ewAdvanced Thermodynamics and Molecular Simulations

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Lecture - 23

Characterizing Mixing and Phase Separation Using Helmholtz Free Energy Density

Hello all of you. So, in the last lecture we have been discussing that if we want to look at the mixing and phase separation behaviour of liquid solutions, we can define something called a Helmholtz free energy density that will characterize the system and using that I can find the mixing and phase behaviour of the system.

So, today I will show you how exactly we will do that looking at the mathematical form f of Φ or how can we find what should be the mathematical form if I want to see a mixing behaviour or phase separation, essentially what we have been looking at the Gibbs free energy that for the incompressible system of liquid can be written something like this,

$$G = V[\,P + f(\Phi,T)\,]$$

where this quantity is what I defined as the Helmholtz free energy density.

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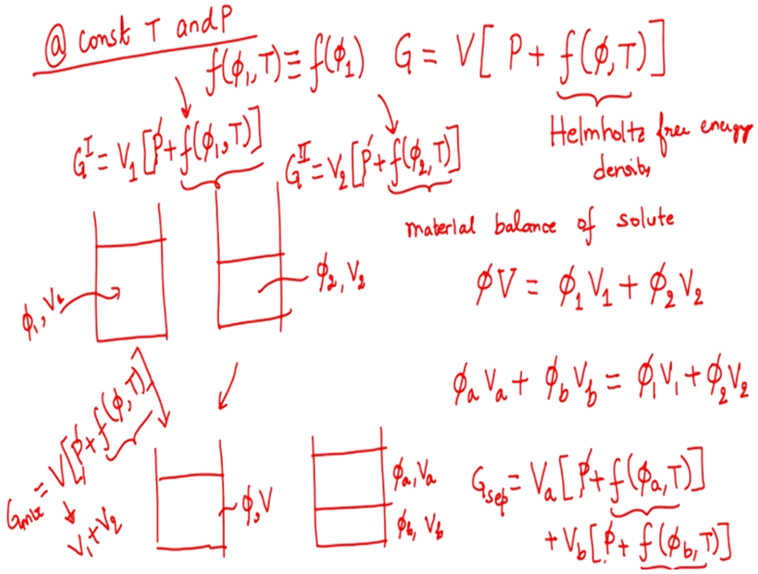
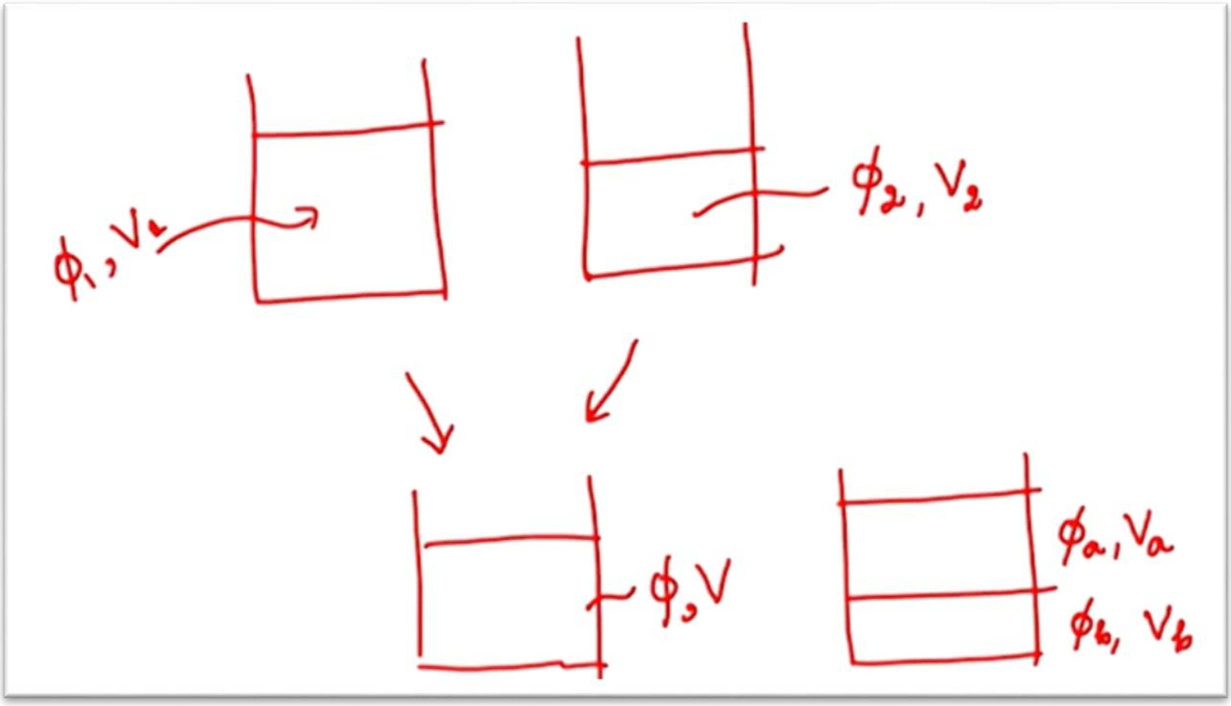


I would like to emphasize here before we proceed that we started with assuming that we are working at constant pressure and temperature condition however, if the liquid is incompressible the constant pressure also translates to a constant volume condition as the volume of liquid is not changing, and therefore we are using the Helmholtz free energy. So, in principle when I am using the constant pressure system, I should use the Gibbs free energy, but in this particular case Helmholtz free energy also makes sense because the volume is not really changing. And that's how, although we write the conditions in terms of Gibbs energy, it is still quite valid to define Helmholtz free energy because the volume is also constant.

So, then if I finally want to go back to the same mixing problem that I have been discussing. So, let us say for example, if I start with a solution containing a solute volume fraction Φ1 and volume V1 and I mix with another liquid that has a solute volume fraction Φ2 and volume V2 both of them are binary system with the same solvent and same solute and if I mix them together, then there are 2 possibilities. When it is mixing then in that case, you will have a homogeneous solution of a fixed volume fraction Φ and volume V or we can have a scenario of phase separation where at equilibrium we can have two phases having volume fraction Φa and Φb keep in mind that the Φa and Φb need not be the same as Φ1 and Φ2, because an equilibrium is established it will be a new equilibrium so as to speak when I mix them together. So, whatever the Φa and Φb will be that will correspond to the equilibrium for this new system.



So, now we can apply the metrical balance, so if I apply the material balance over the solute, what we can find is for the mixing case the volume of solute is Φ multiplied by V and that is equal to the solute volume in the initial two solution, that is-

$$\Phi V = \Phi_1 V_1 + \Phi_2 V_2$$

$$\Phi_a V_a + \Phi_b V_b = \Phi_1 V_1 + \Phi_2 V_2$$

So, if I start with this kind of an idea then I have already said that we will look at the Gibbs free energy of the final state and whichever is giving me a lower Gibbs energy is the one that will go for.

So let us look at the first case of mixing so we are starting with. A system that has a Gibbs free energy equal to

$$G^I = V_1[P + f(\Phi_1, T)]$$

And the other system that has a Gibbs energy

$$G^{II} = V_2[P + f(\Phi_2, T)]$$

Keep in mind now since we have defined the Helmholtz free energy density the f that the function that appears is going to be the same in both these cases because the system is the same, only the value of the arguments are different, the volume fractions are different in the two problems. Now since we are working at constant temperature and pressure we can pretty much write

$$f(\Phi_1, T) = f(\Phi_1)$$

for a given value of temperature. Of course, it is going to be a function of temperature, we will come back to that point. But at a given temperature the function f is a function of the volume fraction alone. Now in the final state if they mix together, then the G of the mixture is going to be the volume

$$G_{mix} = V[P + f(\Phi, \mathrm{T})]$$

And

$$V = V_1 + V_2$$

because we are assuming that the solution is incompressible, so there is no volume change on mixing.

On the other hand, if they are phase separated we are going to have something like

$$G_{sep} = V_a f(\Phi_a, T) + V_b f(\Phi_b, T)$$

And now you can notice that since I am ultimately interested in the difference in the Gibbs free energy, because that difference will drive the process if I compute the differences, this pressure term is going to be inconsequential when I compute the differences in the Gibbs free energy.

And therefore, I can only look at the Helmholtz energy term that is going to be different in the all the cases because the volume fraction are changing.

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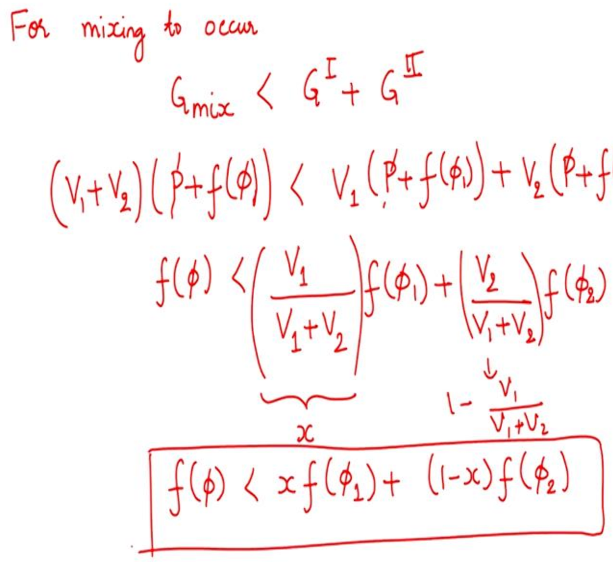

For mixing to occur

$$G_{mix} < G^{I} + G^{II}$$

$$(V_1+V_2)(\cancel{p}+f(\phi)) < V_1(\cancel{p}+f(\phi_1)) + V_2(\cancel{p}+f(\phi_2))$$

$$f(\phi) < \underbrace{\left(\frac{V_1}{V_1+V_2}\right)}_{x} f(\phi_1) + \underset{1-\frac{V_1}{V_1+V_2}}{\underset{\downarrow}{\left(\frac{V_2}{V_1+V_2}\right)}} f(\phi_2)$$

$$\boxed{f(\phi) < x f(\phi_1) + (1-x) f(\phi_2)}$$

So, now, for mixing to occur, we want that

$$G_{mix} < G^{I} + G^{II}$$

that is the Gibbs free energy of the initial solutions that we started with and that gives me

$$(V_1 + V_2)[\cancel{P} + f(\Phi)] < V_1[\cancel{P} + f(\Phi_1)] + V_2[\cancel{P} + f(\Phi_2)]$$

where I will just write as $f(\Phi)$because I am working at a constant temperature. And as I was saying the pressure term is going to cancel out.

And now I can divide this by $V_1 + V_2$, so what we should have

$$f(\Phi) < \frac{V_1}{V_1 + V_2} f(\Phi_1) + \frac{V_2}{V_1 + V_2} f(\Phi_2)$$

So, now I can define this quantity

$$x = \frac{V_1}{V_1 + V_2}$$

that is the volume ratio of the mixtures. So, then this is going to be

$$f(\Phi) < x f(\Phi_1) + (1 - x) f(\Phi_2)$$

because I can write

$$\frac{V_2}{V_1 + V_2} = 1 - \frac{V_1}{V_1 + V_2}$$

So, whenever this is true, then the system has a tendency to mix.

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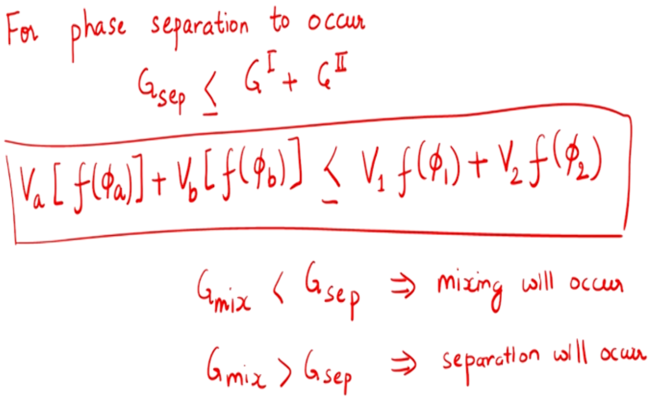

For phase separation to occur

$$G_{sep} \leq G^{I} + G^{II}$$

$$\boxed{V_a[f(\phi_a)] + V_b[f(\phi_b)] \leq V_1 f(\phi_1) + V_2 f(\phi_2)}$$

$G_{mix} < G_{sep} \Rightarrow$ mixing will occur

$G_{mix} > G_{sep} \Rightarrow$ separation will occur

On the other hand, for phase separation to occur, what we should have is the

$$G_{sep} < G^{I} + G^{II}$$

So, I can write this as something like

$$V_a f(\Phi_a) + V_b f(\Phi_b) \leq V_1 f(\Phi_1) + V_2 f(\Phi_2)$$

I am not putting a pressure term there is going to cancel anyway. This was the picture that I have been alluding to in previous figure, except that I have cancelled the pressure terms. So, if you look very closely, then we can actually write the equality also in the last because it can very well be that

$$V_a = V_1, V_b = V_2$$

$$\Phi_a = \Phi_1, \Phi_b = \Phi_2$$

where, after mixing the volume fractions in the 2 phases remain the same as the initial solution that is of course mathematically possible, will seldom happen, but just for the sake of completion we can think in this particular way.

So, now one may ask that, what if both of them are true? That is both the condition of mixing and phase separation is met? So, the answer to this question is both will not really be true, but nonetheless the way to think about it if that is true, then we will go for comparison of those two things. So, if $G_{mix} < G_{sep}$ then mixing will occur and if $G_{mix} > G_{sep}$ then phase separation will occur. So, in principle we do not even have to go to this condition. If the previous condition is not valid, then clearly the system does not have this tendency to mix. So, if it does not have tendency to mix, then it will separate, so we can also say that mixing will occur when

$$f(\Phi) < xf(\Phi_1) + (1-x)f(\Phi_2)$$

And phase separation will occur otherwise.

Otherwise so we simply have to see whether the system has a tendency to mix and if that is not happening when the separation is going to occur. We will come back to the point where we will try to evaluate the free energy in the phase separated state, we will come back to that point. For the time being it is enough to say that we will simply look at these particular conditions and identify whether we will have mixing or not.

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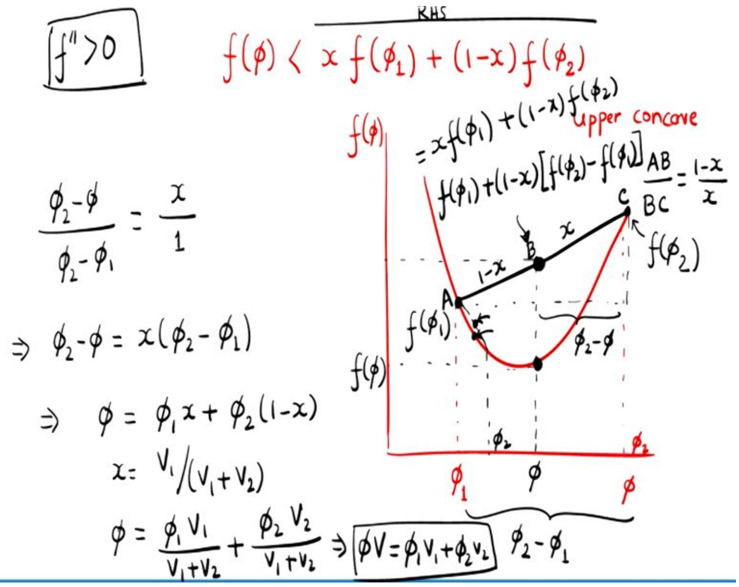


$\boxed{f'' > 0}$

$$f(\phi) < \overbrace{x f(\phi_1) + (1-x) f(\phi_2)}^{\text{RHS}}$$

$$\frac{\phi_2 - \phi}{\phi_2 - \phi_1} = \frac{x}{1}$$

$$\Rightarrow \phi_2 - \phi = x(\phi_2 - \phi_1)$$

$$\Rightarrow \phi = \phi_1 x + \phi_2(1-x)$$

$$x = V_1/(V_1+V_2)$$

$$\phi = \frac{\phi_1 V_1}{V_1+V_2} + \frac{\phi_2 V_2}{V_1+V_2} \Rightarrow \boxed{\phi V = \phi_1 V_1 + \phi_2 V_2}$$

$$= x f(\phi_1) + (1-x) f(\phi_2)$$

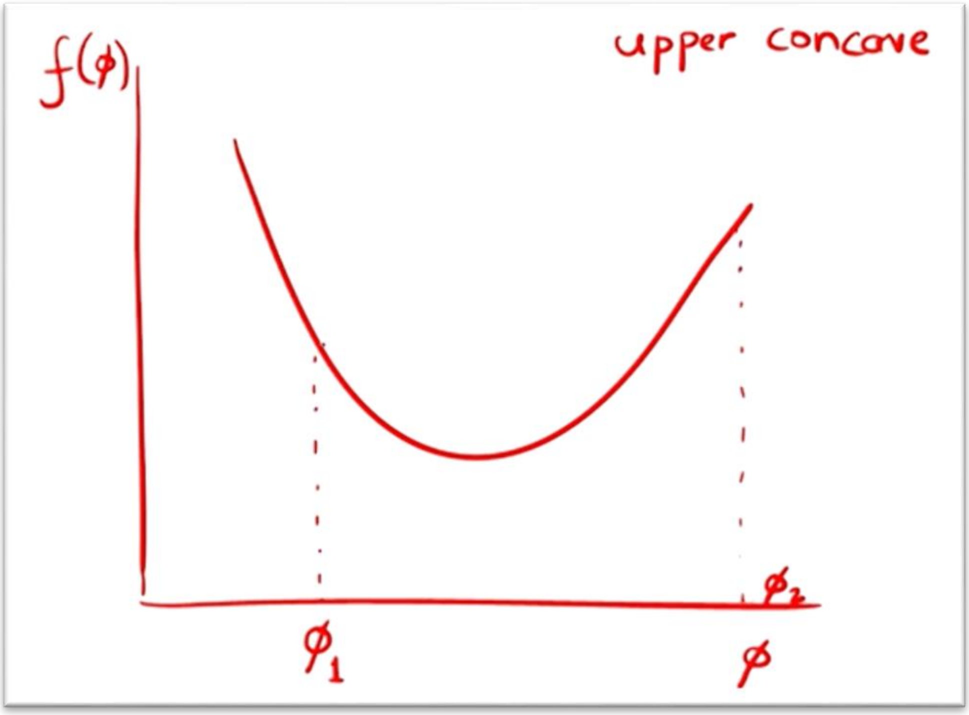
$$f(\phi_1) + (1-x)[f(\phi_2) - f(\phi_1)]$$

$$\frac{AB}{BC} = \frac{1-x}{x}$$

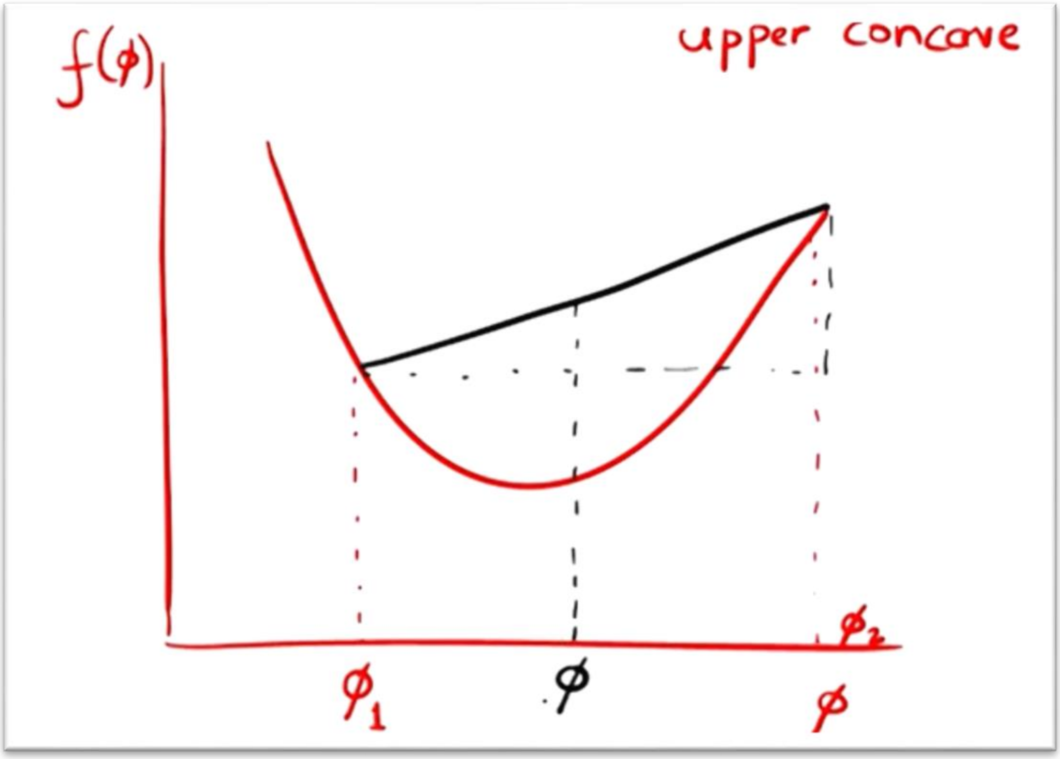
Now so basically, we want to look at this particular condition for mixing to occur,

$$f(\Phi) < xf(\Phi_1) + (1-x)f(\Phi_2)$$

as we have derived in the previous slide. Now we have not really said what is the functional form $f(\Phi)$. So, let us assume some form and see like what does this condition translate to and then going further we can say what should be the form of $f(\Phi)$. Later on we will see how can we derive that but right now I am just looking at the mathematical form of this function. So, let us say for example this function looks like this.

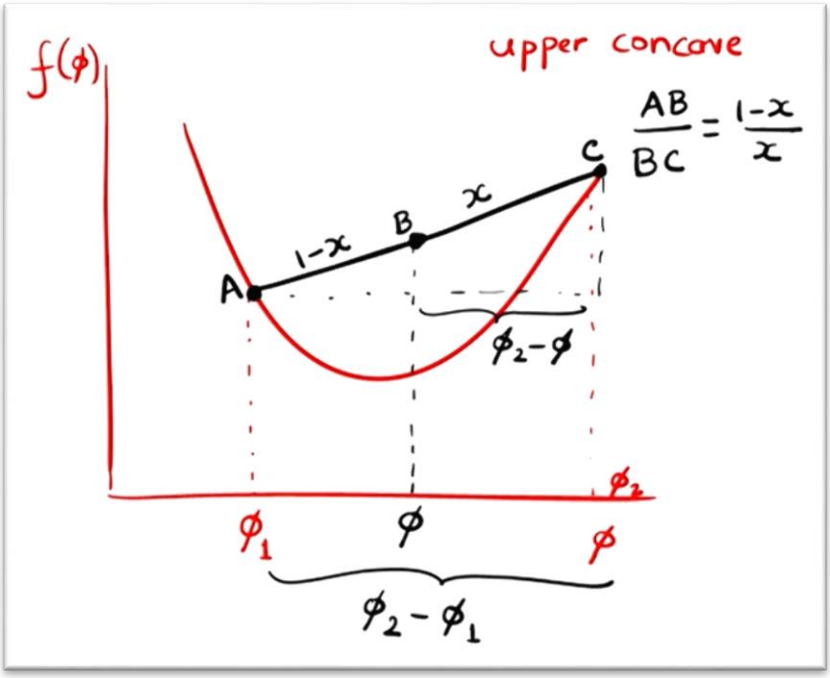


So, I am assuming an upper concave function. And let us say that my initial volume fractions are Φ_1 and Φ_2. So, now, we can draw a line connecting them. And clearly the value of Φ after mixing has to be intermediate between Φ_1 and Φ_2.



So, let say, for example, if I mix 10% of sugar in 20% of sugar, what we know for sure is that the amount of sugar in the final solution has to be between 10% and 20%. We do not know what value is that you can get from material balance, but clearly know that it must be intermediate between 10% and 20% so whatever Φ it is going to be it is going to be intermediate between Φ_1 and Φ_2 values.

So, now, we can say the following.



And

$$\frac{AB}{BC} = \frac{x}{1-x}$$

And let us see why it is true it comes as a consequence of the material balance equation.

So, let us say if I apply the formula of similar triangle here, then what we can see is

$$\frac{\Phi_2 - \Phi}{\Phi_2 - \Phi_1} = \frac{x}{1}$$

By the way, I am looking at the ratio and that is why we get x by 1 the length of AC can be anything but the ratio BC/AC is always going to be x. So, this then becomes

$$\Phi_2 - \Phi = x(\Phi_2 - \Phi_1)$$

And this gives me

$$\Phi = \Phi_1 x + \Phi_2(1 - x)$$

and we have earlier defined

$$x = \frac{V_1}{V_1 + V_2}$$

So, if I put that thing in earlier equation

$$\Phi = \frac{\Phi_1 V_1}{V_1 + V_2} + \frac{\Phi_2 V_2}{V_1 + V_2}$$

and that essentially is

$$\Phi V = \Phi_1 V_1 + \Phi_2 V_2$$

because

$$V = V_1 + V_2$$

Which is the material balance for solute that we had obtained earlier.

So, therefore, AB line segment should be $(1 - x)$ fraction of this AC line segment. And BC line segment should be x fraction of the AC line segment.

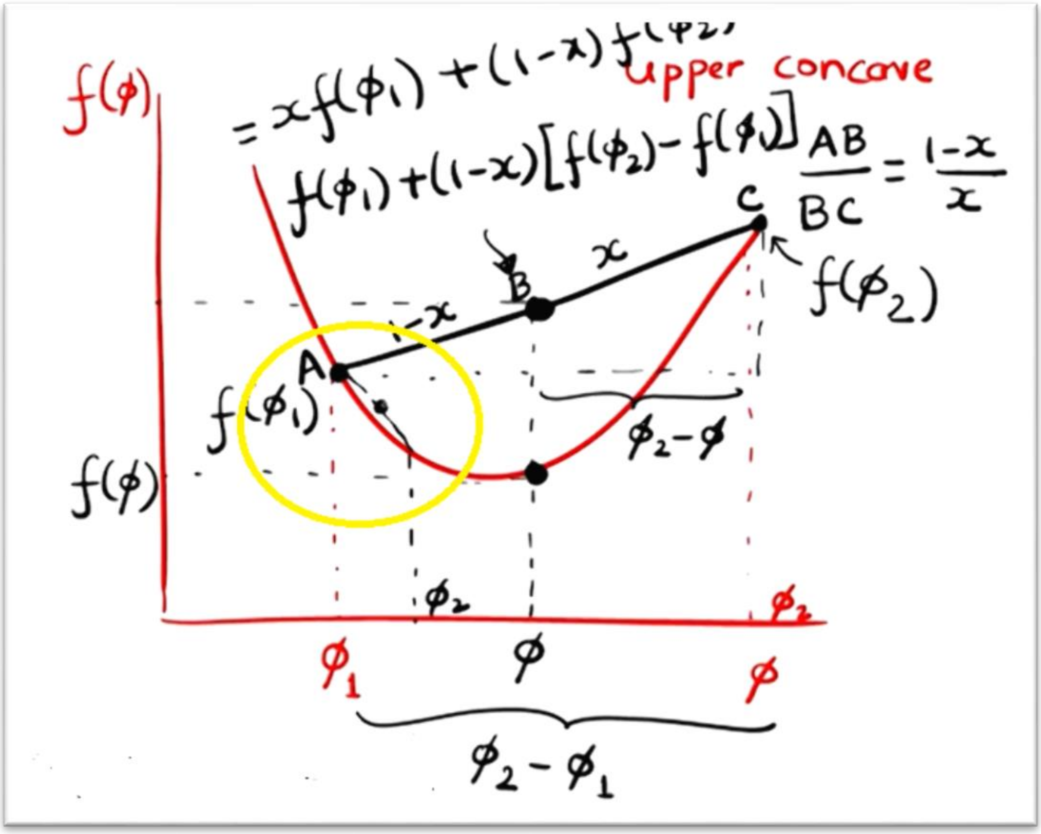
So, if we agree with that, then the next thing that we can do is we can find what should be the function value at point B and it turns out that it is going to be an interpolation between the function value at A that is $f(\Phi_1)$ and the function value of C, that is $f(\Phi_2)$ and this quantity is going to be

$$f(\Phi_1) + (1 - x)[f(\Phi_2) - f(\Phi_1)] = xf(\Phi_1) + (1 - x)f(\Phi_2)$$

So, the function value at B is equal to the right hand side of the expression obtained earlier for mixing case

$$f(\Phi) < xf(\Phi_1) + (1 - x)f(\Phi_2)$$

And the function value at Φ is the value on the curve. So, clearly, if the curve looks like this if f of phi looks like this, the above expression is always true as long as the curve is upper concave that is like what I have drawn here. If it has a minima, and if it has only 1 minima, if it is an upper concave curve, it is going to always mix together. No matter what Φ_1 and Φ_2 I start with. Just for the sake of convenience, I have taken Φ_1 and Φ_2 on different sides of minima, even if my Φ_1 and $\Phi_2$were on same side of minima, then also this argument holds true that (see highlighted section in figure below when Φ_1 and Φ_2 are on same side of minima.



Like the curve is upper concave what so happens that we should have $f'' > 0$ and that simply comes from, if you recall the condition of a minima. So, for the minima $f' = 0$ and $f'' > 0$. So, a curve will have a minima or a curve will be concave if my $f'' > 0$. So, what we can say with certainty is that if f double prime is greater than 0, then we are going to have a tendency of system to mix. Now, let us see if this is not true what really happens.

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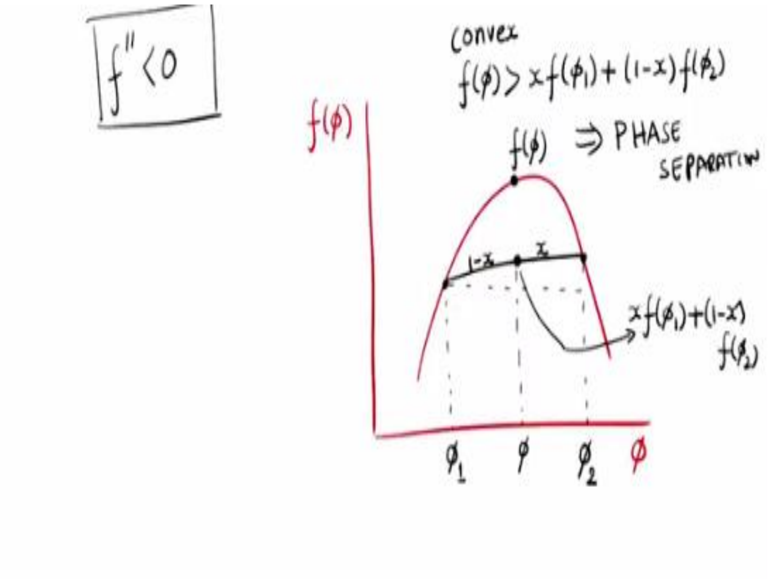
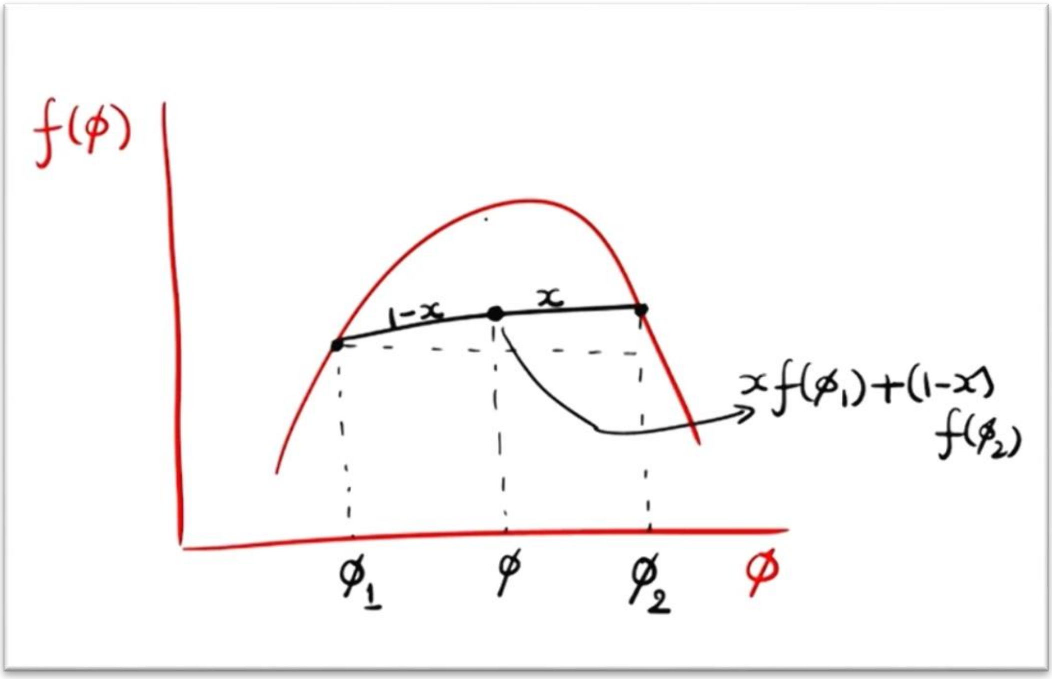


So, let us say for example, now we have a curve that is upper convex. That is my curve, looks like that-



Now in this case again, I can use the same argument. And let us say if I start with some initial volume fraction of solutions. Again, I am going to connect these two points. So, that logic really comes from the material balance and again, I can find the Φ of the final solution and this is going to be 1 - x, this is going to be x. If you recall while doing that, I have not really considered the shape of the curve. I only look at the last, the point at phi 1 and point at phi 2. So, this argument is still is valid. So, this point is till going to be something like-

$$xf(\phi_1) + (1 - x)f(\phi_2)$$

But now my function value is right here, this is my f of Φ. So, if a curve is convex or upper convex, what we are going to have is f (Φ) be higher than x f (Φ_1) + 1 - x f (Φ_2), and in that case, we are going to have a phase separation. So, if you do not have mixing you must have a condition of phase separation. And just like f double prime higher than 0 gave me a concave function f double prime less than 0 that is the condition of maxima gives me a convex function.

So, essentially, even if I do not know f, one thing is clear from here is that the second derivative of ‘f’ will dictate whether the system will have a tendency to mix or to phase separate. If the second derivative is higher than 0, then we have mixing behaviour. If second derivative is less than 0, then we are going to have a phase separation behaviour.

Now in general the curve may not be throughout convex or throughout concave it can be somewhere in between.

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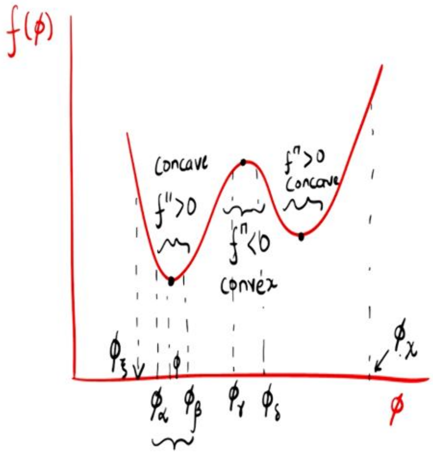

For example, the curve may look something like this. So, now if you see the function has minima’s and maxima’s, so you have 3 points here two of them are minima and one of them is a maxima. If you look in somewhere around here, then my f double prime should be less than 0, that is the function is convex. On the other hand, if I look in here, then my f double prime is higher than 0 that is the function is concave and if I have looked somewhere here again, my f double prime is higher than 0 that is the function is concave.

So, now it becomes important which solutions are we trying to mix- So, let us say for example, if I want to mix 2 solutions with volume fractions Φα and Φβ which happen to come near the concave reason of the plot. In that case, what is going to happen it will have a tendency to mix because Φ anyway is in between these two so, it does not really matter. What the function form is in the other parts of the phase of this diagram, that is what is the function value for other values of Φ because we are looking at only within this range of value. On the other hand, if for example, I am looking at the volume fraction say if some Φγ and Φδ, it happens to be in the convex regime in that case it is going to phase separate.

So, now this, the situation becomes more complicated, because now we have to see what is the function value in the range of Φ between the initial solutions that we started with and if in the range of Φ the function form is concave that is f double prime is higher than 0, we will have a mixing behaviour. If in that range, if the function form is convex. In that case, we will have a phase separation.

Now finally look at a case when if for example, look at two things which are in different parts of the phase diagram. So, let us say this is my Φ ζ and this is my Φ χ and let us say if I want to mix these 2, now the answer is not so trivial. Now we have to see which regime of this function curve will the final Φ value lies and it is that will dictate whether we are going to have a mixing behaviour or a phase separation we gave here.

So, for many cases in thermodynamics, you can have situations where it is not completely or fully convex or a fully concave curve it may look like something like this for example, and in that case we need to see what is the function value in the range of the volume fractions that we are considering and it is then the problem become somewhat more involved and this is what we will discuss in the coming classes.

So, with that I want to conclude here, thank you.