Basic Statistical Mechanics
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Lecture - 50
Binary Mixtures: Towards Understanding Non-Ideality and Osmotic Pressure Part 2

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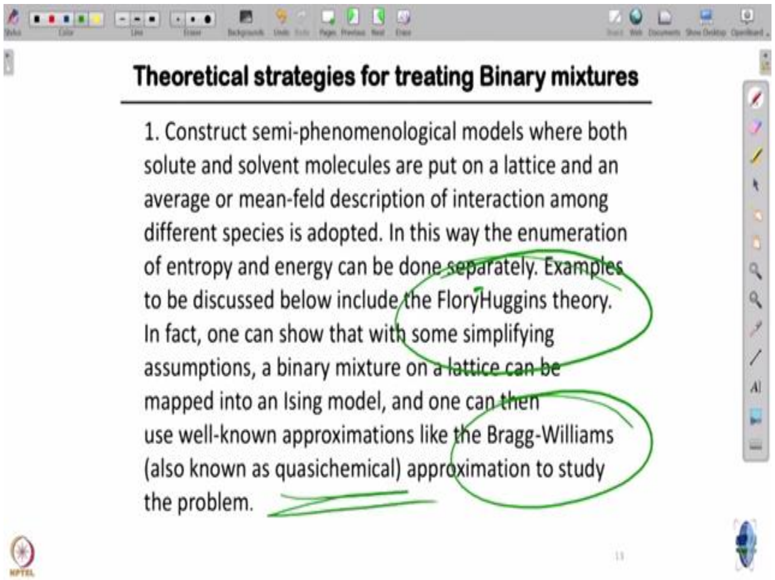

Theoretical strategies for treating Binary mixtures

1. Construct semi-phenomenological models where both solute and solvent molecules are put on a lattice and an average or mean-feld description of interaction among different species is adopted. In this way the enumeration of entropy and energy can be done separately. Examples to be discussed below include the FloryHuggins theory. In fact, one can show that with some simplifying assumptions, a binary mixture on a lattice can be mapped into an Ising model, and one can then use well-known approximations like the Bragg-Williams (also known as quasichemical) approximation to study the problem.

So now let me briefly tell you the theoretical strategies that one of the things fast phenomenological models Mayer came later, but before Mayer around the same time but after Van’t Hoff and Ostwald we started doing a; we put these solute and solvent molecules on a lattice. Because that could be solved because I could now give ε_{AA} , ε_{BB} and ε_{AB} just like we did in binary alloy and I can count now how many ways I can put A and B.

So putting on a lattice has its advantage and that one in a better way in polymer by Flory Huggins theory very famous theory which still plays a very important role in all studies of a polymer solution or even in ordinary solutions. This is very similar to Bragg Williams approximation we did in quasi chemical approximate we did in thin model.

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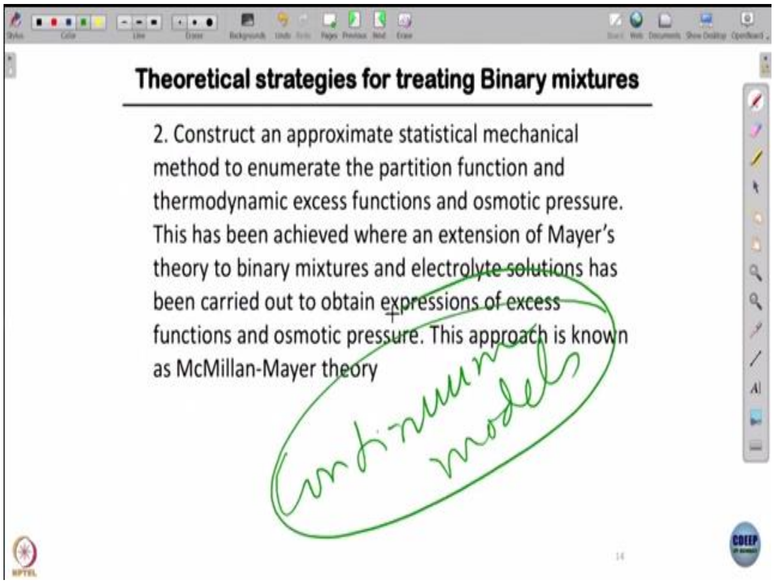

Theoretical strategies for treating Binary mixtures

2. Construct an approximate statistical mechanical method to enumerate the partition function and thermodynamic excess functions and osmotic pressure. This has been achieved where an extension of Mayer's theory to binary mixtures and electrolyte solutions has been carried out to obtain expressions of excess functions and osmotic pressure. This approach is known as McMillan-Mayer theory

Then we have external mechanism the lattice of the Latin language which we will discuss briefly after that is more than you know model will describe it.

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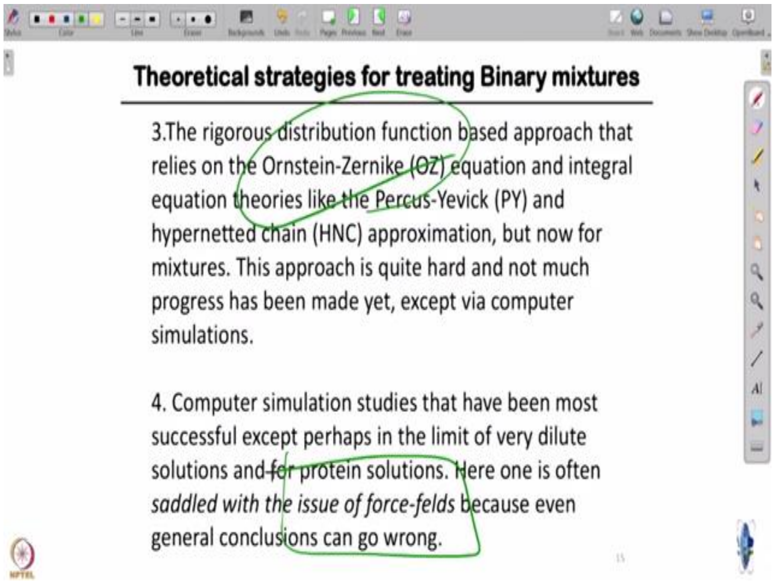

Theoretical strategies for treating Binary mixtures

3.The rigorous distribution function based approach that relies on the Ornstein-Zernike (OZ) equation and integral equation theories like the Percus-Yevick (PY) and hypernetted chain (HNC) approximation, but now for mixtures. This approach is quite hard and not much progress has been made yet, except via computer simulations.

4. Computer simulation studies that have been most successful except perhaps in the limit of very dilute solutions and for protein solutions. Here one is often *saddled with the issue of force-felds* because even general conclusions can go wrong.

Technical description which will just exclude these are the famous things Ornstein-Zernike equation which will discover it will be it and there are many other things we do not need to know now, but everywhere remember everywhere the main central issue remains the issue of the force fields that is where Ostwald equation plays two important role, that gives you it and that is what Flory realized and used it in the polymer and now we go to Flory-Huggins theory.

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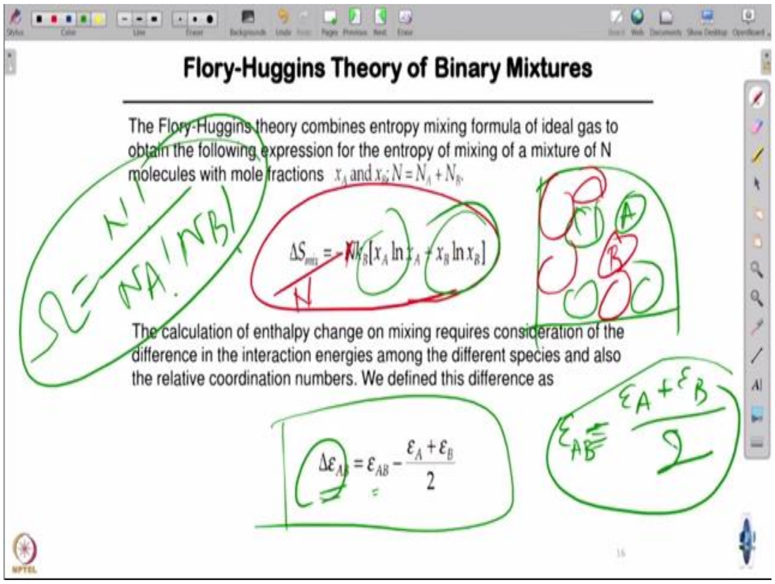

Flory-Huggins Theory of Binary Mixtures

The Flory-Huggins theory combines entropy mixing formula of ideal gas to obtain the following expression for the entropy of mixing of a mixture of N molecules with mole fractions x_A and x_B; $N = N_A + N_B$.

$$\Delta S_{mix} = -Nk_B[x_A \ln x_A + x_B \ln x_B]$$

The calculation of enthalpy change on mixing requires consideration of the difference in the interaction energies among the different species and also the relative coordination numbers. We defined this difference as

$$\Delta\varepsilon_{AB} = \varepsilon_{AB} - \frac{\varepsilon_A + \varepsilon_B}{2}$$

Okay, so as I said when you put A and B together in a mixture A and B together then a first thing I get is an entropy of mixing and that is very well known in the entropy of mixing. Entropy of mixing per particle I would rather take it out from here and put it here by N is KB XA and XA KB is Boltzmann constant so would XA is mole fraction of A B is mole fraction of B so this is say B and this is my A.

Say I have XA in $x_A \ln x_A + x_B \ln x_B$ these things by a mixture know from comes from simple computonics you calculate the Boltzmann omega, number of ways from N factorial by NA factorial by NB factorial that is where lattice lies**.** So N number of lattice sites and you are putting A and B together it is very, very useful to get that. Now so this is the entropy of mixing.

Now comes in extremely important which we have been talking but we have not quantified, that how do I talk up A B and I need something to say A and B different from each other I need a quantification that is done by this guy is discriminate, so epsilon delta I introduce a term delta Epsilon AB in terms of now if Epsilon A B is Epsilon A + Epsilon B by 2, what is this called?

This is Butler rule there is one more called geometric rule. So if A and B interaction is just sum of the average of two, then you get the ideal solution, then you get Raoults law but that is not like water-DMSO you cannot see water-DMSO interaction by Van der Walls interaction, DMSO-

DMSO interaction at the because then the hydrogen bonding between A and B because disappears.

So the interaction between A and B brings a very essential new ingredient and that is captured by this term delta Epsilon A B. So we call it discriminate that how different A and B, how different A and B are in their properties and in their entire interactions that what captures by;

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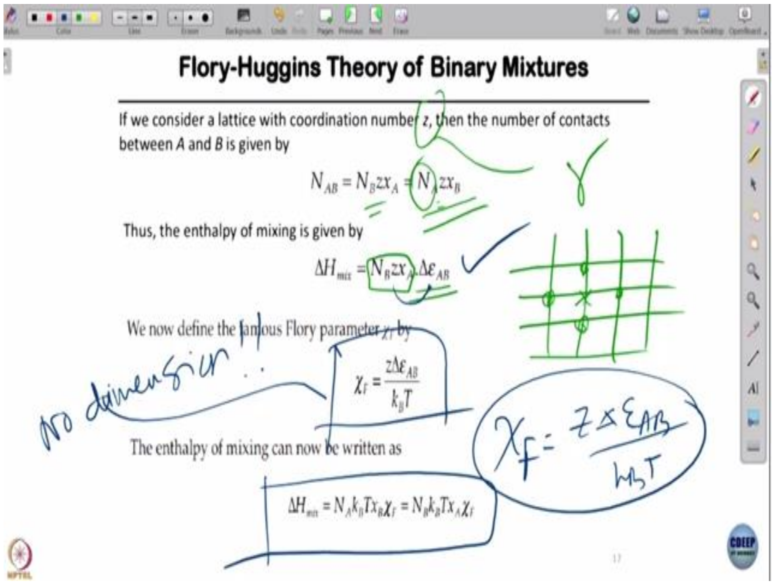

Flory-Huggins Theory of Binary Mixtures

If we consider a lattice with coordination number z, then the number of contacts between A and B is given by

$$N_{AB} = N_B z x_A = N_A z x_B$$

Thus, the enthalpy of mixing is given by

$$\Delta H_{mix} = N_B z x_A \Delta\varepsilon_{AB}$$

We now define the famous Flory parameter χ_F by

$$\chi_F = \frac{z\Delta\varepsilon_{AB}}{k_B T}$$

The enthalpy of mixing can now be written as

$$\Delta H_{mix} = N_A k_B T x_B \chi_F = N_B k_B T x_A \chi_F$$

no dimension !..

$$\chi_F = \frac{Z \Delta \varepsilon_{AB}}{k_B T}$$

This is Flory still we are doing all along Flory so Flory then said okay this is something we discussed a little bit but if Z which is in gamma in my Ising model things is the number of your coordination number. So in a lattice site if this is my lattice site then my coordination number is 4 in 2d simple cubic lattice in 6d would be 6 3 d will be 6, so say it is. So now I want to know that number of contacts between A and B.

Then I can say okay pick up number of A there then I can say okay the coordination number and this is a very mean field means average and the mole fraction so that gives you number of contacts A B these also there they are these two are exactly same quantities. Now I have the entropy I am doing all these things in order to do the enthalpy and sure enough once I know the contact.

Then I say okay I can also write it in terms of N_A it make sense to focus on N little bit more because they are in our mind they are less in number because B is this solute A is this solvent that is kind of kind of picture we have so then N_BZX_A this will be the enthalpy because these are the contact this is the number of contacts and each contact brings a discriminant. So the enthalpy of mixing is the change delta H mixing is the change like entropy of mixing is the change in entropy.

There is a new thing that comes in, okay which was not there because of mixing and that is delta H mixing. So now I add the two enthalpy and entropy I get the free energy. Now define Flory define the following parameter which is famous as a Flory parameter which is this quantity χF is number of coordination number delta Epsilon A B by dimensionless. Dimensionless quantity this is no dimension.

Then we get $\Delta\Delta$ H mixing now this term we are going to rewrite in terms of just introduce this Z into delta A B combine that divide and multiply by KBT and then we get this thing, the delta H mixture. Remember now we have explicitly the Flory interaction parameter or Flory parameter.

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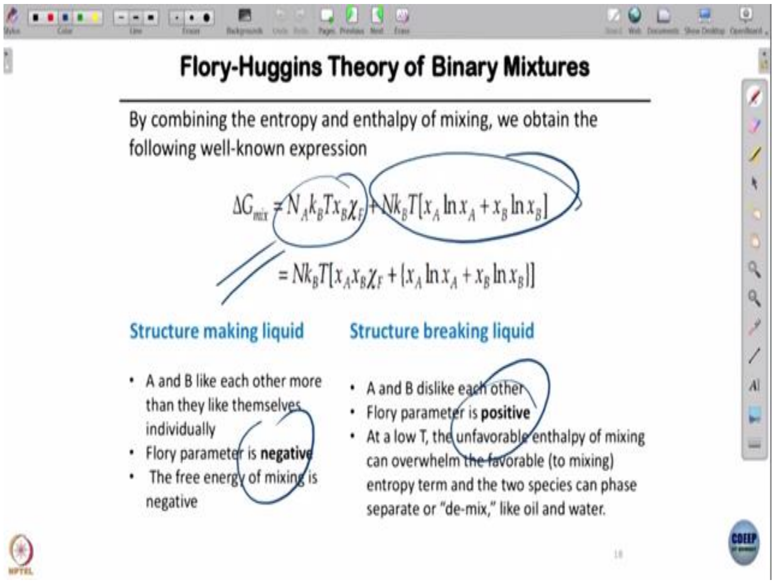

Flory-Huggins Theory of Binary Mixtures

By combining the entropy and enthalpy of mixing, we obtain the following well-known expression

$$\Delta G_{mix} = N_A k_B T x_B \chi_F + N k_B T[x_A \ln x_A + x_B \ln x_B]$$

$$= N k_B T[x_A x_B \chi_F + \{x_A \ln x_A + x_B \ln x_B\}]$$

Structure making liquid

- A and B like each other more than they like themselves individually
- Flory parameter is **negative**
- The free energy of mixing is negative

Structure breaking liquid

- A and B dislike each other
- Flory parameter is **positive**
- At a low T, the unfavorable enthalpy of mixing can overwhelm the favorable (to mixing) entropy term and the two species can phase separate or "de-mix," like oil and water.

Now I get the free energy of mixing I get the free energy of mixing by doing entropy term and the enthalpy term and lower end I have this beautiful thing. Now I have a elementary theory elementary, I am not yet connected with osmotic pressure that is my goal, I will do that. But now

I can start saying some little bit more little bit more teeth into my understanding of physical chemistry the phenomenology that we did in the undergraduate.

And that I already told that now I want to say if their structure making or structure breaking I will be able to tell them in terms of Flory parameter, because the Flory parameter is their negative then the structure making because they like each other more they are more negative but structure breaking is the Flory parameter is positive. So suddenly I am beginning to have little bit of sense of structure making and structure breaking.

And I can now begin to see if I can have some idea of structure making and structure breaking then I can put them into a statistical mechanical theory. So from this structure making delta epsilon A B if I can get an estimate of that then I can take it over to my Lennard Jones parameter and I can do a statistical mechanical theory.

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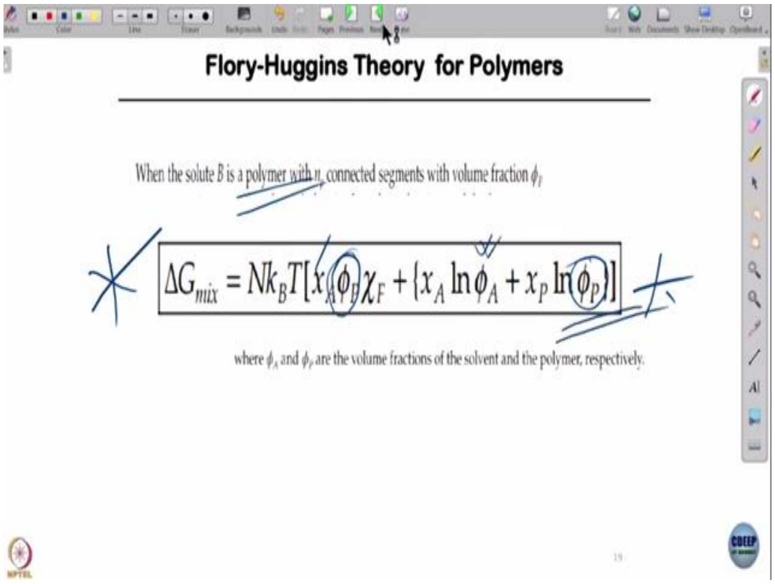

Flory-Huggins Theory for Polymers

When the solute B is a polymer with n_i connected segments with volume fraction ϕ_P

$$\boxed{\Delta G_{mix} = Nk_BT[x_A\phi_P\chi_F + \{x_A\ln\phi_A + x_P\ln\phi_P\}]}$$

where ϕ_A and ϕ_P are the volume fractions of the solvent and the polymer, respectively.

Flory now say that in case of polymer I am not going to go into details of that into polymer what Flory showed that these number that goes in here, these number and these volume fractions so number of contacts that we have done NA NB depends on the volume fraction. If one guy is much bigger than the other then you have to talk of the volume fraction and that is then goes into this will do derive these things when you do the polymer theory of polymers.

But right now I am just going to quote it that because this is a beautiful work of Flory that these same thing goes over and a much more powerful and direct way, where Flory parameter becomes a nearly powerful parameter to talk of feta solvent and many properties of the many, many properties of the polymer solution. Because solvent is so small and so a polymer is so big it now it will be that interaction between polymer effective interaction between solute and solvent becomes very important.

Please remember the term effective interaction and we will come to that. But what Flory parameter is trying to do is an effective interaction and we will come back to that again. But before that I want to these beautiful Theory Delta is H for a polymer is you instead of you have volume fraction but you have the mole fraction of solvent, but in case of solute the polymer it becomes the volume fraction. This I can trivial thing but this is not that trivial.

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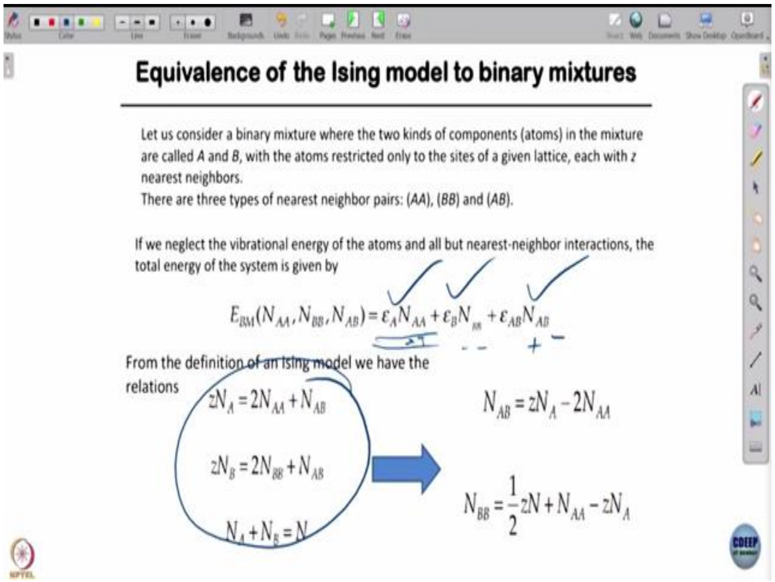

Equivalence of the Ising model to binary mixtures

Let us consider a binary mixture where the two kinds of components (atoms) in the mixture are called *A* and *B*, with the atoms restricted only to the sites of a given lattice, each with *z* nearest neighbors.
There are three types of nearest neighbor pairs: (*AA*), (*BB*) and (*AB*).

If we neglect the vibrational energy of the atoms and all but nearest-neighbor interactions, the total energy of the system is given by

$$E_{BM}(N_{AA},N_{BB},N_{AB}) = \varepsilon_A N_{AA} + \varepsilon_B N_{BB} + \varepsilon_{AB} N_{AB}$$

$$- - \qquad + \; -$$

From the definition of an Ising model we have the relations

$$zN_A = 2N_{AA} + N_{AB}$$

$$zN_B = 2N_{BB} + N_{AB}$$

$$N_A + N_B = N$$

$$N_{AB} = zN_A - 2N_{AA}$$

$$N_{BB} = \frac{1}{2}zN + N_{AA} - zN_A$$

So now I want to do before going on I want to connect the that we have done little bit in the Ising model how these two models are, so I now say spin up is equivalent to a particle A spin down is particle B so in a lattice site I have a spin up that means have A particle spin down and B particle. So when A-A interaction is spin-spin interaction that if it is favored ferromagnetic interaction then epsilon A-A is more negative.

Epsilon and B-B they like each other if I can tune this thing of course and A and B do not like each other, then there is a up and down swing they do not like each other. That is again the ferromagnetic interaction; you down spin like each other them that is anti ferromagnetic interaction that is also very well known thing. But the main idea is that see part of Ising model you remember doing after making all the approximation after those five variables N + and + + and N + - N - - N -.

Eliminating all these things by three conditions of the bonds of by it is neighbors we get N+ N then we did a combinatorial after making a Bragg Williams so it was a chemical or whatever mean field approximation. So here now I do exactly the same thing I write the binary mixture energy as just like I do epsilon A NAA these are the N A are contact in BB N AB so just like there I have N + + this is N- - this is N + -.

So now we just like in model we have these three conditions so the same as 5 variables become equal to 3 variables.

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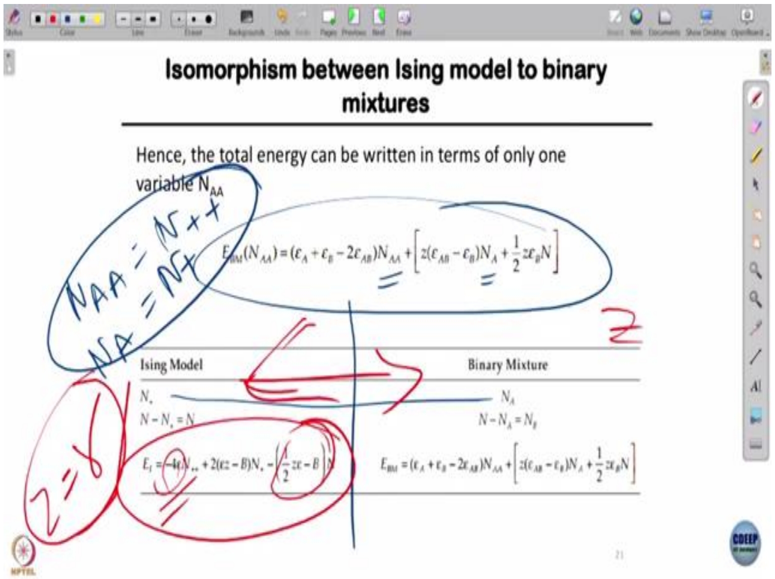

Isomorphism between Ising model to binary mixtures

Hence, the total energy can be written in terms of only one variable N_{AA}

$$E_{BM}(N_{AA}) = (\varepsilon_A + \varepsilon_B - 2\varepsilon_{AB})N_{AA} + \left[z(\varepsilon_{AB} - \varepsilon_B)N_A + \frac{1}{2}z\varepsilon_B N\right]$$

Ising Model	Binary Mixture
N_+	N_A
$N - N_+ = N_-$	$N - N_A = N_B$
$E_I = -4\varepsilon N_{++} + 2(\varepsilon z - B)N_+ - \left(\frac{1}{2}z\varepsilon - B\right)N$	$E_{BM} = (\varepsilon_A + \varepsilon_B - 2\varepsilon_{AB})N_{AA} + \left[z(\varepsilon_{AB} - \varepsilon_B)N_A + \frac{1}{2}z\varepsilon_B N\right]$

$N_{AA} = N_{++}$

$N_A = N_+$

$z = 8$

Z

The exactly same thing goes over we not know as the total energy can be written in the following and by eliminating all the other variables keeping AA and A, this is our NAA is N+ + and NA is N+. So same as before we do not have to do an extra work now or everything has been done by

Bragg and Williams, we just map it into and use the free energy that exactly happens so here is the given the A between then.

Connection between them N+ is NA then N + + is N AA here and then energy of the Ising model is this quantity and that we did in the Ising model class, remember the factor of four, the two and this quantity except Z is gamma in Ising model I am sorry about the change of notation but Z is very common in polymer literature and while gamma is quite common in Ising model. So they are the we went by the kind of they would also use in Ising model.

Or that is coordination number actually chemists like said more and however physicists is kind of gamma is linear it is never interactions partly came from Kerson Huang the famous text books on statistical mechanics. But main thing is that there is a complete isomorphism between them.

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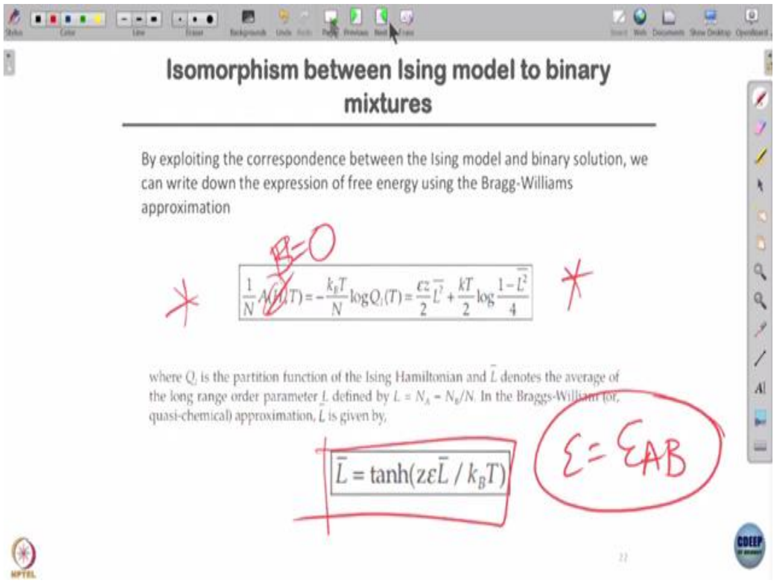

Isomorphism between Ising model to binary mixtures

By exploiting the correspondence between the Ising model and binary solution, we can write down the expression of free energy using the Bragg-Williams approximation

$B=0$

$$\frac{1}{N}A(\cancel{H},T) = -\frac{k_BT}{N}\log Q_I(T) = \frac{\varepsilon z}{2}\overline{L}^2 + \frac{kT}{2}\log\frac{1-\overline{L}^2}{4}$$

where Q_I is the partition function of the Ising Hamiltonian and $\overline{L}$ denotes the average of the long range order parameter L defined by $L = N_A - N_B/N$. In the Braggs-Williams (or, quasi-chemical) approximation, $\overline{L}$ is given by,

$$\boxed{\overline{L} = \tanh(z\varepsilon\overline{L} / k_BT)}$$

$\varepsilon = \varepsilon_{AB}$

As a result of that we can now write down the free energy. So write down the free energy in the case of Bragg Williams approximation this was the free energy wrote down that free energy in the presence of a magnetic field H is this quantity. Now here the free magnetic field H of course we are doing magnetic field H equal to 0 so this is the call H equal to 0 or our B equal to 0 this goes over.

And this is the expression, the equation that we need to solve and epsilon here is epsilon AB. So we get this solution of binary mixture by implicit see that as the beauty is that now

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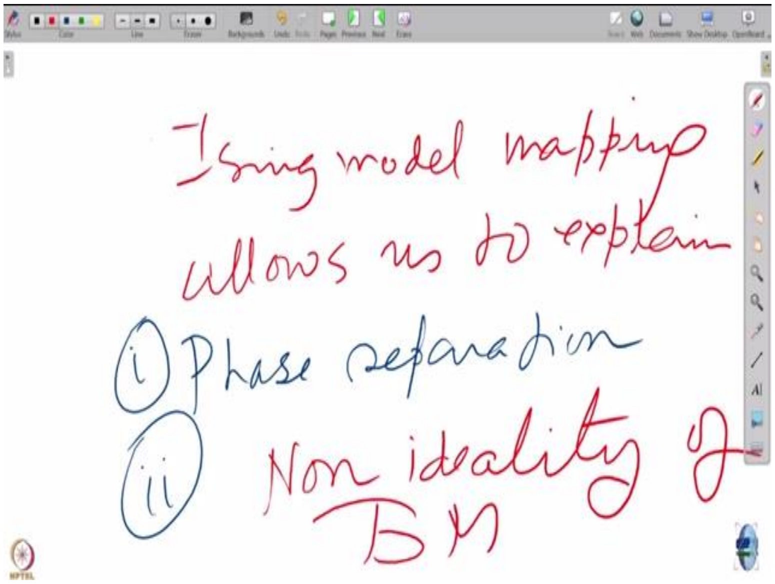

Ising model mapping allows us to explain

(i) Phase separation

(ii) Non ideality of BM

So the Ising model mapping allows us to explain very important this phase separation of binary mixture. Wonderful, that means we need not do any extra work but we realize that it is an isomorphic problem.

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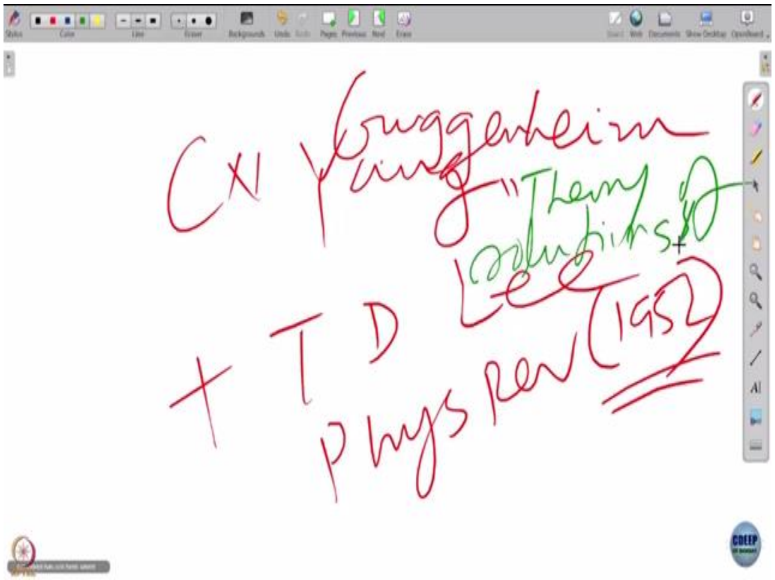

CXI Guggenheim Yang "Theory of solutions"

+ T D Lee

Phys Rev (1952)

This wonderful realization was done by Physical Review 1952 two wonderful papers where did these did and Lattice gas many other people on it has done also by Guggenheim, I should not give only of name the other person who do and he has a beautiful book theory of solutions

Guggenheim beautiful, beautiful book at that all the students would really go through. I was really in fond of.

It is amazing how these days students do not learn in and no I should not deal start dreaming about it, but I find that there is much less until towards is going and because of the internet probably and because of the hour everything at your desktop all the world is coming to you at your computer. But you know at our time we used to go and advantages that we used to discover many old books many classic books like the Guggenheim books.

There is one book by Paul and Guggenheim on statistical mechanics wonderful book and another book is Guggenheim theory of solutions where he does the quasi chemical approximation. Actually quasi chemical approximation was done in respective of the Ising model by Guggenheim, I think I understated and underestimated the contribution of Guggenheim.

So theory of solution and then it was found by TD Lee and C N Yang that there they are exactly the same and but Guggenheim did it I took the force in solving the quasi chemical, quasi chemical name was given by Guggenheim okay, and Brad Williams was running Ising model quasi chemical was done by Guggenheim and these two are the same that was shown later by TD Lee and C N Yang. Okay I think is important to know this history.

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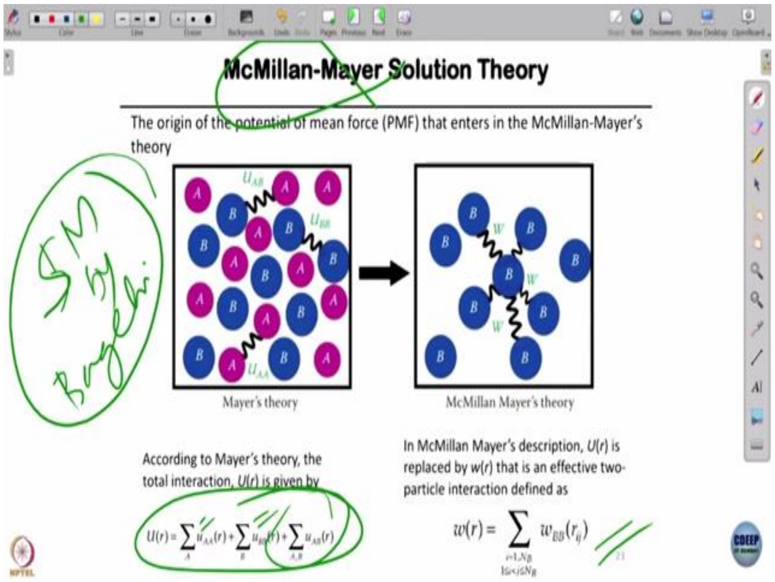

McMillan-Mayer Solution Theory

The origin of the potential of mean force (PMF) that enters in the McMillan-Mayer's theory

According to Mayer's theory, the total interaction, $U(r)$ is given by

$$U(r)=\sum_{A} u_{AA}(r)+\sum_{B} u_{BB}(r)+\sum_{A,B} u_{AB}(r)$$

In McMillan Mayer's description, $U(r)$ is replaced by $w(r)$ that is an effective two-particle interaction defined as

$$w(r)=\sum_{\substack{i=1,N_B \\ 1\le i<j\le N_B}} w_{BB}(r_{ij})$$

Now in the last bit we will try to connect now the importance of the osmotic pressure and so I said that osmotic pressure is so important something not realized in physical chemistry books just give the applications of osmotic pressure osmosis then there are all other biological applications or chemical applications. But first stat- mech guy who is trying to explain binary mixtures and non ideality and phase separation and binary mixture spinodal decomposition many other things, we need the force field and this a measure of the force field comes from the osmotic pressure that is there absolutely goldmine and so we already did osmotic pressure now we kind of connect it together to do and so the basic idea now is that I want an effective interaction which is so important, polymer in every possible way because it is called implicit solvent model.

That means we remove the solvent we are left with only if A and B and there is A is numerous and small B is little larger then I can remove the A and do take only BB but now the BB interaction is not the pure BB interaction. Because it is mediated by A and B it is mediated by A and is actually very different least, how do we do that then? and how do we get an estimate? This is what was done by this great theory on McMillan-Mayer.

Really wonderful theory and a very, very sophisticated theory. So McMillan Mayer did McMillan Mayer was a student of Joseph Mayer and they mapped this problem in a very beautiful and very formidable way very difficult way in our book the stat mech book by Bagchi we have this is what a major thing that was done to really bring home the point. So Mayer's theory we did that interaction potential as in a binary mixture.

If I do a Mayer's theory then it would be way out $\sum_{A} u_{AA}(r) + \sum_{B} u_{BB}(r) + \sum_{A,B} u_{AB}(r)$ and we have here this would be done. McMillan-Mayer now said okay I will use Mayer theory but I will eliminate out A and I want to get that, if I can get that, then I have an effective interaction. Now if I can have a virial series of osmotic pressure my second virial coefficient will have the interaction between B and B. I hope it when there is, I am talking about flow chart and in the flow chart how to get the effective interaction.

So the basic McMillan theory with osmotic pressure gives me this quantity it is very important what that explained the structure making structure breaking all non ideality and these kind of thing.

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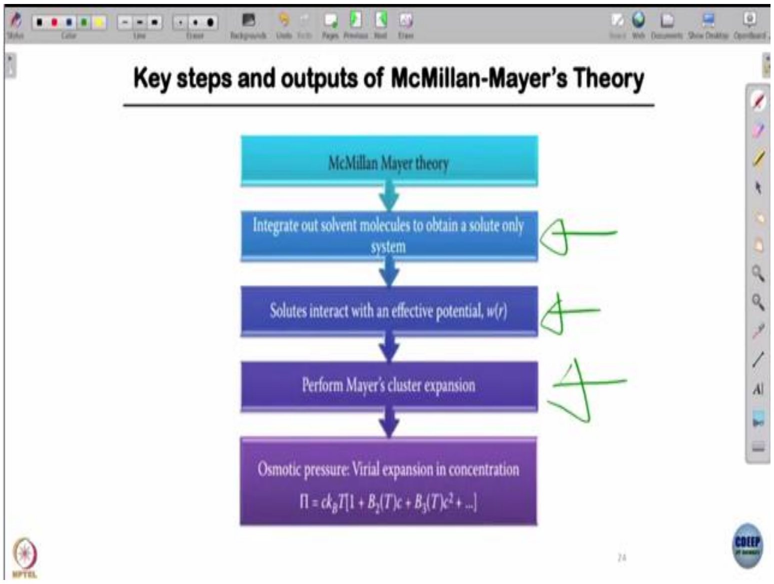

Key steps and outputs of McMillan-Mayer's Theory

McMillan Mayer theory

Integrate out solvent molecules to obtain a solute only system

Solutes interact with an effective potential, $w(r)$

Perform Mayer's cluster expansion

Osmotic pressure: Virial expansion in concentration

$\Pi = ck_BT[1 + B_2(T)c + B_3(T)c^2 + ...]$

So this is a flow chart I hope you can read it that integrate out solvent molecules dropped in solute on the system, solids interact with an effective potential of u(r), perform Mayer's cluster expansion. And then once you do you get these beautiful C's is the concentration now or the mole fraction you get the second virial C. So the osmotic pressure you have a virial expansion of osmotic pressure.

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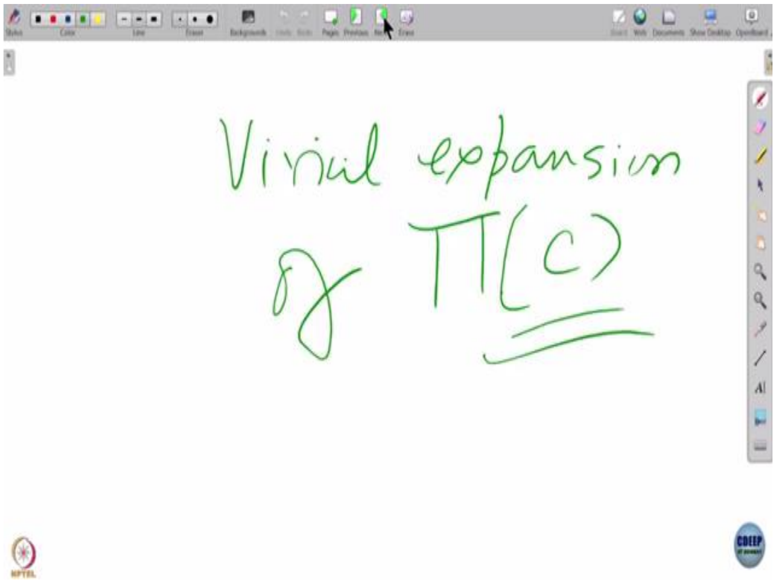

Virial expansion of $\Pi(c)$

So what you have is a virial osmotic pressure pipe which is the concentration dependence so now I can vary the concentration, I can vary of course temperature and I can now get this B to T and then I can measure again with an effective interaction, some form I can use and I can that get that.

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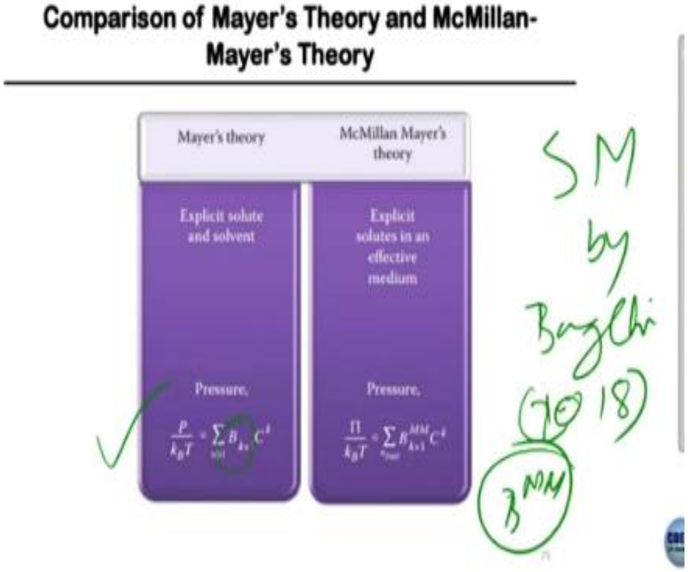

Comparison of Mayer's Theory and McMillan-Mayer's Theory

Mayer's theory	McMillan Mayer's theory
Explicit solute and solvent	Explicit solutes in an effective medium
Pressure, $\frac{P}{k_BT}=\sum B_{k+1}C^{k}$	Pressure, $\frac{\Pi}{k_BT}=\sum B^{MM}_{k+1}C^{k}$

SM by Bagchi (2018)

B^{MM}

So the isomorphism continues McMillan Mayer's theory is very difficult theory it is again given in my book in quite a detail SM by Bagchi will have quite a bit of that, but you are welcome and invited to do this is very important. I write 19 now and then just shows that what where I spend most much of my life in the last century. So this is the Mayer's virial expansion and this is the McMillan Mayer.

Except these are the virial coefficient we know and these BMM and the McMillan Mayer virial coefficient and then this was very important then what this did what McMillan Mayer did derive an expression for BMM and so that it is exactly same thing.

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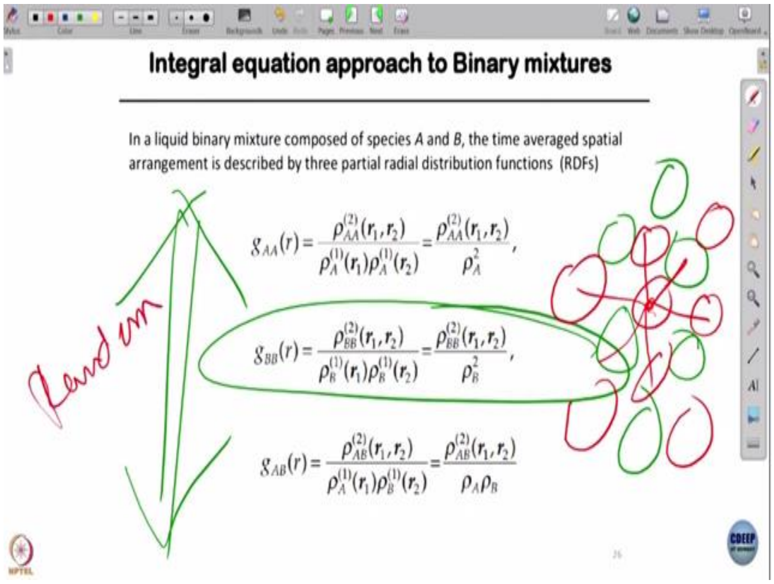

Integral equation approach to Binary mixtures

In a liquid binary mixture composed of species *A* and *B*, the time averaged spatial arrangement is described by three partial radial distribution functions (RDFs)

$$g_{AA}(r) = \frac{\rho^{(2)}_{AA}(r_1, r_2)}{\rho^{(1)}_{A}(r_1)\rho^{(1)}_{A}(r_2)} = \frac{\rho^{(2)}_{AA}(r_1, r_2)}{\rho^{2}_{A}},$$

$$g_{BB}(r) = \frac{\rho^{(2)}_{BB}(r_1, r_2)}{\rho^{(1)}_{B}(r_1)\rho^{(1)}_{B}(r_2)} = \frac{\rho^{(2)}_{BB}(r_1, r_2)}{\rho^{2}_{B}},$$

$$g_{AB}(r) = \frac{\rho^{(2)}_{AB}(r_1, r_2)}{\rho^{(1)}_{A}(r_1)\rho^{(1)}_{B}(r_2)} = \frac{\rho^{(2)}_{AB}(r_1, r_2)}{\rho_{A}\rho_{B}}$$

Random

So it is exactly the; it can be explained, virial coefficient can be expressed in terms of these gBB. So interaction between so these quantities are the radial distribution functions they kind of tailed you A and B how A and B, so now I want to know if this is my B and this is A then how many how B's and A's are connected with these are can are placed with respect to each other in a random system.

In a liquid how A and B are arranged with respect to each other these are post fluctuating these continuously changing so we will have an average description. And that average description is provided by average means it is still microscopic, time averaged description and equilibrium structure. So this G is a very famous thing in the theory of liquid theory of disordered systems one of the most important equilibrium properties these are called the radial distribution functions.

Or the partial radial distribution functions and they form a very important thing of the structure of liquids. So before you go any further we will now go in to do the structure of liquids little bit and then we will come back.

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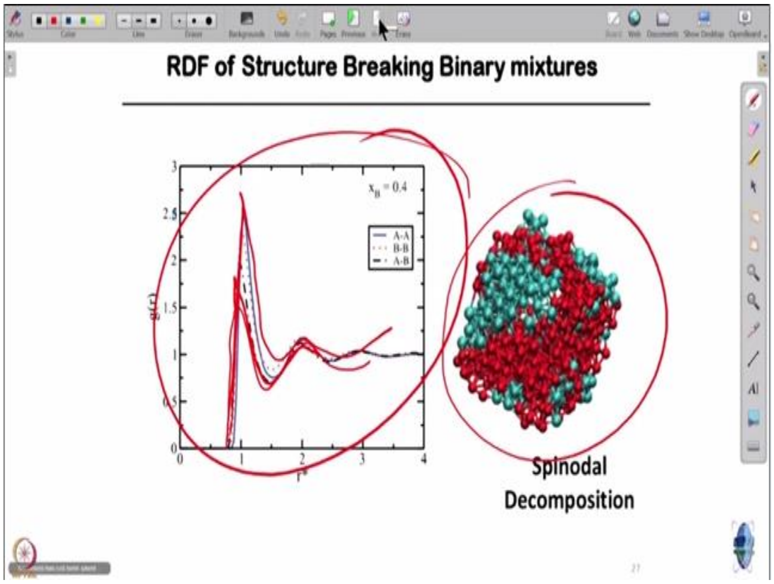

RDF of Structure Breaking Binary mixtures

Spinodal Decomposition

So now as I said that in a very low temperature A and B phase separate if A and B do not like each other. How do I know that they are phase separated microscopically, I can say okay how many A is around B and how many A around A. Then I find in a locally phase separated if A and B do not like each other even at normal temperature when it will appear to be homogeneous they might be locally micro heterogeneity is there.

There will be localized I separated how do I know that I can calculate how many radial distribution function which gives me how many A around B and how many B around A how many A around A how many B? These are the radial distribution function. These are these quantities how A A is the joint probability distribution how many A is around A how many B is around B and how many A is around? They give the time average structure of the liquid.

And now if there then I would know okay A and B will be lowest and that is here A and B this is the A and B, this is the lowest and A and A is maximum number that is A and A. Next is A and B so this A and A, A is around A then B is around B and AAB are depleted. So this is the way one would try to describe now a phase separation, structure breaking liquid or structure making liquid is this the way we will go into it.

So will it now we go to the next class and try to construct and describe these radial distribution functions or how this theory of liquids are built to do these things.