

Materials Science and Engineering Problems

MSE Faculty

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

Link to updated version of this document: <http://msecore.northwestern.edu/MSEproblems.pdf>

Link to main curriculum document: <http://msecore.northwestern.edu/MSEtext.pdf>

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314 Problems

Phases and Components

- (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.
 - 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.
 - A sealed jar of water at room temperature.
 - A sealed jar of water with ice.
 - An open jar of water with NaCl entirely dissolved within.
 - If the jar is left open, in what ways might your description change?
 - How would your answer to (a) change if you take into account equilibrium between water, protons, and hydroxyl ions?

Intensive and Extensive Properties

- (2014) Classify the following thermodynamic properties as intensive or extensive:
 - The mass of an iron magnet.
 - The mass density of an iron magnet.
 - The concentration of phosphorous atoms in a piece of doped silicon.
 - The volume of the piece of silicon.
 - The fraction by weight of copper in a penny.
 - The temperature of the penny in your pocket.
 - The volume of gas in a hot air balloon.

Differential Quantities and State Functions

- (2014) Consider the function $z = 6x^2y^3 \cos^2 u$.
 - Write down the total differential of z . Identify the coefficients of the three differentials in this expression as partial derivatives.
 - Demonstrate that three Maxwell relations (see section 2.3) hold between the coefficients identified under (a).
- (2014) Why are state functions so useful in calculating the changes in a thermodynamic system?
- (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.

Entropy

- (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.
- (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 a hole. 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.
 - Calculate the change in entropy when the valve between compartment A and B is opened.
 - Calculate the change in entropy when the valve between compartment B and compartment C is opened.
 - Without considering the calculations above, how would you know that the overall change in entropy is positive?
 - What would you need to do to the system to restore the initial condition?

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.

- (a) 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	<i>e.g.</i> Gold		
Semiconductor			
Insulator			
Polymer			

- (b) What is a common material with a negative α ?
- (c) How is the coefficient of compressibility related to the bulk modulus?
- (d) Which metal has the highest bulk modulus at room temperature, and what is the value?
- (e) The heat capacity is an extensive quantity. Define the related intensive quantity.
- (f) What trend do you observe in elemental solids?
- (g) 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 $\sim 3.2 \text{ g/cm}^3$. 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/cm^3 . 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:
- (h) 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.
- (i) Using your curve of best fit, determine the optimal speed for driving that maximizes your mileage.
- (j) 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:

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

- (k) Use the system of equations derived in class to determine the coefficients a, b, c, d .
- (l) 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.
- (m) One mole of nitrogen (N_2) at 1000 K is compressed isothermally from 1 to 105 bar.
- (n) One mole of silicon at 300 K is compressed isothermally from 1 to 105 bar.
- (o) One mole of oxygen (O_2) at 300 K is heated isobarically from 300 to 1200 K.
- (p) 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.

- (q) Free expansion into the vacuum to twice the volume, starting from 300 K and 4 bar. Then,
- (r) Heating to 600 K reversibly with the volume held constant. Then,
- (s) Reversible expansion at constant temperature to twice the volume of the previous state. Then,
- (t) 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.

- (u) 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?
- (v) 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:

$$S_2 - S_1 = \int_{T_1}^{T_2} \frac{C_p(T)}{T} dT \quad (.1)$$

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:

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

where the function $f(T)$ in our case is the right hand side of Equation .1, is simply the right hand side of Equation .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.

- (w) What is the difference in entropy at 300 K and 1300 K?
- (x) Previously, we determined that the heat capacity is given by:

$$C_p = 22.83 + 3.826 \times 10^{-3} T - \frac{3.533 \times 10^5}{T^2} + 2.131 \times 10^{-8} T^2 \quad (.3)$$

Use Equation .1 to analytically solve for the change in entropy using Equation .3. Which method do you think is more accurate? Explain your reasoning.

Temperature Equilibration

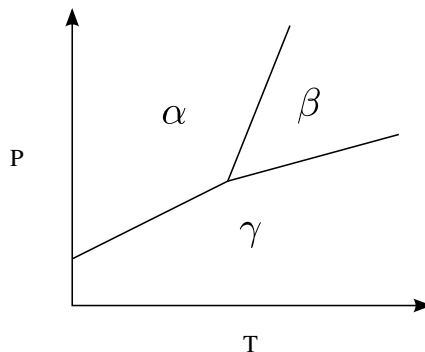
17. (2015) 100 g of ice at 250 K is added to 100 g of water at 300 K, and the mixture is allowed to come to equilibrium in an isolated container at constant pressure. You may assume that C_p is constant for this problem (though it is not the same for water and ice) and that the melting point is 273 K.
- (a) What is the final temperature?
 - (b) How much liquid is present?
 - (c) 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.
- (d) What do you know about the final temperatures of the Al blocks?
 - (e) Will the final temperature(s) be 450 K? Justify your answer.
 - (f) Find the final temperature.

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 ($\epsilon_1, \epsilon_2, \epsilon_3, \epsilon_4$).
- How many distinct microstates are there for this system?
 - List each of the microstates and indicate which microstates have the same energy.
 - How many macrostates are there?
 - 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 .
- Write the partition function for a single particle.
 - Calculate the average number of particles in each state.
 - Determine the number of configurations that have the following occupation numbers for the three states: $n_0 = 4, n_1 = 3, n_2 = 2$.
 - Calculate the entropy of the macrostate described by the occupation numbers above.
 - Calculate the internal energy.
 - 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 entropy ΔS 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}.

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.
- Calculate using the phenomenological thermodynamics of Chapter 4.
 - 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 at 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:
- $\Delta S^{\epsilon \rightarrow \beta} = 3.43 \text{ J/mol} \cdot \text{K}$ (This is the difference in molar entropy 3 between the phases).
 - The change in molar entropy upon melting is $9.02 \text{ J/mol} \cdot \text{K}$.

- $T_m^\beta = 1940 \text{ K}$.

(c) Sketch G^ε , G^β and G^ℓ in the temperature range of interest.

(d) What is T_m^ε ?

(e) 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>

Find the ε phase of titanium (labeled as GHSERTI), the β phase (labeled as GBCCTI), and the liquid phase (labeled as GLIQT) 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 “^”.

Multicomponent 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:

(a) The weight percent of O in the solution.

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

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

(d) 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 $X_{\text{Cr}_2\text{O}_3} = 0.2$. Calculate the resulting changes in the total enthalpy and entropy given the following:

$$T_{m,\text{Cr}_2\text{O}_3} = 2538 \text{ K}; \Delta H_{m,\text{Al}_2\text{O}_3} = 107,500 \text{ J/mol at } T_{m,\text{Al}_2\text{O}_3} = 2324 \text{ K}; \Delta S_{m,\text{Al}_2\text{O}_3} = \Delta S_{m,\text{Cr}_2\text{O}_3}$$

314 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:

$$\begin{aligned} C_p^{\text{Pb}} &= 0.1169 + 4.2 \times 10^{-5} T \frac{\text{kJ}}{\text{kg} \cdot \text{K}} \\ C_p^{\text{H}_2\text{O}} &= 4.2 \frac{\text{kJ}}{\text{kg} \cdot \text{K}} \\ \Delta H_{fus}^{\text{H}_2\text{O}} &= 344 \frac{\text{kJ}}{\text{kg}} \\ \frac{dH}{dt} &= a \Delta T \end{aligned}$$

Here a is a coefficient that controls the heat transfer in conduction, which we will assume to be $3.33 \times 10^{-3} \text{ kJ/K} \cdot \text{s}$, and ΔT is the temperature difference between the two materials.

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

(b) 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?

(c) 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?

32. (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:

$$G_s - X_s \frac{dG_s}{dX_s} = G_\ell - X_\ell \frac{dG_\ell}{dX_\ell} \quad (.4)$$

$$\frac{dG_s}{dX_s} = \frac{dG_\ell}{dX_\ell} \quad (.5)$$

where G_s and G_ℓ are given by the following expressions:

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

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

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. .4 and .5 as follows:

$$G_s - X_s \frac{dG_s}{dX_s} - G_\ell + X_\ell \frac{dG_\ell}{dX_\ell} = 0 \quad (.6)$$

$$\frac{dG_s}{dX_s} - \frac{dG_\ell}{dX_\ell} = 0 \quad (.7)$$

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 $T=700\text{K}$, $\Omega_\ell = 1500 \text{ cal/mol}$ and $\Omega_s = 3000 \text{ cal/mol}$.

33. (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 $R = 1.987 \text{ cal/mol} \cdot \text{K}$

$$G_s(X_s) = \Omega_s X_s (1 - X_s) + RT [X_s \ln X_s + (1 - X_s) \ln (1 - X_s) + X_s \Delta G_\beta^{\ell \rightarrow s} + (1 - X_s) \Delta G_\alpha^{\ell \rightarrow s}].$$

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

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:

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

34. (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 $\Omega_s = 3000$ 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.

- (a) $\Omega_s = 3000$ cal/mol : $\Omega_\ell = 0$
- (b) $\Omega_s = 0$: $\Omega_\ell = 3000$ cal/mol
- (c) $\Omega_s = 0$; $\Omega_\ell = 0$
- (d) $\Omega_s = 3000$ cal/mol : $\Omega_\ell = 3000$ cal/mol

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

315 Problems

- Use the Ellingham Diagram (reproduced here as Figure .1) to answer the following.
 - Find the temperature and partial pressure of O_2 where $Ni(s)$, $Ni(l)$, and $NiO(s)$ are in equilibrium.
 - 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 ?
- Use the Ellingham Diagram to answer the following question. At $1245^\circ C$, 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
- Using the Ellingham diagram, can you safely melt aluminum in a magnesia (MgO) container? Why or why not? What is the resulting reaction and its driving force?
- Establish the T-log P_{O_2} phase diagram between $1000^\circ C$ and $1500^\circ C$ for the Mn-O system at 1 atm total pressure.
- In the days before the industrial revolution the P_{CO_2} in the earth's atmosphere was 275 ppm. Use the data in Figure .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.
- 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 $\Delta C_p \approx 0$ for both end members. Use the following melting points and enthalpies of fusion:

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

- 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	$T_m(^{\circ}C)$	$\Delta H_m(J/mol)$
A	910	34700
B	1300	49800

- Plot the T vs. X phase diagram. Label each region on the diagram with the phases present and the degrees of freedom.
 - For the temperatures $800^\circ C$, $1100^\circ C$, and $1500^\circ C$, 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.
- Based upon the temperature at the top of the miscibility gap in the Cr-W system (see Figure .3), do the following:
 - Predict the miscibility gap (solvus) and spinodals based upon the regular solution model. Use the spreadsheet and plot the results.
 - Compare your miscibility gap with the experimental one in the attached figure. Speculate about why there might be differences.
 - Consider the Pb-Sn phase diagram (see Figure .4).
 - Label each region on the diagram with the degrees of freedom.
 - Sketch free energy vs. composition curves for all phases at $150^\circ C$, $200^\circ C$, $250^\circ C$, and the eutectic temperature.
 - 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 Raoultian. At $150^\circ C$, only plot activity of Sn vs. composition with respect to the solid reference state. At $250^\circ C$, only plot activity of Sn vs. composition with respect to the liquid reference state.

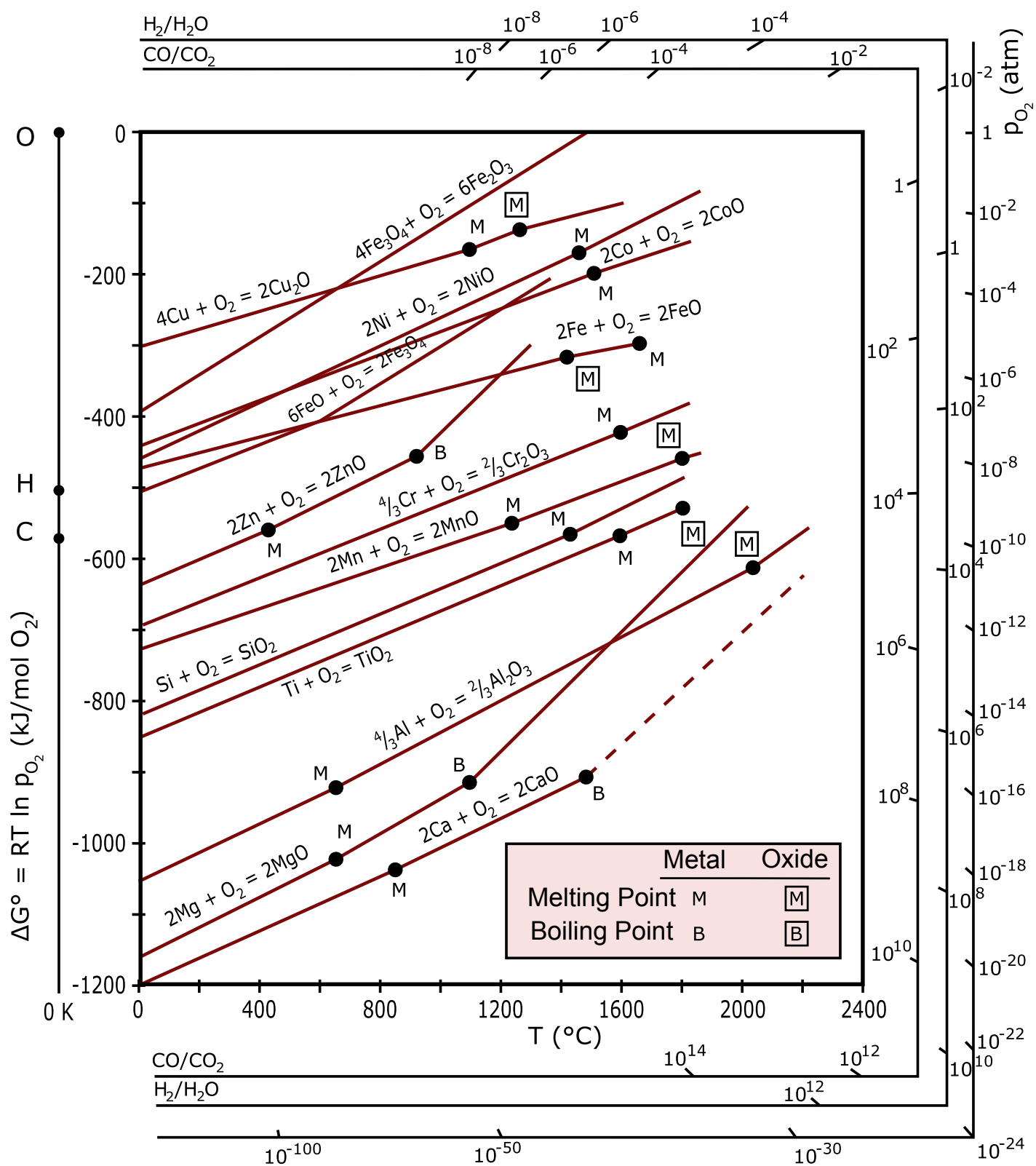


Figure .1: Ellingham diagram.

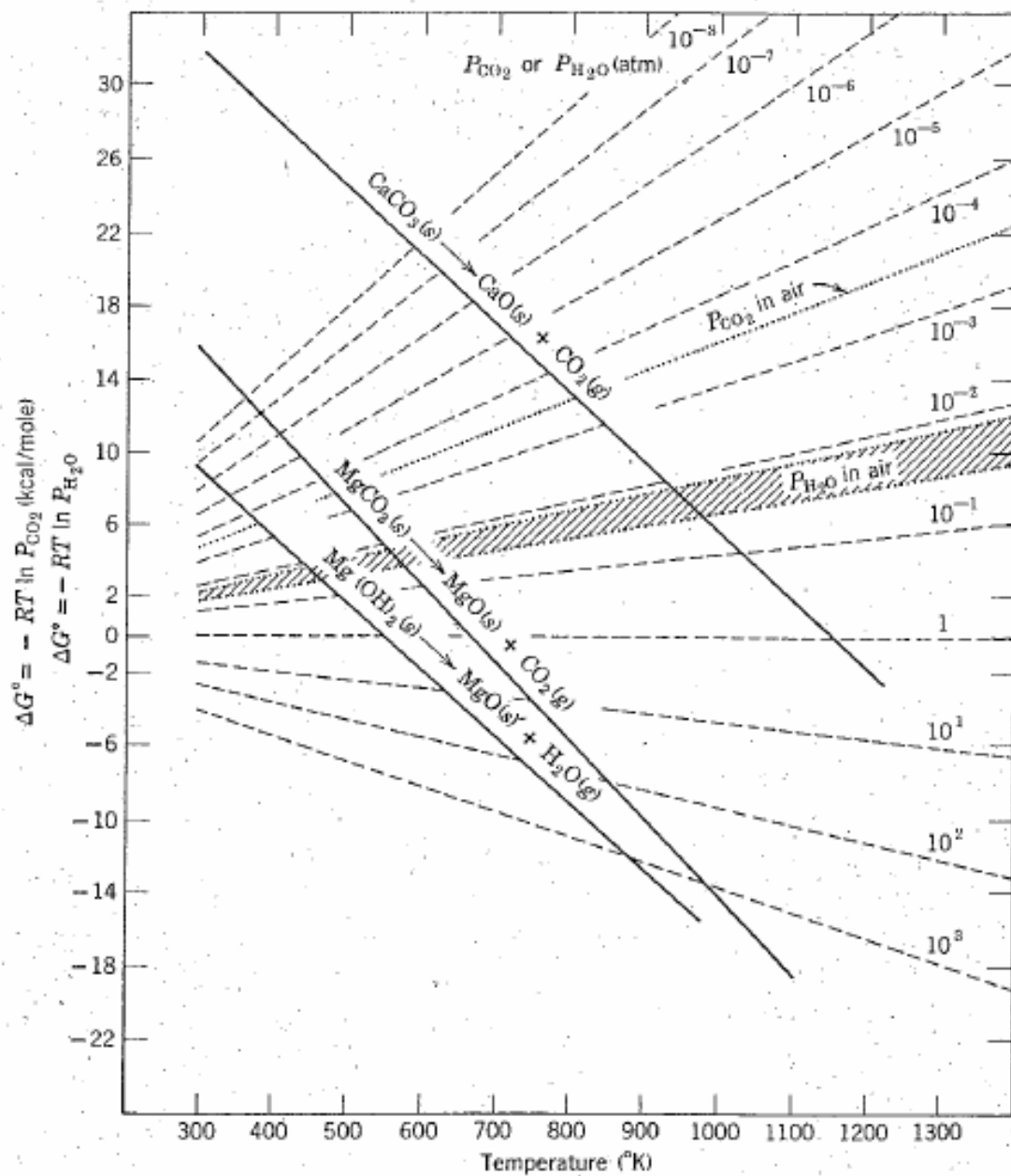


Figure .2: Thermodynamic data for Mg and Ca oxides and carbonates.

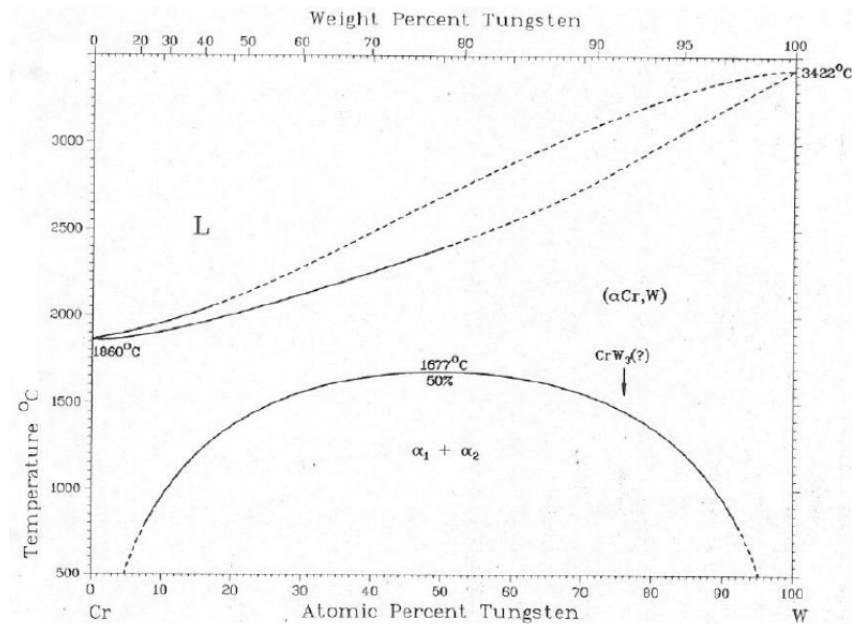


Figure .3: Cr-W Phase diagram.

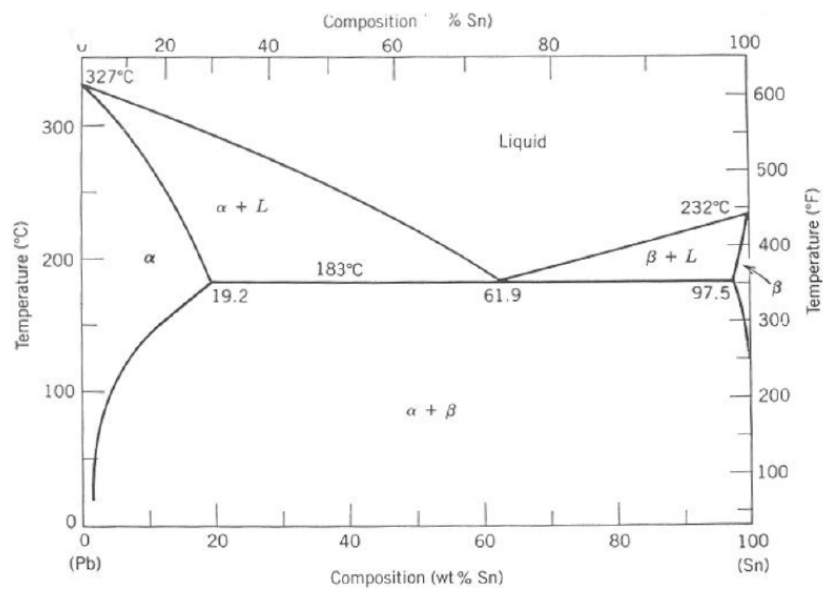


Figure .4: Pb-Sn phase diagram.

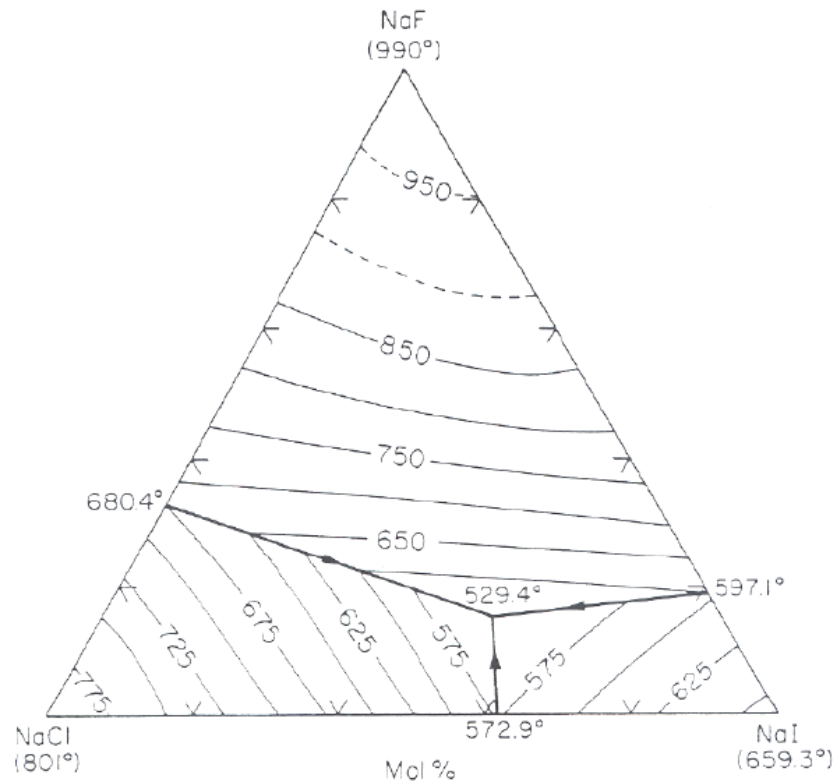


Figure .5: NaF-NaCl-NaI phase diagram. From ref. [?].

10. 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 an ideal liquid solution and negligible solid solubility. Compare your result with the experimental diagram shown in Figure .5. Why might they be different?
11. On the liquidus projection diagram for the hypothetical system A-B-C shown in Figure .6), complete the following:
 - (a) Label primary phase fields
 - (b) Draw the subsolidus compatibility joins.
 - (c) Label all the binary and ternary invariant points.
 - (d) Indicate the directions of falling temperature (binaries and ternary).
 - (e) Sketch all the binary phase diagrams (including those formed by subsolidus compatibility joins).
12. Using the attached liquidus projection diagram for the hypothetical system A-B-C shown in Figure .7, complete the following:
 - (a) Determine the equilibrium crystallization path for the composition marked with the star.
 - (b) Determine the microstructural constituents:
 - i. Just prior to the liquid striking the phase boundary (liquid + solid 1 + solid 2).
 - ii. At the eutectic but just prior to eutectic crystallization.
 - iii. After crystallization is complete.
13. On the $(\text{LiCl})_2 - \text{CaCl}_2 - (\text{KCl})_2$ phase diagram shown in Figure .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)
 - (a) 600°C
 - (b) 450°C
 - (c) 400°C
 - (d) 300°C

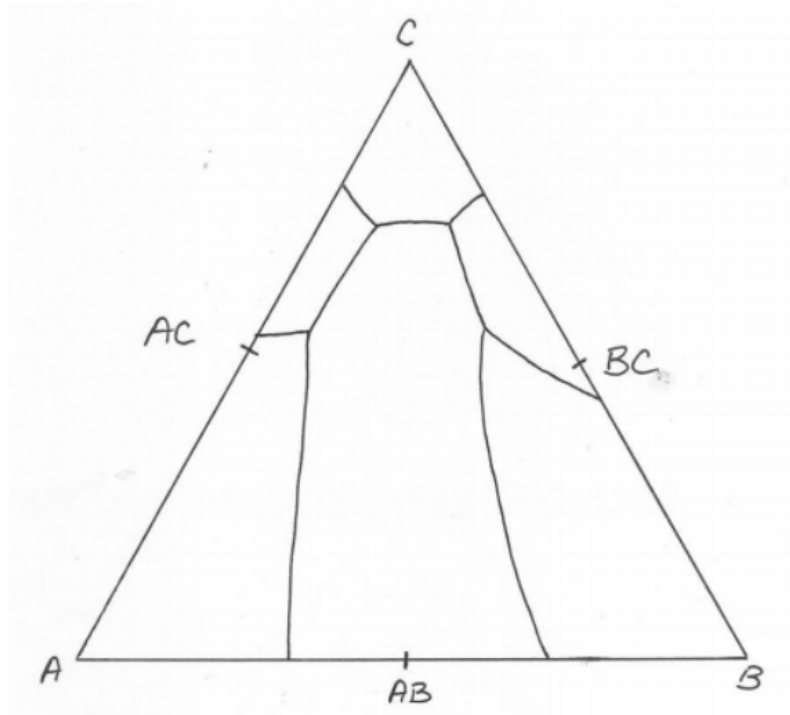


Figure .6: Liquidus projection diagram.

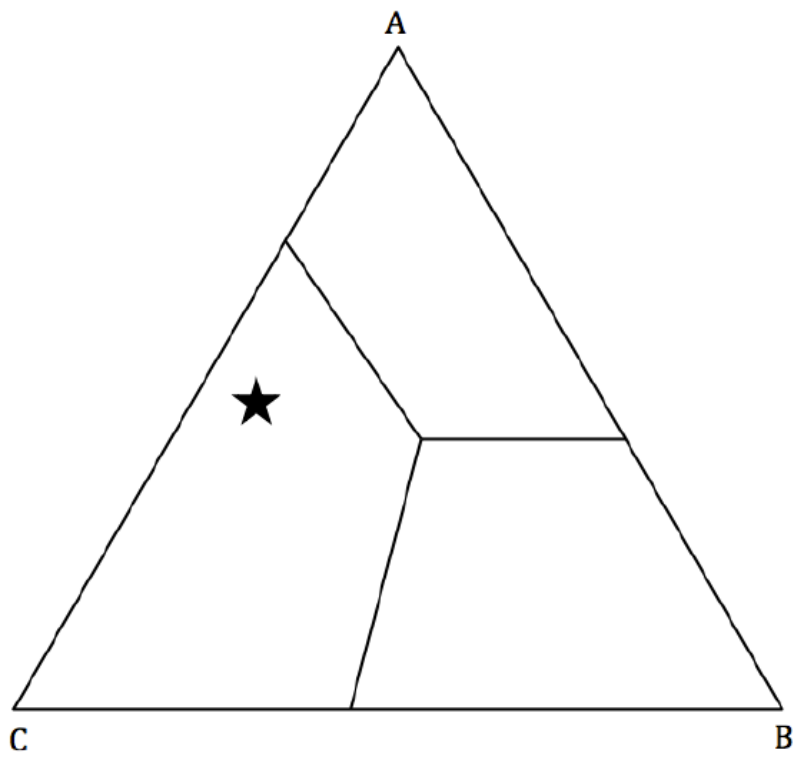


Figure .7: Liquidus projection diagram.

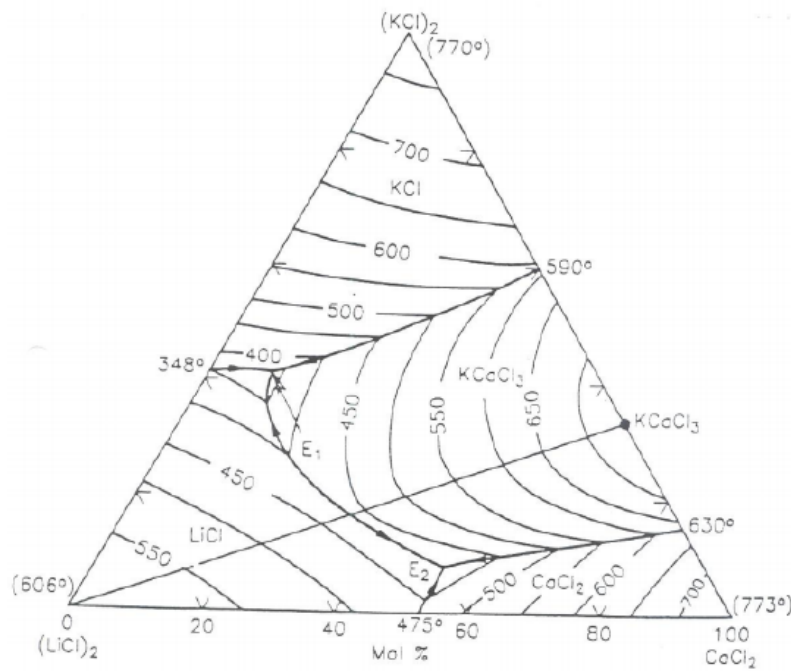


Figure .8: $(\text{LiCl})_2 - \text{CaCl}_2 - (\text{KCl})_2$ phase diagram.

- (e) Also determine the precise (not schematic!) $(\text{LiCl})_2 - \text{KCaCl}_3$ phase diagram.
14. (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 initial 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 ($X_B \rightarrow 1$).
 15. A steel tank contains hydrogen at 15 atm pressure. If the solubility of hydrogen in steel is $1 \times 10^{-2} \text{ g/cm}^3$ under 15 atm pressure, the diffusion coefficient is $8 \times 10^{-5} \text{ cm}^2/\text{s}$ at room temperature and the tank is placed in a vacuum, calculate the flux of hydrogen through a 3.5 mm thick wall.
 16. Austenite ($\gamma\text{-Fe}$) with .85 wt% carbon has a diffusion coefficient of $1.9 \times 10^{-11} \text{ m}^2/\text{s}$ at 900°C .
 - (a) Determine the jump distance in terms of the lattice parameter a_0 and the coordination number for carbon diffusion in this structure.
 - (b) 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?
 - (c) Calculate and compare the random walk distance with the total distance (back and forth) traveled by an interstitial carbon atom in one second.
 17. Ferrite ($\alpha\text{-Fe}$) (BCC structure) dissolves carbon to a lesser extent than austenite (FCC structure).
 - (a) Determine the jump distance in terms of the lattice parameter a_0 and the coordination number for carbon diffusion in this structure.
 - (b) 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 .
 - (c) A different interstitial solute diffuses at a rate of $4.1 \times 10^{-2} \text{ mm}^2/\text{s}$ at 300°C and $7.3 \times 10^{-2} \text{ mm}^2/\text{s}$ at 600°C . Determine its activation energy and pre-exponential factor.
 18. Write a MATLAB code to evaluate the composition as a function of distance for the draining plate problem.
 - (a) 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 $|c(x) - c_{\text{exact}}(x)|/c_{\text{exact}}(c) \times 100$. To determine the exact answer evaluate the summation to $j = 200$. $L = 100 \mu\text{m}$, $C_0 = 0.1 \text{ at. \%}$

- (b) Plot the converged solution as a function of x for $t/\tau = 0.05, 0.5, 1.0, 2.0$.
- (c) 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%?
19. (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.
- (a) 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 D_v is $10^{-5} \text{ cm}^2/\text{s}$.
- (b) Calculate the relaxation time (τ) given a dislocation line length (dislocation density) of 10^7 cm/cm^3 . (Hint: First, calculate the distance between dislocations, i.e, the vacancy sources.)
20. The diffusion coefficient of carbon in austenite can be approximated as:
- $$D_c = 0.2 \exp \left(\frac{-136,000 \text{ J/mol}}{RT} \right) \text{ cm}^2/\text{s}$$
- (a) 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?
- (b) What annealing temperature is required to double the penetration in a given time?
21. 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 $D = 4.5 \times 10^{-11} \text{ m}^2/\text{s}$ and that D is not a function of concentration.
22. 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.
23. Given that $D = \frac{1}{6} \Gamma v \alpha^2$, consider the diffusion of vacancies in an FCC lattice:
- (a) Let $\frac{\Delta S_m}{R} = 2$ and $v = 10^{13} \text{ s}^{-1}$. Calculate the pre-exponential factor D_0 for vacancies (assume $a_0 = 0.4 \text{ nm}$.)
- (b) If $\Delta H_m = 6.5 \text{ kJ/mol}$, calculate D_v for vacancies at 750°C
24. Below are the linear thermal expansion ($\Delta L/L_0$) and X-ray lattice parameter ($\Delta a/a_0$) 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.
25. 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 $\ln X_v$ from this data versus $1/T$ and determine the enthalpy and entropy of vacancy formation in this material. Show all equations used.
26. 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 $\Delta \rho_0$. 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} .
27. Write balanced Kröger-Vink reactions for the following reactions, assuming full ionic charge for all ionic species.
- (a) Schottky defect formation in Li_2O
- (b) Anion Frenkel defect formation in Nb_2O_5
- (c) Oxidation of CdO to yield $\text{Cd}/\text{O} < 1/1$ (write both possible reactions)
- (d) Doping Al_2O_3 with ZnO to produce oxygen vacancies.
28. 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.

- (a) Draw a schematic Brouwer diagram as a function of pO_2 at fixed Al content.
 - (b) 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.
29. 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.

316-1 Problems

Introduction

- Send an email to Prof. Shull (k-shull@northwestern.edu) and Ashley (ashleyepyp@gmail.com) with the following information:
 - 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).
 - Your level of experience and comfort level with MATLAB. Be honest about your assessment (love it, hate it, don't understand it, etc.).

Diffusion

- 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 1. After 56 days at 785 °C the marker velocity was 2.6×10^{-8} mm/s, with a composition at the markers of $X_{Zn} = 0.22$, and a composition gradient, $\partial X_{Zn} / \partial x$ of 0.089 mm^{-1} . A detailed analysis of the data gives $\bar{D} = 4.5 \times 10^{-13} \text{ m}^2/\text{s}$ 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 \bar{D} to vary as a function of composition?

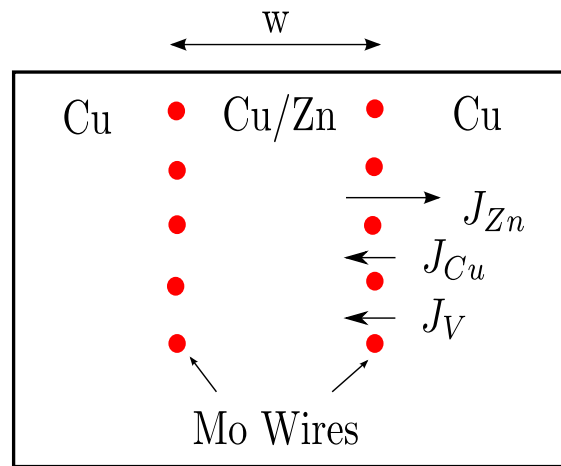


Figure 1: Experimental Geometry for the Kirkendall experiment.

- 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).
- Consider two binary alloys with compositions $X_b = X_1$ and $X_b = X_2$, shown in Figure 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.

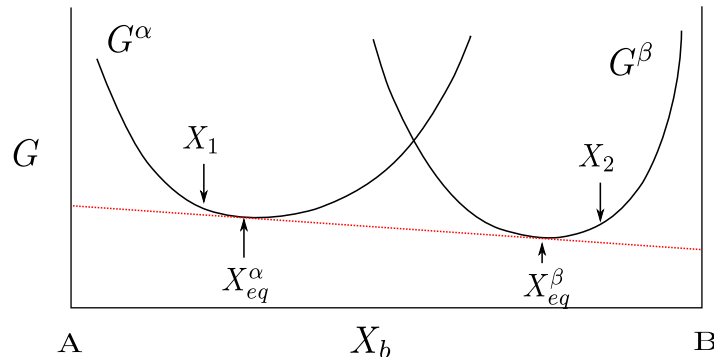


Figure 2: Free energy curves for a model A/B alloy.

5. 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 time 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 will 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=0; % set to zero if you want to speed things up by not showing images, set to 1
19 % if you want to show all the images during the simulation
20 %% now we start to move things around
21 vacancydiff.matrices={}; % make a blank cell array
22 while t<max(times);
23     t=t+1;
24     dir=round(4*rand+0.5);
25     if dir==1
26         in=i+1;
27         jn=j;
28         if in==n+1; in=1; end
29     elseif dir==2
30         in=i-1;
31         jn=j;
32         if in==0; in=n; end
33     elseif dir==3
34         in=i;
35         jn=j+1;
36         if jn>n; jn=1; end
37     elseif dir==4
38         in=i;
39         jn=j-1;
40         if jn==0; jn=n; end
41     end
42     % now we need to make switch
43     neighborix=sub2ind([n n],in,jn);
44     vacix=sub2ind([n n],i,j);
45     matrix([vacix neighborix])=matrix([neighborix vacix]);
46     if showallimages
47         imagesc(matrix);
48         drawnow
49     end
50     if ismember(t,times)
51         vacancydiff.matrices=[vacancydiff.matrices {matrix}]; % append matrix to output file
52         imagesc(matrix);
53         set(gcf,'paperposition',[0 0 5 5])
54         set(gcf,'papersize',[5 5])
55         print(gcf,['vacdiff' num2str(t) '.eps'],'-depsc2')
56     end
57     i=in;
58     j=jn;
59 end
60 vacancydiff.times=times;
61 vacancydiff.n=n;
62 save('vacancydiff.mat','vacancydiff') % writes the vacancydiff structure to a .mat file that we
63 % can read in later
64 toc

```

- (a) run the vacancydiffusion script, and include in your homework the .jpg files generated for time steps of 1e4, 2e4, 4e4 and 1e5.
- (b) 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>):

```

1 load vacancydiff % load the previously saved output.mat file
2 figure
3 figformat % not necessary, this is the standard initialization script I use to standardize
  what my plots look like
4 n=vacancydiff.n;
5 matrix=vacancydiff.matrices{4};
6 matrixsum=sum(matrix,1); % sum of each column in the matrix
7 plot(1:n,matrixsum/n,'+b')
8 xlabel ('x')
9 ylabel ('C')
10 print(gcf,'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
11 saveas(gcf,'vacancyplot.jpg')

```

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,'defaultlinelength',2)
3 set(0,'defaultaxesfontsize',16)
4 set(0,'defaultfigurepaperposition',[0,0,5,5])
5 set(0,'defaultfigurepapersize',[5,5])

```

6. 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.
- (c) 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:

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

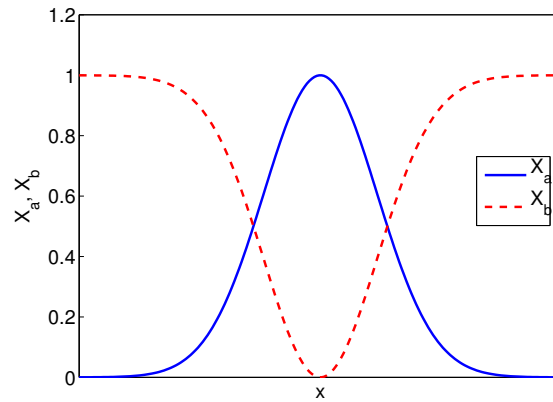
Note: This problem is a curve fitting exercise in MATLAB. The most frustrating part is getting all the syntax right, but once you know the proper format for the MATLAB code, it's pretty straightforward. Take a look at the section entitled 'Fitting a Function to a Data Set' in the MSE MATLAB help file (<http://msecore.northwestern.edu/m>). This section includes a MATLAB script that you can download and modify as needed.

- (d) 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.
- (e) 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 .

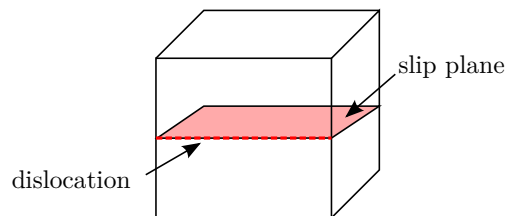
7. A region of material with a different composition is created in an infinitely long bar. The following plot shows the mole fraction of component A as a function of position. Assume that the intrinsic diffusion coefficient of the A atoms is twice as large as the intrinsic diffusion coefficient for the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



- (a) Plot the flux of A and the flux of B relative to the lattice as a function of position in the graph above. Justify your answer in the space below.
- Plot the vacancy creation rate as a function of position in the graph above. Justify your answer in the space below.
 - Plot the flux of A and B in the lab frame as a function of position in the graph above. Justify your answer in the space below.
 - Plot the lattice velocity as a function of position in the graph below. What are the physical implications of this plot?

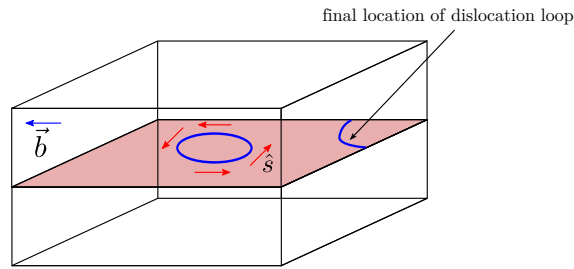
Dislocations

8. 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.



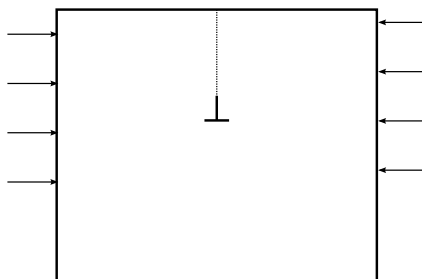
- Sketch the shape of the sample after the dislocation has propagated halfway through the sample, and again when it has propagated all the way through the sample. Use arrows to specify the shear force that is being applied.
 - Repeat part a for a left-handed screw dislocation.
9. Draw an edge dislocation and on the same figure dot in the positions of the atoms after the dislocation has shifted by \vec{b} .
10. How can two edge dislocations with opposite Burgers vectors meet to form a row of vacancies? A row of interstitials.

11. Given a crystal containing a dislocation loop as shown in the following figure:



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.

12. 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.
13. 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.
14. Answer the following questions.
- If edge dislocations with opposite signs of the Burger's vectors meet, does the energy of the crystal increase or decrease? Defend your answer.
 - 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? Defend your answer.
 - If 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? Defend your answer.
 - Draw the compressive and tensile regions surrounding an edge dislocation. Defend your answer.
 - Consider the case of a pure material with a solid spherical particle in a liquid. Is it still possible to use a graphical construction that involves the molar Gibbs free energies as a function of temperature to determine the equilibrium temperature if the molar volume is a function of pressure? Defend your
15. 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):



- If diffusion occurs, which way will the dislocation move? Explain why and tell where the atoms go that leave the dislocation.
- Derive an equation relating the stress, σ to b and the force tending to make the dislocation move in the vertical plane.

- (c) If the edge dislocation is replaced by a screw dislocation, which way will the dislocation tend to move?
16. 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.
17. Repeat the previous problem for edge dislocations of opposite sign.

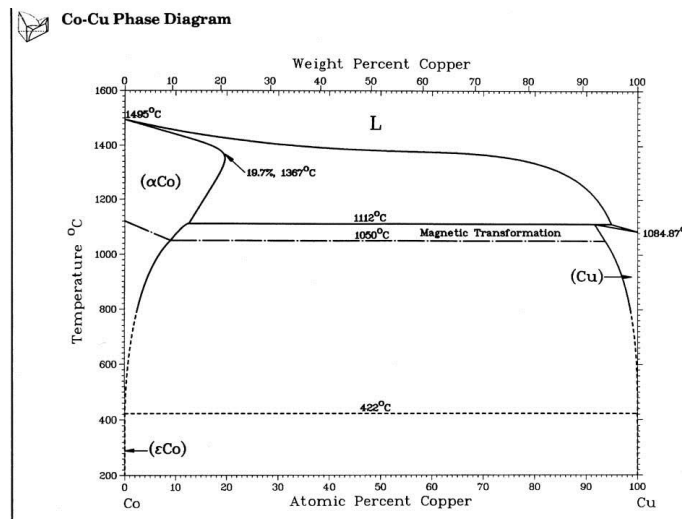
Interfacial Thermodynamics

18. Starting with the expression we derived in class, show that the melting point of a pure solid spherical particle in a liquid can be expressed as follows:

$$T = T_m - \frac{2T_m V_m \sigma}{\Delta H_m r}$$

where ΔH_m is the molar latent heat of fusion, defined as $H_m^l - H_m^s$, where H_m is the molar enthalpy of the liquid or solid.

19. Is the molar latent heat positive or negative? Is the melting temperature, T , greater than or less than T_m ?
20. Consider the case of a pure liquid spherical droplet embedded in a pure solid. Using the graphical construction discussed in class, determine if the melting point above or below the bulk melting temperature?
21. Consider the Co-Cu phase diagram shown below:



- (a) Plot the equilibrium activity of Cobalt as a function of composition across the entire phase diagram at 900°C.
- (b) 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 mJ/m². For what radius of a Co precipitate will this solubility limit be increased by 10%?

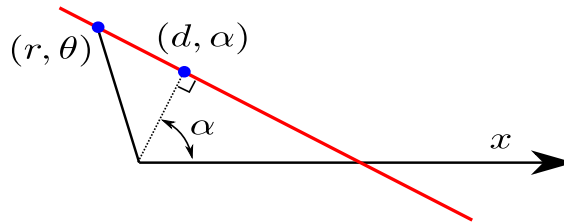


Figure .3: Representation of a line drawn a distance d from the origin.

Surface and Interface Structure

22. 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 .3).
- Determine the equilibrium shape of a crystal where the surface energy is given by $\gamma = 1 \text{ J/m}^2$ (independent of α).
 - 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?
 - Determine the equilibrium shape of a crystal where the surface energy is given by $\gamma = 1 + 0.07 \cos(4\alpha) \text{ J/m}^2$. Are there any corners on the equilibrium shape?
 - Determine the equilibrium shape of a crystal where the surface energy is given by $\gamma = 1 + 0.6 \cos(4\alpha) \text{ J/m}^2$. 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)?

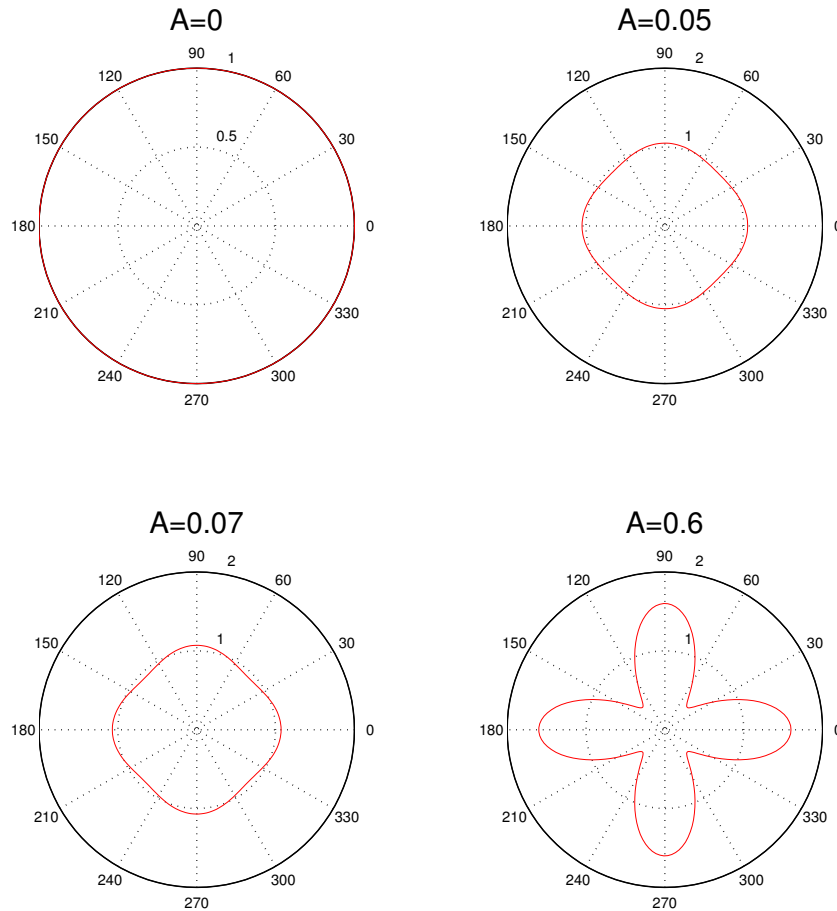
As a headstart on this problem, here's a MATLAB script that generates polar plots of the γ as defined in the problem:

```

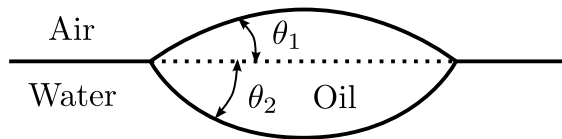
1 close all
2 A=[0,0.05,0.07,0.6]; % these are the 4 values of A defined in the problem
3 % define a function where the radius d is the surface energy and alpha
4 % is the angle
5 d=@(A,alpha) 1+A*cos(4*alpha);
6 figure
7 for k=1:4
8     alpha=linspace(0,2*pi,200);
9     subplot(2,2,k) % this makes a 2 by 2 grid of plots
10    polar(alpha,d(A(k),alpha),'r-'); % polar 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 $\gamma = 1 + A \cos(4\alpha)$).



23. Consider the an oil droplet that forms on the surface of water, as shown schematically in the following Figure:

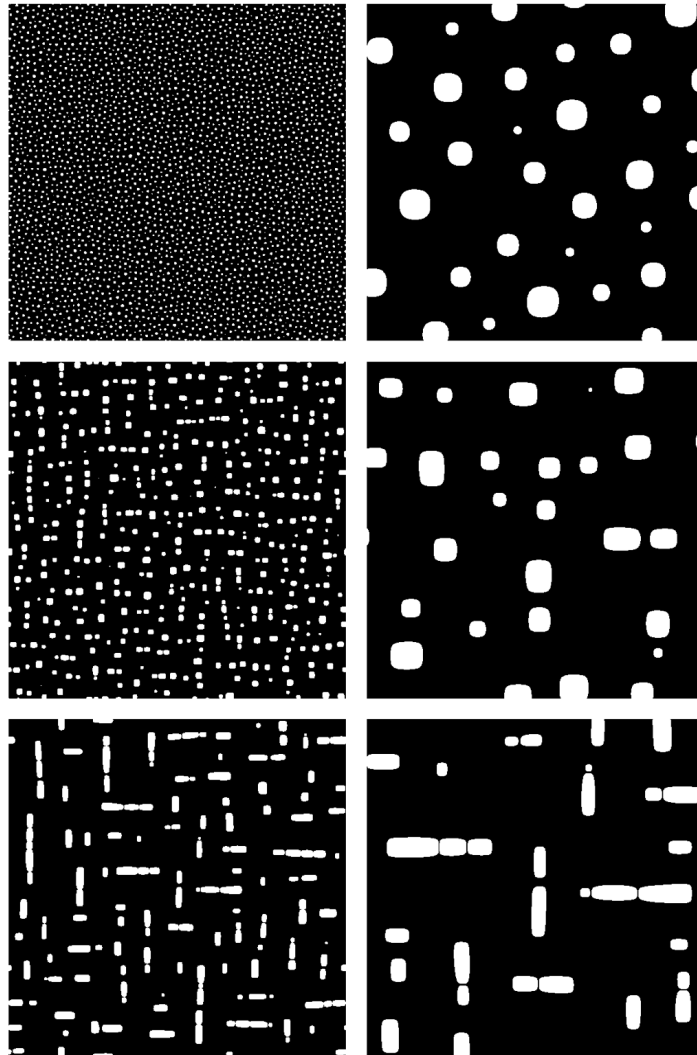


Determine θ_1 and θ_2 if the air/water interfacial free energy is 72 mJ/m^2 , the air/oil interfacial free energy is 30 mJ/m^2 and the oil/water interfacial free energy is 50 mJ/m^2 .

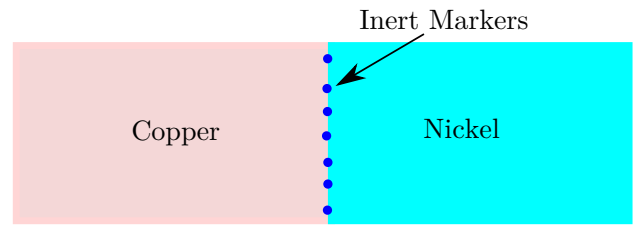
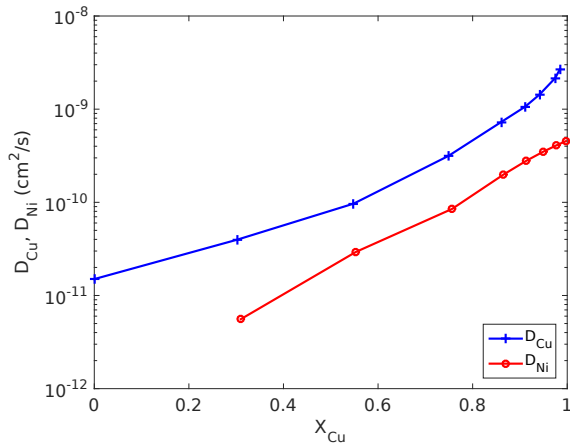
24. The surface energy of the interface between nickel and its vapor is 1.580 J/m^2 at 1100K . The average dihedral angle measured for grain boundaries intersecting the free surface is 168° . Thoria dispersed nickel alloys are made by dispersing fine particles of ThO_2 in nickel powder and consolidating 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.
25. Consider a gold line deposited on a silicon substrate. The film is 0.1 micron thick and all the grain boundaries are perpendicular to the gold-vapor interface. The grain boundaries run laterally completely across the line, giving a "bamboo" structure. 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.
- (a) Compute the dihedral angle where a grain boundary meets the external surface.

(b) Find the critical grain boundary spacing ℓ_c for which the equilibrium grain shape produces a hole in the film.

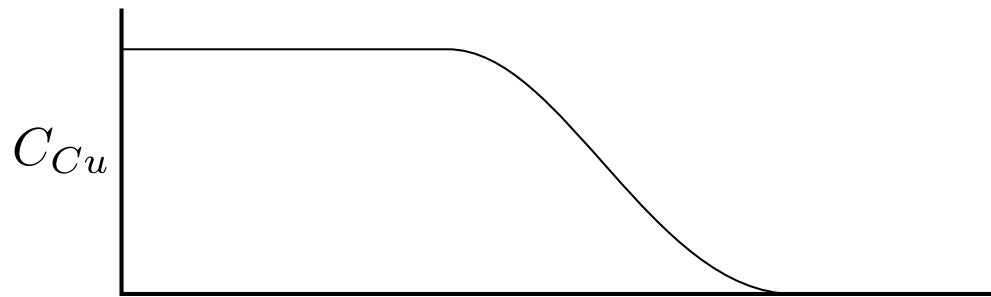
26. The equilibrium shape you calculated in the last homework looks similar to the shape of a few of the particles on the attached simulations of misfitting particles in an elastically anisotropic system. The left column is the entire system, whereas the right column is a magnification of a small region of the figure in the left column. These are snapshots taken as function of time while the particles are growing. Are these cuboidal shapes are due to elastic stress and or anisotropic interfacial energy? Explain your answer.



27. Explain the structure and energies of coherent, semicoherent and incoherent interfaces, paying particular attention to the role of orientation relationships and misfit.
28. Explain why fully coherent precipitates tend to lose coherency as they grow.
29. 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.

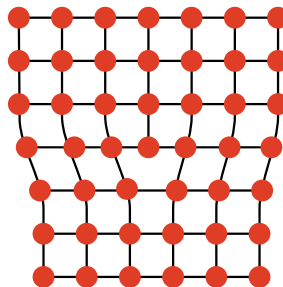


- (c) What is the value of the interdiffusion coefficient \tilde{D} , for an alloy consisting of nearly pure Nickel?
- (d) Will the markers placed initially at the Cu/Ni interface move toward the copper end of the sample, the nickel end of the sample, or stay at exactly the same location during the diffusion experiment.
- (e) The copper concentration across the sample is sketched below after diffusion has occurred for some time.

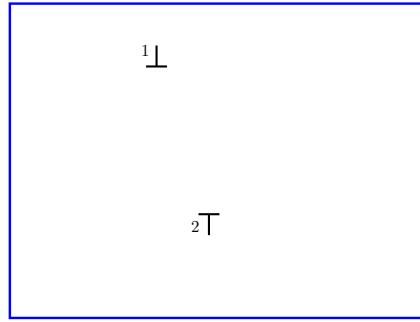


Sketch the fluxes of Copper, Nickel and vacancies, defining positive fluxes as those moving to the right.

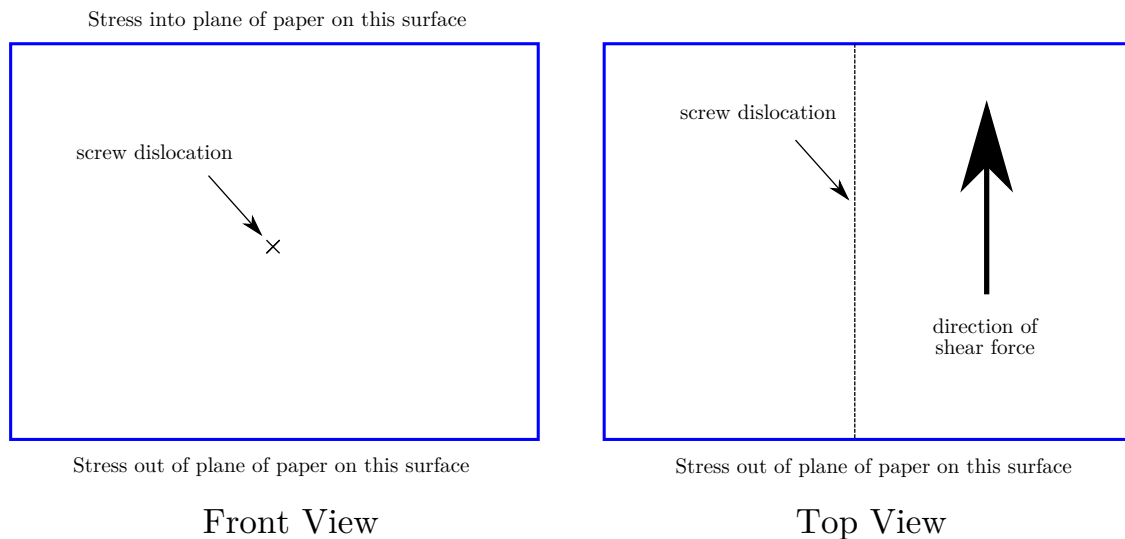
- (f) Now sketch the rate at which vacancies are created or destroyed within the sample in order to maintain a constant overall vacancy concentration throughout.
- (g) On the following sketch of a dislocation, indicate the direction that it must move in order for vacancies to be created.



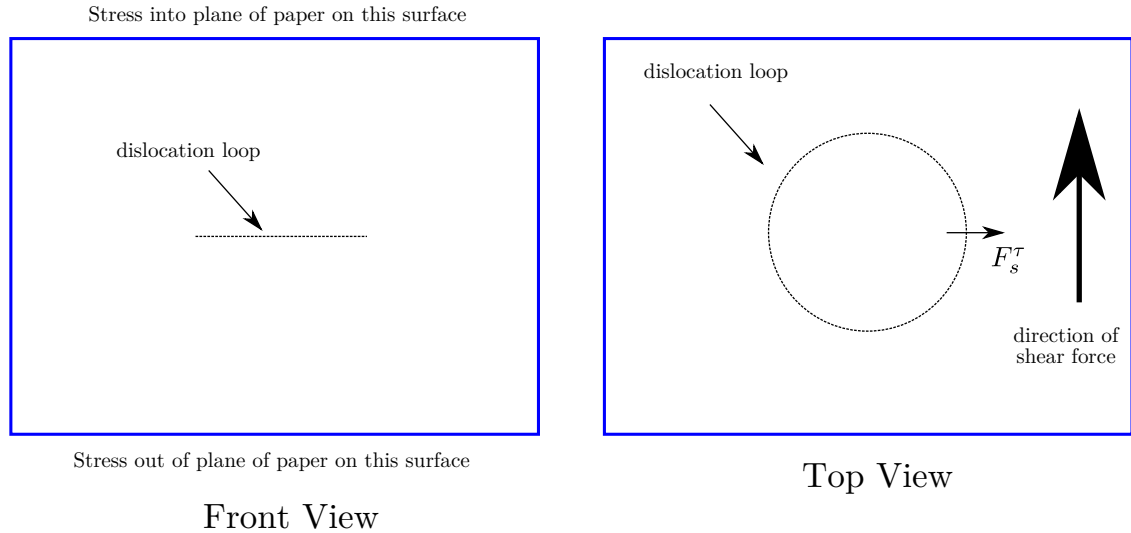
30. Consider the two edge dislocations shown below. Suppose dislocation 1 remains fixed in place, but that dislocation 2 is able to move on its glide plane.
- (a) Assume that the sense vector, \vec{s} , for each dislocation is defined so that \vec{s} points into the page. Indicate the direction of \vec{b} for each of the two dislocations.



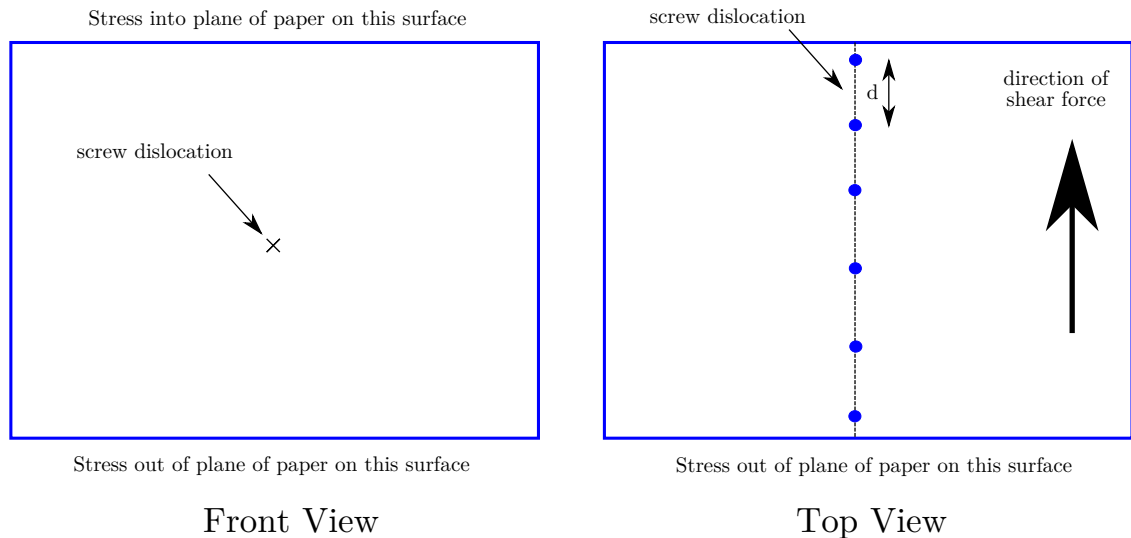
- (b) Indicate the glide plane for dislocation 2 with a dotted line.
- (c) Indicate with an X the location of dislocation 2 at the position within its glide plane that minimizes the total strain energy of the system.
31. Now suppose that dislocation 1 is a fixed, left-handed screw dislocation and dislocation 2 is a mobile right-handed screw dislocation.
- (d) 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.
- (e) Plot the overall strain energy of the system as a function of the distance between the two screw dislocations.
32. Consider an isolated right-handed screw dislocation, identical to dislocation 2 from the previous problem. Suppose a shear force is applied parallel to the dislocation line, as illustrated below.



- (a) What is the direction of the force, F_s^T , that is applied to the dislocation as a result of the applied stress.
- (b) 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^T at different points along the dislocation loop. (The direction of F_s^T has already been indicated at the right edge of the dislocation).



- (c) Describe how the magnitude of F_s^τ changes (if at all) for different locations along the dislocation loop.
- (d) What do 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)?
- (e) Suppose the straight screw dislocation from part b 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.

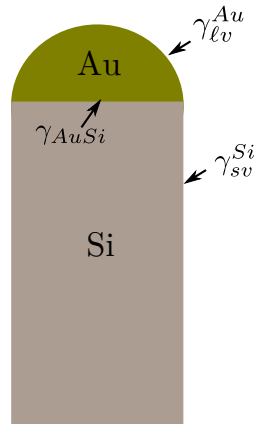


- (f) What do you expect to happen to the critical resolved shear stress of the material if d is decreased by a factor of 2. (Will the critical resolved shear stress increase, decrease or stay the same).
33. The relationship between the the interfacial energy between α and β phases and the pressure difference across a curved interface is obtained from the following expression:

$$-P^\alpha \delta V^\alpha - P^\beta \delta V^\beta + \gamma_{\alpha\beta} \delta A^\Sigma = 0$$

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

- (b) 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.
- (c) Now 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.



34. Why does the velocity of a grain boundary depend on temperature? Assume that the driving force for grain boundary motion is independent of temperature.
35. Assume a simple cubic crystal structure with nearest neighbor interactions. Why does a solid surface with a $\{100\}$ orientation have the lowest surface energy?
36. Why do very small precipitates tend to have coherent interfaces? Defend your answer.
37. A thin film of Zn with a 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. Defend your answer.
38. Does the time to 50% transformed increase or decrease with an increase in nucleation rate? Defend your answer without using any equations.
39. Give an example of an interface between two crystals that displays a very large change in energy with a change in the orientation of the interface.

316-1 Simulation Exercise: Monte Carlo Simulation of Decomposition in a Binary Alloy

Background

Scientific problem We want to analyze the thermodynamic evolution of a A-B alloy by simulation. We assume that this system has the phase diagram presented in Figure 4. In this figure we see that for temperatures lower than T_C , the A-B alloy decomposes in two phases α and β with equilibrium concentrations X_B^α and X_B^β . The experiment that we want to model involves the following steps:

1. We mix together the same number of moles of elements A and B to obtain a homogeneous alloy at some temperature above T_C .

2. The temperature is reduced to T_0 .
3. The temperature is held fixed at T_0 , and the system evolves to form two different phases, with compositions X_B^α and X_B^β .

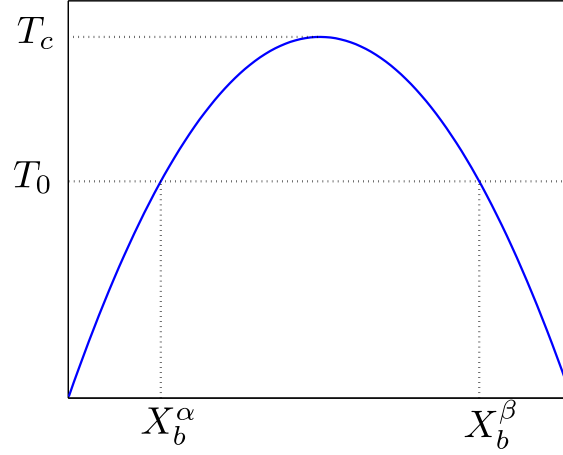


Figure .4: A-B alloy phase diagram

Atomistic Monte Carlo Model In this section, we introduce the Atomistic Monte Carlo model that we will use to model the decomposition of the A-B alloy.

Atomistic model In this model, we suppose that the two elements (A and B) have the same lattice structure. This lattice is represented by a matrix with periodic boundary conditions on its edges (see Figure .5). In 2 dimensions the left edge is connected to the right edge and the upper edge is connected to the lower edge. We reproduce the system evolution at the atomistic level: vacancies present in the lattice migrate from site to site by exchanging their position with their first nearest neighbors. The successive displacements of vacancies make the system evolve toward its equilibrium state.

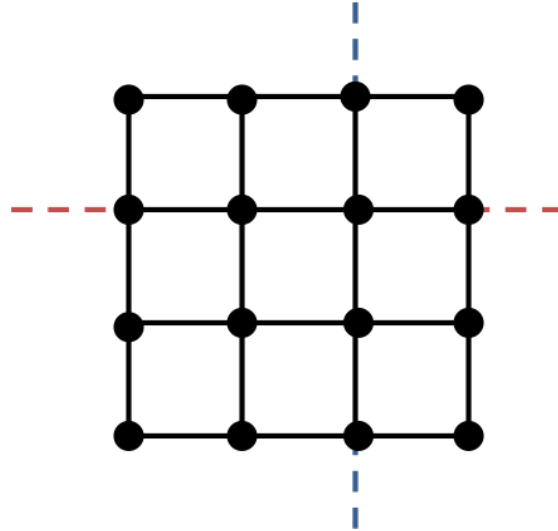


Figure .5: Lattice with periodic boundary conditions. The blue and red dashed lines represent bonds between sites induced by periodic boundary conditions.

Monte Carlo model The thermodynamic evolution of the alloy is modeled with a Monte Carlo process. The principle of Monte Carlo simulations is to model the A-B alloy evolution in a statistic way. To understand this model we can consider individual jumps of a vacancy into one of the z nearest neighbor positions. Within a certain specified time step, Δt , these different possible jumps occur with a probability Γ_μ where μ is an index that indicates which direction the vacancy will

move. In a simple cubic lattice, for example, $z = 6$, and the 6 values of μ correspond to jumps in the positive and negative x, y and z directions. The sum over all possible jump probabilities in the statistical time must sum to 1:

$$\sum_{\mu=1}^z \Gamma_{\mu} = 1 \quad (.1)$$

To figure out which direction the vacancy moves, we draw a random number r_n between 0 and 1. The jump performed by the system during the time Δt is the k^{th} one such that the following condition holds:

$$\sum_{\mu=1}^{k-1} \Gamma_{\mu} < r_n \leq \sum_{\mu=1}^k \Gamma_{\mu} \quad (.2)$$

Probabilities of transitions Γ_{μ} are related to the energetic barrier associated with vacancy motion, which we refer to as ΔE_{μ} . Because vacancy hopping is a thermally activated process, we can use an Arrhenius rate expression:

$$\Gamma_{\mu} = \Gamma_0 \exp \left(-\frac{\Delta E_{\mu}}{k_B T_0} \right) \quad (.3)$$

where Γ_0 is a constant, k_B is Boltzmann's constant and T_0 is the temperature of the system.

The energy barrier is the difference between the maximum energy of the system during the jump (the position of the migrating atom at this maximum energy is called the saddle point) and the energy of the system before the jump.

$$\Delta E_{\mu} = E^{SP} - E^{ini} \quad (.4)$$

Here the superscript *SP* refers to 'Saddle Point' and *ini* means 'initial', as shown in Figure .6.

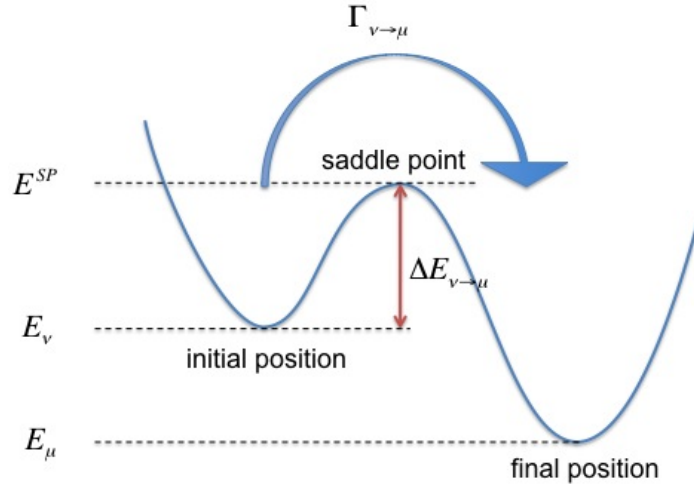


Figure .6: Schematic representation of the evolution of the system energy during a single atomic jump.

Energetic model To compute the energy barriers of the different possible jumps ΔE_{μ} , we have to use an energetic model. In Monte Carlo simulations, we usually use an Ising model or Broken bond model. In this energetic model, we assume that the total energy of the system is equal to the sum of interaction energies ε_{ij} between the different elements (atoms of type A and B and vacancies V) placed on the lattice sites.

$$E_v = \sum_{ij} \varepsilon_{ij} \quad (.5)$$

With this energetic model, the migration barrier of an exchange between an element X and the vacancy V becomes:

$$\Delta E_v = \sum_k \varepsilon_{Xk}^{SP} - \sum_i \varepsilon_{Xi} - \sum_j \varepsilon_{Vj} \quad (.6)$$

where ε_{Ak}^{SP} are interaction energies between the atom migrating and its neighbors at the saddle point, ε_{Ai} are interaction energies between the atom migrating and its neighbors before the jump and ε_{Vj} are interaction energies between the vacancy and its neighbors before the jump. The indices i, j and k indicate the following neighbors:

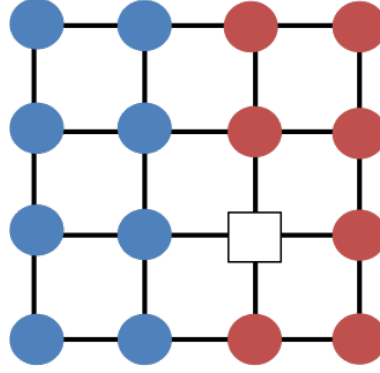


Figure .7: Example of configuration of atoms in the lattice. The red circles are A atoms and the blue circles are B atoms. The square is the vacancy

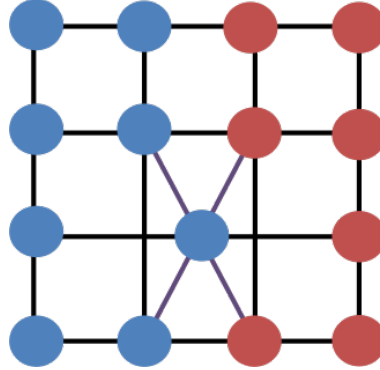


Figure .8: Configuration of the system at the saddle point if the vacancy exchange its position with the B atom on its left

Index	Meaning
i	nearest neighbors of the migrating atom before the jump
j	nearest neighbors of the vacancy before the jump
k	nearest neighbors of migrating atom at the saddle point

In theory, the range of interaction distances between elements are unlimited. In practice, we usually restrict these interactions to first and sometimes second nearest neighbors.

For example, the system presented in figure .7 has:

- 3 A-V interactions
- 1 B-V interaction
- 3 A-B interactions
- 9 A-A interactions
- 12 B-B interactions

Therefore, $E_v = 3\varepsilon_{AV} + 1\varepsilon_{BV} + 3\varepsilon_{AB} + 9\varepsilon_{AA} + 12\varepsilon_{BB}$. If we suppose that the vacancy exchange its position with the B atom on its left side, the configuration of the system at the saddle point is the one presented in figure .8.

In this configuration, the system has:

- 2 B-B interactions at the saddle point
- 2 A-B ineractions at the saddle point
- 3 A-B interactions
- 9 A-A interactions
- 9 B-B interactions

so $E^{SP} = 2\epsilon_{BB}^{SP} + 2\epsilon_{BA}^{SP} + 3\epsilon_{AB} + 9\epsilon_{AA} + 9\epsilon_{BB}$. The migration barrier of this jump is therefore:

$$\Delta E_v = 2\epsilon_{BB}^{SP} + 2\epsilon_{BA}^{SP} - 3\epsilon_{AV} - 1\epsilon_{BV} - 3\epsilon_{BB}$$

Modeling of scientific problem Here we assume that the two elements A and B have the same simple cubic lattice. We model the A-B alloy as a matrix in 2D with nx rows and ny columns and with periodic boundary conditions on its edges. To simplify the problem, we introduce only one vacancy in the lattice (so 1 vacancy for $nx \times ny$ sites), initially located in the middle of the matrix. As we only interest ourselves to the thermodynamic evolution of the system (and not to its kinetic evolution), we assume that the alloy evolves with normalized time steps of 1 until a maximum time t_{max} . At each time step, the vacancy exchanges its position with one of its neighbors.

To simplify the energetic model we suppose that the sum of interaction energies between the atom migrating and its neighbors at the saddle point $\sum_k \epsilon_{Xk}^{SP}$ is a constant equal to $3 eV$. In addition, we suppose that $\epsilon_{AA} = \epsilon_{BB} = \epsilon_{AV} = \epsilon_{BV} = 0 eV$. The only interaction which can be different from zero is thus ϵ_{AB} .

The free enthalpy of the alloy is expressed by

$$\Delta G_{mix} = \Omega X_A X_B - T \Delta S_{mix} \quad (.7)$$

with Ω the ordering energy of the alloy and ΔS_{mix} the configurational entropy of mixing of the alloy given by :

$$\Delta S_{mix} = -k_B [X_A \ln X_A + X_B \ln X_B] \quad (.8)$$

For a symmetrical miscibility gap, the ordering energy is

$$\Omega = 2k_B T_C \quad (.9)$$

where T_C is the critical temperature of the miscibility gap ($T_C = 1000 K$ in this study). In broken bond models with only first nearest neighbors interactions we have:

$$\Omega = z \left(\epsilon_{AB} - \frac{1}{2} (\epsilon_{AA} + \epsilon_{BB}) \right) \quad (.10)$$

where z is the number of first nearest neighbors for a given site.

Algorithmic scheme : Translation of problem in algorithm In this section we translate the problem described previously in an algorithm scheme. As we are modeling an evolution according to time, our code will contain an initial state and an incremental loop on time which will start from the initial time (t_0) and finish at a final time (t_{max}). During the time loop (for example between time t_n and t_{n+1}), the code will repeat the same operations which will make the matrix go from the configuration at t_n to the one at t_{n+1} . In this code we suggest that the system evolves with the following steps in the time loop:

1. Evolution of time from t_n and t_{n+1}
2. Computation of jump frequencies of all possible jumps Γ_μ
3. Drawing of a random number r_n and choice of a jump according to Eq. 2.
4. Completion of chosen jump: exchange of position between vacancy and nearest neighbor chosen.

Exercise

Random walks

In this first work, we model the evolution of the system if the equilibrium configuration of the alloy is an homogenized state. As we only interest ourselves to the thermodynamic evolution of the system (and not to its kinetic evolution), we assume that the alloy evolves with normalized time steps of 1 until a maximum time t_{max} . At each time step, the vacancy exchanges its position with one of its neighbors. The vacancy can exchange its position with all its first nearest neighbors X (and only its first nearest neighbors). The difference is that in this section we suppose that all exchanges have the same jump frequency Γ_{XV} . This is called a "random walk".

Preliminary work

1. Consider a vacancy located on the lattice site (xv, yv) as in Figure (.9). In this figure, identify the first nearest neighbors of the vacancy by numbers and give the coordinates of these neighbors according to (xv, yv) .

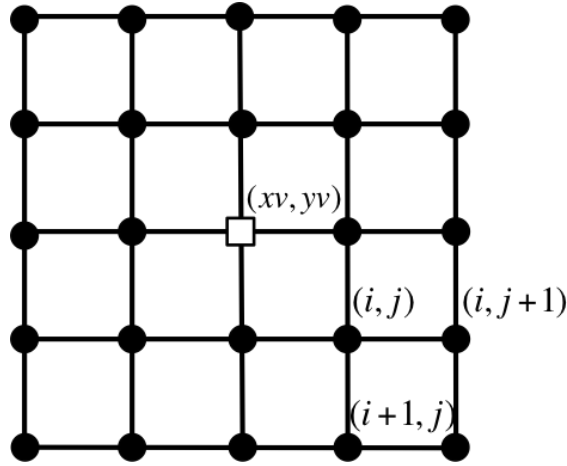


Figure .9: Identification of sites coordinates in the lattice and coordinates of a vacancy (represented by a square)

2. Suppose that all exchanges of the vacancy with its first nearest neighbors have the same jump frequency. Using equation (.1), give the probability of a given jump Γ_μ .

Simulation

3. Create a folder for this MATLAB project. Open a new script in Matlab and save it in your folder as “part1.m”.
4. We first write the initial state of the system in the file part1.m. Save the matrix given in the file called ‘matini.mat’ available from the following link:

<https://www.dropbox.com/s/on914vwpg8hgtj1/matini.mat?dl=0>

Load this matrix in part1.m as “matrix”. Define nx and ny as the number of rows and column respectively of matrix. In this matrix, elements A are identified by a number 1 and elements B are identified by a number 2. Place a vacancy (identified by a 0) in the middle of the matrix:

- define in part1.m the coordinates (xv, yv) (where xv is the row and yv the column of the vacancy position) as the coordinates at the middle of the matrix.
- Place a 0 in the matrix at the coordinates (xv, yv) .

Initialize time t to 0.

5. If the matrix has the configuration of figure X, what does the matrix in Matlab look like (with the numbers)?
6. Create a loop on time t where time evolves by steps of 1 as long as t remains lower than t_{max} . Place $t_{max} = 10$. We now have the part 1 in the algorithm (see section).
7. We now have to create the part 2 of the algorithm: the computation of the jump frequency of all possible jumps. (Remark: in this random walk program, this part could be placed outside of the time loop since all jumps have the same frequency. However, we include it in the time loop to prepare the second part of the problem where we will have to compute the Γ_{XV} according to the environment). In the program, we call Gamma the vector such that $\text{Gamma}(i)$ is the jump frequency of the exchange i . Use a “for” loop to compute the values of the different $\text{Gamma}(i)$ components.
8. We now have to choose a jump amount the different possibilities. For this, we suggest the MATLAB code shown below:

```
1 cumgam=cumsum(Gamma);
2 rn=rand;
3 njump=1;
4 for k=1:4,
5     if cumgam(k)>=rn
```

```

6         break
7     end
8     njump=k+1;
9 end

```

In this code, we draw a random number rn and translate the equation (.2) in a Matlab program which uses the vector $cumgam$ where $cumgam(k) = \sum_{i=1}^k \text{Gamma}(i)$. According to this algorithm, if $rn = 0.3$, what is the number of the jump chosen? What is 'njump' in this code? This part of the code corresponds to the part 3 of the algorithm.

9. For the chosen jump, identify in your code by (xn, yn) the coordinates of the corresponding nearest neighbor according to (xv, yv) . For this, we suggest you to define a matrix $(2 \times z)$ of the different possible evolutions (for example $\begin{pmatrix} +1 \\ 0 \end{pmatrix}$ or $\begin{pmatrix} 0 \\ -1 \end{pmatrix}$) and to write (xn, yn) according to (xv, yv) and the column of the matrix corresponding to the jump.
10. We use periodic boundary conditions in this model (see part). For a site (x, y) , verify that the following function enables to apply boundary conditions presented in figure (.5)

$$\begin{aligned}
 x &= \text{mod}(x - 1, nx) + 1 \\
 y &= \text{mod}(y - 1, ny) + 1
 \end{aligned}$$

For this, respond to the following questions: what is the x returned by this function if the x in input is between 1 and nx ? equal to 0? equal to $nx + 1$? Apply this function to xn and yn .

11. Exchange types of elements corresponding to the vacancy and the neighbor migrating in the matrix.
12. Update the vacancy coordinates to its new site. We now have coded part 4 of the algorithm.
13. In this random walk model, what is the equilibrium state of the system? (Help: the fact that all the $\text{Gamma}(i)$ are equal induces that the migration barriers for all possible jumps ΔE_μ are equal. From equation (.6) it induces that all saddle point interactions ε_{Ak}^{SP} and ε_{Bk}^{SP} are equal, all atom-atom interactions are equal and $\varepsilon_{AV} = \varepsilon_{BV}$. What is thus the value of the ordering energy Ω in equation (.10)? And the value of T_C ? So at any temperature, what is the equilibrium state of the system?)
14. Test: Replace the initial matrix by a matrix of same size with all A atoms on the half left side and all B elements on the half right side. Print an image of this initial matrix. Make the code run until $t_{max} = 10^6$. What do you observe? Print an image of the final matrix.

Introduction of alloy thermodynamic properties We now have to introduce the alloy thermodynamic properties in the code. We thus have to compute the jump frequency of possible exchanges between the vacancy and its neighbors according to the alloy thermodynamic properties. We will therefore only work here on part 2 of the algorithm (see section).

15. We recall here that $\varepsilon_{AA} = \varepsilon_{BB} = 0 \text{ eV}$. Express ε_{AB} according to the ordering energy Ω and then to the critical temperature T_C . Give a numerical value of ε_{AB} in eV if $T_C = 1000 \text{ K}$.
16. We analyze the migration barrier of an exchange between a vacancy V and one of its nearest neighbor X. We note NA the number of X first nearest neighbors of type A and NB the number of X first nearest neighbors of type B. How many first nearest neighbors does X have (we do not count the vacancy)? Express equation (.6) according to NA , NB and ε_{XA} and ε_{XB} (look at the example given in section for help). Using that $\sum_k \varepsilon_{Xk}^{SP} = 3 \text{ eV}$ and that $\varepsilon_{AA} = \varepsilon_{BB} = \varepsilon_{AV} = \varepsilon_{BV} = 0 \text{ eV}$, simplify the equation obtained if X is an element A. Same question if X is an element B. We observe from these calculations that, to compute the migration barrier of a jump, we need to know the type of the element of the exchange (so the type of X) and the type of all X first nearest neighbors (to compute NA and NB).
17. For a given vacancy position, we want to compute the jump frequency of the jump i (so $\text{Gamma}(i)$). We note X the vacancy neighbor corresponding to this jump. We start by computing NA and NB (the number of X first nearest neighbors of type A and B). We note (xn, yn) the position of X and (xnk, ynk) the coordinates of X first nearest neighbor k (k goes from 1 to 3, the vacancy position is excluded from these nearest neighbors). We write

$$\begin{pmatrix} xnk \\ ynk \end{pmatrix} = \begin{pmatrix} xn \\ yn \end{pmatrix} + \text{nveci}(k)$$

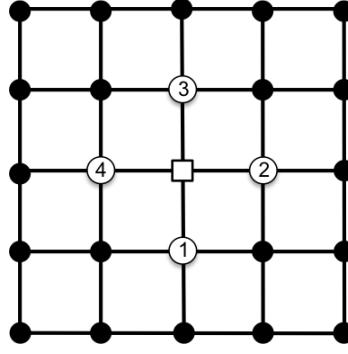


Figure .10: Position of X corresponding to the different possible jumps

where $nveci(k)$ is the column k of the 2×3 matrix of relative position of (xnk, ynk) compared to (xn, yn) . Graph .10 gives the position of neighbors X compared to the vacancy.

For each of these jumps, associate the matrix $nveci$ of the relative position of X first nearest neighbors.

$$(a) \ nveci = \begin{pmatrix} 0 & 0 & -1 \\ +1 & -1 & 0 \end{pmatrix} \quad (b) \ nveci = \begin{pmatrix} 1 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$(c) \ nveci = \begin{pmatrix} 1 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad (d) \ nveci = \begin{pmatrix} 0 & 0 & +1 \\ +1 & -1 & 0 \end{pmatrix}$$

18. Inside the loop to compute $\Gamma(i)$ coefficients write the following steps:
 - (a) define by (xn, yn) the vacancy neighbor corresponding to i (use the $nvec$ matrix). Apply periodic conditions to (xn, yn) .
 - (b) Initialize NA and NB to zero. Compute NA and NB of the exchange by analyzing the type of element on all (xnk, ynk) sites. To define the $nveci$ matrix corresponding to the jump, you can distinguish the different cases with if-statements or you can use a structure with all the $nveci$ matrices and load the one corresponding to the jump. Don't forget to apply boundary conditions to (xnk, ynk) .
19. Express the migration barrier of each jump depending on the type of the neighbor X (located on (xn, yn)) and NA and NB . Compute the jump frequency associated to this migration barrier (place the temperature to an arbitrary value-don't forget to define ϵ_{AB} in your code).
20. Normalize the Gamma vector to 1 so that the sum of $\Gamma(i)$ is equal to 1.
21. Analytic calculation: Suppose that for a given position, the vacancy can exchange it's position with either of 2 different A atoms. One on them is in a local configuration with $NB=0$ (the jump frequency of this exchange is noted $\Gamma_{NB=0}$) and the other one is in a local configuration with $NB=3$ (the jump frequency of this exchange is noted $\Gamma_{NB=3}$). Compute $\Gamma_{NB=3}/\Gamma_{NB=0}$ for $T=100K$ and for $T=2000K$. Explain why these ratios are consistent with the alloy phase diagram.
22. Place the temperature to $100K$. Run the simulation until $t_{max} = 10^6$. What do you observe?

316-2 Problems

General

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

Laplace Pressure Derivation

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

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 $100 \mu\text{m}^3$ 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 $\Delta T = 100\text{K}$ 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}
```

```

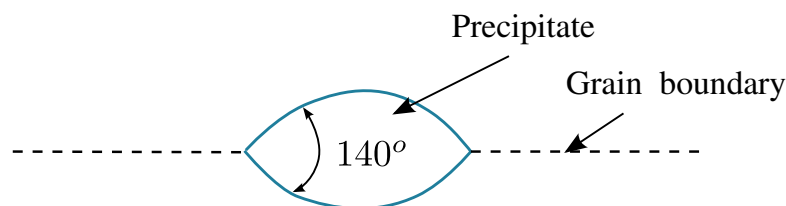
7 Aw: [118x1 double]
8 rho: [118x1 double]
9 gamma: [118x1 double]
10 Vm: [118x1 double]
11 DeltaSof: [118x1 double]
12 Structure: {118x1 cell}
13 Units: {1x8 cell}

```

- (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 $\gamma = 2.38J/m^2$ 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.

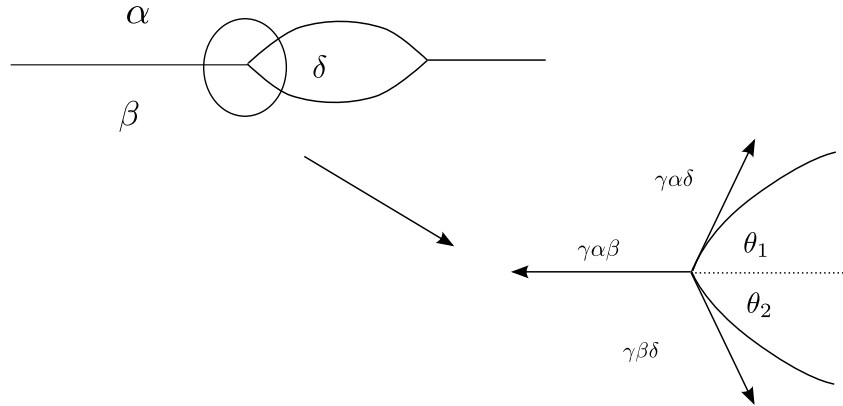
Surface and Interface Effects

7. The surface free energy of solid gold at its melting point ($1063^\circ C$) is $1.400J/m^2$. The surface energy of liquid gold at this temperature is $1.128J/m^2$, and the interfacial energy for the gold solid/liquid interface is $= 0.132J/m^2$. The latent heat of fusion for gold is $1.2 \times 10^9 J/m^3$.
- (a) What is the contact angle for liquid gold on a solid gold surface at $1063^\circ C$?
- (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 $1058^\circ C$ (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:



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 contact 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.



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 ?

Nucleation in a Binary System

13. 3. Consider the formation of a nucleus β^* with composition X^{β^*} 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:

$$\Delta G_m^{\alpha \rightarrow \beta^*} = G_m^\beta(X^{\beta^*}) - G_m^\alpha(X_0^\alpha) - \left. \frac{\partial G^\alpha}{\partial X} \right|_{X_0^\alpha} (X^{\beta^*} - X_0^\alpha) \quad (.1)$$

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

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

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

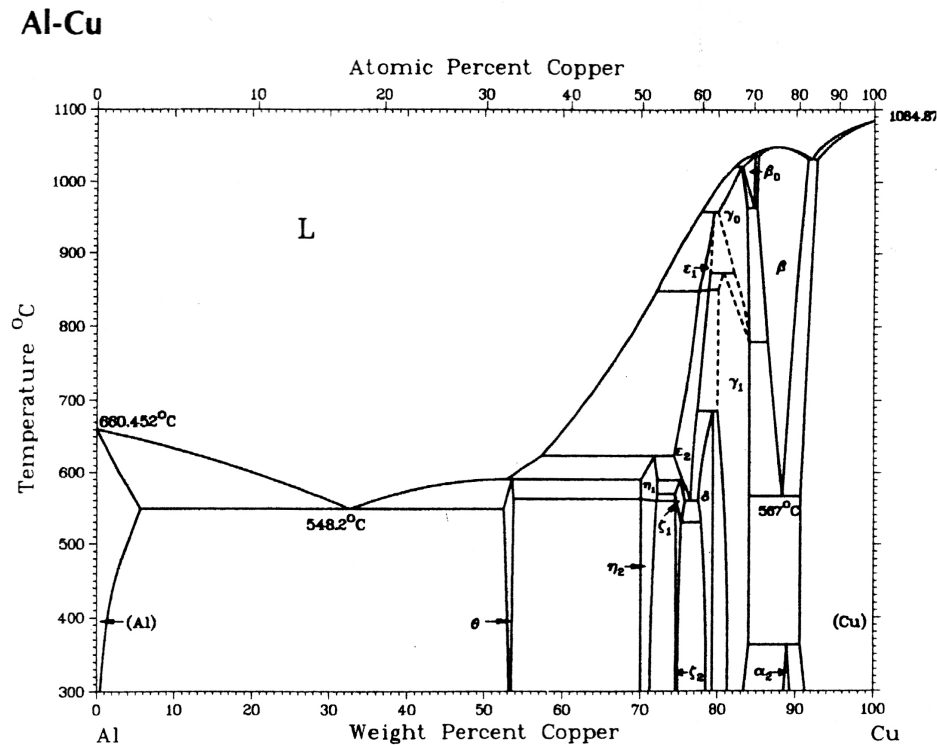
$$\varepsilon = \frac{1}{3} \left(\frac{V_m^\beta - V_m^\alpha}{V_m^\alpha} \right)$$

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

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

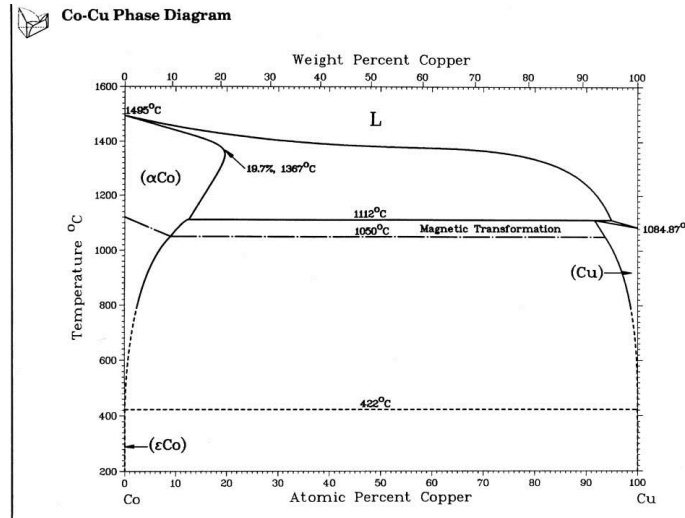
where a is the lattice parameter. Hint: Write ΔV in terms of ϵ_{cubic} and look at the behavior as $\epsilon_{cubic} \rightarrow 0$.

15. A coherent precipitate nucleates much more easily than does an incoherent particle of the same precipitate. To illustrate this:
- 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.
 - 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 $5.46 \times 10^{10} \text{ Pa}$ and bulk modulus of the precipitate of $15 \times 10^{10} \text{ Pa}$.
 - Repeat the previous calculation using a misfit strains of 0.01 and 0.1.
 - 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 $\Delta T = 25 \text{ K}$ and 250 K 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:



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:



- Plot the equilibrium activity of Cobalt as a function of composition across the entire phase diagram at 900°C.
- Suppose the interfacial free energy for the Cu/Co interface is 300 mJ/m². Develop an expression for r^* , the critical radius for a cobalt precipitate, as function of the atomic % cobalt in the alloy.
- 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.

Spinodal Decomposition

- A and B form a regular solution with a positive heat of mixing so that the A-B phase diagram contains a miscibility gap.
 - Starting from $G = X_A G_A + X_B G_B + \Omega X_A X_B + RT (X_A \ln X_A + X_B \ln X_B)$, derive an equation for $d^2 G / dX_B^2$, assuming $G_A = G_B = 0$.
 - Use the above equation to calculate the temperature at the top of the miscibility gap T_c in terms of Ω .
 - Using MATLAB plot the miscibility gap for this system.
 - On the same diagram plot the chemical spinodal.
- 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

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

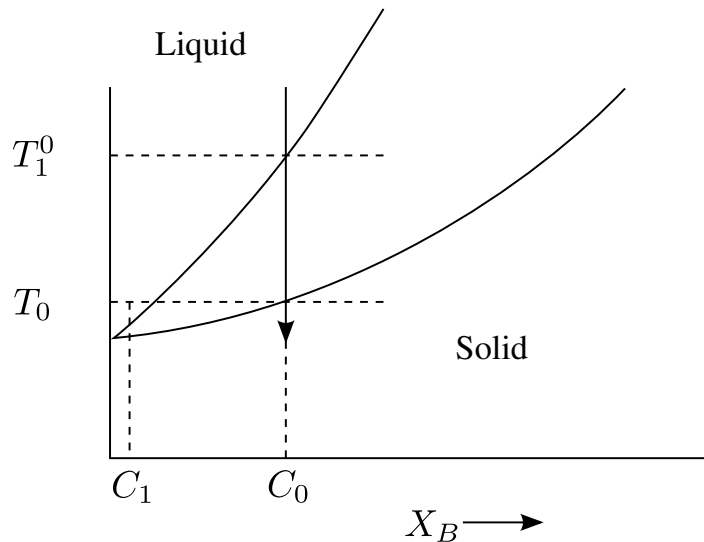
Hint: Express $G(X_0 + \Delta X)$ and $G(X_0 - \Delta X)$ as Taylor series.

- Describe the effect of each of the following, and briefly explain your answer.
 - 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?

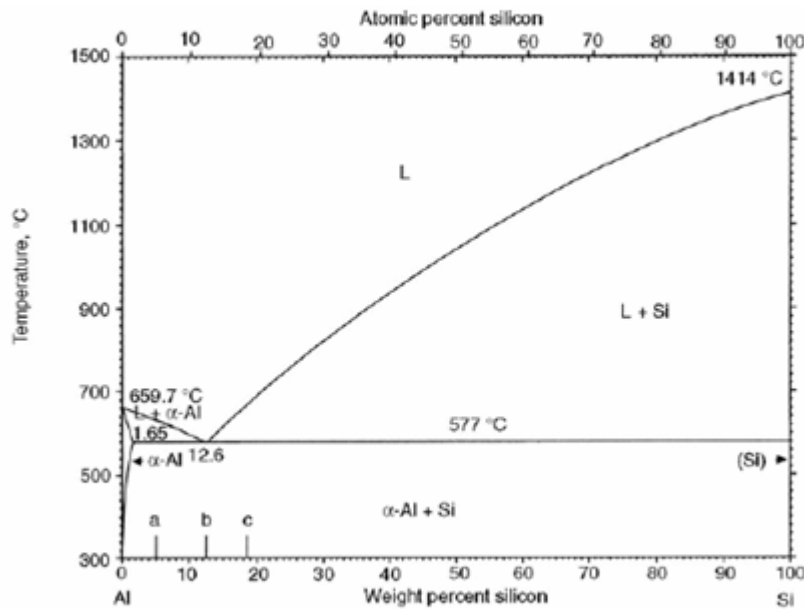
Constitutional Undercooling and the 'Mushy Zone'

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:



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 kJ/mol
- Diffusion coefficient for impurities in liquid Al: $\sim 5 \times 10^{-9} \text{ m}^2/\text{s}$



Suppose an alloy with 0.8 wt. % Si is solidified at a rate of $5\mu\text{m/s}$. (This is the velocity at which the solid/liquid interface is moving.)

- What is the interface temperature in the steady state?
- 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?
- Estimate the temperature gradient required to eliminate the appearance of a 'mushy zone'.

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 \AA , 100 minutes, 35 \AA , 1,000 minutes, 70 \AA .

- 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.
- 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.
- 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

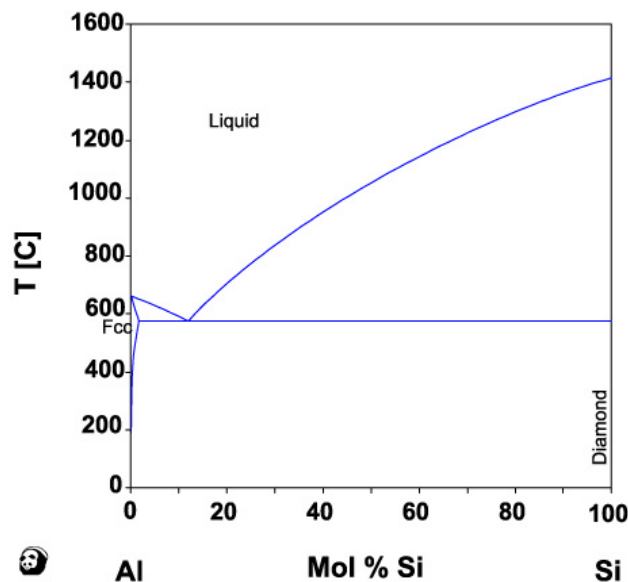
- Determine the value of the exponent m in the above equation by plotting this equation in an appropriate fashion. (Hint: you need to rearrange the equation and take logarithms so that m is the slope of the plot).
- Plot the qualitative temperature dependence that you would expect for the time constant, 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)?

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

- Obtain an estimate for the heat of fusion for the Al/Si eutectic (Joules per cm³ of eutectic).
- 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.

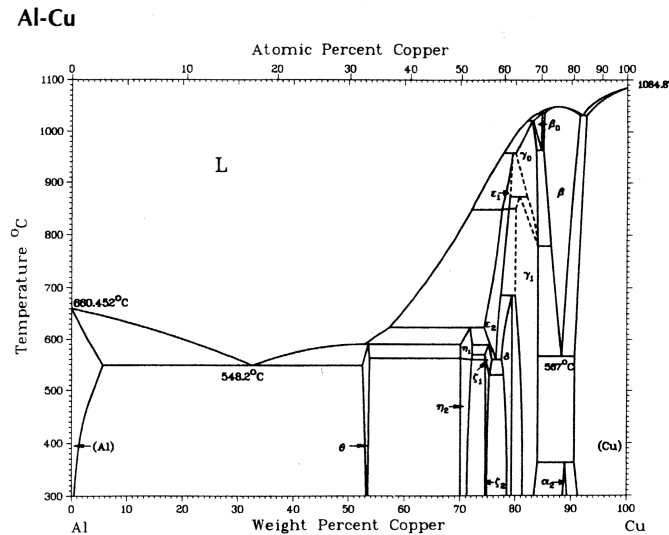
- (c) Calculate the width of the Al and Si phases in a lamellar eutectic for the case where the total free energy change (including the energy associated with the interfaces) on solidification at 560 °C is equal to zero. Assume an interfacial free energy for the Al/Si interface of 350 mJ/m².
- (d) Compare 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.

Eutectoid Transformations

26. Imagine the Fe-0.15 wt% C alloy in the figure below is austenitized above A_3 , and then quenched to 800°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 1 μ m.
- (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. $X_0 = 2.5$ wt.% Cu and $X_0 = 4.5$ 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?

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.



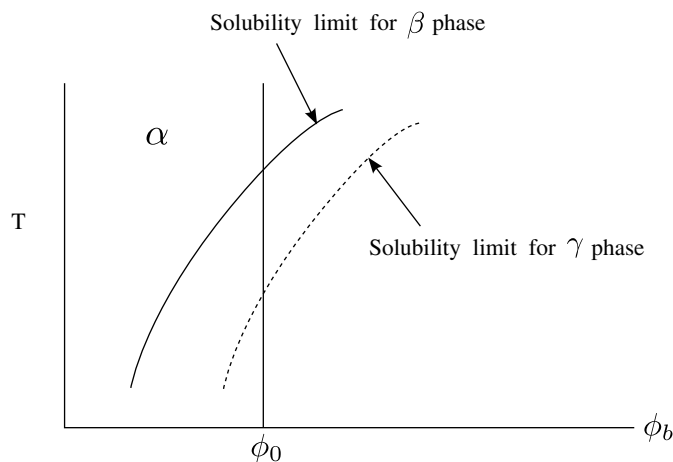
- What phase (or phases) do you expect to be present in the solid immediately after the solidification reaction?
- What phase (or phases) will be present at equilibrium?
- A variety of non-equilibrium phases are observed at intermediate stages in the transformation process. Why are these phases observed?
- 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

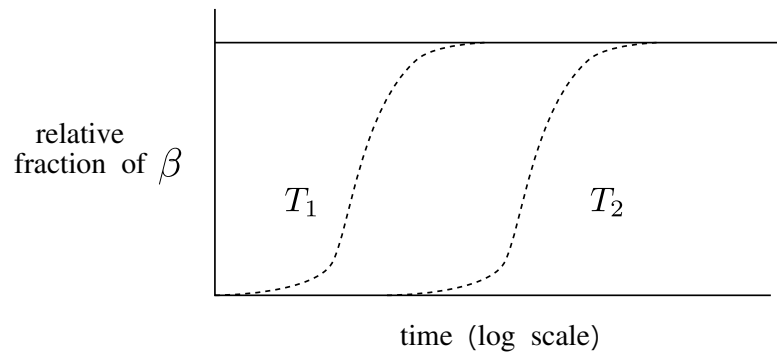
31. Suppose that in the system of interest, χ is inversely proportional to the absolute temperature, and the critical temperature for this system is 350 K. Replot the phase diagram from part a with temperature on the vertical axis.

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.

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.

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 , v_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?

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).

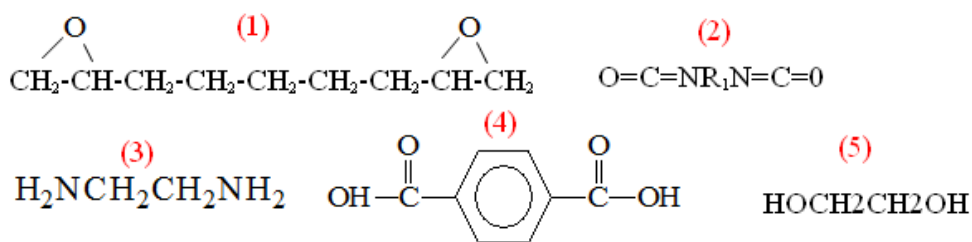
3.

Polymerization Reactions

4. Consider the following monomers:

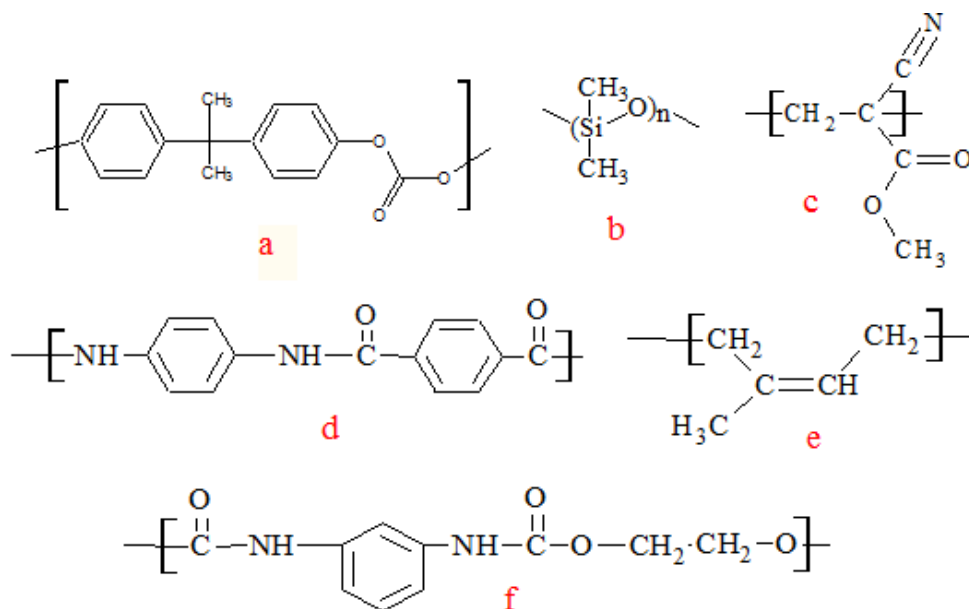
- (a) List all of the monomers that will polymerize by chain growth polymerization.
- (b) Draw the repeat unit structures of 3 different polymer structures that can be formed from (c)
- (c) Which monomers will react with each other to form a linear polyamide?
- (d) Which monomers can you combine to produce a highly crosslinked polymer network by step growth polymerization so that no condensation products are produced?

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?
8. "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?
10. 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?
11. Draw the chemical structures of the monomers from which the following polymers are formed.



12.

332 Problems

Updated February 9, 2016

Course Organization

1. If you are interested in the 3-d printing option of the laboratory, send an email to Boran: (BoranMa2014@u.northwestern.edu). Identify any specific people you would like to work with and have them send an email too.

The Stress Tensor

2. Consider the following stress tensor:

$$\sigma_{ij} = \begin{bmatrix} 4 & 3 & 0 \\ 3 & 1 & 2 \\ 0 & 2 & 6 \end{bmatrix} \times 10^6 \text{ Pa}$$

- (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:

$$\sigma_{ij} = \begin{bmatrix} -2 & 1.4 & 0 \\ 1.4 & 6 & 0 \\ 0 & 0 & 2 \end{bmatrix} \times 10^6 \text{ Pa}$$

- (a) Draw a Mohr circle representation of the stress contributions in the xy plane
- (b) What are the three principal stresses?

Strains

4. An engineering shear strain of 1 (100%) is applied to a rubber cube with dimensions of $1\text{cm} \times 1\text{cm} \times 1\text{cm}$. 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?

Matrix Representation of Stress and Strains

5. For an isotropic system there are only two independent elastic constants, s_{12} and s_{11} . This is because if properties are anisotropic 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:

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

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:

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

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 way to reconcile the results from parts a and b is for s_{44} to be equal to $2(s_{11} - s_{12})$.

Typical Moduli

6. Calculate the sound velocities for shear and longitudinal waves traveling through the materials listed in Table 4.1 of the course notes (332text.pdf).

Yield Criteria

7. 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.
- What is the shear strength of the material according to the Tresca yield criterion?
 - If the value of σ_3^p were increased to 70 MPa, how does this change your result? Explain.
8. 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 .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 $122 \times 10^{-6} \text{ m}^2$.

- What is the slip system for this material.
 - 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.
 - From your calculations, does τ_{RSS} or σ_N control yielding?
 - Plot the Schmid factor versus the normal 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?
9. 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.
10. 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.
- What do you expect for the yield strength of the material in a state of uniaxial compression?
 - What will the yield strength be under a stress state of shear hydrostatic pressure?
 - What is the shear yield strength of the material.

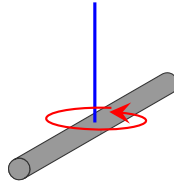
Strengthening Mechanisms

11. Explain which has a larger effect on solid solution strengthening — symmetrical or asymmetrical point defects — and identify which specific defects lead to symmetrical or asymmetrical stress fields. List at least one example of an engineering material in which this factor comes into play.
12. The lower 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.
- Predict the grain diameter needed to cause a lower 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?
- (c) Why might you expect the upper yield point to be more alike in the first two bars than the lower yield point?
13. The lattice parameters of Ni and Ni₃Al are 3.52×10^{-10} m and 3.567×10^{-10} m, respectively. The addition of 50 at% Cr to a Ni-Ni₃Al superalloy increases the lattice parameter of the Ni matrix to 3.525×10^{-10} m. Calculate the fractional change in alloy strength associated with the Cr addition, all other things being equal.

Viscoelasticity

14. Consider a cylindrical metal bar with a density of 7.6 g/cm³, a diameter of 1 cm and a length of 10 cm. It is suspended from a polymer fiber with a length, ℓ , 30 cm and a diameter of 1 mm.

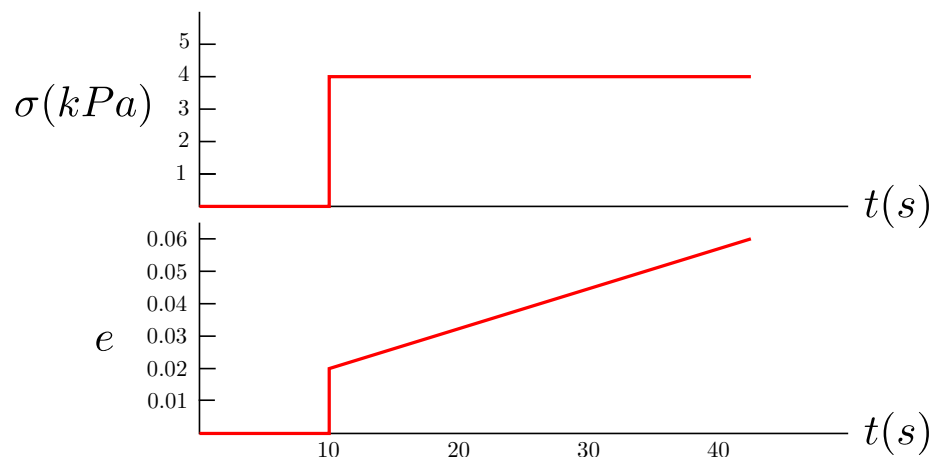


- (a) Suppose the fiber is perfectly elastic, with a shear modulus 10^9 Pa. Calculate the natural frequency of the system if the bar is rotating back and forth, causing the fiber to twist.
- (b) Suppose the fiber is viscoelastic, with G' at the frequency calculated from part a equal to 10^9 Pa, and with $G'' = 10^7$ 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.
15. 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 .
- (a) For what angular frequency are the storage and loss moduli equal to one another for a material that conforms to the Maxwell model? Express your answer in terms of the relaxation time, τ .
- (b) 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.
- (c) 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'' :

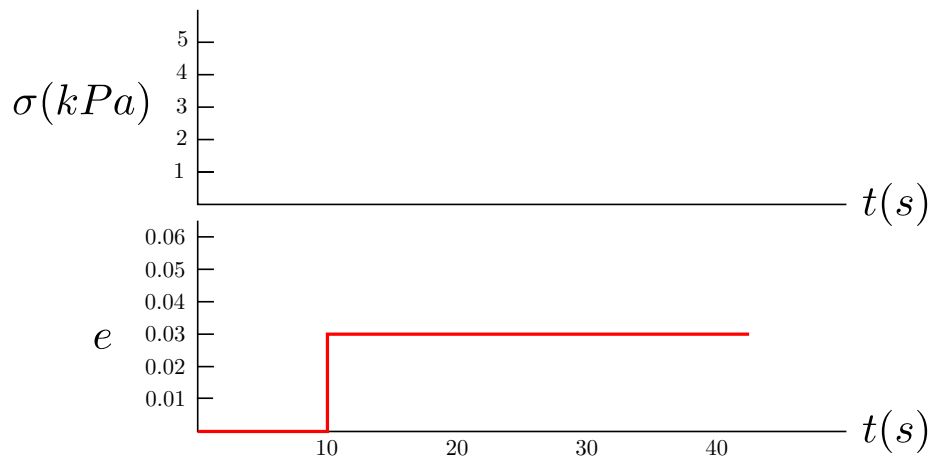
$$\tan \phi = \frac{G''}{G'}$$

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.

16. The following stress and strain response are observed for a material during the initial stages of a creep experiment.



- (a) Draw a spring/dashpot model that describes this behavior. Label moduli and viscosities as quantitatively as possible.
- (b) 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.



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

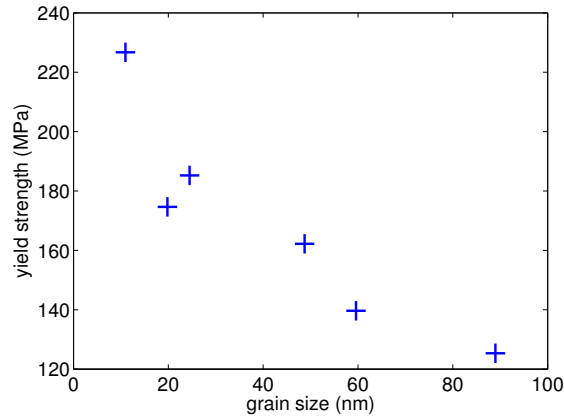
$$\sigma = \begin{bmatrix} 0 & 3 & 0 \\ 3 & 0 & 0 \\ 0 & 0 & -5 \end{bmatrix} \text{ MPa}$$

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.

18. Consider a material with elastic constants given by the following compliance matrix:

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

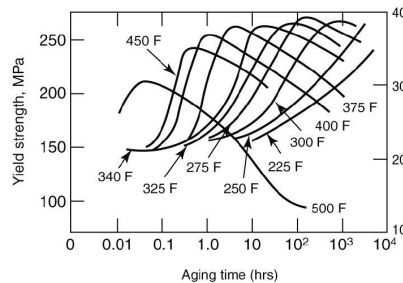
- (a) Describe the symmetry of this material, and explain your reasoning.
- (b) What is the highest value for Young's modulus that you would expect for this material? What direction does it correspond to?
- (c) Calculate the value of Poisson's ratio obtained from an experiment where the materials is pulled in the 3 direction and change in sample width in the 2 direction is measured.
19. The following plot shows values of the yield strength of copper samples as a function of the grain size of these samples.



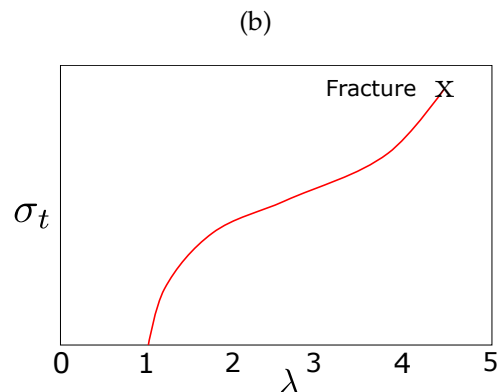
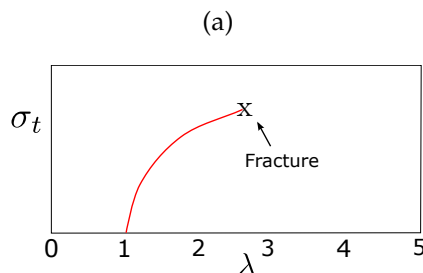
(a) Describe why the yield stress decreases with increasing grain size.

(b) Describe the procedure you would use to determine the limiting value of the yield strength in the absence of grain boundaries.

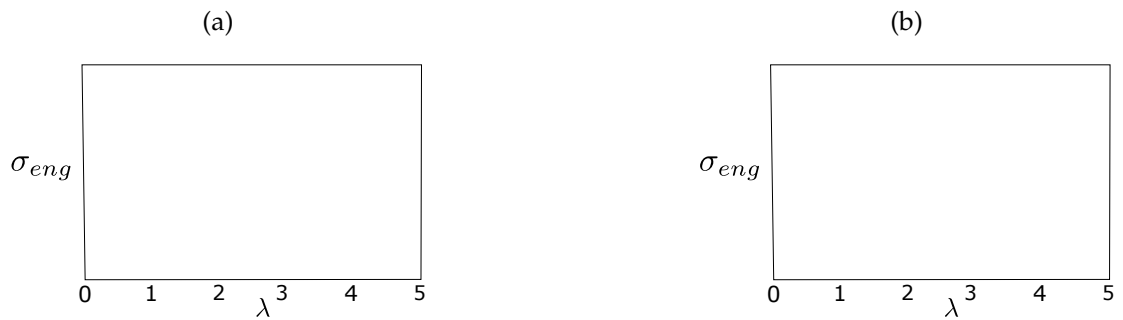
20. The figure below shows the yield strength of a precipitation hardened aluminum alloy as a function of aging time at different temperatures. Note that the yield strength initially goes through maximum and then decreases with time. Explain why this happens in as much detail as possible.



21. 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).



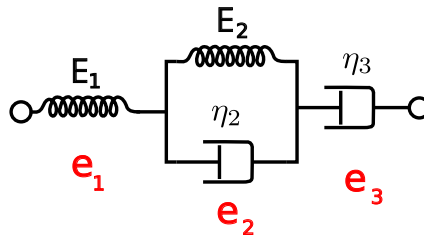
On the axes below, sketch the behavior of the engineering stress (measured tensile force vs. undeformed cross sectional area) vs extension ratio that you expect for each of these samples. Be as quantitative as possible with regard to the x axis.



Briefly describe why you drew the curves the way you did.

Nonlinear Viscoelasticity and Creep

22. 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:



- (a) This model is useful because it includes a non-recoverable creep component, a recoverable time dependent creep component, and an instantaneous, recoverable strain. Identify the element (or combination of elements) in the above model which is associated with each of these three contributions to the strain.
- (b) 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:

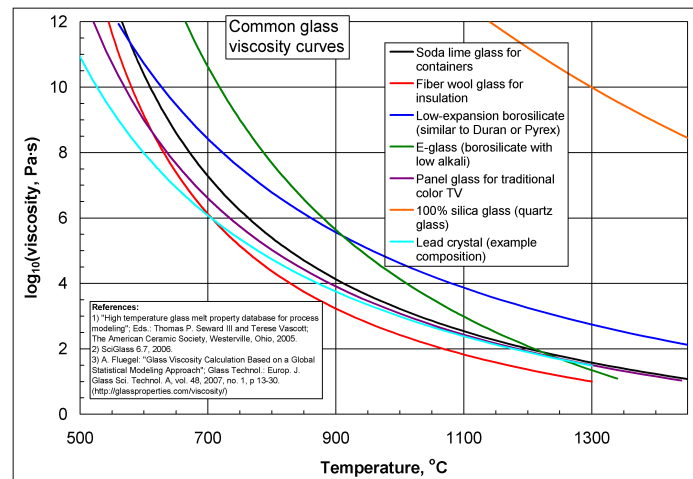
Sample	σ (GPa)	E_1 (GPa)	E_2 (GPa)	η_3 (GPa-s)	η_2 (GPa-s)
Low M	0.025	17.4	33.5	1.8×10^5	4300
Low M	0.05	13.6	35.6	6.3×10^4	5000
Low M	0.1	17.7	26.4	3.1×10^4	2200
Low M	0.15	17.7	26.5	2.6×10^4	2300
Low M	0.2	16.4	26.8	1.2×10^4	2000
High M	0.1	18.3	31.9	3.1×10^6	8.7×10^4
High M	0.15	16.6	21.3	1.7×10^6	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.

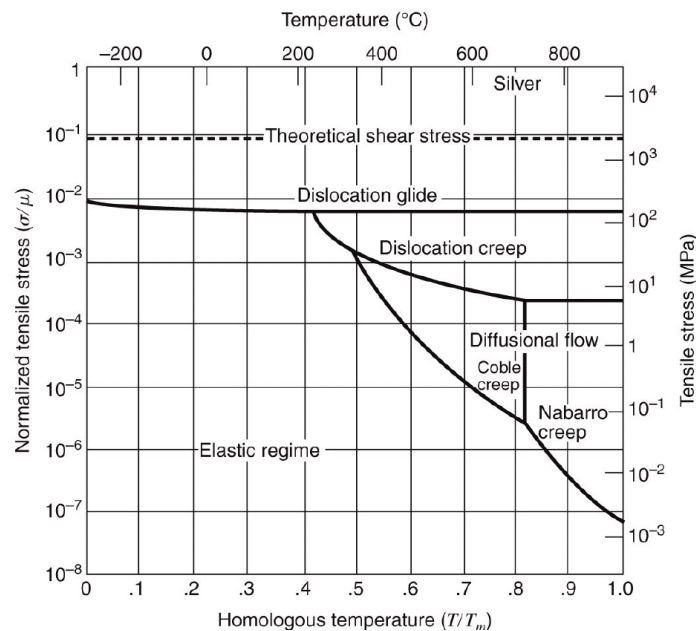
23. In class we briefly talked about the possibility that you could see flow of a glass window over very long periods of time. Can creep of a glass by viscous flow give measurable changes in sample dimensions over a very long period of time? To sort this out, do the following:

- (a) 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).

- (b) Estimate the viscosity that would be needed to give a measurable change in sample dimensions after 400 years.
- (c) 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.

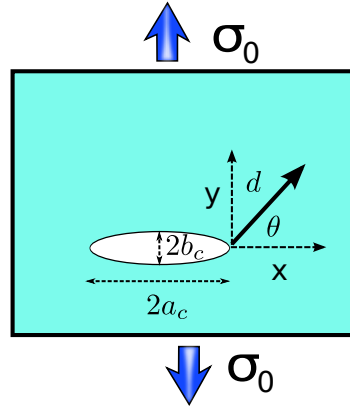


24. Creep in metals at low stresses occurs by a vacancy diffusion mechanism, which means that the activation volume for these creep mechanisms corresponds to the atomic volume. Show using the data below for silver that we can safely replace $\sinh(\sigma v / 2k_B T)$ with $\sigma v / 2k_B T$, so that 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 luck up data you can use to calculate the atomic volume of silver).

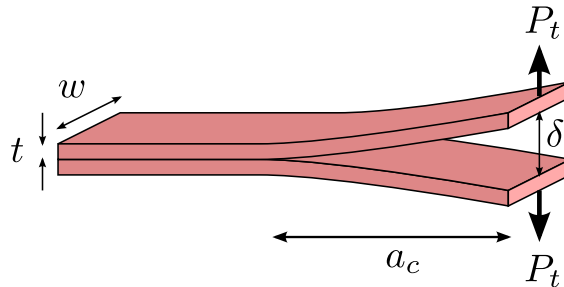


Fracture Mechanics

25. 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.

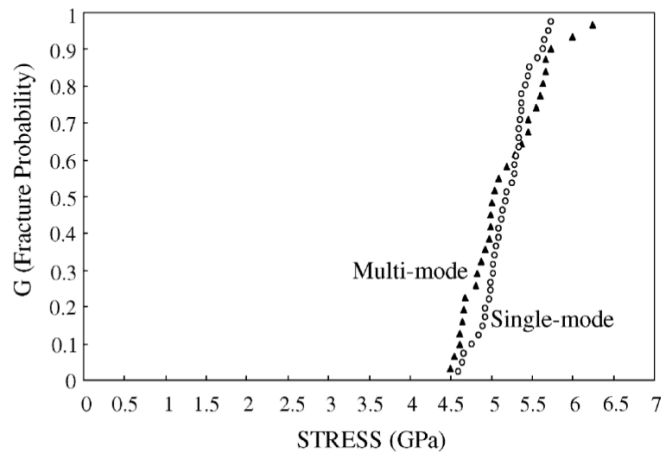


- (a) For a fixed value of d , plot the behavior of σ_{xx} , σ_{yy} and σ_{xy} for a mode I crack as a function of θ .
 - (b) What happens to the stresses for $\theta = 180^\circ$? Why does this make sense?
 - (c) A mode I crack will travel in the direction for which the normal stress acting across the crack surfaces is maximized. What direction is this?
26. 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.
 27. As a crack advances, what happens to the stiffness of the cracked body? What happens to the compliance?
 28. A set of double cantilever beam adhesion test specimens was fabricated from a set of aluminum alloy samples. The geometry 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 , of 10 mm. The critical energy release rate for the adhesive is 65 J/m^2 .

- (d) Calculate the values of the tensile load, P , and the displacement, Δ , where the crack starts to propagate.
 - (e) In a load-controlled experiment, P 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 , Δ and a , describe why the load controlled experiment results in unstable crack growth, but the displacement controlled experiment results in stable crack growth.
 - (f) 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.
29. The following data was 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.

30. 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.

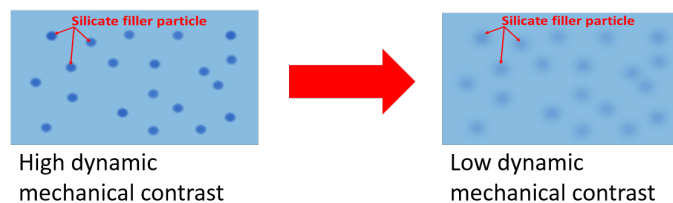
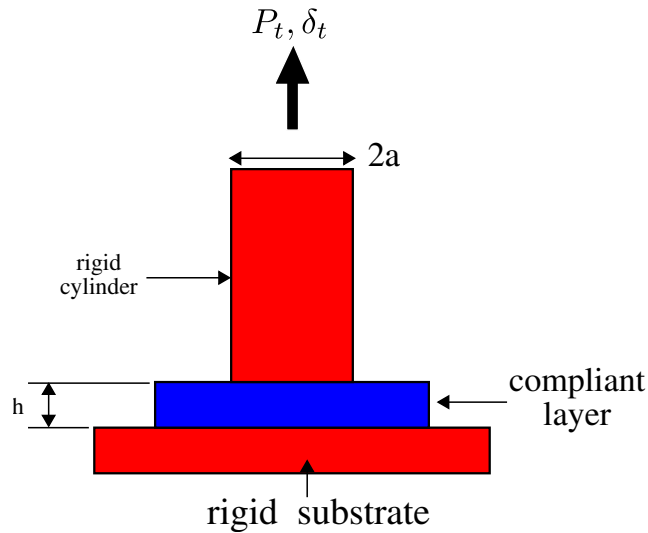


Figure .1: High dynamic mechanical contrast is important

- 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.)
- 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?
- 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)?

Contact Mechanics

31. Consider the contact of a flat rigid punch with a thin elastic layer, as shown schematically below:

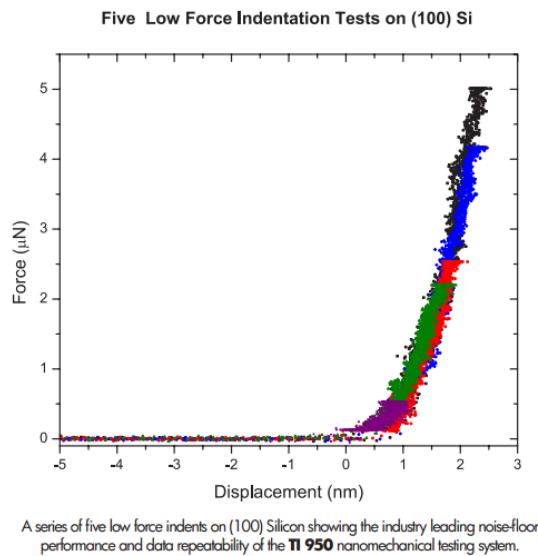


Suppose the compliant layer is incompressible gel ($\nu = 0.5$), with a Young's modulus, E , of 10^4 Pa. The critical energy release rate for failure at the gel/punch interface is 0.1 J/m^2 . The punch radius, a , is 3 mm.

- What is the tensile force required to separate the punch from the layer if the layer is infinitely thick?
- What is the stress intensity factor, K_I , just prior to detachment of the punch from the surface?
- How close to the punch edge do you need to be for the tensile stress at the punch/layer interface to be equal to the modulus of the layer?
- Describe in qualitative terms what happens to the following quantities as the thickness, h , of the compliant layer decreases:
 - The overall compliance of the system.
 - The load required to detach the indenter from the substrate.
 - The displacement at which the indenter detaches from the substrate.
 - The shape of the tensile stress distribution at the punch/substrate interface.

Nanoindentation

- 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) :



- If the data in this figure are obtained with a 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).

- (b) 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 be eliminated by performing the indentation in a suitable liquid.)
33. 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 its weight).

Weibull Statistics

34. A set of glass rods with a Weibull modulus of 30 are fractured in a uniaxial tensile test. If the stress at which 73% of the samples fracture is 100 MPa, what stress should you apply to make sure that less than 1% of the rods fail? What is the maximum stress if you want to make sure that less than one in 10^6 rods fail? (Note that $1/e$ is 0.37). 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?
35. What determines the value of the Weibull modulus in a brittle material?

Fracture Toughness

36. What is crack tip shielding?
37. 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} ?
38. Describe how transformation toughening works to increase the toughness of a ceramic material like ZrO_2 .
39. What is a Charpy impact test conducted, and what does it measure?
40. What is 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.

General Knowledge

41. How are G , ν and K related to one another for an isotropic material?
42. What are typical values of G and K for metals, ceramics and polymers?

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.

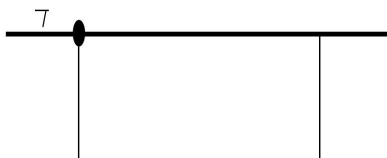
Show that the inversion center and 2-fold rotation axis are not equivalent in three dimensions by doing the same type of operation on a 3D asymmetrical unit "7".

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:

- (a) Fill in the pattern of 7's based on the indicated unit cell and symmetry elements.
- (b) Draw in the additional symmetry elements that are present.
- (c) 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 a_1 , a_2 , 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

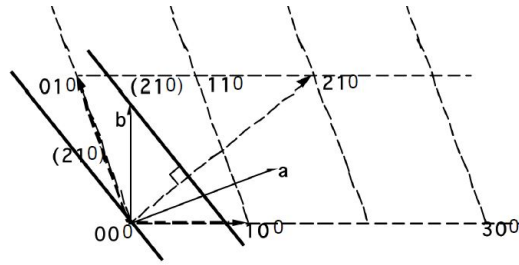
9. C&S Problem 2-13 (Use tracing paper on top of a Wulff net for this problem, in addition to the following two).

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 $a = 2.5 \text{ \AA}$, $b = 3.0 \text{ \AA}$, $c = 5.12 \text{ \AA}$, and $\gamma = 120^\circ$. Note that $\gamma^* = 180^\circ - \gamma = 60^\circ$.

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 $d_{hkl} \cdot r_{hkl}^*$ 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 $a, b, c, \alpha, \beta, \gamma$ and the Miller indices h, k, l . Check answer with C&S A3-1.
15. (a) 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. (b) 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 $\lambda = 1.54 \text{ \AA}$ 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. a) What are the (hkl) Rhombohedral unit cell Miller indices for the three nonparallel faces of the Rhombohedral unit cell?
 b) 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?
 c) Now list these as (hkil) Miller- Bravais indices.
 d) What is the [uvw] direction in the Rhombohedral unit cell for the hexagonal c-axis direction [001]?
 EXTRA CREDIT: Hematite $\alpha\text{-Fe}_2\text{O}_3$ has a rhombohedral crystal structure with $a=5.43\text{\AA}$ 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, and 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.
 - (a) The x ray beam from the x-ray tube is traveling along y. Is this x ray beam:
 - i. preferentially polarized along x ?
 - ii. preferentially polarized along y ?
 - iii. preferentially polarized along z ?
 - iv. not preferentially polarized ? Explain your answer.

- (b) 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 r_n of the n th 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 .

$$f = 2 \frac{\sin kr_K}{kr_K} + 8 \frac{\sin kr_L}{kr_L}$$

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:

$$\frac{\sin^2 \pi Q \cdot a M}{\sin^2 \pi Q \cdot a} = \frac{\sin^2 \beta M}{\sin^2 \beta}$$

$\mathbf{Q} = (\mathbf{S} - \mathbf{S}_0)/\lambda$ is the scattering vector. \mathbf{S} and \mathbf{S}_0 are unit vectors in the scattered and incident directions where $\beta = \pi \mathbf{Q} \cdot \mathbf{a}$ is one-half the phase angle difference (in radians) for rays scattered by planes separated by \mathbf{a} . The crystal contains M planes separated by \mathbf{a} .

- 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 .
 - 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.
 - 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 ?
 - 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 .
33. Consider powder diffraction from CsCl ($a = 4.11 \text{ \AA}$) with Cu $K\alpha$ radiation ($\lambda = 1.542 \text{ \AA}$). 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.)
- What are the hkl indices for the first 7 observed reflections from CsCl?
 - For the first four of these calculate and tabulate $\sin\theta/\lambda$, f_{Cs^+} , f_{Cl^-} , F_{hkl} , 2θ , and LP.
 - Look up multiplicities m_{hkl} (Cullity & Stock Appendix 11). Combine these with your results from part B to calculate the relative 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.
- Sketch the $hk0$ plane of the reciprocal lattice for an HCP crystal, using solid dots (\bullet) to indicate nonzero $|F_{hkl}|^2$. Cover the range from $-2a^*$ to $+2a^*$ and $-2b^*$ to $+2b^*$.
 - 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).
 - 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.

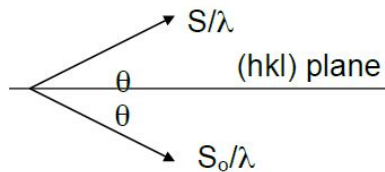


Figure .1: S/λ and S_0/λ

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, $a = 3 \text{ \AA}$, $b = 4 \text{ \AA}$ and $c = 5 \text{ \AA}$. Include 8 reciprocal lattice unit cells (from origin to $2a^*, 2b^*, 2c^*$). Indicate nonzero values of FF^* by dots (\bullet).

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_0/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 $\mathbf{Q} = (S_0/\lambda - S/\lambda)$ must be perpendicular to the hkl plane. From the construction derive Bragg's Law recalling that \mathbf{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 $\mathbf{a}^* = 0.25 \text{ \AA}^{-1}$, $\mathbf{b}^* = 0.15 \text{ \AA}^{-1}$ and $\mathbf{c}^* = 0.36 \text{ \AA}^{-1}$. The radius of the cylindrical camera used for taking this photograph is 50 mm and the x-ray wavelength is 1.542 \AA . 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 \AA . Assume that $\lambda = 1.542 \text{ \AA}$ 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 $K_{\alpha 1} - K_{\alpha 2}$ splitting. Differentiate Bragg's 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 $K_{\alpha 1} - K_{\alpha 2}$ splitting of Cu radiation at $2\theta = 90$.

$$\lambda(K_{\alpha 1}) = 1.5405 \text{ \AA}$$

$$\lambda(K_{\alpha 2}) = 1.5433 \text{ \AA}$$

From this you should appreciate that it is difficult to measure D values greater than about 500 \AA 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 $K_{\alpha 1}$, whose width is approximately 2 eV in comparison to the 20 eV energy separation between the $K_{\alpha 1}$ and $K_{\alpha 2}$.

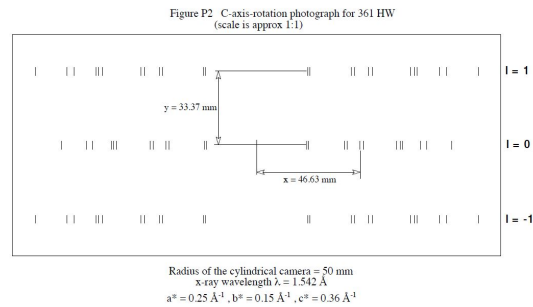
40. Identical powder diffraction scans are made of a diamond powder sample and a germanium powder sample with Cu K_{α} radiation. Each has "diamond cubic" crystal structure with 8 atoms per unit cell. Other pertinent information for this problem is as follows:

Sample	Z	$a[\text{\AA}]$	$\mu/\rho [\text{cm}^2/\text{g}]$	$\rho [\text{g}/\text{cm}^3]$
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

$$K_x = \frac{|F_{hkl}|^2 m_{hkl} L P}{V_C^2}$$

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.



References