Advanced Thermodynamics and Molecular Simulations
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Lecture - 31
Interaction Energy and Force Field

Hello all of you, so in the last lecture we have been discussing the molecular dynamic simulation method and finally we have been discussing the interaction forces and energy between the system.

Today I will take the discussion further and discuss first the interactional energies in more detail and then finally we will come to the Monte Carlo simulation. Before I go further, I want to emphasize that the interaction energy and forces that we have discussed the same idea applies also in the Monte Carlo simulation method because this is what represents the system, so the interactional energy part of the discussion is not really particular to the molecular dynamic simulations.

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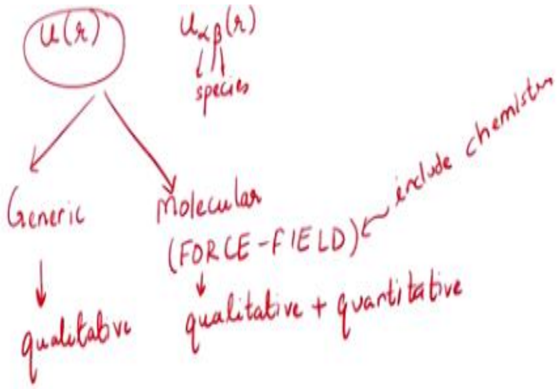

So, I was telling you that ultimately it comes time to finding the interaction between the particles the u(r). I know the mathematical form of that for one component system this is what we are interested in if we have a multi component system. We can find $u_{\alpha\beta}$ (r) where α and β refer to species.

So, let us say if I look at a solvent solute system like a solution, you will have something like ‘u’ between the solvent and solute similar to ε_{ps} in the lattice model ‘u’ between the solutes similar to the ε_{pp} in the lattice model and ‘u’ between the solvents that is similar to ε_{ss} in the lattice model. But this is much more general because now I am accounting for the all possible variations in the separation. In the lattice model, we assumed that the separation is fixed so as to speak because the interactions only occur between the neighboring particles. So, that is only I would say a poor limiting case or the more general scenario because for most interactions, it is not applying only the neighboring molecules or neighboring particles and secondly the particles are not going to be constrained at that particular location. So, by doing that, we have really moved off lattice as to speak by off lattice I mean that now I am doing in a continuous kind of a space. So, what will that interaction look like?

So, there are two ways to think about it. The first way to think in like I would say a more fixed oriented way of what are the possible forces that may possibly adjust and what those forces will give in the form of u of r. The second way is to look at the chemistry in more detail and try to figure out what will be the energy between say a particular species say ethanol and water then we are worried about the chemistry of it and of course that also has to come from the fundamental forces of physics, but then, we are also considering putting the chemistry into consideration and trying to find which chemistry will give rise to which kind of forces.

So, these two ways, I will classify as some sort of generic representation versus kind of a molecular representation the latter is typically referred as force field. So, if I am including chemistry that means you give me a compound and I need to have some mechanism to tell you what are the forces between them or what is the energy between them that is what the force field does, in the generic case, I am only telling you what will happen if the interactions are say coulombic or the interactions are say of the nature of Van der Waals without any regard to a particular system under consideration so, all the systems which are coulombic or ionic will saw that kind of a behavior. So, clearly the generic kind of an approach will not give you accurate predictions when it comes to comparison the experiments but the force field approach where I have including the chemistry will give you the prediction that is more accurate quantitatively. Nonetheless the qualitative picture is captured here as well so, I can see the first approach captures the qualitative picture and the second approach captures both qualitative and quantitative picture.

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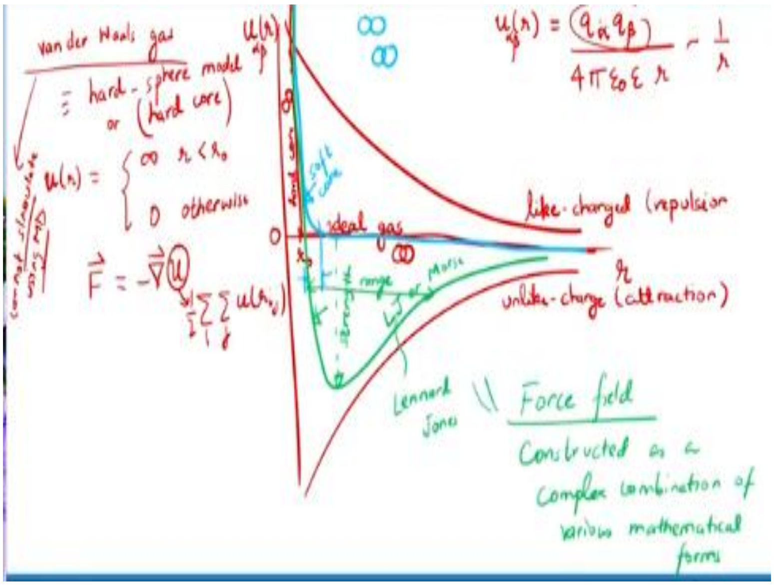
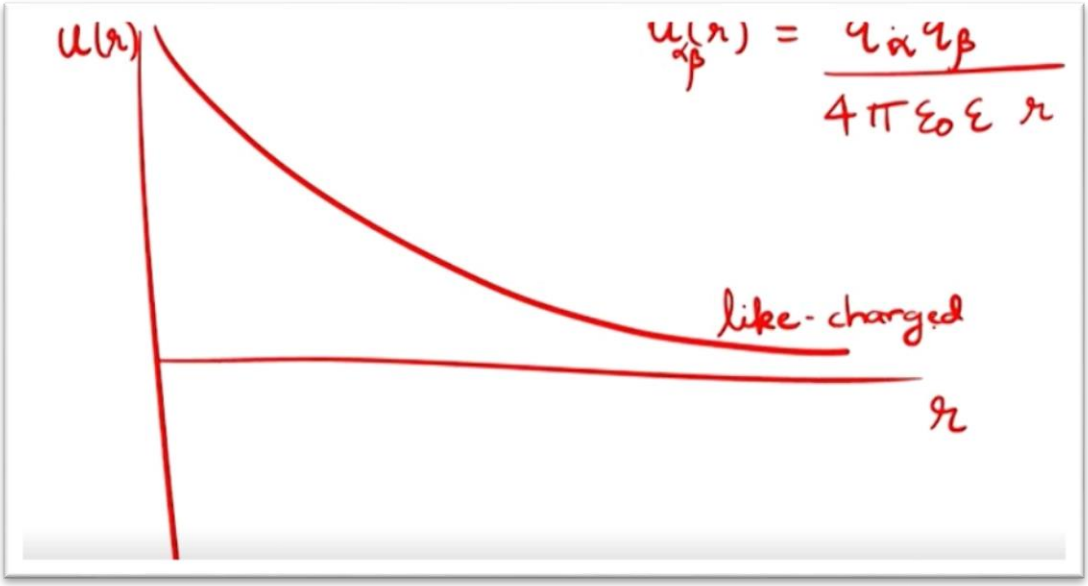


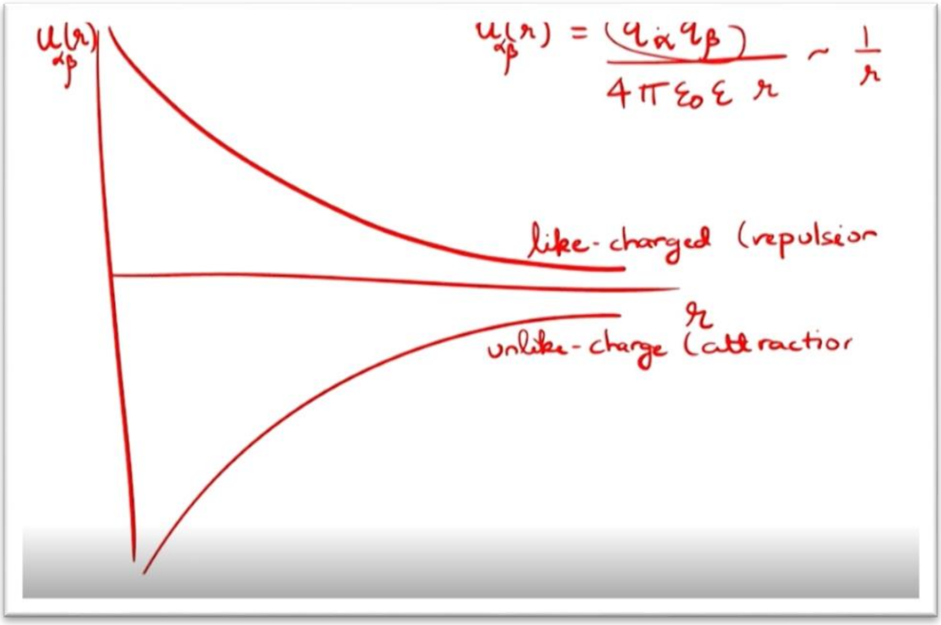
So, let us look at the generic approach to begin with. So, we know for example that, if the columbic interactions are present in the system and we are considering like charged species. So, one component system all the species have to be having the same charge. In that case, there has to be or repulsion between them and the repulsion will give rise to a positive energy. So, columbic energy is represented as something like q_α. So, in general for $u_{\alpha\beta}$, I can write-

$$u_{\alpha\beta} = \frac{q_\alpha q_\beta}{4\pi\varepsilon_0\epsilon\, r} \sim \frac{1}{r}$$

It will look like something like this for the like charged species.

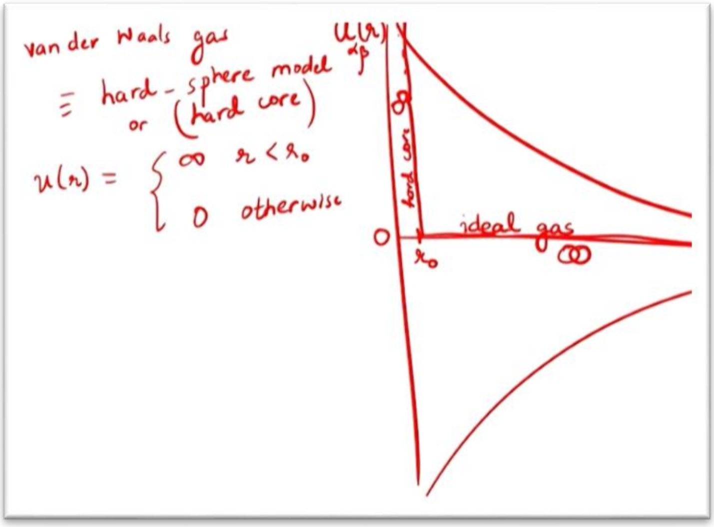


Since I also want to consider the case when they are unlike charged let me put that as something like $u_{\alpha\beta}$ (r) that is I am concerning a multi component system. So, for unlike charge clearly this is going to be negative. So one of them will have positive charge and one of them will have negative charge and in that case we will have attraction between them so this is a repulsion and this is an attraction. So, I have only showing the shape here, of course the magnitude of that will going to change as the charge is changed. But for the sake of like the mathematical form of it this is what it will look like.



Next or I would say when before what we have been discussed we can consider an ideal gas. So ideal gas will be what? Ideal gas is when there is no interaction. It will follow along this line where irrespective of separation there is no interaction whatsoever between the two particles in the system. Then we can consider a Van Der Waals gas or Van Der Waals model and I was telling you that only difference between the Van Der Waals and the ideal gas model is we do not allow the particles to overlap or we are assuming that the particles have a finite size. So, that really limits I would say in an ideal gas this can happen but in a Van Der Waals gas all that could happen is something like this they can come in close contact, but they cannot really overlay. But beyond that as long as they are not contacting there is no interaction whatsoever, so what will that look like?

Since the overlap is restricted what this means is let say if I represent some r_o as the overlap distance then for the values less than this r_o this is going to be like infinite. So, it will be like, pretty much like this and why is that- this is so because once the interactions energy becomes infinity the particles will not overlap because ultimately the system wants to go towards lower energy state. So a positive energy and a positive high energy is something that the system will not like to have so as soon as the, we are less than r_o energy goes to infinity. So, I can say for the Van Der Waal model for the Van Der Waals gas by the way, the model itself is called a hard sphere model that is to say that we assume that there is hard core. So, as to speak, so, hard core is the word that is more common in molecular simulation literature for this particular model the u (r) has the form infinity when r is less than r_o that whatever the overlap distance is when they the close contact distance and 0 otherwise. So, this becomes my hard core model and of course beyond this point it is going to be following the ideal gas like behavior.



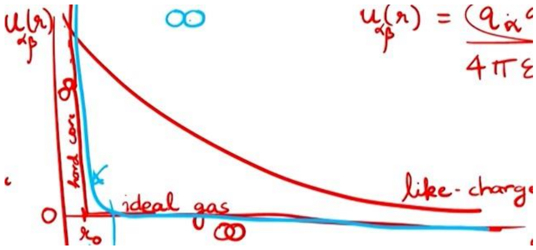
Now there is a problem in this particular function and the problem is let us say if I am using it for molecular dynamics. I have said that the force is given as the gradient of this u-

$$F = -\vec{\nabla}\, U$$

$$U = \frac{1}{2}\sum_{i}\sum_{j} u(r_{ij})$$

This capital U this guy that is total energy of a system that has to be a smooth function without any discontinuities whenever there is continuity then the gradient is not defined. So, therefore what it means that I cannot simulate using MD because in MD we need to find forces and since the function is discontinuous we cannot find the gradient and therefore the forces cannot be evaluated and therefore we cannot do MD we later on we will show that we can still do a Monte Carlo simulation because it approaches the problem a bit differently in terms of energies as opposed to forces but at least MD cannot be done.

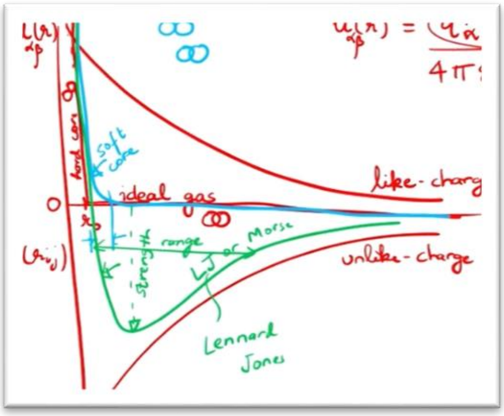
So, instead of that, I mean what difference, will it make in terms of the qualitative behavior if I represent a function that is very close to the hardcore but is not discontinuous that is smooth function. So, I will draw a function that will look like something like this for example so, instead of like having a discontinuity at r_0 it is kind of like going smoothly to 0 and this is still a very small distance. What this means physically is that it is not that I do not allow overlap but as soon as the overlap starts to happen I will have strong energetic penalty as opposed to saying that you are either having 0 interaction or infinite interaction when they come in contact we can say that it is going from 0 to infinity or very large value a bit slowly then having a discontinuous jump. This is what is referred as a soft core interaction that is still repulsive but since it is a continuous function we can use that MD for that. There are small subtle differences in the behavior for this cases but qualitatively there is not too much change in the in the behavior going from hardcore to the soft core model. That is why we typically prefer a soft core model. I will not discuss the form of the potential light here, but keep in mind that this is what the functions will look like.



Now in reality there can also be some other interaction apart from the overlap thing that we have discussed in general, let us say if I am considering the liquid or even for meaning gases, you can have some attraction between the particles at sort distances, you may have some short range interactions. Let us say water molecules, so water interacts with nearby water molecule with a hydrogen bond, hydrogen bond is not as strong as a coulomb interaction but nonetheless it is there this good this gives rise to a negative energy so as to speak and that has to be considered and the fact that both the magnitude is small and the range is small both has to be taken care of. So, in general, one of the most common potential is what is known as a Lennard Jones potential and I will discuss that later in the course. There are other potentials that also achieve the same thing that is called a Mohr's potential.

And we are simply discussing the mathematical forms right now why I am using one why I am not using one is something that we can take on a case to case basis. So, that potential I can represent whether it is a Lennard Jones that is called L J in literature or Morse they have slightly different mathematical forms. But one thing that is common in both of them is they still have no overlap, the particles cannot overlap but they have some short range attraction just like water molecules, two water molecules cannot overlap, but at shorter distances they can form hydrogen bonding.

So, therefore it starts from almost close to infinity at very small values of r then goes negative by negative it means that there is some attraction and this depth of this kind of a well represents the strength of the interaction and this broadness of the plot represents the range of the interaction and using various potentials we can control both of them. So, if I know what is the range in which the interactions are active or interactions have significantly large value then using that information I can construct some kind of a potential that captures this particular behavior.



So, this is an example of the generic kind of models we can build and this is already good enough because if I start thinking from the lattice model that was starting, there we simply had one parameter ε. And there was no control on how the interactions are varying with distance that has been taken care of here and qualitatively it is not very difficult to figure out which kinds of interactions are active in a system, at a qualitative level we can see if the molecules are charged or the atoms in the molecules are charged then there can be a coulomb interaction between them. In fact it turns out that coulomb can be present even within neutral molecules I will come back to that point later but if it if they are charged the clearly there is coulomb interactions, we can expect a Van Der Waal interaction to be present for most liquids, they can be short range attraction that I can represent using Lennard Jones or most potential or some other potential and if it is I want to study the behavior in the ideal gas limit or for the gases we can go for a soft core if I want to do MD simulation. And this will already give me the behavior for a large variety of systems still not considering the I would say the chemistry in any kind of a detail, but considering all possible kinds of behavior that one can obtain that is why I said it is more physics oriented so as to speak so this is a very much possible.

Now let us come to the business of the force fields. Let us say if I am thinking of a force field, what will that entail? The force field should also capture the qualitative behavior that I have described here, but there can be a complex combination of various kinds of interactions. For example there can be electrostatic interactions between some parts of the molecule with some other parts further molecule, there can be Van Der Waals interactions between some parts of molecule, there can be behavior akin to and a soft core there can be a behavior akin to a pure coulomb interaction all this possibilities can happen.

So, a force field is actually constructed as a complex combination of these things the combination of various mathematical forms. Now how will I get that mathematical form? There are two ways to get that. First of all I can again do experiments I can assume some mathematical form of force field. I do some kind of fitting just like I was telling you for the χ in a similar way I can fit the parameters of the force field and I can get the course field for the system. It turns out that most of us do not have to do it most of us working in the application of the molecular dynamics or Monte Carlo simulation can benefit from the force field development efforts that has already happened since like last 20 30 years. In fact, there was a noble prize coming from a group who has developed a force field.

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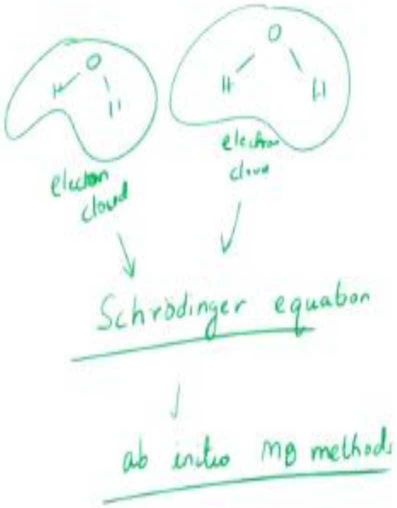

So, this has been there are force fields of various names and I will come back to that when I discuss the molecular dynamics, who are doing this fitting exercise and they will tell you that for these kind of molecules with those kind of molecules use this kind of force field. So, there are prescriptions so in some sense the force fields are still empirical if we are doing some kind of fitting exercise. So, why do I have to do a fitting is the question that you can we can try to answer.

So, if I think of like actually at a molecular level the forces between the molecules really have to think that every molecule is some sort of an electron cloud. If I really zoom in and are able to see the molecules let us say when two water molecules we are in fact dealing with interaction between two electron clouds there. If I really want to find the interaction between these two electron clouds what I should do is I should solve the Schrodinger equation because the whole idea of considering the interaction at the level of electrons and protons and so on that comes in the regime of Schrodinger equation. So, ideally we should solve Schrodinger equation, find the interactions and feed that into molecular dynamics.

In fact that is exactly what is done in what is known as ab initio method, ab initio molecular dynamics method. Now it is not very difficult to imagine that is going to be a very complicated exercise. So, I want to simulate a large relatively large thermodynamic system the Schrodinger equation is already complicated even for very simple molecules the whole quantum chemistry as of now can only work for very small systems. So if I want to take that approach to like slightly microscopic system or systems contain large number of molecules, then it is going to be a very cost consuming affair and therefore even though the ab initio methods are in principle the correct way of doing it, they are not typically employed in molecular dynamics instead what people do is they develop this force fields and force fields are developed earlier of mostly using exponential data but now they are also using some small quantum chemistry semi simulations for smaller systems and using that to parameterize or to fit the force field equations. So, these can be done and these will then include the effect of the chemistry of the molecules. It just turns out that it is mathematically more involved and therefore numerically more involved than compared to the generic method that I have been discussing. So, if you go back to the literature, the generic methods are the ones that have been used. I would say a lot in the initial era of computers the molecular methods starting from a force field even if it is empirical force field have come a bit later and right now we are at a stage where we can do at least for a small systems, ab initio simulations.

So, keep in mind that whenever we say that we are using an empirical force field or we are even generic model we are still not in a fully predictive kind of a method. The method is not really first principle when I am doing quantum mechanics the method is the first principle method we give me a chemistry I will give you the behavior, in molecular simulation the method is not completely first principle, because the force fields are trained using experimental data. If they have been trained using quantum mechanics simulation data, then we can still say as first principle that approach is coming up now but if we are using experiments to train the force field it is not completely a first principle method nonetheless it turns out that once I have the force field under given conditions that really works pretty well for a variety of conditions. Let us say if I now vary temperature or I vary the composition the force field have been shown to be efficient in a multiple of the scenarios.

So, it is just that there is now a transition from getting the generic behavior to an emphasis more on including the detailed chemistry and the molecular approaches aim to do just that. So, I want to complete the discussion here what we will see in the in the next few lectures is that I can use the same interaction potentials in what is known as the Monte Carlo simulation that really is a very attractive alternate way of doing MD first of all as I already hinted I can for example do hardcore interactions but that is not the key idea or the key benefit of the molecular, the Monte Carlo simulation.

The key benefit is it tells me a better way to sample the phase space because if you recall I started with saying that the molecular dynamics is starting from one state point and doing the trajectory for a limited time. So in a sense we are looking at only a small portion of the large phase space and Monte Carlo gives me a better way to sample the phase space but the key idea that we will borrow from the discussion that we have already done is that the Hamiltonian is not going to change the description of the phase space is not going to change the interaction potentials or the u of r are not going to change, the fact that we can do a generic simulation or a molecular simulation using force field that is not going to change. What will change however is how exactly the simulation is being conducted? How exactly are we moving within the phase space? And in the molecular dynamic simulations we have used the Newton's laws of motion to evolve the system and in Monte Carlo you will see it is based on a completely different idea, but still gives the same equilibrium behavior as the molecular dynamic simulations.

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