Advanced Thermodynamics and Molecular Simulations

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Lecture - 22
Pure Components Phase Diagram; Solution Thermodynamics: Helmholtz Free Energy Density

Hello all of you. So, in the last class, we have derived the Gibbs phase rule for a multiphase multi component equilibrium. Before that, I gave some motivation towards the idea of mixing and phase separation and why we are doing this particular system.

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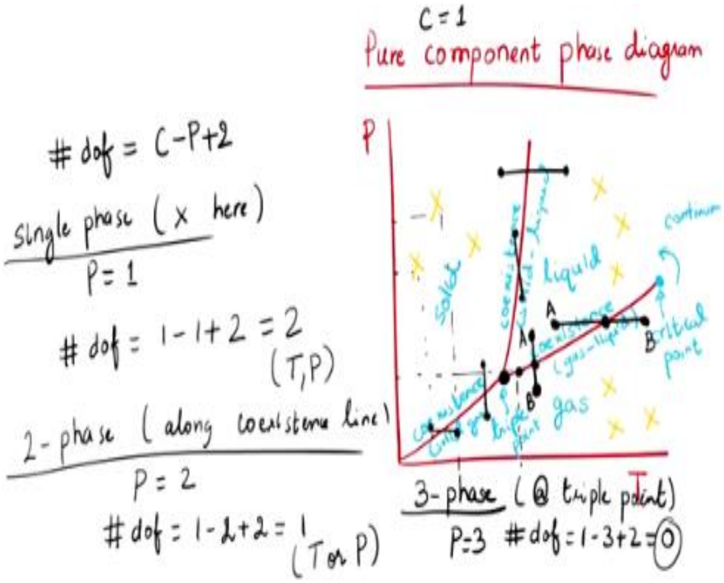


C = 1
Pure component phase diagram

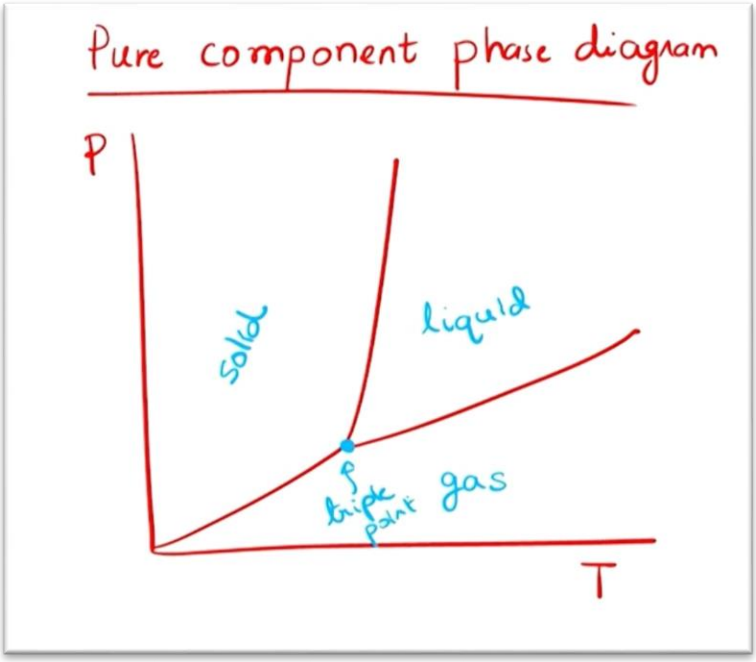
dof = C-P+2

single phase (x here)
P = 1
# dof = 1-1+2 = 2 (T,P)

2-phase (along coexistence line)
P = 2
# dof = 1-2+2 = 1 (T or P)

3-phase (@ triple point)
P=3 # dof = 1-3+2 = 0

So, today I will take that a bit further, I will first discuss the consequences of the Gibbs phase rule taking an example of the pure component phase diagram and then we will go towards a more systematic way of doing the thermodynamics for liquid solutions. If you may recall the pure component phase diagram for the case of liquid looks something like this.



So, this is the diagram looks like, so when we look at this part of the phase diagram, we have a solid phase in along this part of the phase diagram, we have the liquid phase and this part of the phase diagram we have gas or vapor phase. This particular point is referred as the triple point, at this particular point all the three phases exist together. . So, let us say if you look at water as a system then we can have ice, liquid water and water vapour in coexistence it at this particular condition. This point is where this line ends is what is referred as the Critical point. Beyond this point we can go from a gas to a liquid phase or a liquid phase to a gas phase continuously. So, in the literature of phase transition, what is it referred as the second order phase transition.

So, let say for example, if I look at temperatures below the critical point we observe a jump in the properties let say if I look at the densities, densities undergo a jump as soon as I go from a water vapor to a liquid state or a solid to a gas state and vice versa. On the other hand beyond the critical point, we have a continuous phase transition. These red lines that we see on the diagram they are referred as coexistence lines. Now depending on which two phases they are connecting, they have accordingly we name them. For example this line is connecting the gas and liquid part of the phase diagram. So, this is coexistence for gas liquid. This will be coexistence for solid liquid and this will be coexistence for solid gas we can also say the coexistence of gas liquid as something like a boiling curve, so a liquid boils and becomes a gas. So, if I want to represent that on this particular phase diagram. I can say that let us say a liquid is here and then we heat it becomes a gas by increasing temperature. So, we pass through the coexistence line at this particular point we are having a state where the liquid and gas phases coexist.

So, now I am showing you a path when the temperature was increasing the pressure was constant you can have some other path were I keep the temperature fixed and I change the pressure. So, if I lower the pressure I can also go from a liquid to a gas state. So, these are the showing, depicting essentially a liquid gas or a gas liquid phase transition and you will always have a point in between where the two phases coexist. And these points if we connect we are getting the coexistence curve. Similarly you can think of going from a liquid to a solid phase by decreasing the temperature or by increasing the pressure at the same temperature.

Similarly, you can also imagine starting from a solid lowering the pressure to become a gas. This is solid gas part is called sublimation curve just like solid liquid will be a freezing curve and so on. And we can imagine all the processes by which the phase transition may happen.

So, what the Gibbs phase rule tell me is the number of d of dof that is the number of degree of freedom is given as C - P + 2. and let us see what does it, mean at different parts in the phase diagram. So, let us first look at points which are located inside one of those phases. So, let us say if the points are right here I am in a solid phase, if the points are right here then I am in a liquid phase, if the points are right here I am in a gas phase. And for all these points the number of phases is equal to 1 because there is no coexistence so as to speak because; we are looking at deep inside one particular phase. So, for that single phase represented by these crosses here we are having the P value is equal to 1. And for pure component C is always equal to 1. So, what does it mean? So, the number of dof is 1 - 1 + 2 that is equal to 2.

So, we have two variables under control or two intensive variable under control what does it mean? In this case, I am looking at a temperature and pressure as the variable in the diagram. And you can see there for each of these points I am at perfect liberty to choose the temperature and pressure value as long as I am in the single phase regime. So, we have a perfect control on the pressure and temperature they can be independently varied so as to speak as long as we are in the single phase part of the phase diagram so, these variables are going to be temperature and pressure.

Now, let us look at the cases when I am along the coexistence line except that particular triple point will come to that in a minute. So, let us say if I am in a two phase regime that is along coexistence line. Now, if I am there then the P value is equal to 2. So, the number of DOF is equal to 1 - 2 + 2 and that is equal to 1 that means we have only one variable under control, and why is that because let us say for example, if I pick temperature as the value if I am say at this point in the curve, then as soon as I pick the temperature the pressure is already determined. So, for any given temperature, the pressure value is given by the curve for any given pressure the temperature value is given by the curve. So, we do not have a liberty to control temperature and pressure both so, we can say that variable can be temperature or pressure. So, I can independently vary pressure but once I very pressure then the temperature has to be what comes on the coexistence curve. So, therefore we do not have control over temperature in that case.

On the other hand, I can independently vary temperature but then I will not have control over the pressure value or by control I also mean that the pressure value is determined as soon as I choose temperature and vice versa.

Now, we can have a 3-phase part and that will happen at triple point. So, if I am at triple point. In that particular case, we are having a coexistence of the 3 phases. So, we are having P is equal to 3. So, the number of DOF is 1 - 3 + 2 and that comes out to be 0 and why is that because there is only one triple point that corresponds to one particular value of pressure and one particular value of temperature we cannot choose to have any particular triple point because the value is predetermined for the component under consideration. If I change the component it may have a different triple point but none the less the triple point is a unique value of temperature and pressure.

So, therefore we have no control on any variable, whether it is temperature or pressure that is how this Gibbs phase rule becomes useful because for any multiphase multi component system. I can figure out what are the control variables we have and in terms of chemical process design what are the design variables we have, how can I control the process if I want to establish this particular type of equilibrium.

So, this was I can say the picture that we have learnt in the undergrad thermodynamics. Now let us try to build the advanced thermodynamics idea of liquid solutions where the goal is to determine the Helmholtz free energy to derive the Helmholtz free energy for this system and we will see why we are doing Helmholtz free energy and using that I can find the properties of interest first of all, I will develop the basic framework and then I will discuss what is known as the lattice model of solution and using that we can find the expression of the Helmholtz free energy for this particular problem.

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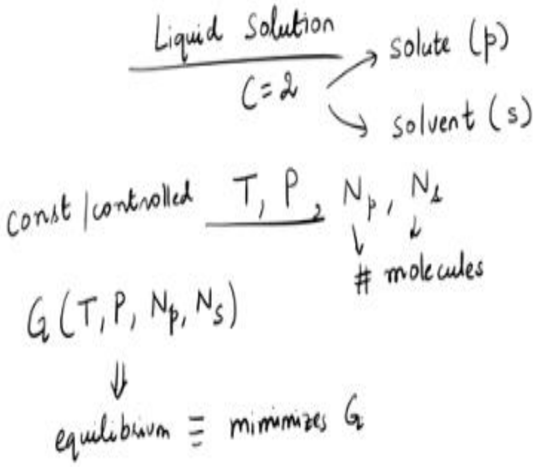

So, for this purpose, I will focus on a binary system that is for C = 2 you can generalize the idea for a multi component system more than two components, but we will do it for two that clearly one of them is a solute. I will use the symbol p for the solute the subscript p will refer to solute. And we will have a solvent and I will represent using s right. And let say we are controlling or working at controlled temperature and pressure conditions. Now, we can choose to have an open system or a closed system, let us say the system is a closed system then the number of molecules of the solute and solvent is also controlled, this is the number of molecules.

And now we have already said that when the temperature, pressure and the number of molecules are the control variable the appropriate energy function will be the Gibbs energy and Gibbs energy is going to be a function of the temperature, pressure, number of molecules of solute and solvent. So, the equilibrium will correspond to what minimizes the G. Ultimately if I want to find the equilibrium condition or the most probable distribution for this problem, as we have discussed earlier, we need to minimize the Gibbs free energy. So, what this tells me alluding to the idea that I have done earlier that ultimately thermodynamics dictates that whether two things will mix or will separate.

Now we can say that I can find the Gibbs free energy and figure out whether we will have a mixed state or we will have a separated state.

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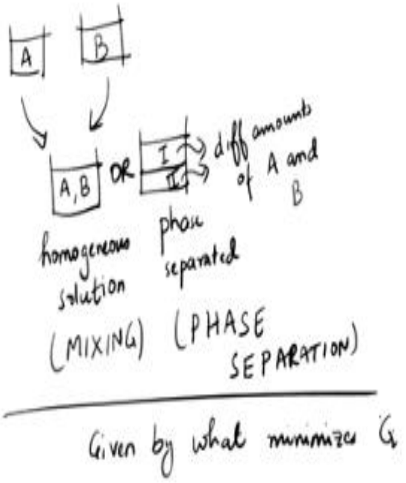

So, let us say for example, if I pour some A with some B. You can have two possibilities, you can have this forming a homogenous solution or this forming a phase separated solution. So, when it is homogeneous then A and B are perfectly mixed. So, this is a mixing case, when it is phase separated then clearly one possibility you may imagine that all the A will stay away from all the B as you typically see in oil water situation but more generally speaking you can have two or more phases containing different amounts of A and B. So, you can have one phase rich in A and dilute in B other phase rich in B and dilute in A and that is what I called as phase separated state. So, that is when I will say we have a phase separation. Now, what is going to happen? So, whether we have this or this is given by what minimizes the G.

So, ultimately we write the expression for Gibbs free energy we can write it for a mixed state. You can write for the phase separated state and whichever gives me a lower value of Gibbs free energy gives me the equilibrium state for the system and using that we can figure out whether we will have mixing or phase separation the only difficulty is we do not know how to find G. And this is what is the goal of the exercise that we are ultimately doing but let us say if the G is given to you then how can we proceed in this particular problem.

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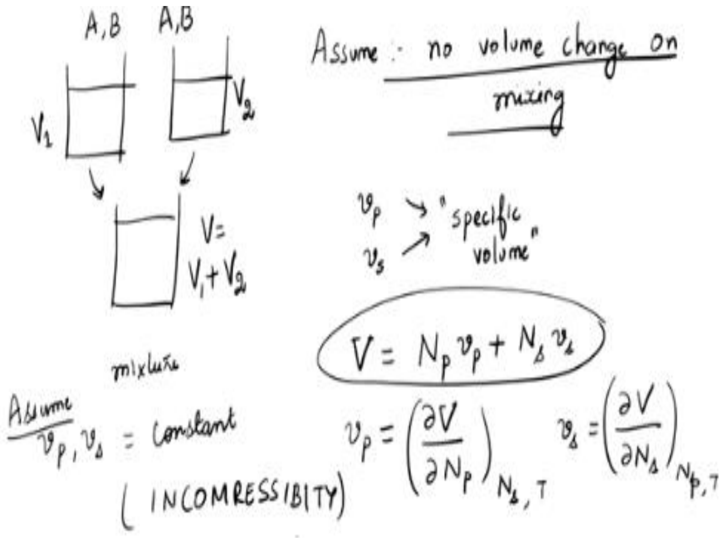

So, I will make some more approximations here that is particular to the liquid. So, first of all, what I will say- Just to keep the picture a bit more rigorous. I am trying to mix two things A and B and I am getting a mixture. Now, in general both may contain variable amount of A and B. I have said I will mix pure A and pure B that need not be the case you can have varying amounts of A and B that I mix and I will form the mixture.

So, now the question is whether we will have a mixing or phase separation, this is what we are ultimately interested in. So, the first thing to note is let us say if I start with different amounts of volume the final thing will have a sum of these two volume. Now although that seems to be very intuitive that is not completely correct because there can be a volume change when we mix two substances.

So, the first assumption that we make is that we have no volume change on mixing and that is actually a very important assumption. If you are confused why are we having volume change on mixing that is happening because new interactions develop between the molecules once we put them together. So, when they, were existing as separate solutions or separate pure component things, they did not have those interactions once we mix them together we have new interaction. Let us say we have a glass of water and glass of alcohol, now there was no water alcohol interaction in those systems. Now when I mix them together now new interactions because of the alcohol and water will form and that may result in the change in the volume can discuss that later but for the time being we can assume that the volume change is not so appreciable or we can ignore that.

The next thing is we can attribute some volume to the different components. This is the volume I say, it is a volume of every molecule. More specifically I am defining what is known as the specific volume? And what essentially it means is that this is the volume that will change when I add one molecule in the system. So, v_p is the volume change by adding one molecule of solute in the system, v_s is the volume change when I add one molecule of solvent in the system. So, the way it is defined is like let us say if V is my final volume. I can define V as something like-

$$V=N_p\,V_p+N_sV_s$$

Were,

$$V_p=\left(\frac{\partial V}{\partial N_p}\right)_{N_s,T}\ and\ V_s=\left(\frac{\partial V}{\partial N_s}\right)_{N_p,T}$$

and of course at constant temperature that particular definition is important why? Because as I was saying; just now that the volume may change because of the change in interactions.

Now you may imagine, if I have more alcohol you will have more of those interactions. So, the volume change that we are getting by adding a molecule is actually not a constant that is going to vary in reality not for the assumption that we are saying. In reality the volumes may change because of the changes in the direction value. So, when we say that there is no volume change on mixing what essentially we are saying, is we are assuming that v_p and v_s are constant because, only then the; volume is going to be constant for a constant number of N_p and N_s. If that is not true then we have to be somewhat more careful in the analysis. So, clearly it is not true for the gases, and this assumption is the assumption of an incompressible liquid. So, the assuming incompressibility. So, there is in some in other words the density of that thing does not vary the density remains constant. This is what exactly incompressibility refers to for liquid systems, that is clearly not valid for the gases. So, for water it is ok to say that if I increase temperature or if I add something else the density does not change appreciably but clearly it is not true for gases they undergo a changes in density and for those cases we have to relax this particular assumption of that. So, if I assume the v_p and v_s to be constant our problem becomes somewhat simpler to that extent.

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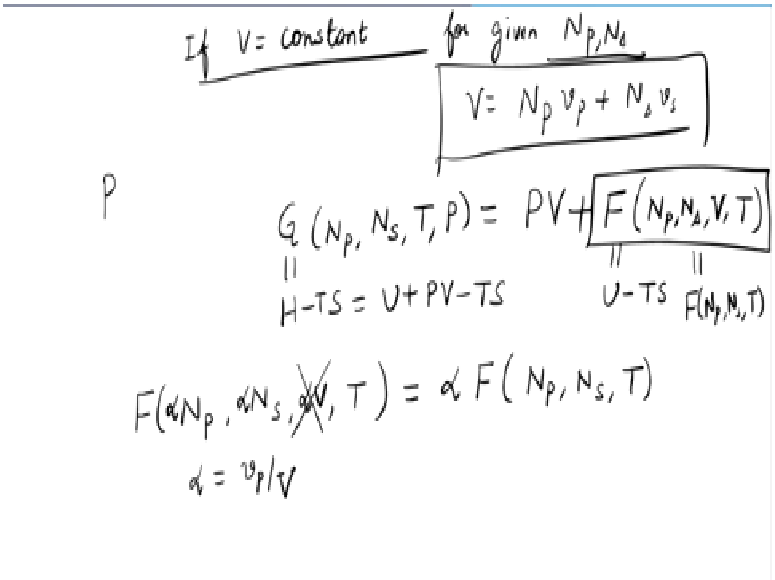

If $V =$ constant for given N_p, N_s

$$\boxed{V = N_p v_p + N_s v_s}$$

P

$$G(N_p, N_s, T, P) = PV + \boxed{F(N_p, N_s, V, T)}$$

$$H - TS = U + PV - TS \qquad U - TS \qquad F(N_p, N_s, T)$$

$$F(\alpha N_p, \alpha N_s, \cancel{\alpha V}, T) = \alpha F(N_p, N_s, T)$$

$$\alpha = v_p / V$$

So, now if that is true. If V is constant there is a bit of a problem if you think about it. So, what I am saying is if V is constant for given value of Np and Ns. So, V is clearly changing when Np and N s is changing because my V is equal to $N_p v_p + N_s v_s$. But since vp and vs are constant for a given value of N_p and N_s the volume is constant. But now I have said earlier that is how I started with I have said that I am working at constant pressure or pressure is the control variable. So, what does it mean because earlier I have said that if I am controlling the pressure, I cannot control the volume. So, how can both of them be controlled? How can both be constant? And the answer to that comes back to the assumption that we have made right here. In reality the volume is going to undergo fluctuations, but we are going to ignore the effect of those fluctuations. Assuming that those volume changes are I would say can be neglected or they are very small or not appreciable.

So, under those conditions, I can say that instead of working with G that is a function of N_p, N_s, Temperature and Pressure. I can work with the Helmholtz free energy because volume is also constant. So, I did not be working for the Gibbs free energy in this case because volume is constant. So, we can say volume is the control variable. So, it is fine to work with the Helmholtz free energy and the reason why we are doing that is that it makes things simpler and we already know that my

$$G = P V + F \text{ and } F = U - TS \text{ and}$$
$$G = H - TS = U + PV - TS.$$

So, now, what we can then say is once we have figured out this my F, I can figure out the G because PV is anywhere constant. P, I am already controlling and I am assuming that V is not changing. So, V is also constant for a given value of N_p and N_s. N_p and N_s is already given or already being controlled. So, therefore we can work with the Helmholtz free energy.

So, now, if I look at the Helmholtz free energy we know that the Helmholtz free energy is an extensive quantity that means if I multiply the number of molecules of solute and solvent it alpha. Then clearly the volume is also going to be α times and that clearly comes from this equation. In fact if you think about it in this case volume is no longer an independent variable because once I find N_p and N_s volume is found. So, we can pretty much remove volume from there because as for increase N_p and N_s α times the volume is also α times volume is not changing independently.

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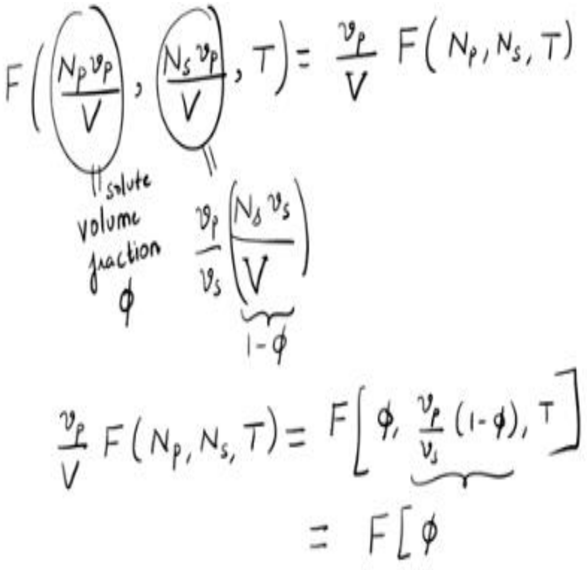

So, we can say F is a function of only N_p N_s and T. So, if I increase the number of α times the energy will be α times the energy of the original system that just means that if I double the number of molecules the energy will be doubled if I make the system four times the energy will be four times that really comes from the extensive nature of the Helmholtz free energy and at the same is true also for the Gibbs energy and all that.

So, using this idea I can now say and let us say if α is equal to something like-

$$\alpha = \frac{v_p}{V}$$

Then,

$$F\left(\frac{N_p v_p}{V}, \frac{N_s v_p}{V}, T\right) = \frac{v_p}{V} F(N_p, N_s, T)$$

Now if I look at this particular quantity, what does that represent? So, I am multiplying the number of solute molecules with the volume of solute molecules, so actually it is specific volume but we have assumed that to be constant so we can say to the volume of a solute molecule. So the numerator here and N_p v_p is the volume occupied by the solute in the system and volume is the V is a total volume. So, this is actually the volume fraction which I can name as some Φ. Now if I look at this quantity we can right this as something like N_s v_s by V multiplied with V_p by v_s and this is going to be the volume fraction of solvent. So, this is a solute volume fraction and this is going to be the solvent volume fraction.

Now clearly since only we have only two components both of the volume fractions must add to 1. So, this has to be 1 – Φ and therefore we can say that my vp by V F Np, Ns, T is equal to F of Φ vp by vs 1 - Φ, T. Now you can see here that the second variable here also becomes a function of Φ, vp and vs are constant and the left side. So, we can therefore say that this is something like function of Φ and T.

$$\frac{v_p}{V}F(N_p, N_sT) = F[\phi, \frac{v_p}{v_s}(1-\phi), T]$$

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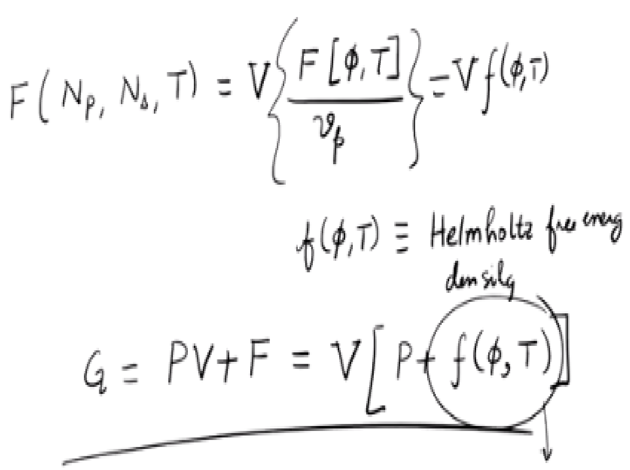

$$F(N_p, N_s, T) = V\left\{\frac{F[\phi,T]}{v_p}\right\} = V f(\phi,T)$$

$f(\phi,T) \equiv$ Helmholtz free energy density

$$G = PV + F = V[P + \boxed{f(\phi,T)}]$$

So, therefore, we can say my original function, the Helmholtz free energy can be written as, so, you will have V by v_p going on the other side. So, you will have V multiplied with F Φ, T by v_p and this quantity you can identify as something like the density of the Helmholtz free energy. Helmholtz free energy density or Helmholtz free energy per unit volume. I will name this as something like F of ΦT.

$$F(N_p, N_s, T) = V\{\frac{F[\phi, T]}{v_p}\}$$

Thus,

$$f(\phi, T) = Helmhotz\ free\ energy$$

So, before we go further, let us pause for a moment and think why we did that? So, by doing that we have been able to reduce one variable because, F indeed was a function of the number of molecules of P number of molecules of S and temperature. On the right hand side we are having a single variable volume fraction because ultimately N_p and N_s depended on quantity, when I was doing in the discussion of the Gibbs phase rule I said that only the intensive variables will characterize the equilibrium state Φ happens to be an intensive variable. So, Φ already captures the effect of composition. So, this not only gives rise to a reduction in the number of variables in the function but also it is more intuitive because now we are considering only the intuitive variables in the problem. So, therefore going back to the expression of G. So G was-

$$G = PV + F = V[P + f(\phi, T)]$$

So, now we can start from this particular expression of the Gibbs free energy or the expression of this f (ΦT), and use that to determine the condition for mixing and phase separation why because ultimately; it has to refer to minima of Gibbs free energy. I can write G as a function of this small f. If I look if I know the function is small f I pretty much know what is going to be mixing and separation. Because once I control pressure the volume is already controlled and we have assumed that the liquid is incompressible so volume is also constant. So, ultimately if I know this then I know the mixing and phase behavior. So, have got a handy function you do not know what the function value is. What I am going to show you in the next lecture is even when I do not know that simply by looking at the mathematical form of that f we can figure out what should be the mixing and separation tendency.

In other words, I can say what mathematical form of f will give rise to a tendency of mixing and what mathematical form of f will give rise to tendency of phase separation and going further using a lattice model. We will try to derive the expression of f that will be under a particular condition right. So until so far we have only assumed that it is an incompressible liquid but the treatment is quite general. Going further we will try to find that small value of f using the latest model and again we will be making more approximations to make that happen.

So, with that I conclude here, thank you.

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