Introduction to Polymer Physics
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Lecture-27
Solution Thermodynamics-I

Welcome, so in the last class we have been discussing about the Monte Carlo and molecular dynamics simulations and I ended up saying about thermodynamic concepts that we discussed in the context of simulations. So today I will build up on that further to discuss what is known as a solution thermodynamics and based on that we will develop the thermodynamics of polymer solutions, so just to put this in context what we have discussed earlier in the very beginning where the models of a random walk that we applied to a single polymer chain, after this I have discussed different cases where we have some interaction between segments like good solvent or poor solvent cases but again you are looking at a single polymer chain.

So now I want to take a slightly zoomed out view a look at the behaviour of a solution and by behaviour I really mean a macroscopic behaviour to begin with and then will come back to a microscopic model for that behaviour of polymer solutions, but let us say we are zooming out and we do not look at a polymer chain, we look at the solution of polymer chains that is contained in there so it is very microscopic or macroscopic compared to the view that we had earlier.

Before that let me just recap some idea of thermodynamics of simple solutions that does not contain polymer right. So let us think about a liquid solution and for the sake of simplicity let us say there are only 2 components that we call solute and solvent, these are my 2 components and it is in a single phase liquid to begin with. If I use Gibbs phase rule it tells me a number of intensive variables I need to specify in order to get thermodynamic behaviour of system-

$$F = C - P + 2$$

Here C is the number of components which is 2, P is the number of phases which is 1, so we get 3, so we can have 3 intensive variables which will perfectly characterize the system.

Now we can make various choices again keeping in mind the idea that we discuss regarding the conjugate variables. So let us say I pick temperature, pressure and composition. So the composition I can specify in 2 ways. I can say either in terms of number of solute and number of solvent, so we are refer solute as P, the solvent as S, but now if I say in terms of number of molecules then these 2 are not intensive, therefore extensive variables-

$$N_p, N_s (Extensive\,Variables)$$

If I want to use an intensive variable we can just define as-

$$x = \frac{N_p}{N_p + N_s} (Intensive\,Variable)$$

So we can either the specified (T, P, x) or we can specify (T, P, N_P, N_S) because using N_P, NS I can find x ok essentially we only need 3 intensive variables. So if I am given both N_P and N_S that is the number of molecules of solute and solvent I can get the x that is the mole fraction.

So now the relevant energy function in this case is the Gibbs free energy which I can write in terms of Helmholtz free energy as-

$$G(N_p, N_s, T, P) = A + PV$$

Here A is a function of (N_p, N_s, T, V). So it can be written as-

$$G(N_p, N_s, T, P) = A(N_p, N_s, T, V) + PV$$

So now we will note here that we started with a Gibbs free energy which was a function of temperature pressure and composition. If I write in terms of the temperature, volume and composition that is if use the Helmholtz free energy of course I can separate out the PV term or it gives me certain mathematical convenience when I am doing this, and I will elaborate on that in this lecture.

So before this, if I want to define the volume fraction of solute I can find it as something like the following-

$$\phi=\frac{V_p N_p}{V_p N_p+V_s N_s}$$

Where V_p and V_s are specific volumes of solute and solvent molecules.

So keep in mind that we do not refer to the actual volume of molecules ,let us say we have water, how do we define its volume, is it the volume of electron cloud, is it some sort of a volume occupied the molecule it is very arbitrary concept. So the way we are defining a specific volume is the change in a volume if I add a molecule of water to a certain volume and it is present already. So this is defined as a change in volume not as a volume of the molecule itself, it makes some difference in the actual meaning, what it means is that it can be dependent on the composition, the change in volume may be different by adding one molecule if I add in say a solvent that is favourable to that molecule for a solvent that is not favourable, will come back to this later but the basic idea is that we defined as-

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

The change in volume, if I change, if I keep temperature, pressure and number of solvent molecules fixed, if I add a molecule of solute. It can be different, a dilute solution compare to a concentrate solution because change in volume may in turn depend on the interactions present inside the system.

Similarly I can define v_S as the following-

$$v_s=\frac{\partial V}{\partial N_s}$$

So with this particular means some specific volumes we can talk in terms of volume fraction of solute of course for solvent it has to be 1-ϕ because both of them must add to 1 because there is no void it is either containing a solute or containing solvent.

So now although I have just said than v_P and v_S can be not constant, it can differ with the concentration and so on we will now assume that let us what happens when they are constant. It is an assumption until so far what we are doing is somewhat rigorous now what we are making is an assumption so we assume that v_P and v_S are constant. So now by the way before I do this I can write my volume V as v_p $N_p+v_sN_s$ and this is also quite general, it is before the assumption that I am just made.

So if the v_p and v_s are constant then for a constant value of N_p and N_s the volume is also constant because if v_p and v_s are constant here Np,Ns is anyway constant. So V will be constant, what this means is the solution is what is known as an incompressible volume because there is no pressure here in the expression I am writing of course the pressure may appear in actual definition of specific volumes but if I ignore that in that case what I am assuming is that the specific volumes are constant that means volume is constant and when the volume is constant the system is considered incompressible so the pressure does not change the volume. So although pressure and volume are conjugate variables and they should work in terms of either P or V. Since we assume V to be constant, it does not matter I can work in terms of both P and V. I can equivalently work in Helmholtz free energy as I can do in work in terms of Gibbs free energy and that is the reason why we use the Helmholtz free energy because it will simpler for the analysis that we will do. So now

$$G(N_p, N_s, T, P) = PV + A(N_p, N_s, V, T)$$

Since V is constant here we can write this expression as-

$$G(N_p, N_s, T, P) = PV + A(N_p, N_s, T)$$

So now if I look at this particular A term then A is also an extensive variable because energy will change if the quantity of matter will change, energy is extensive, so now what it means is since A is extensive, I can write as-

$$A(\alpha N_p, \alpha N_s, T) = \alpha A(N_p, N_s, T)$$

It is just a mathematical trick that will give you some dividend in a moment. If I set $\alpha = \frac{V_p}{V}$ then I get the following-

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

$$\phi = \frac{v_p}{v_s}\left(\frac{N_s v_s}{V}\right)(we\,have\,derived\,this\,earlier)$$

$$so, now\, \frac{v_p}{v_s}(1-\phi)$$

I will note down like what do you have in the left hand side, the first 2 terms I have represented as a function of ϕ and temperature because v_p, v_S anyway constant so this term is anyway constant so I can write it as a function of ϕ and temperature, so we have reduced one more variable you no longer talk about the number of molecules of solute and solvent. I talk about the volume fraction of solute and then what I can write it as-

$$A\left(N_p, N_s, T\right) = Vf\left(\phi, T\right)$$

So the basic idea is I am writing the Helmholtz free energy in terms of something we can refer to as Helmholtz free energy density. So,

$$f\left(\phi, T\right) = Helhmholtz\ Free\ Energy\ Density$$

Now going back to our G we get-

$$G\left(N_p, N_s, T, P\right) = V\left[P + f\left(\phi, T\right)\right]$$

So now I have a simple expression of the Gibbs free energy of the system in terms of PV terms and something that we refer to as the Helmholtz free energy density, we do not know what is the functional form of that f (ϕ,T) yet, but we can I will show you that why is that particular form is very convenient to look at the mixing behaviour and the phase separation behaviour of the systems.

Before this let us define what I mean by mixing and phase separation. So let us say if I start with 2 volumes of containers containing different volumes and different amounts of the solute, let us see the first one has a volume V_1, the other one has a volume V_2 and they have volume fraction of solute ϕ_1 and ϕ_2. If I add them together we may form a new volume V with a net volume fraction ϕ. This only happen if the system has a tendency to mix, on the other hand if somehow even if I manage to mix a system to have a certain volume fraction ϕ and volume V but the system does not have a tendency to remain homogenous or remain in the mixed state, it will phase separate. So, one of them you can call a concentrate, other one you can come later dilute phase there are other things are basically we can talk in terms of equality of chemical potential in the two phases when we discuss the phase separation. The basic idea that I want to point out here is the system phase separates to two phases.

So now the question is how does the function that we have derived does the Gibbs free energy that was in terms of Helmholtz free energy density f (ϕ,T) so how does this function f(ϕ,T) can characterize the mixing and phase behaviour. What should be the form of the function that will give you a mixing behaviour in systems what will be the form that will give you a phase separation behaviour?

First of all before this we want to know whether that function is sufficient to characterize the mixing and phase separation behaviour or not. We will see like when this mixing or separation will occur, what is the criteria for that to happen. So if for example we look at the first situation Helmholtz energy of the system is-

$$V_1 f(\phi_1)$$

Then our Gibbs free energy becomes-

$$G^1 = V_1 P + V_1 f(\phi_1) \wedge G^2 = V_2 P + V_2 f(\phi_2) \wedge G^3 = VP + Vf(\phi)$$

Assuming here temperature is constant.

So now we know from thermodynamics that the process will be favoured if the resulting Gibbs free energy will be less than the sum of the Gibbs free energy of the phases that I have a mixed together which means-

$$V$$

$$(¿¿1P+V_1 f(\phi_1))+(V_2 P+V_2 f(\phi_2))$$

$$VP+Vf(\phi)<¿$$

The first thing to note here is since the volumes assume to be constant when I add them together V_1+V_2 become equal to V, that means specific volume is assume to be constant. So what this means is V terms will cancel out and we are left with-

$$Vf(\phi)<V_1 f(\phi_1)+V_2 f(\phi_2)$$

Which is a Helmholtz free energy density term. So the mixing will happen if this is the case or if I divide by V_1 and we get-

$$f(\phi)<x_1 f(\phi_1)+(1-x_1) f(\phi_2)$$

Here $x_1=\frac{V_1}{V}$

Similar idea we can apply to phase separation so for phase separation you should have to V f(ϕ) now the final state is phase separated which has 2 phases the energy in the states will be lesser than the energy in the homogenous state. So this should be higher-

$$Vf(\phi)>V_1 f(\phi_a)+V_2 f(\phi_b)$$

$$f(\phi)>x_a f(\phi_a)+(1-x_a) f(\phi_2)$$

Here, $x_a=\frac{V_a}{V_b}$

So now we have a simple mathematical relation in terms of the function ϕ that characterizes the mixing and separation behaviour. We haven’t yet discussed what the mathematical form is, but we have already discussed what the mathematical form should be to have certain type of behaviour that we can see. So the next class I will elaborate on this in more detail. Then I will discuss that the other ideas that we discuss in thermodynamics like osmotic potential and osmotic pressure and chemical potential. They can also be written in terms of this function f(ϕ) for liquid solution and then finally we can extend the idea to polymers solution and try to find what that function f is and based on that we can talk about the mixing and phase separation behaviour in polymers solutions and other polymeric systems.

Thank you.