Introducing Interfacial Stress into Phase Diagrams

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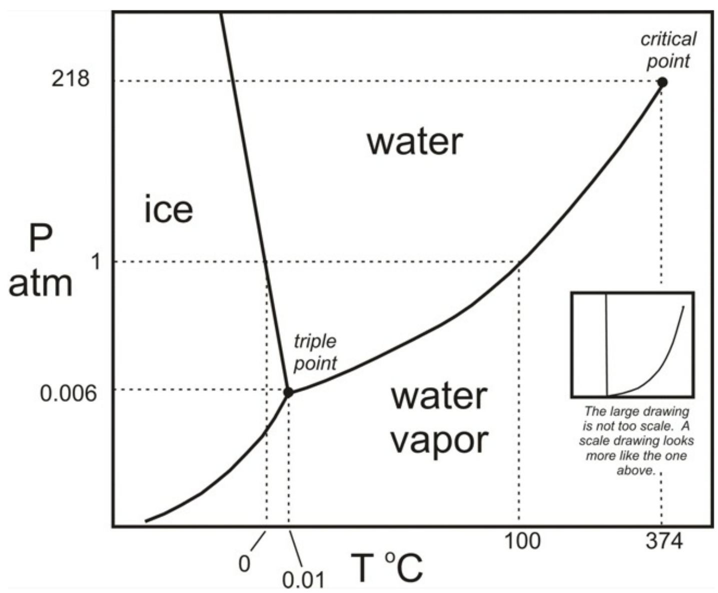
1 Introduction

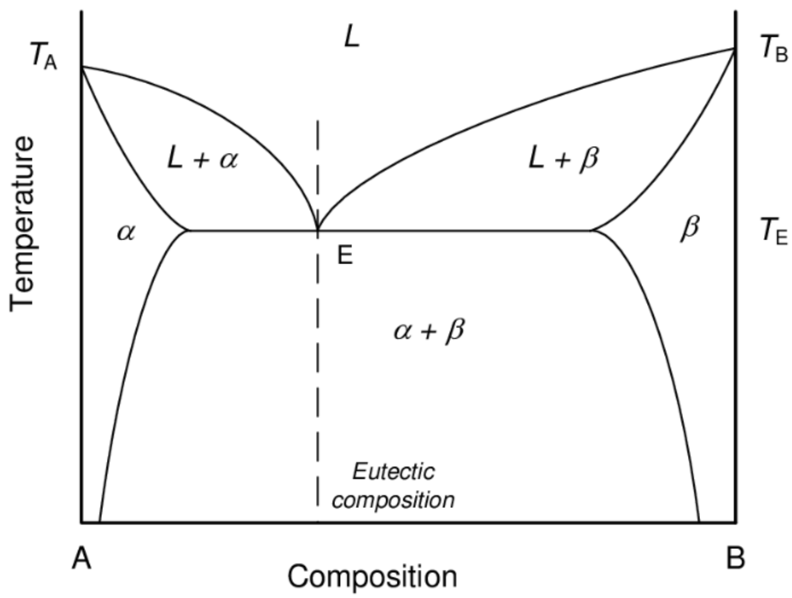
Phase diagrams are ubiquitous in materials science and often referred to as the beginning of wisdom for many materials systems [8]. They are typically the first step in new materials understanding and discovery. Historically, phase diagrams were created through laboratory experiments by taking different compositions of materials at different temperatures and plotting a point on the phase diagram. These points would be connected to create what we now know as a phase diagram. While these phase diagrams have led to much better understanding of current materials and material processes, it is clear this process is heavily time consuming and very expensive. Recent work has leveraged the use of numerical algorithms to create phase diagrams through computational methods which allow for quicker, more accurate descriptions as well as easier extraction to other systems yet to be experimentally tested. The most popular current method is that of Computer Coupling of Phase Diagrams (CALPHAD) [5, 6, 9, 10]. This method relies on the minimization of the Gibbs Free energy to find the most stable phase for a given composition and temperature. For the purpose of this paper, we will focus on Binary systems (that containing two components) and build off of the current CALPHAD methods. While many Binary phase diagrams have been studied experimentally and computationally, there is often a gap between the two approaches. One reason may be due to the stress in the interfaces that is difficult to measure. Take for instance Silicon and Germanium. This system is known to have discrepancies between the experimental and computational phase diagrams and it is also known to have great inter-facial stress [3]. We will examine the impacts of stress on phase diagrams using theoretical free energy functions to gather a better understanding of the discrepancies we see.

2 Review on Phase Diagrams

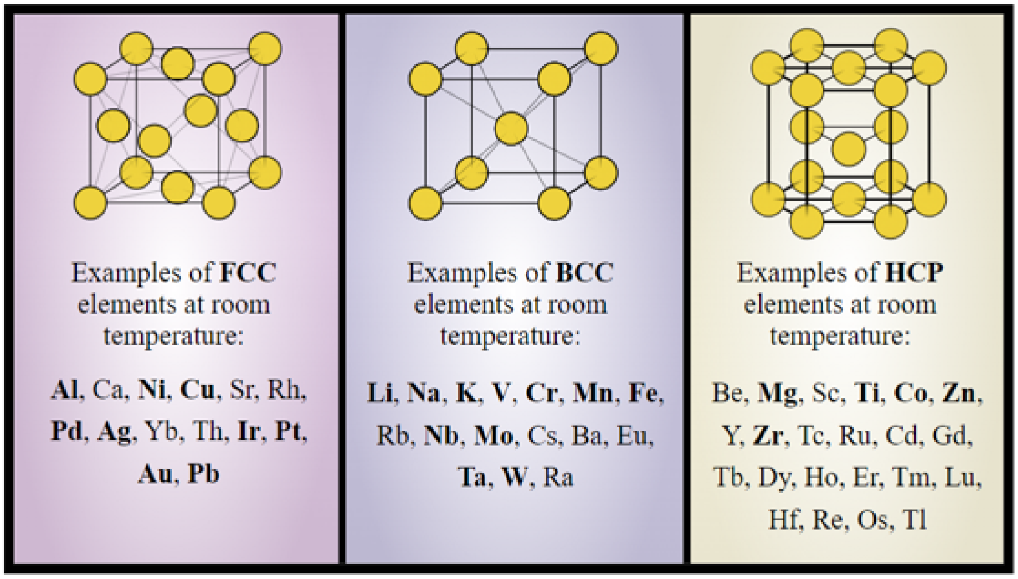
For a brief overview of phase diagrams, recall early chemistry courses on the phase diagram of H20.



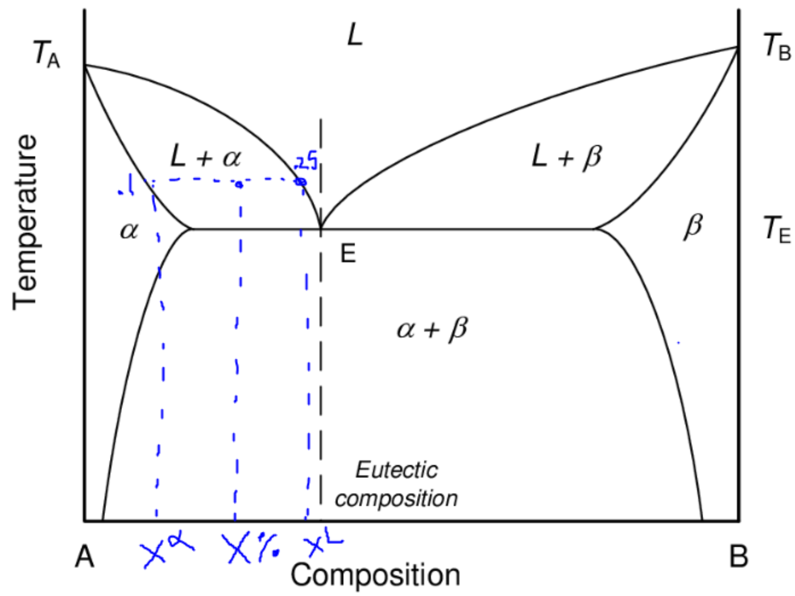
To understand the vocabulary, this diagram has one component and three phases. The component being H20 and the phases of ice, water, and vapor. At the point labeled "Triple point" is the intersection of all three phases and is where they are in equilibrium together. This can also be thought of as a breaking point as the change in temperature or pressure in any direction will result in a pure phase.
We can now extend this logic to binary phase diagrams, that which has two components and for the purpose of this paper we will focus on systems with 2 or 3 phases (while in reality, many more are possible but the same logic can be extended).



The phase diagram above is two components and three phases. The components being A and B, and the phases of α, β,L. Here L is for liquid and below is an image of some possibilities of α, β, in which the underlying lattice structure determines that phase. Notice how the axes have changed from our single component system. The axes here read composition and temperature where pressure is not accounted for. For most systems, we assume a pressure of 1 atm for all compositions and temperatures. Reading from left to right, the left most edge consists of 100 percent component A, 0 percent B. As we move right, more component B is added until we reach the right most edge which has 0 percent component A, 100 percent component B.



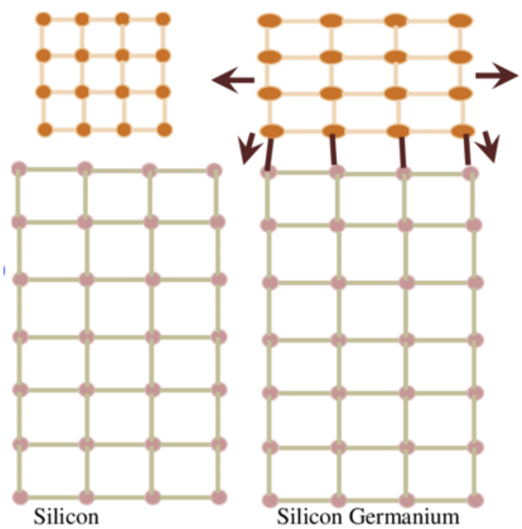
1. **Reading the Phase Diagram**
   By design, a phase diagram is created under thermodynamic equilibrium assumptions. That is why it is often referred to as the beginning of wisdom, but not the end as equilibrium is often not achievable. To read the phase diagram we begin with some composition X percent of B. X will always refer to the fraction of B, which gives the fraction of A as $100 - X$. Let us choose $X = .2$ in the diagram directly below and heat the composition to T_A(melting temperature of pure component A). Here we can see the Liquid phase is the only one present. As we begin to cool to around $.8T_A$, we see our system is in $L + \alpha$ meaning it is in come combination of the two phases. This is what is known as a two phase region. To find the molar fractions of L and α phases we can use the "Common tangent rule" which tells us to remain at the same temperature and draw a line to the connecting single phase regions. The length between X and the individual phases determines the amount of each phase. If $x^L = .25, x^\alpha = .1$ we find the two phase region is has molar fractions of α , $z_\alpha = \frac{X - x^L}{x^\alpha - x^L} = \frac{.2 - .25}{.1 - .25} = \frac{1}{3}$ and the fractions of Liquid, $z_L = \frac{X - x^\alpha}{x^L - x^\alpha} = \frac{.2 - .1}{.25 - .1} = \frac{2}{3}$ or simply could of been found by $1 - z_\alpha$. This "rule" is due to the conservation of mass and will be further discussed as too why it holds physically.



2. **Why is the Eutectic point important?**
The eutectic point is the point labeled "E" on the phase diagram. Here, we see a singular point where the α, β, L phases intersect. It is important to understand the goal is to often find a mixture of the $\alpha + \beta$ phase that is randomly organized, as this produces the best structure. Also recall the phase diagram is under equilibrium so we want the best possible chance of achieving the $\alpha + \beta$ phase, that is randomly organized, when the system is quickly cooled (rather than the infinite time a phase diagram assumes). Liquid itself is a random mixture of atoms. Thus, if we take a composition of $X = E$, and heat the system into the L phase, we can rapidly cool the mixture to become $\alpha + \beta$ without worries that one phase will form before the other. In summary, the three phase region is extremely important as it is often the wanted composition and that which reality closely follows the phase diagram. For more reading regarding the eutectic point [2].

3 Introduction of Stress

Naturally, stresses arise in the interfaces of two phases due to a lattice mismatch. Take for example the image below of Silicon-Germanium. The two elements in their solid phases have mismatched lattices which create a stress when mixing the two. As one would suspect, the higher the stress is the less likely the two phases will blend and instead create an unwanted gap between the two [3, 7].



For the rest of this paper we will take the previous ideas of CALPHAD under no stress conditions and theoretically study the impact stress has on these phase diagrams.

4 2-Phase under stress

Let us examine first the effects on the two phase region in a system with two components and two solid phases. Consider two solid phases,α and β in equilibrium with each other. Both phases are solid solutions of chemical species 1 and 2. Composition of the phases are described in terms of concentrations of species 1 per phase: x_1^α and x_1^β (because $x_2^\alpha = 1 - x_1^\alpha$ and the same for same for β). The two phases have an interface, which has an associated stress that adds to the energy of the system. The stress is assumed to be proportional to the amounts of the two phases described by the molar fractions z^α and z^β: $Az^\alpha z^\beta$.

The goal is to find the compositions and molar fractions that correspond to both solid phases in thermodynamic equilibrium. To do so we must find the minimum of the Gibbs free energy of the system according to the following optimization problem which was first introduced in [1].

Minimize

$$g(z^\alpha, z^\beta, x_1^\alpha, x_1^\beta) = z^\alpha g^\alpha(x_1^\alpha) + z^\beta g^\beta(x_1^\beta) + Az^\alpha z^\beta$$

Subject to

$$\begin{gathered} X = z^\alpha x_1^\alpha + z^\beta x_1^\beta \\ z^\alpha + z^\beta = 1 \\ 0 \leq z^\alpha, z^\beta, z^\alpha + z^\beta, x_1^\alpha, x_1^\beta, X \leq 1 \end{gathered}$$

The first equality constraint represents the conservation of of the selected composition X. The second equality constraint represents preservation of Mass. The inequality constraint represents the necessary conditions for the existence of a phase. To solve the generalized optimization problem we have. Solving by the method of Lagrange Multipliers,

Minimize

$$\begin{aligned} l(z^\alpha, z^\beta, x_1^\alpha, x_1^\beta, \lambda) = {} & z^\alpha g^\alpha(x_1^\alpha) + (1 - z^\alpha) g^\beta(x_1^\beta) + Az^\alpha(1 - z^\alpha) \\ & - \lambda((z^\alpha x_1^\alpha + (1 - z^\alpha) x_1^\beta - X) \end{aligned}$$

Subject to

$$0 \leq z^\alpha, z^\beta, z^\alpha + z^\beta, x_1^\alpha, x_1^\beta, X \leq 1$$

Finding the partial derivatives with respect to all variables we get the following equations,

$$
\begin{aligned}
\frac{\partial l}{\partial z^\alpha} &= g^\alpha(x_1^\alpha) - g^\beta(x_1^\beta) + A(1-2z^\alpha) - \lambda(x_1^\alpha + x_1^\beta) = 0 \\
\frac{\partial l}{\partial x_1^\alpha} &= z^\alpha(\frac{dg^\alpha}{dx_1^\alpha} - \lambda) = 0 \\
\frac{\partial l}{\partial x_1^\beta} &= (1-z^\alpha)(\frac{dg^\beta}{dx_1^\beta} - \lambda) = 0 \\
\frac{\partial l}{\partial \lambda} &= z^\alpha x_1^\alpha + (1-z^\alpha)x_1^\beta - X = 0
\end{aligned}
$$

The following system of equations has 3 possible solutions.

1. $z^\alpha = 1, \implies x_1^\alpha = X$
   Minimum: $g^\alpha(X)$

2. $z^\alpha = 0, \implies x_1^\beta = X$
   Minimum: $g^\beta(X)$

3. $0 < z^\alpha < 1, \implies z^\alpha = \frac{X - x_1^\beta}{x_1^\alpha - x_1^\beta}$
   Minimum:

$$\frac{dg^\alpha}{dx_1^\alpha} = \frac{dg^\beta}{dx_1^\beta} = \frac{g^\alpha(x_1^\alpha) - g^\beta(x_1^\beta) + A(1-2z^\alpha)}{x_1^\alpha - x_1^\beta}$$

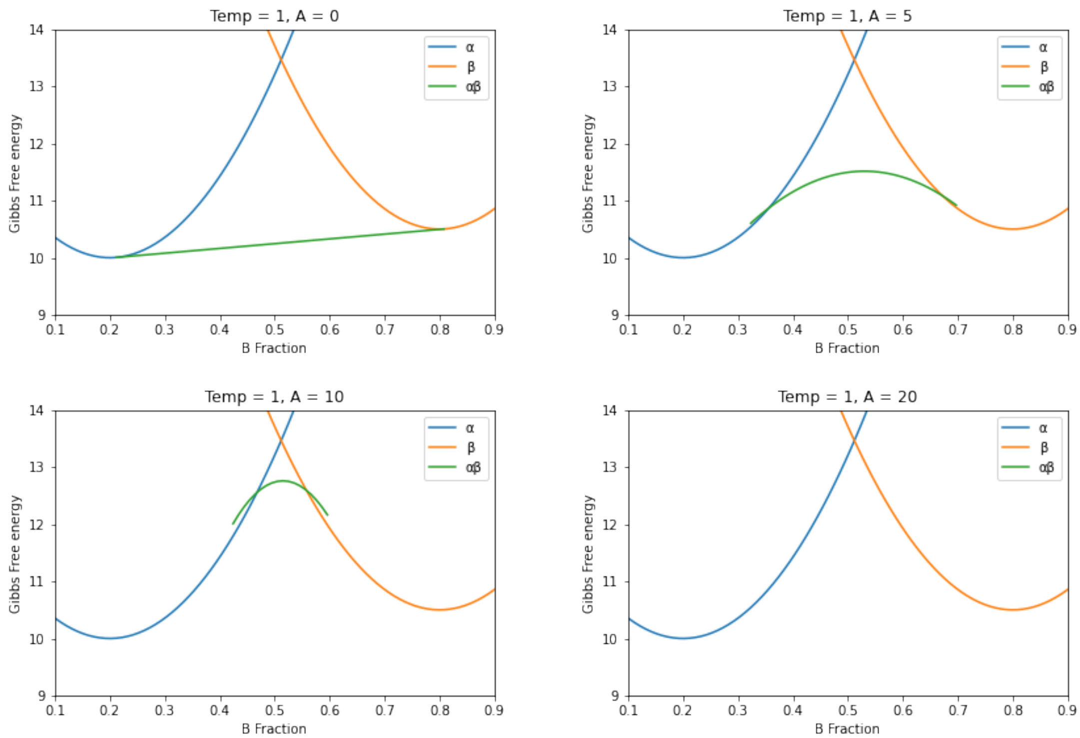
In the case where there is no stress between two solid interfaces i.e. $A = 0$, we get the popular common tangent rule,

$$\frac{dg^\alpha}{dx_1^\alpha} = \frac{dg^\beta}{dx_1^\beta} = \frac{g^\alpha(x_1^\alpha) - g^\beta(x_1^\beta)}{x_1^\alpha - x_1^\beta}$$

which states the solution is in either one phase or lies on the common tangent between two phases. This is depicted in the phase diagram above where the molar fractions of two phases were found. To depict this, let us choose two free energy functions at a specific temperature. Free energy functions are typically convex with parabolic shape thus we will choose 2 parabolas to depict these.

$$g^\alpha(x^\alpha) = a(x_1^\alpha - x_0^\alpha)^2 + b^\alpha, g^\beta(x^\beta) = a(x_1^\beta - x_0^\beta)^2 + b^\beta$$

For graphing purposes we choose, $a = 40, x_0^\alpha = .2, x_0^\beta = .8, b^\alpha = 10, b^\beta = 11$. The following depicts these two functions.



The plots above are of the free energies given above along with the common tangent at the same temperature under different levels of stress. To read these first start with no stress $A = 0$. Here we determine at the given temperature the α phase exists from $[0, .2]$, $\alpha + \beta$ from $[.2, .8]$ and β from $[.8, 1]$. Similarly lets examine the diagram with $A = 10$ (Significant stress). Here we determine at the given temperature the α phase exists from $[0, .45]$, $\alpha + \beta$ from $[.45, .55]$ and β from $[.55, 1]$. Finally under very high stress $A = 20$, the two-phase region disappears which makes physical sense as the higher the stress between two phases the more likely they are to choose one single pure phase. While the two-phase region is of some interest, the three phase eutectic point is of much greater interest. Using the same principles, let us extend this work to a three phase system.

5 3-Phase under stress

Consider two solid phases,α,β, and a L (Liquid) phase in equilibrium with each other. Both α, β phases are solid solutions of chemical species 1 and 2. Composition of the phases are described in terms of concentrations of species 1 per phase: x_1^α,x_1^β, and x_1^L (because $x_2^\alpha = 1 - x_1^\alpha$ and the same for same for β,L). The two phases have an interface, which has an associated stress that adds to the energy of the system. The stress is assumed to be proportional to the amounts of the two phases described by the molar fractions z^α and z^β: $Az^\alpha z^\beta$. It is noted there is no stress in the interface between liquid and any other phase.

The goal is to find the compositions and molar fractions that correspond to all three phases in thermodynamic equilibrium or known as the eutectic/peritectic point. To do so we must find the minimum of the Gibbs free energy of the system according to the following optimization problem.

Minimize

$$g(z^\alpha, z^\beta, x_1^\alpha, x_1^\beta, x_1^L) = z^L g^L(x_1^L) + z^\alpha g^\alpha(x_1^\alpha) + z^\beta g^\beta(x_1^\beta) + Az^\alpha z^\beta$$

Subject to

$$X = (1 - z^\alpha - z^\beta)x_1^L + z^\alpha x_1^\alpha + z^\beta x_1^\beta$$
$$z^\alpha + z^\beta + z^L = 1$$
$$0 \leq z^\alpha, z^\beta, z^\alpha + z^\beta, x_1^L, x_1^\alpha, x_1^\beta, X \leq 1$$

The first equality constraint represents the conservation of of the selected composition X. The second equality constraint represents preservation of Mass. The inequality constraint represents the necessary conditions for the existence of a phase. To solve the generalized optimization problem we have

Minimize

$$l(z^\alpha, z^\beta, x_1^\alpha, x_1^\beta, x_1^L, \lambda) = (1 - z^\alpha - z^\beta) g^L(x_1^L) + z^\alpha g^\alpha(x_1^\alpha) + z^\beta g^\beta(x_1^\beta) + A z^\alpha z^\beta \\ - \lambda((1 - z^\alpha - z^\beta) x_1^L + z^\alpha x_1^\alpha + z^\beta x_1^\beta - X)$$

Subject to

Finding the partial derivatives with respect to all variables we get the following equations,

$$\frac{\partial l}{\partial z^\alpha} = -g^L(x_1^L) + g^\alpha(x_1^\alpha) + A z^\beta - \lambda(-x_1^L + x_1^\alpha) = 0 \tag{1}$$

$$\frac{\partial l}{\partial z^\beta} = -g^L(x_1^L) + g^\beta(x_1^\beta) + A z^\alpha - \lambda(-x_1^L + x_1^\beta) = 0 \tag{2}$$

$$\frac{\partial l}{\partial x_1^L} = (1 - z^\alpha - z^\beta)(\frac{dg^L}{dx_1^L} - \lambda) = 0 \tag{3}$$

$$\frac{\partial l}{\partial x_1^\alpha} = z^\alpha(\frac{dg^\alpha}{dx_1^\alpha} - \lambda) = 0 \tag{4}$$

$$\frac{\partial l}{\partial x_1^\beta} = z^\beta(\frac{dg^\beta}{dx_1^\beta} - \lambda) = 0 \tag{5}$$

$$\frac{\partial l}{\partial \lambda} = (1 - z^\alpha - z^\beta) x_1^L + z^\alpha x_1^\alpha + z^\beta x_1^\beta - X = 0 \tag{6}$$

In the case where we $0 < z^\alpha, z^\beta, z^\alpha + z^\beta < 1$ we get the following equations,

$$\frac{dg^L}{dx_1^L} = \frac{dg^\alpha}{dx_1^\alpha} = \frac{dg^\beta}{dx_1^\beta} = \frac{g^\alpha(x_1^\alpha) - g^L(x_1^L) + A z^\beta}{x_1^\alpha - x_1^L} = \frac{g^\beta(x_1^\beta) - g^L(x_1^L) + A z^\alpha}{x_1^\beta - x_1^L}$$

$$X = (1 - z^\alpha - z^\beta) x_1^L + z^\alpha x_1^\alpha + z^\beta x_1^\beta$$

We can see when A = 0 we get the known common tangent equation,

$$\frac{dg^L}{dx_1^L} = \frac{dg^\alpha}{dx_1^\alpha} = \frac{dg^\beta}{dx_1^\beta} = \frac{g^\alpha(x_1^\alpha) - g^L(x_1^L)}{x_1^\alpha - x_1^L} = \frac{g^\beta(x_1^\beta) - g^L(x_1^L)}{x_1^\beta - x_1^L}$$

telling a three phase region is only possible when the slope between α and Liquid is equal to the slope between β + Liquid at the same point on Liquid.

In general there are seven possible solutions.

1.
$$g^L(X) \rightarrow z^\alpha, z^\beta = 0$$

2.
$$g^\alpha(X) \rightarrow z^L, z^\beta = 0$$

3.
$$g^\beta(X) \rightarrow z^L, z^\alpha = 0$$

4.
$$(1 - z^\beta)g^L(x^L) + z^\beta g^\beta(x^\beta) \rightarrow z^\alpha = 0$$

Where, z^β, x^L, x^β are found by the equations,

$$\frac{dg^L}{dx_1^L} = \frac{dg^\beta}{dx_1^\beta} = \frac{g^\beta(x^\beta) - g^L(x^L)}{x^\beta - x^L}$$

$$z^\beta = \frac{X - x^L}{x^\beta - x^L}$$

5.
$$(1 - z^\alpha)g^L(x^L) + z^\alpha g^\alpha(x^\alpha) \rightarrow z^\beta = 0$$

Where, z^α, x^L, x^α are found by the equations,

$$\frac{dg^L}{dx_1^L} = \frac{dg^\alpha}{dx_1^\alpha} = \frac{g^\alpha(x^\alpha) - g^L(x^L)}{x^\alpha - x^L}$$

$$z^\alpha = \frac{X - x^L}{x^\alpha - x^L}$$

6.
$$z^\alpha g^\alpha(x^\alpha) + z^\beta g^\beta(x^\beta) + Az^\alpha z^\beta \rightarrow z^L = 0$$

Where $z^\alpha, z^\beta, x^\alpha, x^\beta$ are found by,

$$\frac{dg^\alpha}{dx_1^\alpha} = \frac{dg^\beta}{dx_1^\beta} = \frac{g^\alpha(x_1^\alpha) - g^\beta(x_1^\beta) + A(1 - 2z^\alpha)}{x_1^\alpha - x_1^\beta}$$

$$z^\alpha = \frac{X - x^\beta}{x^\alpha - x^\beta}$$

7.
$$(1-z^{\alpha}-z^{\beta})g^{L}(x^{L})+z^{\alpha}g^{\alpha}(x^{\alpha})+z^{\beta}g^{\beta}(x^{\beta})+Az^{\alpha}z^{\beta}$$

Where $z^{\alpha}, z^{\beta}, x^{L}, x^{\alpha}, x^{\beta}$ are found by,

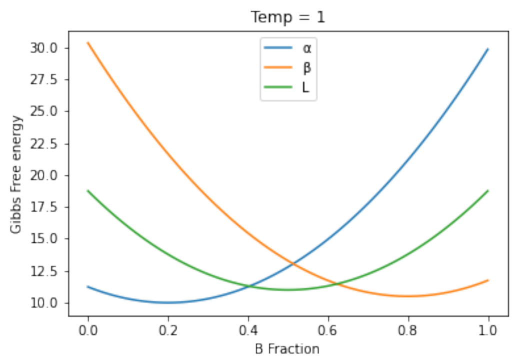
$$\frac{dg^L}{dx_1^L}=\frac{dg^{\alpha}}{dx_1^{\alpha}}=\frac{dg^{\beta}}{dx_1^{\beta}}=\frac{g^{\alpha}(x_1^{\alpha})-g^{L}(x_1^{L})+Az^{\beta}}{x_1^{\alpha}-x_1^{L}}=\frac{g^{\beta}(x_1^{\beta})-g^{L}(x_1^{L})+Az^{\alpha}}{x_1^{\beta}-x_1^{L}}$$

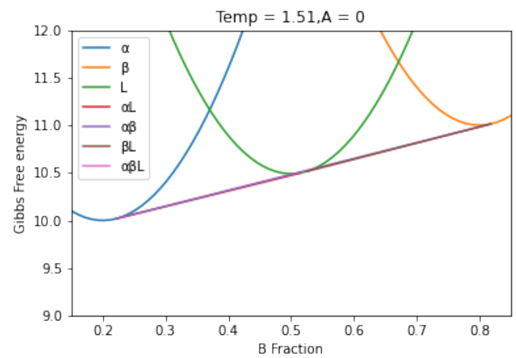
$$X=(1-z^{\alpha}-z^{\beta})x_1^{L}+z^{\alpha}x_1^{\alpha}+z^{\beta}x_1^{\beta}$$
$$\implies z^{\alpha}=\frac{X-x^{L}}{x^{\alpha}-x^{L}}+z^{\beta}\left(\frac{x^{L}-x^{\beta}}{x^{\alpha}-x^{\beta}}\right)$$

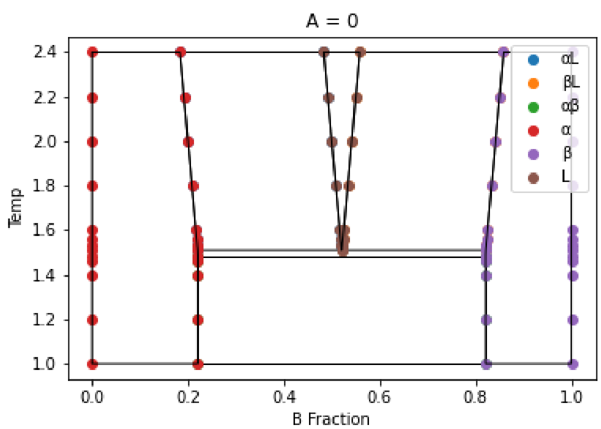
To depict the solutions, let us choose three free energy functions, where only the liquid varies with temperature. Free energy functions are typically convex with parabolic shape thus we will choose 3 parabolas to depict these.

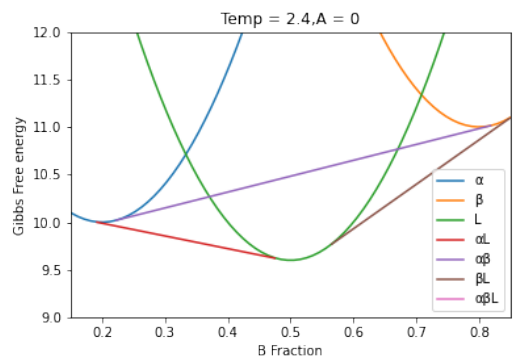
$g^{\alpha}(x^{\alpha})=a(x_1^{\alpha}-x_0^{\alpha})^2+b^{\alpha}, g^{\beta}(x^{\beta})=a(x_1^{\beta}-x_0^{\beta})^2+b^{\beta}, g^{L}(x^{\beta})=a(x_1^{L}-x_0^{L})^2+b^{L}-T$

For graphing purposes we choose, $a=40, x_0^{\alpha}=.2, x_0^{\beta}=.8, x_0^{L}=.5 b^{\alpha}=10, b^{\beta}=11, b^{L}=12.$

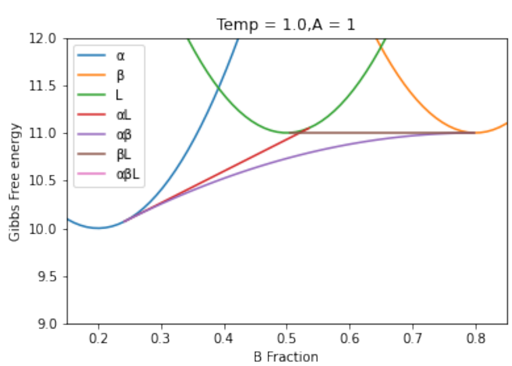


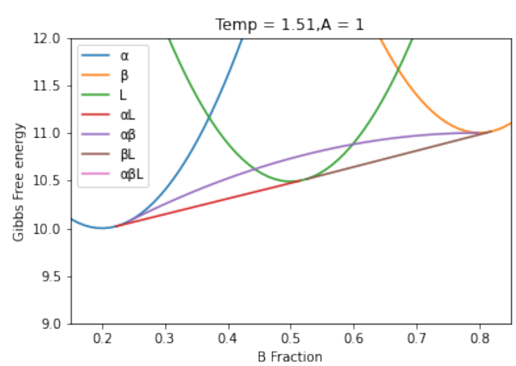


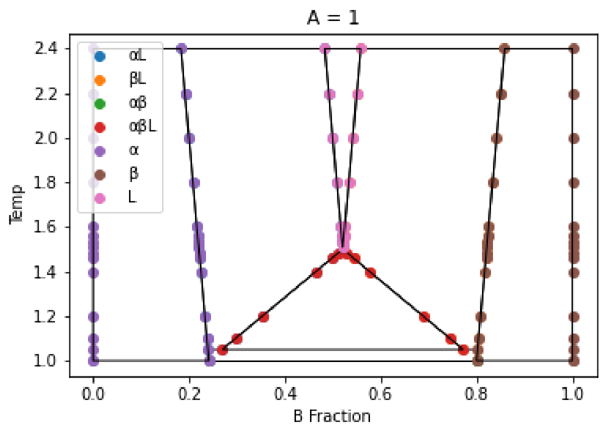


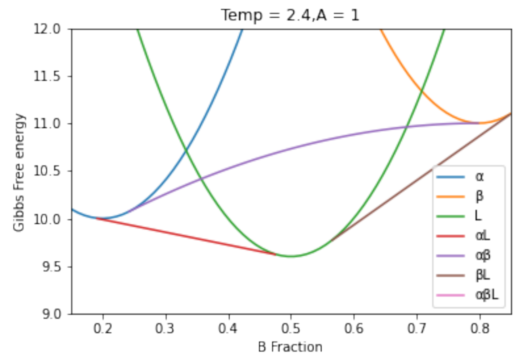


The solutions above are under no stress. The phase diagram is computed by finding the phases at different compositions and temperatures, where the free energy functions which depict which phase a solution is in are depicted around it.









The solutions above are under small amounts stress, $A = 1$. The phase diagram is computed by finding the phases at different compositions and temperatures, where the free energy functions which depict which phase a solution is in are depicted around it. Here we can see the growth in the three phase region along with a lessening of the two solid phase region, $\alpha + \beta$

6 Algorithms

After finding the equations for the three-phase equilibrium under stress, we first refer to the complete simplified algorithm (Algorithm 1) that takes in a temperature and composition and returns the phase.

Running this algorithm over an arbitrary composition and temperature grid is computationally expensive. To find the composition of pure α, β, L phases is straightforward and computationally inexpensive, but the process needs to be sped up for compositions lying in two and three phase regions. To do so, the algorithms used are symbolic but future work will extend this to numerical algorithms where free energy functions become more complex. To simplify the algorithm we first find the common tangents for a given temperature T. This allows X from Algorithm 1 to be variable rather than an input. To find the common tangents we refer to Algorithm 2.

After the common tangents have been found, we need to find where they intersect the free energy functions, as between these points are the feasible

Algorithm 1 Return Phase

Require: $g^\alpha, g^\beta, g^L, X, T$

$\alpha \leftarrow g^\alpha(X, T)$
$\beta \leftarrow g^\beta(X, T)$
$L \leftarrow g^L(X, T)$

$[x^\alpha, x^L] \leftarrow \frac{dg^L}{dx_1^L} = \frac{dg^\alpha}{dx_1^\alpha} = \frac{g^\alpha(x^\alpha) - g^L(x^L)}{x^\alpha - x^L}$
$z^\alpha \leftarrow \frac{X - x^L}{x^\alpha - x^L}$
$\alpha L \leftarrow z^\alpha g^\alpha(x^\alpha, T) + (1 - z^\alpha) g^L(x^L, T)$

$[x^\beta, x^L] \leftarrow \frac{dg^L}{dx_1^L} = \frac{dg^\beta}{dx_1^\beta} = \frac{g^\beta(x^\beta) - g^L(x^L)}{x^\beta - x^L}$
$z^\beta \leftarrow \frac{X - x^L}{x^\beta - x^L}$
$\beta L \leftarrow z^\beta g^\beta(x^\beta, T) + (1 - z^\beta) g^L(x^L, T)$

$[x^\alpha, x^\beta] \leftarrow \frac{dg^\alpha}{dx_1^\alpha} = \frac{dg^\beta}{dx_1^\beta} = \frac{g^\alpha(x_1^\alpha) - g^\beta(x_1^\beta) + A(1 - 2z^\alpha)}{x_1^\alpha - x_1^\beta}$
$z^\alpha \leftarrow \frac{X - x^\beta}{x^\alpha - x^\beta}$
$\alpha\beta \leftarrow z^\alpha g^\alpha(x^\alpha, T) + (1 - z^\alpha) g^L(x^L, T) + A z^\alpha z^\beta$

$[x^\alpha, x^\beta, x^L, z^a, z^b] \leftarrow \frac{dg^L}{dx_1^L} = \frac{dg^\alpha}{dx_1^\alpha} = \frac{dg^\beta}{dx_1^\beta} = \frac{g^\alpha(x_1^\alpha) - g^L(x_1^L) + A z^\beta}{x_1^\alpha - x_1^L} = \frac{g^\beta(x_1^\beta) - g^L(x_1^L) + A z^\alpha}{x_1^\beta - x_1^L}$
$z^L \leftarrow 1 - z^\beta - z^\alpha$
$\alpha\beta L \leftarrow z^L g^L(x^L, T) + z^\alpha g^\alpha(x^\alpha, T) + z^\beta g^L(x^\beta, T) + A z^\alpha z^\beta$
return $\arg\min(\alpha, \beta, L, \alpha L, \beta L, \alpha\beta, \alpha\beta L)$

Algorithm 2 Find Common Tangents (CT)

Require: $g^\alpha, g^\beta, g^L, T$

$[x^\alpha, x^L] \leftarrow \frac{dg^L}{dx_1^L} = \frac{dg^\alpha}{dx_1^\alpha} = \frac{g^\alpha(x^\alpha)-g^L(x^L)}{x^\alpha - x^L}$

$z^\alpha \leftarrow \frac{X-x^L}{x^\alpha-x^L}$

$\mathrm{CT}_{\alpha L}(X) \leftarrow z^\alpha g^\alpha(x^\alpha, T) + (1-z^\alpha) g^L(x^L, T)$

$[x^\beta, x^L] \leftarrow \frac{dg^L}{dx_1^L} = \frac{dg^\beta}{dx_1^\beta} = \frac{g^\beta(x^\beta)-g^L(x^L)}{x^\beta - x^L}$

$z^\beta \leftarrow \frac{X-x^L}{x^\beta-x^L}$

$\mathrm{CT}_{\beta L}(X) \leftarrow z^\beta g^\beta(x^\beta, T) + (1-z^\beta) g^L(x^L, T)$

$[x^\alpha, x^\beta] \leftarrow \frac{dg^\alpha}{dx_1^\alpha} = \frac{dg^\beta}{dx_1^\beta} = \frac{g^\alpha(x_1^\alpha)-g^\beta(x_1^\beta)+A(1-2z^\alpha)}{x_1^\alpha - x_1^\beta}$

$z^\alpha \leftarrow \frac{X-x^\beta}{x^\alpha-x^\beta}$

$\mathrm{CT}_{\alpha\beta}(X) \leftarrow z^\alpha g^\alpha(x^\alpha, T) + (1-z^\alpha) g^L(x^L, T) + A z^\alpha z^\beta$

$[x^\alpha, x^\beta, x^L, z^a, z^b] \leftarrow \frac{dg^L}{dx_1^L} = \frac{dg^\alpha}{dx_1^\alpha} = \frac{dg^\beta}{dx_1^\beta} = \frac{g^\alpha(x_1^\alpha)-g^L(x_1^L)+Az^\beta}{x_1^\alpha - x_1^L} = \frac{g^\beta(x_1^\beta)-g^L(x_1^L)+Az^\alpha}{x_1^\beta - x_1^L}$

$z^L \leftarrow 1 - z^\beta - z^\alpha$

$\mathrm{CT}_{\alpha\beta L}(X) \leftarrow z^L g^L(x^L, T) + z^\alpha g^\alpha(x^\alpha, T) + z^\beta g^L(x^\beta, T) + A z^\alpha z^\beta$

return $\mathrm{CT}_{\alpha L}(X), \mathrm{CT}_{\beta L}(X), \mathrm{CT}_{\alpha\beta}(X), \mathrm{CT}_{\alpha\beta L}(X)$

region for the phase to exist. To do so we refer to Algorithm 3.

Algorithm 3 Find Common Tangent and Free energy Intersections

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Require: $g^\alpha, g^\beta, g^L, T, \mathrm{CT}_{\alpha L}(X), \mathrm{CT}_{\beta L}(X), \mathrm{CT}_{\alpha\beta}(X), \mathrm{CT}_{\alpha\beta L}(X)$
  function INTERFREE(g_1, g_2,CT)
    $x_1 = \mathit{Solve}(CT - g_1(X) = 0)$
    $x_2 = \mathit{Solve}(CT - g_2(X) = 0)$
  return $[x_1, x_2]$
  end function

  function INTERCT(CT_1, CT_2, CT_3)
    $x_1 = \mathit{Solve}(CT_1 - CT_2 = 0)$
    $x_2 = \mathit{Solve}(CT_1 - CT_3 = 0)$
  return $[x_1, x_2]$
  end function

  $x = []$
  $x.\mathit{append}(\mathrm{INTERFREE}(g^\alpha, g^L, \mathrm{CT}_{\alpha L}))$
  $x.\mathit{append}(\mathrm{INTERFREE}(g^\beta, g^L, \mathrm{CT}_{\beta L}))$
  $x.\mathit{append}(\mathrm{INTERFREE}(g^\alpha, g^\beta, \mathrm{CT}_{\alpha\beta}))$
  $x.\mathit{append}(\mathrm{INTERCT}(\mathrm{CT}_{\alpha L}, \mathrm{CT}_{\alpha\beta}, \mathrm{CT}_{\beta L}))$
  $x.\mathit{append}(\mathrm{INTERCT}(\mathrm{CT}_{\beta L}, \mathrm{CT}_{\alpha\beta}, \mathrm{CT}_{\alpha L}))$
  $x.\mathit{append}(\mathrm{INTERCT}(\mathrm{CT}_{\alpha\beta L}, \mathrm{CT}_{\alpha L}, \mathrm{CT}_{\beta L}))$
  return x

Now we have the compositions at which the breaking point between phases is possible, the common tangents, and the free energy functions. Putting it all together, we first symbollically find the common tangents, find the breaking points, and check the phases at these points. By doing this over a grid of temperatures we can very precisely plot the wanted compositions at each phase.

The solutions below are with the same free energy functions as previously used in the three-phase problem. Here we similar behavior, as stress increases the two solid phase region shrinks (similar to the two phase problem as well), while all other phases grow.

Algorithm 4 Find Common Tangent and Free energy Intersections

Require: $g^\alpha, g^\beta, g^L, T$

$\mathrm{CT}_{\alpha L}(X), \mathrm{CT}_{\beta L}(X), \mathrm{CT}_{\alpha\beta}(X), \mathrm{CT}_{\alpha\beta L}(X) \leftarrow \text{Algorithm2}(g^\alpha, g^\beta, g^L, T)$

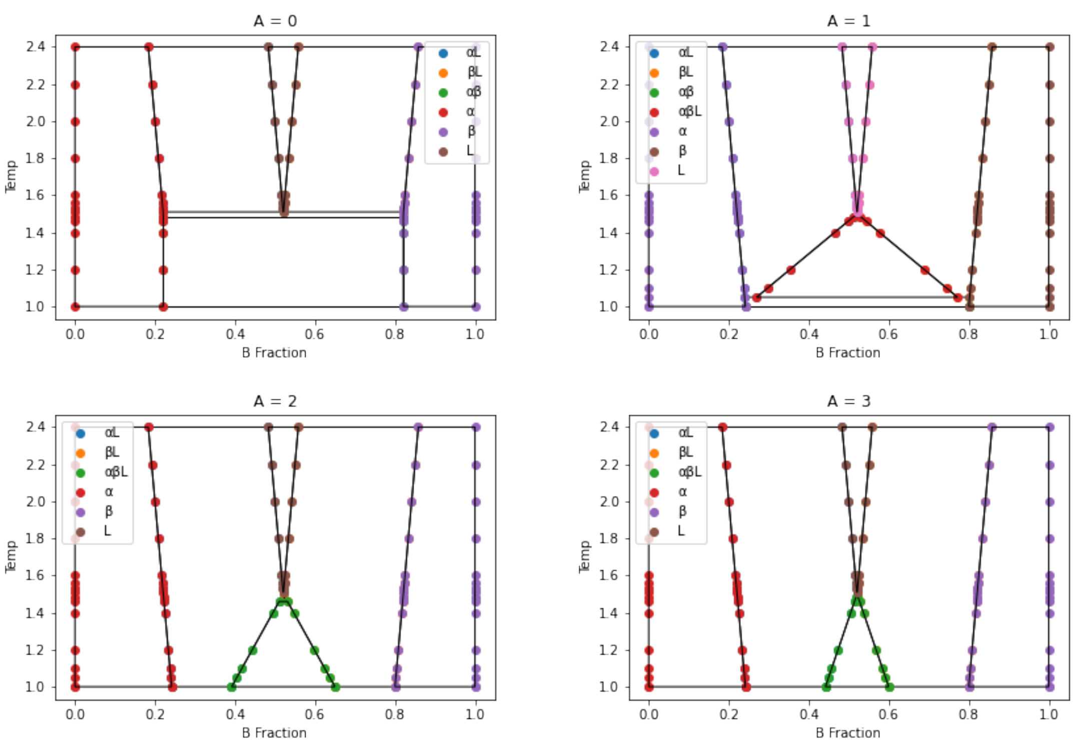
$x_{\text{grid}} \leftarrow \text{Algorithm3}(g^\alpha, g^\beta, g^L, T, \mathrm{CT}_{\alpha L}(X), \mathrm{CT}_{\beta L}(X), \mathrm{CT}_{\alpha\beta}(X), \mathrm{CT}_{\alpha\beta L}(X))$

phases = []

$x \leftarrow x_{\text{grid}}[i]$

phases$[i] \leftarrow \arg\min(g^\alpha(x), g^\beta(x), g^L(x), \mathrm{CT}_{\alpha L}(x), \mathrm{CT}_{\beta L}(x), \mathrm{CT}_{\alpha\beta}(x), \mathrm{CT}_{\alpha\beta L}(x))$

return phases



7 Future work

1. Currently the important compositions are solved for to reduce computation, but the temperature grids are not. Future work would need to find computational methods for resolving the temperature grid.

2. Currently all solutions shown were done symbolically. Some numerical techniques were implanted but for initial accuracy we did not go this route. With more complex functions on real systems, it is realistic to move to numerical optimization approaches. Many current approaches use the convex hull algorithm [4] but this method will be inneficient without the use of linear tangents.

3. Figure out how to interpret the three-phase region under stress. What are the actual fractions of each phase now that we do not have the simple to use common tangent rule?

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