Basic Statistical Mechanics

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Lecture -07

From Postulates to Formulation

In the very first lecture, I talked about why we need to do Statistical Mechanics. It is a difficult subject, very difficult subject and in the evolution of Statistical Mechanics, physicists and chemists, almost, you know, they were hand in hand. Many-many things were done together. Willard Gibbs (he was one of the fathers of Statistical Mechanics), many times, was considered to be a chemist. When I was doing PhD, he was referred to as an American chemist. Now I think physicists claim him as much as chemists.

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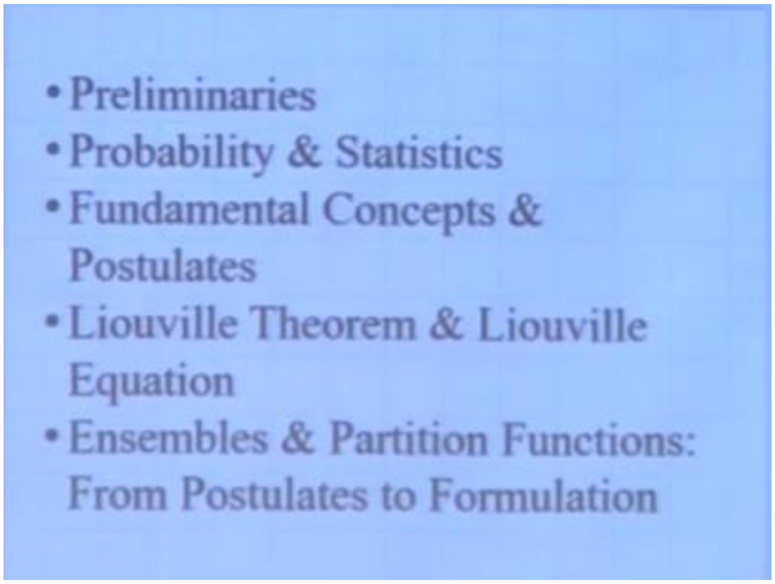

- Preliminaries
- Probability & Statistics
- Fundamental Concepts & Postulates
- Liouville Theorem & Liouville Equation
- Ensembles & Partition Functions: From Postulates to Formulation

So in the very first lecture, we did the preliminaries. We talked about if you take an undergraduate physical chemistry or even MSc level physical chemistry book what you will find is that the chapters except for the wave mechanics (quantum mechanics), 1 or 2 chapters on spectroscopy if there are 32 chapters you will find 20-25 chapters are things like kinetic theory of gases, thermodynamics (entire 3-4 chapters of thermodynamics), then you have a phase equilibrium, then you have a phase transition, then you have a binary mixture, you have solution, electrochemistry. All these chapters that you study, they are all.

You remember, when you study of the conductivity the ions such as lithium, sodium, potassium etc., then conductivity- times- viscosity ($\Lambda_0 \times \eta$) is plotted against the size; they are supposed to go as one over the size of the ion ($1/r_{ion}$). (Here the size of the ions refers to their crystallographic radius). But it just goes instead of going like a straight line, it just goes the maximum and falls back. If you remember, conductivity- times- viscosity is called Walden product and that non-monotonic behaviour is called the breakdown of the Walden product. The reason I am talking of the breakdown Walden product is that because I want to make a point and a very important point which is the following.

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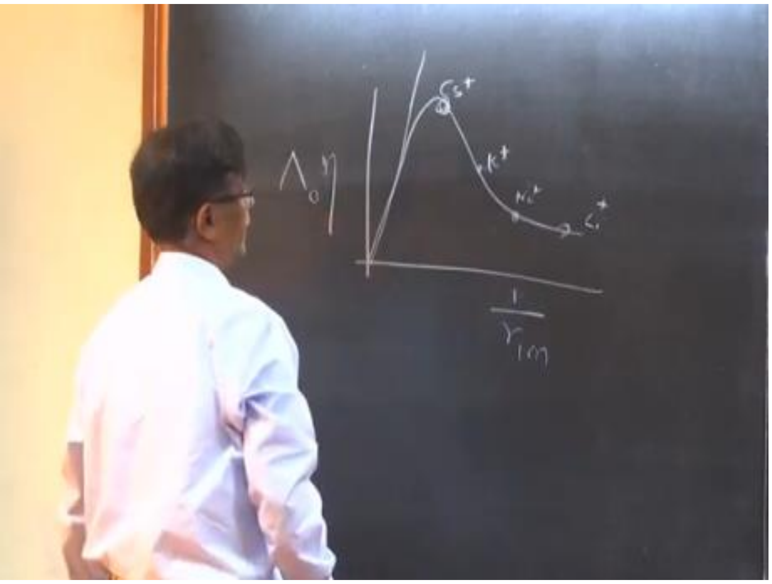

So, Λ_0 is the limiting ionic conductivity. In electrochemistry, you have read Debye-Huckel theory and the limiting ionic conductivity. η is the viscosity. Λ_0 is nothing but what is called the diffusion. And diffusion is inversely proportional to viscosity. So this product ($\Lambda_0 \times \eta$) should vary as $1/r_{ion}$, which is like this (straight line). Instead of that what happens, it just comes down like that and this is lithium, then sodium, then potassium it goes like that and this is here where caesium, rubidium and all these guys lie. Maybe the potassium will be closer to caesium.

So, in the undergraduate physical chemistry textbooks of Castellan or Moore or Glasstone or Atkins, they call this breakdown of Waldan product and give some pictorial description like ice-berg formation around the small ions. So the basic idea of my telling this is that in much of physical chemistry, in undergraduate, whenever we have anything interesting going on, we have a picture that came but that picture was mostly very approximate.

However behind all these pictures, there is a quantitative theory that was largely developed in the post 1950 and or maybe 1960, 70s and aided enormously by the computer simulations.

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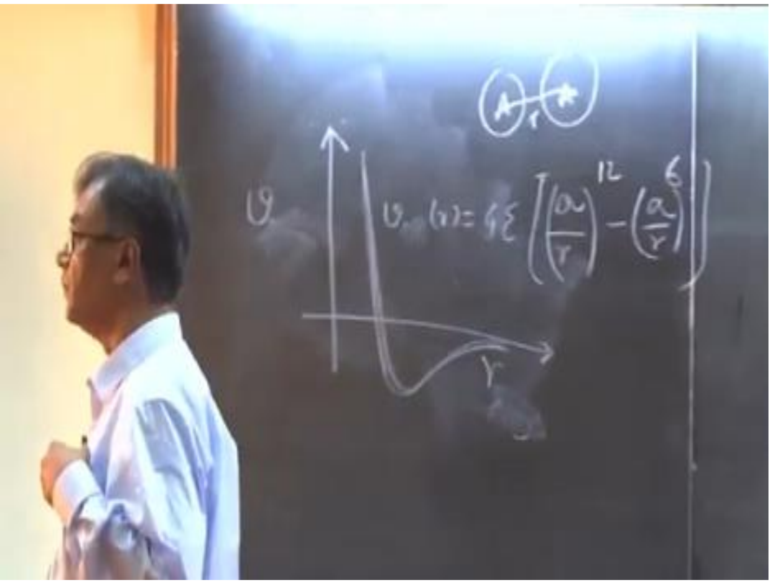

So, Statistical Mechanics has come of age now and like in quantum chemistry you have all the packages. So, a student working in a quantum chemistry laboratory can always have these packages and they use these packages, for example, doing organic chemistry calculations and other things. In Statistical Mechanics, those kinds of packages are just coming now in terms of GROMACS or AMBER or independent force fields. It has become much more institutional wise now.

So there are a lot more calculations going on and it has pretty very important interesting things. It is a rapidly developing field; a huge amount of work is going on. It is not that much visible still in India, though there are now significant numbers of people doing Statistical Mechanics in chemistry and physics (the number of people is huge in physics). So this was the preliminaries. I explained, why you need to invoke Statistical Mechanics to understand what we call the “large-scale phenomena”.

Large-scale phenomena include many particles. Examples of large-scale phenomena are phase transitions, conductivity or understanding thermodynamics, or phase equilibrium, all these things. We discussed that in the first lecture. In the second lecture, we had a little bit of mathematics where we did probability and statistics. Because this name is Statistical Mechanics which combines mechanics.

Mechanics is very deterministic, it starts with Newton's equation. If the initial conditions are given to you, you can predict the future. But, as I told you, unfortunately, we cannot even solve what is called a 'three-body problem', that is even if you have three particles, we cannot solve that analytically. Even two-particles, having a little complicated potential such as radial potential or Lennard-Jones potential,l even that has to be done through a quadrature.

So this is an interaction between A and B. r_{AB} is the distance between A and B. This is the Lennard-Jones potential, we call it 6-12 potential. The form is $v_{AB}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r_{AB}}\right)^{12} - \left(\frac{\sigma}{r_{AB}}\right)^{6}\right]$. It is a universal notation. Let me say A and B are the same, two particles both are A, then I do not need the B. I can do without this index (subscript AB). There is a separation between them that is *r*. and this is the form of potential. It is very important to understand these things i.e. the interaction potential between two particles.

When they come from a distance, they attract each other. But when they come too close, electrons overlap and there is a huge repulsion. This simple potential, apparently simple potential, plays a very important role in the understanding of many phenomena such as solvation, phase transition and many things. However, coming back to the point, even these potential in a two-body, we have to do by quadrature and by the time I go to three-body potential (i.e. if I bring one more particle), I cannot solve Newton's equation anymore.

However, when you think of the properties of water then you think of properties of water in a glass which are Avogadro number of molecules and they are strongly interacting and we cannot use Newton's equation anymore to solve them. If we want some really very complicated and sophisticated effect like polarization i.e. one molecule is polarizing another molecule then we have to do quantum mechanics that is even more difficult.

So, we have faced a situation where we have to explain natural phenomena like why ice melts? And then why water at 100 degree centigrade becomes steam? When I put a solute in a solvent, why depression of freezing point and elevation of boiling point happens? These kinds of things if you want to understand, you cannot, do from the first principles. What do I mean by the first principles? These are the terms we use again and again in Statistical Mechanics. We also use these in Quantum Mechanics.

In Quantum mechanics, when you say the first principle, we think that we are starting from Schrodinger equation and interaction potential and going about it. Of course, they are looking at the electronic properties and there are approximations and there are answers. In Statistical Mechanics, while one can do Quantum Statistical Mechanics, right now let me focus on Classical Statistical Mechanics because of the large-scale phenomena like phase transition or as I am saying why steam bites you more than water at the same temperature, depression of freezing point when you add salt. That is what the principle of ice cream that you get, you can go to minus 20 degree centigrade that is where ice cream falls. You can do that experiment by doing that. There is an ice cream maker and there is liquid there which then goes very low temperature and you put milk and you can make the ice cream.

So these many large-amplitude phenomena that you want to understand, we cannot do by following Newton’s equation anymore. So then we need to go further but how do we go. Classical Mechanics means Newton’s equation or Hamilton's equation or whatever. Let us continue with Newton's equations which you know. Newton's equation then is not going to help us because we cannot even solve a three-body problem.

That is where Statistical Mechanics comes in. It was formulated starting with Maxwell-Boltzmann, then Willard Gibbs. So, what is then I do? I cannot do mechanics as I know it. So I had to drag the other. This was a huge conceptual and philosophical problem at the end of 19th century when people started introducing the concepts of statistics. It all started with the work of Maxwell. You all know the Maxwell velocity distribution.

Maxwell is the first guy who told if I have, in a glass jar, a bunch of atoms or molecules at a temperature T, I do not need to follow properties of each atom and molecule. Instead, I can talk in terms of distribution. So Maxwell said, Boltzmann also said what are the properties we want to know? I want to know the viscosity of the gas and later viscosity of the liquid.

I need to know the pressure, equation of state. You know $PV = nRT$ is the ideal gas law but if you go to a little high-density ideal gas law breaks down and then comes the Virial equation. How do then I get the Virial coefficients? So, then Maxwell said, I do not need to know individual atoms and molecules in a striking departure from classical mechanics, instead I will talk of a probability distribution.

As soon as the concept of probability distribution came in, then came the question of statistics. How do I define probability? I need statistics to define probability. So that is what it was the second lecture where we discussed probability and statistics. Then in the last lecture, the third lecture, we started talking the postulates. So fundamental concepts and postulates, I will revise a little bit of that but then I will not go to Liouville theorem in this lecture. I will do it later.

I will directly go to something which has little bit more applications: ensembles and partition functions. These are from my book and what I have written there that, actually earlier I have this, from postulates to formulation. So we will go to the formulation of Statistical Mechanics. Today so it is a very important class in that sense, this and the next class. What I had before the title is that from promises to realization.

Because there was this promise that was made by Boltzmann and Willard Gibbs. Willard Gibbs mostly realized it. So, both Boltzmann and Willard Gibbs played a role in giving us the main postulates of Statistical Mechanics. From there will directly go now because this is more to do with dynamics and we will do that at some stage but not now. There are two postulates which are connected by the one hypothesis and based on that Statistical Mechanics promises to explain the natural phenomenon which is very high.

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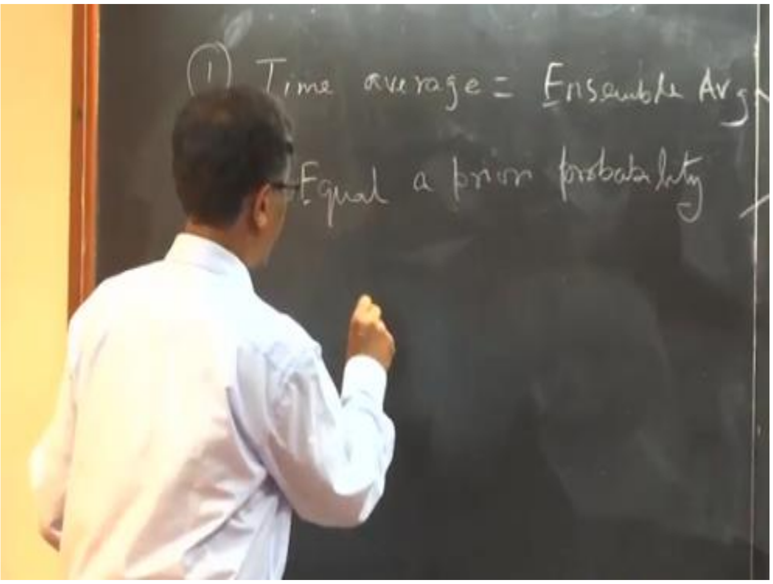

So, there are postulates that I did last time also but this is so important so that there is no harm in doing it once more. So the first postulate is called time-average is equal to ensemble average. And the second postulate is called equally a priori probability. What is not told in a not any book is that why do we need the hypothesis? These two postulates are connected by Ergodic hypothesis. I will spend next 5 minutes talking about it then we will go to the partition function and ensembles.

How did that come? It came because Boltzmann tried very-very hard to develop a kinetic theory of gases. So, when you read, as I mentioned this last time, in Quantum Mechanics if you noticed, I did not notice, but I realized later partly because of a book I picked up, of the Ryogo-Kubo in Presidency College, the old books next to presidency college that when you study quantum mechanics since all the way from hydrogen molecule, you do not have any name.

You know there is no name because particle in a box, rigid rotator, harmonic oscillator, hydrogen atom, hydrogen molecule that because everything was done by Schrodinger alone. You know when he first hit upon the idea he went to a resort area and stayed 3 months there and solved everything. So the whole quantum mechanics as we read in MSc, you know is that done by one man.

Similarly kinetic theory of gases again, there is no name. Almost entire of the kinetic theory of gases was done by Maxwell and a bit here and there by Boltzmann later. So when this beautiful paper of Maxwell appear, there are other papers around that but not as clear as Maxwell and also not went to English-speaking world, then Boltzmann fell completely in love with that paper until the end of his life. He died early, in 1906.

He carried that paper and then he tried to extend Maxwell's work. Maxwell had this funny mix of assumptions that particles are like billiard balls but then, on the other hand, he is also talking of an ideal gas, ideal gas do not interact they pass to each other. So, there were these contradictions in all the ideal gas, in our study of kinetic theory of gases. So Boltzmann set out to extend it to real gases and separate and there is a famous equation i.e. Boltzmann kinetic equation.

But Boltzmann did not fully succeed, he tried very hard. He could go only to very dilute gas and he also made some assumptions, which were heavily criticized to the extent that probably caused his death. Now, when Boltzmann tried very hard and could not take into account even, he is the first one. Maxwell had it, the concept of probability distribution but he did not explicitly state that in his formation and that was done by Boltzmann.

He explicitly added probabilistic concepts. He said, if I have a probability of a particle at a position r with momentum p, I call it $f(r,p,t)$. Another particle at position r_1, p_1 there r_2, p_2 then together I have a two-particle distribution like I call up $f_2\,(r_1, p_1, r_2, p_2, t)$ that at a given time, a particle as r_1 and p_1 another particle as r_2, p_2 i.e. a two-particle distribution. It is so difficult because it has r_1 and r_2 all of 3 dimensions i.e 3+3= 6; and p_1 and p_2 have another 3+3 = 6. What a beast it is! So, he made an approximation that $f_2\,(r_1, p_1, r_2, p_2, t) = f_1(r_1,p_1,t)\, f_1(r_2,p_2,t)$.This was called random chaos approximation and he was immediately and hugely criticized for making this approximation. But there was no other option. Subsequent whole century people have tried, 100 years people have tried to extend that and have done to some extent. So when Boltzmann tried these, he could extend all little.

On the other side of Atlantic, one person who looked with concerned at the difficulty faced by Boltzmann, who was equal fan of Maxwell and Maxwell distribution, his name is Willard Gibbs. Willard Gibbs then thought what Boltzmann did is not tenable anymore, we cannot go that way because we cannot do two-particle. Three particles are out of the question and there are also many other complexities.

So then Willard Gibbs made the important observation that, as I told in the last class also, let me have 10 glasses, 10 glasses of water half full, now I look into it. By that time the microscopic motions and all these things, kinetic theory of gases were somewhat already understood. So if I think of the microscopic state and a microscopic state now is defined by giving the position and momentum of each particle.

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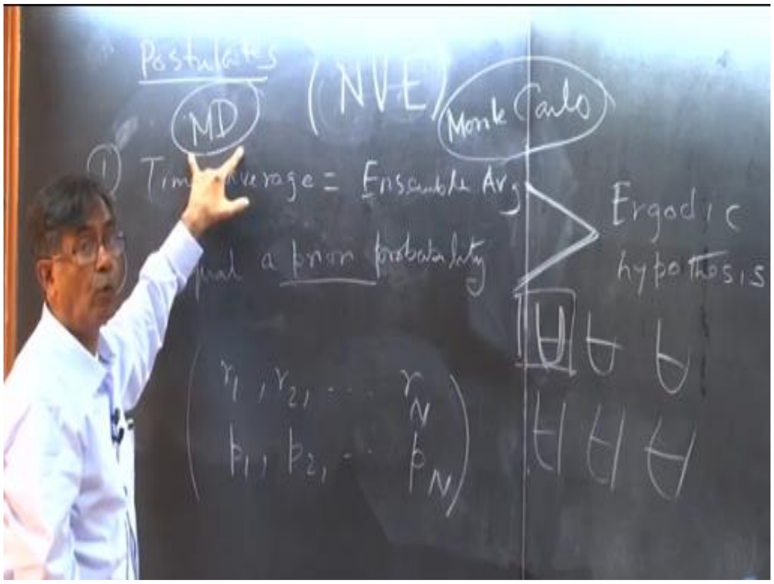

So I have N particles then I give you $r_1, r_2 \ldots r_N$, I give you $p_1, p_2, \ldots p_N$ that together determines my macroscopic state of the system. Now in my 10 glasses, all these have water, now all of them have the same properties, they are at the same temperature, they have the same volume, they have the same pressure, they have the same specific heat, they have the same conductivity, same entropy, every property is the same.

But certainly, the microscopic state of all of them would be different because there is such a huge number of microscopic states. Atoms and molecules are moving around. So, then Willard Gibbs realized that if I can now have a mental replica; I have just one, this is my system in course this is my real system. Now I mentally construct billions and billions of my mental objects such that they are thermodynamically same but their microscopic states are different.

This mental construction is called an ensemble. Then he said if I wait for a long time then my this system, my system in question going to go through all the microscopic states, so these are essentially same microscopic states in which all these particles are. If I now in my mental replica I create a mental, billions and billions of copies of these things which I call ensemble, the collection is called ensemble.

If I can take an average of that then that would be same if I now study what Boltzmann tried to do, study the detailed trajectories; trajectory means the path that the particle takes, all the particles take together, that will be the same. That if I can do the time averaging over infinite time as Boltzmann tried and if it can be placed by the ensemble averaging, averaging over all this mental replicas, both will be the same.

So that was the first postulate of Statistical Mechanics i.e. time average equal to ensemble average. Now as soon as Gibbs did that, there is a problem, a problem came that when I am doing time averaging, I have one system which I am studying for a very long time and I am studying the motion of atoms and molecules their positions and momenta; and then I am averaging a property for example pressure, I am averaging a property, for example, the internal energy, their enthalpy, entropy but now I have a replaced it by my mental construction. But what is the guarantee that the system I am following for infinite time will go to all the microscopic states? And second, even if they go to all the microscopic states how do I give a probability to it?

So that is the time, he introduced that I am going to talk of the systems with a constant number N, constant volume V and constant energy E. So all my mental replicas have a constant energy E. So all the microscopic states have the same energy. If all the microscope states have the same energy E, then I can now assume (and I have no other option but to assume under this ensemble) that there is equally a priori probability i,e. all the microscopic states are equally probable.

There is no other option than to do that. It turned out, it is correct. It worked out but that means all the subsequent work said that is okay. All the microscopic states with equal energy are equally probable. People still work on this. So these are the two postulate. The first postulate introduced the ensemble, one of the most brilliant ideas that mankind has ever come up with. This probably does not get the sufficient credit that how brilliant this construction is! Then time average is equal to ensemble average.

But as soon as this was made, here to average over all the microscopic states and he needed the probability of being in a microscopic state. But since they are all the same energy, the natural postulate was that they are all are equally probable that is equal to a priori probability. But there are no other options and it turned out to be. Now came what as in between started talking about that now, he faced the problem, following problem.

I have done time average, I have done some ensemble average and I have set equal probability, in ensemble average, I am going to billions and billions of microscopic states. But what is the guarantee that when I do a time-averaging, the system goes through all the microscopic states in a given time, what is that guarantee? Then comes the constrain, the hypothesis which is Ergodic hypothesis which means the system indeed given sufficient amount of time, it visits every microscopic state equal likely.

So the first postulate requires the second postulate because to average over the ensemble and once this is set then I have to make sure that my system visits every state. So this is then they made the Ergodic hypothesis which connects these two postulates. So this is the very important point of the statistical mechanics and why it is important because armed with these two postulates and hypothesis, that is where everything whole of statistical mechanics is built on. It is very amazing.

This is what you can say equivalent to the wave function. And the wave function has to have these properties, satisfying Schrodinger equation, ψ^2 has to be positive and square-integrable. The similar kind of things that comes here in this statistical mechanical formulation. This is very-very important to understand.

This part is more important to understand because now as I was talking you a while ago about the different packages, the time average is what we call now the molecular dynamics simulations and this is the ensemble average what is called Monte Carlo. So these are the two major branches of computer simulations that we do. And the same problem, emphasized by Gibbs, so many years ago, more than 100 years ago it is exactly the problem we face now.

So when I do equilibrium statistical mechanics, equilibrium properties like a phase transition, I land up the problem by one phase to another phase that cannot be done in molecular dynamics simulation because it cannot explore all these things, it gets stuck in a minimum. We will talk about it. Now that is where you go to Monte Carlo, which is much better to calculate time-independent equilibrium properties.

Now Students are asking me today, why do we mix these two? The reason we mix the two is that many times molecular dynamics get stuck. So we follow a hybrid where you start with a multiple, not too many maybe 10 or 20 initial condition, then do molecular dynamics from that and then the probability of initial state given by the energy. So the hybrid simulation is a very popular thing now, to study really complex problems like in biology or like water at very low temperatures. There are a lot of interests now, you know at low temperature there is some presumably liquid-liquid transition.

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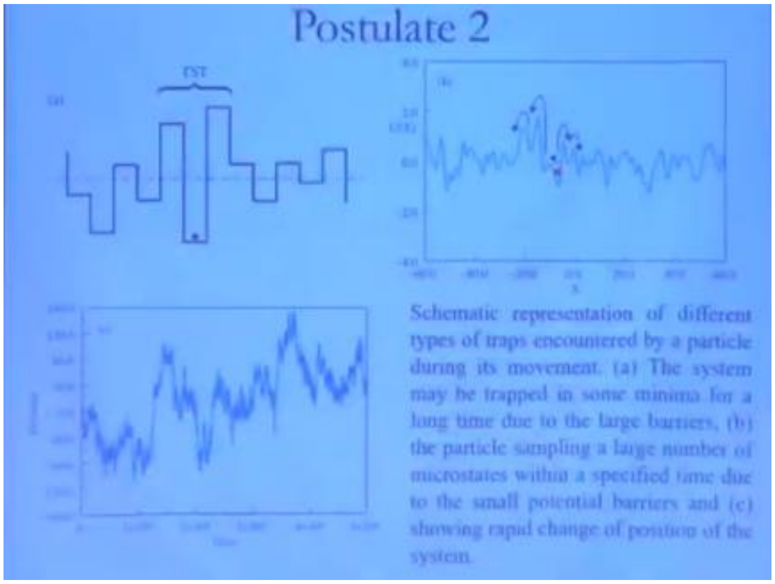

Postulate 2

Schematic representation of different types of traps encountered by a particle during its movement. (a) The system may be trapped in some minima for a long time due to the large barriers, (b) the particle sampling a large number of microstates within a specified time due to the small potential barriers and (c) showing rapid change of position of the system.

So, now I will slightly talk if I have. Now this is the kind of thing that I want to point out. Say I have a particle which is undergoing some kind of motion. So this is a particle but I have a kind of energy landscape like this. In that case, the particle can get stuck here. This is a very simple thing, a one-dimensional walk, random walk, but in an ordinary random walk, drunkard's random walk you have flat energy. What you have here is called rugged energy landscape. Such a simple problem, one-dimensional with energy distribution, it is just hell to get a molecular dynamics simulation going into this kind of a system because it becomes non-Ergodic very quickly. And so if you want to calculate equilibrium properties you do a Monte Carlo, you just sample. That is very easy to do. On the other hand, if you want to calculate dynamical properties, it becomes very- very difficult.

So this is an example of what we call compromised Ergodicity. So the Ergodic hypothesis was particularly made to make sure these kinds of situations are not done. Now, why is it less serious? In many of the cases, in NVE, because all of them are the same energy, these will be ruled out if I can do this simulation in NVE because these kinds of things are not allowed. However, in the real systems, we do not do NVE, we do the other ensemble which I am now going to discuss.