# Advanced Thermodynamics and Molecular Simulations
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## Lecture - 26
## Lattice Model of Liquid Solutions I

Hello all of you. So, in the last few lectures, we have been discussing how can, we analyze the liquid solutions, especially their mixing and phase separation behaviour using the idea of Helmholtz free energy density and we have been able to relate that quantity with the osmotic pressure at chemical potential and all of them can be considered to be a driving force for the mixing or for phase separation.

So, now we will try to complete the other part of the story is how, will I actually get that function f of Φ. So, we know that once we have that double prime of that the second derivative is if it is more than zero then we have mixing behavior otherwise we have phase separation behavior and so on we discussed that in detail that if you give me the form of f of Φ I can tell you what is the mixing and phase separation behavior but we have not so far discussed how will we derive that particular expression, how we will get that expression. So, with that will be the story that I will start again for liquid solutions but we will go in the next week to the molecular simulation part that also in some sense is giving me the Helmholtz free energy density, perhaps more rigorously than what we are discussing right now.

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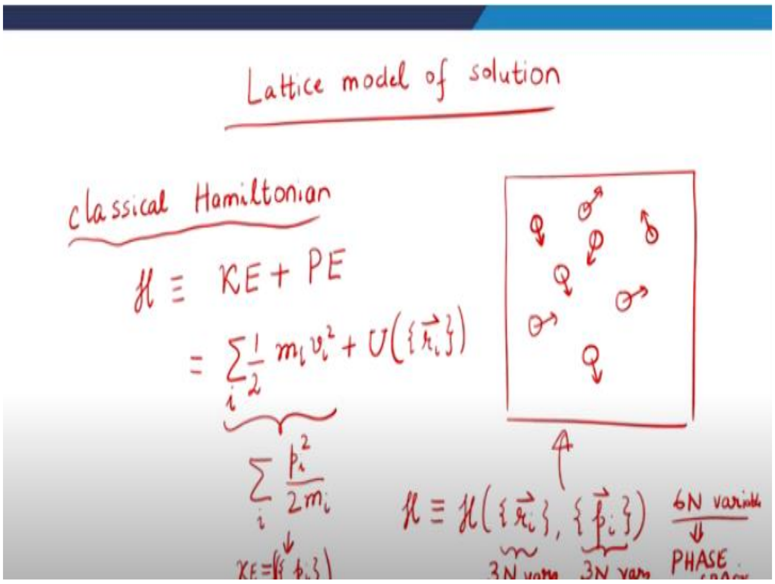

Lattice model of solution

classical Hamiltonian

$$\mathcal{H} \equiv KE + PE$$

$$= \underbrace{\sum_i \frac{1}{2} m_i v_i^2}_{\sum_i \frac{p_i^2}{2m_i}} + U(\{\vec{r}_i\})$$

$$KE = f(\{p_i\})$$

$$\mathcal{H} \equiv \mathcal{H}(\underbrace{\{\vec{r}_i\}}_{3N \text{ vars}}, \underbrace{\{\vec{p}_i\}}_{3N \text{ vars}})$$

6N variables ↓ PHASE

So, what we will discuss is known as the lattice model of solution where my solute and solvent will occupy positions on a lattice. So, before I even get there let us first try to see like why exactly we have to make a model where we started with saying that if I know the molecular motion, let us say if you have a system of molecules and I know the molecular motion and I know the kinetic energy and potential energy I mean, if I have the energy I can get the molecular motion and then we have I would say the properties that we are interested in although that idea is quite valid the only difficulty is that it cannot be applied to a very large number of molecules. It is computationally impossible at least for microscopic systems that we are typically interested in.

So, with that why there is a need for a new model and how exactly we are building the model will be the part of the story I will discuss this week and later on I will return to this problem, the actual problem where molecules are moving under the influence of forces of other molecules and try to say that if I do a simulation I can also get the same quantity perhaps more rigorously.

So, the basic idea behind both these approaches is that we are trying to get what is known as the classical Hamiltonian that is the statistical mechanics way to describe energies. So So, Hamiltonian is described as the sum of the kinetic energy and the potential energy of the molecules. So, let us say if you have 'm' molecules in the system they will have a kinetic energy and there will be some energy in the system that is going to change as the position of the particles change. A more common way to write the first part is to use the idea of the momentum.

$$H \equiv KE + PE$$

$$H = \sum_i \frac{1}{2}\, m_i v_i^2 + U\{(\overline{r_i})\}$$

We can write it as-

$$\sum_i \frac{1}{2}\, m_i v_i^2 = \sum_i \frac{pi^2}{2m_i}$$

because momentum is mass multiplied with the velocity and the reason we prefer the representation is that I can then write the first term that is my kinetic energy term as some function of the momentum variables. So, the way to think about it is there are two kinds of variables in the system that characterizes the system. One is the momentum of particles and the second is the positions of the particle.

So, as the system evolves over time or even in a state of equilibrium since the molecules are particles still moving we are having many possible configurations corresponding to different positions accordingly, we can have many different momenta of particles according to the history of the collisions every time a collision takes place momentum is being exchanged, that results in change in momentum over time so as to speak even in a condition of equilibrium because equilibrium is not a frozen state. So, if I really have to think about it, I can say that my Hamiltonian happens to be a function of the position and momentum.

$$H \equiv H(\{\overline{r_i}\},\{\overline{p_i}\})$$

And now I am looking at Hamiltonian as a function of that and that function will have how many variables- We will have for each of the n particles we will have three coordinates if we are working in three dimensions. So, you will have 3N variables and 3N variables also of the momentum because momentum also is a vector. So, in total we have 6N variables. These 6N variables are what is referred to as the phase space. Why? Because Hamiltonian; is changing as a function of all these 6N variables. So, as any of the position of any of the molecules changes the Hamiltonian changes. As any of the momentum of any of the particle changes the Hamiltonian changes. So, in totality there are 6N variables in that particular function which pretty much determines the state of a system and this is what we call a phase space by the way this phase has nothing to do with the phase separation that we have been discussing in this case we are looking at really the molecular states as opposed to complex phases that we have discussed earlier.

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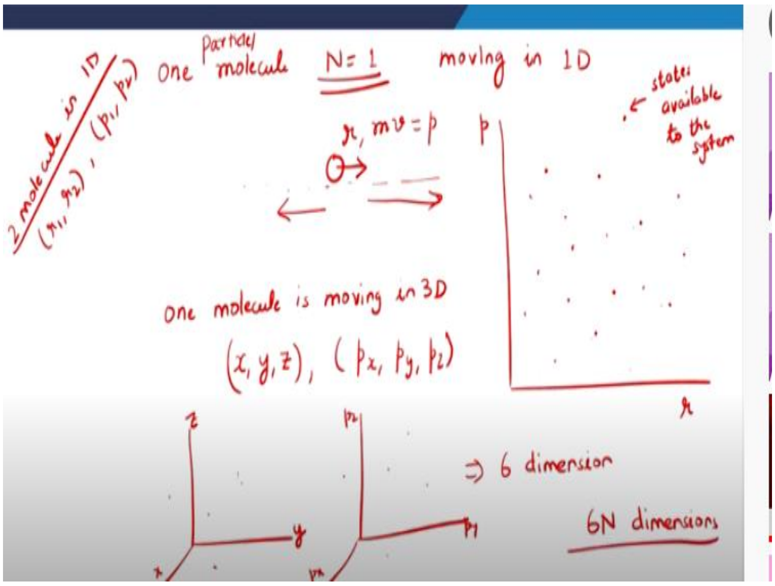
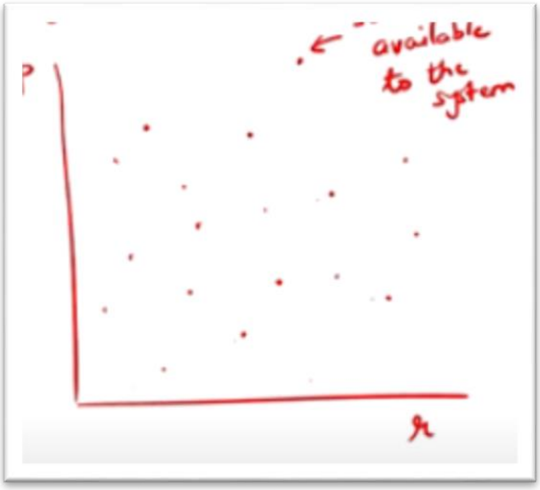


So, essentially just to think of like the complexity of this. Let us say we were looking at just one molecule N equal to one that is clearly not a thermodynamic system and let us say this molecule is moving in only one dimension along the line. Let us say from a molecule is there just for sake of hypothesis we assume that it is moving along the line in any particular direction we can go left or to the right.

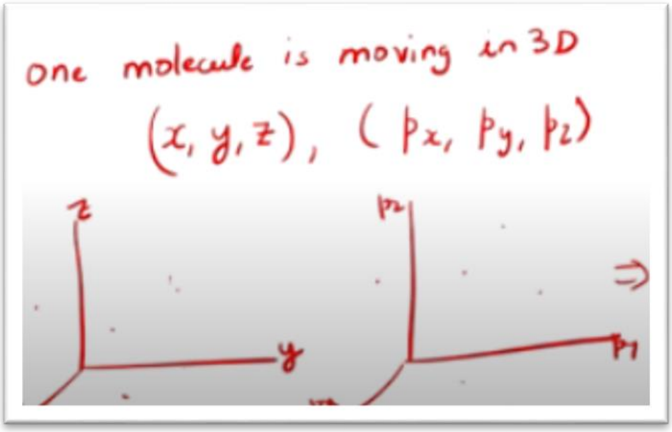
So, how will I characterize this molecule or I have been using the word particle because it can be an atom or a collection of molecules we will come to these things later but for all that we are discussing we are referring it to as particles. So, I can characterize this as some of the its position let me call it some ‘r’ and its momentum and now the momentum is in terms of only one component because it can only go in one direction. So, there is one momentum and one position variable correctly this particle. Now over time this particle can go to any position in space, we precise you can keep moving if I wait until infinite time it can go from this part of the universe to a different part of the universe. Similarly it can have a whole range of possible momentum values, in fact zero to infinity or minus infinity to plus infinity if I also consider the sign of the velocity.

So, with that in mind if I have to represent where the molecule is at any particular state, it can be anywhere in this ‘rp’ space each of these points refers to states available to the system. Although I have drawn only a few points, a point is that I can pretty much put any point anywhere on this plot and that will be a valid state of the system because momentum can take any value and position can take any value.



Now under given considerations for a given system it may not be from minus to plus infinity or zero to infinity. It may be in a certain range, let us say from within like 1 meter to the left or 1 to the right depending on a boundary condition like a wall that is preventing the particle movement or the momentum can also be limited but the key point is that even in that limited range the number of points which are possible are still huge. It can take pretty much any value in the continuous space. So, that is already complicated if I am looking at just one molecule.

Now we imagine that let us say if this molecule is moving in 3D. Now we will have three variables characterizing the position of the particle and three variables characterizing the momentum of the particle. Now if I start thinking around these lines then position wise the particle can be anywhere and similarly momentum wise the particle can be anywhere and in fact since for every given position I can have any momentum in fact although I have drawn it separately because I can only draw a three-dimensional graph on board.



The point is actually in reality we have a six dimensional graph because whatever position we can have any value of the momentum. So, this tells me that we have six dimensions for one molecule. Now let us say what will happen if we have two molecules. Let us say if we have two molecules in 1D, now you will have position of these two and momentum of these two. So, now in totality you will have 4 variables to take care of. Now if I do in 3D we are going to have 12 variables. So, if I keep on extending the argument in 3D we have in total 6N dimensions and that even if I try to approximate by representing the continuous space by a discrete space, even then the number of possibilities are going to be extremely large and that is the problem that we are trying to address when I am trying to represent the motion and the positions of particles and using that to get the properties of interest in thermodynamics.

So, there are two approaches to kind of go around this problem. I mean, this is the exact way of doing it but clearly we cannot do that for a large collection of particles. So, there we have to find alternate way of doing it which have to be approximate because the actual problem is computationally impossible so as to speak.

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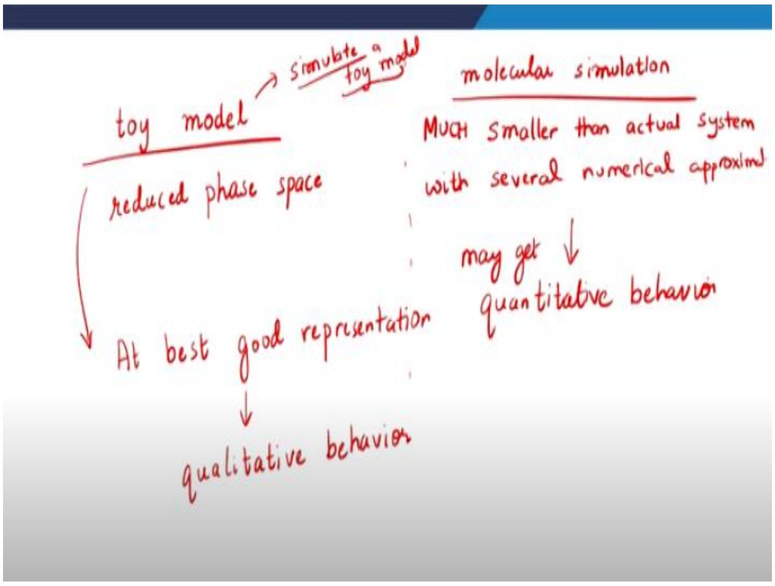

So, one of the ways is I can develop what is known as a toy model where I try to limit the phase space. I basically work with a much reduced phase space and lattice model is an example of that in fact the random walk model of drunkard who was going left and right the example we did long back was also an example of a toy model. The other approach is we can try to do a molecular simulation now clearly we cannot do it for the actual system, but we can do for smaller I must say much smaller than actual system with several numerical approximations. We will get to that molecular simulation part in the next week, but let us first look at the toy model part of it and see how exactly it can achieve that.

So, although I will discuss a lattice model for liquid solutions the possibilities of toy models are endless when you imagine like many kinds of models but keep in mind these toy models are not really same as the actual system at hand because we are working with a reduced phase space clearly it can be at best a good representation of the system but it cannot be the same as the system. For the toy model itself I can get an exact solution or I can get an approximate solution. So, even if we are solving the toy model exactly even in that case, we are not actually modeling the system because as soon as I introduce a toy model we; are working on a reduced phase space but for that particular model I can get a correct answer.

Let us say for example, when I say a gas is an ideal gas now within the assumptions of the ideal gas law, we can say PV equal to nRT and that may very well be exact assuming that we have point like particles and we have no interaction but that is not the reality because in reality we never have a point like particles and we never have absence of interactions. So, we have to keep in mind that even if we are putting an effort into getting an exact solution of a toy model it remains still far from the actual reality at best it is a good representation. At best we can get qualitative behavior but not really I would say quantitative behavior without some kind of like experimental input and we can see later as we as we discuss that.

In the molecular simulation part it is slightly different paradigm. So, we are modeling a very small system and for that system we can be close to exact within the numerical approximation we are making. So, the toy model case the model itself is an approximation. In the molecular simulation case, the model is what the system is except that we are doing it for a smaller system. Then we are applying some numerical approximation. For example, I can numerically integrate something so, the numerical accuracy will increase as I am going for better scheme. So, as I am going for like larger systems and so on and so forth. But the model itself is representing the reality. So, that is the key difference. In the toy model case we can get an exact solution but even then it is far from reality.

In the molecular simulation, if we even if we approximate numerical solution, we are getting actually a quantitative behavior so as to speak or we may get quantitative behavior that may be at least closer to the reality as opposed to a toy model. Having said that I can also simulate the toy model that is going to go towards a better solution of the toy model. If we cannot analytically solve it we can go for a simulation of that but even then since the model is a toy model we are still far from the actual solution.

So, we have to understand these I would say two or three different paradigms. One is the molecular simulation that framework wise it is modeling the exact system, but we can only do a very small system within certain numerical approximations. One is a toy model that can be exact but it is not representing the actual system. For the toy model also we can do simulation and in fact we can use same tools of molecular simulation, let us say Monte Carlo and molecular dynamics on the actual molecules and on the toy models in fact as we go further in the discussion what you will realize that in fact everything to some extent is some sort of a toy model but maybe closer to the actual reality but let us not get there right now. We will see as the discussion proceeds.

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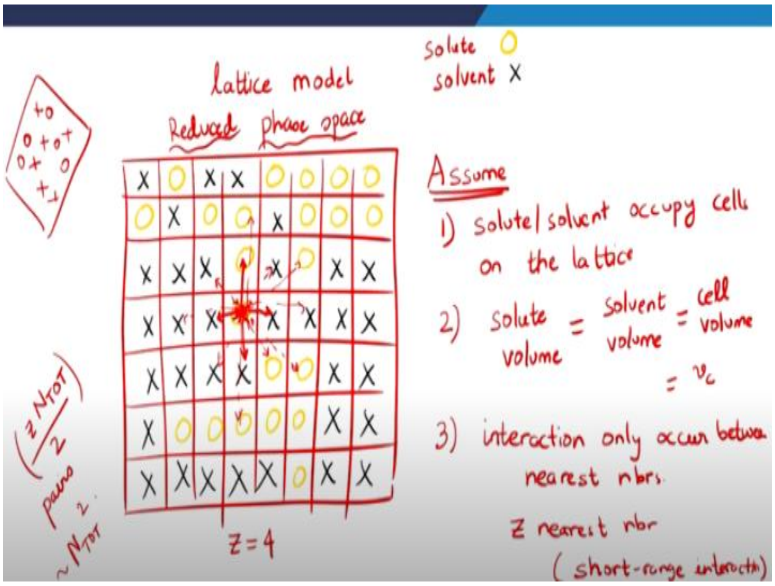

Assume

1) Solute/solvent occupy cells on the lattice

2) Solute volume = Solvent volume = cell volume $= v_c$

3) interaction only occur betwn nearest nbrs.

z nearest nbr (short-range interactn)

So, with that kind of an argument what the lattice model assumes is that I still have a system of solute and solvent but I assume that they are occupying positions on a lattice. And that is like a chess board so as to speak. So, we have a solute and a solvent. I will use different symbols for them, so let us say this is my solute and this is my solvent. So, each of the cells can be occupied by the solvent. I am leaving some space for the solute. So, all these cells can be occupied by a solute or a solvent. So, let us say this is where my solvents are and let us say this is where my solute are you can already see that we have already met while doing that in comparison to the actual system.

Solute- O and solvent-X in the above diagram

So, we already have assumed that my solute and solvent occupy cells on the lattice. So, now imagine an actual situation in actuality you can have a continuous space where the solute and solvent can be anywhere.

Now if I have to elaborate what are the possible positions and possible momenta that are going to be huge for the continuous space in fact infinite. On the other hand for the lattice model since the positions of this solute and solvents are constrained to the cells like slots that I have assigned, now there are much fewer number of positions. Let us say if I am doing an 8 by 8 chess board we have only 64 positions where the particles can be. On the other hand if the same area was occupied by a continuous kind of a distribution then there are infinite numbers of ways I can place a particle. So, by constraining or by limiting the positions that where the particles can be we have actually got a huge reduction in the dimension of the problem we are trying to solve. That is the first advantage that is why I say I am working with a reduced phase space but nonetheless if you notice here, I have tried to put the solute and solvent quite randomly.

So, we can think of let us say if I have to think of an ensemble of this system or thermodynamic ensemble that will correspond to an ensemble of these lattices and for each state in the ensemble, you will have different positions of solute and solvent that is still possible. So, at a qualitative level we are accounting for the fact that the distribution of solute and solvent can be random but we are getting a reduction in the dimension of the problem because we are representing a continuous space with a lattice. And I would say greatly simplifies the problem at hand.

The second assumption that we make is that the solute volume is the same as solvent volume and that is already implicit from the diagram. And that is the same as the cell volume. Let me call it $v_c$. Now, you may imagine a situation where you can try to make different kinds of cells where a smaller cell will correspond to a smaller solvent, a larger cell will correspond to a larger solute molecule or vice versa but there is not too much benefit in doing that. First of all, it is going to be mathematically complicated. The reason why we are doing toy model is because we want simplicity. And secondly, even when we do that, even then we are not very close to the actual system at hand because an actual system was in a continuous space so, even by accounting for this small integrity that the volumes of these molecules are different or volume of particles are different we are putting so much numerical effort and modeling effort and we are gaining very little in terms of the quantitative prediction unless the volume difference between solute and solvent is very large, that is probably not worth doing.

The last assumption that we make that is very important one is that interactions only occur between nearest neighbors. What this means here is let us say if I want to focus on one of the solute molecules, let us say this guy this can only interact with its four nearest neighbors that it finds on the top, on the bottom, on the left, on the right. By the way, even though I have drawn a square lattice here, you may imagine that if you want to do a three dimension, I can draw a cubic lattice. If I want to have somewhat better representation then I have the triangular lattice. The lattice form is not really very important here that will not change the results that I am going to discuss.

So, in general, I can say that there are 'z' nearest neighbors. In this case, z is equal to 4. You may as well ask that why not count the diagonal things we can very well count that that is only going to change my 'z' in the thing. So, if I also count the diagonals then in that case, we will have 8 neighbors. But the way the models are it is always better idea to go for simplicity and try to improve the model only if there is a need in terms of the qualitative behavior you want to predict. The lattice model is still good enough to give me a good picture then why make some other model.

So, the idea is that we have substantially I would say to a very large degree that used the phase space we have reduced the dimensionality of the problem and once we have done that then I am making some more approximations around it. Now once we have got the final results for this kind of a model, we can go back and compare with the actual results if we have available and try to improve the model later on then doing it in the very beginning because as soon as we can keep on adding the integrities the model starts becoming more complicated. It is always good to have a good enough reference case, let us say an ideal gas model serves like a very good reference case using that I can develop a Van der Waal's gas model. Similarly we can start with this model as a reference case and I can include more features like effect of the volumes of solute and solvent, the interactions which are the neighbors and so on.

So, while doing that essentially what we are capturing is only the short range interactions. So, the molecules or particles have say only Van Der Waals interactions; the Van Der Waals are rather short range. They exist only over a small distance so molecules which are farther enough are anyway going to have lesser influence only the close enough molecules will have a significant influence on a particular molecule or particle. So, we should keep in mind that this model is therefore by design applicable only when we have short range interactions. Again, we could have included that but you can imagine that it will make the simulation much more complicated because the number of pairs simply becomes large. So, as of now every molecule has only z neighbors. So, in total we are looking at z multiplied with $N_{TOT}$ divided by two pairs because every pair will double count if I multiply $N_{TOT}$ with z.

So, right now we have only these pairs. If on the other hand if I am counting interaction between all possible particles in the system we are going to have in total something like $N_{TOT}^2$ multiplied with some pre factor pairs. So, that will really make whatever derivation I am doing or simulation I am doing on the toy model more expensive than comparison to what we are trying to do.

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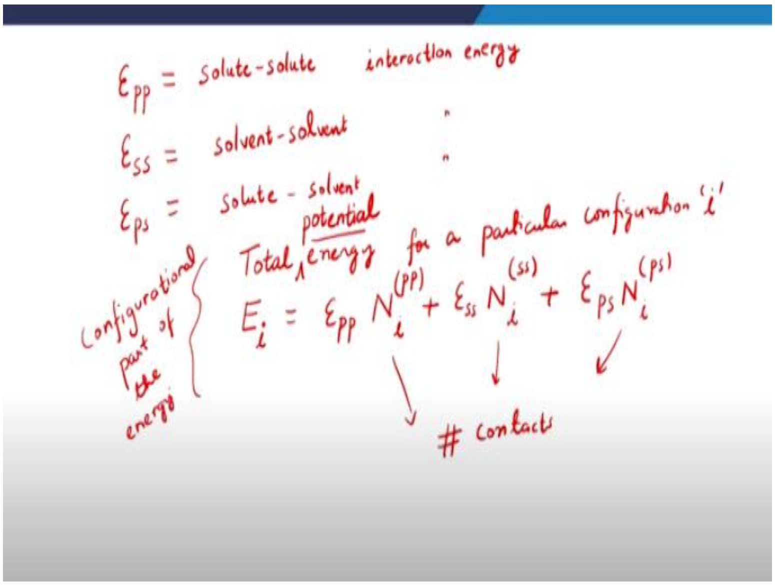

$\epsilon_{pp}$ = solute-solute interaction energy

$\epsilon_{ss}$ = solvent-solvent "

$\epsilon_{ps}$ = solute-solvent "

Total potential energy for a particular configuration 'i'

Configurational part of the energy

$$E_i = \epsilon_{pp} N_i^{(pp)} + \epsilon_{ss} N_i^{(ss)} + \epsilon_{ps} N_i^{(ps)}$$

# contacts

So, with this particular idea, I can then define these interactions as the following. I can say $\epsilon_{pp}$, $\epsilon_{ss}$ and $\epsilon_{ps}$ represent the solute-solute, solvent-solvent and solute-solvent interaction energy respectively.

So, if I have to find the total energy of the system assuming that it is an equilibrium there is no external latency and so on. We can say that the total energy is something like-

$$E_i = \epsilon_{pp} N_i^{(pp)} + \epsilon_{ss} N_i^{(ss)} + \epsilon_{ps} N_i^{(ps)}$$

where these represents the number of contacts. So, $N^{pp}$ is the number of solute-solute contacts, $N^{ss}$ is the number of solved-solvent contacts and $N^{ps}$ is the number of solute-solvent contacts.

Now the two points here is that the first point is that this is going to be applicable only to a particular configuration because as soon as the positions of the solute and solvent changes the number of contacts also changes and therefore, we need to say that it is applicable only for a configuration that I call some i. So, for that configuration I can define the $E_i$.

The other thing is that this is only the potential energy of a system because in the model so far we have not discussed the momentum of the particles and there is a reason why we did not do that. The reason is like since we are fixing the position of the molecule, the molecules can only move so as to speak in by moving from one position to the other and that is I mean, like intuitively speaking is going to be from one slot to a nearby slot. So, in this construction there is no scope to include changes in momenta and all these factors because that velocity will give me a position that is like not lying on these slots. So, what is the meaning of talking about momentum when the positions are pre specified where a molecule can only jump from one side to the other so, in some way we are also constraining the movement by constraining the positions in the system. So, as of now we do not have the momentum in the system. We are only looking at the potential energy or we only look at the configurational part of the energy.

The next is going to be the kinetic part of that, but we will see that it is not so consequential for what we are trying to discuss. So, with that I wanted to conclude the discussion today.

In the next lecture you will introduce what is known as a mean field approximation that further simplifies that problem and using that we can then evaluate the partition function for this lattice model and once we have the partition function we can clearly find the Helmholtz free energy and the Helmholtz free energy density and once we have that we can talk about the mixing and phase separation of solutions and once we have obtained that then we can compare with what we were expecting or if we have any experimental results is the qualitative trend same as the experimental results and using that we can be convinced that our model is correct and if that does not happen then we have to build a new model.

So, any intuition based toy model we are developing is as good as the results of the model if the results are convincing enough then the model is good, if the results do not work then we have to think of a new model or try to see which assumption in the model needs to be lifted to have a more convincing representation of what is going on.

So, with that I wanted to conclude here. Thank you.