Advanced Thermodynamics and Molecular Simulations
Prof. Prateek Kumar Jha
Department of Chemical Engineering
Indian Institute of Technology, Roorkee

Lecture – 41
Particle Simulations: Comparison with Quantum Chemical and Continuum Simulations; Bridging Length and Time Scales

Hello all of you. So, in the last week we have been discussing the numerical implementation of the Monte Carlo scheme. Before that we have discussed the theoretical basis of molecular simulations and I told you that both Monte Carlo and molecular dynamics methods, which are theoretically very different gives you the same equilibrium behavior of systems, in many instances the Monte Carlo provides a much more efficient sampling of phases compared to molecular dynamics, but nonetheless molecular dynamics is actually I would say more common in description of atomic systems because it captures the true dynamics of the system. So, it can be extended even for none equilibrium behavior or dynamic behavior of systems.

So, I will now discuss the molecular dynamics of MD scheme. But before that and along the lines of what we have been discussing there are several commonalities between the Monte Carlo and molecular dynamics. For example, the system constructions the way we define the boundary conditions and also the forces or energies are pretty much the same between the two simulation and therefore they say are several features in common only the basic algorithm is essentially different in both MD and Monte Carlo scheme.

So, what I will first present, is a general overview of particle simulations. I will also discuss how it falls in lines with the other simulations you may have heard of let us say quantum chemistry simulations or any of the continuum simulations like CFD and all that. And then what are the time and length scales we are probing and then finally we will come to how can we define the forces and the energies in the system.

So, broadly speaking both Monte Carlo and molecular dynamics comes under a class of particle simulations, there are other methods also in that class but these are the one which are used a lot in thermodynamics. So, whenever we say a particle simulation, we are representing our entities using particles in continuum models, let us say computational fluid dynamics, we do not have the motion of particles instead, we have a continuum control volume or fluid element, which has some properties like density velocity and all that that is defined over a fluid element that is a continuous element, we do not talk about molecules there indeed control volume has to be composed of infinitely many molecules or very large number of molecules so, that we define an average behaviour but nonetheless we do not concern about the particle how they are moving and so on in particle simulations, it is not the case, we are actually implementing particles.

Now depending on what we define a particle there are several classes of these simulations. For example, when I say I am doing an atomistic simulations I am dealing with particles which are atoms or molecules and we can do atomistic Monte Carlo or we can do atomistic molecular dynamics then in some cases we also want to look at particles as some collection of atoms or molecules, they constitute some kind of a building block. This is what is referred as a coarse grained simulation.

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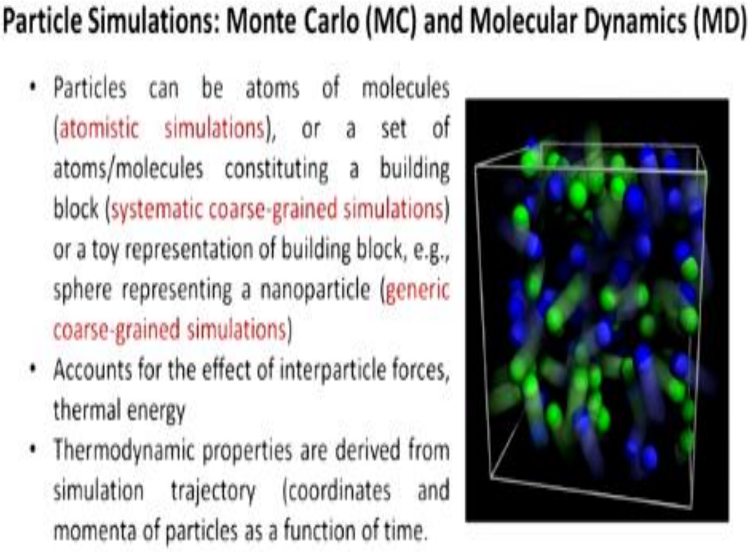

Particle Simulations: Monte Carlo (MC) and Molecular Dynamics (MD)

- Particles can be atoms of molecules (atomistic simulations), or a set of atoms/molecules constituting a building block (systematic coarse-grained simulations) or a toy representation of building block, e.g., sphere representing a nanoparticle (generic coarse-grained simulations)
- Accounts for the effect of interparticle forces, thermal energy
- Thermodynamic properties are derived from simulation trajectory (coordinates and momenta of particles as a function of time.

We can do in two ways, in one way we are actually representing the chemistry we know what the building block is composed of. Let us say a collection of carbon atoms or carbon hydrogen atoms. In that case, we say it is a systematic coarse grained simulations in some other case, we simply have a building block let us say is fair or a cube and that in principle would represent an atomic system, but we are not actually implementing any chemistry into that. So, essentially we are modeling just some is spherical particles under some model potentials or some cubic particles or some other safe particles without any regard to their actual chemistry.

So, those come under the class of a generic coarse grained simulations, I would emphasize here that the algorithm of the Monte Carlo or molecular dynamics would not change depending on what kind of simulations we are doing here, whether it is atomistic or generic coarse grained or systematic course grained. What would change is how we construct the system and how we define the forces between the particles in the system and more or less all these methods that we have been discussing account for essentially two things one is the inter particle forces and other is thermal energy. If you compare that to typical continuum methods, let us say computational fluid dynamics, we typically do not account for these two factors. So, we look at for example in CFD how the flow will occur in the presence of an applied pressure drop that is external to the system but we do not really concern about the interactions of water molecules themselves. This comes under the regime of particle simulations.

Similarly thermal energy is thought to be not so important when we are doing any kind of continuum simulations. In this case of particle simulations since we are modeling the particles, we are actually modeling the kinetic energy of particles and therefore we are accounting for thermal energy, very precisely. So, whenever we are interested in looking at a system where the inter particle forces or thermal energy is very significant or thought to be playing an important role, in those cases we should resort to a particle simulations having said that there are some field based methods nowadays that can also achieve something similar but I will not discuss them in the class, you will focus more on the particles in this methods and then the basic idea irrespective of whether we are doing Monte Carlo or molecular dynamics is we have some starting coordinates and momenta particle in Monte Carlo momenta is not so relevant and they defined some point in the phase space of the system and then we basically look at a trajectory of the system that trajectory in the case of MD is the actual motion of a system starting from a starting state.

In the case of Monte Carlo it is purely artificial we are simply jumping from one state to the other. But nonetheless we get some sort of a trajectory or some sort of a collection of phase space points, which is what I will use to compute the average properties. In other words, we compute the property value whatever we are interested in be it, the temperature be the pressure be it some property like density or something else, we compute at each of these points along the trajectory and then average over that and then we can compute the property of the interest that is the basic idea of particle simulation common between both Monte Carlo and molecular dynamics methods.

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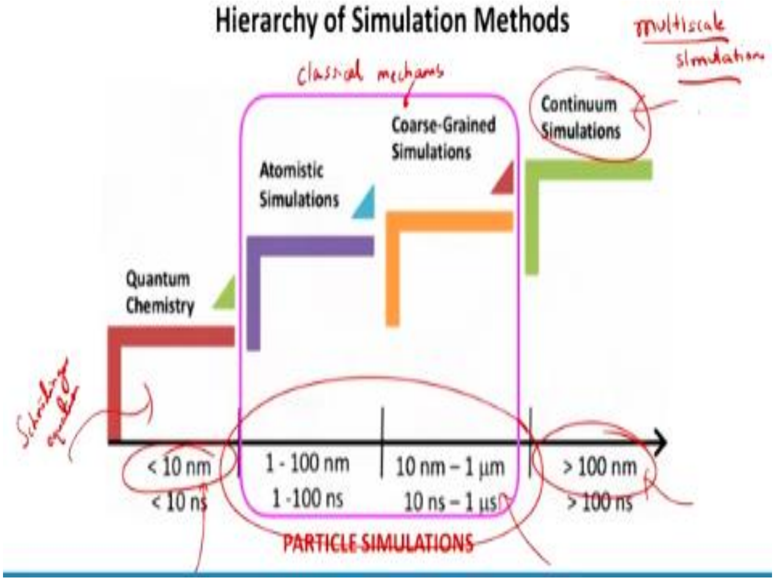
Hierarchy of Simulation Methods



multiscale simulation

classical mechanics

Quantum Chemistry

Atomistic Simulations

Coarse-Grained Simulations

Continuum Simulations

Schrodinger equation

< 10 nm
< 10 ns

1 - 100 nm
1 -100 ns

10 nm – 1 μm
10 ns – 1 μs

> 100 nm
> 100 ns

PARTICLE SIMULATIONS

So, if you want to compare that to the other methods out there, of course we could have done quantum chemistry where we are essentially solving the Schrodinger equation and in this case we are actually solving for so as to speak the density of electron clouds. So, we are not only looking at the motion of the nuclei, but we are also looking at the motion of the electrons as well. So, quantum chemistry definitely is the most accurate method because many phenomena are driven by electron cloud interactions. Let us say for example chemical reactions by the ability to model the density of electron clouds we are able to represent chemical reactions in a quantum chemistry simulation.

The same is not true in the atomistic or coarse grain simulations that are the particle simulations we have been discussing that is because we are in the regime of classical mechanics. So, we assume that the motion of the electrons essentially follow the nucleus. So, we are not solving for the electrons and nuclear separately instead we represent the motion of atoms as such or collection of atoms or the twine particles in the twine models. So, in this case, we completely disregard electronic motions and therefore clearly we cannot capture chemical reactions or anything that requires the information regarding the electron clouds. Then finally we have continuum simulations where we do not look at the particles at all, we represent I would say the system as composed of some fluid element where every element is composed of many-many particles where we are not interested in the particles themselves, we are interested in the average behavior of a large collection of particles.

So, clearly this would also mean that the length is scale where this is going to apply is going to be very different. If we think about very small length scales, let us say less than 10 nanometers or so we may start to expect that the quantum chemical effects will be more important because we are looking at atomic or subatomic systems. On the other hand in continental limit we are thinking of really microscopic systems where we are dealing with very large collection of molecules such as fluid flowing in a pipe. So, this will apply I would say more in the micron or above regime at least starting from like point 1 micron 100 nanometers. In between these two extremes actually slightly overlapping with both of them we can define the regime of particle simulations. This is the regime where inter particle interactions and thermal energy are found to have significant role.

In continuum limit thermal energy and inter particle interactions typically are lesser important than compared to the particle simulation or quantum chemistry.

Now these numbers also depend on our ability to simulate. So, yes, Schrodinger equation is the most accurate equation and there is no reason to think that it will not apply to a large microscopic system we could as well simulate a pipe flow using Schrodinger equation the only problem is that it is computationally impossible to do. So, these pretty much limits how much we can go in terms of length scale in these simulations. It is not that the quantum chemistry cannot be applied to larger than this scales or atomistic cannot be applied to larger length scales. These limits I have put here also is pretty much our computational restrictions which are of course improving over time, but not quite to an extent where we can apply a single method over the entire spectrum.

So, this is why and there is a word of this part multi scale modelling or multi scale simulations and the reason why it becomes important is because this harnesses our ability to use best simulations or most appropriate simulations at the length scale of interest. Let us say if I look at a microscopic system in which there are certain nano scale features for which quantum chemistry is important. Let us say a chemical reaction is going on in chemical reactor. The reactor itself is large, but the chemical reaction is happening over very small length scale. So, in that case we can apply quantum chemistry for that scale but for simulation of the flow inside the reactor I can do continuum simulations.

In a similar manner, if you have for example a catalyst and there is a chemical reaction going on the surface of catalyst. So, the physical absorption of the reactant to the catalyst surface can be modeled using atomistic simulations because there is no chemical reaction happening in the adsorption process and the chemical reaction itself can be modeled using quantum chemistry stimulations. And therefore if we are able to combine these methods and we have not discussed in this course and we will not discuss so much detail. Anyway, we can get the best out of all these worlds and we can basically represent any microscopic phenomena by using different methods to represent different lengthy scales and therefore capturing the physics with the computational power we already have and this is what comes under the regime of multi scale. In this slide what I told you about the computational limitations of quantum chemistry or atomistic simulations. As computers get better there is in principle lesser need of multi-scale simulations or in the same words we can say that as computers get better we can study more complex systems using the same multi-scale method. The way you want to look at it the complexity of systems that we are able to study now is much-much better than what we could do. I would say 10 years ago and 20 years ago, at the same time we can do larger systems and we can apply quantum chemistry, two cases where it cannot be applied earlier where atomistic we are used earlier, but now I am doing quantum chemistry for that.

Similarly, atomistic simulation have been pushed to the regime of macroscopic scales and therefore in the regime where we typically use continuum simulations now we can use atomistic or coarse grained simulations. These abilities are improving as time is evolving.

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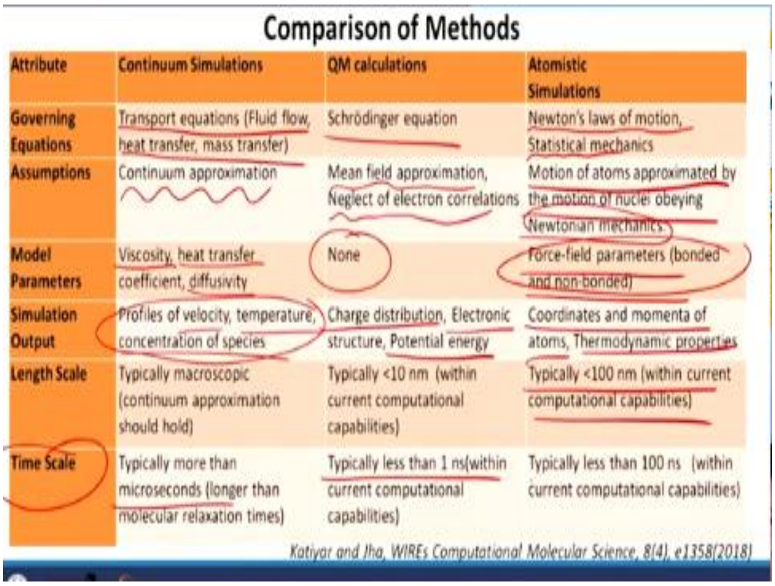

Comparison of Methods

Attribute	Continuum Simulations	QM calculations	Atomistic Simulations
Governing Equations	Transport equations (Fluid flow, heat transfer, mass transfer)	Schrödinger equation	Newton's laws of motion, Statistical mechanics
Assumptions	Continuum approximation	Mean field approximation, Neglect of electron correlations	Motion of atoms approximated by the motion of nuclei obeying Newtonian mechanics
Model Parameters	Viscosity, heat transfer coefficient, diffusivity	None	Force-field parameters (bonded and non-bonded)
Simulation Output	Profiles of velocity, temperature, concentration of species	Charge distribution, Electronic structure, Potential energy	Coordinates and momenta of atoms, Thermodynamic properties
Length Scale	Typically macroscopic (continuum approximation should hold)	Typically <10 nm (within current computational capabilities)	Typically <100 nm (within current computational capabilities)
Time Scale	Typically more than microseconds (longer than molecular relaxation times)	Typically less than 1 ns(within current computational capabilities)	Typically less than 100 ns (within current computational capabilities)

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So, here is a brief comparison in terms of the features of these methods. So, in continuum simulations, the governing equations are the transport equations that you may have learnt in transport phenomena course. Let us say for example, the equations of fluid flow, the Bernoulli equations and Navier Stokes equations. The equations of heat transfer which are the Fourier law for conduction. The equations for mass transfer such as the fixed law of diffusion.

In the quantum mechanical or quantum chemical regime, we are solving the Schrodinger equation and atomistic or coarse grained simulations, we are solving the Newton's laws of motion for the case of MD and we are using the tool bar of a statistical mechanics both for MD but more for the, Monte Carlo simulations and the assumptions that we make in these methods are again, very different you have very lesser number of assumptions and quantum chemistry. So, it is called a first principle method on the other hand you have many assumptions inherent in a continuum simulation method. So, the basic assumption is the continuum assumption that we assume that the molecules in a control volume give rise to an average property such as density or velocity, whatever.

In the quantum mechanical case we use something known as a mean field approximation different from what we discussed in lattice model case but that is solved during the numerical solution of Schrodinger equation, I will emphasize here that the exact solution of Schrodinger equation is only possible for various small molecules like hydrogen and so on. If you really want to apply quantum chemistry to slightly more complicated systems or more realistic systems, we need to make certain numerical approximations to solve Schrodinger equation. For example, typically we also neglect electron correlations they are found to be of lesser importance than compared to the other terms in the Schrodinger equation.

Similarly, in the atomistic simulation case, we are approximating the motion of atoms as the motion of nuclei. In other words, we are saying that the electron follows in the nucleus wherever it is going and then we assume that the motion is actually following the Newtonian mechanics we are in the classical regime.

The model parameters are very different, because they depend on the problem we are trying to solve in these cases. For example in continuum simulations, we typically have model parameters like viscosity, the heat transfer coefficient or the diffusivity which are really microscopic parameters that we can get from experiments. We can also get from higher level theory such as doing a quantum mechanical or atomistic simulations if it is possible so these are two ways, we can get the parameters of continuum simulations.

In quantum chemistry in principle, there are no model parameters. Because as I said, it is a first principle method you give me a molecule and I will solve Schrodinger equations. I do not need any experimental data as such. Of course we will make some numerical approximations. But that is not to say that we are using any information from experiments or from any lower level theory.

In atomistic simulations, we have something known as force fields, they represent the forces between atoms of molecules and I will come to that later in the course and then the simulation output is clearly very different in all these cases.

In continuum simulations, we typically look at the profile or the variation with respect to space and time of the velocity, temperature, or concentration of species depending on whether we are solving for fluid flow heat transfer or mass transfer. In many cases, we are looking at combination of them, we have some fluid flow happening along with heat transfer or mass transfer which is what is now known in fancy terms as a multiphysics simulations. So, this is the typical output of that and more derived variables along those lines.

In quantum chemistry calculations, we are interested in the electron cloud. So, we are interested in the charge distribution around the nucleus. We are interested in the electronic structure of the molecules, we are interested in the potential energy of the molecules.

In the case of atomistic we are as I said interested in the coordinates and momenta of particles and using that we can evaluate the thermodynamic properties of interest.

And length scale we had already mentioned in the case of continuum, we are typically in micro to macro kind of a lengthy scale. In quantum chemistry, we are limited to something like less than 10 nanometers. That is the regime that we can solve as of now. And in atomistic we are typically limited to less than 100 nanometers, but it is really improving over time.

And in terms of time scale as well in the case of continuum, we can go to like pretty much to seconds or minutes much more than microsecond scales. In the case of quantum mechanics, we are pretty much in the regime of less than one nanosecond. It is also important to know is that many a times the features we are interested in are typically happening also over very short time. I given example of chemical reactions, the time it takes for the actual reaction to take place once two reactants come together are pretty small. So, therefore it is not really a limitation, it is really that is where the physics occurs. Unlike in the case of continuum simulations where in one nanosecond pretty much nothing happens. So, in that case, we are interested in behavior for longer lengthy scale. Atomistic clearly serve in between clearly we can go up to 100 nanoseconds and most phenomena we are interested in we can capture within that time scale but clearly there are certain phenomena that require a longer simulations and many of that is not possible with the current resources that we have.

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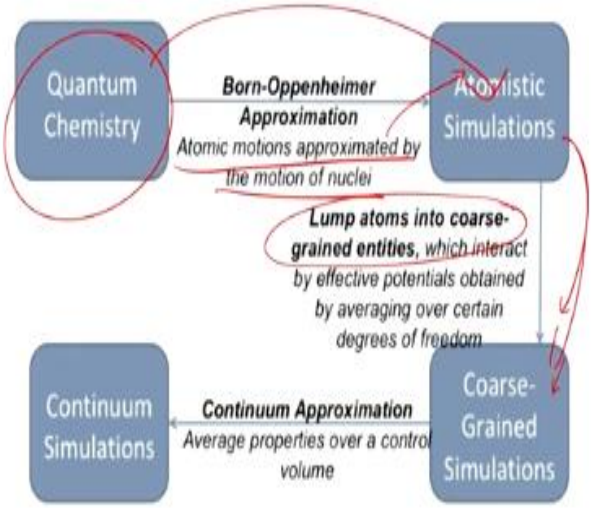
Bridging Length and Time Scales



Quantum Chemistry

Born-Oppenheimer Approximation
Atomic motions approximated by the motion of nuclei

Atomistic Simulations

Lump atoms into coarse-grained entities, *which interact by effective potentials obtained by averaging over certain degrees of freedom*

Coarse-Grained Simulations

Continuum Approximation
Average properties over a control volume

Continuum Simulations

So, I was telling you about the multi-scale simulations. So, this is a way in which I can think of like bridging several methods. For example, I can start from a quantum chemistry simulations and I have pretty much the whole data of the electron cloud, the density of electron cloud, the conical structure and all that. And then I can use an approximation known as the Born Oppenheimer approximation where using this data I can use the approximation where I will approximate the motion of atoms as the motion of nuclei so as to speak we can assume that the electron follows the nucleus and using that we can then go to atomistic simulations or in other words atomistic simulation is a representation of the quantum chemical system where I am not looking at the motion of electrons individually.

Similarly, I can go from atomistic to coarse grained by lumping atoms into coarse grain entities. Let say you have 10 atoms in a molecule; I can make them into 2 entities of 5 atoms each which is what I do in a systematic course gradient approach and then I can basically use the atomistic simulation data to kind of find the forces or energy for the case, of course grained simulations and using that I can come to this scale.

And when I am moving from one to the other method by this way I am doing basically a multi-scale simulations and the advantage now is that I can include the quantum chemical details at lower lengthy scales in atomistic simulations performed over larger lengthy scales. Similarly, I can include the particle movement details that I get or whatever inference they have at nanometer scales in I would say micro micrometer scales of micron scales and coarse grained simulations and then similarly I can use the continuum approximation we can average properties over a control volume and we add in the regime of continuum simulation.

So, this is like I would say a by enlarge the broad framework of multi-scale modeling. This is not a course on multi-scale modeling, but something that any person doing simulation should keep in mind because this is where the world is going, this is how we are designing materials in current around.

So, with this kind of a broad overview I want to conclude this lecture. In the next lecture we will start discussing the model potentials, which are common between Monte Carlo and molecular dynamics schemes. And then I will tell about certain tricks that we apply in the case of particle simulations. And so if you look at the pattern in which we have been going I am now going into actually application of the molecular simulation methods. We have already discussed the theoretical background on where this model is built on. But now I will be focusing more on how can we apply these methods to common use.

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