RAFAEL JARAMILLO: So let's talk about phase coexistence. Phase coexistence in a common tangent construction. Right, so what's the situation here? We have two phases. We'll just label them 1 and 2. And they can freely exchange components A and B. So two phases, two components.

And we know that phased coexistence at equilibrium requires that the Gibbs free energy is stationary. So here's our little picture. We have phase A, phase one, phase two. And let's say A is-- it can be red squares. And B can be green circles.

And we know that this boundary is open. If this boundary is open, then what? Components can freely jump between phases. That's something that can happen-- it's an unconstrained, internal process. We're not going to stop that from happening.

So given that these matter exchanges can happen, how do we determine the equilibrium condition? And I say, these fluctuations must leave G stationary at equilibrium. OK, so this is now zooming in at the molecular level.

And I think people understand that if you have a glass of ice water, there's a boundary between the ice and the water, the liquid water and the solid water. And ice and water molecules will be jumping back and forth between the two phases at that boundary. On a molecular scale, and on a molecular timescale.

So what does it mean for that process to leave G stationary? That would be our equilibrium condition. So we can get into the math with that. We say, the change of G-- now we're going to be at fixed temperature and pressure. So we're not going to worry about that.

And we know the total differential of Gibbs free energy from weeks past. It's a sum over components and phases, chemical potential of each component in each phase times the change in mole number of each component in each phase. So K going-- let's see A, B-- these are components. I going one, two, these are phases.

So let's write this out. This goes mu, A, 1 d mu-- d n, sorry, let me start over. Mu A 1 d n a 1 plus mu B 1 dn B 1 plus mu a 2 dn a 2 plus mu B 2 dn B 2.

OK, so we're written that out. Now, we're going to use conservation of mass. And conservation of mass tells me that I can have molecules or atoms jumping back and forth, but I can't have them just disappearing. Or just appearing. I've got to have mass conserved.

So conservation of mass tells me that dn a 1 equals minus dn a2. And dn b1 equals minus the dn b2. So two equations, and so we're going to reduce our number of independent variables from four to two.

So I'm going to reduce-- I'm going to do that. And I get this-- mu a 1 minus mu a 2 dn a 1 plus mu b 1 minus mu b 2 dn b 1. So I have four independent variables, I applied two constraints, I end up with two independent variables.

This has a familiar form for us-- these here, these here, are the unconstrained, independent variables. Those are the unconstrained, independent variables. And what do we call the multipliers in front of the independent variables in this differential form?

What do we call this thing and this thing? This is a differentiable form for a dependent variable, and how it varies with two independent variables. And we have--

STUDENT: It's the coefficient.

RAFAEL JARAMILLO: Their coefficients, thank you. I didn't notice who that was, but thank you.

Right, coefficients. Good. So this is a form that we are familiar with. And we know from when we've solved equilibrium conditions before in this class, that d g p t equals 0 requires coefficients to be 0. That's our equilibrium condition. And in this case, what that means-- the chemical potential of A is the same in both phases.

And the chemical potential of B is the same in both phases. When that happens, phases can exchange mass freely without changing-- overall Gibbs free energy. Or in other words, Gibbs free energy is stationary.

So the math is the same. There's a lot of pattern recognition that kicks in, in this class. The math is the same formally, as we've seen before. We're just exploring different cases of this.

And so right, chemical potential is the same. So these particles, they can move back and forth. They can change their phase, but the chemical potential remain unchanged. So the overall Gibbs free energy will remain unchanged.

Now, how do we analyze that? Right, in general, in general, each phase has its own solution model, and partial molar properties of mixing.

So what do I mean by that? Mu a in phase one equals mu a in its reference state, plus delta mu a of mixing in phase one. Mu a in phase two equals mu a in its reference state, plus delta mu a in phase two mixing.

And I can write the same for the other component-- mu B in phase one, equals mu B naught plus the change in chemical potential of B due to mixing in phase one. Chemical potential of B in phase two equals the reference state plus the change in chemical potential of B due to mixing, phase two.

Why did I write it in this way? I wrote it in this way because we see that these pure components-- pure component A, and pure component B-- those terms are the same in this equation as this equation. Or they're the same in this equation as this equation.

It's the chemical potential of A in its pure state. It's the chemical potential of A in its pure state. It doesn't care what kind of mixture you're going to make out of it. This is like ingredients on the shelf-- if you've got sugar on the shelf, that's pure sugar, it's thermodynamic properties don't care whether you're going to go make cupcakes or you're going to make syrup out of it. It's just pure sugar.

So its reference state is unchanged, doesn't depend on what you're about to mix it into. So in words, the reference states-- the reference states are fixed, and the mu k naught don't depend on mixing. The properties of the ingredients don't depend on your recipe.

So if we have mu a 1 equals mu a 2 as our equilibrium condition, this becomes delta mu a of mixing 1 equals delta mu a of mixing 2. And similarly, mu B 1 equals mu B 2 delta mu B of mixing, 1 equals delta mu B of mixing 2.

And these are our two-phase co-existence equilibrium conditions. Those are our equilibrium conditions.

So now, we're going to use something which we introduced maybe a week or more ago, which is the graphical-- the graphical solution for parsing all the properties. And to remind you what that was, we had-- now, specific to the case of Gibbs, because that's pretty much the only way we're going to be using this-- we had here Gibbs free energy, and we had this concept of a solution model.

So let me just draw a section of a solution model. Draw the whole thing, because I don't need the whole thing. And let's imagine some system composition here, that would be x 2-- that's x 2. The way that we found the partial molar Gibbs free energy of mixing was we drew the tangent to the solution model at that composition.

And the intercepts were the partial molar properties of mixing. So this intercept here is mu 2 at x 2. And this intercept here is mu 1 at x 1. So I hope you do remember this-- if you don't, just rewind for a couple of lectures.

So we had this graphical solution. Now, we introduce this for one solution model. So what we're going to do now is use this tangent construction for the case of two different phases. This becomes a common tangent construction. It's called-- or if you like, you just call it a condition-- for two-phase equilibrium.

So how does that look? Well, let's drive one phase. There's part of a solution model for one phase. Let's draw another phase. There's part of a solution model for another phase.

And now, I'm going to look for a common tangent. Let's say that I drew that accurately, and we have a tangent, which is common to both curves. This is phase one, this is phase two. But say, now using our notation from the previous slides, let's say this is composition of component B and phase one. This is composition of component B in phase two.

These intercepts are the chemical potentials B and A. So what we've shown is a common tangent, which is satisfied at compositions xb 1 and xb 2. Right, it's only satisfied with these compositions. If you look at these curves, the way I've drawn them, there's no other common tangent. It's only those two particular compositions.

And for those two particular compositions, common tangent satisfied composition, that ensures that the chemical potential mu a 1 equals mu a 2 mu B 1 equals mu B 2. This is the equilibrium condition.

So a common tangent on a free energy composition diagram is the same as the equilibrium condition. When you can draw the common tangent, then you can have two-phase equilibrium. And only at those compositions that satisfy the common tangent. If there's no common tangent you can draw, then there's no two-phase equilibrium possible.

So we're knitting things together here across different lectures.

I'm going to spend the rest of the class on how this works in the case of spinodal systems. So before I make it a little bit more specific to spinodal systems, are there any questions on the concept, or on the math of this, so far? OK.

So let's move on, then. OK, so now, we're going to make this a little more specific. We're going to talk about an example of common tangent construction. And that is spinodal systems. So something a little bit familiar to us.

So here's the general view of a free energy composition diagram for a spinodal system. This is going to be delta G of mixing, and let's draw a solution model for a phase that exhibits spinodal decomposition. So let's draw something like-- that works.

You've been playing with stuff, something like this in PSETs and in previous lectures. And so this has a common tangent. Let me draw it.

OK, so it has a common tangent, let's say, here, and let's say, here. Just eyeballing this, obviously. And so let's note the composition of the system when it satisfies common tangent.

Let's say, we have x b, we'll call that phase one, x b, we'll call that phase two. The 0 of the free energy mixing is there. And these intercepts are delta mu b of mixing, and delta mu a of mixing.

And so what's happened in this system? What happens at equilibrium? The system has phase-separated. It has spontaneously unmixed into two different phases, with what? These two compositions. So you could say, this is a composition rich in component a.

So that composition were a-rich. And here's a composition rich in component. And we saw some examples of this on the slides from Monday's lecture.

So there's the common tangent construction-- [INAUDIBLE] system. When the common tangent is possible, the free energy of two-phase system is lower then that of fully mixed one phase system-- as you would expect for equilibrium. It's got the lowest free energy.

I'm not going to prove this to you right now, but I'm going to show you graphically how it comes about. Here, again, is a free energy composition diagram. And let me say, my solution model looks kind of like this-- [INAUDIBLE] here. I'd say it looks like that.

And here is my common tangent, points of tangency. And my composition is here at those points of common tangency. And let's imagine an overall system composition here. Let's imagine an overall system composition there. It can be shown that relative to a fully mixed system, the free energy can be decreased by exactly this amount, by splitting into two different phases.

So spontaneous un-mixing lowers the free energy by exactly the amount that I drew here on the plot. So the single phase, the single phase, the Gibbs free energy of the single phase system equals the Gibbs free energy of the components in their pure state. Plus just the value of this curve evaluated at the overall composition, plus delta G mixed evaluated, at overall x b.

And two phase, two phase, the Gibbs free energy is, again, the Gibbs free energy of the components unmixed, plus the Gibbs free energy of each of those two phases-- sorry.

Right, so single phase, it's just the reference state plus the evaluation of this solution model at that composition. Two phases, it's the reference state, plus the evaluation of the solution model at these two compositions, weighted by the phase fractions. So this here's a solution model, solution model. This is solution model.

And these are phase fractions. OK, so you're working some of these concepts on the problem set. All right, so now we're going to continue exploring the spinodal case. The common tangents-- they define the tie lines on a binary phase diagram.

So again, for the example of spinodal system, example of a spinodal system-- here, I'll draw a phase diagram. So we have temperature, composition, and we have a region of spontaneous-- or I should say, region of phase separation.

And let's see, we have the highest temperature here, which is sometimes marked as star-- different notations there. I'll just say T star. And we have these tie lines-- these tie lines define the compositions that can coexist at equilibrium with each other.

So in a system like this, mixing-- mixing favored at high temp. All right, in fact, it's fully immiscible at high temp. At low temp, the system spontaneously unmixes. Spontaneously unmixes, and the tie lines that are drawn in the two-phase region, connect compositions that co-exist at equilibrium.

And so this is a reminder, basically, of what tie lines are. How do the common tangents define the tie lines? They do it through the free energy composition diagrams. So phase diagram emerges from temp dependence of free energy composition diagrams.

So I'm going to draw some snapshots here of how that happens, and then we're going to spend a lot of time in the next couple of weeks on this. So let's say, low temp, T1, let me draw a free energy composition diagram for this spinodal system at low temperature. At low temperature, T1, delta G of mixing is basically positive-- that's why we have-- let me draw it like this.

This is an example. It could look like this. This system has a common tangent, right? So now, right below this, we're going to draw the phase diagram.

There's going to be temperature. I'm going to drop down those compositions. This is x b. What I've just learned from this complement tangent, is that these two compositions can coexist at equilibrium at temperature T1. So those are two points on the phase diagram.

And I know what's going to happen if I vary temperature. So I'm just going to draw those as two points on little line segments, and I'm going to connect them with a tie line. What about medium temp?

What about medium temp? So as I raise the temperature, my free energy composition diagram will change. As I raise the temperature, mixing becomes more favored.

So now, my 0 of delta G of mixing will be there. And I'll draw it maybe like this. I've got a common tangent, right? There and there.

Let's draw the corresponding phase diagram. And this is x b. At T1, I had coexistence at-- let's say, here, and here, being a little bit rough with that. So we had a tie line here. Now, at T2, I've got coexistence.

OK, let's say this is T2. Let's say my coexistence is here and here. All right, I'm calling this T2. And I've got a tie line there.

And now, I'm only drawing discrete points in temperature, but you can imagine this now starts to define a family of tie lines. So I've shown you how the tie lines at T1 and T2 emerge, but you can imagine that as I sweep the temperature, I have a family of tie lines. And this starts to sweep out the two-phase region.

And then, a high temp-- T3-- we see it again. At high temp, I know that my free energy mixing will pretty much be strictly negative. So I'm going to draw the 0 way up there. And I can say, my solution model might look like that.

So no common tangents, no inflection points. Strictly positive curvature throughout. And so that section of my phase diagram will show full miscibility.

Here's x and b. Here's T1, here is T2. And let's say this up here is T3. I'm just going to sketch this now. We'll see if we have-- all right. So now, my region of two-phase region has closed. And I have finished drawing my spinodal phase diagram.

So the way I did this here is I did a very, very slow motion animation for you. At each temperature, you have a free energy composition diagram. At each temperature, that free energy composition diagram determines for you whether or not there are any tie lines in the phase diagram. It tells you about the phase stability and equilibrium as a function of composition at that temperature.

And so as you tune the temperatures and knob, you sweep through a series of free energy composition diagrams. And you gradually build up the phase diagram.

So you can imagine a flipbook style version of this. The textbook has some nice examples of this-- of these free energy composition diagrams giving rise to phase diagrams. These single temperature snapshots.

And in the weeks ahead, we're also going to play with an online kind of animated version of this, which we've coded up for use in this class.

OK, that's where I want to leave it for today. We're finishing about five minutes early, so we have plenty of time for questions. I just saw there was a chat-- does a common tangent construction help us to say anything about the kinetics of the process of segregation?

No, it doesn't. This doesn't tell us anything about kinetics. So this tells us about the equilibrium, the common tangent construction tells us about the equilibrium configuration of the system. Now, we can infer a lot of things about kinetics from the phase diagrams, and we can also infer things about kinetics from the driving force for phase segregation.

It goes beyond the scope of the class, but kinetics is really interesting. And it starts from this point-- kinetics studies start from phase diagrams like this. And a tendency of a system to spontaneously unmix-- that is, a tendency for pattern formation. And what patterns actually form depends on the kinetics-- depends on diffusion coefficients, depends on temperature.

And that's where this curriculum takes off in the fall.