Advanced Thermodynamics and Molecular Simulations
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Lecture - 29
Critical Review of Lattice Model, Theoretical Basis of Molecular Dynamics Simulation

Hello all of you, so in the last few lectures, we have been discussing the lattice model of solutions. So, in today's lecture, we will critically review that lattice model and try to find its shortcomings and going further, I will discuss the theoretical basis of molecular simulations and how molecular simulations can address those shortcomings of lattice model. So, just to, quickly recap on what we have been doing.

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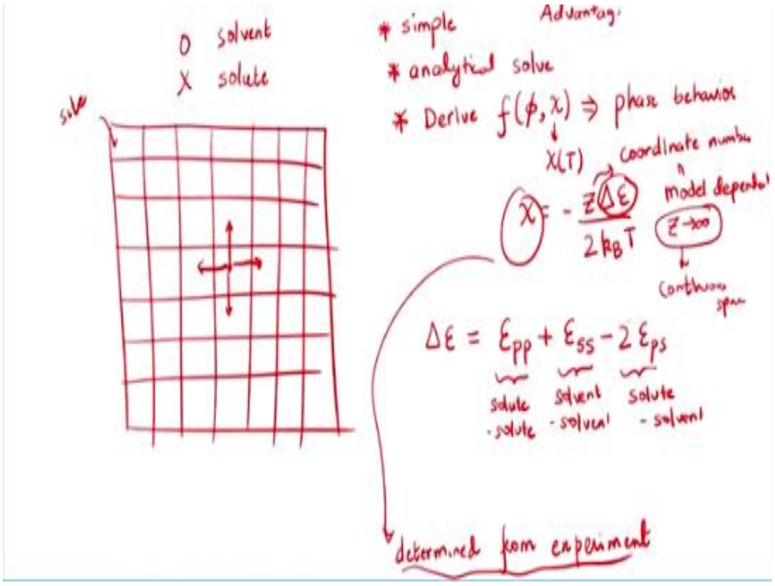

So, we had assumed that we are discussing a system of solute and solvent that is a solution and they cannot just be anywhere in space, but they are occupying sites on a lattice so each of these sites are occupied by a solvent or a solute. So, there are some problems with that model, but before that lets try to see what is the big advantage of the model So, first of all the model is clearly very simple, we can analytically solve it and what we are able to show is that, I can derive the expression of f of (Φ) or f of (Φ_t) but temperature we have replaced by the variable χ and using that we then have a expression for the phase behavior we can characterize the mixing and all that.

So, if you have looked at it carefully, the only variable that is kind of not known a priori is the variable χ. Of course, we know the expression of chi that is-

$$\chi = -\frac{Z\Delta E}{k_B T}$$

where z is the coordination number of the lattice for square lattice it is going to be 4 in two dimensions, in cubic lattice is going to be 6. We can think of any kind of a lattice that will have a different coordination number but clearly since the original idea was that the solute and solvent is occupying the continuous space there was no lattice in reality it was only an assumption. This z happens to be in some sense model dependent in fact, we can think of the continuous space as the limit when z is going to infinity because molecules can be anywhere. So, if that is true, then we are doing that to our system but you may imagine that as z increases the complexity somewhat increases and all that.

So, clearly we have more number of sites and that if I am analytically solving it, it is not really a problem but as we have discussed even there we had made many assumptions and if we try to numerically solve it without those assumptions then it is clearly going to be difficult as the number of sites confuse.

$\Delta\ \varepsilon$ in some sense is still model dependent because we have assumed that at any particular site you have interactions only between the nearest neighbors. But nonetheless $\Delta\ \varepsilon$ included the solute-solute, solute-solvent and solvent-solvent interactions - 2 ε_{ps}. Solute solvent, ε_{ss} is solvent-solvent and ε_{pp} is solute-solute.

$$\Delta\varepsilon = \varepsilon_{pp} + \varepsilon_{ss} + \varepsilon_{ps}$$

Clearly this $\Delta\ \varepsilon$ has to be determined somehow and we will look at in more detail in a minute but before, that let us say that I know the phase behavior from an experiment or a particular system of solute and solvent or a particular liquid solution. If I know the phase behavior I expect that at the qualitatively level the behavior is going to be the same as we have obtained in the lattice model. If that is not true, then the lattice model is not a good representation of the system in the first place so whatever assumptions that we have made in the model, it should be such that at least the qualitative features are captured of the phase behavior.

So, if we have an experimental data available then I can therefore fit my lattice model the results of lattice model and using that I can then find the value of χ. So, χ in principle can be determined from experiment and this is not really something I would say so bad as a chemical engineers that is what we are used to doing so most of the models that we; are used to see, they always have some model parameters, and the model parameters of course come from experiments. Let us say if I look at the pressure drop in a pipeline, we need to know the viscosity and viscosity has to be coming from the experiments typically of course, we can get that from molecular simulations as well, we can get to that later but in most cases we do enough experiment and can find the particular parameter. The simplicity of the model is such that there is only one fitting parameter that is χ and therefore it is quite natural that the model will have a wide applicability even without worrying about the fact that χ is indeed a fitting parameter. There are tables for many systems where the experimental data has been used to find the χ values.

So, if I want to look for any experimental system in most cases there are ways to estimate chi or there are already the tracer data on the values of chi that has been obtained by fitting some kind of experimental data particularly in the literature of polymer solutions, this has been the practice since very long time. So, that is I would say the advantage part of it. Now, let us look at the disadvantage part of it and that really comes from the assumptions that we have made in the lattice model.

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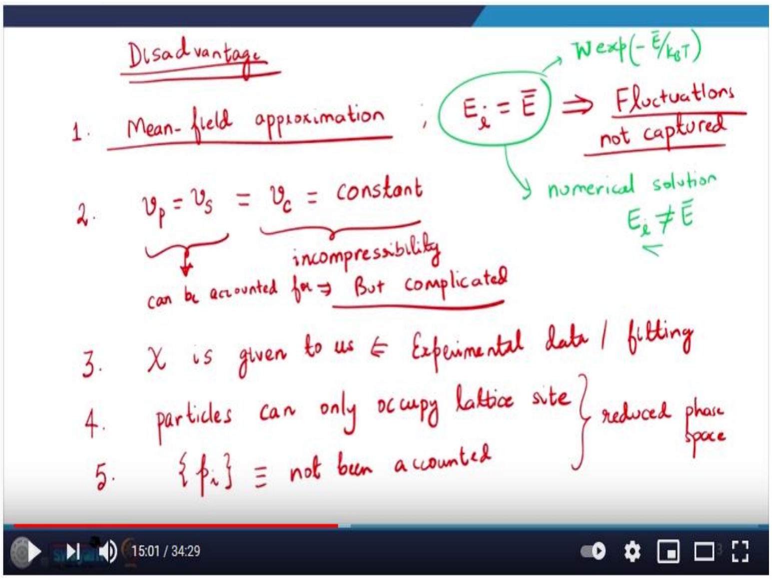

Disadvantage

1. Mean-field approximation ; $E_i = \bar{E}$ $\Rightarrow$ Fluctuations not captured

$W\exp(-\bar{E}/k_BT)$

numerical solution $E_i \neq \bar{E}$

2. $v_p = v_s = v_c = \text{constant}$

can be accounted for $\Rightarrow$ But complicated

incompressibility

3. χ is given to us $\Leftarrow$ Experimental data / fitting

4. particles can only occupy lattice site

5. $\{p_i\} \equiv$ not been accounted

reduced phase space

So, disadvantage really is from the assumption that we have made. So, the first assumption that we made was a mean field assumption or mean field approximation and that says that I did not consider all possible configuration because I did for the perspective of entropy but I did not consider in the perspective of energy I assumed that the energy of all the configurations I mean different arrangements of solute and solvent are the same and that is equal to the mean energy that is to say that my Ei is equal to some evidence value E bar and we estimated that and then basically we looked at the number of contacts in an evidence sense.

$$E_i = \bar{E}$$

And that is how we got the E bar value and once we have that we can get the partition in the entropy component of it. We did account for the number of configurations, but energetically we assumed that all the configurations have the same energy. So, clearly, this means that we do not have the effect of fluctuations in the model.

So, any property that is expected to vary with energy fluctuations such as specific heat for example is not being captured. That is the assumption in the model as long as the fluctuations are not so important or what we are interested in it is fine but nonetheless it is problem, I would say even in those cases because the accuracy will not be appropriate but in the cases where fluctuations are important for the description of property in that case, clearly the mean field will fail.

The second assumption that we made and not in the particular order that I described but that is consumption we made was that v_p that is the volume of the solute is equal to the v_p the volume of the solvent, and this is then equal to the volume of the site or the cell, and this is then equal to a constant and if you think about it, the last bit of it is coming from incompressibility. And the first bit is coming from the fact that we are assuming that the solute and solvent occupy the same volume.

So, we are basically disregarding the molecular structure of solute and solvent. Therefore the model is quite general. We are not differentiating between say an ethanol molecule and a water molecule clearly ethanol is with respect to be much larger in volume than compared to water. For the case of polymer solution, we said that we can divide the polymer into various small units, which will have the same volume as a solvent. So, there are ways to account for that in some sense but it is still going to be not very accurate.

We can also think of models which will have different sites for the solute and solvent but you can imagine, that is model will be going to be complicated. So, therefore these can be accounted for but that is going to be complicated. The whole idea why we started doing the lattice model was that the inherent simplicity we can get analytical solutions in the limit of mean field. If that is not happening probably the lattice model is not so much worth doing because anyway, it is a toy model.

The third assumption that we are making is that, the χ is kind of given to us and I was telling you that means that we have some kind of experimental data we are doing some kind of fitting exercise to get the value of χ or someone else has found it using whatever method that they are doing in the model itself. We do not have a way to find the χ value.

The final assumption in the lattice model, actually the first one when I was describing is that we are working on a reduced phase space. So, particles can only occupy lattice site and I can put the second term separately that the fact that the momentum value of particles can be different has not been accounted for. In fact, we have not mentioned the momentum anywhere in the development of the model, because what we have been looking at was only the configurational part of the partition function we are not looking at the distribution of momenta. I said that we can factor out that contribution from momenta but I did not tell you, like how to do that. At least it is not inherent in the lattice model. So, therefore we are doing a reduced phase space.

Now let us try to address these limitations one by one. So, the first one we have a mean field approximation and we said that my Ei is equal to E bar. If you think about it that need not have been assumed, because inherent in the model is the fact that we have some ε interaction between different species ε_{pp}. ε_{ps} ε_{ss}. So, within the lattice model framework if I know the configuration I can find the energy value. And clearly that energy value will be different for different states. The only difficulty then would be that if I want to address this then we will have to go for a numerical solution because the simplicity is kind of lost there in this particular case, we were able to the write our partition function as something like that is not going to be possible in this case we really have to sum over the various possible configurations and that is clearly going to be more complicated and you may imagine that we will need a numerical solution.

So, within the context of the lattice model is still we have a way to find the Ei value but that will not give me as simple solution that we have got within the mean field approximation, but that is not really the main concern as we can discuss.

The next concern is right here, I was telling you this can be accounted for by doing a more complicated lattice. This part in fact is even though there can be liquids which are not incompressible. I mean, in if I want to put it correctly all the liquids will be compressible but the amount of the compressibility will vary. So, gases, of course are highly compressible the liquids are less compressible that means the density changes in the gas with, for example temperature are going to be quite significant, but it is going to be quite a small for the case of liquids and so is true with pressure and so on. So, that is not really a big concern so as to speak as long as we are looking at a liquid. If I want to simulate a gas, then, yes then of course, we have to be concerned. If I want to for example look at the transition from a gas state to a liquid state, that means we are looking at some kind of a phase transition then this is a concern and this has to be accounted for then also we can think that we can do because I assumed that my every site on the lattice is being occupied by the solute or solvent that need not have been assumed we can assume that some sites are empty kind of vacuum between the two molecules that is still a possibility even if we want to consider a gas within the context of a lattice model that is also not a big concern.

The last two are the ones which should be of great concern to us- First of all, we are doing on a much reduced phase. So, clearly we are not sampling all the possibilities by constraining the particles to the lattice site, we have really made a big assumption in terms of the entire physics by which the particles are moving. And the so is true for the value of χ because first of all, I have assumed that the interactions are only between the neighboring particles that also in some sense we can relax by assuming that I will consider interactions between the next nearest neighbors and so on but it is going to be complicated in the context of lattice model but even then, even if I assume interaction with the next nearest neighbors or let us say all the molecules are particles in the lattice, even then the fact, that the particles are constrained would mean that my interactions are not being captured well and clearly the moment are not being accounted for.

So, let us try to argue that all, this thing can be addressed when I am doing a molecular simulation and of course that is going to set the ground for what I will discuss in the next week, that is the Monte Carlo simulation and the following weeks when we discussed the molecular dynamic simulations.

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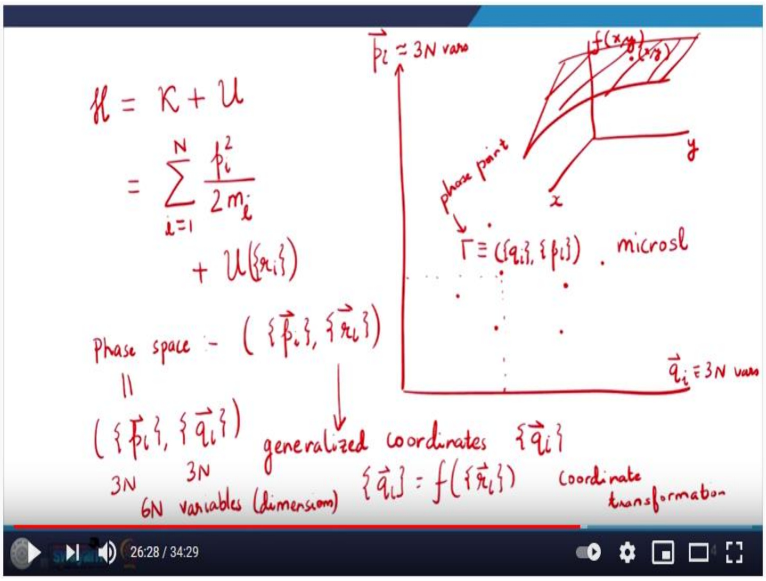

So, I want to return to the picture of the phase space. I said that the Hamiltonian that represents the energy of the system has two components the kinetic energy and potential energy. I can write the kinetic energy as sum over all the particles in the system, the momentum squared by twice their masses and I can write the potential energy as some function of the coordinate’s r i.

$$H = K + U$$

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + U(\{r_i\})$$

So, therefore we can imagine that we have a phase space formed by these momentum values and these coordinates by the way, when I talk about coordinates, although I always tend to draw a Cartesian kind of coordinates or Cartesian plots. It does not really matter if I work in cylindrical coordinate or is spherical coordinate. In general, we can replace this with something like a generalized coordinates $\{q_i\}$ and by the way all of them are vectors, which would then be in any coordinate system we are working with and the reason why we could do that is because different coordinate systems are related by coordinate transformation. So, yes the $\{r_i\}$ values and the $\{q_i\}$ values, let us say if I compare the Cartesian and cylindrical coordinates would be different. But they are related still by some kind of coordinate transformation.

$$\{\vec{q_i}\} = f(\{\vec{r_i}\})$$

So, you can always write the coordinates in any coordinate system as a function of the coordinates in the Cartesian system by some sort of a coordinate transformation. So, let me represent the phase space in general as something like the momenta and the generalized coordinates.

So, H is going to be a function of these variables and how many are there? So, for n particles, we have n momenta value and n coordinate values. Now each of the individual momentum that is moment or every particle will have three components in three dimensional space. So, in total we will have 3N momenta in the three dimensional space and 3N coordinate in that give me 6N variables. We can also call them as dimensions, because the Hamiltonian depends on the 6N variables. you may imagine that the function of 6N variables and I want to plot this function. So, for 1 or 2 variable it is still very intuitive to plot.

Let us say for example, we have a function that is a function of x and y. So, let us say there is some function of x and y. How will I represent that so I can plot f of x y in on one axis and x and y on the other two axis. And this function is then going to be some surface in this plot, in this 3 dimensional plot. Now, you may imagine that function is a function of 6N variables. So, how many dimensions we need? We need 6N dimensions and clearly beyond 3 dimensions. I can no longer plot on board.

So therefore it is important to develop some kind of representation of that sixth and dimensional space and let us try that. So, what I would then say is I would represent the momenta along the so called y axis and the coordinates along the so called x axis. But then this is some sort of a representation of 3N variables and this is a representation of 3N variables. So, we should not think of it as a 2 d plot, as it looks like on board we are simply drawing a 2d plot because we cannot draw a 6N dimensional plot.

Nonetheless if I look, at any point on this particular plot that would correspond to a particular value of the momenta and the coordinates. So, a set of coordinates and set of momenta will give rise to a unique point on this 2d plot or a unique point in the 6N dimensional space. Just like a point on this plot give me a unique value of x and y.

So, therefore if I have to represent the phase space, this is one way of doing it. And always keep in mind that this is not no longer a 2d plot that we are used to, but nonetheless every point on the plot represents a unique value of the set of momenta and a set of generalized coordinates and this point is what I would then represent as some term γ and I would say it is a phase point.

So, therefore a phase space is actually a space of this phase point, which are every point is a set of the generalized coordinates and a set of momentum value. So, now if I go back to the idea of ensembles that I have been discussing you will note that every microstate in any of the ensembles that we discussed corresponded to a given set of momentum and a given set of coordinates. So, every microstate has a unique value of the momenta and the coordinates. I mean the entire set is unique. So, individual momenta can be same between the two microstates but the entire set of the momenta and generalized coordinates will be unique for a given state.

So, therefore this phase space in some sense is representing the microstates of the system. So, if I look at the; system, so if I look at any molecular system at any given time. I may have a particular value of the momenta and the coordinates and that will correspond to a point on this particular plot, I have drawn that will be a phase point γ . So, γ will represent state of the system at any given time and that will clearly, will change with time. So, if I take a picture at say 10 different times or at 10 different locations, I will get different values of γ because the coordinates and movement are changing way to, often then we can imagine because we are dealing with molecular systems. They are experiencing collisions, the molecules are moving and so on and so forth. So, the γ is really a dynamic variable that keeps on evolving as a function of time and as a function of space so as to speak.

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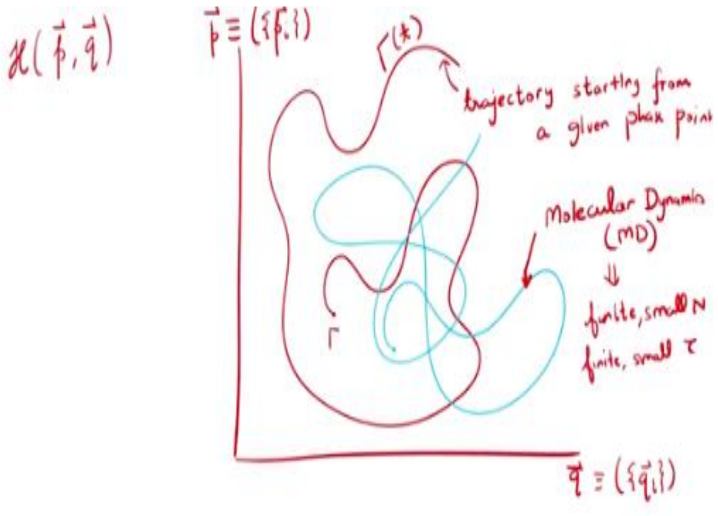

So, then, what we can then say is, if I start looking at any of the system from at any particular time at any particular location or whatever I am always starting with some particular value of γ and then this γ is changing with time. So, you will have some sort of a trajectory starting from a given phase point. And we can call the trajectory some γ as a function of t.

So, now if I start with some other state, let us say if I start from here I will have some other trajectory but nonetheless the key point here is that if I can study all possible trajectories starting from all possible states of the system. So, going back to the idea of ensemble, we said that we have some a states and ‘a’ is really a large number. You can imagine that is most infinite right but if we can hypothetically speaking if we can start from each of those states and, If I can run the some kind of a simulation for very long time and that simulations if it captures the γt as it evolves we will therefore have a clear representation of the system dynamics and since; my Hamiltonian is a function of this p and q. I am writing in a compact notation now because p is the set of pi and q is the set of qi. So, always keep in mind that this p and q are 3 and 3 and variables each.

So, if I know the p and q value, I know the Hamiltonian. So, I know the energy of the system and if you recall that all that goes in our thermodynamic apparatus of the ensembles and so on because once I know this then I am pretty much done because I can then figure out the energy in different states and using the energy value I can then find the average energy I can define the partition function depending on the ensemble, you will have different partition functions and then once we have that then we can find the properties of interest.

So, in the end although that hypothetical picture that I was telling you of counting all the trajectories is looks to be very difficult to do are the most impossible to do, if we are able to do that, then we will have the complete thermodynamics of the system that we are considering. And it is it turns out that even though that particular thing that I mentioned is not quite possible of starting from every possible state and looking at the trajectories what is indeed possible is I can look at one of these trajectories. Let say if I focus on this guy I can do this for a reasonable amount of time, this is what we do in a Molecular Dynamic simulation that is an MD simulation.

So even though we cannot do starting from all possible state for one possible state for a finite amount of time, we can clearly do that. I mean, that is the capability that computers currently have and of course whenever I say that I am also saying for a finite this small value of N but for finite small time for finite small, value of time we can simulate this starting from one particular state.

Now the question then is that starting from that particular information of a trajectory that has started from one of those states or that information of one of the trajectory out of all possible trajectories what we can then infer because even in this situation we are not in a sense capturing the entire phases.

So, the reason why we set out doing this was because the lattice model was not capturing the phase space but even after doing this we have so that yes we can do MD but since there are too many states and infinitely many states doing all this all of them is not possible. So, at least one of them for a given amount of time, I can do. So, is that any better than the lattice model and the answer is yes and the reason gets into because not only we can do that but we can also account for the interactions in much better sense while doing that it is not like a lattice model where I had assumed that there is interaction between only neighboring particles. We can account for interactions in a more general sense in this particular framework.

So, I would like to stop here. In the next lecture, we will discuss the I would say a very basic framework of molecular dynamic simulations and then I will try to compare with a basic framework of the Monte Carlo simulations and in the following weeks, we will first discuss the Monte Carlo simulation is in more detail because that is somewhat simpler to think about and after that we will discuss the molecular dynamic simulations.

So, with that, I want to conclude here, thank you.