Basic Statistical Mechanics
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Lecture - 49
Binary Mixtures: Towards Understanding Non-Ideality and Osmotic Pressure Part 1

Welcome back to today's lecture, we have been studying statistical mechanics, more importantly we are trying to understand many aspects of natural phenomena that we study in the name of physical chemistry and chemical physics. And those things are the understanding of the huge number of physical and chemical phenomena like solutions, chemical reaction dynamics, and phase transitions.

All these things are important both in physics, chemistry, biology, material science, physical chemistry, get you started on them. Because it is through physical chemistry you learn about properties of solvents, it is through physical chemistry you learn chemical kinetics, you learn electrolytes. Now how does physical chemistry do that? If you reflect a little bit, on the physical chemistry that you studied in your undergraduate books Or even in some time in advanced schools.

Physical chemistry introduces many, many concepts in certain sense it starts with kinetic theory of gases as we have told many times. Then it might also take the help of thermodynamics and we get Gibbs free energy and Helmholtz free energy, all these different conditions and then goes into a little bit of phase transition. So physical chemistry tends to phenomena and tends to a sudden phenological explanation of that.

And to be specific to today's lecture, let me take the case of binary mixtures. A mixture of two species A and B in the language of physical chemistry I will talk one as the solvent and one as the solute. The other alternative language more popular in organic chemistry is solvent and co-solvent, solvent and solute has the disadvantage because it always assumes that one is in small quantity which is the solute.

But many times we have a 50-50 percent mixture of two species and the. Now we know from physical chemistry that a binary mixture of two species like the very common binary mixture is water and ethanol and they show enormous number of range of properties. Binary mixtures are very common because these are much of our common solvents or a binary mixture because many things are not soluble in water.

So you add a little co-solvent like I did with ethanol and water is a fantastic medium for reactions and it has a lot of properties like polarity. So another solvent if we can mix it together and tune the properties then we get a huge amount of diverse range of properties by tuning and varying the composition. But how do you know about the interactions between them? How do you know how water and ethanol are interacting?

We might know about water, we might be able to construct a force field that means how water molecules interact, there is a huge amount of work that has gone into it or even ethanol some amount water has gone into it, what ethanol still is somewhat least thing but this is very important. So you are starting into a mixture of binary characteristics or binary mixed, it starts in the following way.

We have constructed, study a property P and we vary the mole fraction, we go on adding increasing the solute little by little and then start the property. What are the properties we are going to study? We can start the properties, for example, what is the volume, excess volume and I will define what is excess volume. What is the volume of the mixture? We can add constant pressure sometime when you add co-solvent, the volume of the two decreases that what it should be if they are ideally mixed.

We talk of viscosity and dynamical properties like diffusion. So the range of property is that an experimentalist measures and you really study in that experiment is binary mixtures. In India it was a very common and very popular research of the study of binary mixtures, I know many people who studied their whole life on binary mixtures and it was quite significant work. Another method of doing experimental study of binary mixtures is through sound attenuation.

You send sound waves and you find out how the sound gets attenuated and absorbed. There are a host of thermodynamics and dynamic experimental tools that we bring in to understand these binary mixtures. So what I will do now in this lecture today, we will talk of binary mixtures, motivate it and tell you how this very important class of physical systems for physics, chemistry, biology and material science.

How we would begin and understand the physical properties of these things and this is done but as I said the statistical mechanics.

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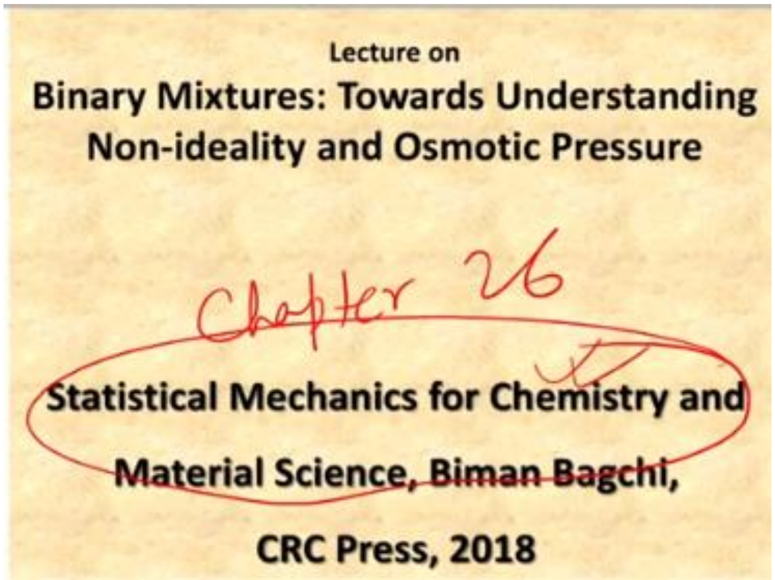

Lecture on

Binary Mixtures: Towards Understanding Non-ideality and Osmotic Pressure

Chapter 26

Statistical Mechanics for Chemistry and Material Science, Biman Bagchi,

CRC Press, 2018

And this is what we describe in this book that we have written and this is in chapter 19 or chapter 26 in this book that we have discussed the subject in quite great detail and will follow this book closely but there will be some simplifications. So I just recap what I said.

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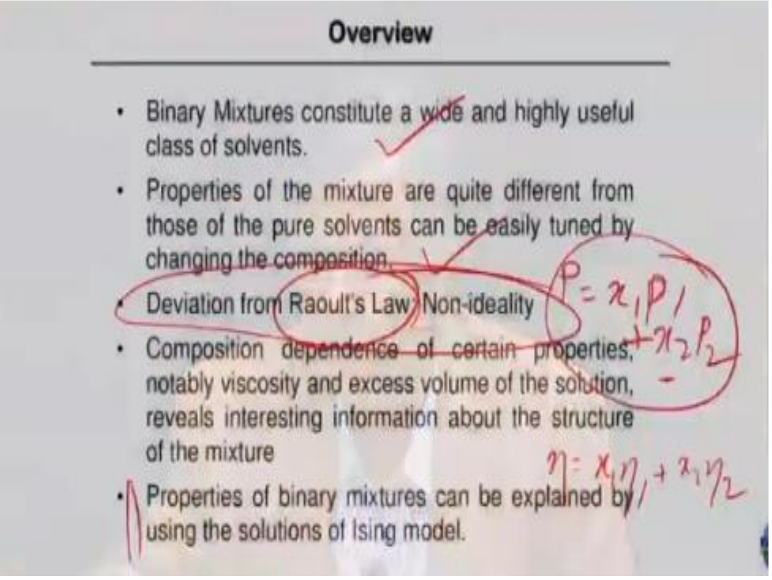

Overview

- Binary Mixtures constitute a wide and highly useful class of solvents.
- Properties of the mixture are quite different from those of the pure solvents can be easily tuned by changing the composition.
- Deviation from Raoult's Law/ Non-ideality
- Composition dependence of certain properties, notably viscosity and excess volume of the solution, reveals interesting information about the structure of the mixture
- Properties of binary mixtures can be explained by using the solutions of Ising model.

Binary mixtures constitute a wide and highly useful class of solvents. Then properties are quite different from those of the pure solvents, that means I have properties of A and protein of B when it mixes them A and B has properties which are very different from that away. Then something which you have studied at length, probably even in schools but certainly in your physical chemistry is, Raoult's law and says that the properties of a point P is X1, P1, X is the mole fraction.

So if there are two species 1 and 2, if I mix them then property P of the mixture becomes a mole fraction of species 1 multiplied by the property P1, then for example I can take a viscosity then viscosity would be written as, x1n1+x2n2. Then the composition dependence, so mole fraction ideal Raoult's law gives you certain dependence on mole fraction which is here but you find a very large deviation from that.

Now many properties are obtained by using the Ising model as we discussed in a previous lecture that how the Ising model, the binary mixture can be mapped quite well into the Ising model, it was nearly done in the compound and really appropriate in the context of the binary alloy. The reason is the binary alloy because I can put a binary alloy in lattice like beta brass that is copper lattice. These are the space centered cubic lattice.

And then I can easily map liquid in a disordered system and in the next lecture or two will be discussing the property in the structure of liquids that is different from that of a binary alloy. Because here we have more use of statistical mechanics because properties are much more statistical, that means we will have to talk in terms of probabilities.

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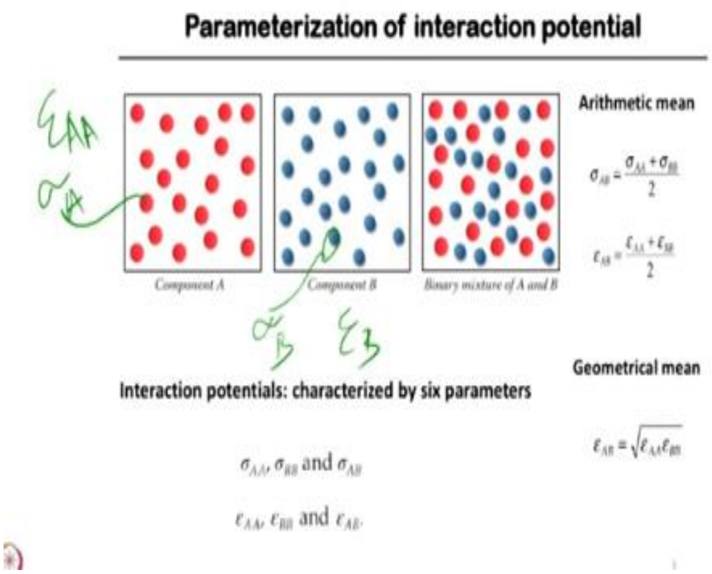

Parameterization of interaction potential

Arithmetic mean

$$\sigma_{AB} = \frac{\sigma_{AA} + \sigma_{BB}}{2}$$

$$\epsilon_{AB} = \frac{\epsilon_{AA} + \epsilon_{BB}}{2}$$

Geometrical mean

$$\epsilon_{AB} = \sqrt{\epsilon_{AA}\epsilon_{BB}}$$

Interaction potentials: characterized by six parameters

σ_{AA}, σ_{BB} and σ_{AB}

ϵ_{AA}, ϵ_{BB} and ϵ_{AB}.

So let us get started with some simple eye opening kind of things. You have one space is A by the red balls and the blue by the B and we mix them and one thing that you realize immediately that A and B can interact differently. So if I have an interaction potential and they can have diameters differently, let us say this diameter is Sigma A and this diameter is Sigma B. Then AA interact with an interaction potential AA, then BB interact with interaction potential BB.

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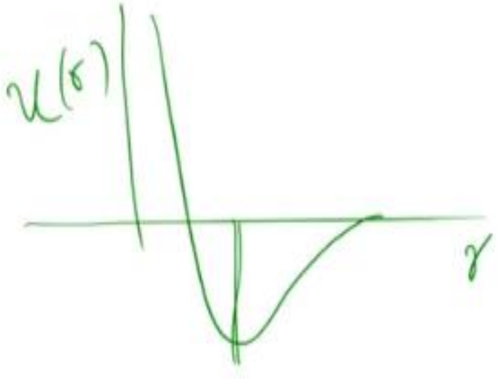

So I have one in back of my mind essentially an interaction potential u(r) and I have this kind of potential Lennard Jones then it is the depth that I am talking. Of course half sure the part of the potential is important but half part of the potential makes its presence fail in giving you the structure of the liquid. And in thermodynamics the internal energy enthalpy, many things which are manifestation property of the structure is really a very interesting role that, this part and this part place.

That means one part gives you the structure, then the structure of course determines the thermodynamics and dynamics but on that structure you have a liquid because you have intermolecular interactions this epsilon. So these two play a very interesting role together and that I think I want you to appreciate. So now back to Raoult's law, as I say it is a law which is called the ideal solution.

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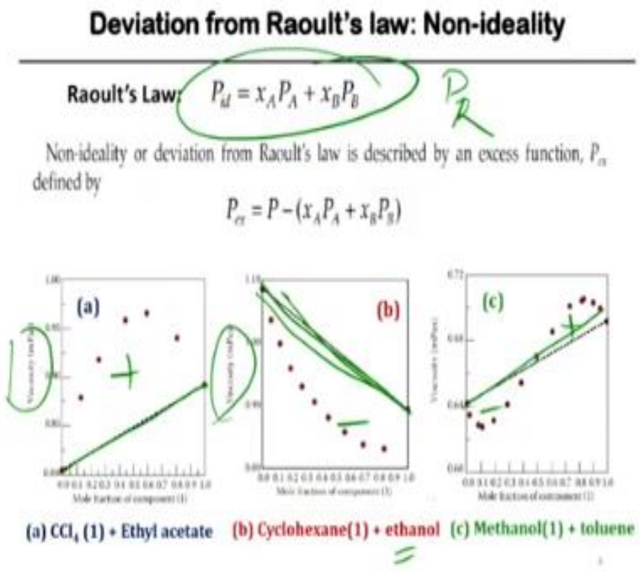

Deviation from Raoult's law: Non-ideality

Raoult's Law: $P_{id} = x_A P_A + x_B P_B$ P_R

Non-ideality or deviation from Raoult's law is described by an excess function, P_{ex} defined by

$$P_{ex} = P - (x_A P_A + x_B P_B)$$

(a) CCl_4 (1) + Ethyl acetate (b) Cyclohexane(1) + ethanol (c) Methanol(1) + toluene

So ideal solution, ideal will be P ideal or P Raoults or PR, you can call it P Raoults is just what I wrote down. However if you have many solvents remarkable deviation from this ideal, if it were ideal then these should be the straight line, but what you find all kinds of behaviors. The real number is like here carbon tetrachloride ethyl acetate, here you have a cyclohexane, it is very inert solvent and then ethanol that has mark deviations, this is a positive deviation of viscosity.

And this is a negative deviation of viscosity and here in the methanol and toluene is fairly common solvents, we all chemists know about it that carbon tetrachloride, ethyl acetate, cyclohexane, ethanol, methanol and toluene. But look at the kind of behavior they show, one is a positive deviation and there is a negative deviation and there it is negative-positive. This kind of behavior has given rise to certain nomenclature and this nomenclature is the one that we will go into and they will try to do statistical mechanics.

So the purpose of this chapter is partly to try to tell you how we can understand these things. This is still very much an active area of research and a lot of papers are being published and that one of the reasons that such sudden interest in the last 10-15 years in this area is the use of computer simulations. As you can see carbon tetrachloride or ethyl acetate or cyclohexane, they are common solvents but they are complex molecules.

They are not like the spheres we just drew in the previous slides, so they are more complex molecules and so the interactions are very complex. So our analytical work towards this has been slow, our progress in analytical work and so it is needed for computers who become really boarded and then of course they work in order to get the computer going, I need the interaction potential which is the force field.

And that force field also has been developed or being developed for all these systems and that is a very rigorous and respectable way right now the forcefield development of the force field which allows us to simulate the system is a very respectable branch of work in physical chemistry. That is why I will tell you what are the fields, that one is working so that you basically know what is the kinetic status.

Then physical chemistry attained, statistical mechanics attained so this is what physical chemistry handed us from undergraduate and now physical chemistry, Statistical mechanics rather wants to provide an explanation for these things.

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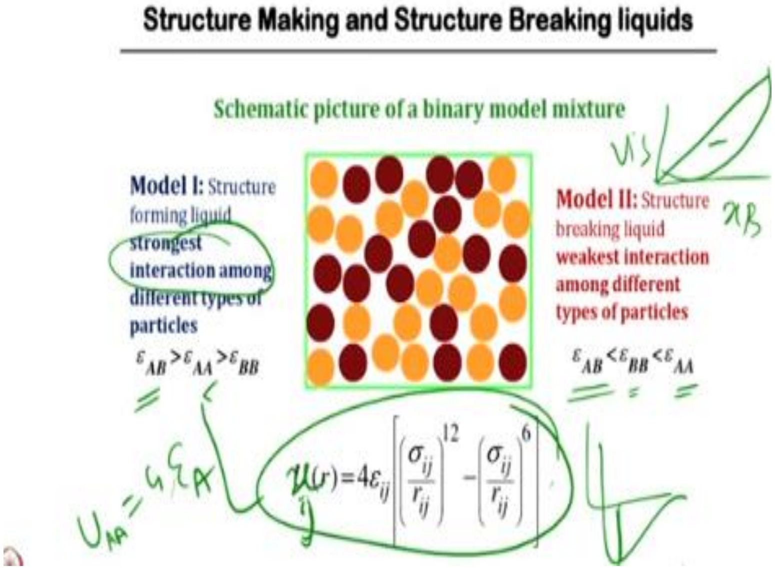

Structure Making and Structure Breaking liquids

Schematic picture of a binary model mixture

Model I: Structure forming liquid strongest interaction among different types of particles

$\varepsilon_{AB} > \varepsilon_{AA} > \varepsilon_{BB}$

Model II: Structure breaking liquid weakest interaction among different types of particles

$\varepsilon_{AB} < \varepsilon_{BB} < \varepsilon_{AA}$

$$u(r) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$$

And how do we do? Now we start with an interaction potential and we find that this kind of thing where the viscosity goes up, that means structure becomes more rigid that is called structure forming here viscosity becomes less and we call this structure breaking and here there is a crossover from structure breaking in the negative part to structure making.

So any structure breaking these structures A and B like each other and structure making the weakest structure which is coherent and that becomes more rigid viscosity goes up and when there is structure breaking, there they are stay away from each other and there is always an entropic component but there is an enthalpy component. But they interact with each other in these two cases to give this kind of bizarre and widely different behavior.

Then in statistical mechanics everything starts with interaction potential shows that we called a structure forming liquid stronger interaction between A and B. Now A and B like each other more than AA like each other, BB like each other. Similarly there is a model to which is structure breaking in this case we assume by convention AA like each other more than BB like each other.

But most importantly both of this interaction potential that I continuously draw this thing is more than A and B, that means A and B who do not like each other or they might like each other but they are like less than B likes B and A likes A. This is the structure breaking and structure breaking is the one that gave this viscosity if I wrote viscosity against composition, this is Raoult's law.

This goes like the negative deviation in viscosity and will be positive deviation, excess volume, if I plot the excess volume in exercise because we go in another way when the volume increases excess volume is positive, then volume increases in addition to two solvents. Then the viscosity goes down because the molecules kind of expand, they go away from each other and that is the structure breaking.

Structure making becomes close to each other, so the excess volume goes down becomes negative and your viscosity goes up. So we are doing the simplest possible thing now, then we will go into making it much more rigorous but we are starting to build a theory understanding it based on statistical mechanics. So we start with the force field, the force field is the Lennard Jones interaction potential and our old friends 4 epsilon but now A and B have these for U_{IJ}.

So when I have U_{AA} then that would be 4 epsilon AA and the rest of the things Sigma A, sigma B, so this IJ is important and should actually be lower.

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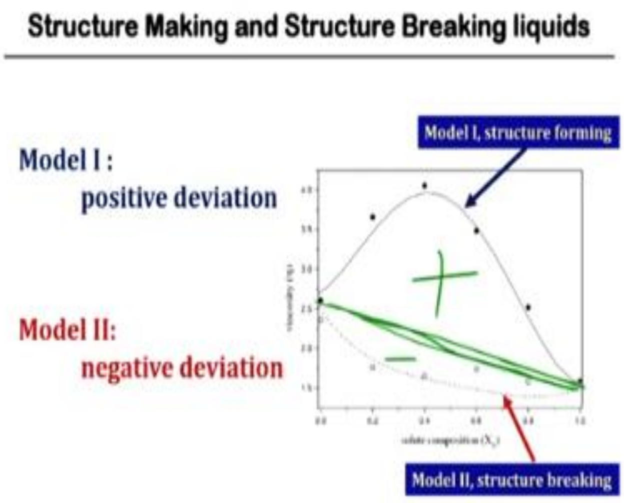

Structure Making and Structure Breaking liquids

Model I :
positive deviation

Model II:
negative deviation

Model I, structure forming

Model II, structure breaking

So again recap the whole thing if this is positive, this is a taking a model like that they did from theoretical what both computer simulations and some sophisticated statistical mechanical theory and you can generate by this kind of a model that we describe here, these kind of model one can indeed describe, so this would be the Raoult’s law, you have the positive deviation and negative deviation.

So this model is structure breaking and these structure making. So what I am telling you in pictorially one can do, I will describe how one does that in the next half an hour.

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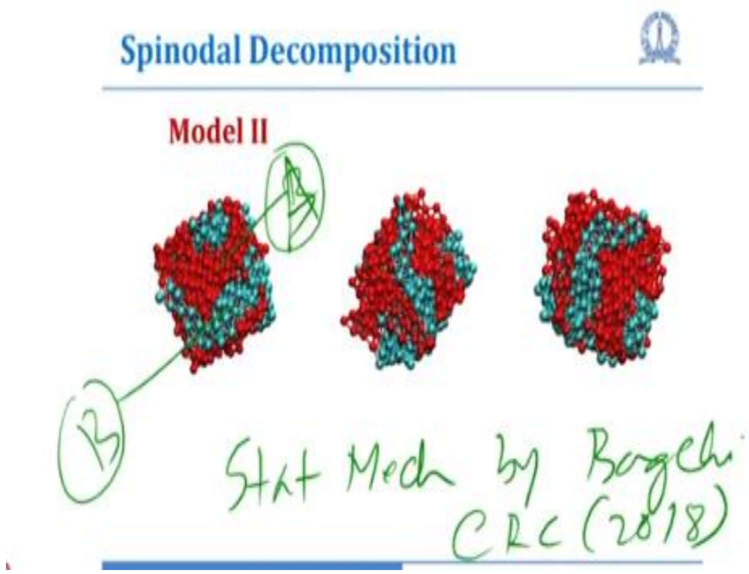

Spinodal Decomposition

Model II

Stat Mech by Bagchi
CRC (2018)

There are some beautiful phenomena we studied a little bit of each and it is given in the Stat Mech book by Bagchi CRC. Now there are very important interesting phenomena that A and B that I was just going to address if A and B, they do not like each other, how come they are still together in a liquid? If I asked you the question I think some of you already know and will be able to give the answer, they stay with each other because the entropy gets.

When you form a binary mixture you get a large entropy that is the entropy of mixing. So that entropy of mixing contributes to making free energy negative, so the mixture remains, but what happened if I suddenly cooled the temperature? Then entropic contribution become less then they cannot stay together, then the phase separates. So two structures breaking liquid where A and B they do not like each other but still are together in high temperature.

They lower temperature they phase separate to be a beautiful pattern formation which is we see in nature all the time in volcanic rocks and in all of any other systems and these are those kind of beautiful structures that I am showing you here that is also A and B are two different species so the red and blue are two different species, if this is our A and this is our B then when you lower temperature then they become beautiful if I separate.

This is another very interesting aspect of binary mixtures which is very popular in binary alloys and very popular in material science.

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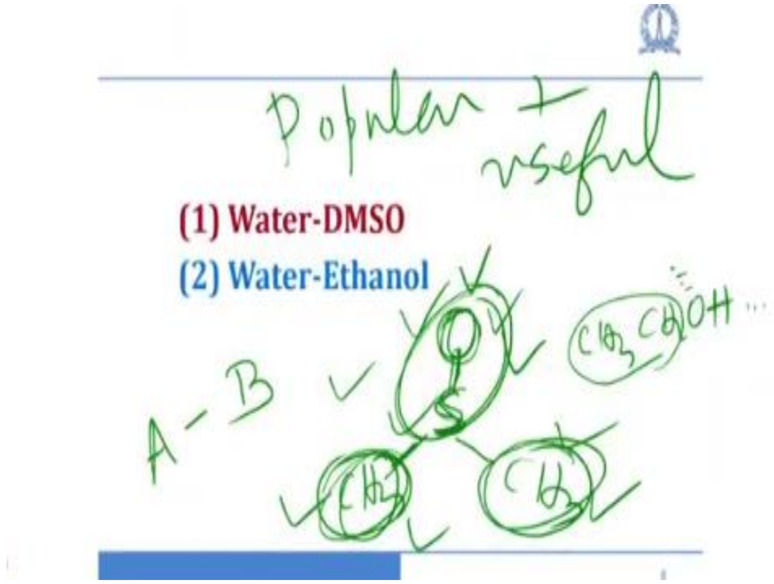

(1) Water-DMSO

(2) Water-Ethanol

Next we go and describe two cases which are very common I am still in the process of entering introducing the students to this beautiful world of binary mixtures, one is water and dimethyl sulphoxide, two popular and highly useful in chemistry and biology is water dimethyl sulphoxide DMSO and water-ethanol. So let me draw the DMSO then DMSO is sulphur oxygen CH3 CH3, this is the dimethyl sulphoxide and ethanol you know, CH3 CH2 OH and then I have water.

So everywhere there is water here, these are water molecules. Now you notice something very interesting in the dimethyl sulphoxide, oxygen is negatively charged, sulfur is positively charged and the methane group nearly spherical has very little charge. So water molecules just surround this oxygen and water molecules kind of go away from methane groups, they kind of form a cage structure, but there little distance having because they do not want to disrupt a hydrogen bond.

Ethanol again has these two parts which are not very polar, so they do not form hydrogen bonds but these guys form hydrogen bonds like; oxygen form 2 hydrogen bonds, hydrogen form one hydrogen bond. So these kinds of molecules are particularly good because in these molecules A and B together, so I have a molecule where A and B together I would say, this is my structure making thing and this is my structure breaking thing.

If A is structure making and B is structure making, then together with respect to water molecules, this is called a hydrophilic group, this is called a hydrophobic group. And these kinds of solvents which are very important are called amphiphilic solvents.

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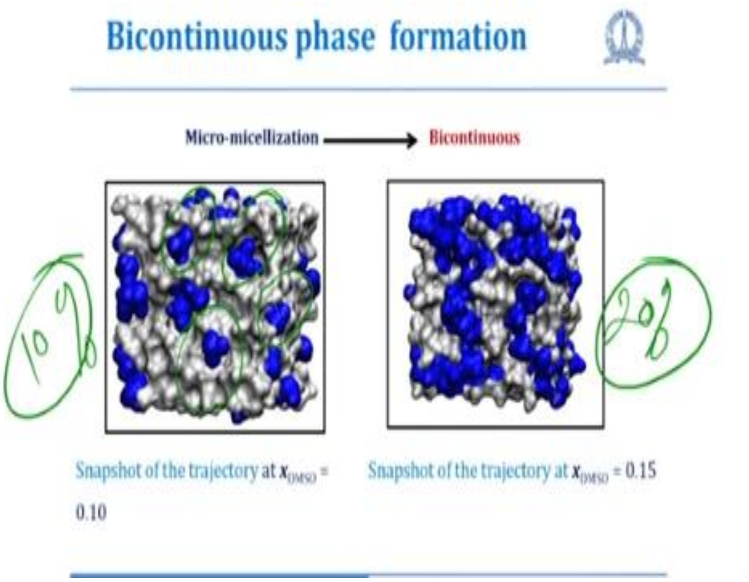

Bicontinuous phase formation

Micro-micellization → Bicontinuous

Snapshot of the trajectory at x_{DMSO} = 0.10

Snapshot of the trajectory at x_{DMSO} = 0.15

And when you do that then the kind of spinoidal decomposition of dimethyl sulphoxide, you see this kind of beautiful phase separation. First they are together and so they are small compositions, they form kind of micro droplets like this droplets showing here but when I increase the composition this will be maybe 10% and this would be by 20%. Here their Islands very interconnected a lot of many beautiful properties of water because of these two phenomena.

So what I am trying to tell you now is, we are going to explain a quantitative theory but you should never fail to appreciate that there is a certain understanding which is coming from physical chemistry. The understanding in terms of structure making and structure breaking is a very powerful paradigm, then hydrophobic and hydrophilic, this is again a very powerful concept.

So what statistical mechanics does is take these powerful concepts and terminology and picture from physical chemistry and then put them into a quantitative predictive theory. So these beautiful languages that we use and the concept they are not predictive, they do not give you numbers they give you some understanding but they are not quantitative, they are qualitative. But now statistical mechanics gives you a quantitative, they give you how to do that.

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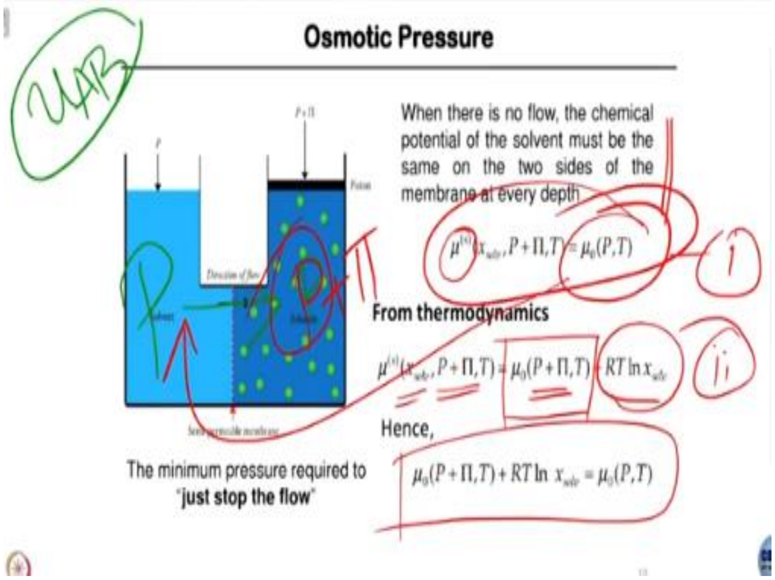

Osmotic Pressure

When there is no flow, the chemical potential of the solvent must be the same on the two sides of the membrane at every depth

$$\mu^{(s)}(x_{solv}, P+\Pi, T) = \mu_0(P,T)$$

From thermodynamics

$$\mu^{(s)}(x_{solv}, P+\Pi, T) = \mu_0(P+\Pi, T) + RT\ln x_{solv}$$

Hence,

$$\mu_0(P+\Pi, T) + RT\ln x_{solv} = \mu_0(P,T)$$

The minimum pressure required to "just stop the flow"

As I am telling you that we want two A and B, interaction potential, so I have some idea of the interaction between A and A, some idea of interaction between B and B but I do not have any idea about understanding between A and B. How do you find the interaction between A and B? Now remember to go back, again and again I told you something about the force field, how do we get the force field?

The first force field was done after the expression of the second virial coefficient, B 2 in terms of interaction potential u(r) remember the expression of B 2 is, integration over dr, r square, e to the power '-Ur', by KBT-1. So I have experimentally determined temperature dependence of the second virial coefficient. So now I can put it into your form like Lennard-Jones potential.

But now I can evaluate these if I have this temperature then I should have this second virial coefficient and I already have measured the second virial coefficient so I have a nonlinear feet and I gave the properties the epsilon and Sigma of Lennard-Jones potential. That is called a force field, then I can do many other things.

For A and B we have a host of properties, diffusion constant, the equation of state, second virial coefficient, we have control over Sigma and epsilon the forceful parameters. But how about the binary mixtures, how about A and B? That is much more complicated because if I want to say let me play the game of second virial coefficient, but when I do that I do not just have to deal with A and B, I have to deal with AA and BB also.

So then the basic idea is that divide and conquer we get A and A, we get B and B, then I want to make A and B but then I need a phenomena, certain particular experiments which are sensitive to interaction between A and B. Because I already have two other interactions hanging around and confusingly and that is the osmotic pressure. Osmotic pressure gives you inroad into interaction between A and B.

The reason their osmotic pressure is so important is that osmotic pressure has been taught in such great detail as well as in physical chemistry. It is a very big thing in biology, if it is in biophysical chemistry then osmotic pressure is the extremely important thing and we will explain how that goes and what the major thing of this particular lecture of statistical mechanics is bringing home that particular point.

Statistical mechanics gives you an expression for osmotic pressure and then you conform if the essential defines a second virial coefficient of the solute and from there you can find the interaction potential between A and B is very important, I need to know how A and B interact experimentally. So osmotic pressure as defined here that you say when I put A and B together, then I put them in a semipermeable membrane that allows A but does not allow B.

So A starts coming from one side to the other like shown here it goes from A to B and how do you stop that? I stopped it by putting a pressure up there, so these guys in pressure P but these guys in pressure P +$\pi$and Pi is the osmotic pressure we know. So we put a pressure on the right side where I have solute due to pressure on the solution to stop the flow and that excess pressure is the osmotic pressure.

When I stop the flow then the systems are in equilibrium now, chemical equilibrium, mechanical equilibrium, thermodynamic equilibrium. Chemical potential of the two are the same which is seen here, so chemical potential of the solvent molecules because in the solvent molecule, that was coming from left to right was the same on the two sides. So the chemical potential of the solvent must be the same of the two sides.

'S' means in the presence of this solution, this I know the 'mu naught PT', this is the chemical potential of this guy. So now from thermodynamic if I have mu in the presence of small concentration of a solute then, I can write that the chemical potential is written as the that of the pure solvent, so this is a interesting list at a mole fraction of the solvent that P + π is the pressure which I am talking of this right-hand side of my slide and then at temperature T.

Then I write it in terms of the pure solvent but it has to be at pressure P + π and then the correction term that is RT Ln X solvent, this comes from thermodynamics. Since I have this thing and this thing now must be by equation 1 and equation 2, I equate these two and I get $\mu_0(P+\Pi,T)+RT\ln x_{solv}$, so this is the one equation that I derived. The base is only one of the equations on the way we are going to derive but remember this equation.

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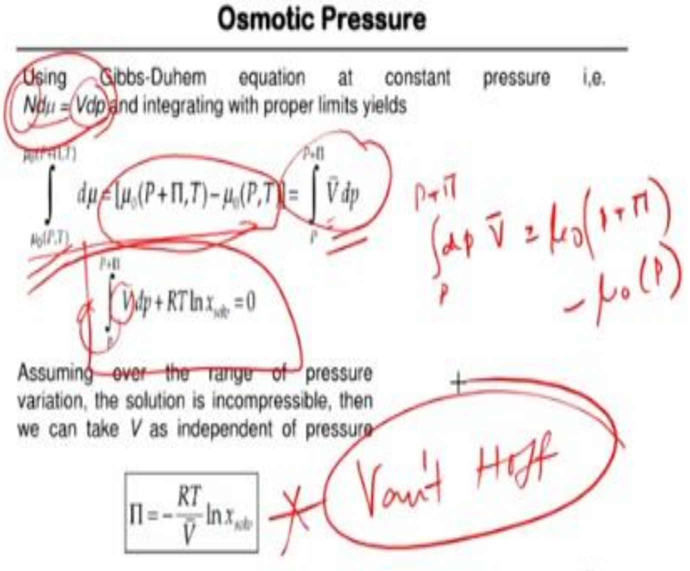

Osmotic Pressure

Using Gibbs-Duhem equation at constant pressure i,e. $Nd\mu = Vdp$ and integrating with proper limits yields

$$\int_{\mu_0(P,T)}^{\mu_0(P+\Pi,T)} d\mu = [\mu_0(P+\Pi,T)-\mu_0(P,T)] = \int_P^{P+\Pi} \bar{V}\,dp$$

$$\int_P^{P+\Pi} \bar{V}\,dp + RT\ln x_{solv} = 0$$

Assuming over the range of pressure variation, the solution is incompressible, then we can take V as independent of pressure

$$\boxed{\Pi = -\frac{RT}{\bar{V}}\ln x_{solv}}$$

$$\int_P^{P+\Pi} dp\,\bar{V} = \mu_0(P+\Pi) - \mu_0(P)$$

Van't Hoff

Next equation we are going to do is the following. Now we have to use the Gibbs-Duhem equation, now we are going to the whole idea if you are smart enough you would be knowing from ideal gas law or from gas law that the whole idea is to get an expression for the osmotic pressure, that is the goal. That is why I am doing all these things, that is what I have derived an equation in chemical potential.

So now if I do that, it is my star equation here, I want to use it but how do I go about it? Then the next piece of the puzzle is to find out the variation of chemical potential as a function operation. I have done variation of chemical potential in terms of mole fraction, what I am going to do now as a function of pressure and who gives you that, who gives you the variation of chemical potential at pressure? That is the Gibbs-Duhem equation, one of the virial equations I like and is a very powerful equation.

And that is why the Gibbs-Duhem equation is so important, so here is a Gibbs-Duhem equation, Ndμ equal to VdP. Sorry about the notation of P, there are various kinds of P, actually P is pressure here. I divide this by N and divide this equation by volume V then I integrate from pressure P to pressure P +π , π is osmotic pressure, then I integrate dμ, then this guy and I of course integrate this one in a minute.

And then I can do this integration is $[\mu_0(P+\Pi,T)-\mu_0(P,T)]$, the same thing as indication of VdP because the indication of that term. So I have first done that integration and got this thing then I put it equal to VdP, I probably would have written the other way around. Now this integration is from P to P + π $\int_P^{P+\Pi}\bar{V}dp=[\mu_0(P+\Pi)-\mu_0(P)]$, so I would have probability to need dP, Vd equal to then integration mu naught P + Pi, forget about T.

So now we are almost there, I bring this to combine the two things together and I get VdP and now we are going to go back to the previous slide, we have already derived that is why I bring this on the side, so $\mu_0(P+\Pi)-\mu_0(P)$ equal to RT ln, so my equation is done. Now assume these will be dependent on pressure, the molar volume is increased depending on pressure then the integration V comes out.

And then this integration does give me Pi, so V Pi equal to RT ln x and I take on the right hand side, so I derive this beautiful equation. This was done by great Van't Hoff one of the three major people who is physical chemistry, one is Arrhenius, the other is Ostwald and other is Van’t Hoff. And the first Nobel Prize in Chemistry went to Arrhenius, second one went to Van’t Hoff, third one would have gone to Ostwald.

But presumably I know that Arrhenius did not like Ostwald at all, so there is 1907 was the Ostwald prize, 1901 was Arrhenius, 1902 or 1903 was Van’t Hoff. I remember I was asked this question in one of the quizzes because in India we have very strange kind of fact oriented exams and I was asked who got the first Nobel Prize in Chemistry. I thought about why I chewed my pain and then I selected Van’t Hoff, but no it was Arrhenius who got the first Nobel Prize.

But Van’t Hoff is one of the fathers of the solution phase physical chemistry and thought that was what was the early 20th century that was the most important and people realize the master under the solution. So now something even more interesting we are going to do, this is RT ln x solvent.

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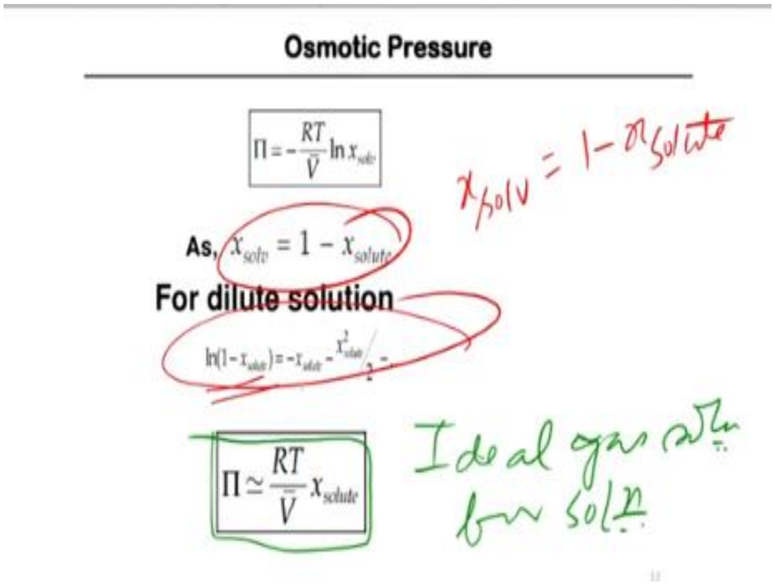

Osmotic Pressure

$$\boxed{\Pi = -\frac{RT}{\bar{V}} \ln x_{solv}}$$

$x_{solv} = 1 - x_{solute}$

As, $x_{solv} = 1 - x_{solute}$

For dilute solution

$$\ln(1 - x_{solute}) = -x_{solute} - \frac{x_{solute}^2}{2} - \ldots$$

$$\boxed{\Pi \simeq \frac{RT}{\bar{V}} x_{solute}}$$

Ideal gas eqn.

for soln.

Now I write it as; x solvent is 1 - x $_{solute}$, this is here then ln 1 - X $_{solute}$ is - x solute - logarithmic expansion and behold I take this first term - and - + and I get my ideal gas law, it is the ideal gas law for solutions. This is one of the most important things of the binary mixture, osmotic pressure is perhaps the most important thing and this equation Van’t Hoff, all these things were done by Van’t Hoff.

So we now beginning to get an idea this is how it goes that I have been able to derive the ideal gas law, if I get a deviation from the ideal gas law in terms of the concentration x solute, then I will be able to get a second viral coefficient thing like that so I will then get an idea of effective interaction between B and B and which will be very useful and also interaction between A and B.

So that was exactly the strategy followed by Mayer many years later and it was also the strategy that Van’t Hoff and Ostwald had, it really all these easily makes a beautiful story.