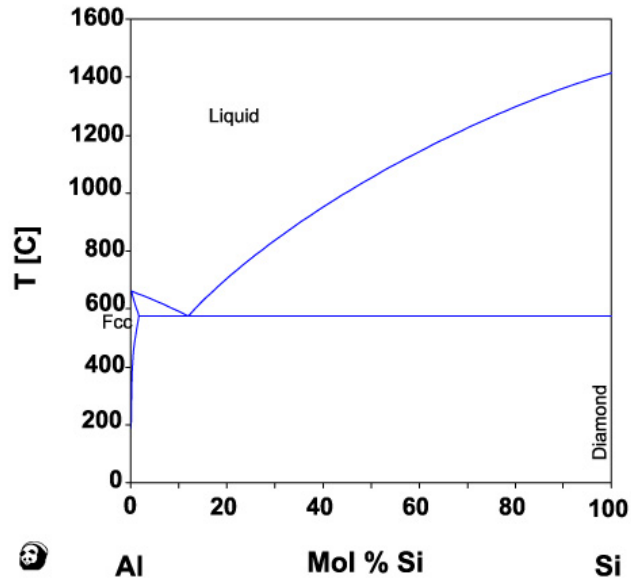
Calculated Al-Si phase diagram assessed by Murray and McAlister

NIMS

a Obtain an estimate for the heat of fusion for the Al/Si eutectic (Joules per cm^3 of eutectic).

b Calculate the bulk free energy gain (ignoring the energy associated with the Al/Si interfaces) associated with the solidification of 1 cm3 of eutectic at 560 °C.

c Calculate the width of the Al and Si phases in a lamellar eutectic for the case where the total free energy change (including the energy associated with the interfaces) on solidification at 560 °C is equal to zero. Assume an interfacial free energy for the Al/Si interface of 350 mJ/m^2.

d Compare the phase widths from part c to the critical radii for the solidification of pure Al and pure Si at an undercooling of 20 °C. Assume that the solid liquid interfacial free energies are similar in magnitude to the Al/Si (solid/solid) interfacial free energy.

e How good is the assumption of ideal liquid mixing in this case? Plot the liquidus lines for the Al-rich and Si-rich phases, using the equation that was developed in class. Compare the location of these lines with the location of the actual eutectic point, and comment on the agreement that you observe.

5.11 Eutectoid Transormations

(26) Imagine the Fe-0.15 wt% C alloy in the figure below is austenitized above A_3, and then quenched to800°C where ferrite nucleates and covers the austenite grain boundaries.

a Draw a composition profile normal to the α/γ interface after partial transformation assuming diffusion-controlled growth.

b Derive an approximate expression for the thickness of the ferrite slabs as a function of time.

(27) The eutectoid temperature for the Fe/C phase diagram is 723 °C. Pearlite formed at 713 °C has a lamellar period (λ) of 1μm.

a Calculate the lamellar period for pearlite that you would expect if the pearlite were formed at a temperature of 623 °C.

b Pearlite forms initially at grain boundaries within the parent austenite phase. Briefly describe why this is so.

c Describe what happens to the microstructure of the steel and to the hardness as increasingly large cooling rates are used. Discuss the role of carbon diffusion, and the role of both equilibrium and non-equilibrium phases.

(28) In the reading about the Wright Flyer Crankcase, the authors assert "In an Al-Cu alloy with significant supersaturation, GP zones develop by spinodal decomposition. The spacing between zones (before coarsening) is determined by the fastest growing wavelength during decomposition. The favored wavelength is inversely related to the second derivative of the free energy versus composition function,which is zero at the spinodal line (located inside but near the GP zone solvus curve) and increases(negatively) with an increase in Cu or a decrease in temperature. Thus, the favored wavelength in the region with a large amount of Cu is smaller than in the regions with small amounts of Cu, and the resulting spacing between zones is smaller."

  d Support their argument using the equations derived in class for spinodal decomposition. A good way to approach this is to postulate a spinodal line and then consider two cases, i.e. $X_o = 2.5$ wt.% Cu and $X_o = 4.5$ wt.% Cu, in detail, based on this spinodal. Be sure to also explain why the authors made the parenthetical statement "(before coarsening)".

  e Is their argument entirely valid or do certain conditions need to be met? If so, what qualifications should be made to make it more accurate?

  f The authors claim that "The growth of [GP] zones is ultimately limited by solute depletion in the matrix. Despite its high solute concentration, the region with a large amount of Cu is depleted of solute by the time the zones have grown to about 10 nm." Let's assume with them the GP zones grow at 100°C from a matrix with 4.5 wt.% Cu. How do the authors arrive at this statement, what evidence did they likely use, and what calculations did they perform to arrive at this statement?

5.12 Transitional Phases

(29) Suppose an alloy containing 97 wt. % aluminum and 3 wt. % copper is poured into a mold and solidified by extracting heat from the external surfaces of the mold.

Al-Cu
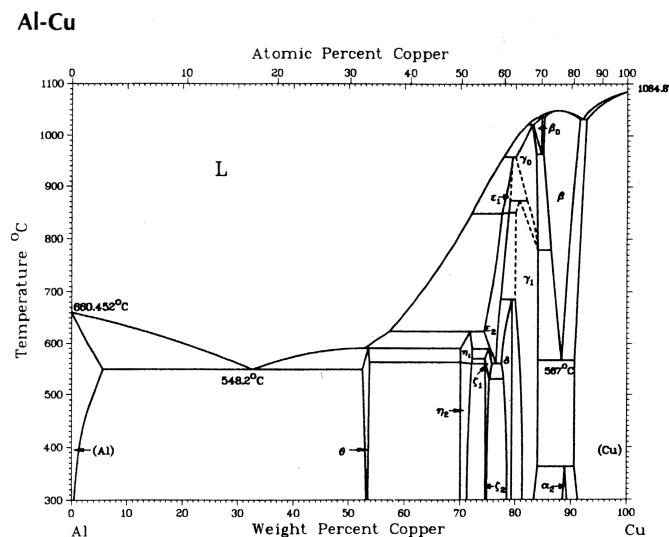
  a What phase (or phases) do you expect to be present in the solid immediately after the solidification reaction?

  b What phase (or phases) will be present at equilibrium?

  c A variety of non-equilibrium phases are observed at intermediate stages in the transformation process. Why are these phases observed?

  d Once the equilibrium phase is formed, its rate of growth is found to decrease with time. Why is this? What is the rate limiting step in the transformation?

(30) Porter and Easterling, prob. 5.6

(31) Suppose that in the system of interest, χ is inversely proportional to the absolute temperature, and the critical temperature for this system is 350 K. Replot the phase diagram from part a with temperature on the vertical axis.

5.13 TTT diagrams

(32) Consider the following blowup of the low concentration region of a phase diagram similar to the Co-Cu diagram shown above:
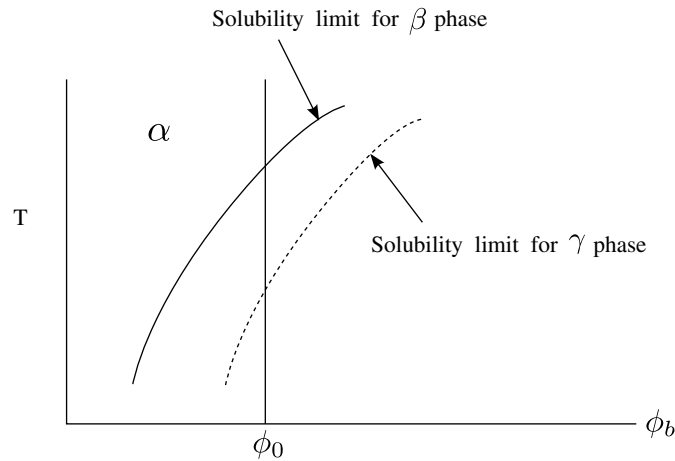
a At an average alloy composition ϕ_0 shown on this plot, it is determined that only β precipitates form (no γ is ever observed) at two temperatures, T_1 and T_2. The time dependence of the appearance of β is plotted at these two temperatures as shown below. On the plot above, indicate locations of T_1 and T_2 that are consistent with these curves, and briefly describe your reasoning.
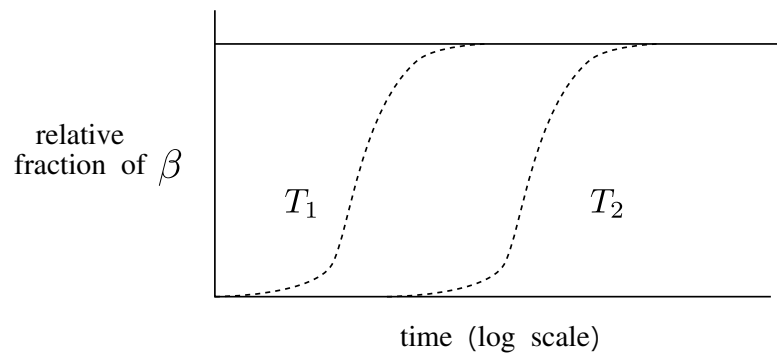
b Draw TTT curves for the precipitation of both β and γ for an alloy with the composition of ϕ_0, making connections to specific temperatures from the phase diagram where possible.

5.14 Mineralization

(33) Calculate the CO_3^{2-} concentration in equilibrium with seawater and with each of the following three forms of calcium carbonate: calcite, aragonite, vaterite. You'll need to use the solubility products provided in class, and look up the calcium concentration in seawater.

5.15 Review Questions

- What does the liquid composition look like in front of an advancing solid phase?

- What controls length scale of the composition variation?

- What is the criteria for interface stability with respect to the formation of dendrites?

- Under what conditions are dendrites formed during the solidification of a pure material?

- What is the qualitative behavior of $S(\theta)$ for nucleation at a flat interface, and at grain boundary surfaces, edges and corners?

- How are equilibrium contact angles related to surface and interfacial free energies?

- What is meant by complete wetting?

    – What is the effect on nucleation for the complete wetting case?

- What are the characteristic frequencies and concentrations (C_0, ν_0) that determine the homogeneous and heterogeneous nucleation rates?

- Why is coherent nucleation generally the favored homogeneous nucleation mechanism?

- How is the work to form the critical nucleus calculated?

- What is the 'incoherent solvus', and how does it relate to the expressions listed above?

- Where does the Laplace pressure come from?

- How do you know that kinetic factors must be controlling complex morphologies (dendrite formation, shapes of snowflakes, etc.)?

- What controls the size of the depletion zone in front of a flat or curved precipitate that is growing?

- How does it evolve with time?

- What limits the growth velocity of a precipitate phase boundary at high and low temperatures?

    – Which of these limits are connected to the phase diagram?

- Why are flat, plate-like precipitates sometimes formed?

- How does the molar free energy depend on the radius of curvature of a precipitate?

- How does curvature effect the equilibrium concentration of solute that is in equilibrium with a precipitate?

- What does the concentration dependence look like for precipitates that are larger than r*?

    – What if the precipitate is smaller than r*?

- What are transition phases, and why do they form?

    – What is the mechanism by which transition phases shrink at the expense of equilibrium phases?

- How are TTT curves for transition phases related to the phase diagram?

- What are the basic physical assumptions of the Lifshitz/Slyosov coarsening theory discussed in class?

    – What do the depletion zones look like?
    – What determines the average solute concentration in the matrix phase?

- What does the distribution of precipitates look like if coarsening occurs by the Lifshitz/Slyosov mechanism?

- What do the binodal and spinodal curves look like for the regular solution model?

    – What is the critical temperature?

- What determines the size of the characteristic phase size when phase separation occurs by spinodal decomposition?

- What is meant by uphill diffusion?

  – When is it observed?

- How is this phase size modified (in qualitative terms) by coherent strains?

- How do these strains modify the phase diagram to give coherent spinodal and binodal curves?

- How can the liquidus lines be estimated for an ideal eutectic system?

  – What are the assumptions made in the approximation?

- What determines the size of the individual phases for eutectic solidification?

- What determines the size of the individual phases for a eutectoid transformation?

- What is the physical significance of the squared gradient term in the free energy expression?

- How can the shapes and sizes of metallic nanoparticles be controlled?

- What is the growth mechanism of Si nanowires catalyzed by Gold?

  – What is the importance of the Au/Si phase diagram.

- How does the solubility of calcite compare to the solubility of aragonite or vaterite, and why?

  – How is the concept of the solubility product used?

- In the two-phase mixture of n-type and p-type materials used to form an organic solar cell, what sort of phase morphology is desired, and why?

6 332 Problems

Notes:

- If you use MATLAB or Python to solve any of these problems, include the code that you used.

6.1 Course Organization

1) Send an email to Prof. McCue (ian.mccue@northwestern.edu), Qihua Chen (r6p5t6@u.northwestern.edu), and Donghoon Shin (donghoonshin2023@u.northwestern.edu). If you have not taken CE 216 or the MSE 316 sequence, let us know why. Otherwise, let us know how comfortable you feel with the material from CE 216 and MSE 316-1. Also let us know what you have enjoyed most about MSE so far, what you like least (if such a thing exists!) and if you are involved in any research within the department or elsewhere.

6.2 The Stress Tensor

2) Consider the following stress tensor:

$$\sigma_{ij} = \begin{bmatrix} 4 & 3 & 0 \\ 3 & 1 & 2 \\ 0 & 2 & 6 \end{bmatrix} x10^6 \, \text{Pa}$$

(a) Calculate the stress tensor for coordinate axes rotated by $30°$ about the z axis (the 3 axis).

(b) Repeat the calculation for a $30°$ rotation around the x axis (the 1 axis).

(c) Calculate the three principal stresses.

(d) Calculate the maximum shear stress in the sample.

3) Consider the following stress tensor:

$$\sigma_{ij} = \begin{bmatrix} -2 & 1.4 & 0 \\ 1.4 & 6 & 0 \\ 0 & 0 & 2 \end{bmatrix} x10^6 \, \text{Pa}$$

(a) Draw a Mohr circle representation of the stress contributions in the xy plane

(b) What are the three principal stresses?

(c) Show that the the sum of the diagonal components from original stress tensor is equal to the sum of the three principal stresses. What is the hydrostatic pressure for this stress state?

6.3 Strains

4) An engineering shear strain of 1 (100%) is applied to a rubber cube with dimensions of 1cm×1cm×1cm. Young's modulus for the rubber sample is 10^6 Pa, and you can assume it is incompressible.

(a) Sketch the shape of the object after the strain is applied, indicating the dimensions quantitatively.

(b) On your sketch, indicate the magnitude and directions of the forces that are applied to the object in order to reach the desired strain.

(c) Calculate the 3 principal extension ratios characterizing the final strain state.

6.4 Typical Moduli

5) Calculate the sound velocities for shear and longitudinal waves traveling through the materials listed in the 'Representative Moduli' table from the course text.

6.5   Matrix Representation of Stress and Strains

6)   For an isotropic system there are only two independent elastic constants, s_{12} and s_{11}. This is because if properties are isotropic in the 1-2 plane, the compliance coefficient describing shear in this plane, s_{44}, is equal to $2(s_{11} - s_{12})$. We can use the Mohr's circle construction to figure out why this equality must exist.

(a) Start with the following pure shear stress and strain states:

$$\sigma = \begin{bmatrix} 0 & \sigma_{12} & 0 \\ \sigma_{12} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} ; \ e = \begin{bmatrix} 0 & e_{12} & 0 \\ e_{12} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

Use the matrix formulation to obtain a relationship between σ_{12} and e_{12} in this coordinate system.

(b) Rotate the coordinate system by $45°$ so that the stress state looks like this:

$$\sigma = \begin{bmatrix} \sigma_1^p & 0 & 0 \\ 0 & \sigma_2^p & 0 \\ 0 & 0 & 0 \end{bmatrix} ; \ e = \begin{bmatrix} e_1^p & 0 & 0 \\ 0 & e_2^p & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

Use the Mohr's circle construction to write these principal stresses and strains in terms of σ_{12} and e_{12}. Then use the matrix formulation to obtain an expression between σ_{12} and e_{12} in this rotated coordinate system.

(c) For an isotropic system, the relationship between σ_{12} and e_{12} should not depend on the orientation of the coordinate axes. Show that the only to reconcile the results from parts a and b is for s_{44} to be equal to $2(s_{11} - s_{12})$.

7)   Consider a material with orthorhombic symmetry, with different properties along the 1, 2 and 3 directions. Young's moduli are measured along the 3 different directions, and we obtain the following results:
$E_1 = 5.5$ GPa; $E_2 = 2.0$ GPa; $E_3 = 3$GPa

(a) Is this material a metal, a ceramic or a polymer? How do you know?

(b) The compliance matrix, s, is a symmetric 6x6 matrix as shown below. For this material, cross out all of the elements that must be zero.

$$\begin{bmatrix} s_{11} & s_{12} & s_{13} & s_{14} & s_{15} & s_{16} \\ s_{12} & s_{22} & s_{23} & s_{24} & s_{25} & s_{26} \\ s_{13} & s_{23} & s_{33} & s_{34} & s_{35} & s_{36} \\ s_{14} & s_{24} & s_{34} & s_{44} & s_{45} & s_{46} \\ s_{15} & s_{25} & s_{35} & s_{45} & s_{55} & s_{56} \\ s_{16} & s_{26} & s_{36} & s_{46} & s_{56} & s_{66} \end{bmatrix}$$

(c) What are the values of s_{11}, s_{22} and s_{33} for this material?

(d) A value of 0.38 is obtained for Poisson's ratio is measured in the 1-2 plane by applying a tensile stress in the 1 direction and measuring the strains in the 2 direction. What is the value of s_{12} for this material?

8)   Consider a material with elastic constants given by the following compliance matrix:

$$s_{ij} = \begin{bmatrix} 14.5 & -4.78 & -0.019 & 0 & 0 & 0 \\ -4.78 & 11.7 & -0.062 & 0 & 0 & 0 \\ -0.019 & -0.062 & 0.317 & 0 & 0 & 0 \\ 0 & 0 & 0 & 31.4 & 0 & 0 \\ 0 & 0 & 0 & 0 & 61.7 & 0 \\ 0 & 0 & 0 & 0 & 0 & 27.6 \end{bmatrix} \text{GPa}^{-1}$$

(a) Describe the symmetry of this material, and explain your reasoning.

(b) What is the highest value for Young's modulus that you would expect for this material? What direction does it correspond to?

(c) Calculate the value of Poisson's ratio obtained from an experiment where the materials is pulled in the 3 direction and change in sample width in the 2 direction is measured.

6.6 Other Linear Properties

9) Quartz has the 32 point group which has a coefficient map that looks like this:
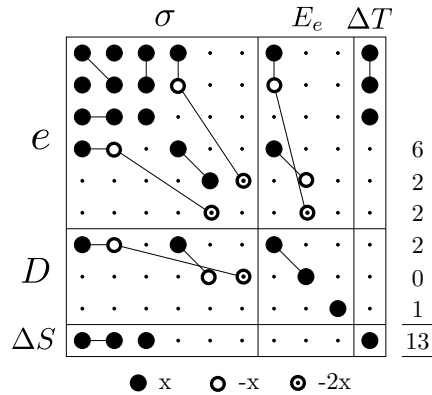
(a) Consider the converse piezoelectric effect, where an electric field is applied along a particular direction and we are interested in determining the resulting strains in the material. Will any strains be generated in the material if I apply an electric field along the '3' direction of the crystal? Why or why not?

(b) Compare the normal strains in the 1 and 2 directions that are obtained when an electric field is applied in the 1 direction.

(c) Are any shear strains developed in the material when an electric field is applied in the 1 direction? If so describe the orientation of this shear strain.

(d) How many independent elastic constants are there for quartz?

(e) Does the shape of a chunk of single crystal quartz change when you heat it up? (Note: this is another way of asking if the thermal expansion of quartz is isotropic).

6.7 Yield Criteria

10) A cube of material is loaded triaxially resulting in the following principal stresses at the point of plastic yielding: $\sigma_1^p = 140$ MPa, $\sigma_2^p = 20$ MPa, and $\sigma_3^p = 35$ MPa.

(a) What is the shear strength of the material according to the Tresca yield criterion?

(b) If the the value of σ_3^p were increased to 70 MPa, how does this change your result? Explain.

11) From the work of D. C. Jillson, Trans. AIME 188, 1129 (1950), the following data were taken relating to the deformation of zinc single crystals:

Table 6.1: Applied tensile force for slip of single crystal Zn.

ϕ	λ	P (N)
83.5	18	203.1
70.5	29	77.1
60	30.5	51.7
50	40	45.1
29	62.5	54.9
13	78	109.0
4	86	318.5

In this table ϕ is the angle between the loading axis and the normal to the slip plane, λ is the angle between the loading axis and the slip direction and P is the force acting on the crystal when yielding begins. The crystals have a cross-sectional area, A_0, of $122 \times 10^{-6} \text{m}^2$.

(a) What is the slip system for this material.

(b) For each combination of P, ϕ and λ, calculate the resolved shear stress, τ_{RSS} and normal stress, σ_N acting on the slip plane when yielding begins.

(c) From your calculations, does τ_{RSS} or σ_N control yielding?

(d) Plot the Schmid factor versus the applied stress, P/A_0, acting on the rod. At what Schmid factor value are these experimentally-measured yield loads at a minimum? Does this make sense?

12) The tensile yield stress of a materials is measured as 45 MPa by a uniaxial tensile test.

(a) What will the shear stress of the material by if the materials yields at a specified value of the Tresca stress?

(b) Now calculate the same quantity (shear yield stress) if the material yields at a specified value of the Von Mises stress.

(c) Suppose the material is a glassy polymer like Plexiglas, and Tresca yield stress is obtained from a uniaxial compression experiment and from a uniaxial tensile experiment. Which of these experiments to you expect to give the largest Tresca yield stress?

13) What is the effect of the resolved normal stress on the yield behavior of crystalline metals and ceramics? What about polymers? Describe any differences between the two cases.

14) A sample of pure iron has a uniaxial tensile yield strength of 100 MPa. Assume that the yield behavior is described by the Von Mises yield criterion.

(a) What do you expect for the yield strength of the material in a state of uniaxial compression?

(b) What will the yield strength be under a stress state of pure hydrostatic pressure?

(c) What is the shear yield strength of the material.

15) Consider the following two stress-strain curves obtained from a glassy polymer material. In these plots σ_t is the true stress and λ is the extension ratio ($1+e$, where e is the tensile strain).
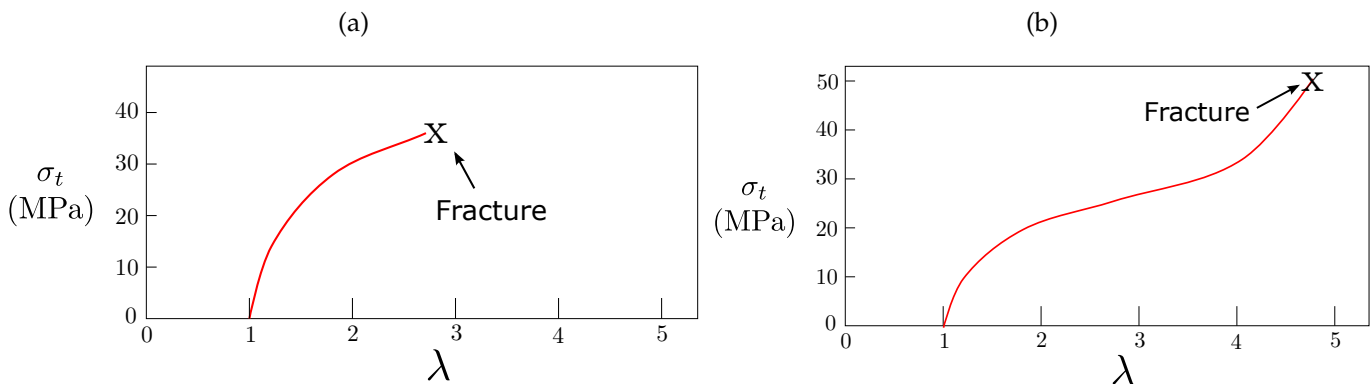
(a) Sketch the behavior of the engineering stress vs extension ratio that you expect for each of these samples in a uniaxial tensile test. Be as quantitative as possible. Briefly describe why you drew the curves the way you did.

(b) Which of these samples can be cold drawn? What value do you expect for the draw ratio? (The plastic strain in the drawn region of the sample)?

(c) Suppose the cross sectional area of each sample is $1\ \text{cm}^2$. What is the maximum load that the sample will be able to support prior to failure for each of the two samples?

16) Consider a material with the following true stress vs. engineering strain behavior, measured in uniaxial extension:
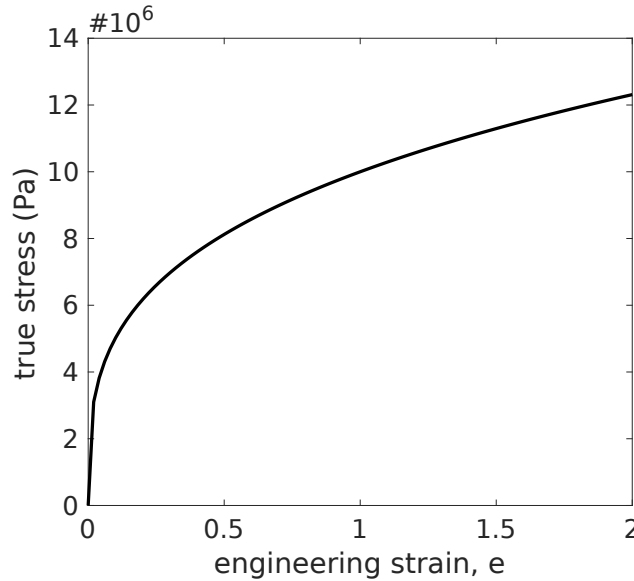
(a) Suppose the cross sectional area of this material is 1 cm². Calculate the maximum force that this material would be able to support prior to failure.

(b) Will this material form a stable neck? If so, what is the characteristic strain in the necked region?

17) The following stress tensor describes the state of stress of a material at its yield point:

$$\sigma = \begin{bmatrix} 0 & 3 & 0 \\ 3 & 0 & 0 \\ 0 & 0 & -5 \end{bmatrix} \text{MPa}$$

Suppose the same material is subjected to stress state of simple shear. At what value of the applied shear stress do you expect yielding to occur, assuming that the material obeys a Tresca yield criterion.

6.8 Strengthening Mechanisms

18) Consider the two red dislocations at the center of the two diagrams shown below: (All of the dislocations are perpendicular to the plane of the paper.) We are interested in the effect that the central dislocation has on each case on the 4 surrounding black dislocations.

$$R = \text{right-handed screw dislocation}; \quad L = \text{left-handed screw dislocation}$$
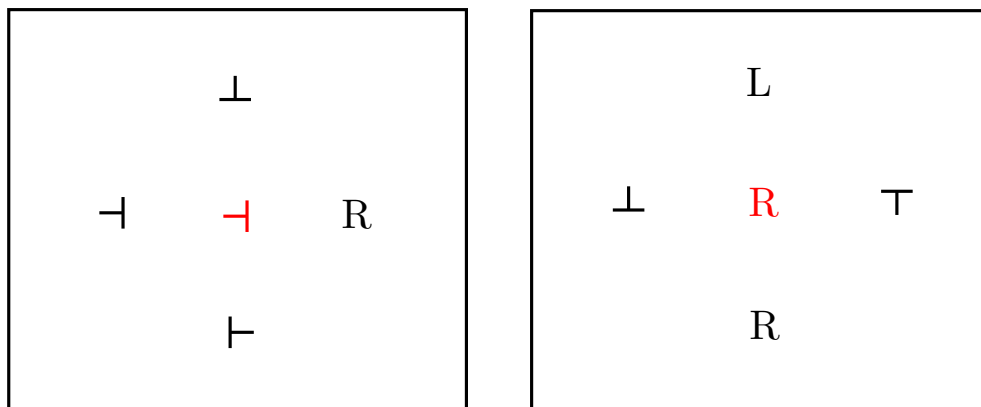
(a) For each of the 5 black edge dislocations, indicate the slip planes with a dashed line.

(b) Draw an arrow on each of the black edge dislocations, showing the direction of the force within its slip plane that is exerted by the red dislocation. If there is no force within the slip plane, circle the black dislocation instead.

(c) For the three black screw dislocations, draw an arrow on them to indicate the direction of the slip force exerted by the red dislocation. If the slip force is zero, circle the black screw dislocation instead.

19)   Consider the two edge dislocations shown below. Suppose dislocation 1 remains fixed in place, but that dislocation 2 is able to move on its glide plane.

(a) Assume that the sense vector, $\vec{s}$, for each dislocation is defined so that $\vec{s}$ points into the page. Indicate the direction of $\vec{b}$ for each of the two dislocations.
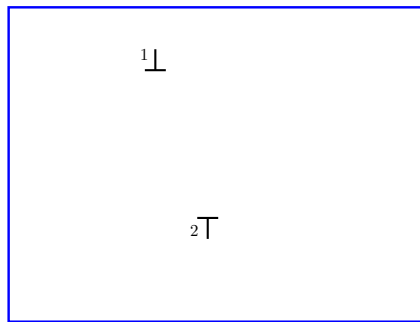
(b) Indicate the glide plane for dislocation 2 with a dotted line.

(c) Indicate with an X the location of dislocation 2 at the position within its glide plane that minimizes the total strain energy of the system.

(d) Now suppose that dislocation 1 is a fixed, left-handed screw dislocation and dislocation 2 is a mobile right-handed screw dislocation.

   i Use a dotted line to indicate the plane on which you expect dislocation 2 to move in order to minimize the overall strain energy of the system.

   ii Plot the overall strain energy of the system as a function of the distance between the two screw dislocations.

20)   The figure below shows the yield strength of a precipitation hardened aluminum alloy as a function of aging time at different temperatures. Note that the yield strength initially goes through maximum and then decreases with time. Explain why this happens in as much detail as possible.
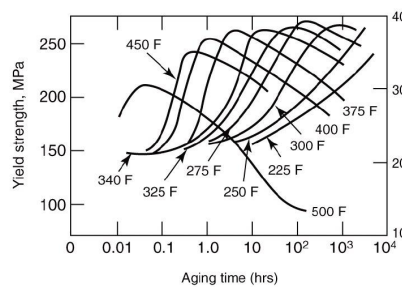
21)   The following plot shows values of the yield strength of copper samples as a function of the grain size of these samples.
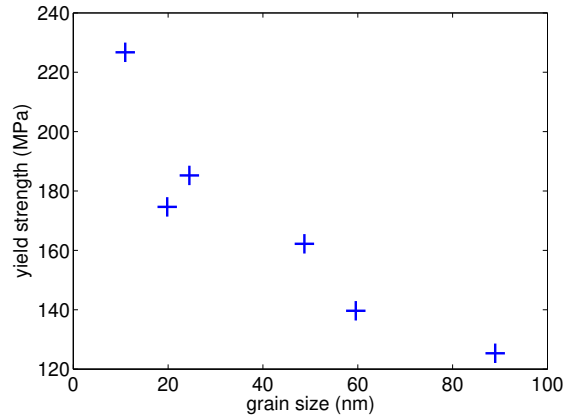
(a) Describe why the yield stress decreases with increasing grain size.

(b) Describe the procedure you would use to determine the limiting value of the yield strength in the absence of grain boundaries.

21).1

22) The yield point for a certain plain carbon steel bar is found to be 135 MPa, while a second bar of the same composition yields at 260 MPa. Metallographic analysis shows that the average grain diameter is 50 μm in the first bar and 8 μm in the second bar.

(a) Predict the grain diameter needed to give a yield point of 205 MPa.

(b) If the steel could be fabricated to form a stable grain structure of 500 nm grains, what strength would be predicted?

23) The lattice parameters of Ni and Ni_3Al are 3.52×10^{-10} m and 3.567×10^{-10} m, respectively. The addition of 50 at% Cr to a Ni-Ni_3Al superalloy increases the lattice parameter of the Ni matrix to $3.525 \times 10\text{-}10$ m. Calculate the fractional change in alloy strength associated with the Cr addition, all other things being equal.

24) General Knowledge

24).1 How are G, ν and K related to one another for an isotropic material?

24).2 What are typical values of G and K for metals, ceramics and polymers?

6.9 Contact Mechanics

25) Consider the contact of a flat rigid punch with a thin elastic layer, as shown schematically below:
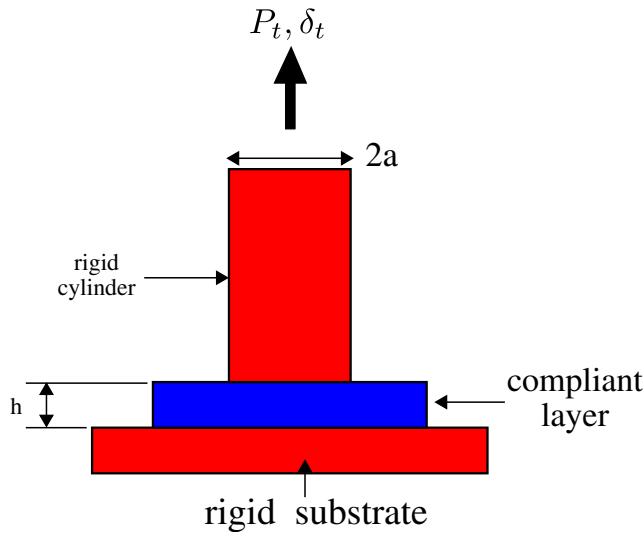
Suppose the compliant layer is incompressible gel ($\nu = 0.5$), with a Young's modulus, E, of 10^4 Pa. The critical energy release rate for failure at the gel/punch interface is 0.1 J/m^2. The punch radius, a, is 3 mm.

(1) What is the tensile force required to separate the punch from the layer if the layer is infinitely thick?

(2) What is the stress intensity factor, K_I, just prior to detachment of the punch from the surface?

(3) How close to the punch edge to you need to be for the tensile stress at the punch/layer interface to be equal to the modulus of the layer?

26) Describe in qualitative terms what happens to the following quantities as the thickness, h, of the compliant layer from the previous problem decreases:

(1) The overall compliance of the system.

(2) The load required to detach the indenter from the substrate.

(3) The displacement at which the indenter detaches from the substrate.

(4) The shape of the tensile stress distribution at the punch/substrate interface.

6.10   Nanoindentation

27) Commercial nanoindenters are generally not suitable for the characterization of soft materials. To understand why this is the case, consider the following indentation data from the Hysitron web site (this is for the same instrument that Northwestern has in the NUANCE facility):
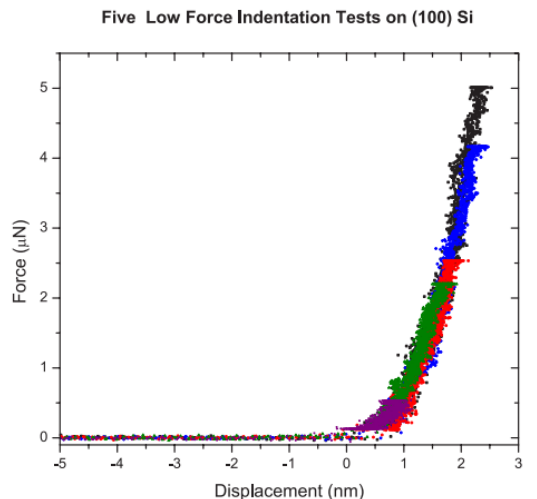
A series of five low force indents on (100) Silicon showing the industry leading noise-floor performance and data repeatability of the **TI 950** nanomechanical testing system.

(1) If the data in this figure are obtained with a rigid spherical indenter of radius R, use the data from this figure to estimate the value of R. Assume that the material is being indented elastically and that adhesion can be neglected. (You'll need to look up mechanical property data for silicon).

(2) Suppose that the material is replaced by an elastomer with a modulus of 10^6 Pa. What value of R would need to be used to obtain the same Force displacement curve for this much softer material? (Assume that the effects of adhesion can eliminated by performing the indentation in a suitable liquid).

28)   Suppose an elastomeric sphere with a radius of 1 mm and a reduced modulus, E^*, of 10^6 Pa is placed on a flat, rigid substrate. Suppose also that the adhesion between the sphere and the substrate is characterized by a critical energy release rate of 0.05 J/m^2, independent of the crack velocity or direction of crack motion. Calculate the radius of the circular contact area that develops between the elastomer and the surface, assuming that there is no external load applied to the sphere (apart from it's weight).

29)   Obtain the hardness and elastic modulus from the following nanoindentation curve, obtained from a Berkovich indenter:
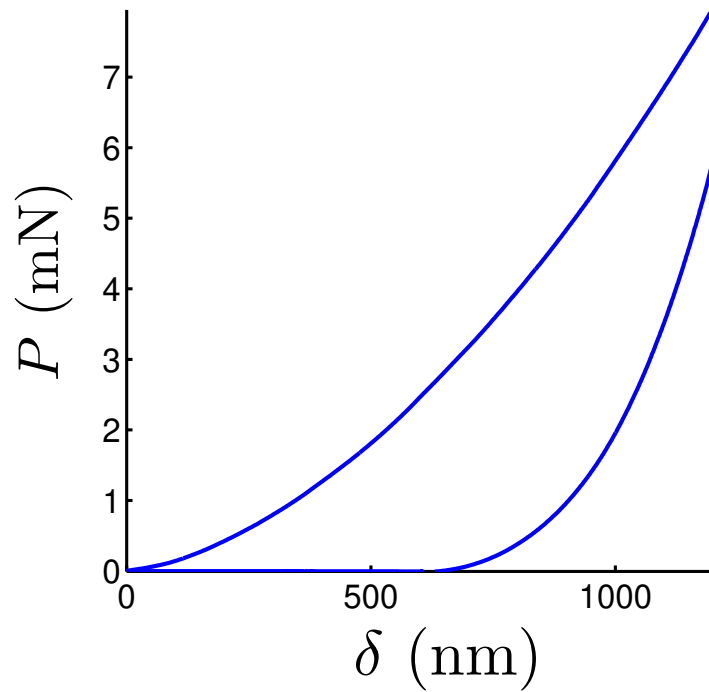
6.11   Fracture Mechanics

30)   The stress fields in the vicinity of a crack tip in a material are determined by the distance, d, from the crack, and the polar angle θ, defined in the following diagram.
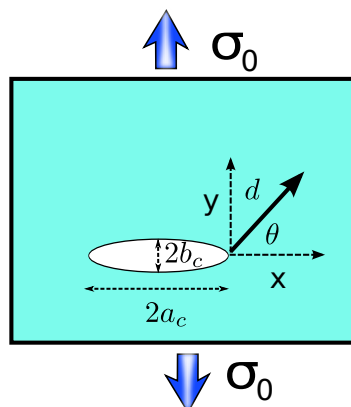
(1) For a fixed value of d, plot the behavior of σ_{xx}, σ_{yy} and σ_{xy} for a mode I crack as a function of θ.

(2) What happens to the stresses for $\theta = 180°$? Why does this make sense?

(3) A mode I crack will travel in the direction for which the normal stress acting across the crack surfaces is maximized. What direction is this?

31) Look up the fracture toughness (K_{IC}) and Young's modulus (E) for window glass. Assuming that the maximum local stress is $\approx E/10$, estimate the crack tip radius of curvature for a crack propagating through window glass.

32) As a crack advances, what happens to the stiffness of the cracked body? What happens to the compliance?

33) A set of double cantilever beam adhesion test specimens was fabricated from a set of aluminum alloy samples. The geometry as as shown below:
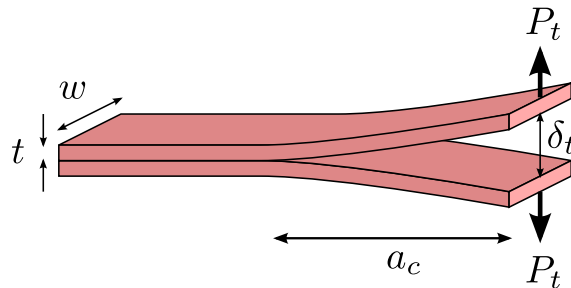
Suppose each of the two beams has a thickness (t) of 10 mm, a width (w) of 20 mm and a length of 80 mm. The double cantilever beam sample was produced by using an adhesive to glue the two beams together. Assume the precrack with a length, a_c, of 10 mm. The critical energy release rate for the adhesive is 65J/m^2.

(1) Calculate the values of the tensile load, P, and the displacement, Δ, where the crack starts to propagate.

(2) In a load-controlled experiment, P_t is held constant once the crack starts to propagate, and in a displacement controlled test Δ is held constant once the crack starts to propagate. From the relationship between $\mathcal{G}$ and P_t, Δ and a, describe why the load controlled experiment results in unstable crack growth, but the displacement controlled experiment results in stable crack growth.

(3) From your answer to part b, describe how you would design an experiment where you measured the energy release rate required to propagate the crack at a specified velocity.

34) What is crack tip shielding?

35) Describe the difference between a crack and a craze? How is the maximum width of a craze related to $\mathcal{G}_c$ and K_{IC}?

36) Describe how transformation toughening works to increase the toughness of a ceramic material like ZrO$_2$.

37) What is a Charpy impact test conducted, and what does it measure?

38) What the difference between the side windows of your car and the windshield? Include the role of tempering, thermal annealing and composite layering, and describe how the desired properties are obtained for the two different applications of glass.

39) The following data were obtained for the fracture stress of a series of silica glass fibers used for optical communications:
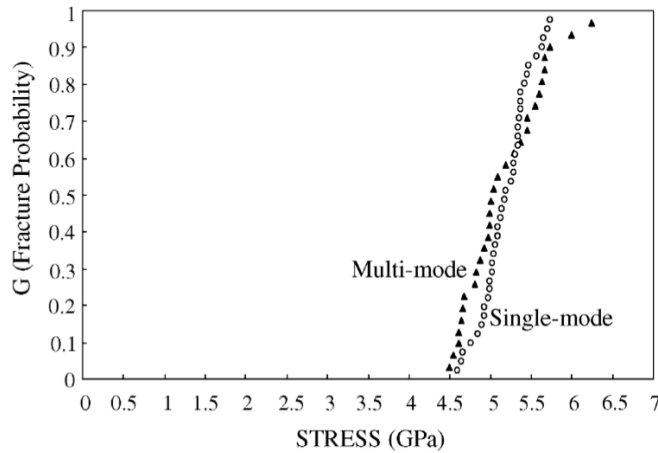
The graph shows the distribution of failure probabilities as a function of the applied tensile stress. None of the samples had fractured at a stress of 4.5 GPa, but they had all fractured at a stress of 6 GPa. From these data, and from fracture toughnesses given for inorganic glass in class (and in the course notes), estimate the intrinsic flaw sizes that are present at the surface of the glass fibers. Comment on these sizes, and if you think the fracture mechanics analysis makes sense to use in this case.

40) Silicones containing resin fillers are used as an encapsulant materials in light emitting diodes (LEDs) in order to protect the electronics from harsh environments and to aid in heat dissipation. Near the surface of the electronic components, temperatures can go as high as 200 °C for extended time periods.
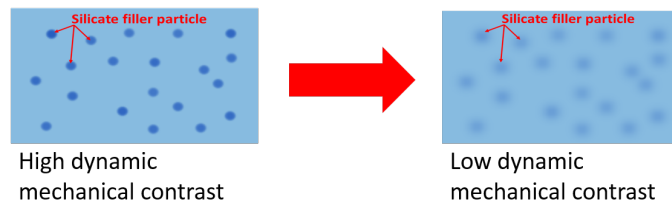
Figure 6.1: High dynamic mechanical contrast is important

(1) Given that a high dynamic mechanical contrast is desirable in creating a soft material with high fracture toughness, what would you suggest as a design criteria in order to maintain high dynamic mechanical contrast at high temperatures? (Hint: think about the role of the T_g of the matrix and filler content.)

(2) Thermal mismatch at the interface between the encapsulant and electronic can lead to residual stresses that promote crack propagation. In assessing the performance of the encapsulant at the interface, should a failure stress or a failure strain criteria be used? Why?

(3) From a thermal management and mechanics perspective, why do you think a soft encapsulant (e.g. silicone) will be more preferable over a hard encapsulant (e.g. glass)?

6.12 Weibull Statistics

41) A set of glass rods with a Weibull modulus of 30 are fractured in a uniaxial tensile test. The stress at which 63% of the samples fracture is 100 MPa.

(1) What is the maximums stress if you want to make sure that less than one in 100 rods fail? (Note that $1/e$ is 0.37).

(2) What is the maximums stress if you want to make sure that less than one in 10^6 rods fail?

(3) What does the stress need to be to get less than 1 failure in 10^6 if the Weibull modulus is 10 instead of 30?

42) What determines the value of the Weibull modulus in a brittle material?

43) A brittle material with a specified geometry fails with a 50% probability at a tensile stress of 100 MPa. From the failure statistics, it is determined that the Weibull modulus for this material is 40. What fraction of these materials will fail at a tensile stress of 70 MPa?

6.13 Viscoelasticity

44) The following questions relate to the DGEBA-PACM/Jeffamine system that was introduced in class.

(1) For the D230-based system, make a plot comparing the temperatures where the slope in $\log(E')$ vs. temperature is maximized, and also the temperature where $\tan(\delta)$ is maximized. Comment on the relationship between these two temperatures.

(2) How many moles of D230 need to be combined with one mole of DGEBA to make a stoichiometric mixture? (no PACM added)

(3) How many grams of D230 need to be combined with one mole of DGEBA to make a stoichiometric mixture? (again assume that no PACM is added. Note that 230 in this case is the molecular weight of the Jeffamine in g/mole. You'll need to calculate or look up the molecular weight of DGEBA to do this DGEBA stands for diglycidyl ether of bisphenol A, but DGEBA is pretty standard abbreviation for it).

(4) What happens to the amount of jeffamine you need to add to get a stoichiometric ratio as the molecular weight of the jeffamine is increased as you move from D230 to D400 to D2000 to D4000? (a qualitative answer is okay - you don't need to be quantitative for this. Continue to assume that no PACM is added).

(5) What happens to the glass transition temperature for samples without any PACM as the molecular weight of the Jeffamine increases from 230g/mole to 400 g/mole? Describe how you obtained T_g from the data shown in the lecture. Also describe why the trend in T_g is as you describe.

(6) Mixtures with DGEBA and an equal amount of jeffamine and PACM become cloudy as the molecular weight of the jeffamine increases. Why is this?
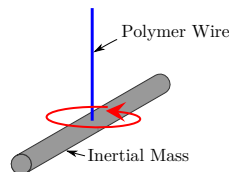
45) Consider a cylindrical metal bar with a density of 7.6 g/cm^3, a diameter of 1 cm and a length of 10 cm. It is suspended from a polymer fiber with a length, ℓ, of 30 cm and a diameter of 1 mm.

(1) Suppose the fiber is perfectly elastic, with a shear modulus 10^9 Pa. Calculate the natural frequency of the system if the bar is rotating back and forth, causing the fiber to twist.

(2) Suppose the fiber is viscoelastic, with G' at the frequency calculated from part a equal to 10^9 Pa, and with $G'' = 10^7$ Pa. How many periods of the oscillation will take place before the magnitude of the oscillation decays by a factor of e (2.72)? Note: the rotational moment of inertia for the suspended metal bar in this geometry is $m\ell^2/12$, where m is the total mass of the bar and ℓ is its length.

46) As mentioned in class, the Maxwell model, with a viscous element and an elastic element in series with one another, is the simplest possible model for a material that transitions from solid-like behavior at short times, to liquid-like behavior at long times. For a shear geometry we refer to the elastic element as G_0 and the viscous element as η.

(1) For what angular frequency are the storage and loss moduli equal to one another for a material that conforms to the Maxwell model? Express you answer in terms of the relaxation time, τ.

(2) Suppose the material is oscillated at a frequency that is ten times the frequency you calculated from part a. Does the material act more like a liquid or a solid at this frequency? Describe your reasoning.

(3) Calculate the values of G' and G'' at the frequency from part b, and calculate the phase angle, ϕ describing the phase lag between stress and strain in an oscillatory experiment. Note that the following expression relates ϕ, G' and G'':

$$\tan \phi = \frac{G''}{G'}$$

Does this phase angle make sense, given your answer to part b? Compare your value of ϕ to the values you expect for a perfectly elastic solid and a perfect liquid.

47) The following stress and strain response are observed for a material during the initial stages of a creep experiment.
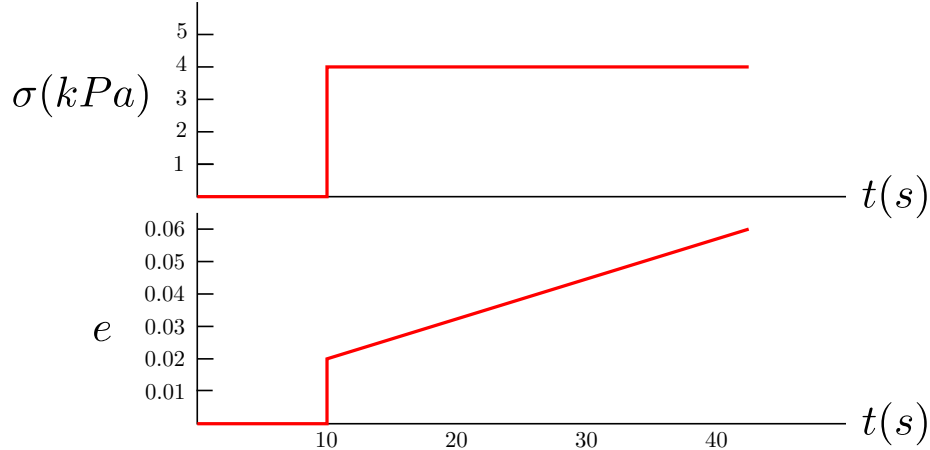
(1) Draw a spring/dashpot model that describes this behavior. Label moduli and viscosities as quantitatively as possible.

(2) A stress relaxation test (strain shown below) is performed on the same material. On the stress axis below, draw the stress response that you expect for the model you have drawn from part a.
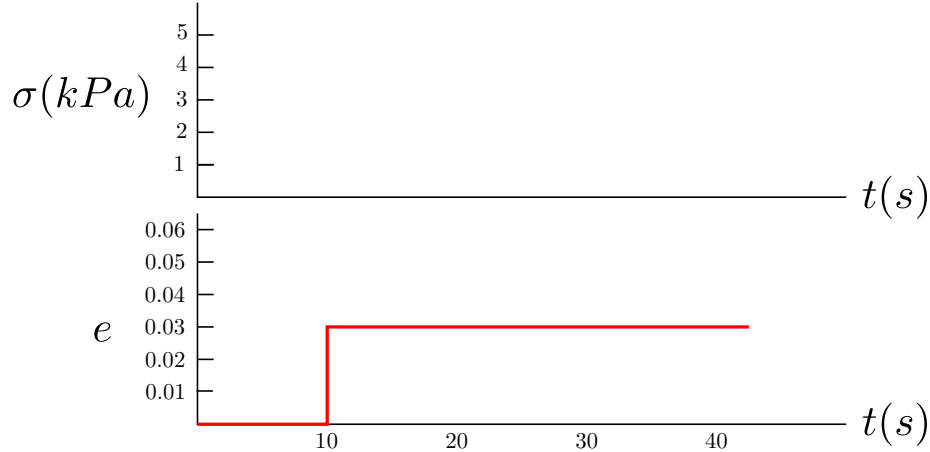
48) A tensile experiment is performed on a viscoelastic material, with the tensile strain (e) and tensile stress (σ) exhibiting the time dependence shown in the following figure:
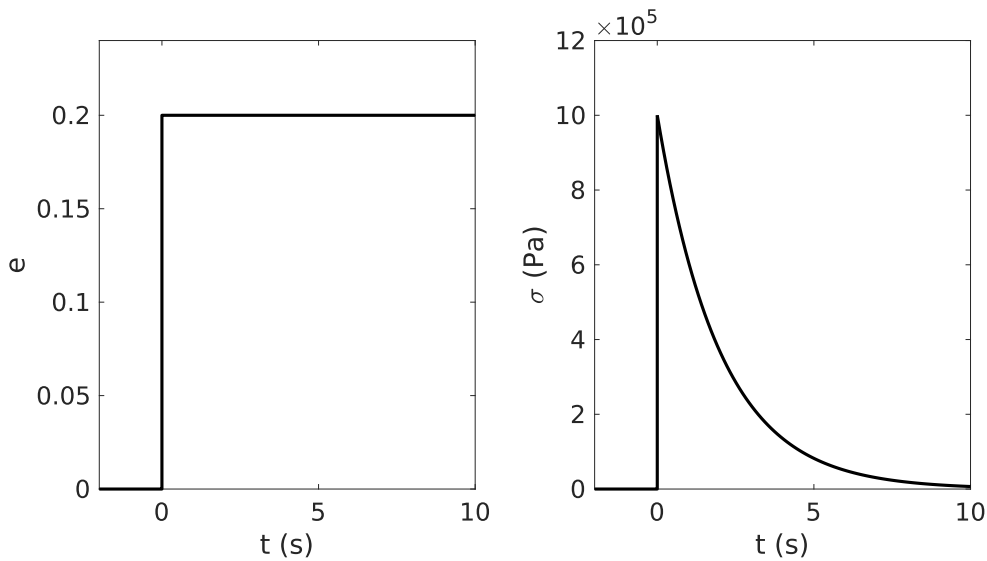
(1) Draw a spring and dashpot model that would give this response. Give values (modulus or viscosity) for each element in your model (the values of these quantities are not expected to be exact).

(2) Suppose the sample were vibrated in tension at a frequency of 1000 Hz (cycles per second). Estimate the value of $|E^*|$ (magnitude of the complex shear modulus) that you would expect to obtain.

(3) For what range of frequencies do you expect the loss modulus (E'') to exceed the storage modulus (E') for this material?

49)   Can creep of a glass window by viscous flow give measurable changes in sample dimensions over a very long period of time? To sort this out, do the following:

(1) Estimate the stress at the bottom of a very tall pane of window glass, due to the weight of the window itself. Look up the density of silica glass, and a height of the window that makes sense (choose a big one).

(2) Estimate the viscosity that would be needed to give a measurable change in sample dimensions after 400 years.

(3) Using the data below, does it make sense to you that observable flow could noticeably change the dimensions of the window? (You'll need to make some assumptions about how the viscosity will extrapolate to room temperature.
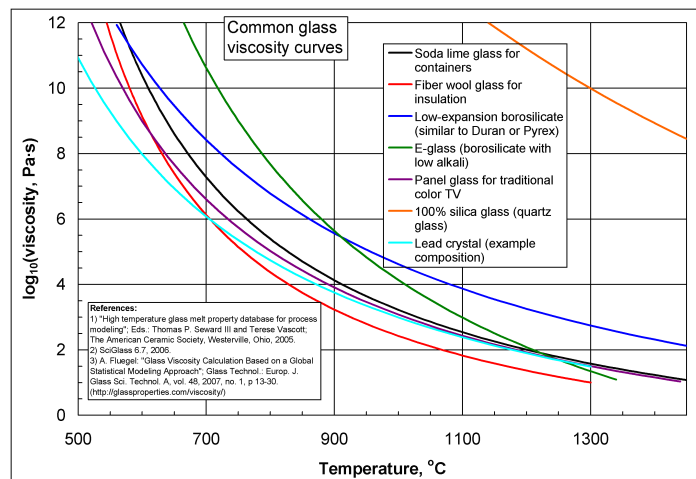
6.14   Nonlinear Viscoelasticity and Creep

50)   A step stress (0 for t<0, σ for t>0) is applied to a solid which can be modeled by the following combination of linear springs and dashpots:
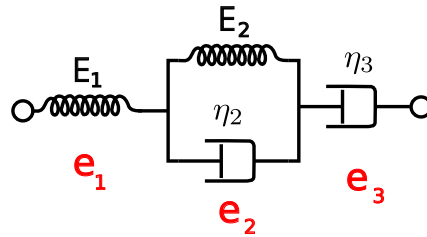
(1) This model is useful because it includes a non-recoverable creep component, a recoverable time dependent creep component, and an instantaneous, recoverable strain.

   a) Identify the element (or combination of elements) in the above model which is associated with each of these three contributions to the strain.

   b) Write down the expression for the total strain, $e(t)$, after the imposition of the step increase in stress.

   c) Suppose the stress is applied for a long time, so that the strain is increasing linearly with time. At some time, t', the stress is removed. Derive an expression for the change in strain after the stress is removed.

(2) This model has been applied to creep data for oriented polyethylene at room temperature. Model predictions were compared to data obtained from samples of high molecular weight (High M) and low molecular weight (Low M). Both samples were drawn to the same draw ratio. The following values of E_1, E_2, η_2 and η_3 were obtained from experimental data:

Sample	σ (GPa)	E_1 (GPa)	E_2 (GPa)	η_3 (GPa-s)	η_2 (GPa-s)
Low M	0.025	17.4	33.5	1.8×10^5	4300
Low M	0.05	13.6	35.6	6.3×10^4	5000
Low M	0.1	17.7	26.4	3.1×10^4	2200
Low M	0.15	17.7	26.5	2.6×10^4	2300
Low M	0.2	16.4	26.8	1.2×10^4	2000
High M	0.1	18.3	31.9	3.1×10^6	8.7×10^4
High M	0.15	16.6	21.3	1.7×10^6	7.3×10^4
High M	0.2	15.8	32.7	7.7×10^5	3×10^4
High M	0.3	25.4	39.1	4.8×10^4	2800
High M	0.4	25.0	43	3×10^4	3000
High M	0.5	21.7	46	2.5×10^4	5000

From the values of η_3 given in this table, determine the stress dependence of the steady state creep rate. From this stress dependence, calculate the activation volume for non-recoverable creep in the high and low molecular weight samples, and compare these values to one another.

51) Creep in metals at low stresses occurs by a vacancy diffusion mechanism, which means that the activation volume for these creep mechanisms corresponds to the atomic volume. Show using the data below for silver that we can safely replace sinh $(\sigma v / 2 k_B T)$ with $\sigma v / 2 k_B T$, so that the creep rates are linear in stress at all relevant temperatures and stresses where the dominant creep mechanisms involve vacancy diffusion. (You'll need to look up data you can use to calculate the atomic volume of silver).
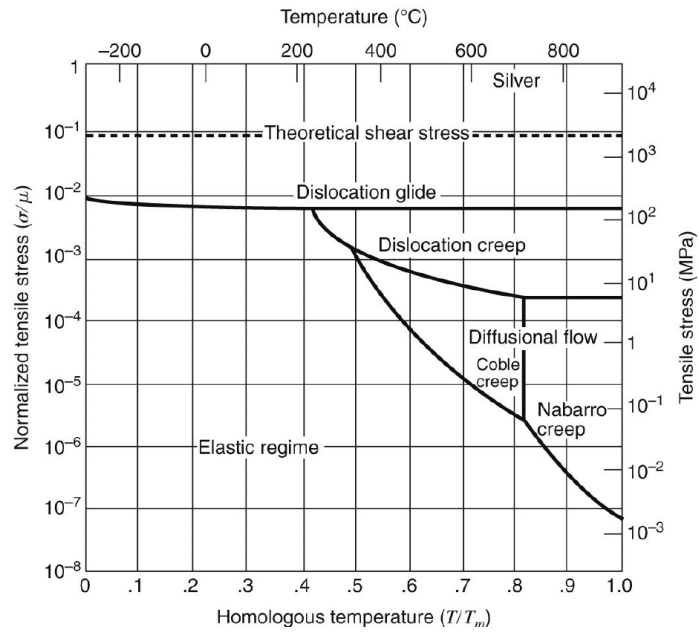
7   331 Problems

Basic chemistry review

Some basic problems having to do with the chemical structures of polymers.

1)   Calculate the repeat unit molecular weights for each of the 22 polymers shown in the 'common polymers' section of the text.

2)   Draw Lewis diagrams illustrating the valence shell configurations for polystyrene, poly(methyl methacrylate) and poly(dimethylsiloxane).

3)   Draw Lewis diagrams illustrating the valence shell configurations for amide, ester and urethane linkages.

Polymerization Reactions

4)   Suppose a polyester is formed by combining 1.00 mol of a diacid (2 acid groups per molecule) with 1.01 mol of a dialcohol in a homogeneous solution. The molecular weight of the diacid is 160g/mol and the molecular weight of the dialcohol is 180 g/mol.

  (a) What is the highest value of M_n that can be expected from this combination?

  (b) How many grams of water will be produced during the polymerization reaction?

5)   Consider the following 5 monomers:
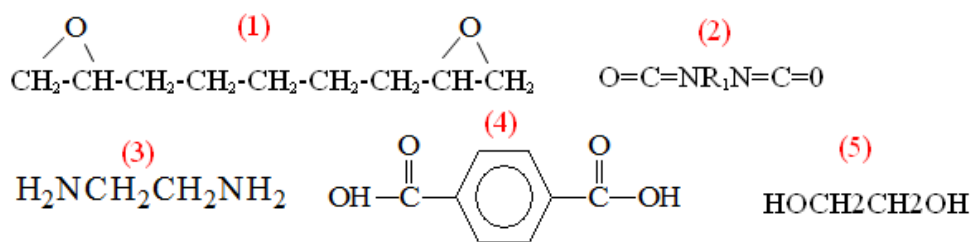
  (a) Draw the repeat units for three linear polymers that can be produced by reactions between the monomers in this list. Identify these polymers according to their type (polyamides, polyesters, etc.), and indicate whether each polymerization reaction is condensation reaction or not.

  (b) What combination of monomers from this list would you choose in order to produce a three-dimensional network?

  (c) Draw the repeat unit structure of a linear polyamide formed by a condensation polymerization involving a combination of the molecules from this list, and identify the condensation product.

6)   Suppose a diamine (primary amines at each of the molecule) is reacted with a di-epoxide (epoxide groups at each end of the molecule).

  (a) What ratio of diamine molecules to di-epoxide molecules would you use in order to optimize the ability of the system to gel (i.e., form a network)?

  (b) Estimate the fraction of amine groups will need to react in order for a gel to form? Identify any assumptions that you have made in arriving at this number.

7)   Why is tacticity relevant for polystyrene or polypropylene, but not polyethylene?

8) Describe methods that could be used to make the following two block copolymers:

(a) A polystyrene/polyisoprene diblock polymer

(b) A mutiblock copolymer consisting of alternating Nylon 6-6 and Nylon 6-10 blocks.

(c) Comment on the polydispersity of block lengths, and of the number of blocks within a molecule, which can obtained by the methods described in parts a and b.

9) A step-growth reactions takes place between 1.2 moles of dicarboxylic acid, 0.4 moles of glycerol (a trifunctional alcohol) and 0.6 moles of ethylene glycol (a difunctional alcohol). Calculate the critical extent of reaction for gelation using the Carothers theory. Describe why you would expect gelation to occur for values of p that are different from this predicted value. (Hint: you will need to generalize the expression for the average functionality, f_{av}, to include the possibility of more than two different monomers.)

10) In 1963 Karl Ziegler and Giulio Natta received the Nobel prize in chemistry for the development of processes which could be used to produce (among other things) linear, unbranched isotactic polypropylene. Why was this an important development? What useful properties does isotactic polypropylene have when compared to atactic polypropylene? Describe some applications where isotactic polypropylene could be used, but where it would be impractical to use atactic polypropylene. (Note: the glass transition temperature of both forms of polypropylene is well below room temperature.)

11) "Living" polymerizations are chain growth polymerizations that proceed without termination or chain transfer reactions.

(a) Discuss the conditions that must be met in order for polymers with a low polydispersity to be formed by a living polymerization.

(b) What type of reactions must be avoided in order to produce block copolymers by radical chain growth polymerization.

(c) Proteins are perfectly disperse copolymers, with a polydispersity index of exactly 1. While relatively monodisperse polymers ($M_w/M_n < 1.05$) can be made by living polymerization methods like anionic polymerization, it is not possible to make perfectly monodisperse polymer by these methods, even when termination and chain transfer events are completely eliminated. Why is that?

12) Suppose 100 moles of styrene monomer are polymerized by anionic polymerization, using 0.1 mole of initiator.

(a) Draw the repeat unit structure of the polymer which is formed in this reaction.

(b) Below what temperature will this polymer behave as a rigid material?

(c) Suppose that there are no chain transfer or termination events during the resulting polymerization. Calculate the number average molecular weight (M_n) of the polymer that is produced.

13) Suppose nylon is formed in two separate batches by reacting the same sets of monomers with one another. In the first reaction, an extent of reaction of 0.999 is obtained. In the second reaction, an extent of reaction of 0.9999 is obtained. Assume that an ideal distribution of molecular weights is obtained for each reaction.

(a) What is the ratio of M_w for the second reaction to M_w for the first reaction?

(b) Suppose equal weights of the polymers formed by these two reactions are mixed with one another. What is the polydispersity index of the resultant mixture?

14) Draw the chemical structures of the monomers from which the following polymers are formed.

(a)

(b)

(c)

(d)

(e)

(f)
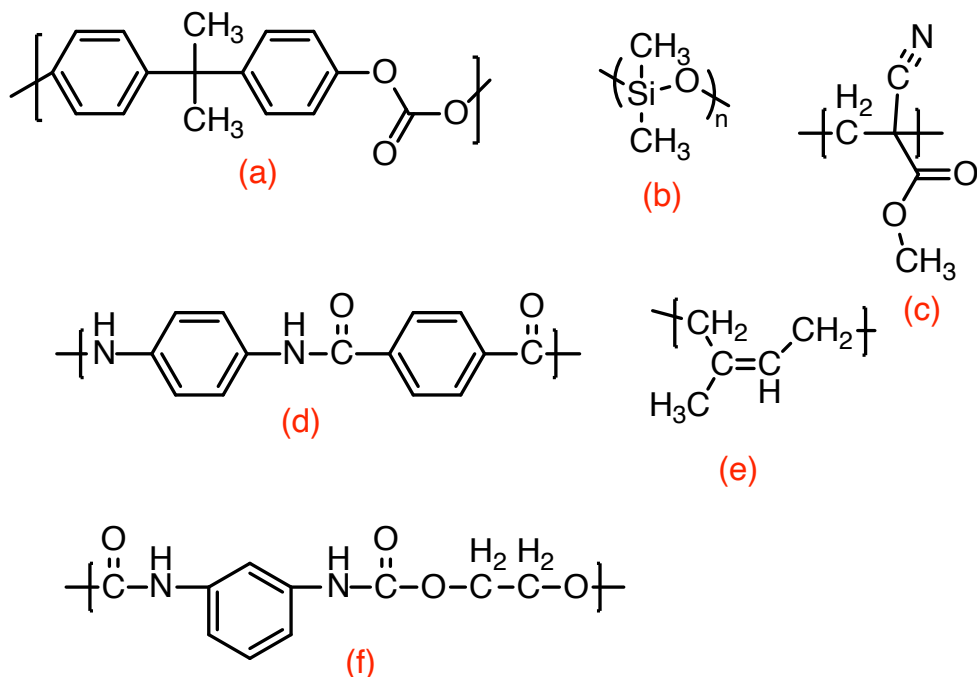
15) Suppose you want to sell a set of cheap plastic mugs which are suitable for drinking coffee. Briefly discuss the potential applicability of the following materials for this purpose:

(a) atactic polystyrene

(b) atactic poly(vinyl chloride)

(c) high density polyethylene

16) Consider the the piece of the highly crosslinked chemical structure shown below.

(a) Draw the chemical structures of the two different monomers that were used to form this material. (Note that the R groups just represent connections to the rest of the material, they are not part of the structures you need to draw).
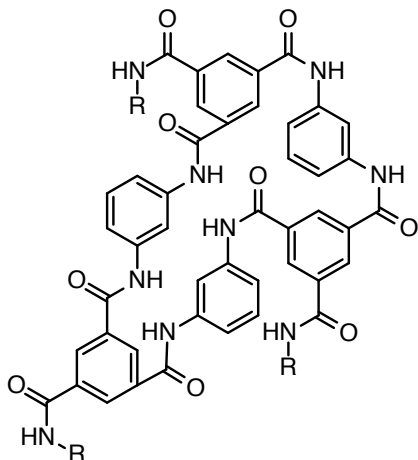
(b) What type of polymer is this (polyester, polyamide, polyurethane, epoxy, etc.)

(c) Next to each structure that you have drawn in part a, indicate its chemical functionality.

(d) What is the relative amount of each of the two monomers from part a (in moles) that you should be added to one another to optimize the polymerization?

(e) Assuming that the two monomers are added together in optimum proportions you mentioned in part d, what fraction of reactive groups need to react to form an insoluble gel.

The Glass Transition

17)   An amorphous polymer has $T_\infty = 50°C$. The thermal expansion coefficient in the glassy state is $3 \times 10^{-4}/°C$, and the thermal expansion coefficient in the liquid state is $4.5 \times 10^{-4}/°C$.

   (a) Calculate the glass transition temperature if the fractional free volume at the glass transition is 0.025.

   (b) The glass transition temperature measured at a different cooling rate is found to correspond to a fractional free volume of 0.021. Is this cooling rate higher of lower than the cooling rate from part a?

   (c) Rank these three polymers in the order of high T_g to low T_g, and provide an explanation for your prediction:

<div align="center">Polystyrene   Poly(para butylstyrene) Poly(α-methylstyrene)</div>
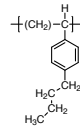
18)   The DSC curves below correspond to the 3 polymers listed below. Identify which is which, and identify on the curves any crystallization (T_c), glass transition (T_g) or melting (T_m) temperatures, and give your reasoning in each case.
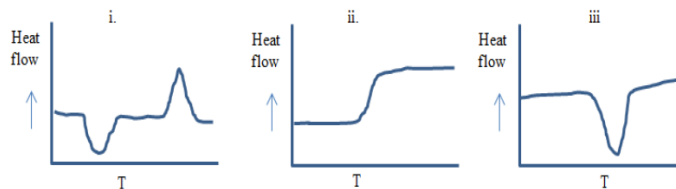
   (a) Atactic polystyrene being heated from room temperature to 200^oC.

   (b) High density polyethylene being cooled from 200^oC to room temperature.

   (c) Poly(ethylene terephthalate) that had originally been cooled rapidly from 300^oC to room temperature, and is now being slowly heated from room temperature back up to 300^oC.

19)   Short, bulky side groups (like methyl of phenyl groups) increase the fractional free volume required for the motion of polymer chain segments, whereas long, thin groups (like the n-butyl group $-CH_2CH_2CH_2CH_3$) increase the available free volume.

   (a) Describe how each of these two types of groups is expected to affect the glass transition temperature.

   (b) Polymers with very little flexibility along the backbone of the polymer chain have very high glass transition temperatures. Give a brief explanation for this in terms of free volume theory.

Chain Dimensions

20)   The value of R_0, the rms (root mean squared) end-to-end distance for a polystyrene molecule in the bulk material (no solvent) is 200Å. The molecular weight, M, of this molecule is 100, 000 g/mol.

   (a) What is the rms end-to-end distance for a polystyrene molecule with M=250,000 g/mol?

   (b) What is the characteristic ratio (C_∞) for polystyrene?

   (c) What is the statistical segment length (equivalent length of a repeat unit in a random walk model of chain dimensions) for polystyrene?

   (d) The volume pervaded by a single molecule is given approximately by R_0^3. For a polystyrene molecule with M=250, 000 g/mol, compare this volume to the volume actually occupied by the polystyrene molecule. How many different molecules overlap with one another in polystyrene with this molecular weight?

   (e) Consider a simple model of polystyrene for which all of the bonds are in either gauche or trans configurations. What fraction of bonds are in the trans configuration?

<div align="center">93</div>

21) Consider a simple model for the chain dimensions of amorphous poly(vinyl chloride) where only trans and gauche bonds are possible.

Poly(vinyl chloride)	Trans Configuration	Gauche Configuration
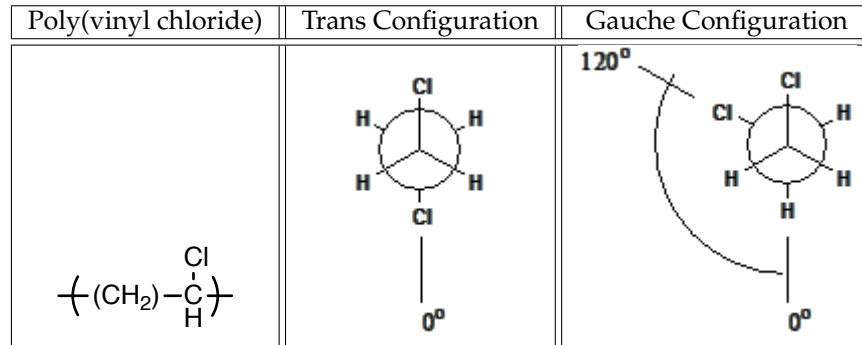
(a) What fraction of the backbone bonds are in the gauche configuration if C_∞ for the polymer is 8?

(b) Calculate the statistical segment length of a repeat unit, assuming the value of C_∞ from part a.

22) What fraction of molecules in an equilibrated amorphous polymer melt have end-to-end vectors with magnitudes larger than the root-mean-square end-to-end distance? (note – this will require a numerical or graphical solution.)

Mechanical Properties

23) A thermoset is cooled to a very low temperature. As the temperature is increased, the elastic modulus remains roughly constant until T_g, at which point the elastic modulus rapidly decreases. Above the glass transition temperature the elastic modulus slowly increases. Describe in qualitative terms what is going on at the glass transition, and why the modulus actually increases slightly above T_g.

24) Values of Young's moduli (E) for elastomers are typically near 10^6 Pa (1 MPa).

(a) What is the average molecular weight between crosslinks for a polymer with this value of E? Assume the polymer has a specific gravity of 1. What fraction of cis 1-4 polyisoprene repeat units contain crosslinks if the modulus is 10^6 Pa?

(b) Plot the predicted tensile stress/strain curve for this material for engineering strains from -0.5 to 2 (extension ratios from 0.5 to 3).

25) The yield point of a material is often defined as the onset of nonlinear behavior in the stress-strain curve. Can this definition be used for an elastomeric material that is deformed in tension? Why or why not?

26) Suppose a sample of Sylgard 184 is cured, and the degree of polymerization of the prepolymer is 60. Estimate the value for both the shear modulus and Young's modulus of this polymer. Describe any assumptions that you've made.

27) Consider the deformation behavior of a uniaxially stretched rubber.

(a) Plot the free energy of a uniaxially stretched rubber as a function of the extension ratio from $\lambda = 0.1$ (compressive strain to $\lambda = 4$ (tensile strain). (The extension ratio of interest here corresponds to the direction in which the rubber is stretched.)

(b) At what value of the strain is the free energy minimized?

(c) For what compressive value of the extension ratio is the free energy of the rubber equal to the free energy it has for an extension ratio equal to 4?

28) Calculate the force required to fix the ends of a 1,4 polyisoprene molecule with M = 100,000 g/mol at the separation of 1000Å. Assume $C_\infty = 8$, and that the double and single bonds have equal lengths of 1.54 Å.

29) Consider a material which is defined between two circular plates that are parallel to one another. Each plate has a diameter of 2.5 cm, and the plates are separated by 1mm.

(a) Calculate the maximum shear strain at the outer periphery of the disks, if the top disk is rotated by 1° with respect to the bottom disk.

(b) Calculate the torque required to rotate the top plate by1°, in terms of the magnitude of the complex shear modulus,$G*$. (You will need to integrate contributions from all portions of the disk, keeping in mind that the local stress is equal to the shear modulus multiplied by the local strain.)

(c) Suppose the material between the two plates is a purely viscous fluid ($G' = 0$ at the appropriate frequency), and that the viscosity of the fluid is 1000 Pa-sec. Calculate the magnitude of the torque which must be applied to give a sinusoidal rotation with a magnitude of1°. Assume that the angular frequency of the applied torque is 100 radians/second.

30) Consider a polymer with a density of 1g/cm^3 that has the following relaxation modulus at room temperature (the molecular weight is much higher than the average molecular weight between entanglements).

$$G(t) = G_1 \exp\left(\frac{-t}{\tau_1}\right) + G_2 \exp\left(\frac{-t}{\tau_2}\right)$$

Suppose$G_1 = 10^9$ Pa, $G_2 = 3x10^5$ Pa, $\tau_1 = 10^{-6}$ s and $\tau_2 = 1$ s.

(a) Calculate the zero shear viscosity for this polymer.

(b) Is this polymer crosslinked? How do you know?

(c) Calculate the average molecular weight between entanglements.

(d) Describe what happens toτ_1 andτ_2 when the temperature is increased (do they remain constant, increase or decrease)?

(e) What vibrational frequencies do you expect to be most efficiently damped by this polymer?

(f) Describe what happens toτ_1 andτ_2 when the molecular weight of the polymer is increased (do they remain constant, increase or decrease)?

31) Consider a polymer with the behavior of the relaxation modulus ($G(t)$) and temperature shift factor(a_T) plotted below. Assume the polymer has a density of 1 g/cm^3.
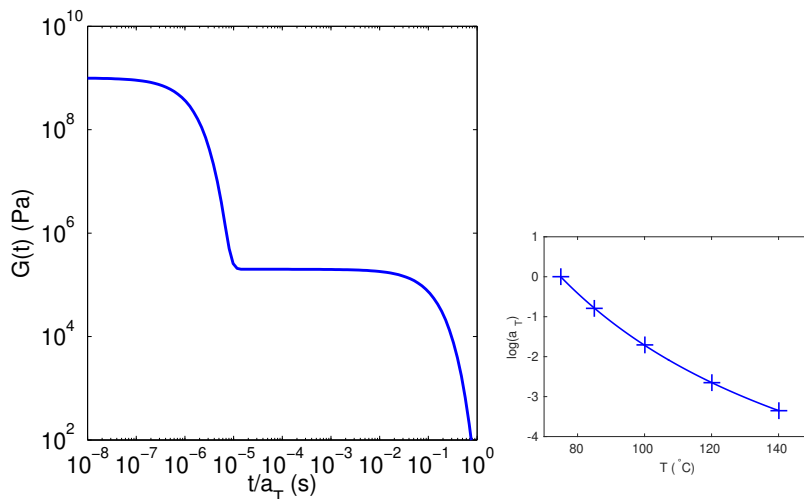
(a) Describe in qualitative terms what is going on at each of the two characteristic values of t/a_T where $G(t)$ decreases substantially.

(b) Is this polymer crosslinked? Briefly explain your answer.

(c) Estimate the entanglement molecular weight for this polymer.

(d) Estimate the viscosity of this polymer that is obtained at very low shear rates, at a temperature of 40°C.

(e) What is the ratio of viscosity of the polymer at -40°C to the viscosity at 40°C?

(f) Suppose that $G'(\omega)$ is measured at a very high frequency of 10^9 s^{-1}. What value of G' do you expect to obtain from this experiment?

32) Use the PtBA data in the appendix to address the following:

(a) Determine the shift factors as a function of temperature for poly(t-butyl acrylate) (PtBA), using 75°C as the reference temperature. Plot these shift factors as a function of temperature, and determine a value for T_∞ by fitting to the Vogel equation. Compare this value of T_∞ to T_g for PtBA. Values of G' and G'' at different temperatures are included in the data tables at the end of the text.

(b) Determine the zero shear viscosity of PtBA with M=350,000 g/mol at 75°C.

(c) Determine the entanglement molecular weight, M_e, for PTBA. Assume a density of 1 g/cm^3 for PtBA.

33) Using the appendix data for poly(2-vinylpyridine), repeat the previous 3 sub-problems for poly(2-vinylpyridine) with a molecular weight of 82,000 g/mol, using 160°C as the reference temperature (where $a_T = 1$), and 130° C for the viscosity calculation.

34) An elastomer is made from a poly(n-butyl acrylate) precursor molecule with double bonds at either end that are able to react with a tetrafunctional crosslinker. The chemical structure is shown at the left below, and a schematic representation of the crosslinked structure is shown at the right.

Crosslinks

n = 100
M_0 = 128 g/mole
density = 128 g/cm^3
a = 0.7nm
T_g = -45°C
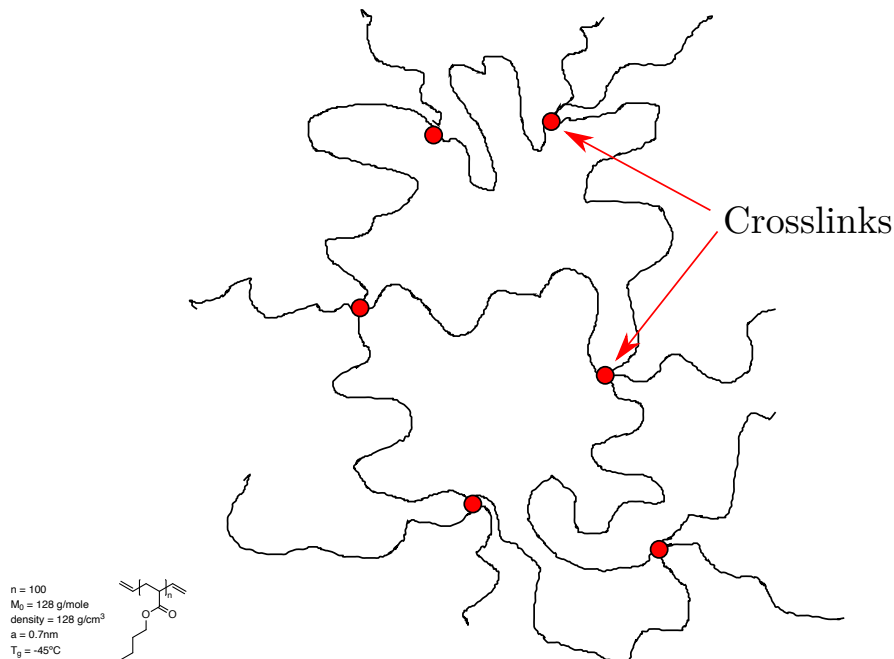
(a) Calculate the shear modulus, G, for this material at room temperature.

(b) Give Young's modulus (E) and the Poisson's ratio (ν) for this material.

(c) What is the root mean square end-to-end distance $\langle R^2 \rangle^{1/2}$ for crosslink points at either end of the one of the precursor chains when the material is in its undeformed state?

(d) What is the value of C_∞ for poly(n-butyl acrylate)?

(e) Express the deformation free energies of the elastomer, divided by the shear modulus, G, for the following strain states:

    i Simple shear at a shear strain, γ, of 1.

    ii Uniaxial extension to an engineering strain of 100 % ($\lambda = 2$).

    iii Uniaxial compression to a engineering strain of -50% ($\lambda = 0.5$).

35) For each if the following pairs of quantities, circle the **largest** one. If you expect them to have the same value, write 'same'.

quantity 1	quantity 2
The thermal expansion coefficient of poly(n-butyl acrylate) at temperatures **above** -45 C.	The thermal expansion coefficient of poly(n-butyl acrylate) at temperatures **below** -45 C.
the free volume for a poly(n-butyl acrylate) sample **above** -45 C.	the free volume for a poly(n-butyl acrylate) sample **below** -45 C.
The **free energy** of an undeformed poly(n-butyl acrylate) sample.	The **free energy** of poly(n-butyl acrylate) sample at a shear strain of 0.3
The **entropy** of an undeformed poly(n-butyl acrylate) sample.	The **entropy** of poly(n-butyl acrylate) sample at a shear strain of 0.3
T_g for poly(n-butyl acrylate)	T_g for poly(methyl acrylate) (where the 4-carbon butyl group in poly(n-butyl acrylate) is replaced by a methyl group.

Crystallinity

36) Consider a polyethylene molecule with a molecular weight of 150,000 g/mol.

(a) Estimate the number of times the molecule folds back on itself within a lamellar crystallite with a thickness of 100 Å. Assume for the purposes of this calculation that the molecule remains in the crystallite, and does not move into the amorphous regions of the polymer.

(b) From your answer to part a, what can you say about the ability to stretch a polymer molecule in a semicrystalline polymer without breaking any bonds?

37) Describe how axis of the unit cell in polyethylene is oriented with respect to a spherulite, with respect to an individual lamellar crystallite, and with respect to the molecular chain axis.

38) Consider a polymer that crystallizes with an orthorhombic unit cell (all angle= 90°). The polymer has a carbon backbone, and crystallizes with a 4*1/1 helical structure. The unit cell dimension are a=10.4Å, b=5.3Å with 1.27Å per backbone carbon along the c axis. The molecular weight of a polymeric repeat unit is 125 g/mol, and there are two of these units per unit cell.

(a) What is the theoretical density of a completely crystalline version of this polymer (100% crystalline)?

(b) The percent crystallinity of a sample with a density of 1.35 g/cc is 60%. What is the density of the amorphous regions of this polymer?

39) Poly(ethylene terephthalate) has a relatively high equilibrium melting point (265 °C), but the polymer at room temperature is almost completely amorphous. Based on this result, do you expect that T_g for PET is above room temperature or below room temperature? Explain your reasoning.

40) Consider two perfect single crystals of polyethylene and polypropylene. Polypropylene forms a 3/1 helix, and polyethylene forms a 2/1 helix. Which of these single crystals would you expect to have a higher modulus along the C axis? Include in your discussion the relative importance of bond bending and bond rotation during elastic deformation of the two materials. Also mention the importance of the lateral packing (i.e., the number of helices per unit area in the AB plane).

41) High density polyethylene has an equilibrium melting temperature of 138 °C. Two identical batches of this polymer are crystallized at different temperatures: one at 100 °C and one at 125 °C. Describe one important difference in the resulting structures of these two semicrystalline polymers, and explain the origin of the difference.

42) A linear homopolymer was crystallized from the melt at crystallization temperatures (T_c) within the range 270K to 330K. Following complete crystallization the following melting temperatures (T_m) were measured by differential scanning calorimetry (DSC).

Given:

T_c(K)	T_m(K)
270	300
280	306.5
290	312.5
300	319.0
310	325.0
320	331.0
330	337.5

Graphically determine the equilibrium melting temperature, T_m^0.

43) Small angle x-ray scattering experiments using x-rays with a wavelength of 1.54 Å were used to measure the distance between crystalline regions. Peaks corresponding to the lamellar period were obtained at the following angles:

$T_c(K)$	$\theta(degrees)$
270	0.44
280	0.39
290	0.33
300	0.27
310	0.22
320	0.17
330	0.11

(a) Use the Bragg equation to calculate the values of the lamellar period for each crystallization temperature.

(b) The degree of crystallinity was measured to be 45% for all samples. Calculate the lamellar thickness in each case, and use this information to graphically obtain the fold surface energy, γ_e. Assume the enthalpy of fusion of the polymer is $150J/cm^3$, and the value of the equilibrium melting temperature from the previous problem.

44) Poly(ethylene oxide) (PEO) is a semicrystalline polymer with melting point of 65°C and a glass transition temperature of -60°C. Suppose a series of crystalline samples is made by performing the crystallization at temperatures of 40°C and 60°C.

(a) Describe any differences you expect rate of crystallization, and the crystal thickness ℓ_c, at these two temperatures. Be as quantitative as possible.

(b) Suppose the two samples are slowly heated. Describe any differences you expert to observe in the melting temperatures for these two samples.

(c) PEO is always crystalline at room temperature, but PET is often amorphous at room temperature, even though PET has a much higher melting temperature than PEO. Why is this?

Liquid Crystals

45) Consider the liquid crystalline texture from the nematic liquid crystal texture page of a nematic liquid crystalline material confined between two crossed polarizers.

(a) Give an example of the type of defect that can lie at the places where 4 dark bands come together. (show how the molecules are oriented in these regions)

(b) Describe why alternating light and dark bands emanate from these defect points.

(c) Is it possible to obtain a completely black image from a sample that has good nematic order? If so, describe a situation where this would be the case.

Thermodynamics of Solutions and Blends

46)   Which contribution to the free energy (enthalpy of entropy) dominates at low temperature?

47)   What are the signs of $\triangle h_{mix}$ and $\triangle s_{mix}$ for a system which has an LCST phase diagram?

48)   For what values of χ will a polymer be able to completely dissolve in a small-molecular solvent?

49)   Measured values of χ for a blend of polymer A with polymer B have the following temperature dependence:

$$\chi = \frac{0.326}{T} - 2.3 \times 10^{-4}$$

where T is the absolute temperature.
Consider a blend with $N_a = 2500$, $N_b = 3500$

(a) What is the predicted critical composition, and the predicted critical temperature for this blend?

(b) Plot free energy curves (free energy as a function of composition) for $\chi/\chi_{crit} = 1.1, 1.2, 1.3, 1.4$, and 1.5. Using the common tangent construction from these five curves, construct a phase diagram with χ/χ_{crit} on the vertical axis and the blend composition on the horizontal axis.

50)   Consider the following phase diagram:
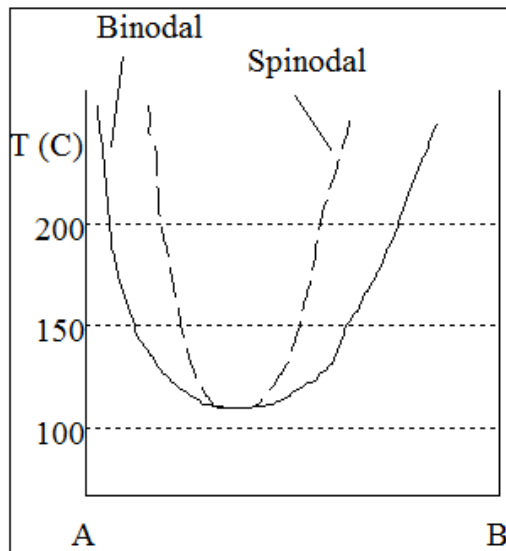
(a) Is the enthalpy of mixing positive or negative for this system?

(b) Is the entropy of mixing positive or negative for this system?

(c) Draw free energy of mixing vs. composition curves at 100°, 150°, 200° that are consistent with this phase diagram. Show any common tangents points and points of inflection.

51) Consider a polymer/solvent mixture for which the ratio of polymer to solvent volume is 10,000.

(a) Determine the critical value of the chi parameter (χ_{crit})

(b) What is polymer volume fraction at the critical point?

(c) Plot the solvent chemical potential for this system as a function of polymer volume fraction for $\chi/\chi_{crit} = 0.9$, $\chi/\chi_{crit} = 1.0$, $\chi/\chi_{crit} = 1.2$, $\chi/\chi_{crit} = 1.5$.

(d) Suppose that the polymer is dipped into a pure solvent (solvent chemical potential equals zero). Solvent will diffuse into the polymer until the solvent chemical potential in the polymer reaches zero. From the plots made for part c, determine the equilibrium solvent volume fractions for $\chi/\chi_{crit} = 1.2$, and $\chi/\chi_{crit} = 1.5$.

52) Describe in your own words why most pairs of different types of polymers do not mix with each other in the liquid state.

53) Most liquids mix better at high temperatures than they do at low temperatures. However, polymeric liquids often mix better at low temperatures than high temperatures. Explain in as much detail as possible why this is the case.

54) Consider the following osmotic pressure data obtained for polyethylene oxide solutions in water (1MPa $=10^6$ Pa) at 20 °C.

ϕ_P	$\Pi(MPa)$
0.0457	0.0411
0.0917	0.145
0.138	0.346
0.185	0.685
0.232	1.212
0.280	2.010
0.329	3.161
0.377	4.868
0.427	7.323
0.476	10.77
0.516	14.54

(a) Plot the osmotic pressure as a function of the polymer volume fraction, using logarithmic axes for both the pressure and the polymer volume fraction. On the same plot, include the Flory Huggins expression for Π, using the value of χ that gives the best fit to the data.

(b) Repeat part a, but now compare the data to the scaling expression for ϕ in the semidilute regime (Eq.), where a_o^3/v_s is the adjustable parameter. (Note that v_s is the solvent molecular volume, obtained from the molar volume, V_s, by dividing by N_{av}).

55) Use the PEO solution data from the previous problem to calculate the following:

(a) The concentration of PEO at 20°C that gives an osmotic pressure large enough to support a column of water that is 100 meters tall.

(b) What is the correlation length ξ, for a PEO solution in water with $\phi_P = 0.1$?

56) For charged molecules, the osmotic pressure is often dominated by the counterions. Suppose a solution of sodium polyacrylate at a concentration of 0.05 g/cm^{3}is made in water. Estimate the osmotic pressure, assuming that the counterions can be treated as an ideal gas.

57) The interfacial free energy characterizing the interface high molecular weight versions of polystyrene (PS) and poly(2-vinyl pyridine) (P2VP) is $3x10^{-3}$ J/m^2 at 180 °C. Assume the volume per repeat unit is the same for both polymers (165Å^3, and use this as your reference volume. Also assume that the statistical segment length for both polymers is 6.7 Å.

<div align="center">PS   P2VP</div>

(a) What is χ for the PS/P2VP system at 180 °C?

(b) Suppose PS and P2VP polymers with equal degrees of polymerization are mixed with one another. What range of molecular weights will form mixtures that are completely miscible with one another at all compositions at 180 °C?

(c) Suppose monodisperse PS and P2VP samples with degrees of polymerization of 1000 are mixed with one another. What is the solubility of the PS in the P2VP at 180 °C? (hint: for a symmetric system like this, where both degrees of polymerization are equal to one another, the common tangent construction is satisfied at the point where the first derivative of the free energy of mixing with respect to volume fraction is equal to zero).

58) Use the data from the PS/P2VP system from the previous problem to answer the following questions:

(a) A diblock copolymer is synthesized that has a PS block with a degree of polymerization of 500 attached to a 2nd block with a degree of polymerization of 500. Calculate the periodicity of the lamellar structure that is formed by this material at equilibrium.

(b) Describe in qualitative terms the equilibrium geometries of the structures formed when the P2VP block length is fixed, but the PS block degree of polymerization is steadily increased.

59) Poly(n-isopropylacrylamide) (chemical structure shown below) exhibits a lower critical solution temperature in water. It is fully soluble in water at temperatures below 32°C, but the phase diagram with water has a two phase region for temperatures above 32°C.

(a) The temperature dependence of χ for the Poly(n-isopropylacrylamide)/water system can be written in the following form: $\chi = A + BT$, where A and B are constants and T is the temperature in °C. What is the sign (positive or negative) of B in this equation?

(b) Is the entropy of mixing for this system positive or negative? Briefly explain your answer.

(c) Calculate the osmotic pressure of an aqueous solution of high molecular weight poly(n-isopropylacrylamide) with a polymer volume fraction of 0.2.

Capillarity

60) A hollow glass tube is immersed in water as shown in the illustration below:
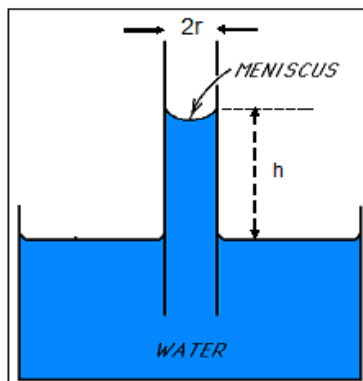
(a) Calculate the internal tube diameter that gives a capillary rise of 10 cm, assuming that water completely wets the glass (contact angle of zero).

(b) Calculate the capillary rise if the same glass tube from part a is coated with a thin layer of polystyrene, changing the contact angle to 90° .

61) Answer the following:

(a) Calculate the force required to push a cylindrical fiber with a radius of 1 μm into water, if the contact angle the fiber makes with the water is 130°.

(b) What stress can be supported if you create an array of these fibers on a square lattice, with a spacing between fiber centers of 4 μm? (Assume the density of the fibers is equal to the density of water, so you don't need to worry about forces due to buoyancy).

(c) How much weight could be supported by an object like this with a total area of 1 cm^2?

331 Computational Exercises

62) In binary blends where the two components have very different molar volumes (often the case with polymers), the following form of the free energy expression is commonly used:

$$\frac{v_0 G_v}{k_B T} = \frac{\phi_b ln \phi_b}{N_b} + \frac{(1 - \phi_b) \ln (1 - \phi_b)}{N_a} + \chi \phi_b (1 - \phi_b)$$

The expressions for the chemical potentials for the A and B molecules are given by the following expression:

$$\frac{\mu_a}{k_B T} = \ln (1 - \phi_b) + \phi_b (1 - N_a/N_b) + \chi N_a \phi_b^2$$

$$\frac{\mu_b}{k_B T} = \ln (\phi_b) + (1 - \phi_b) (1 - N_b/N_a) + \chi N_b (1 - \phi_b)^2$$

Here G_v is the free energy per volume, ϕ_b is the volume fraction of B in the system, and N_a and N_b are proportional to the molecular volumes of the two components. The quantity v_0 is a reference volume, so the molecular volume of the 'A' molecule is $v_0 N_a$ and the molecular volume of the 'B' molecule is $v_0 N_b$. Adapt the MATLAB script below to do the following:

```
1  global na nb chi % these values also get used in function definitions
2  set(0,'defaultaxesfontsize',16)
3  set(0,'defaultlinelinewidth',2)
4  phi=linspace(0.001,0.999,1000);
5  na=150;
6  nb=100;
7  chi=0.02;
8  % fv is the expression for the free energy of mixing
9  fv=@(phi) phi.*log(phi)/nb+(1-phi).*log(1-phi)./na+chi.*phi.*(1-phi);
10
11 %mua and  mub are the chemical potentials of A and B
12 mua=@(phi) log(1-phi)+phi*(1-na/nb)+chi*na*phi.^2;
13 mub=@(phi) log(phi)+(1-phi)*(1-nb/na)+chi*nb*(1-phi)^2;
14
15 % now write the function that is equal to zero when the A and B chemical
16 % potentials are equal to one another for phi=phi(1) and phi=phi(2)
17
18 ftosolve=@(phi) [mua(phi(1))-mua(phi(2));
19     mub(phi(1))-mub(phi(2))];
20
21 plot(phi,fv(phi));
22 xlabel('\phi_{b}')
23 ylabel('G_{v}V_{0}/RT')
24
25 % start with a guess for the equilibrium volume fractions
26 phiguess = [0.2; 0.8];    % Make a starting guess at the equilibrium compositions
27 [phicalc,fval] = fsolve(ftosolve,phiguess);  % Call solver
28
29 % now we add the tangent line
30 slope=(fv(phicalc(2))-fv(phicalc(1)))/(phicalc(2)-phicalc(1));
31 intercept=fv(phicalc(1))-slope*phicalc(1);
32 tangentline=intercept+slope.*phi;
```

```
33  hold on
34  plot(phi,tangentline,'r')
35  hold off
36  title(['\chi=' num2str(chi) ', N_a=' num2str(na), ', N_b=' num2str(nb)], 'fontsize', 11)
37
38  % now save the plot as a jpg file
39  saveas(gcf,'commontangent.jpg');
40
41  % this saves the file a .eps file, used to embed the figure into the
42  % solution set - students can comment out this next line if they don't wan
43  % the .svg file
44  print(gcf,'-dsvg','commontangent.svg')
```

(a) Plot the free energy expression $\chi = 0.02$, $N_a = 200$, and $N_b = 100$, along with its common tangent construction, and report the values of the equilibrium compositions of the two phases. Include the plot with your solution.

(b) Repeat the previous calculation for $\chi = 0.025$ and $\chi = 0.05$ (you may need to adjust the initial guess for the volume fractions).

(c) Decrease χ to the critical value, χ_{crit}, which can be calculated analytically. Include a plot of G_v as a function of ϕ_b for value of χ.

63)　　Extend work from the previous problem to obtain a MATLAB code that generates the full phase diagram (with χ on the vertical axis and ϕ_b on the horizontal axis) for a system with $N_a = 200$ and $N_b = 100$. Show both the bimodal and spinodal curves, and turn in a printout of your actual MATLAB code. **Hint:** You'll want to solve the equations for a variety of χ values above the critical value of χ, which you can calculate analytically. You can use a 'for' loop in MATLAB to do this. Calculation of the spinodal curve is pretty easy, because there's an analytic expression for that. When you're developing your initial guesses for the bimodal compositions to pass to the 'fsolve' command, keep in mind that the bimodal compositions must lie outside the spinodal compositions. This can help you develop sensible guesses to use for this quantity.

8   351-1 Problems

(1) Newton's Laws Can be derived from Hamilton's equations.

    a) Identify the Hamiltonian from conservation of energy using only momentum p (for Kinetic Energy) and position x (for potential Energy):

$$H = KE + PE$$

    Use the Hamiltonian for a particle in a 1-D quadratic potential like a mass on a spring. What is KE, PE?

    b) Hamiltion's equations are

$$\frac{dp}{dt} = -\frac{\partial H}{\partial x}$$
$$\frac{dx}{dt} = \frac{\partial H}{\partial p}$$

    Show these give Newton's laws of motion for the mass on a spring.

    c) Derive the 1-D differential equation of motion from Hamilton equation. For a particle of total energy E and spring constant $k, x = 0$ at $t = 0$, what is the equation of motion $x(t)$. what is $p(t)$. show the region of Phase Space (p vs x) that describes the particle throughout its motion.

    d) Use the equipartition theorem (where <A> is time average of A, and i is index for each spatial dimension):

$$\left\langle p_i \frac{\partial H}{\partial p_i} \right\rangle = \left\langle x_i \frac{\partial H}{\partial x_i} \right\rangle = k_B T$$

    to derive the relationship between thermal velocity and temperature $\frac{1}{2}mv_{th}^2 = \frac{3}{2}k_B T$

    e) Derive the Dulong-Petit law for atoms in a 3-D potential from the equipartition theorem:

$$\langle E \rangle = 3k_B T$$

    f) What is the heat capacity $C = dE/dT$ in this case?

(2) Problem 1.1 from Solymar and Walsh:

A 10 mm cube of germanium passes a current of 6.4 mA when 10 mV is applied between two of its parallel faces. Calculate the resistivity of the sample. Assuming that the charge carriers are electrons that have a mobility of 0.39 $m^2 V^{-1} s^{-1}$, calculate the density of carriers. What is their collision time if the electron's effective mass in germanium is 0.12 m_e where m_e is the free electron mass?

(3) Give a one line description of each of these experiments and their significance to modern physics: Photoelectric Effect, Compton Effect, Black Body Radiation, Rutherford Backscattering (Bohr model), Electron Diffraction, Atomic spectra.

Classical: https://www.youtube.com/watch?v=yXsHflXB7QM

Bohr Atom: https://www.youtube.com/watch?v=ydPzEZTd-98

Wave Particle Duality - photoelectric effect: https://www.youtube.com/watch?v=frNLtEm1glg

Schrödinger waves: https://www.youtube.com/watch?v=C8XGIYz1PCw

Probability interpretation: https://www.youtube.com/watch?v=p7xIKoBdViY

Compton Effect: https://www.youtube.com/watch?v=0Y648TNGAIo

(4) Problem 2.1 from Solymar and Walsh.

Find the de Broglie wavelength of the following particles, ignoring relativistic effects:

(i) an electron in a semiconductor having average thermal velocity at $T = 300K$ and an effective mass of $m_e^* = am_o$,

(ii) a helium atom having thermal energy at $T = 300K$

(iii) an α particle (He^4 nucleus) of kinetic energy 10 MeV.

Hint: See question 1. For a gas of non-interacting particles, $\frac{1}{2}mv_{th}^2 = \frac{3}{2}k_B T$.

(5) A particle of mass, m, is confined to a 1-D region $0 \le x \le L$. In class, we derived the following stationary state wavefunctions and energies for this 1-D infinite square well potential:

$$\psi_n(x) = A sin\left(\frac{\pi n}{L}s\right)$$

a) Normalize the wave function to find the value of A.

b) Find the Energy of these stationary states

Assuming that the initial normalized wavefunction of this particle at $t = 0$ is:

$$\Psi(x, t = 0) = \sqrt{\frac{8}{5L}} \left[1 + \cos\left(\frac{\pi}{L}x\right)\right] \sin\left(\frac{\pi}{L}x\right)$$

a) Derive an expression for the wavefunction $\Psi(x, T)$, at all later times $t > 0$.

b) Show that the probability of finding the particle in the left half of the box (i.e., in the region $0 \leq x \leq L/2$) at time $t > 0$ is: $\frac{1}{2} + \frac{16}{15\pi} \cos\left(\frac{3\pi^2 ht}{2mL^2}\right)$

(6) Assuming that $\Psi(x,t)$ is a solution of the 1-D Schrödinger Equation, the current density is defined as:

$$J(x) = -\frac{i\hbar e}{2m} \left[\Psi^* \frac{\partial \Psi}{\partial x} - \Psi \frac{\partial \Psi^*}{\partial x}\right]$$

In this problem, consider the potential barrier of height (V) and width (d) that is depicted in Fig. 3.3 of Solymar and Walsh. Assume that the electron energy (E) is less than V.

a) By applying suitable boundary conditions and your knowledge of quantum mechanics, develop a system of equations that could be solved to determine the transmitted current through the barrier (J_t) in terms of the incident current on the barrier (J_i).

b) By solving your system of equations from part (a), show that:

$$\frac{J_t}{J_i} = \frac{1}{1 + \frac{V^2}{4(V-E)E} \sinh^2(\gamma d)}$$

where $\gamma = \frac{\sqrt{2m(V-E)}}{\hbar}$ and $\sinh(\gamma d) = \frac{1}{2}(e^{\gamma d} - e^{-\gamma d})$

c) In the limit where $\gamma d \gg 1$, show that: $\frac{J_t}{J_i} = \frac{16(V-E)E}{V^2} e^{-2\gamma d}$

d) The exponential dependence of the "tunneling" current on distance is utilized for atomic resolution imaging of conductive surfaces with the scanning tunneling microscope (STM). Conservatively assume that the STM can detect changes in the tunneling current of 1%. Under typical tunneling conditions (e.g., $V - E$ 1eV, d ~ 10 Å), estimate the vertical spatial resolution of the STM. Hint: The answer can be expressed in picometers (10^{-12} m)!

(7) Derive the solution of the 2-D particle in a box (particle is constrained in both x, and y directions; $V \rightarrow \infty$ at the boundaries).

a) Solve for the energies and wave functions of the ground and first excited states.

b) What is the degeneracy of the first excited state?

c) Plot the probability distributions 2 ψ of the first excited states as surface plots.

d) Optional: plot probability distributions of the ground state, first excited states, and 2nd excited states, and comment on the evolution.

(8) Consider the infinite spherical well: $V(r) = 0$ if $r \leq a$, $V(r) = \infty$ if $r > a$.

a) For $l = 0$, determine the allowed energies (E_n).

b) For $l = 0$, show that the corresponding wavefunctions are:

$$\Psi_n(r) = \frac{1}{\sqrt{2\pi a}} \frac{\sin(n\pi r/a)}{r}$$

In class, we worked through the Schrödinger equation in spherical coordinates for spherically symmetric potentials by breaking the solution into radial and angular functions. You should be able to solve the radial equation for the conditions given here.

(9) Consider the infinite spherical well: $V(r) = 0$ if $r \leq a$, $V(r) = V_o$ if $r > a$.

a) For $l = 0$, show that there is no bound state if: $V_o a^2 < \frac{\pi^2 \hbar^2}{8m}$. This can be shown without resorting to numerical computation.

b) Given $V_o = \frac{2\hbar\pi^2}{ma^2}$, find the energies of the two bound states by graphing in MATLAB or Excel. You can also use MATLAB to check your solution by solving the transcendental equation directly.

This problem is analogous to the finite square well problem solved in 3.8 of Solymar and Walsh, but in the spherical coordinate system. Through the appropriate application of boundary conditions, you should arrive at a transcendental equation whose argument can be analyzed to establish the condition for the existence of bound states.

(10) Suppose that the nucleus of a hydrogen atom is located at a distance d from a two-dimensional infinite potential wall which, of course, tends to distort the hydrogen atom. As d approaches zero, determine the following items:

a) The ground state wavefunction.

b) The degeneracy of the first excited state (ignore degeneracy due to spin).

c) The wavelength of light that is emitted upon transition between the first excited state and the ground state (express your answer in nanometers).

With the exception of part (c), this problem does not involve mathematical calculation. The proper choice of coordinate system can make the relationship between these solutions and the usual hydrogen atom solutions clear. Bear in mind that the ground state refers to the lowest energy state that exists.

(11) Consider a double finite potential well in one dimension. Suppose that the depth V_0 and the width a are fixed such that the following equation is obeyed:

$$\beta^2 = \frac{V_0 m a^2}{2\hbar^2} = 4\pi^2$$
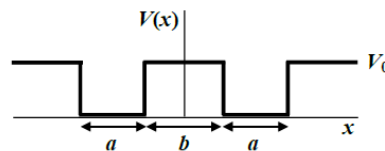
(12) Qualitatively sketch the ground state wavefunction ψ_1 and the first excited state wavefunction ψ_2 for: (i) $b = 0$, (ii) $b = a/2$, and (iii) $b \gg a$.

a) For $b = 0$, show that the ground state energy (E_1) is given by: $E_1 = \frac{\hbar^2 x_1^2}{2ma^2}$, where x_1 is the solution of the following equation: $\tan x_1 = \sqrt{\left(\frac{2\beta}{x_1}\right)^2 - 1}$. Calculate E_1 in units of $\frac{\hbar}{ma^2}$.

b) For $b = 0$, show that the first excited state energy (E_2) is given by: $E_2 = \frac{\hbar^2 x_2^2}{2ma^2}$ where x_2 is the solution of the following equation: $-\cot x_2 = \sqrt{\left(\frac{2\beta}{x_2}\right)^2 - 1}$. Calculate E_2 in units of $\frac{\hbar^2}{ma^2}$.

c) For $b \gg a$, estimate E_1 and E_2 in units of $\frac{\hbar^2}{ma^2}$.

d) Use the MATLAB code derived from Garcia, R., Zozulya, A. & Stickney, J. MATLAB codes for teaching quantum physics: Part 1. *arXiv* **physics.ed-ph**, (2007). http://arxiv.org/pdf/0704.1622.pdf

Consult the original publication for background on the code, which is reproduced below.

   i. What is the Heaviside function? How is it used in this code (for what purpose)?

   ii. Using the MATLAB code, generate the plots you sketched in part (a) (ground and first excited states for b=0, b=a/2, and b>>a). You should have three graphs with two curves on each. Label the graphs and the wave functions.

   iii. Generate 2 more plots with intermediate barrier widths, and sketch the trends in E_1 and E_2 as a function of barrier width (you should have 5 different widths).

   Note: in the code, you can change the potential profile quite easily (e.g. the quadratic harmonic oscillator potential or single square well). Parameters can be varied to develop insight into how the wavefunctions vary with the potentials.

e) Provide a physical explanation for the variation of E_1 with b that you observed in part (e).

f) The double well is a primitive one dimensional model for the potential experienced by an electron in a diatomic molecule (the two wells represent the attractive force of the nuclei). If the nuclei are free to move, they will adopt the configuration of minimum energy. In view of your conclusions in (b), does the electron in the ground state (E_1) tend to draw the nuclei together or push them apart? What about E_2? Provide a physical reason for these behaviors, considering your answer to the previous question.

```matlab
1  % Program 4: Find several lowest eigenmodes V(x) and
2  % eigenenergies E of 1D Schrodinger equation
3  % -1/2*hbar^2/m(d2/dx2)V(x) + U(x)V(x) = EV(x)
4  % for arbitrary potentials U(x)
5  % Parameters for solving problem in the interval -L < x < L
6  % PARAMETERS:
7  L = 5;% Interval Length
8  N = 1000; % No of points
9  x = linspace(-L,L,N)';% Coordinate vector
10 dx = x(2) -x(1); % Coordinate step
11
12 % POTENTIAL, choose one or make your own
13 U = 1/2*100*x.^(2); % quadratic harmonic oscillator potential
14 %U = 1/2*x.^(4); % quartic potential
15
16 % Finite square well of width 2w and depth given
17 %w = L/50;
18 %U = -500*(heaviside(x+w)-heaviside(x-w));
19
20 % Two finite square wells of width 2w and distance 2a apart
21 %w = L/50; a=3*w;
22 %U = -200*(heaviside(x+w-a) -heaviside(x-w-a) ...
23 % + heaviside(x+w+a) -heaviside(x-w+a));
24
25 % Three-point finite-difference representation of Laplacian
26 % using sparse matrices, where you save memory by only
27 % storing non-zero matrix elements
28 e = ones(N,1); Lap = spdiags([e -2*e e],[-1 0 1],N,N)/dx^2;
29
30 % Total Hamiltonian hbar = 1; m = 1;
31 % constants for Hamiltonian H = -1/2*(hbar^2/m)*Lap + spdiags(U,0,N,N);
32
33 % Find lowest nmodes eigenvectors and eigenvalues of sparse matrix
34 nmodes = 3; options.disp = 0;
35 [V,E] = eigs(H,nmodes,'sa',options);% find eigs
36 [E,ind] = sort(diag(E));% convert E to vector and sort low to high
37 V = V(:,ind); % rearrange corresponding eigenvectors
38
39 % Generate plot of lowest energy eigenvectors V(x) and U(x)
40 Usc = U*max(abs(V(:)))/max(abs(U)); % rescale U for plotting
41 plot(x,V,x,Usc,'- k '); % plot V(x) and rescaled U(x)
42
43 % Add legend showing Energy of plotted V(x)
44 lgnd_str = [repmat('E = ',nmodes,1),num2str(E)];
45 legend(lgnd_str) % place lengend string on plot
```

(13) Consider a cesium chloride crystal where the potential energy per formula unit is:

$$E(r) = \frac{A}{r^n} - \frac{Me^2}{4\pi\epsilon_0 r}$$

where A is a constant, $n > 1$, r is interionic distance, and M is the Madelung constant.

a) Express the binding energy (E_0) in terms of M, n, r_0, and fundamental constants. *Hint: first express A in terms of these constants by considering the equilibrium condition.*

b) The cesium chloride crystal structure consists of cations located on a simple cubic lattice (lattice constant = a) with an anion located at the center of the cube. What is the volume per formula unit (v) in terms of r?

c) From thermodynamics, the bulk modulus (B) is known to be: $B = v\frac{\partial}{\partial v}\left(\frac{\partial E}{\partial v}\right)$. Show that B_o is of the form $B_0 = \frac{C}{r_o}\frac{d^2E}{dr^2}|_{r=r_o}$, and find C. *Hint: use your result from the previous problem to rewrite the derivatives in terms of r.*

d) Using the result from part (c), express the equilibrium bulk modulus (B_0) in terms of M, n, r_0, and fundamental constants.

e) The experimentally determined values of B_0 and r_0 for CsCl are 19.8 GPa and 3.571 Å respectively. Calculate E_0 for CsCl in eV. <u>Note:</u> M = 1.7627 for CsCl.

9 351-2 Problems

(1) An abrupt Si p-n junction has $N_a = 10^{18} cm^{-3}$ on one side and $N_d = 10^{15} cm^{-3}$ on the other.

    a) Calculate the Fermi level position at 300K on both sides.

    b) Draw an equilibrium band diagram for the junction.

    c) Determine the contact potential Φ_o for this junction.

(2) A silicon $p^+ - n$ junction $10^{-2} cm^2$ in area had $N_d = 10^{15} cm^{-3}$ doping on the n-side. Calculate the junction capacitance with a reverse bias of 10V.

(3) For metallic aluminum, calculate:

    a) The valence electron density.

    b) The radius of the Fermi sphere k_F.

    c) Fermi energy in eV.

(4) From the Schrodinger equation for a quantum well, show that the wave vector is equal to $n\pi/L$ where L is the well width.

(5) Calculate the energy of light emitted from a 10 nm wide AlGaAs/GaAs quantum well structure that is photoexcited with 2.5 eV laser light.

(6) What is the luminescent energy for a CdSe quantum dot with a 2 nm radius.

(7) For a MOSFET device briefly describe how the three types of device work: a) enhancement mode b) depletion mode c) inversion mode.

(8) Calculate the capacitance of an MOS capacitor with a 10 nm thick HfO_2 dielectric oxide. What is the ratio of capacitances for C_{HfO_2}/C_{SiO_2}. The relatie dielectric constant for HfO_2 is 25.

(9) Problem 9.9 in Solymar and Walsh

(10) Problem 9.14 in Solymar and Walsh

(11) Problem 9.16 in Solymar and Walsh

(12) Problem 12.10 in Solymar and Walsh

(13) Consider a quantum cascade laser (QCL) made from GaAs and GaAlAs. What well thickness is needed for laser emission at 3 microns?

(14) Derive the expression for the average value of the dipole moment. Show that it is given by:

$< \mu >= \mu[\coth a - \frac{1}{a}]$

(15) The saturation polarization P_s of $PbTiO_3$, a ferroelectric, is 0.8 coulombs/m^2. The lattice constant is $4.1\dot{A}$. Calculate the dipole moment of unit cell.

(16) Calculate the polarization P of one liter of argon gas at 273 K and 1 atm. The diameter of an argon atom is 0.3 nm.

(17) Consider the frequency dependence of the atomic polarizability. The polarizability and its frequency dependence can be modeled as a damped harmonic oscillator. Derive the expression for α in this case.

The expression is given by:

$m\frac{dx}{dt^2} + b\frac{dx}{dt} + \omega_0^2 x = -e\varepsilon_{loc}\sin\omega t$

Plot α vs. ω for this case.

(18) Problem 4.6 in Solymar and Walsh.

(19) Problem 4.7 in Solymar and Walsh.

(20) Problem 4.8 in Solymar and Walsh.

(21) Problem 4.9 in Solymar and Walsh.

(22) Calculate the magnetic susceptibility of metallic copper. How does it compare to the measured value of -1.0?

(23) Calculate the effective magneton number p for Mn^{2+}, Co^{2+}. Show work.

(24) Consider Mn doped GaP. There are $10^{20} Mn^{2+}$ ions.

(25) What is the electron configuration Mn^{2+} in spectroscopic notation.

     a) Calculate its magnetic moment at saturation in Bohr magnetons.
     b) Calculate its magnetic susceptibility.

(26) For metallic Co, which has a Curie temperature of 1388 K, calculate the Weiss constant λ. Calculate the exchange constant in meV.

10 361 Problems

Homework Policy: You may consult with other class members when preparing your homework answers; indicate clearly on your paper the names of the students with whom you worked. The solutions you submit should, nevertheless, be your own and in your own hand.

Reading Assignments: See the Syllabus, which is published on the NU Blackboard for this course.

1)   By operating on a "7" in the plane of the paper, show that an inversion center is equivalent to a 2-fold rotation axis (perpendicular to the plane of the paper) in two dimensions.

Show that the inversion center and 2-fold rotation axis are not equivalent in three dimensions by doing the same type of

operation on a 3D asymmetrical unit " 7."

2)   Below are sketched a 2-fold axis parallel to a mirror and two perpendicular mirrors. Operate on the "7" with the indicated symmetry elements and show that a third symmetry element is present in each case and that the two cases are equivalent. Which point group does this pattern of 7's belong to ?

3)   For the following 2D primitive rectangular unit cell:

(1) Fill in the pattern of 7's based on the indicated unit cell and symmetry elements.

(2) Draw in the additional symmetry elements that are present.

(3) Indicate which 2D space group this pattern belongs to.
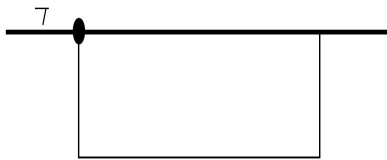
4)   From Azaroff 1-7
Examine the crystal on page 22 of Week 1 notes (Azaroff Fig. 1-29) and list all the symmetry elements that you find present. Determine the correct crystal class and system.

5)   From Azaroff 1-8
Consider the tetragonal crystal shown on page 21 of Week 1 notes (Azaroff Fig. 1-24). Using the axis labeled a1, a2, and c in that figure, what are the indices of the four faces visible? What is the form?

6)   C&S Prob. 2-6

7)   Hammond Prob. 2-3

8)   C&S Prob. 2-10

9)   C&S Problem 2-13 (Use tracing paper on top of a Wulff net for this problem, in addition to the following two).

10)   C&S Problem 2-14

11)   C&S Problem 2-15

12)   Prepare a drawing of the $hk0$ layer in the reciprocal lattice of a monoclinic crystal for which a = 2.5 Å, b = 3.0 Å, c = 5.12 Å, and γ=120°. Note that $\gamma^* = 180° - \gamma = 60°$.

13) Using the figure from lecture notes Week 2 slide 11, draw two lines that represent the edge-on view of the (010), (110) and (210) hkl planes. Draw the corresponding reciprocal lattice vectors, noting that they are perpendicular to the hkl planes. This is already done below for the (210) plane. Using a ruler, measure the interplanar spacing, d_{hkl}, and the length of the reciprocal lattice vector r^*_{hkl}. Verify that the product $d_{hkl} \bullet r^*_{hkl}$ is the same for each set of planes, thus demonstrating that reciprocal lattice vector lengths are inversely proportional to d-spacings in direct space.
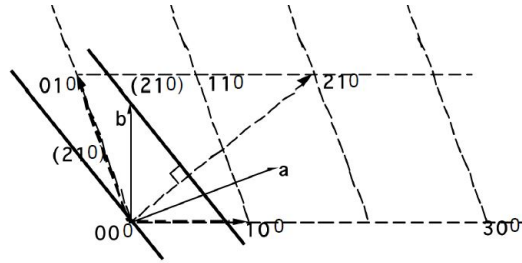
14) Using the general definition of the reciprocal lattice vector (see Week 2 Lecture Notes), derive the relation for d_{hkl} for the tetragonal, orthorhombic, and monoclinic systems in terms of the unit cell parameters a, b, c, α, β, γ and the Miller indices h, k, l. Check answer with C&S A3-1.

15)

(1) Determine the lattice constant "a" in terms of R for a BCC (body centered cubic) structure with spheres of radius R at each lattice point packed as closely as possible.

(2) repeat part (a) for an FCC lattice.

16) GaAs is a zinc blende structure, which has Ga atoms at FCC positions and As atoms at FCC + (1/4, 1/4, 1/4) positions. Write out the 4 coordinates for Ga and the 4 coordinates for As for a unit cell. Make a sketch of this unit cell with the 8 atoms or use Crystal Maker.

17) Hammond Prob. 5.6. Plus use MatLab to perform the matrix transformations between cubic-I (HKL) and rhombohedral (hkl) for HKL = {100, 111, 110} and hkl = {100, 111, 110}.

18) C&S Problem 2-7

19) C&S Problem 2-8

20) Hammond Exercise 5.2

21) One formula weight of NiO equals 74.69 amu, and the density of a NiO crystal is 6.67 g/cm^3. (a) Calculate the length of the unit cell edge, a. (b) Using λ = 1.54 Å prepare a list of the first 6 allowed reflections (hkl) and the corresponding Bragg angles, θ_{hkl}. Refer to CS Appendix 9 which lists the allowed reflections for various Bravais direct-space lattices.

22) Prepare a 3-d drawing of the reciprocal lattice for a body-centered-cubic direct space lattice. Show and label all reciprocal lattice points for $0 \leq h,k,l \leq 2$. Show and label the reciprocal space axes, $\mathbf{a^*}$, $\mathbf{b^*}$, and $\mathbf{c^*}$. Identify the Bravais lattice type for this reciprocal space lattice.

23)

(1) What are the (hkl) Rhombohedral unit cell Miller indices for the three nonparallel faces of the Rhombohedral unit cell?

(2) Read Hammond Section 5.9, make sure you understand how the transformation matrices were generated for trigonal crystals with rhombohedral lattices. Using the transformation matrix derived in Sec. 5.9, what are the (HKL) Hexagonal unit cell Miller indices for the three nonparallel faces of the Rhombohedral unit cell?

(3) Now list these as (hkil) Miller- Bravais indices.

(4) What is the [uvw] direction in the Rhombohedral unit cell for the hexagonal c-axis direction [001]?

(5) EXTRA CREDIT: Hematite α-Fe2O3 has a rhombohedral crystal structure with a=5.43Å and $\alpha = 55.3°$. What is the angle between the hexagonal c-axis and the rhombohedral c-axis? What is the angle between the hexagonal c-face and the rhombohedral c-face?

24) Find Azaroff Chapters 6 and 8 on BlackBoard, Read Azaroff Ch 6. pp 86-113, an Azaroff Ch. 8 pp. 155-165

25) [Azaroff 6-1]

26) Refer to Azaroff Fig. 6-2 on page 88. This experiment is with continuous radiation.

(1) The x ray beam from the x-ray tube is traveling along y. Is this x ray beam:

   a) preferentially polarized along x ?
   b) preferentially polarized along y ?
   c) preferentially polarized along z ?
   d) not preferentially polarized ? Explain your answer.

(2) Is radiation scattered by the block stronger in detector 1 (along x) or in detector 2 (along z)? Again explain your answer.

27) [Azaroff 6-2]

28) [Azaroff 6-3]

29) [Azaroff 8-1] **Hint** : According to the Bohr model, the radius rn of the nth orbit is proportional to n^2/Z, where Z is the atomic number. Plot the scattering-factor curves f_K, f_L and f as functions of kr_K.

$$f = 2\frac{sinkr_K}{kr_K} + 8\frac{sinkr_L}{kr_L}$$

Note that there is a typo in the text book. "a missing factor of 8".

30) [Azaroff 8-2] (see Cullity & Stock Appendix 10)

31) [Azaroff 8-9]

32) The one dimensional interference function is:

$$\frac{sin^2\pi Q \cdot aM}{sin^2\pi Q \cdot a} = \frac{sin^2\beta M}{sin^2\beta}$$

$Q = (S - S_o)/\lambda$ is the scattering vector. S and S_o are unit vectors in the scattered and incident directions where $\beta = \pi Q \cdot a$ is one-half the phase angle difference (in radians) for rays scattered by planes separated by a. The crystal contains M planes separated by **a**.

(1) Use a computer with a suitable program or spreadsheet and plotting program (MSE Ugrads must use MatLab) to plot this function over the domain $0 \leq \beta \leq \pi$. Note that this is a periodic function repeated every π radians. Make separate plots of the function for the cases of M = 2, 4, and 16. You will have to appropriately adjust the evaluation interval $\Delta\beta$ to accommodate the sharpness of the function that varies with M.

(2) For each M above, tabulate the height of the primary maxima, the height of the first subsidiary maxima, and the ratio of the height of the first subsidiary maxima to the height of the primary maxima. This demonstrates how the subsidiary maxima become less significant as M increases.

(3) By numerical integration determine the area under the $\beta = 0$ primary diffraction peak between the first intensity minima (nulls) for each M above. How does this vary with M?

(4) The integral breadth of a peak is the quotient of the area over the height. This represents the full width of a rectangle that has the same height and area as the peak in question. Calculate the integral breadth of the primary maximum for the three cases, and consider its relation to M.
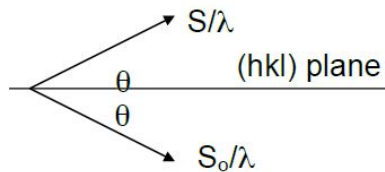
Figure 10.1: S/λ and $S_o/\tilde{}$

33) Consider powder diffraction from CsCl (a = 4.11 Å) with Cu Kα radiation (λ = 1.542 Å). This is a simple cubic structure with Cs^+ at 0,0,0 and Cl^- at 1/2,1/2,1/2. (Note: CsCl is not BCC.)

(1) What are the *hkl* indices for the first 7 observed reflections from CsCl?

(2) For the first four of these calculate and tabulate $\sin\vartheta/\lambda$,f_{Cs^+}, f_{Cl^-}, F_{hkl}, 2ϑ, and LP.

(3) Look up multiplicities m_{hkl} (Cullity & Stock Appendix 11). Combine these with your results from part B to calculate the <u>relative</u> intensities of the four peaks in question. Assign the value of 100 to the most intense peak.

34) The relation of multiplicity factors m_{hkl} to powder diffraction intensities can be appreciated with the reciprocal lattice.

(1) Sketch the hk0 plane of the reciprocal lattice for an HCP crystal, using solid dots (•) to indicate nonzero $|F_{hkl}|^2$. Cover the range from -2a* to +2a* and -2b* to +2b*.

(2) Show that there are 6 reciprocal lattice vectors of the same length $r_{hkl}* = a* = b*$. Give the *hkl* indices for these six vectors. In a powder sample, these will all diffract at the same value of (scalar) Q (or in the same 2θ direction).

(3) The six planes responsible for this diffraction are of the form {100}, though this is seen more clearly in the 4 axis Bravais-Miller system hkil , where i = -(h+k). Write the indices hkil for these six planes.

35) Write the structure factor for a crystal with two atoms of the same type per unit cell at x, y, z and $x + 1/2, y + 1/2, z + 1/2$. This conforms to a body centered (I) unit cell with an arbitrarily displaced origin at x,y,z.
Now evaluate the product $FF*$ for all possible values of h, k, and l. You should see that the result is independent of x,y,z. Therefore, the intensity (FF*) depends only on the separation between atoms; absolute positions are not relevant.
Make a perspective sketch of the reciprocal lattice for an orthorhombic I crystal, a = 3Å, b = 4 Å and c = 5 Å. Include 8 reciprocal lattice unit cells (from origin to 2a*, 2b*, 2c*). Indicate nonzero values of FF* by dots (•).
You should notice two things: the "missing" reciprocal lattice points result from the choice of the nonprimitive unit cell; the pattern of nonzero points forms a face centered (F) array in reciprocal space. The same is true for cubic I and tetragonal I Bravais lattices, the reciprocal lattices of which are face centered.

36) (Cullity & Stock Prob. 4-4) Derive simplified expressions for F and F^2 for diamond, including the rules governing observed reflections. This crystal is FCC and contains 8 atoms per unit cell located at: FCC and FCC + 1/4 1/4 1/4 . Note, silicon and germanium are diamond structure.

37) Construct a diagram that illustrates the *hkl* Bragg condition, showing S/λ, S_o/λ and an (hkl) reflecting plane such that the two unit vectors originate from the same point as shown below. Continue the diagram and show that the vector $Q = (S_o/\lambda - S/\lambda)$ must be perpendicular to the hkl plane. From the construction derive Braggs' Law recalling that Q must be the same as a reciprocal lattice vector.

38) Figure P2 is a c-axis-rotation photograph of an orthorhombic crystal which has $a* = 0.25 \text{ Å}^{-1}$, $b* = 0.15 \text{ Å}^{-1}$ and $c* = 0.36 \text{ Å}^{-1}$. The radius of the cylindrical camera used for taking this photograph is 50 mm and the x-ray wavelength is 1.542 Å. Construct the appropriate reciprocal lattice nets (l=0 and l=1) to index all the reflections shown. What is the lattice type of this crystal?

39) Use the Scherrer equation $(\delta(2\theta) = 2\varepsilon_{1/2} = 0.94\lambda/D\cos\theta)$ to evaluate the FWHM peak width $\delta(2\theta)$ (in degrees) for crystallite sizes D = 25, 75, 125, 450, and 900 Å. Assume that λ = 1.542 Å and that the peak in this $\theta - 2\theta$ scan whose width we are considering occurs at $2\theta = 80°$.

The ability to measure small peak widths is hampered by instrumental broadening. Even if the incident and diffracted beams were perfectly collimated, the peaks would still be broadened by the $K_{\alpha1} - K_{\alpha2}$ splitting. Differentiate Braggs law to obtain an expression for $d\theta$ as a function of θ, λ, and $d\lambda$. Using this expression, calculate $d\theta$ for the $K_{\alpha1} - K_{\alpha2}$ splitting of Cu radiation at $2\theta = 90°$.

$\lambda(K_{\alpha1}) = 1.5405Å$.

$\lambda(K_{\alpha2}) = 1.5433Å$

From this you should appreciate that it is difficult to measure D values greater than about 500 Å. when using the Cu K_α doublet as a radiation source. Note that the wavelength resolution $\lambda/d\lambda$ can be improved by an order of magnitude by using a single crystal monochromator to select out the Cu $K_{\alpha1}$, whose width is approximately 2 eV in comparison to the 20 eV energy separation between the $K_{\alpha1}$ and $K_{\alpha2}$.

40) Identical powder diffraction scans are made of a diamond powder sample and a germanium powder sample with Cu K_α radiation. Each has "diamond cubic" crystal structure with 8 atoms per unit cell. Other pertinent information for this problem is as follows:

Sample	Z	a[Å]	μ/ρ [cm^2/g]	ρ [g/cm^3]
Carbon	6	3.5671	4.22	3.51
Germanium	32	5.6577	67.9	5.91

The scans were done in symmetric reflection. One might think that the ratio of observed intensities would be given by the ratio of the quantities

$K_x = \dfrac{|F_{hkl}|^2 m_{hkl} LP}{V_{C^2}}$

where x is C or Ge. However, the observed intensity of diamond, relative to that of germanium, was 25 times larger than that calculated from the ratio K_C/K_{Ge}. Explain where this factor of 25 comes from.

Figure P2   C-axis-rotation photograph for 361 HW
(scale is approx 1:1)
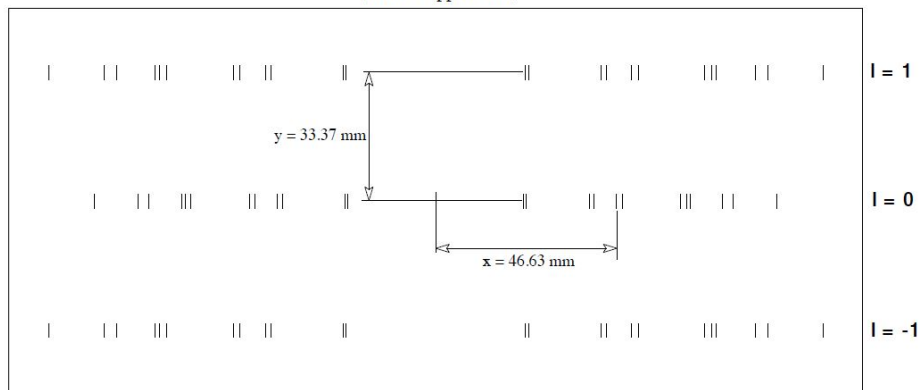
Radius of the cylindrical camera = 50 mm
x-ray wavelength λ = 1.542 Å
$a* = 0.25$ Å^{-1}, $b* = 0.15$ Å^{-1}, $c* = 0.36$ Å^{-1}

11 390 Problems

11.1 Materials Selection in Mechanical Design

Note: Because the CES Materials Selector Software only works on PCs, which not everyone has, these projects will be done in your project groups, with 1 report submitted per group. Upload the completed report to Canvas as a pdf file on the due date.

In order to receive credit for the CES materials selection problems, you must:

- answer the questions

- explain the process used to get your answers

- include ALL relevant CES plots with explanations of the information given on each plot in all problems. CES plots should be properly enlarged in specific regions if needed, and failed records of materials (materials that do not satisfy the criteria shown in gray) should be hidden.

There is no unique answer to the questions. Therefore, your grade will not be determined by the particular materials you choose. You can select any materials that satisfy the criteria and as long as you explain the process used to get your answer.

Start from "Level 3" database and "All bulk materials" for all problems.

To change units go to: tools → settings → units → <automatic-metric> or <metric>

1) General use of the CES database: Answer the following using CES database:

(a) A component is currently made of soft commercially pure Gold. Due to high cost of gold, please use CES to suggest two other materials that have greater thermal conductivity.

(b) Find a material with $250 < E < 350$ GPa and density $7,000 < \rho < 8,000$ kg/m^3.

(c) Which have higher specific stiffness, E/ρ : titanium alloys or tungsten carbides?

(Hint: use 'Tree' in the selection stage to select titanium alloys and tungsten carbides only)

(d) Is the fracture toughness, K_{IC}, of common engineering polymers like PVC elastomer (Shore A60) higher or lower than those of engineering ceramics like silicon carbide (HIP)?

2) Multi-stage materials selection using CES database You are employed by a company that manufactures various sports goods except tennis rackets. Even though the company is doing well, in an effort to expand company's market the management decided to introduce a new product: tennis rackets. Being the only Materials Engineer in the company your new assignment is to select four different materials that would be suitable for manufacturing tennis rackets.

Since you have already used CES, you should not have any problem in getting started. First, let us examine the essential functions of a body of a tennis racket: structural support for the string, transfer of force, absorption of energy (damping) etc. Often, the tennis rackets are also subjected to mechanical abuse (due to bad temper or frustration of the players). Thus, the optimal materials must be light, stiff, strong, and should have reasonably good fracture toughness. In conjunction with the CES database, the following multi-stage criteria may be applied to select off-the-shelf materials suitable for manufacturing tennis rackets.

Stage I: Assume that due to the complex shape of the body of the tennis racket the maximum stiffness at minimum weight is given by the following performance index:

$$M_1 = \frac{\sqrt{E}}{\rho} \tag{11.1}$$

where E is the Young's Modulus, and ρ is the density.

Stage II: The maximum ductile strength of rods at minimum weight is given by the following performance index:

$$M_2 = \frac{\sigma_y^{0.8}}{\rho} \tag{11.2}$$

where σ_y is the yield stress (Elastic Limit in CES).

Stage III: The maximum fracture toughness of rods at minimum weight is given by the following performance index:

$$M_3 = \frac{K_{IC}}{\rho} \tag{11.3}$$

where K_{IC} is the fracture toughness.

Stage IV: Selection of materials that will give minimum density and maximum damping capacity. In CES, the damping behavior is represented by the Mechanical Loss Coefficient under Optical, aesthetic and acoustic properties. A higher mechanical loss coefficient implies a better damping capacity. Use Box Method for selecting a subset of materials (with ρ < 2,000 kg/m3 and mechanical loss coefficient greater than 0.008) in this stage.

Use the above four stages of selection to determine the optimal materials for tennis racquets. The materials must also satisfy the following:

- $M_1 > (10^3 \, \text{Pa})^{0.5}/(\text{kg/m}^3)$

- $M_2 > (10^4 \, \text{Pa})^{0.8}/(\text{kg/m}^3)$

- $M_3 > (10^4 \, \text{Pa}\sqrt{\text{m}})/(\text{kg/m}^3)$

(See the note in section **??** to better understand how to interpret these values of the performance index).

Turn in the following:

(a) Graphical output for each stage showing the selection line/box. In the report, you must explain how you have drawn the selection line in each stage;

(b) Table for Materials passing 4 of the 4 stages

(c) Select four different materials that passed all the stages for manufacturing tennis rackets. At this stage you may consider cost (listed in CES) so that rackets will have a wide range of price. List the Young's modulus, the yield stress, the fracture toughness, the loss coefficient, and price of the materials you selected, in a table like the one outlined below:

Material	E (Pa)	σ_y (Pa)	K_{IC} (MPa$\sqrt{\text{m}}$)	Mech. Loss Coeff.	Price

3) Multi-stage materials selection using CES database: As an engineer at a minor aircraft company, you have been given the task of determining the proper material for use as an aircraft door. After research you have determined nine properties that the material must possess. They are as follow:

- Fracture toughness, $K_{IC} > 40 \, \text{MPa}\sqrt{m}$

- Young's Modulus, $E > 100 \, \text{GPa}$

- Density, $\rho < 5,000 \, \text{kg/m}^3$

- Thermal Expansion $< 20 \times 10^{-6}/°C$

- Elongation $> 10 \, \%$

- Cost $< 20 \, \text{USD/kg}$

- Recycle fraction in current supply $> 20 \, \%$

- Flammability = {non-flammable}

- Durability in fresh water = {excellent}

Determine a suitable material for this application

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11.2 Thermo-Calc

Requirements for Thermo-Calc questions:

- Your answers to all of questions must be substantiated by calculated diagrams and I should be able to make out as to what you have to plot in the figure(s)

- Everyone must submit his/her own calculated diagram(s)

- The title of the phase diagrams MUST be your name

- All phase fields must be labeled; and (v) a copy of the equilibrium results obtained from the TC 2017b window must accompany the answers that require equilibrium calculations

- You will receive an automatic zero if it is found that you have submitted someone else's phase diagram or graph.

- **Warning:** The phase labeling function of TC2017b occasionally gives you obviously wrong results. You may try removing all labels and adding them again, or adjusting window/graph sizes. If you can't get it right from the software, clarify the situation and give your answers in your homework.

4) Pb-Sn solders are widely used in electronic packaging (chip-to-chip and chip-to-carrier interconnections) and various other applications related to soldering. However, due to toxicity of Pb and environmental concerns, Pb-Sn solders have been banned in many applications, such as, food packaging (e.g., beverage cans), certain plumbing applications etc. The Sn-In phase diagram is important for designing multicomponent Pb-free solders.
Hints: (i) Use SSOL2 database; (ii) For both the Pb-Sn and In-Sn systems, consider the following phases only: LIQUID, FCC_A1 and BCT_A5; (iii) temperature limits for mapping: 0 – 400°C for both alloys. In the SSOL database, the Sn-phase is defined by BCT_A5, because its structure is body centered tetragonal, the In-phase and Pb-phase are defined by FCC_A1, because both of their structures are face centered cubic.

(a) Calculate Pb-Sn and In-Sn equilibrium phase diagrams. You have to submit the calculated phase diagrams with all phase fields labeled.

(b) What are the calculated eutectic temperatures in Pb-Sn and In-Sn systems?

(c) What are the calculated solid solubilities of Pb in Sn and In in Sn at their respective eutectic temperatures? Answer this question both in weight and atomic percents of Pb and In.

(d) Despite toxicity/environmental concerns, Pb-Sn solders are widely used in all microelectronic packages. In particular, the Pb-Sn eutectic alloy. For a Sn-38 wt.% Pb alloy, answer the following:

    i What are the phases present at 50°C and 130°C? (Note: many devices, such as computers operate in this temperature range)

    ii What are the amounts and composition (in wt%) of the phases present at 50 and 130°C?

    iii What are the important differences you notice between the calculated results at these two temperatures?

5) Calculation of the Ms temperature (temperature when martensite starts to form) is a very crucial step in designing ultra-high strength, secondary hardening martensitic steels. Such a calculation allows us to select the alloy(s) whose Ms is sufficiently high so that upon quenching (from solution treatment temperature) to room temperature a fully martensitic microstructure is obtained. If the Ms is not high enough, then we may get incomplete transformation at room temperature and the alloy will need to be quenched at sub-ambient temperatures. Therefore, an alloy with an Ms>300°C would be desirable.
Hints: (i) Use the SSOL2 database; (ii) consider the following phases for 2.1-2.4: BCC_A2 and FCC_A1, consider the following phases for 2.5: LIQUID, BCC_A2, FCC_A1, HCP_A3, SIGMA, CEMENTITE, M23C6, and M7C3 (iii) stepping ranges for 2.1-2.4: 200 to 1000°C for temperature; mapping ranges for 2.5: 750 to 1250°C for temperature (iv) A solution treatment temperature is defined as the temperature at which all solutes will be in solid solution in one phase.
The alloy is based on iron with different concentrations of C, and with 14 wt. % Co, 8 wt. % Cr , 6 wt% Ni, 0.5 wt. % Mo and 0.3 wt. % V.

(a) What is the T0 temperature of the above alloy as a function of C content? Consider carbon concentrations 0.1 wt%, 0.3 wt%, 0.5 wt%, 0.7wt% and 0.9 wt%?

(b) Comment of the effect of C on the T0 temperature.

(c) Assuming that the martensitic transformation starts at a Driving Force of -1500 J/mol, what is the Ms temperature of the above alloy as a function of C content at 0.1 wt%, 0.3 wt%, 0.5 wt%, 0.7wt% and 0.9 wt%?

(d) Comment on the compositional dependence of Ms temperatures and determine which alloy(s) would be appropriate for the application stated in the above question.

(e) Calculate the vertical section of this alloy. For a solution treatment temperature of 1000°C, what is the maximum amount of C that can be put in the alloy? Show this point of the phase diagram.

11.3 DICTRA

To receive credit:

- Your answers to all of questions must be substantiated by calculated diagrams or table renderer results
- everyone must submit his/her own calculated diagram(s)
- the title of the phase diagrams MUST be your name

6) γ to α transformation in a ternary Fe-0.15wt%C-0.50wt%Si steel, when cooled from 1173K down to 1050K with the cooling rate of 10K/minute, and then isothermally held at 1050K until total heat-treatment time reaches 107 sec.

(a) Provide a plot of carbon concentration vs distance at t=1,000, 100,000, 10^7 sec.

(b) Provide a plot of silicon concentration vs distance at t=1000, 100000, 107 sec. Compare with the plot of the carbon concentration. Which element do you think is more mobile in this steel at this temperature, C or Si?

Hints:

- Use the SSOL2 database as thermodynamics database, and MOB1 database as mobility database
- Consider the following phases: FCC_A1 (γ, austenite) and BCC_A2 (α, ferrite)
- assume fully homogenized austenite (FCC_A1) at the beginning of the heat-treatment
- apply 50 grid-points of geometric grid with ratio = 1.05 in the initial austenite region
- assume ferrite starts to form when the driving force exceeds 10-5 (vi) use potential (not activity) for finding tie-line at the phase interface

11.4 TC-PRISMA

To receive credit:

- Your answers to all of questions must be substantiated by calculated diagrams or table renderer results
- everyone must submit his/her own calculated diagram(s)
- the title of the phase diagrams MUST be your name

11.4.1

Isothermal precipitation calculation of γ-γ′ Ni-12Al (at%) alloy at 450 °C for 1e15 s
Hints:

- Use the Demo Ni alloys database package

- Consider the following phases: DIS_FCC_A1 (matrix) and FCC_L12 (precipitate)

- Precipitate nucleation sites: bulk, interfacial energy 0.035 J/m2

(a) What is the maximum number density of precipitate? How long does it take to reach the maximum number density of precipitates (in hours)?

(b) What is the volume fraction of precipitate phase and matrix composition (Al concentration in at%) at 1e15 s?

11.4.2

3. Isothermal precipitation calculation of metastable and stable carbides in Fe-0.1C-12Cr (wt%) at 750 °C for 1e6 s

(a) From the volume fraction vs. time figure, can you tell the sequence of precipitation?

Hints:

- Use the Steel and Fe alloys database package;
- consider the following phases: BCC_A2 (matrix), CEMENTITE (precipitate), M23C6 (precipitate), and M7C3 (precipitate)
- precipitate nucleation sites: grain boundaries
- interfacial energy: CEMENTITE (0.167 J/m^2), M23C6 (0.252 J/m^2), M7C3 (0.282 J/m^2)
- plot volume fraction of all three carbides (linear) vs. time (log 10)

(b) Can you obtain this precipitation sequence without doing this isothermal calculation?

Hint:

Example 2 in Lab 5b tutorial

(c) What the volume fraction of the stable precipitate phase at 10^6 s? How about its equilibrium volume fraction?

Hint:

TC single point equilibrium calculation using TCFE9 database with BCC_A2, CEMENTITE, M23C6, and M7C3 entered

References

[1] C. E. Johnson, E. J. Hathaway, Solid-Liquid Phase Equilibria for the Ternary Systems Li(F,Cl,I) and Na(F,Cl,I), J. Electrochem. Soc. 118 (4) (1971) 631–634. doi:10.1149/1.2408125. 38