

1 316-2 Problems

1.1 General

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

1.2 Laplace Pressure Derivation

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

1.3 Homogeneous Nucleation

3. Consider the following data for nickel:

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

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

- (a) The molar volume of nickel.
 - (b) The work of nucleation (W_R^*).
 - (c) The dimensionless ratio, $W_R^*/k_B T$.
 - (d) The radius of the critical nucleus.
 - (e) The pressure of the critical nucleus in pascals (assume the surrounding liquid is at atmospheric pressure).
 - (f) The molar enthalpy of melting at T_m .
 - (g) Suppose a Ni droplet with a volume of about 100 μm^3 is solidified. Approximate the temperature to which the droplet must be cooled in order for solidification to occur by homogeneous nucleation.
4. Import the file labeled ElementData.mat that includes the required data for various elements on the periodic table into Matlab and:
 - (a) Derive the expressions for ΔP , R^* , W_R^* , and $W_R^*/k_B T$ in terms of T_m , ΔT , V_m , ΔS_f , and γ .
 - (b) Plot V_m , ΔS_f , γ , ΔP , R^* , W_R^* , and $W_R^*/k_B T$ using $\Delta T = 100\text{K}$ 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:

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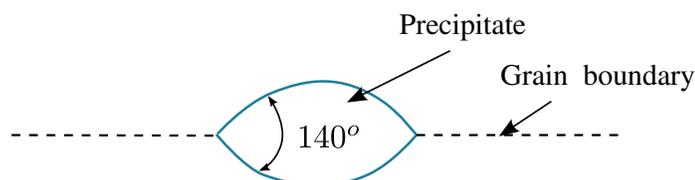
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2 Name: {118x1 cell}
3 Symbol: {118x1 cell}
4 DeltaH0f: [118x1 double]
5 Tm: [118x1 double]
6 Z: [118x1 double]
7 Aw: [118x1 double]
8 rho: [118x1 double]
9 gamma: [118x1 double]
10 Vm: [118x1 double]
11 DeltaS0f: [118x1 double]
12 Structure: {118x1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

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- (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.

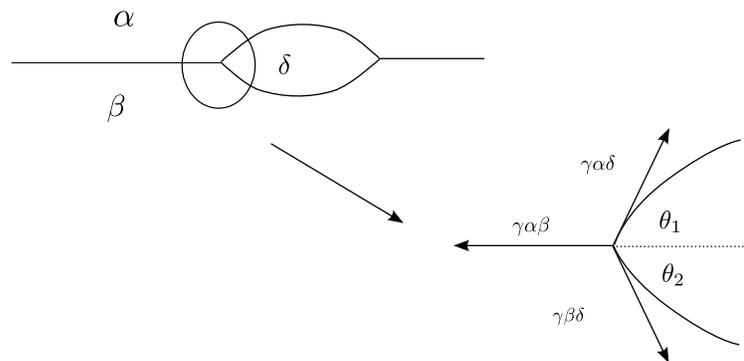
1.4 Surface and Interface Effects

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?

- 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).
- 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.



1.5 Heterogeneous Nucleation

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

1.6 Nucleation in a Binary System

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:

$$\Delta G_m^{\alpha \rightarrow \beta^*} = G_m^\beta(X^{\beta^*}) - G_m^\alpha(X_0^\alpha) - \left. \frac{\partial G^\alpha}{\partial X} \right|_{X_0^\alpha} (X^{\beta^*} - X_0^\alpha) \quad (1.1)$$

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

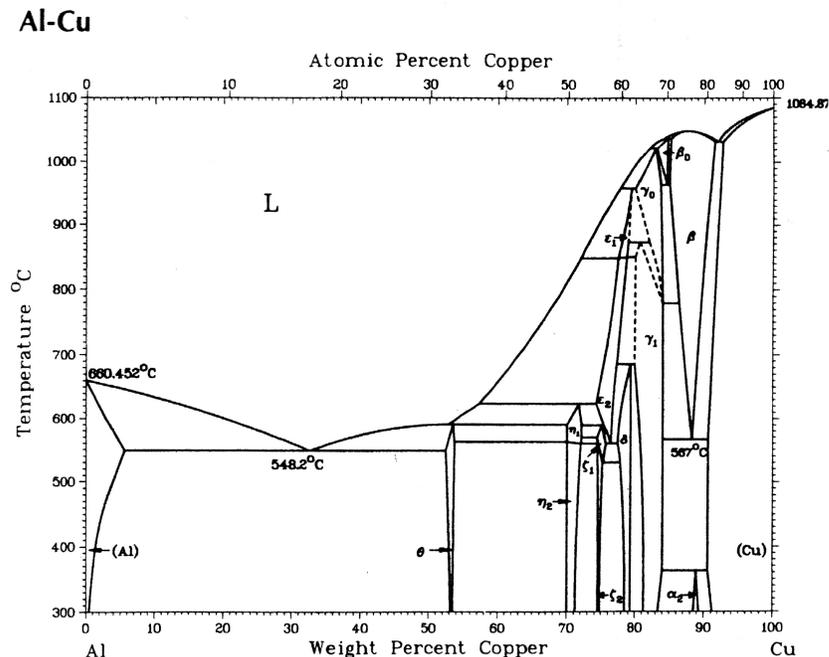
$$\varepsilon = \frac{1}{3} \left(\frac{V_m^\beta - V_m^\alpha}{V_m^\alpha} \right)$$

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

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

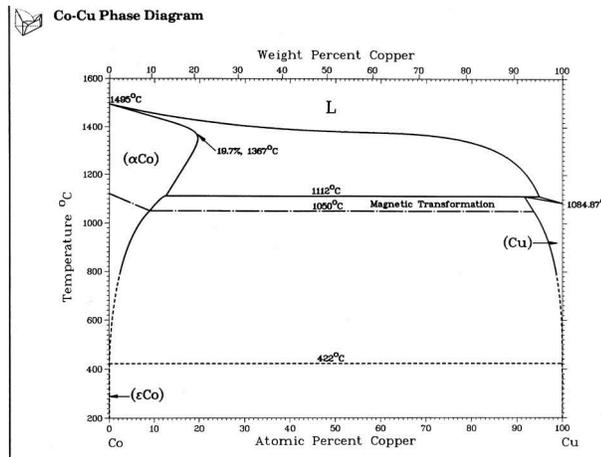
where a is the lattice parameter. Hint: Write ΔV in terms of ε_{cubic} and look at the behavior as $\varepsilon_{cubic} \rightarrow 0$.

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/m² and a molar volume for the α and β phases of 7 cm³.

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.

1.7 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

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

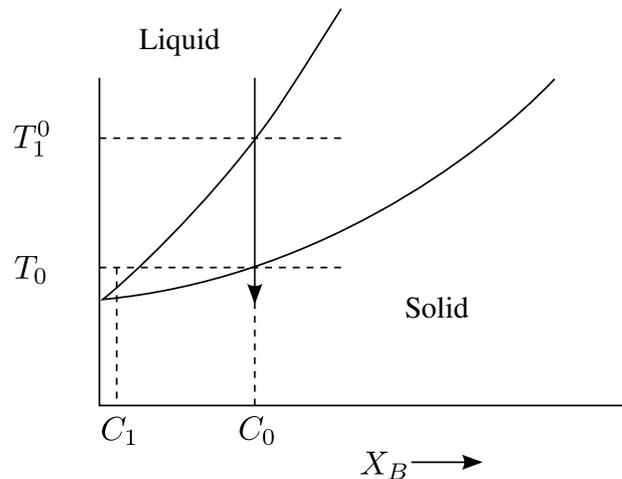
Hint: Express $G(X_0 + \Delta X)$ and $G(X_0 - \Delta X)$ as Taylor series.

- 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.
- The effect of a reduction of the surface free energy on the nucleation rate.
- The effect of a decrease in the contact angle of a precipitate on its heterogeneous nucleation rate.
- Can a diffusion coefficient ever be negative? If so, when is this the case?

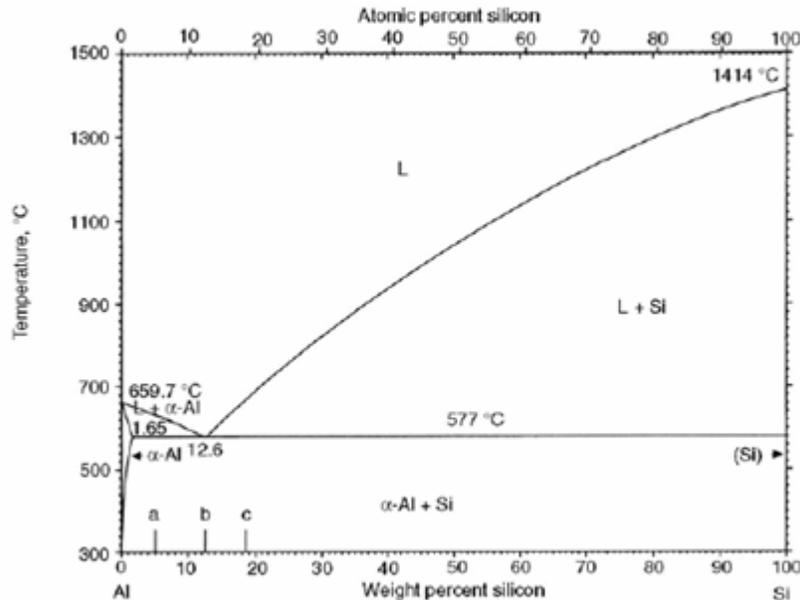
1.8 Constitutional Undercooling and the 'Mushy Zone'

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



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

- 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.
 - 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.
 - 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 $5\mu\text{m}/\text{s}$. (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'.

1.9 Coarsening

- 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:

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

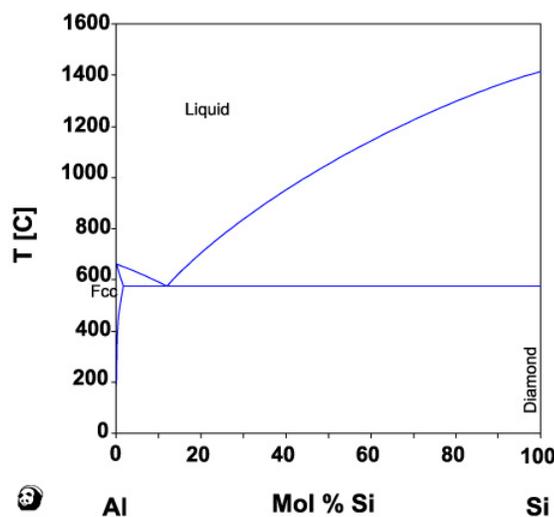
Consider the following experimental data for the formation of Guinier-Preston zones in Al-2 wt.% Cu at 0°C for $X(t)$ less than 0.25. .

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

- (a) Determine the value of the exponent m in the above equation by plotting this equation in an appropriate fashion. (Hint: you need to rearrange the equation and take logarithms so that m is the slope of the plot).
- (b) Plot the qualitative temperature dependence that you would expect for the time constant, τ . Note that you cannot obtain this from the data provided – you need to make some assumptions about what you expect this to look like) Comment on the factors that cause τ to become very large at high and low temperatures. From Fig. 5.25 in Porter and Easterling, what can you say about the behavior of τ in the high temperature regime (i.e., at what temperature must τ diverge to infinity)?

1.10 Eutectic Solidification

25. Refer to the Al/Si phase diagram and thermodynamic data below to answer the following questions.
 Heat of fusion for Al: 395 J/g
 Heat of fusion for Si: 1408 J/g



Calculated Al-Si phase diagram assessed by Murray and McAlister

NIMS

- (a) Obtain an estimate for the heat of fusion for the Al/Si eutectic (Joules per cm^3 of eutectic).
- (b) Calculate the bulk free energy gain (ignoring the energy associated with the Al/Si interfaces) associated with the solidification of 1 cm^3 of eutectic at 560°C .
- (c) Calculate the width of the Al and Si phases in a lamellar eutectic for the case where the total free energy change (including the energy associated with the interfaces) on solidification at 560°C is equal to zero. Assume an interfacial free energy for the Al/Si interface of 350 mJ/m^2 .
- (d) Compare the phase widths from part c to the critical radii for the solidification of pure Al and pure Si at an undercooling of 20°C . Assume that the solid liquid interfacial free energies are similar in magnitude to the Al/Si (solid/solid) interfacial free energy.
- (e) How good is the assumption of ideal liquid mixing in this case? Plot the liquidus lines for the Al-rich and Si-rich phases, using the equation that was developed in class. Compare the location of these lines with the location of the actual eutectic point, and comment on the agreement that you observe.

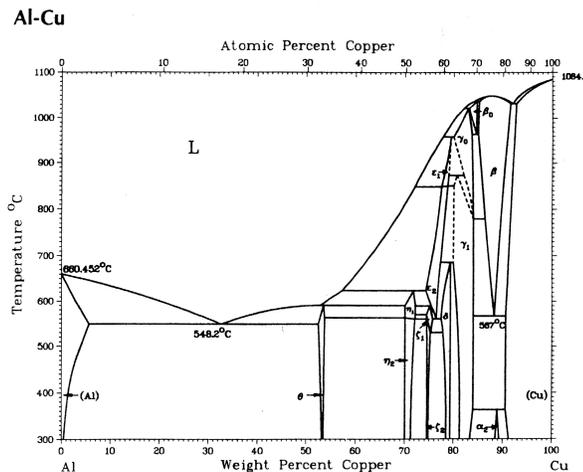
1.11 Eutectoid Transformations

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 $1 \mu\text{m}$.
 - (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. $X_o = 2.5 \text{ wt.\% Cu}$ and $X_o = 4.5 \text{ wt.\% Cu}$, 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?

1.12 Transitional Phases

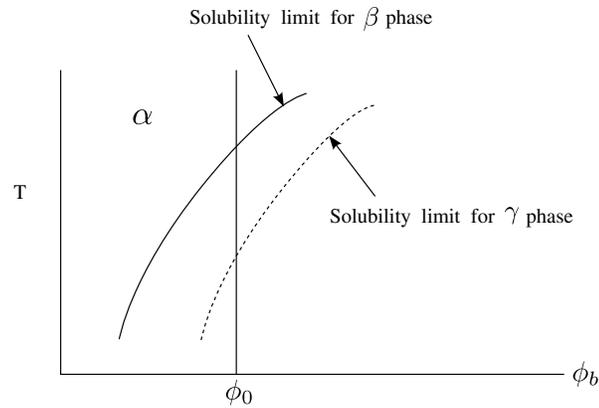
29. Suppose an alloy containing 97 wt. % aluminum and 3 wt. % copper is poured into a mold and solidified by extracting heat from the external surfaces of the mold.



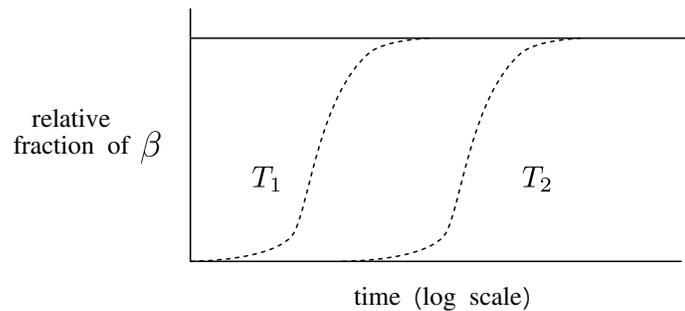
- (a) What phase (or phases) do you expect to be present in the solid immediately after the solidification reaction?
- (b) What phase (or phases) will be present at equilibrium?
- (c) A variety of non-equilibrium phases are observed at intermediate stages in the transformation process. Why are these phases observed?
- (d) Once the equilibrium phase is formed, its rate of growth is found to decrease with time. Why is this? What is the rate limiting step in the transformation?
30. Porter and Easterling, prob. 5.6
31. Suppose that in the system of interest, χ is inversely proportional to the absolute temperature, and the critical temperature for this system is 350 K. Replot the phase diagram from part a with temperature on the vertical axis.

1.13 TTT diagrams

32. Consider the following blowup of the low concentration region of a phase diagram similar to the Co-Cu diagram shown above:



- (a) At an average alloy composition ϕ_0 shown on this plot, it is determined that only β precipitates form (no γ is ever observed) at two temperatures, T_1 and T_2 . The time dependence of the appearance of β is plotted at these two temperatures as shown below. On the plot above, indicate locations of T_1 and T_2 that are consistent with these curves, and briefly describe your reasoning.



- (b) Draw TTT curves for the precipitation of both β and γ for an alloy with the composition of ϕ_0 , making connections to specific temperatures from the phase diagram where possible.

1.14 Mineralization

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

1.15 Review Questions

- What does the liquid composition look like in front of an advancing solid phase?
- What controls length scale of the composition variation?
- What is the criteria for interface stability with respect to the formation of dendrites?
- Under what conditions are dendrites formed during the solidification of a pure material?
- What is the qualitative behavior of $S(\theta)$ for nucleation at a flat interface, and at grain boundary surfaces, edges and corners?
- How are equilibrium contact angles related to surface and interfacial free energies?
- What is meant by complete wetting?
 - What is the effect on nucleation for the complete wetting case?
- What are the characteristic frequencies and concentrations (C_0 , ν_0) that determine the homogeneous and heterogeneous nucleation rates?
- Why is coherent nucleation generally the favored homogeneous nucleation mechanism?
- How is the work to form the critical nucleus calculated?
- What is the 'incoherent solvus', and how does it relate to the expressions listed above?
- Where does the Laplace pressure come from?
- How do you know that kinetic factors must be controlling complex morphologies (dendrite formation, shapes of snowflakes, etc.)?
- What controls the size of the depletion zone in front of a flat or curved precipitate that is growing?
- How does it evolve with time?
- What limits the growth velocity of a precipitate phase boundary at high and low temperatures?
 - Which of these limits are connected to the phase diagram?
- Why are flat, plate-like precipitates sometimes formed?
- How does the molar free energy depend on the radius of curvature of a precipitate?
- How does curvature effect the equilibrium concentration of solute that is in equilibrium with a precipitate?
- What does the concentration dependence look like for precipitates that are larger than r^* ?
 - What if the precipitate is smaller than r^* ?
- What are transition phases, and why do they form?
 - What is the mechanism by which transition phases shrink at the expense of equilibrium phases?
- How are TTT curves for transition phases related to the phase diagram?
- What are the basic physical assumptions of the Lifshitz/Slyosov coarsening theory discussed in class?
 - What do the depletion zones look like?
 - What determines the average solute concentration in the matrix phase?

- What does the distribution of precipitates look like if coarsening occurs by the Lifshitz/Slyosov mechanism?
- What do the binodal and spinodal curves look like for the regular solution model?
 - What is the critical temperature?
- What determines the size of the characteristic phase size when phase separation occurs by spinodal decomposition?
- What is meant by uphill diffusion?
 - When is it observed?
- How is this phase size modified (in qualitative terms) by coherent strains?
- How do these strains modify the phase diagram to give coherent spinodal and binodal curves?
- How can the liquidus lines be estimated for an ideal eutectic system?
 - What are the assumptions made in the approximation?
- What determines the size of the individual phases for eutectic solidification?
- What determines the size of the individual phases for a eutectoid transformation?
- What is the physical significance of the squared gradient term in the free energy expression?
- How can the shapes and sizes of metallic nanoparticles be controlled?
- What is the growth mechanism of Si nanowires catalyzed by Gold?
 - What is the importance of the Au/Si phase diagram.
- How does the solubility of calcite compare to the solubility of aragonite or vaterite, and why?
 - How is the concept of the solubility product used?
- In the two-phase mixture of n-type and p-type materials used to form an organic solar cell, what sort of phase morphology is desired, and why?