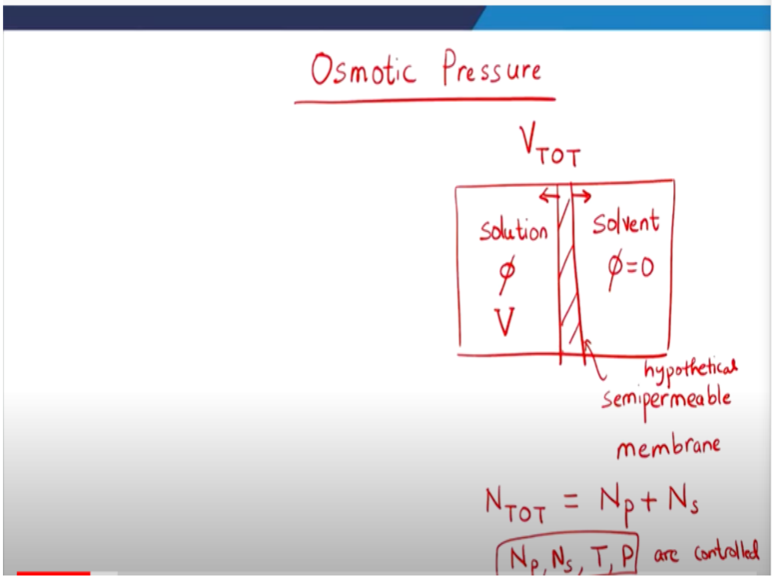
Advanced Thermodynamics and Molecular Simulations
Prof. Prateek Kumar Jha
Department of Chemical Engineering
Indian Institute of Technology, Roorkee

Lecture - 25
Osmotic Pressure and Chemical Potential

Hello all of you. So, in the last lecture we have discussed the idea of binodal and spinodal. And today we will discuss how can, we use the Helmholtz free energy density to also get the osmotic pressure and chemical potential and how osmotic pressure and chemical potential are also a measure of the driving force or mixing and phase separation.

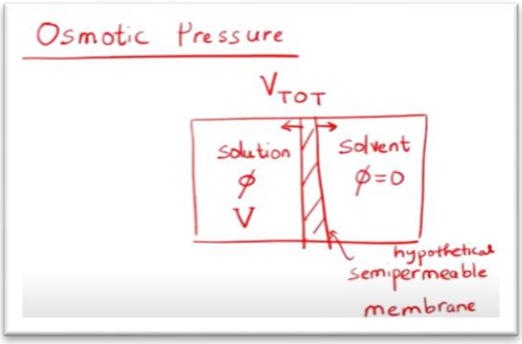
(Refer Slide Time: 00:49)



Let us first start with the Osmotic Pressure. So, general picture in which we use the word osmotic pressure refers to an idea of the osmosis process where we assume that there is a membrane that is permeable only to the solvent and we look at the migration of solute and solvent in the particular problem, but that idea itself is more general there need not be a membrane material exert an osmotic pressure by itself.

So, we will start with the idea of a membrane, but keep in mind that this membrane is just a hypothetical construct in reality what we are discussing is that it is a property of the material itself. It is a membrane that we physically be there present for this pressure to exert.

So, the picture is something like this. So, let us say if I start with solution that contains both solute and solvent which has a volume fraction Φ for the solute and on the other side of membrane, let us say we have the pure solvent or we can say Φ is equal to 0. And then we have a semi permeable membrane are emphasize that it is just a hypothetical kind of a construct. The idea is applicable whenever we have a solution and solvent the membrane does not have to be physically present there.



So, in this particular scenario, we are we also allow the movement of the membrane to the left and right. In general, we can say that the solution may occupy some volume V and in total we have some V_{TOT} volume. Similarly, we have N_{TOT} molecules, which is N_p+ N_s and just like what we have been doing we are working for the situation we are N_p, N_s temperature and pressure are controlled and therefore, we are interested in the Gibbs free energy for particular system and that is how we have been developing the idea of Helmholtz free energy density and all that you always talking Gibbs free energy because when we have this thing constant then the applicable energy function is the Gibbs free energy.

So, for this particular system, what we can say is that the movement of this membrane will be in some sense driven by what is the movement of a solute of the solvent in this particular case because solute anyway cannot move through the membrane. So, if for example the solvent wants to come here since the liquid assumed to be incompressible the movement of solvent must be accompanied by the movement of the membrane to the right or we can say that the V increases as solvent comes in solution. So, generally if I start particular system the solvent will have a tendency to pass through the membrane to the solution and whenever that happens there is a change in the volume of the solution.

So, now if I want to stop that from happening what I have to do is I have to apply some pressure let me give it a name π to keep the to keep the membrane at a fixed location. If I want to keep well volume fixed or the solution, we have to apply an external pressure on the solvent side so that it compensates the tendency of the solvent to move because as solvent was moving the barrier was or the membrane was coming to the right so, we apply a counteracting force to stop that from happening. So, what this is also means is that in some sense by the idea of force balance is that the solution itself is exerting a pressure. So, if I look at the force balance for the membrane since we have to apply an osmotic pressure π, I have given the name but I will call that osmotic pressure. If I have to apply pressure π from solvent side then it means that the solution is exerting the pressure π from its side.

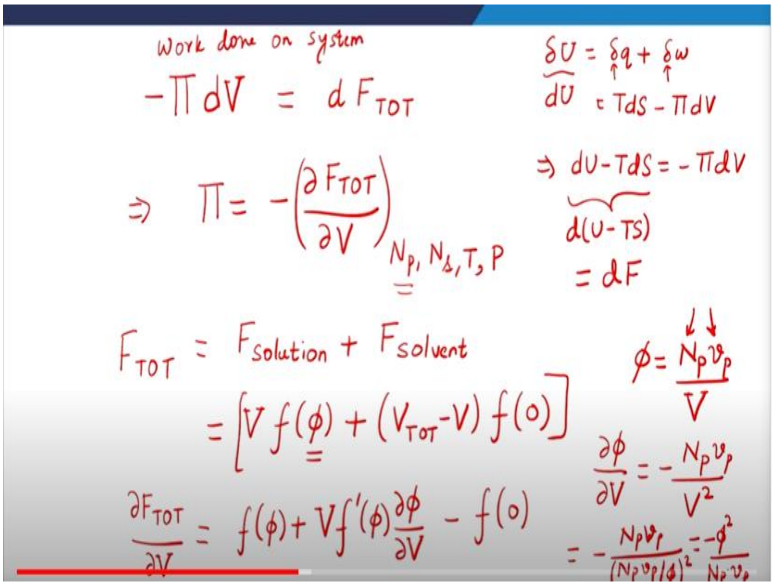
So, therefore we can say that there is some Osmotic Pressure of solution. And as you may imagine this should be a function of Φ because let say for example. When Φ is very high in that case the amount of solvent in solution side is less and then we have pure solvent on the other side so you have a large concentration gradient so as to speak to begin with. When Φ decreases as volume increases that concentration gradient becomes smaller so, that should result in a lower osmotic pressure or a lower requirement of pressure to keep the membrane at a fixed volume. This must be a function of the volume fraction and this in some sense then is what characterizes the mixing behavior for this particular problem.

So, let us say for example if we solute likes the solvent of a solute wants to mix in the solvent then it will tend to increase its volume because only then the solvent can come from the other side of the membrane. So, therefore whenever we have case where we tend to favor mixing the volume has a tendency to increase and therefore the pressure is large. On the other hand, if there is less tendency of mixing what this means is we have to apply lesser magnitude of pressure to keep the membrane intact because anyway the tendency of solvent to migrate is less. So, the higher value of osmotic pressure implies a higher tendency of mixing or we can say that Φ is a driving force of mixing.

Just to think of like analogous situation where there is no membrane, you can imagine let us say for example at the smoke start coming from one side of this room the smoke is has a tendency to fill the entire room because the smoke wants to be dissolved in the air in the entire room is more does not have a tendency to phase separates more content you mix. So, when this process begins what we can say that a smoke brings along with it some must osmotic pressure and it is that osmotic pressure that is driving the movement of the smoke. So, the volume of the smoke is increasing until we have a scenario where smokes fills the entire room while that is happening, of course the volume fraction of solute particles and smoke is decreasing. So, in this problem the Φ will decrease as the volume increases. So, that is the case when we have tendency to mix.

If on the other hand if we; did not have a tendency to mix in that case that osmotic pressure will be very small. So, in that case whatever substance we have will remain as it is or we undergo a small change in volume. So, therefore Φ pretty much becomes the driving force of mixing. But we have earlier established that I can characterize mixing with the function F,that is the Helmholtz free energy density.

(Refer Slide Time: 10:35)



Work done on system

$$-\Pi dV = dF_{TOT}$$

$$\Rightarrow \Pi = -\left(\frac{\partial F_{TOT}}{\partial V}\right)_{\underline{\underline{N_p}}, N_s, T, P}$$

$$F_{TOT} = F_{solution} + F_{solvent}$$

$$= \left[V f(\underline{\underline{\phi}}) + (V_{TOT} - V) f(0)\right]$$

$$\frac{\partial F_{TOT}}{\partial V} = f(\phi) + V f'(\phi)\frac{\partial \phi}{\partial V} - f(0)$$

$$\underbrace{\delta U}_{dU} = \overset{\uparrow}{\delta q} + \overset{\uparrow}{\delta w}$$

$$= TdS - \Pi dV$$

$$\Rightarrow \underbrace{dU - TdS}_{d(U-TS)} = -\Pi dV$$

$$= dF$$

$$\phi = \frac{\overset{\downarrow}{N_p}\overset{\downarrow}{v_p}}{V}$$

$$\frac{\partial \phi}{\partial V} = -\frac{N_p v_p}{V^2}$$

$$= -\frac{N_p v_p}{(N_p v_p/\phi)^2} = -\frac{\phi^2}{N_p v_p}$$

So, if that is possible then it also means that this phi has to be a function of that small f. So, let us see how that happens. So, if you think about its ΠdV with minus sign because the volume change that is happening is against the pressure that is being applied on the system or if you think about what done by the system it is going to be ΠdV work done by the system. Work done on the system is going to be ΠdV. And this must be then equal to the change in the total free energy of the system. So, the work, done needs to go into changing of the energy of the system.

$$-\Pi dV = dF_{TOT}$$

So, we can think in terms of the first law of thermodynamics where I said that change in U is given as change in q plus change in w by the way typically represented that as-

$$\frac{\delta U}{dU} = \delta q + \delta w = TdS - \Pi dV$$

since U is state function and these are delta q and delta w because these are path functions. So, I say this is equal to TdS and the second term is - Πdv. So, if I move this on the other side you have-

$$dU - TdS = -\Pi dV$$

and this at constant temperature you can say is dU-TS and that is equal to mine Helmholtz free energy.

$$d(U - TS) = dF = helmholtz\, free\, energy$$

So, change in Helmholtz free energy is therefore equal to the work done on the system and therefore we can define Π as-

$$\Pi = -\left(\frac{\partial F_{tot}}{\partial V}\right)_{-}(N_p, N_s, T, P)$$

And that is happening at constant value of the number of molecules the temperature and the pressure of the system. In this case, pressure is if you think about these inconsequential because we are assuming both pressure and volume to be related because the system is incompressible essentially the temperature is the one that is more important so as to speak.

So, now the free energy in the total will be equal to free energy of the solution plus free energy of the solvent. And that we can write in terms of the free energy densities as-

$$F_{TOT} = Vf(\phi) + (V_{TOT} - V)f(0)$$

because on the solvent side the volume fraction of solute is 0 solved. It appears on it. So, now keep in mind that this Φ is related to volume N_p and v_p are fixed we assuming constant v_p because system is incompressible and N_p is also fixed because we have kept at fixed in the partial derivative.

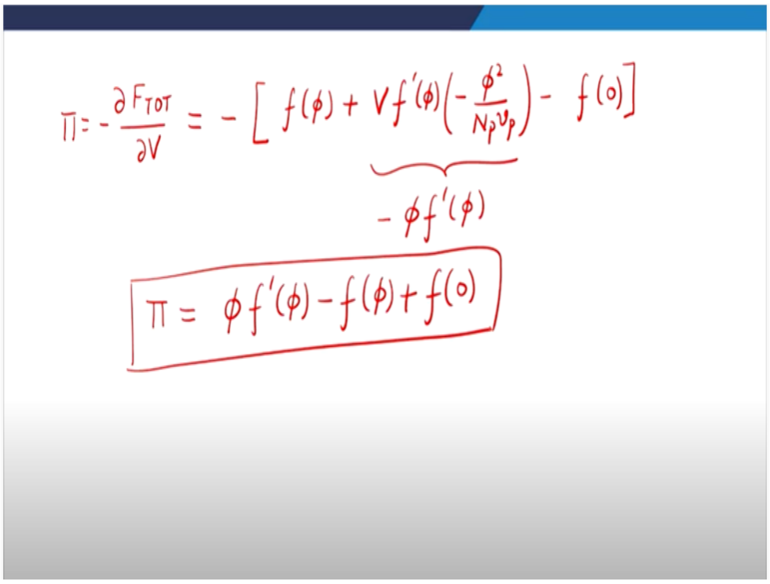
So, therefore, I can write this as-

$$\frac{\partial F_{TOT}}{\partial V} = f(\phi) + Vf'(\phi)\frac{\partial \phi}{\partial V} - f(0)$$

Now let us find what is-

$$\frac{\partial \phi}{\partial V} = \frac{-N_p v_p}{V^2} = -\frac{N_p v_p}{\left(\frac{N_p v_p}{\phi}\right)^2} = -\frac{\phi^2}{N_p v_p}$$

(Refer Slide Time: 15:33)



$$\Pi = -\frac{\partial F_{TOT}}{\partial V} = -\left[f(\phi) + \underbrace{V f'(\phi)\left(-\frac{\phi^2}{N_p v_p}\right)}_{-\phi f'(\phi)} - f(0)\right]$$

$$\boxed{\Pi = \phi f'(\phi) - f(\phi) + f(0)}$$

So, if I put that thing in here. What we then have is my Π as-

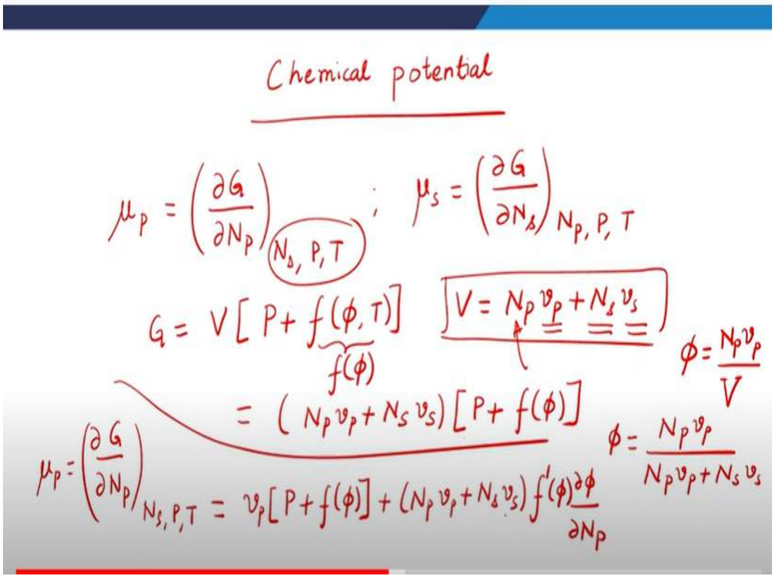
$$\Pi = -\frac{\partial F_{TOT}}{\partial V} = -\left[f(\phi) + Vf'(\phi)\left(-\frac{\phi^2}{N_p v_p}\right) - f(0)\right]$$

So, if I look at this quantity- $Vf'(\phi)\left(-\frac{\phi^2}{N_p v_p}\right)$ we can notice that Np vp by capital V is still phi so one of the Φ will cancel and so we can write this as minus Φf ‘ Φ and therefore I can write my Π as-

$$\Pi = \phi f'(\phi) - f(\phi) + f(0)$$

so this is the expression of the osmotic pressure and surely it is the function of f. So, this for expected because Π is the driving force of mixing and we already said if I know is small f I can characterize mixing. So, both has to be related.

(Refer Slide Time: 16:55)



Chemical potential

$$\mu_p = \left(\frac{\partial G}{\partial N_p}\right)_{N_s, P, T} \; ; \quad \mu_s = \left(\frac{\partial G}{\partial N_s}\right)_{N_p, P, T}$$

$$G = V[P + \underbrace{f(\phi, T)}_{f(\phi)}] \qquad \boxed{V = N_p v_p + N_s v_s} \qquad \phi = \frac{N_p v_p}{V}$$

$$= (N_p v_p + N_s v_s)[P + f(\phi)]$$

$$\phi = \frac{N_p v_p}{N_p v_p + N_s v_s}$$

$$\mu_p = \left(\frac{\partial G}{\partial N_p}\right)_{N_s, P, T} = v_p[P + f(\phi)] + (N_p v_p + N_s v_s) f'(\phi) \frac{\partial \phi}{\partial N_p}$$

Now let us look at the Chemical potential. So, by definition the chemical potential of the solute is given as-

$$\mu_p = \left(\frac{\partial G}{\partial N_p}\right)_{N_s, P, T}$$

And,

$$\mu_s = \left(\frac{\partial G}{\partial N_s}\right)_{N_p, P, T}$$

Now,

$$G = V[P + f(\phi, T)] = V[P + f(\phi)] (assuming\ constant\ temperature)$$

So, then when I am to compute μ_p again, we have meant a bit careful here, because as the Np is changing the volume is also changing. So, we have to have volume is equal to-

$$V = N_p v_p + N_s v_s$$

Whenever we are doing this math the key thing is to see what is the variable that is being held fixed. In this case Ns, P and T are fixed we are not saying anything regarding the volume and volume is clearly changing when V changing because P is constant Ns is constant and vs is constant. So, will put that; form here so I can write G as-

$$G = (N_p v_p + N_s v_s)[P + f(\phi)]$$

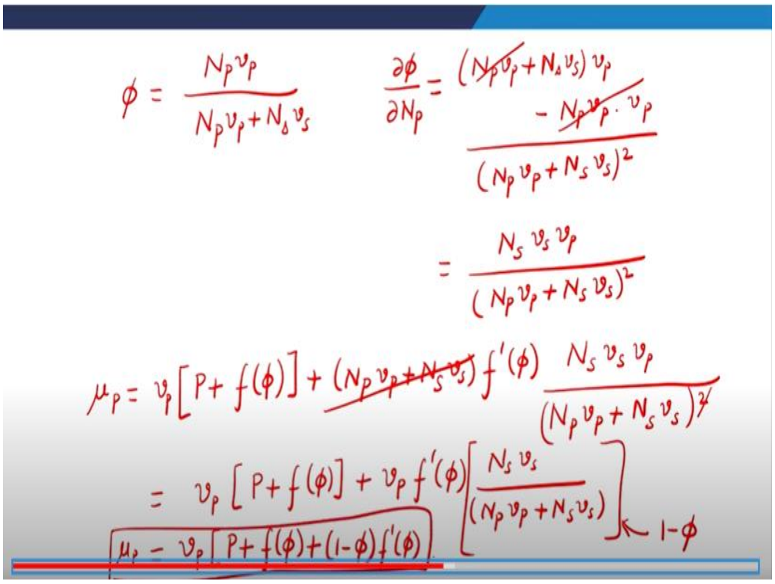
Now if I take that derivative,

$$\phi = \frac{N_p v_p}{V}$$

we still have to use the fact that Φ will also change as volume will change and this again, we can write this as-

$$\phi = \frac{N_p v_p}{N_p v_p + N_s v_s}$$

(Refer Slide Time: 20:26)



$$\phi = \frac{N_p v_p}{N_p v_p + N_s v_s}$$

$$\frac{\partial\phi}{\partial N_p} = \frac{(\cancel{N_p v_p} + N_s v_s)\, v_p - \cancel{N_p v_p} \cdot v_p}{(N_p v_p + N_s v_s)^2}$$

$$= \frac{N_s v_s v_p}{(N_p v_p + N_s v_s)^2}$$

$$\mu_p = v_p\left[P + f(\phi)\right] + \cancel{(N_p v_p + N_s v_s)}\, f'(\phi)\, \frac{N_s v_s v_p}{(N_p v_p + N_s v_s)^{\cancel{2}}}$$

$$= v_p\left[P + f(\phi)\right] + v_p f'(\phi)\left[\frac{N_s v_s}{(N_p v_p + N_s v_s)}\right] \leftarrow 1-\phi$$

$$\boxed{\mu_p = v_p\left[P + f(\phi) + (1-\phi) f'(\phi)\right]}$$

So, now this quantity-

$$\mu_p = \left(\frac{\partial G}{\partial N_p}\right)_{N_s,P,T} = v_p[P + f(\phi)] + (N_p v_p + N_s v_s) f'(\phi)\frac{\partial\phi}{\partial N_p}$$

Let us first find what is dou Φ by dou Np here. So, I said-

$$\phi = \frac{N_p v_p}{N_p v_p + N_s v_s}$$

So therefore,

$$\frac{\partial\phi}{\partial N_p} = \frac{(N_p v_p + N_s v_s) v_p - N_p v_p . v_p}{(N_p v_p + N_s v_s)^2} = \frac{N_s v_s . v_p}{(N_p v_p + N_s v_s)^2}$$

So, if I put that thing in the expression, we have obtained earlier what we going to have-

$$\mu_p = v_p[P + f(\phi)] + (N_p v_p + N_s v_s) f'(\phi)\frac{N_s v_s v_p}{(N_p v_p + N_s v_s)}$$

$$= v_p[P + f(\phi)] + v_p f'(\phi)\left[\frac{N_s v_s}{N_p v_p + N_s v_s}\right]$$

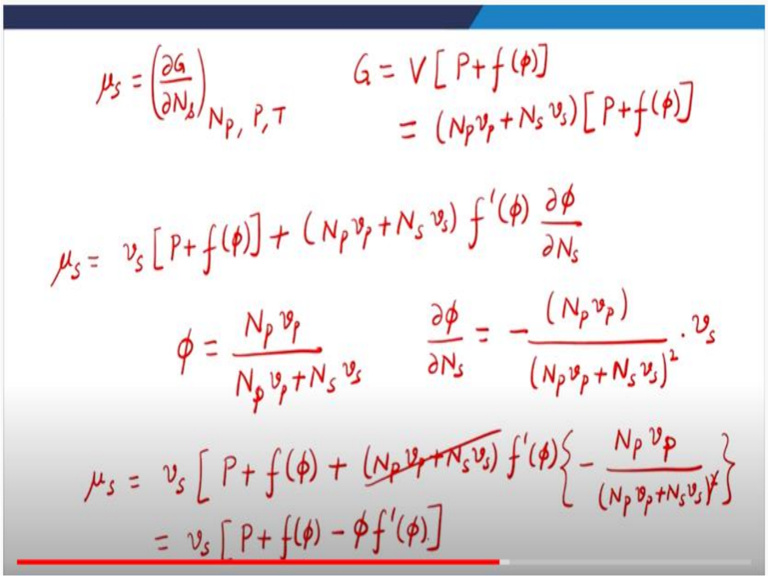
And as we know,

$$\left[\frac{N_s v_s}{N_p v_p + N_s v_s}\right] = 1 - \phi$$

Therefore,

$$\mu_p = v_p[P + f(\phi) + (1 - \phi)f'(\phi)$$

(Refer Slide Time: 23:39)



$$\mu_s = \left(\frac{\partial G}{\partial N_s}\right)_{N_p, P, T} \qquad G = V[P + f(\phi)] = (N_p v_p + N_s v_s)[P + f(\phi)]$$

$$\mu_s = v_s[P + f(\phi)] + (N_p v_p + N_s v_s) f'(\phi) \frac{\partial \phi}{\partial N_s}$$

$$\phi = \frac{N_p v_p}{N_p v_p + N_s v_s} \qquad \frac{\partial \phi}{\partial N_s} = -\frac{(N_p v_p)}{(N_p v_p + N_s v_s)^2} \cdot v_s$$

$$\mu_s = v_s\left[P + f(\phi) + \cancel{(N_p v_p + N_s v_s)} f'(\phi)\left\{-\frac{N_p v_p}{(N_p v_p + N_s v_s)^{\cancel{2}}}\right\}\right.$$

$$= v_s[P + f(\phi) - \phi f'(\phi)]$$

So, now I can do the same exercise for the chemical potential of the solvent that will be-

$$\mu_s = \left(\frac{\partial G}{\partial N_s}\right)_{N_p, P, T}$$

Again, we start with G being equal to-

$$G = V[P + f(\phi)] = (N_p v_p + N_s v_s)[P + f(\phi)]$$

And,

$$\mu_s = v_s[P + f(\phi)](N_p v_p + N_s v_s) f'(\phi) \frac{\partial \phi}{\partial N_s}$$

$$\phi = \frac{N_p v_p}{N_p v_p + N_s v_s}$$

So,

$$\frac{\partial \phi}{\partial N_s} = -\frac{(N_p v_p)}{(N_p v_p + N_s v_s)^2} . v_s$$

$$\mu_s = v_s[P + f(\phi) + (N_p v_p + N_s v_s) + f'(\phi)\left\{-\frac{N_p v_p}{N_p v_p + N_s v_s}\right\}$$

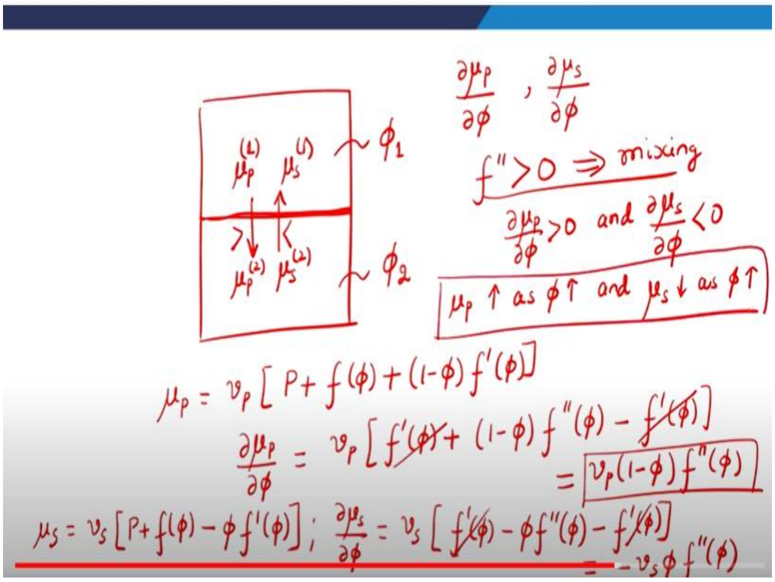
Therefore,

$$\mu_s = v_s[P + f(\phi) - \phi f'(\phi)]$$

Thus Chemical potential can also be represented as a function of the f of Φ.

Now let us pause for a moment and see that how chemical potential can this can also be a driving force so, let us imagine that we have two phases that is not under equilibrium. So, clearly when that is present then there is some exchange happening in the two phases.

(Refer Slide Time: 26:54)



$$\frac{\partial \mu_p}{\partial \phi}, \frac{\partial \mu_s}{\partial \phi}$$

$$f'' > 0 \Rightarrow \text{mixing}$$

$$\frac{\partial \mu_p}{\partial \phi} > 0 \text{ and } \frac{\partial \mu_s}{\partial \phi} < 0$$

$$\boxed{\mu_p \uparrow \text{as } \phi \uparrow \text{ and } \mu_s \downarrow \text{as } \phi \uparrow}$$

$$\mu_p = v_p\left[P + f(\phi) + (1-\phi) f'(\phi)\right]$$

$$\frac{\partial \mu_p}{\partial \phi} = v_p\left[\cancel{f'(\phi)} + (1-\phi) f''(\phi) - \cancel{f'(\phi)}\right]$$

$$= \boxed{v_p (1-\phi) f''(\phi)}$$

$$\mu_s = v_s\left[P + f(\phi) - \phi f'(\phi)\right]; \quad \frac{\partial \mu_s}{\partial \phi} = v_s\left[\cancel{f'(\phi)} - \phi f''(\phi) - \cancel{f'(\phi)}\right]$$

$$= -v_s \phi f''(\phi)$$

So, let us say one of the phases has some volume fraction Φ1 and the other phase has some volume fraction Φ2. And I want to what is the direction of the transfer of the solute and solvent in this particular case. So, clearly the transfer is going to occur in the direction where the total Gibbs energy is minimized but in terms of chemical potential it is driven by the gradient of Chemical potentials. For example, μ_p in the first phase if it happens to be more than the μ_p in the second phase you will have transfer of solute from phase 1 to phase 2. In other words, transfer happens in the direction of decrease of the chemical potential or transfer happens from a higher chemical potential to a lower chemical potential.

Similarly, for solute if μ_s in the second phase happens to be more than the μ_s in the first phase that will be giving me the direction of the solute solvent transfer. So, in this case solvent will going this way because I am still going from a high chemical potential of solvent to low chemical potential solvent because the second phase the chemical potential solvent is more, so ultimately, we are interested in the gradients of these chemical potentials because it is these gradients that dictate in this direction the transverse will take place.

So, let us start with let expressions that we have obtained for μ_p and μ_s and find these gradients. As we start with the first one. So, I have found-

$$\mu_p = v_p[P + f(\phi) + (1-\phi)f'(\phi)$$

$$\frac{\partial \mu_p}{\partial \phi} = v_p[f'(\phi) + (1-\phi)f''(\phi) - f'(\phi)]$$

On the other hand μ_s we have obtained as-

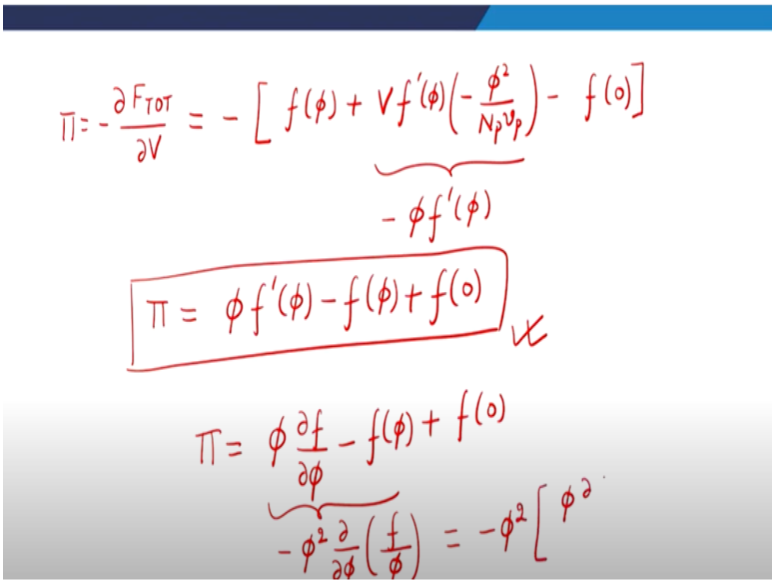
$$\mu_s = v_s[P + f(\phi) - \phi f'(\phi)]$$

So therefore,

$$\frac{\partial \mu_s}{\partial \phi} = v_s[f'(\phi) - \phi f''(\phi) - f'(\phi)] = -v_s \phi f''(\phi)$$

Now we look at the scenarios that we have obtained earlier. So, I said when f double prime is greater than 0 then we have a tendency of mixing. What does it translate to in terms of the dou μ_p by dou Φ and dou μ_s by dou Φ what means is that by dou μ_p by dou Φ that is this particular term it is also going to be positive because Φ is the number between 0 to 1, vp is positive number. So, if double prime is positive then dou μ_p by dou Φ is also positive. And dou μ_s by dou Φ is going to be negative because we had a negative sign. So, this means that μ_p is actually increasing as Φ is increasing. And μ_s is decreasing as Φ is increasing. So, now starting from this argument, let us say I want to consider a situation.

(Refer Slide Time: 32:37)



$$\Pi = -\frac{\partial F_{TOT}}{\partial V} = -\left[f(\phi) + \underbrace{Vf'(\phi)\left(-\frac{\phi^2}{N_p v_p}\right)}_{-\phi f'(\phi)} - f(0)\right]$$

$$\boxed{\Pi = \phi f'(\phi) - f(\phi) + f(0)}$$

$$\Pi = \underbrace{\phi \frac{\partial f}{\partial \phi}}_{-\phi^2 \frac{\partial}{\partial \phi}\left(\frac{f}{\phi}\right) = -\phi^2\left[\phi \partial\right.} - f(\phi) + f(0)$$

Where, I start with pure solvent and the solution. Solution had some Φ and pure solvent has Φ equal to 0. Let us say I put them together there is no membrane between them or something like that so in that case I have just said that if f double prime is more than 0 this means that μ_p

is going to increase as Φ increases. But μ_s is going to decrease as Φ increases. So, clearly in this particular case, if the solute moves from the solve solution to the pure solvent, then Φ is decreasing so for solute movement Φ will decrease when we go from solution to the pure solvent phase and only that will result in loading of chemical potential because if the transfer is other way round that will result in increase in the chemical potential and I just said we want to go in the direction of decrease in the chemical potential. So, pretty much this tells me that solute has to go from solutions to the pure solvent phase.

However, for the solution the chemical potential is decreasing as Φ is increasing. So, begin with Φ= 0. So, when the solute comes into there, then the Φ increases and that is favored because chemical potential of solvent is decreasing. So, a motion of solute from the solution phase to the solvent phase is favored both by the chemical potential of solute because that results in lowering of the chemical potential of solute and it also favored by the chemical potential of solvent because increase in Φ results in lowering of the chemical potential of solvent and therefore, we have a tendency of mixing.

On the other hand, if f double prime is less than 0 in that case what is going to happen and let us say again start with solution with some volume fraction Φ and a pure solvent that is with Φ = 0. In this case we will have the opposite situation. So, μ_p will decrease as Φ increases. But μ_s will increase as Φ increases. In this case the solute movement should be other way round that means if I have pure solvent there is no movement, why is that because if I go in the opposite direction that will result in a lowering of the Φ and the lowering of Φ will give me an increase in the chemical potential because chemical potential decreases as Φ increases. So, if we have decrease in Φ that will give rise to increase in the chemical potential and that will clearly not be favored. So, we cannot have the tendency for solute to go from solution phase to the solvent phase.

Similarly, the chemical potential of solvent also increases as phi increases. So, any solute transfer from solution to the solvent will result in increase in chemical potential and that is also not favored. So, therefore the system will have a tendency to phase separate. So, the key point of the discuss on they want to emphasize is that the tendency of the mixing phase separation can be described also in terms of osmotic pressure and chemical potential but since they are related to the Helmholtz free energy density or they can be written as a function of Helmholtz free energy density we do not have to consider them independently if one of them is telling me that mixing will happen you should be confident that mixing is going to happen.

So, the final point I want to make here is that although I have derived the expression of the osmotic pressure in terms of f of Φ and similarly the expression of chemical potential as a function of Φ it is not necessary that I first calculate f of Φ and then calculate Π it can be other way around. If I have the expression of Π I can also calculate expression of f of Φ and the same is true for the chemical potential. If I know chemical potential, I can use that to find the f of Φ where it becomes important is because for many equations of states it is more convenient to write the equation of state in terms of the osmotic pressure as opposed to the Helmholtz free energy density. So, in those cases if we need to compute the Helmholtz free energy density, it is very much possible. So, if you just think of doing the opposite of what we are doing. So, I can write my Π as-

$$\Pi = \phi \frac{\partial f}{\partial \phi} - f(\phi) + f(0)$$

$$\phi \frac{\partial f}{\partial \phi} - f(\phi) = \phi^2 \frac{\partial}{\partial \phi}\left(\frac{f}{\phi}\right) = \phi^2 \left[\frac{\phi \frac{\partial f}{\partial \phi} - f(\phi)}{\phi^2}\right] = \phi \frac{\partial f}{\partial \phi} - f$$

Therefore,

$$\Pi = \phi^2 \frac{\partial}{\partial \phi}\left(\frac{f}{\phi}\right)$$

So, if I know the expression of Π I can integrate this and find the expression of f.

So, with that I want to conclude the discussion here. In the coming classes I will discuss how can we obtain this Helmholtz free energy expression of f (Φ) using the lattice model of solutions.

Thank you.