Advanced Thermodynamics and Molecular Simulations
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Lecture - 30
Theoretical Basis of Molecular Dynamics Simulation

Hello all of you. So, in the last lecture we have been discussing the theoretical basis of the molecular simulations and how the molecular simulations can address the challenges that we saw in the lattice model. So, today I will take it further and discuss about the molecular dynamics approach in a little bit more detail and I will focus more on, how do we capture the interactions and after that in this the following lectures we will be discussing how can, we think of another method that is the Monte Carlo method of the simulations that essentially captures the same kind of thermodynamics behavior.

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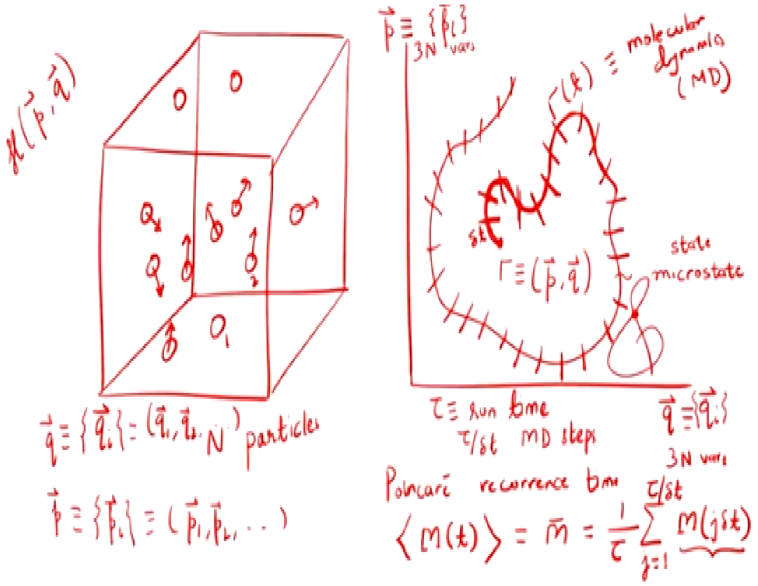
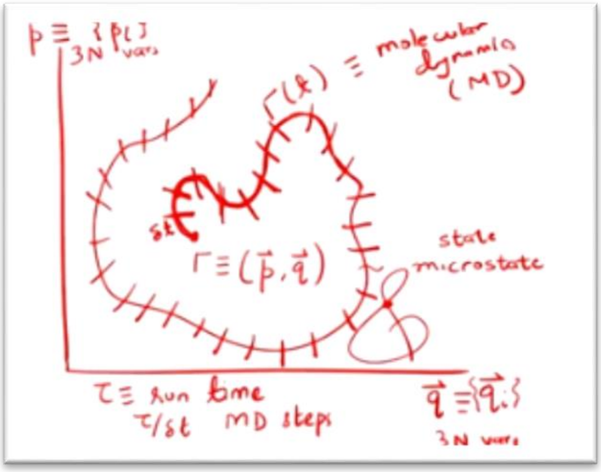


So, just to quickly recap what I have been telling in the last lecture is, we can think of the phase space as the space formed by the momenta of the particles and I used a collective or compact representation P for all the momenta of all the particles and all the coordinates of all the particles. These are 3N variables, these are 3N variables. The only reason I am doing a 2d plot is because I do not know how to do a 6N dimensional plot that simply impossible and then I said that I can represent a phase point as some γ that represents the state of the system at a given time in terms of our ensemble-based idea that is kind of a microstate or we can refer as state.

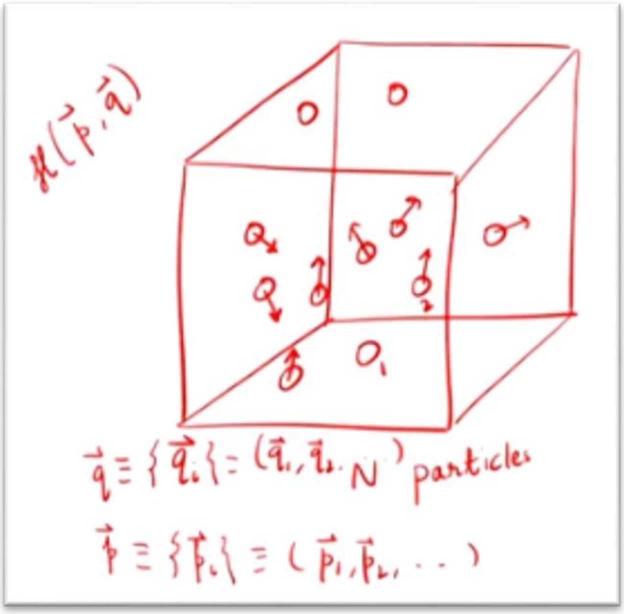
And then I said in reality, this is all the information that we need if I know what is the phase space since Hamiltonian depends on the phages space the P and Q we have the energy and we can do the all thermodynamics that we are interested in simply it is impossible to do that because it may imagine there are infinitely many trajectories in starting from infinitely many state points which are possible out there but what is possible and that is what I was starting to claim is the starting from a given state point or few state points. I mean, I can do simulations from various configurations and look at the trajectory of that particular state. And this is when I am looking at this γt is the basis of the molecular dynamics or MD simulation.



So, although I have drawn the trajectory here we should not confuse this with the actual motion. So, I am not saying that the molecules are moving in this way or the system is moving in this way. This is a trajectory in a phase space that is formed by the momentum and the coordinates there is not very intuitive to look at the shape of the trajectory and make any clear inference starting from there. So, keep in mind that the trajectory is there using that I can infer information and there is whole mathematical apparatus for doing that but as it is shape of the trajectory is not too much to worry about right now because it is not very intuitive on the shape that we can we can say anything is happening.

So, then let us see what we will then do in the molecular dynamics? How will we make it happen? How will we get γ (t)?

So, what I will do is- I will start with the system that is typically done. I will start with the system of certain number of molecules and I will place them in some kind of a box. So, these are the molecules or particles in the system and there are N of them and all of them are essentially moving and it is their generalized coordinates that can be any coordinate system or q and their generalized momenta that is p that is essentially a collection of q1 q2 and so on and p1 p2 and so on if we have labeled the particles in any particular way.



So, they are evolving and therefore if I look at the evolution of the system, we are essentially evolving using the definition of Hamiltonian that is a function of p and q and at any given time you will have a particular value of p and q. After very long time and there is a name for this it is called Poincare recurrence time the molecules may come back to the same configuration but imagine that for a large number of particles that is not really going to happen. So, if you are interested it is called Poincare recurrence time that is when you can revisit a state or in terms of our trajectory kind of logic it may be something like that. So, whenever we cross the same point. So, we are revisiting the same point in the trajectory and when that is happening when like intuitively you can see from diagram it is happening but in reality, since we are running only for a finite time that will seldom happen for very large number of particles.

So, after so much time it may come back but essentially for all we care we will have unique states of the system corresponding to different value of p and q for most of the time. So, let us say we have a mechanism to evolve this and I will come to how to do that and let us say we are able to find how this γt is changing with time.

Now you may imagine that if I am having some kind of an analytical expression then clearly, I can solve in this continuous domain along the trajectory, but any kind of numerical method will not be quite doing that. So, essentially what you will be doing is solving for small time points. And using those time point values we can then infer the trajectory that is nothing to do with molecular dynamics in general whenever we have doing things numerically, we always have to discretize the domain or the where the motion is taking place, I am moving in the phase space here. So, the motion is not like a trailing emotion, but nonetheless you will be typically solving for a finite intervals of time, let me call that some δt.

So, then I can since at every phase point using the Hamiltonian, I can find the properties and let us say I am interested in some property M of t this can be anything. So, let us say at every time point I can evaluate that then if I take the average value of that this will give me the average value of to property of interest that I am working. So, essentially in our logic this is going to be something like-

$$< M(t) > = \frac{1}{\tau} \sum_{j=1}^{\frac{\tau}{\delta t}} M\,(j\,\delta t)$$

What I am doing essentially here is let us say if I am running for so τ is my total run time of the simulation, so then I will be making τ by δt MD steps that will correspond to different lines that I am drawing here. And for each of them I will be computing the property value and the time value is j multiplied with delta t. And if I sum over all the property values and divide by the total time, I will get the basically arithmetic mean of that. And this is what I will represent as the average of the particular property that I am interested in this is I would say, the basis of the molecular dynamics. Now try to see how exactly I will find the Hamiltonian.

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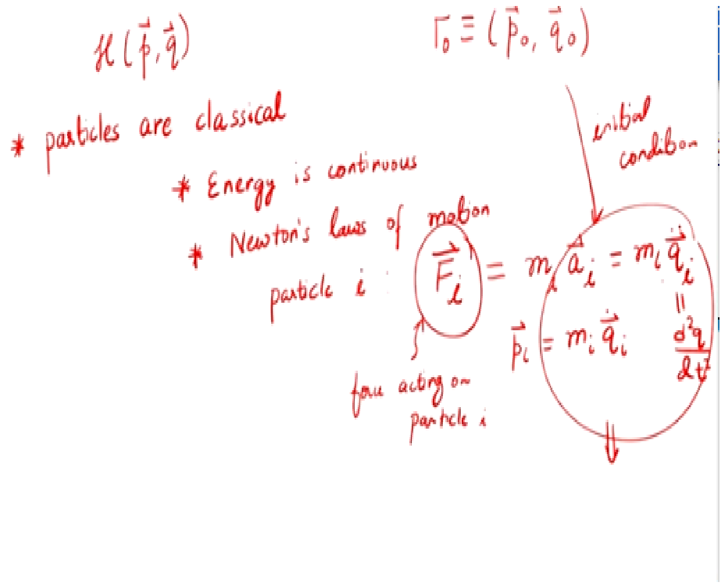

So, essentially scheme goes like this-

$$H(\vec{p}, \vec{q})$$

So, I assume that the particles are classical and by classical means several things here. First of all, whenever I say the particles are classical that means they are moving like say a typical example of balls or the pieces on a carom board. So, when that is happening, so one of the things that is an outcome of classical mechanics is that the energy happens to be no longer quantized and quantum mechanics, the energy is quantized in classical mechanics, there is no such thing. The energy is like really continuous in fact, quantum mechanics is what is valid for a very small scale if I really go to within a molecule or a smaller scale then it is indeed true that the energy is quantized but if the total energy is very large in comparison to the quantum units then in that case that assumption is barely important. Let us say if quantum unit or one quantum corresponds to something like one in some unit of energy. And let us say we are dealing with billions of that energy units. Then in that case the fact that energy is changing in the units of 1 is barely important because the energy unit is so small in comparison to the energy of the system.

So, that quantum mechanical effect vanish in the regime of classical mechanics as long as we are dealing with much larger systems than compared to individual molecules what this also means is if the particles are classical then they have to follow the Newton's laws of motion. And what do I mean by the Newton's laws of motion, it is simply F = ma. So, first of all I can say energy is continuous and I will revisit this point in a minute and the second thing I am saying is in the particles follow the Newton's laws of motion. So, when the particles follow the Newton's law of motion, that is F = ma and that is true for every particle.

So, let us say if I look at particle i we will compute the force acting on the particle i and this has to be equal to the mass of the particle multiplied with its acceleration and both acceleration and force are vectors. In terms of our generalized coordinates or any coordinate I can write this ai as the second derivative of my qi. So, we can find the positions the first derivative is my velocity and the second derivative is my acceleration.

$$\vec{F}_i = m_i \vec{a}_i = m_i \vec{q}_i$$

$$\vec{p}_i = m_i . \vec{q}_i$$

So, then if I know the forces, I can know how the positions are changing with time. And I also know the momenta are because momenta is simply mass multiplied with the acceleration that is mass multiplied by qi. So, let us say if I start with a given value of p and q that means I start with given coordinates and momenta of the system. I know how they will evolve with time if I know the forces acting between the particles or forces acting on that particular particle at this moment.

Now we can discuss like what is the force acting on the particle i? So, Fi is the force acting on particle i. So, in terms of our space representation, I only note need to know my initial state γ_0 that will be corresponding to some initial value of p_0 and q_0. And that will be the initial condition for this second order differential equation because second this q_0 is something like-

$$F_0 = (\vec{p}_0, \vec{q}_0)$$

$$= \frac{d^2 q}{dt^2}$$

in the second order kind of a differential equation and we know the initial condition in terms of the momentum and the coordinates of all the particles.

So, we can do it for every particle in the system and then we know how the system is evolving. Now this kind of makes it clear why I used a δt why I use a discrete domain because we have solved being a differential equation so in a sense to find q or to find the momenta, we need to do some kind of a differentiation and integration. The numerical way of doing that is by discretizing the domain and that is what we have already done in the time space.

Now why do I say that we cannot solve it analytically- The reason being, that how we will I find these forces acting on the particle that is first point. And the second point is how many equations do I have to solve? So, let us say even if I know the forces by whatever means then this quantity essentially is meaning how many differential equations. So, you have this equation written for every each of the N particles in the system, so you have N second order differential equation for the acceleration and N first order differential equation for the momenta and clearly there are too many differential equations because we are dealing with N that is really large that is a thermodynamic system for 2 or 3 particles we can clearly do that this is how you do a multi particle system in classical mechanics. But as soon as the number of particles becomes large this becomes a very much interactable problem for analytical stuff and therefore, there is no way we can do that.

It is more important point because these forces are also kind of complicated. So, in a classical system the way we are used to seeing the forces are often external to the system. Let us say when the apple is falling from the tree then it is experiencing a gravity force and that is given by the mass of the apple multiplied by the gravity is the force is external to the system.

What we are dealing with are systems at equilibrium. So, that implicitly means that there is no external force acting on the system. In most cases where we will apply molecular dynamics in this case when we are interested in the equilibrium behaviour that is in the absence of any external force. The external force can also be accounted forward and there are whole set of methods to do that will briefly touch on that later. But for the time being let us assume that we are dealing we are interested in equilibrium, so the forces are not external. So, then the only way the forces appear in the system that I have drawn is because of forces between the particles of the system so every two particles will experience a force. So, try to look at that in a bit more detail.

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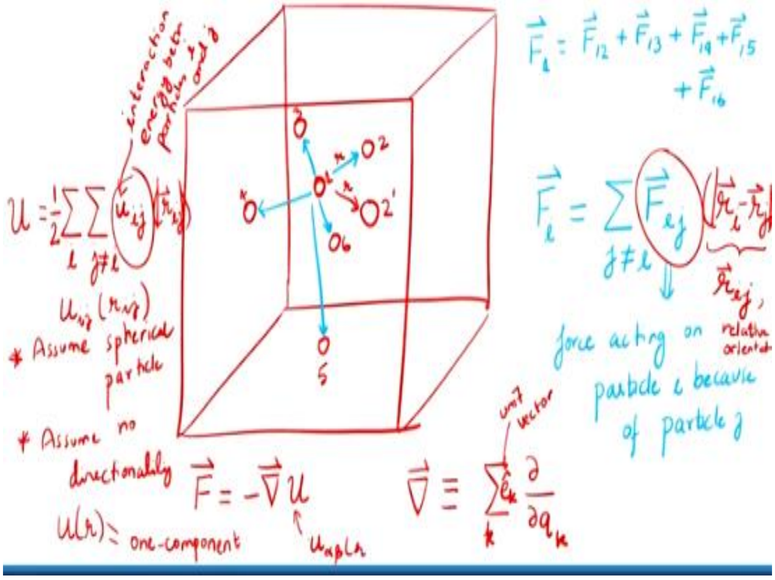
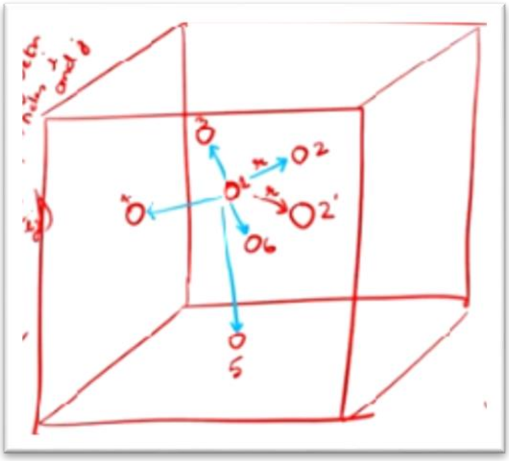


So, let say this is the big other particles that I am looking at right, of course there are too many of them. But just for the sake of drawing I am drawing only few particles. So, let us say if I am interested in this particle number 1 and there are others near labeled 1, 2, 3, 4, 5, 6 keep in mind the labels do not have meaning because the particles are in distinguishable but that’s beside the point for every particle it is experiencing forces from every other particle in the system.



So, if I have to find the net force on the particle number 1, it is going to be a sum of the forces because of every other particle in the system. So, let us say if I want to look at F of 1 that is going to be the force between 1 and 2 the force between 1 and 3 and the force between 1 and 4, 1 and 5 and 1 and 6.

$$\vec{F}_1 = \vec{F}_{12} + \vec{F}_{13} + \vec{F}_{14} + \vec{F}_{15} + \vec{F}_{16}$$

In general what we can therefore say is the force acting on any particle i in the system is sum over all the particles in the system. Let us label them j except that particle itself. So, one does not apply force on itself. If I sum over all the other particles apart from the particle i and find the forces between them we have essentially find the total force acting on this particular particle. So, F ij is the force acting on particle i because of particle j.

$$\vec{F}_i = \sum_{j \neq i} \vec{F}_{ij}$$

It turns out that instead of forces it is many a times more convenient to discuss in terms of the energy of these interactions and ultimately forces and energies are kind of related. The only difference is that the force is kind of acting on every particle. So, it is a well-defined thing to look at the force on every particle. Energy on the other hand is defined globally for the entire system.

So, there is not much meaning to look at the energy of one of the particles in the system, of course there can be defined. But in general, the energy is typically defined for the entire system that we have. But nonetheless the force and the energy are defined in this particular way. So, I can write my F as the gradient of the energy between the particle. So, at any point in the space if I find the gradient of the energy, I will get the system.

$$\bar{F} - \nabla U$$

So, u is defined globally for the system, of course that does not mean that u does not depend on the particle position you depends on that for a given configuration, you will have a given value of u, if I take the gradient of that that will give me the force acting at any point in the system. So, now it is defined in a continuous domain so as to speak. Because we are dealing with large number of particles, it is not really pretty important.

$$\vec{\nabla} = \sum_k e_k \frac{\partial}{\partial q_k}$$

we are k are the components of the coordinate the three-dimensional space k will go from 1 to 3 multiplied with the unit vector in the k direction. That is my gradient operator. So, instead of saying the forces acting on all, the particle I can then say that I can find the u of the system and what does the u of system come from?

The u of system come from the interactions between every pair of particles that means I will sum over all particles and for that I will again sum over all the particles, except the particle i. And I compute the energy of interaction let me use small u to represent the energy of interaction between particles i and j

$$U = \frac{1}{2}\sum_{i}\sum_{j\neq i} u_{ij}$$

This is the interaction energy between particles i and j and clearly when we do that, we will be counting every interaction twice because let us say if I count the interaction between 1 and 2 in this picture in the sum, you will have u 1 2, but then you will also have u 2 1. But both are representing the same energy in terms of forces they are acting on different particles but in terms of energy, it has to be counted only once not twice, because every interaction is only contributing once to the sum. So, therefore we need to divide this by 1 by 2.

So, now what will this u_{ij} or F_{ij} depend on- so, clearly you may imagine that as the particles come closer or farther.keep in mind that I have been trying to develop a generic representation from day one I did not say what are the interactions. So, let us say if the particles are coming farther or closer what is going to happen? The forces has to change it does not matter what forces are there. If it is columbic force, it is going to change the columbic force goes like inverse of the distance between them. If it is Van der Waal's force then also it is going to change. It is very into to see that the particles further apart have lesser forces and therefore lesser energy of interaction. And particles closer will contribute more energy or will have more forces. So, therefore this is going to depend on the r_i - r_j, that is the separation between the two particles i and j. I can call this something like r_{ij}. So, therefore, this will also depend on r_{ij}.

We will see later that we also may have to worry about the orientation of the particles. If we are not doing a spherical particle so something else may also come as an argument here let us say the angle between the two particles if they are not a spherical. But nonetheless that will also be changing as the states are changing. So, it is a function of the separation and it is a function of the relative orientation. So, you can say r_{ij}, relative orientation of the particles we can leave it for later because I am assuming that the balls are is spherical in the picture. So, in that case, the orientation is not so important.

So, going further what we can also say is that in most cases that one can imagine there is no directionality to the interaction, right? So, let us say, for example, you have 1 and 2 and they are let say here or here this is 2 was here as long as the distance is the same, we may imagine the forces are also going to be the same. It is not that the vector distance is important in fact, it is the magnitude of that is more important. This is not completely true particularly when there is some directionality to that we can also worry about that later.

So, assuming spherical particles and assuming no directionality that is true for most all the cases that we will discuss in this particular course. We can say that we will not worry about the vector distance will worry about the scalar distance. We can say we want to compute u_{ij} as a function of r_{ij}.

And finally, if all the particles are identical in the system then we can now say that all the particles will have the interaction energy with other particles changing by the same function, right? So, let us say for example, all the particles have the same mass same charge everything the identical particles in that case, you will not have different mathematical forms of interactions between them, right?

So, in general, we can write u(r) for one component system. If you have a multi component system in that case, you will define something like $u_{\alpha\beta}$ (r). But then the α β refers to my species. Let us say you have a species a and b then you will have u_{aa} u_{bb} and u_{ab}. So, you will have different mathematical forms for different pairs of species, not at the particle level but at the level of species for a one component system, you will have a single u of r. So, now the idea is how can, I represent this u (r).

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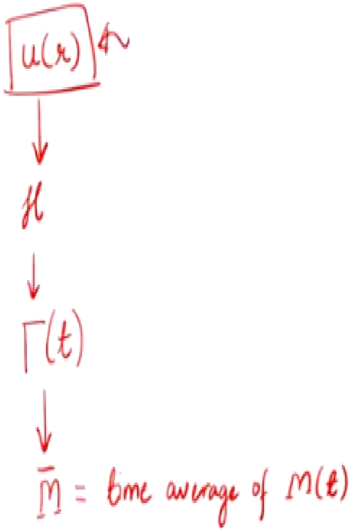

So, then to conclude the discussion, our objective is to find this mathematical form u (r) between every pair of particles or the pairs of species, whatever. Once we have that then we can find the Hamiltonian. Why I am saying that? Because once I have this small u, I can find the capital U and the kinetic energy is a function of the momenta. And momenta anyway, I can find in terms of the generalized coordinates. So, the only thing that we have to find is the energy of the system and the energy of a system will be characterized with this u (r). clearly, if I look at different states with different p and q values in that case the r will also change between every pair of particles.

And therefore, the energy will also change and therefore the Hamiltonian will also change but this is I would say the basic mechanism that we can think of right. And that is what is done in a molecular dynamic simulation. You give a feed or input value of u of r and I will discuss in the next class that what exactly it is called and so on that becomes the feed variable you find the Hamiltonian or energy and you solve the Newton's laws of motion and the particles evolve.

And you essentially have the description of the trajectory in terms of γ of t and once we have that then we can find the evidence value of the property I am interested in as time average of M of t. The next lecture we will discuss how can we estimate u of r or what are the ways we can represent this u of r.

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