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

Lecture – 59
Simulations of Chemical Reactions using Kinetic Monte Carlo Simulations

Hello all of you. So, in the last couple of lectures of this course I will discuss some topics that really goes beyond the idea of thermodynamics that we have discussed in the first part of the course. These are I would say comes under the periphery of molecular simulations but not based on the idea of the equilibrium simulations that we have discussed or even the non-equilibrium that we have discussed towards the end.

So, the first class of these methods involved treating chemical reactions and I want to cover that because as chemical engineers we are interested in chemical reactions and the second part I will discuss briefly on quantum chemistry simulations. None of these are going to be I would say an introduction that will be sufficient but just to give a flavor of like what else is out there in the world of molecules simulations.

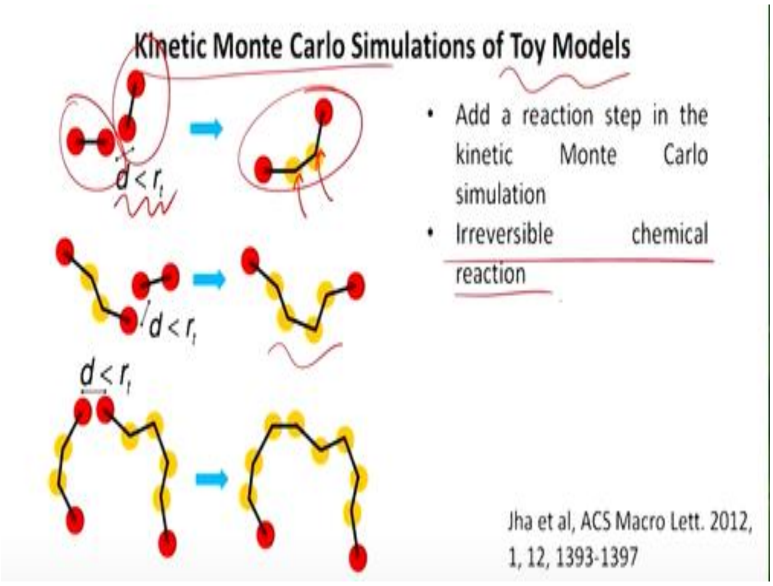
So, let us first discuss the chemical reactions and see why first we are saying that we need a different class of methods for that and the reason for that is that when we think of the classical mechanics framework, the identities of molecules are kind of fixed we cannot change the entity of molecules. Let us say for example, if I begin with ethanol in water. Ethanol will remain ethanol the chemical structure cannot undergo a change because chemical reaction itself is a quantum chemical phenomenon. It involves electrons it involves the overlap of electrons that forms a bond and unless we are accounting for the motion of electrons and the overlap of electron clouds and all these stuffs, we cannot really study chemical reactions.

And clearly in classical mechanics the assumption that we made is that the atom is a single entity and the motion of atom represents the motion of both the nuclei and the atoms in our classical mechanics framework and therefore, clearly, we do not have a way to include the electrons and the electron motions and electron overlaps all the phenomena that would be relevant for discussion of the chemical reactions.

So, therefore we need a separate set of tools to study chemical reactions and quantum chemistry is clearly one of that. So, therein we are solving the Schrodinger equations that is the equation for the electron cloud density or the density of electron in the in the cloud and using that we can now discuss the chemical reactions because now we can see the overlap of cloud happening in the formation of a chemical bond happening and so on and so forth.

Nonetheless there are some I would say rudimentary methods that do account for chemical reactions in somewhat approximate way using a framework similar to the classical mechanics framework that we have already discussed. That kind of; simulations that we already discussed.

(Refer Slide Time: 03:32)



Kinetic Monte Carlo Simulations of Toy Models

- Add a reaction step in the kinetic Monte Carlo simulation
- Irreversible chemical reaction

Jha et al, ACS Macro Lett. 2012, 1, 12, 1393-1397

So, the first class of method is the kinetic Monte Carlo simulation method and we can do in pretty much two ways. In the first way we can develop some Toy model that has some kind of a reaction modeled in I would say a very crude manner and the second class of method we actually include the chemical reactions but that method then will require input from the quantum chemistry calculation.

So, the first class of methods on Toy models what we can imagine, for example is let us say I want to study the polymerization process. So, polymerization process involves beginning from monomeric units or monomers which combine together and form a polymer chain. So, I am doing example here.

So, you start with this monomer in red, they combine together and form a chain containing four repeat units these yellow guys now become the repeat units of the polymer chain. They further combine with other monomers or they can combine with other polymer chains they are formed and form longer chains and even longer chains and so on. And this is essentially what the process of polymerization is.

Now one way to include that in the kind of simulation that we have been doing is we can do a Monte Carlo simulation and say that whenever two monomers come within a distance less than some threshold distance, we form a bond. This is how we analyze hydrogen bonds in molecular dynamics but in the case of hydrogen bond the geometric criteria is a still okay because hydrogen bond is not really a kind of a covalent bond unlike in the case of the polymer chains where you are forming a covalent bond. So, hydrogen bonds can really break easily and form again. But these covalent bonds are quite strong and therefore, when we do that in this kinetic Monte Carlo's framework, we say that this process is somewhat irreversible that is to say that once the bonds are formed, they remain there unlike say the hydrogen bond that forms dynamically in a molecular dynamic simulation.

So; by doing that we lose the actual flavor of the metropolis algorithm and the detailed balance condition because we cannot go back to the state we begin with. In a sense, we cannot simulate thermodynamic equilibrium there because, the system will simply grow in the size the polymer chains become larger and larger as simulation proceeds. The equilibrium in this case will correspond to the case when you have the longest possible change in the system and that is probably not what we are interested in, we are interested in the rates of the polymerization process.

So, actually both the purpose of the simulation and the outcome of the simulation are towards the non-equilibrium state or non-equilibrium phenomena that involves the chemical reactions between the monomers and the clearly does not satisfy the detailed balance condition. And therefore, it remains somewhat theoretically vague scheme but still as long as we want to get a qualitative picture it is one way to look at the polymerization process.

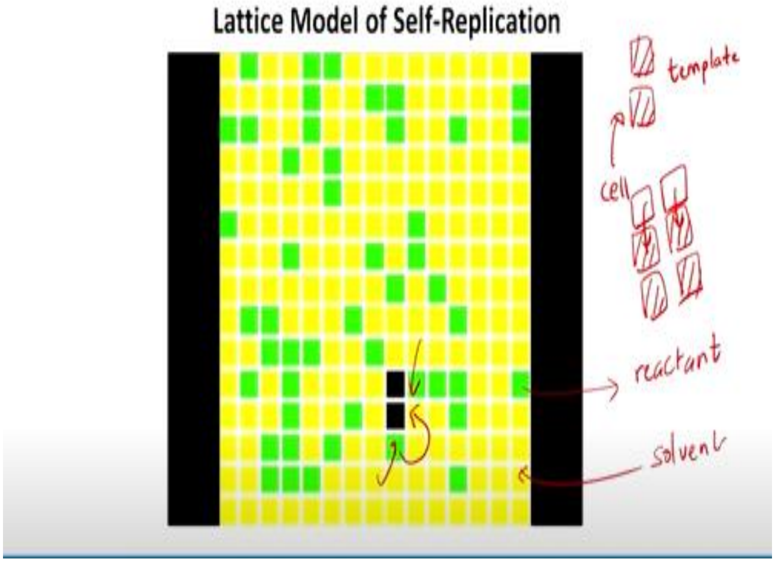
The second concern is that when I say 'd' less than some threshold distance be the condition of the chemical reaction, we are only accounting for the fact that the reactants have to come together to form any kind of a product but when they come together there is only certain probability with which the reaction will take place. There is a whole idea of activation energy and the rate constant that also has to be included in the kinetic monte formalism.

Again, we can assign some probability for the reaction to occur but again, that is going to be somewhat crude way of doing it because we do not have a clear sense of how can we estimate such parameters using experiments.

So; with this kind of a background and with these limitations this is still quite possible to look at least qualitatively how the polymerization pressure process happens because the fact that monomers form the polymers in this particular way or by this particular mechanism is well known and we can visualize this process by performing a kinetic Monte Carlo simulation. And as long as the idea is to get a qualitative understanding this kind of a toy model picture works pretty well.

So, one example that I am giving you is a model of a self replication or the similar thing can also happen whenever we are using a template in a chemical reaction. The template will grow and form more and more species.

(Refer Slide Time: 08:50)



So, in this case I will show you a movie where these black guys we are at begin with are my template all you can think of some cells which are trying to replicate this process itself with other complex. And we are not hoping to model the actual biological phenomena or the phenomena that takes place in templates synthesis but we are simply trying to capture whether a very simple model can at least capture the basic physics or basic flow of how the phenomena, takes place and in that kind of a context this model is already good enough.

So, we are saying that the molecules can only be on a lattice. So, these squares are my molecules similar to the lattice model of solution. In this case, we have green guys, which refer to my reactants so as to speak. Yellow guys is my solvent molecules, which do not react and the reaction takes place whenever two green guys, that is two reactants come in contact with the template it can be a cell it is trying to replicate the kind of phenomena we are trying to model.

Now as soon as these two guys come here, they also become same as the black guys that means they can also become template themselves. And therefore, other green guys can come here and now for these two green guys, the newly formed black guys also serve as template. The only criteria are that two green guys, two reactants would come together on the template.

So, now as I will play the movie what you will see is wherever these two green guys come in contact with two black guys so both green should come in contact with black in the condition. If only one comes there then it will not turn to black. So, in this particular configuration I start with these guys cannot turn to black. So, one of these green guys come so come near the black guy and both the greens will be together and both the blacks will be together in order to form a new template that is in order for the black guys to replicate itself the green to become black.

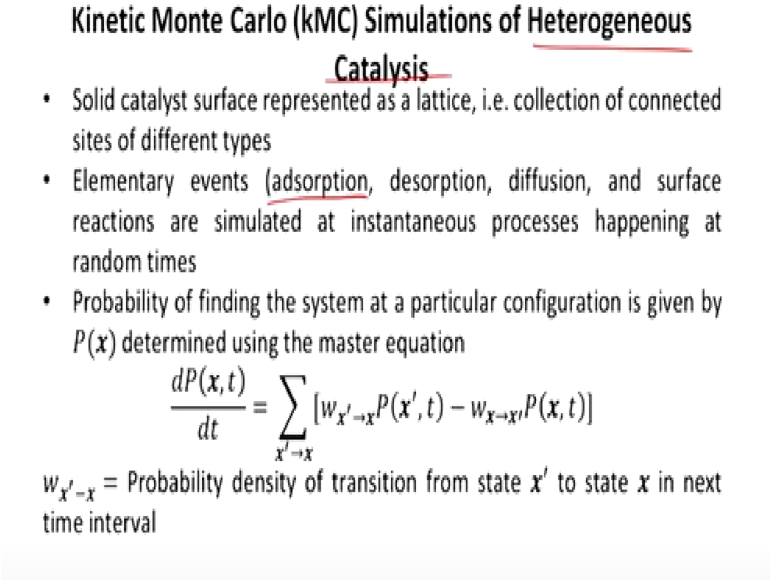
This is a very simple model of the self replication process and in between all the green and yellow guys are doing random movements, the think of that you have some kind of a solution of reactants and reactants are diffusing through the solution whenever the reactant comes in contact with the template only then the reactant may turn to the template otherwise they will remain simply diffusing in the solution.

So, let us see how the movie looks like and does it represent the replication process or not at least qualitatively do we have the picture that we want to see.

So, now you see we have formed two green into black and again, the simulation is going on. And then as time proceeds the template keeps growing it is an irreversible process. So, once you form a black from green, it can no longer turn back to green although in this Toy model we can do that as well. And you see the template just keeps on growing and growing and system essentially is replicating itself as the simulation proceeds and eventually if we wait long enough all the green guys will turn to black.

So, as long as the purpose is only to get a qualitative understanding of the underlying phenomena these kinds of models can be used which are very much similar to the methods that we have discussed in this course, it can be even simpler models of systems that can explain some of the complex phenomena happening in biological systems or the chemical systems but nonetheless keep in mind that we cannot really make any quantitative predictions unless we have some understanding of the rate processes that are going behind these particular systems and that has to be somehow included in these models.

(Refer Slide Time: 13:58)



Kinetic Monte Carlo (kMC) Simulations of Heterogeneous Catalysis

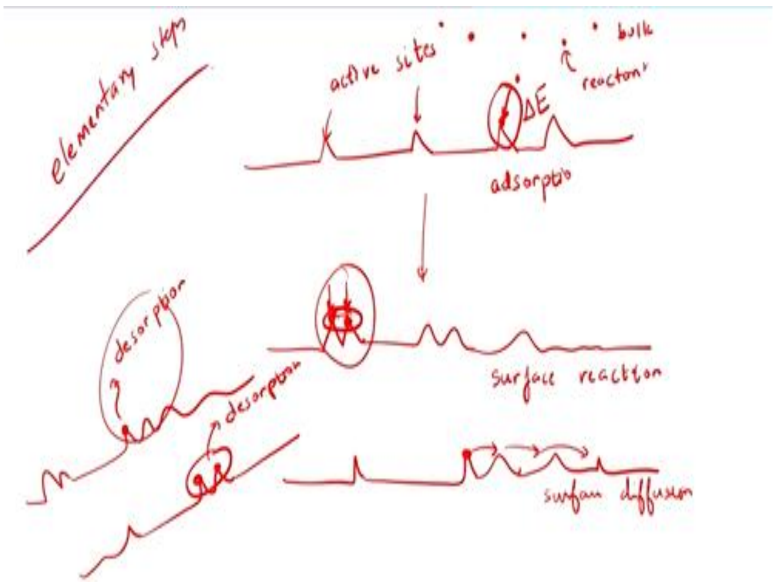
- Solid catalyst surface represented as a lattice, i.e. collection of connected sites of different types
- Elementary events (adsorption, desorption, diffusion, and surface reactions are simulated at instantaneous processes happening at random times
- Probability of finding the system at a particular configuration is given by $P(\boldsymbol{x})$ determined using the master equation

$$\frac{dP(\boldsymbol{x},t)}{dt} = \sum_{\boldsymbol{x}'\to \boldsymbol{x}} [w_{\boldsymbol{x}'\to \boldsymbol{x}}P(\boldsymbol{x}',t) - w_{\boldsymbol{x}\to \boldsymbol{x}'}P(\boldsymbol{x},t)]$$

$w_{\boldsymbol{x}'-\boldsymbol{x}}$ = Probability density of transition from state $\boldsymbol{x}'$ to state $\boldsymbol{x}$ in next time interval

So, one of the ways to do that is the kinetic Monte Carlo simulation again, but in this case, we are following a very different approach with this method has been particularly successful in the context of hydrogen catalysis. So, you want to model the reaction at the surface of a solid catalyst. So, there is a theory of catalysis that says that that reaction would involve basically four steps. The reactant had to adsorb on the surface then it can diffuse on the surface, of course the reactant can also diffuse in the bulk. Then there can be surface reaction happening on the catalyst surface between two reactants. And finally, once the product is formed the product may desorb from the surface of course, the reactant may also desorb without undergoing a reaction we can do it like pictorially.

(Refer Slide Time: 14:56)



So, let us say for example. This is my catalyst surface and these are some active sites where the reactants can come and sit. Let us say if these are my reactants present in the bulk. The adsorption step is when the reactants come and sit on the active site. This is my adsorption this is my reactant. So, reactant will of course diffuse in the bulk and then at some point they can adsorb on the surface and there may be some energetics there some adsorption energy of the reactant in there and that has to be negative really for the reactant to absorb on the surface.

And then once we have several such reactants on the catalyst surface and they are sufficiently close to each other. So, there is really no change in the location of active sites in the two pictures. But all I am trying to show is that two reactants may come very close on the catalyst surface both are on the active side but they can be sufficiently closed.

So, in that case now these two guys can undergo a reaction. Let us say in this case they form a product right here. So, that is my surface reaction part. Also, what may happen is the reactant may hop between sites on the catalyst surface that is a surface diffusion. And finally, the reactant on the site may go back to the bulk that is desorption and the same can be true for a product that is formed this entire thing can desorb so, it can be also desorption process of the product.

So, any catalytic reaction happening on a solid surface of a catalyst basically undergoes these four steps. Now let us say for example I want to analyze this reaction in detail. And let say for example, we have the capability of for performing quantum chemistry calculations. Now we can perform that only for the reaction part of it because the timescale of the chemical reactions are pretty small and even the length is scale is pretty small. So, we can simulate two molecules in quantum chemistry and depending on the molecule size this may take less time or plenty of time when we impossible but nonetheless even if we do that we are not accounting for the other steps in the process. The adsorption desorption surface diffusion, which are happening at much longer time scale in comparison to the chemical reaction. So, to model the adsorption desorption and surface diffusion or the bulk diffusion, we cannot really use the concept of quantum chemistry.

So, in that case, we need some sort of a multi-scale method that uses the quantum chemistry to analyze the chemical reaction part of it and use some kind of a classical kind of a framework outside quantum chemistry or some kind of a physical framework to look at the adsorption desorption processes.

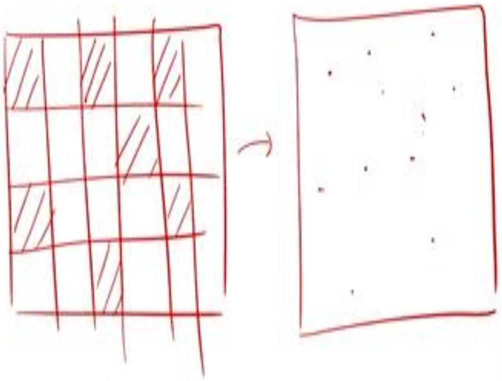
Now if I look at individually all these processes. There is certain energetics with all these processes at a local level. For example, when the adsorption is taking place there may be some energy change with that and I said this strategy change has to be negative. Same is true for the surface reaction, same is true for desorption process and all that.

So, although the time is scales of the adsorption and desorption and diffusion and surface diffusion may be very different from the chemical reaction itself. The actual energy change that is happening in these processes can still be computed using quantum chemistry calculations because in there you simply have to place a molecule of reactant near an active site and simulate the site along with the molecule or few sides around the molecule with the molecule and look at the energy rates are difficult to compute in quantum chemistry but the energy is we can compute because therein we can do very small systems.

So, this is the kind of idea that motivates the use of kinetic Monte Carlo’s scheme and the main thing in here is that with compute these energy changes of these different steps which are refer as elementary steps using quantum chemistry calculations and using that we; somehow compute the rate constants and once we have the rate constant, we put that into some kind of a Monte Carlo formalism and we perform some kind of a classical simulation and get the entire catalysis process that includes all these step adsorption desorption surface reaction and so on.

So, in a sense, it is a multi-scale modeling paradigm that has been particularly successful in the area of catalysis. So, the basic idea behind the method is to solve some sort of a master equation where we are basically looking at the probability of finding the system at a particular configuration and the way that we define the configuration in this case can be many but one of the common ways is we assume that my catalyst surface can be represented as some sort of a lattice. And I can assume a variety of lattices.

(Refer Slide Time: 21:26)



So basically, I am looking at only the 2d surface now that on the 3d volume of the catalyst. And then we say that some of these cells are my active sites or may be all of them are my active sites. And then I basically look at elementary steps happening on these active sites where the surface has been represented by a lattice this is one of the most common frameworks.

But we can also do it of lattice we can simply say that this is my catalyst surface and you have some random locations or some given locations of my active sites and then the reactant may come and sit on top of that.

In both these cases the basic physics remains the same but clearly this is going to be computationally difficult when compared to this and fortunately, most of the solid catalysts we are working with are having crystalline surfaces and that would make sense then to use lattice kind of picture because you always have well defined crystalline plane which can be represented using some kind of a lattice or repetition of some kinds of unit cells.

So, this is the motivation behind most of the kinetic Monte Carlo simulation in this area and we essentially solving them probability of finding the system in a particular configuration which would then be the configuration with respect to the lattice in the picture of the lattice. So, where the; species are in the lattice and then basically I look at the evolution of that probability using the difference of two processes.

One is a forward process and one is the backward process. So, forward process is one that brings the system into state x and the backward process is one which essentially takes away the system from the state x.

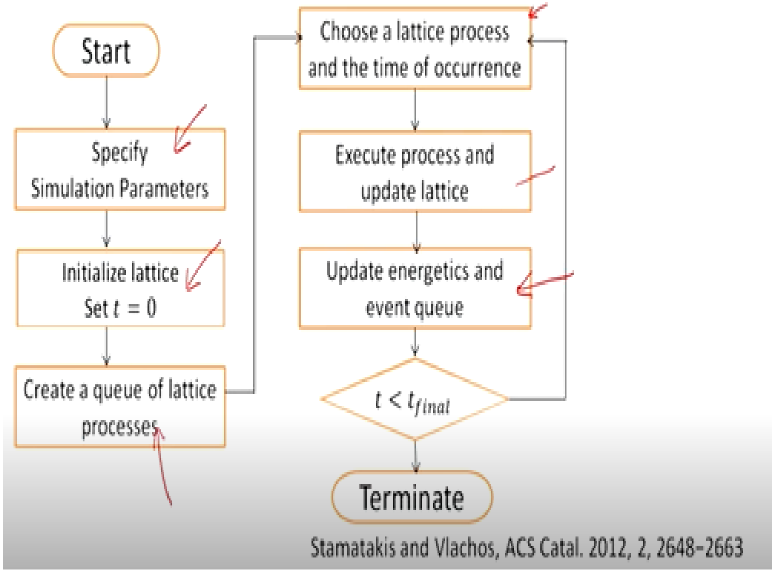
$$\frac{dP(x,t)}{dt} = \sum_{x' \to x} [w_{x' \to x} P(x',t) - w_{x \to x'} P(x,t)]$$

And since we are doing on a lattice, we have only discrete number of states we do not have infinitely many states as in the case of various spaces that we have been discussing earlier. Since we are doing on a lattice and typically, we are working with rather small lattice. Let us say 64 by 64. So, in that case we can pretty much enumerate the total number of possible states and then out of that all the processes that are coming to that particular state is defined as the forward processes and all the processes going out of the state is called the backward process.

So, another way to think about it is if these are my possible state then all the forward processes for this particular point are the ones which are coming here and all the backward processes are the ones which are going out of there.

Now, I want to emphasize here that it is precisely this kind of a quantity that we had set to 0 when we were doing a detailed balance condition because we were looking at the equilibrium in that case and at equilibrium the forward processes become equal to the backward process what we are looking at here is essentially the opposite of that we are interested in the evolution of the system not the final equilibrium state and therefore, we also have a dP by dt term, that was not present in the condition retailed balance. And therefore, this is not really the standard Metropolis Monte Carlo it is a totally different method even if the techniques may be similar to the Monte Carlo, but the method itself is very different both theoretically and also in terms of the algorithm of the method.

(Refer Slide Time: 25:56)



Stamatakis and Vlachos, ACS Catal. 2012, 2, 2648-2663

So, then W becomes the probability density of transition from state some state x prime to some state x and then basically the simulation proceeds like this we start and specify by simulation parameters which in this case may be the dimensions of the lattice the concentration of the reactants the concentration of the active sides on the lattice the rate constants of adsorption and adsorption processes. I was telling you that they can come from the quantum chemistry calculations but let us wait on that but let us say they are just known to you then we initialize our lattice the initial state can be for example a bare catalyst surface without any reactant that can be possible let say if I start the reaction at time t equal to 0 or we can start with some concentration of reactant in the beginning and want to see how the evolution takes place and then I create a queue of lattice processes.

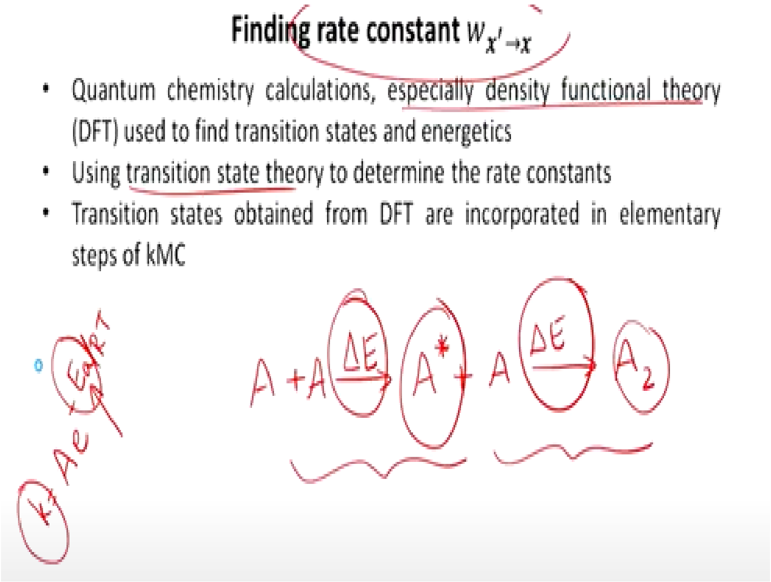
The processes here are at least the 4 adsorption, desorption diffusion and surface reaction but we can define even more number of processes depending on the system under consideration and then finally in here we start doing some kind of a Monte Carlo simulation.

So, we choose one of these lattice processes. Let us say ten things are possible then we can pick one of them that is a choice that we can make and we can do it by some kind of stochastic algorithm and we choose when, will that process happen and then we execute the process and as soon as we execute that we have two update the lattice because I have to say somehow save the changes that has occurred in the lattice.

Now as soon as, that change happens we have to also update the energetics because the energy changes have occurred because of that process that has to be accounted for just like the energy changes that happened in the metropolis Monte Carlo. But in this case, we are interested in the dynamics and this we continue until whatever time that we want to simulate we do not wait for the equilibrium or anything let us say I want to study for one minute. I want to look at the evolution that we run for only one minute.

So, in this case the idea is totally not to look at the equilibrium behavior but only the evolution is starting from an initial state and for most chemical reactions only the initial part is important because the reaction rates are pretty large in the beginning that are only in the catalyst is bare then the reactions are much faster than compared to the case when the catalyst is all occupied by the reactants.

(Refer Slide Time: 28:48)



Finding rate constant $w_{x' \to x}$

- Quantum chemistry calculations, especially density functional theory (DFT) used to find transition states and energetics
- Using transition state theory to determine the rate constants
- Transition states obtained from DFT are incorporated in elementary steps of kMC

$k = Ae^{-E_a/RT}$

$A + A \xrightarrow{\Delta E} A^* + A \xrightarrow{\Delta E} A_2$

So, with this particular idea what remains to be done is we have to find the rate constant. I was telling you that we can of course take it as some guess value to begin with but the better way to work with this as I said is the quantum chemistry calculations. And in this area, especially the density functional theory method, the DFT method in quantum chemistry is particularly used not only to get the energy changes but also to find the transition states in chemical reaction.

So, you may recall from the chemistry class that many reactions involved transition states. Let say this particular reaction. I am showing here where A and A_1 to combine to form A_2, but it does not happen in one step it may involve the conversion of a transition state. And depending on the specifics of the reaction the transition states may be different or there can be multiple transition state or there can be no transition state.

So, when I look at the chemical reaction in this picture, we will not represent the chemical reaction as a whole as an elementary step but each of these individual steps from the reactant to a transition state from a transition state to other transition states and a transition state to a product as separate elementary steps and therefore, this method can then track the mechanism that is basically incorporated in your model framework. And of course, the transition state should be known to us and that and that is where the quantum chemistry calculations can help us it can provide us the transition state and therefore, we can build a mechanism and based on the mechanism we can define the elementary steps and we will know also from quantum chemistry the energy changes for all these elementary steps.

Now using this energy changes, we can also find the rates of these elementary processes using a theory known as the transition state of theory. As an example of such calculation, you can look at the Arrhenius law the rate constant is given as –

$$k = Ae^{-\frac{Ea}{RT}}$$

where Ea is the activation energy.

Transition state theory is somewhat more detailed version of the Arrhenius law but the essential idea remains the same that were relating the rate constant with the energy. And energies we can find using the quantum chemistry calculation in this case the DFT calculation.

So, with this particular idea then we have some sort of first principle method that can predict the fate of a catalytic reaction happening on the solid surface. The reason why I am saying it first principle is because the elementary rate constants are coming from quantum chemistry calculations, of course coupled with transition state theory we are accounting for the presence of transition states that also has been computed in the quantum chemistry.

The only bit where the Monte Carlo simulation is coming in is when we want to look at all the steps together how the elementary steps couple with each other and how can we find the total rate of chemical reaction or total rate at which the products are formed which in this case depends on the fate of multiple reactions happening at multiple x to active sites and also, other processes like adsorption desorption and diffusion and all of that can be done in the kinetic

Monte Carlo simulation.

So, in this way we have an excellent multi-scale paradigm where we can simulate a large catalyst surface large compared to what we were typically doing in the molecular simulations or what we could do in the quantum chemistry but still pretty small when I compared to bulk systems that we are used to but this pretty much provides one of the best possible examples of how the multi-scale paradigm can be useful in the design of catalytic materials.

So, with that I want to conclude todays lecture. In the next lecture I will discuss another class of method that is known as the reaction force field or reacts FF.

With that I want to conclude. Thank you.