Advanced Thermodynamics and Molecular Simulations
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Lecture - 32
Liouiville Theorem; Theoretical Basis of Monte Carlo Simulation

Hello all of you. So, in the last class I have been discussing the interaction energies or the potentials that we use in a molecular simulation and before that we have discussed the molecular dynamics simulations that is one way to sample the phase space.

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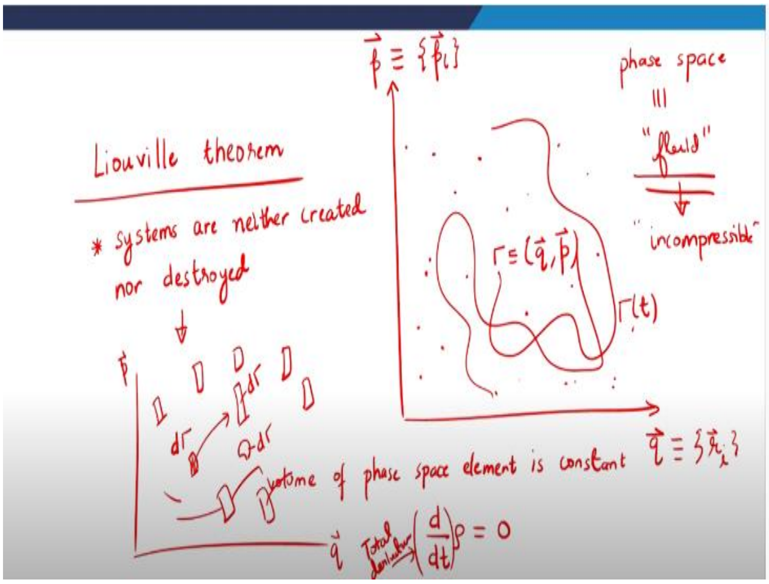


Liouville theorem

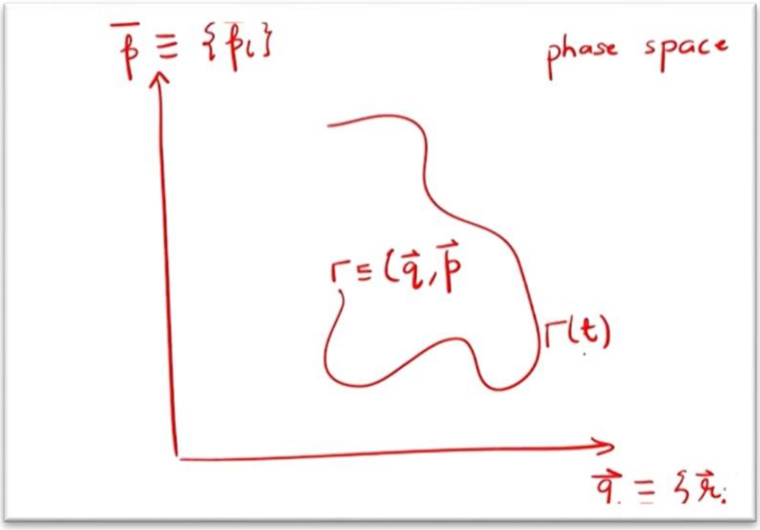
* systems are neither created nor destroyed

volume of phase space element is constant

Total derivative $\left(\frac{d}{dt}\right)\rho = 0$

phase space ≡ "fluid" → "incompressible"

So, today I will introduce the Monte Carlo simulation that is another way to sample the phase space or another method of molecular simulation. So, I want to go back to the drawing that we had of the phase space and we have said that I can represent the state of the particle on something known as the phase space where 'p' is the momentum of the particles and 'q' are the generalized coordinates of the particles. So, I can represent any point on the phase space as 'q' and 'p' and in molecular dynamics what we do is essentially we look at the trajectory γ (t) as a function of time of course for a finite time.



So, in this kind of a picture there is something that is defined there is a theorem that is called the Liouiville theorem which essentially says the following. So, what we imagine that the phase space is some kind of a hypothetical fluid, I mean we are not plotting in a typical coordinate like the x-y axis so we should not think of any kind of a real fluid but some kind of a hypothetical fluid because it is moving so you can move from one point in the phase space to another point. So, that motion we can characterize as some fluid moving within the phase space, it is not really a real space in terms of coordinates you will not see that happening in this particular way because it is not really a space that we can visualize because it is extended dimensional space the fluid is somewhat hypothetical so as to speak but the definition of that undercoat fluid is useful in defining this particular theorem of its defined on the phase space.

It says that fluid that we can imagine in the phase space is actually incompressible. So, we make an analogy with incompressible fluids in fluid mechanics and think of the hypothetical fluid that is the phase space as an incompressible fluid. So, what this essentially means are two things- first we are essentially saying that systems are neither created nor destroyed so clearly I can be anywhere in the phase space at any given time or any given spatial location and all these are valid starting point for us to visualize how the system is moving. So, in some sense each of these phase points each of these Γ values are different systems so as to speak.

So, when I am looking at the trajectory in the molecular dynamics I am looking at a particular system starting from one particular Γ value. Now that system remains of course the Γ of that system will change but that system is not being created or destroyed. Similarly you can have some other system that is here to begin with and then it is like going in this particular way. So, you can define systems as different individual states and at any given time I can identify a system that is moving with time. If I look in some other time I will look in some other system moving with time but all these systems are essentially always present in the universe of the phase space because there is no creation or destruction system they evolve over time and as a result of that what we can then say is that if I look at any small volume in the phase space let me define the volume as some dΓ it is like a small range of possible values of Γ.

Now of course that dΓ is also going to evolve with time and in the phase space plot it is quite difficult to visualize what it will look like but clearly the shape of that small dΓ may not remain the same but since the systems are neither created nor destroyed what we can then say as a consequence of the incompressibility assumption that I am saying is that the volume of that phase space element is constant that is similar to like what happens in an incompressible fluid.

Incompressible fluid what do we say, we say that the density remains constant. So, if I look at any small volume in the fluid that is the fluid element that volume remains the same. The fluid of course moves, the shape of the volume may change, it may distort, it may get shrink whatever. But the volume of that cannot change because overall the density of the system is constant. So, if the volume of an element changes that would necessitate a change in the volume of the entire system and since that is not happening the volume of the element is also not happening and therefore we say the fluid is incompressible.

The same idea also applies here since the systems are neither created nor destroyed we can imagine the phase space as a collection of many of these systems each of which are evolving in their own way but their volumes remain constant. So, they fill the phase space and there is no way they can expand or shrink in terms of the volume. Their shape may change but the volume of the element will remain constant. Mathematically speaking this means the condition that the total derivative

$$\frac{d}{dt}\rho = 0$$

And that is true regardless of whether we are at equilibrium or not. It has nothing to do with equilibrium this is simply coming from a standard principle in classical mechanics. There is no thermodynamics involved in whatever we have discussed in the Liouiville theorem. Now this total derivative d by dt is actually defined in kind of a frame that is moving with the fluid element. So, I am looking at a derivative of rho with respect to time as I am moving with a particular fluid element. So, this derivative can then be represented as the partial derivative with respect to time and derivative with respect to the momentum and derivative with respect to the coordinates.

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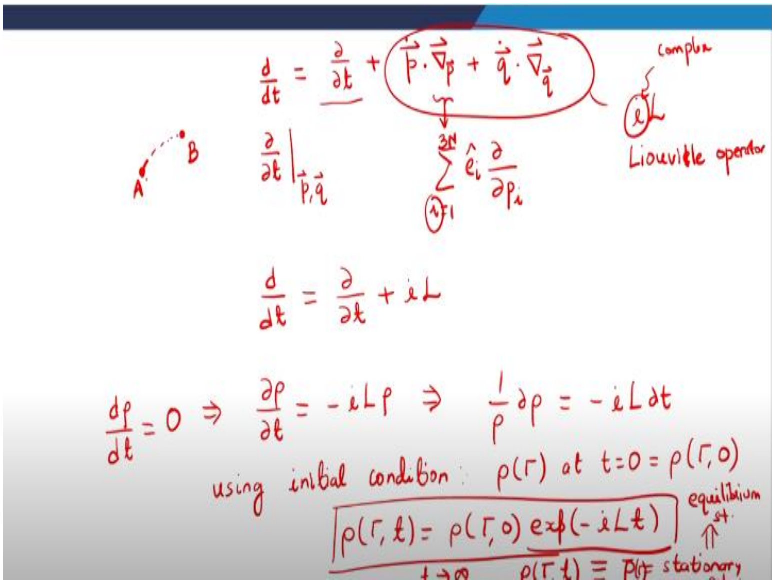

$$\frac{d}{dt} = \underline{\frac{\partial}{\partial t}} + \underbrace{\left(\dot{\vec{p}}\cdot\vec{\nabla}_{\vec{p}} + \dot{\vec{q}}\cdot\vec{\nabla}_{\vec{q}}\right)}$$

complex

$i\mathcal{L}$

Liouville operator

$$\left.\frac{\partial}{\partial t}\right|_{\vec{p},\vec{q}} \qquad \sum_{i=1}^{3N} \hat{e}_i \frac{\partial}{\partial p_i}$$

$$\frac{d}{dt} = \frac{\partial}{\partial t} + i\mathcal{L}$$

$$\frac{d\rho}{dt} = 0 \Rightarrow \frac{\partial \rho}{\partial t} = -i\mathcal{L}\rho \Rightarrow \frac{1}{\rho}\partial\rho = -i\mathcal{L}\partial t$$

using initial condition: $\rho(\Gamma)$ at $t=0 = \rho(\Gamma,0)$

$$\boxed{\rho(\Gamma,t) = \rho(\Gamma,0)\,\underline{\exp(-i\mathcal{L}t)}}$$

equilibrium st.

$t\to\infty$ $\quad \rho(\Gamma,t) \equiv P(\Gamma)$ stationary

The other way to think about it is let us say if I am going from this point to this point in phase space, when I am computing the d by dt, I am moving with the point. Let us say if I am going from A to B, I am moving with the point. So, my frame is also moving from A to B and derivative is defined in that particular frame.

On the other hand if I compute the partial derivative that will be fixated to the point A. So, even though that particular system at A has moved to B, it has evolved to be our reference frame for the computation of the time derivative dou by dou t will remain fixed at A. So, this is keeping the p and q constant.

So, if I do the math it turns out that I can represent the total derivative as-

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \dot{\vec{p}}\,.\vec{\nabla}_{\vec{p}} + \dot{\vec{q}}\,.\vec{\nabla}_{\vec{q}}$$

So, the gradient operator is defined as it is. So, in the first case we are defining the gradient with respect to the momentum and again these are with respect to the 3N momentum variables that we have. So, you will have 3N components in the del of p. It will look like something like a unit vector in each of the momentum directions-

$$\vec{\nabla}_{\vec{p}}= \sum_{i=1}^{3N} \hat{e_\iota} \frac{\partial}{\partial p_i}$$

And similarly we can do the same for the coordinate variables.

So, then this quantity is defined as the Liouiville operator and it tells me that my d by dt can now be represented as something like-

$$\frac{d}{dt} = \frac{\partial}{\partial t} + iL$$

By the way this is the complex i and this i is not same as that i. This i was an index ranging from 1 to 3N and this i here is the complex i. So, i square is equal to minus 1.

So, that means since the Liouiville theorem says that-

$$\frac{d\rho}{dt} = 0$$

What we have is-

$$\frac{\partial \rho}{\partial t} = -i\ L\ \rho$$

So this I can integrate as-

$$\frac{1}{\rho} \partial \rho = -i\ L\ \partial t$$

using the initial condition that ρ is clearly a function of the phase space at t equal to 0 is equal to something like ρ (Γ,0). So, therefore what we have is-

$$\rho(\Gamma, t) = \rho(\Gamma, 0) \exp - i\ L\ t$$

Keep in mind that in the exponential the L is the operator. L is not really a number. So, therefore we can expand it but it still remains kind of an operator just like dou by dou t is an operator. So, only when it is applied to something it has some meaning. But nonetheless what this gives rise to and I will not really go over the math is that this gives the fact that if I go to a large value of time that is if I go in the limit of t going to infinity this will tend to some stationary solution.

$$t \to \infty \; \rho(\Gamma, t) = \bar{\rho}(\Gamma) = stationary\ solution$$

So, over time since you have multiplying with an exponential function it is a decaying functions kind of although keep in mind that L is an operator but nonetheless it tends towards some kind of a stationary solution. So, this has certain consequences. So, one of the consequences of this result is that I will of course start with some distribution of the probability density in the space and this is going to evolve with time but provided I wait long enough I will reach a stationary distribution of probability density in the phase space and this is what we refer to as the equilibrium state of the system. So, I will repeat this point here.

So, when we begin or when we look at start looking at any particular system or when the system is not in a condition of equilibrium the system has some probability density, that probability density as a function of the phase space point Γ is changing as a function of time until we reach the equilibrium state and at equilibrium state it becomes a constant value of course it remains a function of the phase space point, the phase space variable but it is no longer a function of time and that is what we refer to as the equilibrium state of the system. After equilibrium that probability density no longer changes so as to speak so this is very much in line is our idea of the ensembles.

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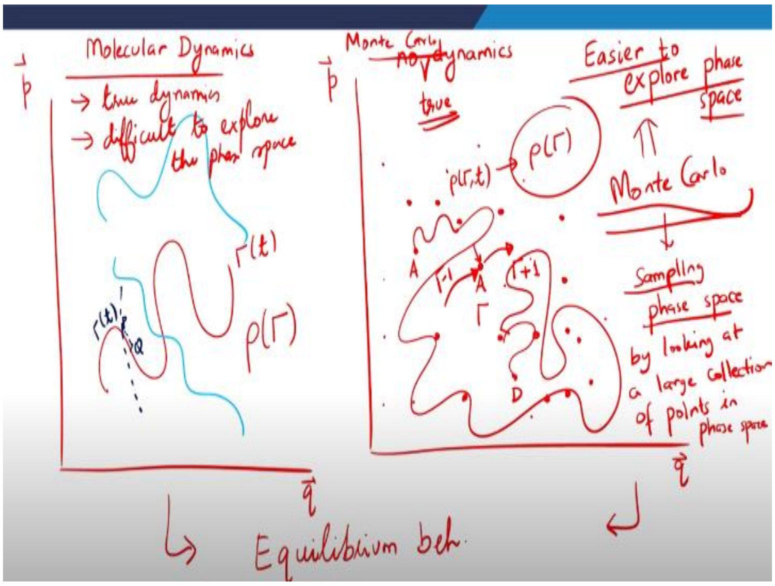
Molecular Dynamics
→ true dynamics
→ difficult to explore the phase space

Monte Carlo ~~no~~ dynamics
true

Easier to explore phase space
⇑
Monte Carlo
↓
Sampling phase space by looking at a large collection of points in phase space

↳ Equilibrium beh.

So, when we said that I will look at my ensemble as a collection of states it clearly corresponds to different points in the phase space and clearly at all of these points if I start looking at the ρΓ of t that probability density will keep on changing with time and only at the equilibrium state this goes to something that is independent of time but in ensemble we always define the probability density of a given state. So, we implicitly assume that the probability density is kind of independent of time and that is the equilibrium state that we are referring to. So, that is one of the consequences.

The second consequence is if for example, let us say if I am at A that is some particular phase space point Γ. If for example from here I go to a new state that is let me call this something like Γ + 1 just for the sake of convenience. Let us say in any given time I go from Γ to some Γ + 1. Now this particular phase space point A will therefore in some sense get empty because we have moved from Γ to Γ + 1. But since the fluid is incompressible and since the probability density is stationary what this means is something else needs to come at this particular point from Γ - 1 that is the past state. So, as soon as a system leaves a phase space point some other system occupies that phase space point because if that does not happen then the probability density will not remain constant. Because at any given point; you should have a stationary value of the probability density. As soon as the system has moved from there clearly the number of systems or number of states at that particular point has decreased so that means that unless something else comes there to fill in the void the probability density cannot be constant. So, this means that something else must come to that particular point if the system is at the equilibrium state.

And this has a very deep consequence not only for the Monte Carlo simulation we will discuss but also for the molecular dynamic simulation, why is that because I have said that although the system in principle can be just anywhere in the phase space to begin with. I am starting from a particular phase point and I look at the trajectory over a finite time. So, clearly if I started from somewhere else you may have some other trajectory what it tells me is that as soon as my previous state as soon as let us say if I am following this particular trajectory, as soon as I leave from here to there let us say from point p to point q something else must come at p. So, that means some other trajectory must be coming at p as soon as the trajectory of the system that I am looking at has moved from p to q. So, as soon as the system moves from p to q some other system occupies p. So, the other trajectory should pass through or cross the trajectory that we are considering we are not actually doing those trajectories; we are looking at only one system but we know that some other trajectory is also crossing this trajectory at every point because as soon as I leave every point on the trajectory something else must come there if the system is at equilibrium.

So, this means that since the trajectories cross each other we can therefore say that I need not look at all the possible trajectory because ultimately if I keep following the same trajectory over time that is in some sense a representation of all the trajectories because that trajectory that I am following for one given system is being shared point by point by every other trajectory. Every other trajectory is crossing each of the points of this particular trajectory provided if I look at it long enough. So, there is no unique point on the trajectory that I am considering that is not being revisited by any other trajectory in the system. In fact every point that I am passing through will be visited by some other trajectory at that particular time when I have moved past it.

So, therefore if I look at any given trajectory for a very long time that is in some sense equivalent to looking at multiple trajectories because ultimately every trajectory is a collection of points and every point is being visited by one trajectory or the other as the time passes. So, when I have traced a trajectory for one particular system I have been basically able to look at the trajectory of all possible systems provided that I have evolved long enough and this is the idea of ergodicity.

So, an easier way to think about it is let us say for example, if I look air in this particular room that is a much easier example. What I am saying is kind of saying that every molecule in this particular air will eventually pass through every other point in the room provided I wait long enough. So, in this case I am only looking at the coordinates. So, every molecule is having some trajectory now in the real space over time but every time I am passing through any particular point in the air some other molecule will occupy that point. So, therefore if I just keep following one particular molecule over time it is essentially capturing the entire room because any place in the room can be occupied by the molecule but we do not know how much long it takes. But if I just keep waiting for a very, very long time this trajectory of a single molecule will pass through every point in the particular room so in a similar manner now in the; phase space compared to the air with the real space. Now in the phase space since trajectories cross each other if I just wait long enough I will be able to basically sample the entire phase space. That is a very deep consequence of the Liouiville theorem and this essentially gives rise to the idea of the ergodicity in the system.

It is not always true. There can be systems which can be non-ergodic. So, for those systems what will happen is that there will be regions in the phase space that will not be visited starting from any given state. So, let us say for example if I start from a given point I only visit part of the phase space and some part is never visited. If that is happening then we can say that the system is non-ergodic but when it is ergodic and that is the assumption that we typically make then we can say that no point in the phase space will remain untouched by the system no matter where I start from provided I evolve the system for a very long time.

So, that is one important consequence that goes into the idea of molecular dynamics then there is another consequence that is important for the Monte Carlo simulation and that is what this means is since my ρ Γ is independent of time why does it matter that I look at trajectories starting from any given point because in the end I am interested in the stationary solution. In the stationary limit ρ Γ is independent of time. So, instead of looking at dynamics of any given system what I can instead do is I can sample points in the phase space in some other way and precisely this is what we are doing when we are defining the ensemble.

So, ensemble is a collection of states where we are not interested in how will I get from one state to the other. I simply list out all the possible states and once I average over the properties in all those states I get the average behaviour. So, I am not really concerned how the states are connected or I am not concerned about the dynamics of one state going to the other. When we are concerned about it we can do molecular dynamics that is actually a fair representation of that provided I wait long enough. So, if I just pick two states from the ensemble yes it is true that they will be connected by some sort of a trajectory but how long that is going to be that we do not know. It may take a very small number of steps, it may take a very large number of steps. So, instead of trying to connect the states instead of looking at dynamics from a given state and all that what we can instead do as done in the thermodynamic ensemble approach is we simply sample the phase space without worrying about the dynamics of those points and that is only valid when we are at the equilibrium condition.

So, in Monte Carlo simulation this exactly is what we are doing, we are simply sampling phase space by looking at a large collection of points in phase space and then we can sample in a variety of ways and we will discuss how we can sample that. But you can already see the beauty of this.

Let us say for example, I am looking at two particular phase space points A and D. So, in a Monte Carlo simulation I can clearly sample A and D very easily and these are arbitrarily located in different places in the phase space. On the other hand if I am following the molecular dynamics approach then I will start a trajectory from A or from D and I have to wait long enough until they meet each other. So, starting from A we can never be sure that I will get to D if I am following the molecular dynamics but in Monte Carlo it is trivial to do because I can always sample A and D because I am not worried about how A is evolving how D is evolving. I am only interested about stationary states A and states D. I will have some mechanism to choose how I will generate the states that is the secondary point. But let us say if I am interested in a particular state I can always pick that and I can pick a collection of states that I am interested in.

So, what this means in Monte Carlo provided that the scheme has been designed appropriately it is easier to explore the phase space. I can pretty much pick points the way I like. On the other hand in molecular dynamics it is much more difficult to explore the phase space.

The demerit however is there is no dynamics or we can say there is no true dynamics because we are not following Newton's laws of motion there, of course when we are doing simulation we have some mechanism to generate the points and that may appear like some kind of a dynamics but it is not following the Hamilton's equation of motion. It is not starting with Hamiltonian and therefore the dynamics is not really a true dynamics.

On the other hand in molecular dynamics as opposed to the Monte Carlo in molecular dynamics it is having the true dynamics. I can really capture how any state would evolve particularly when we are looking at the behaviour in the non-equilibrium regime when we have not reached the stationary solution. In that case molecular dynamics will kind of guide the study of how the system will evolve to the equilibrium state and that will be a true dynamics because we are solving the Newton's laws of motion or Hamilton's equation of motion.

On the other hand it will be difficult to explore the phase space, we are limited by the natural trajectory of individual states and the natural trajectory may take a very long time to explore the entire phase space. It may not be efficient in many of the situations.

Nonetheless as long as we are interested in the equilibrium state both should give you the same answer because ultimately in both the approaches we are trying to sample the entire phase space we are trying to get the probability densities and on the basis of those densities we want to evaluate the average properties. So, whatever $\rho \Gamma$ we will have here the same $\rho \Gamma$ we will have here in the equilibrium state.

So, therefore the equilibrium behaviour must be the same between the molecular dynamics and Monte Carlo simulation provided we can get to the equilibrium state. That is naturally true, so when I start a simulation I am not certain and that is true also for Monte Carlo simulation we will discuss that point later that I am actually simulating a thermodynamic equilibrium. Am I correctly representing the density of states as what should be in the equilibrium condition if I am able to do that then in that case we will have the same equilibrium behaviour because then we are studying the equilibrium. If we are not able to do that then in molecular dynamics still it is fortunate because we are still capturing the non-equilibrium behaviour the dynamics whatever we are following is still valid.

But in Monte Carlo it is kind of meaningless because dynamics is not the true dynamics and as long as we are not in the equilibrium regime we are that simulation is pretty much meaningless because Monte Carlo hinges on the idea of the stationary solution of the probability density that is when the probability density becomes independent of time. As long as that condition is not met the Monte Carlo does not have any meaning, having said that you will read some approaches and I will also discuss this towards the end of this course where Monte Carlo is applied in non-equilibrium settings but in what we will discuss in this week and the following week we will be confined to equilibrium simulations whenever we apply Monte Carlo in the non-equilibrium setting it is not still the true dynamics as molecular dynamics but there are some ways it still captures some sort of physics.

So, it is not really a very correct way to simulate non-equilibrium behaviour but nonetheless there are methods called kinetic Monte Carlo schemes that can do that and we will discuss it towards the end of the course but for most applications Monte Carlo is applied in the equilibrium setting, molecular dynamics also in most applications tries to simulate equilibrium behaviour because that is what is a practical interest but there are cases when molecular dynamics is also used to look at the non-equilibrium behaviour of a system.

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