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

Lecture – 53

Monte Carlo in Gibbs Ensemble and Semi - Grand Canonical Ensemble, Thermodynamic Integration

Hello all of you so in the last lecture we discussed the grand canonical ensemble simulations and we have said that it is very convenient when we are interested in the phase equilibria and the reason that we gave was that if for example I am looking at two phases in equilibrium let us say 1 and 2, I want to equate their chemical potentials at equilibrium and therefore it would therefore make sense to simulate in the constant chemical potential case because then I can vary the chemical potential and look at the phase equilibrium behavior.

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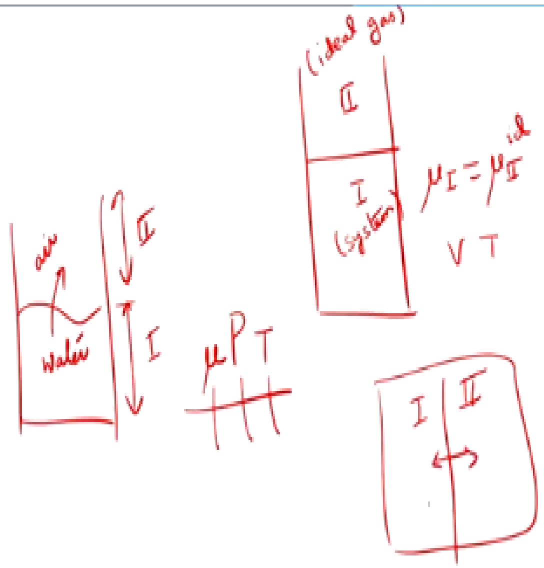

For example, if 2 is an ideal gas and 1 is my system we have kind of a convenient regime where I can do the phase 2 using the ideal gas thing where I know the expression and I only have to simulate the system and therefore I can simulate a different chemical potential and therefore we can find when will we have the phase equilibrium condition.

However in the grand canonical ensemble the volume and temperature are also controlled. In most realistic cases when we have an open system it is not really the case because let us say for example we are looking at an open system containing water in contact with air, where water can evaporate and go into the air. So, in that case clearly if water forms a phase a thermodynamic phase then the volume of water is also not fixed.

So, what would have been more convenient is, so we can keep the chemical potential control variable or chemical potential constant, but we can let the volume change because volume in the phase one is changing here and the same is true for other cases of phase equilibrium we can imagine whenever we have an open system and therefore we want the volume to change we can work at constant temperature so ideally we want to work as something like a μPT ensemble where volume may also vary and I can work at a constant chemical potential, so it turns out that μPT is not really a valid thermodynamic ensemble because all of these are intensive variables so there is no variable containing the system size and therefore we cannot really work on that, something closer to that we can achieve using a method called the Gibbs ensemble method where the volume is allowed to vary but then we are also simulating the system two and in some sense it is good because we do not have to assume that the system two is an ideal gas.

So, we have one and two and these can be pretty much anything, but the volume of each of these systems can change and the chemical potential can be held constant or a controlled variable. So, it is something that looks like a μPT ensemble in principle but it turns out that it is indeed a canonical ensemble still in some limit and I will not go into the math behind it but it is just some approximation of the canonical ensemble under some limit this gives me the canonical ensemble behavior,

So the idea here is that I assume a large box and the large box is at constant volume and constant number of molecules and there are two parts of the box you can imagine there are two boxes if that is more convenient and the two boxes are in contact. So, they are exchanging molecules but they can also exchange volume.

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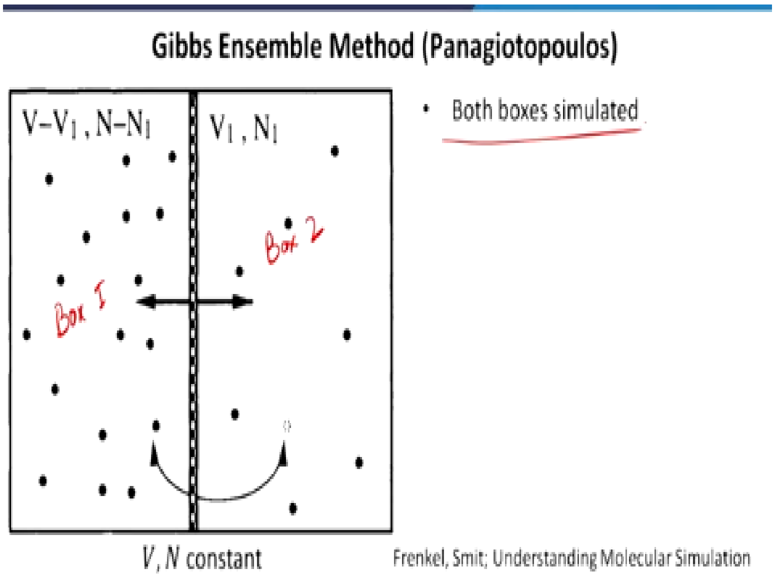

Gibbs Ensemble Method (Panagiotopoulos)

- Both boxes simulated

Frenkel, Smit; Understanding Molecular Simulation

So, they are doing both the volume change and the molecule transfer between each other and now I am simulating both these boxes so let say this is my box 1 and this is my box 2 I am simulating both of them so I am basically able to transfer molecule from one box to the other and I can transfer the volume or if I decrease the volume in one box then I increase the volume by same amount in the other box and vice versa. Both these boxes are being parallelly simulated this is very intelligent method by Panagiotopoulos but now it has been used for a variety of calculations of phase equilibrium it turns out to be like one of the most commonly used methods for phase equilibrium particularly in the liquid like media.

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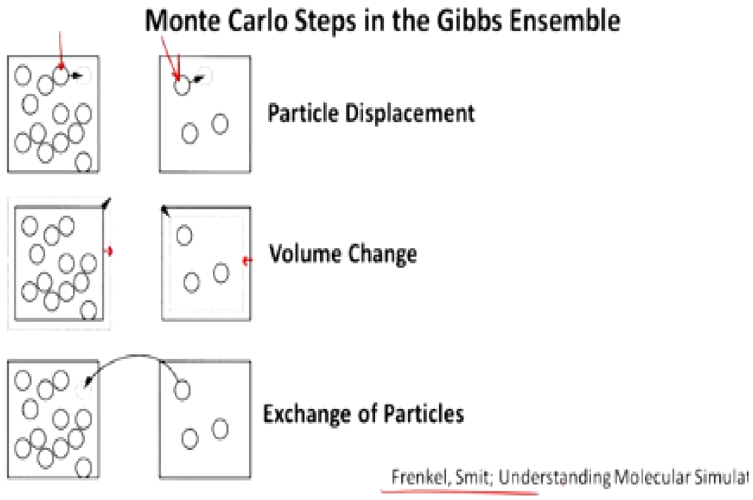

Monte Carlo Steps in the Gibbs Ensemble

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So, we are simulating both of them and then the kind of movements that we make in the Monte Carlo algorithm is I start with the two boxes 1one and box 2 and there can be individual particle displacement in both of these boxes. So, in this case for example one particle in box 1 is moving and one part particle in box 2 is moving and both of them are pretty much happening together then there is some volume change.

So, if box 1 increases in volume then box 2 decreases in volume and finally there can be an exchange of particle in this case a particle from box 2 is coming to a location in box 1 and this process is continued until we get the condition of equilibrium in this case the phase equilibrium. So, this is the basics of the Gibbs ensemble simulation I will not go into the detail numerical implementation of that but I would refer to the book by Franklin and Smith that has I would say the detailed algorithm and description of what exactly is a theoretical foundation behind the Gibbs ensemble.

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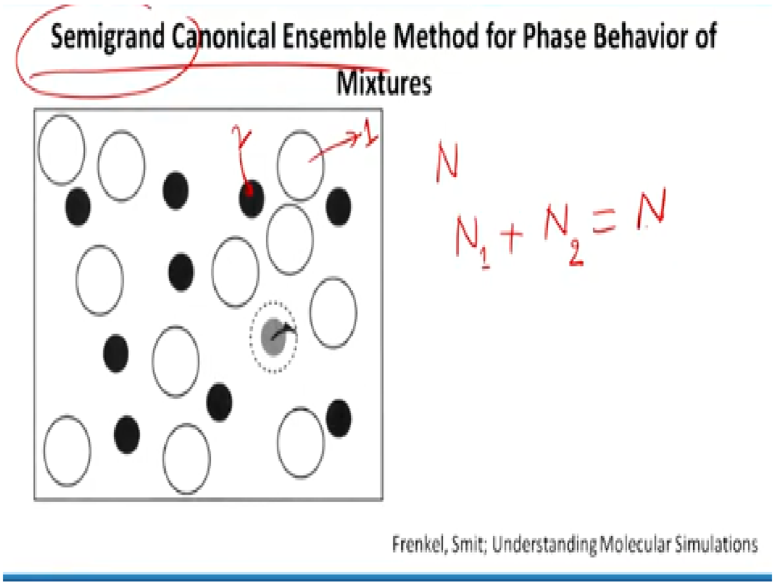

Semigrand Canonical Ensemble Method for Phase Behavior of Mixtures

N

$N_1 + N_2 = N$

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One of the other methods that are particularly convenient for mixtures and along the lines of what we have discussed is the following. So, it is called the Semi-grand Canonical Ensemble Method and in this case what we do is we start with the system containing a binary system of particles, we can have more than two components as well in this case this white guys are one component and black guys are another component and what we do in the simulation along with particle displacements are we change the identity of the particles in this simulation. So, you can have a Monte Carlo step where particle of species one become particle of species two and vice versa.

Now this is not really happening in the physical sense because Monte Carlo is not looking at the true dynamics this is only happening in the artificial sense, because I am interested in the equilibrium composition of the mixture for example, at a particular chemical potential and so on and therefore we can do this kind of artificial displacement and we can keep on doing it and find the composition of individual phases at different chemical potentials and so on and the method is called semi-grand Canonical because the total number of molecules are fixed but the number of molecules of individual species let us say species 1 that is N 1 here and species 2 that is N 2 here they can change but their sum has to be constant and therefore we call the name semi-grand Canonical ensemble.

So, all the methods that we have discussed so far they were focusing on the phase equilibrium problem where I want to look at the coexistence behavior of the two phases we have discussed the Grand Canonical Ensemble the Gibbs ensemble and semi-grand ensemble.

Now I want to come to the general problem of the free energy calculations because if I can compute the free energy not only I can look at the phase behaviour but also it is important to look at phase transition in more general and several other cases where we have large free energy barriers and that cannot be simulated within the conventional Monte Carlo or molecular dynamics simulations.

The first question however that we can pose is why did we not compute the free energy in the conventional Monte Carlo molecular dynamics because we; have been sampling the phase space, so in principle we should have had the partition function because all the evidences that we had computed. All the canonical or other evidence for different ensembles that we have computed they were done by already an integration over the dr and dp variables in the phase space then what is the problem with the partition function?

And the answer to this lies in the fact that we have always preferred to choose configurations which are of lower energy that is in the metropolis algorithm. For example, we assign more weight to the configurations that have higher probability that is larger value of exponential of minus βu. So, that by default ignores many configurations that are of higher energy on the other hand when we look at the partition function it is not difficult to see that the higher energy configurations have a big role to play in the partition function itself.

$$Q \propto \int dr^N e^{-\beta u} = \frac{\int dr^N}{\frac{\int dr^N e^{\beta u}\, e^{-\beta u}}{dr^N e^{-\beta u}}}$$

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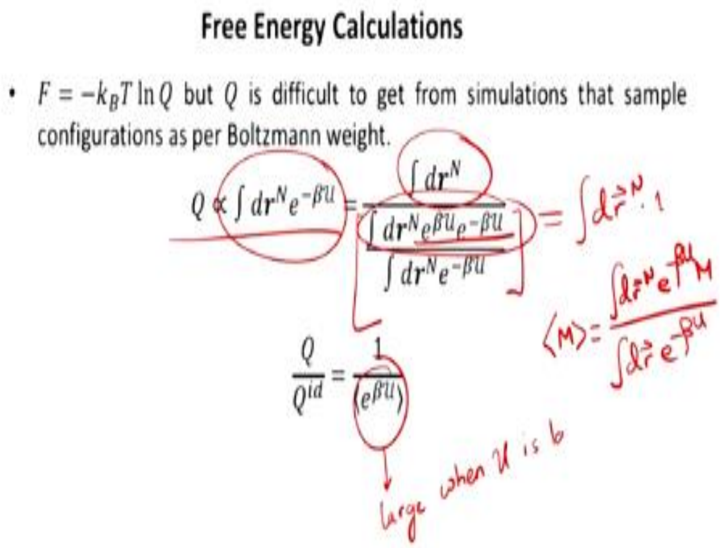

Free Energy Calculations

- $F = -k_B T \ln Q$ but Q is difficult to get from simulations that sample configurations as per Boltzmann weight.

$$Q \propto \int dr^N e^{-\beta U} = \frac{\int dr^N}{\left[\frac{\int dr^N e^{\beta U} e^{-\beta U}}{\int dr^N e^{-\beta U}}\right]} = \int d\vec{r}^N \cdot 1$$

$$\langle M \rangle = \frac{\int d\vec{r}^N e^{-\beta U} M}{\int d\vec{r}\, e^{-\beta U}}$$

$$\frac{Q}{Q^{id}} = \frac{1}{\langle e^{\beta U} \rangle}$$

large when U is b

So, let us say for example, I start with the configuration part of the partition function that is simply an integral of exponential of bit minus beta u, I can rearrange in the following way. So, I can write the ideal gas part that will correspond to essentially u equal to 0 and I can divide again by the same quantity dr N but instead of 1 I have put e to the power beta u multiplied with e to the power minus beta u and then whatever we had here that goes in the denominator of that and this rearrangement tells me that the denominator of this expression now is basically if you look carefully, is the canonical average of exponential of βu because in general evidence of any property is-

$$< M >= \frac{\int dr^N e^{-\beta u} M}{\int dr e^{-\beta u}}$$

the denominator is the partition function.

If I put M = $e^{\beta u}$ I will get whatever we have in the denominator here and the numerator already is we have said is the partition function of the ideal gas. We are not keeping the pre factors here because they anyway cancel out. So, what this means is the partition function of a system can be written as the partition function of the ideal gas that we can compute analytically multiplied with 1 over the economical average of $e^{\beta u}$.

Now clearly this quantity is going to be large when U is large and the metropolis algorithm we are actually giving less preference or less importance to the large energy configurations. So, the parts of the phase space which are contributing to my canonical averages are the parts which are having lower energies. On the other hand the parts of the phase space which are contributing to my Q includes the larger use as well and therefore we never really compute the partition function or I will not say that it is impossible to compute, but it will be very time consuming affair to compute the partition function of the canonical ensemble and one of the reasons is because you have too many states of larger energy that has to be considered and since $e^{\beta u}$ is an exponential function and there are plenty of states of large energy this calculation will take very long, I mean we have to take many Monte Carlo step and of course we have to modify the metropolis criteria because that by default assigns more importance to configurations of lower u and in this case we want to give importance to higher U configuration because those are the ones which are contributing significantly or I would say mainly to the partition function.

So, then clearly we do not compute the Q and therefore although we said that Q is a generating function and once we have Q, I can get f that approach is almost never followed in any molecular simulation. Instead what we typically do is we work with the derivatives of the free energy and in most cases those are some things that we can easily get from a molecular simulation. For example, the evidence energy we can easily compute in a molecular dynamic simulation let us say performed in the NVT ensemble.

$$\langle E \rangle = -\left[\frac{\partial \ln Q}{\partial \beta}\right]_{V,N} = \left[\frac{\partial\left(\frac{F}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right]_{V,N}$$

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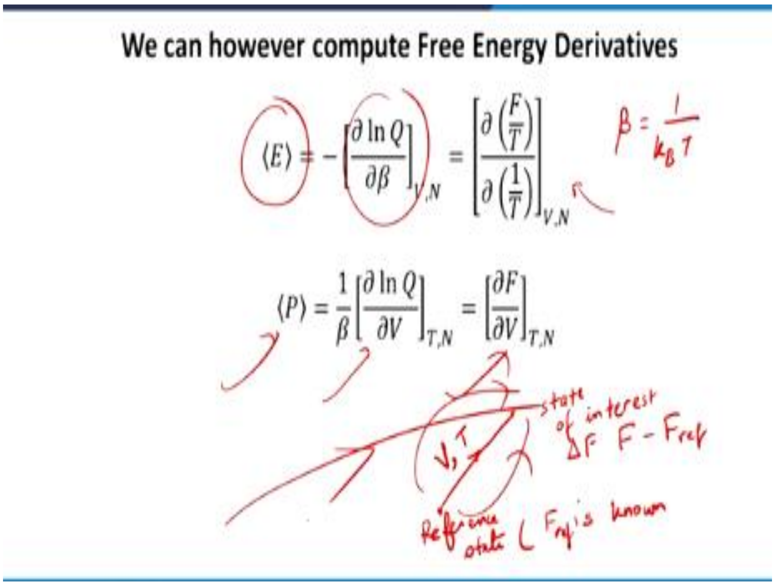

We can however compute Free Energy Derivatives

$$\langle E\rangle = -\left[\frac{\partial \ln Q}{\partial \beta}\right]_{V,N} = \left[\frac{\partial\left(\frac{F}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right]_{V,N}$$

$$\langle P\rangle = \frac{1}{\beta}\left[\frac{\partial \ln Q}{\partial V}\right]_{T,N} = \left[\frac{\partial F}{\partial V}\right]_{T,N}$$

You can simply compute every energy of every configuration and then average over that quantity is given as the derivative of the ln Q with respect to β where beta is 1 over K_BT or we can write that as derivative of 1 by K_BT divided by derivative of 1 by T. Now this is something that we can easily get, because average energy can be computed in a simulation.

In a similar manner I can find the average pressure that is again a derivative of the ln of the partition function and also a derivative of the free energy because F is simply minus K_BT In Q or minus ln Q by β and therefore I can easily compute that derivative.

$$\langle P\rangle = \frac{1}{\beta}\left[\frac{\partial \ln Q}{\partial V}\right]_{T,N} = \left[\frac{\partial F}{\partial V}\right]_{T,N}$$

Now once we have the free energy derivative we can find the free energy differences from any particular state. Now, let say you have a reference state for which you know the energy for which my F is known. Now if I am looking at some other state where I am interested in although I cannot find the free energy of that in state directly if I am able to imagine a path between these two states by changing for example, volume and temperature since we know how the derivatives of free energy with respect to volume are and how the derivative with respect to temperature are we can basically find the free energy difference of the state from the reference state in this case F minus F_{ref} that is ΔF this is something that we can compute.

Now the interesting thing here is that reference state is completely arbitrary for us to choose from it does not have to be physically a reference state where the system is coming from it can be any arbitrary state let us say for example, I can say my reference state is a perfect crystal at 0 kelvin or an ideal gas at a certain temperature it is completely up to us, how we can choose the reference state as long as we can define a path from that reference state to the current state of the system in the volume temperature plane, that is by going varying the volume and temperature if I can get from the reference state to the current state I can find the free energy difference and once I find the free energy difference, I can find the absolute free energy of a given state and since free energy is a state function it does not depend on the path.

So, if we would have started from somewhere else or if we would have followed some other path to get here, let us say I follow some other path or let us say if I come from somewhere well somewhere else to here it does not really matter. The free energy in that state is completely independent of where I came from and which path did I follow, because it is only a state function.

The only reason why we are introducing a reference state is because we know the free energy value there and we can pick any of the reference state for which the free energy value is known that also means that even the choice of path can be completely arbitrary it may not be really a physical path that is being followed in the experiment or that can even be created in the experiment, it can be a completely arbitrary path as long as it is connecting the two states and as long as it involves the changes in the volume and temperature whatever variable that we are looking at we can find the free energy in the state of interest and this is precisely what we do in the method known as the thermodynamic integration.

So, the way we do in this particular method is we start with a reference system 1 and for that reference system or the reference state, I know the free energy this can be an ideal gas system that is kind of example that we have discussed earlier or this can be a perfect crystal or an ideal liquid or any other arbitrary reference state for which free energy is known to us and system 2 is my system of interest and now we typically define a linear coupling parameter although it can be any other relation as well going from 0 to 1 to λ is a coupling parameter from 0 to 1 and I introduce the energy function Uλ as-

$$U(\lambda) = (1-\lambda)U_I + \lambda U_{II}$$

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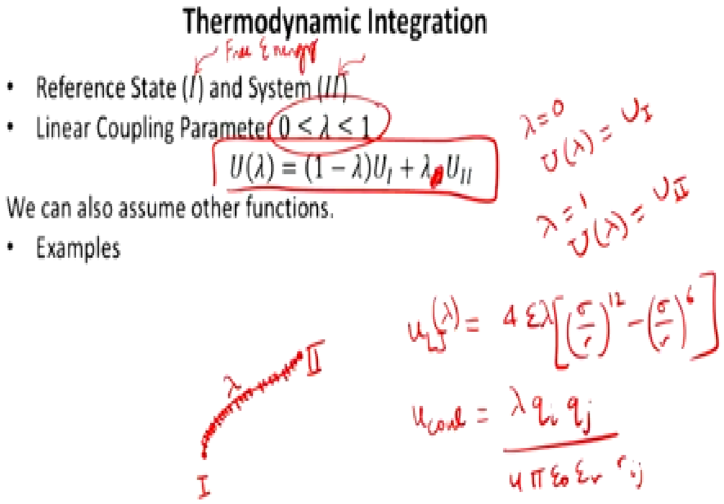

Thermodynamic Integration

Free Energy

- Reference State (I) and System (II)
- Linear Coupling Parameter $(0 < \lambda < 1)$

$$\boxed{U(\lambda) = (1-\lambda)U_I + \lambda U_{II}}$$

We can also assume other functions.

- Examples

$\lambda = 0$ $U(\lambda) = U_I$

$\lambda = 1$ $U(\lambda) = U_{II}$

$$u_{LJ}(\lambda) = 4\varepsilon\lambda\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

$$u_{coul} = \frac{\lambda q_i q_j}{4\pi\varepsilon_0\varepsilon_r r_{ij}}$$

For lambda equal to 0 my Uλ is equal to-

$$U(\lambda) = U_I$$

And for λ equal to 1-

$$U(\lambda) = U_{II}$$

So, basically we are imagining some path along a variable that we have defined. So, we are saying that the energy of the system or the interactions between the, particles are changing in this particular arbitrary way. Now as I said this need not be a physical path because you may not be able to envision systems at which interactions have this particular value linearly changing in this particular way. Let us say for example, I can say that if I want to simulate a system interacting with a Lennard Jones interaction, let us say if it is given by some particular functional form-

$$U_{LJ} = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

and let us say if it is the only interaction in the system what I am trying to say here is that I will envision systems where the U is multiplied with λ.

So, for λ equal to 0 we will have no interaction in the system so it becomes an ideal gas and for λ equal to 1 becomes the system that we are interested in so for all the intermediate λ value those systems we do not need to create or do not need to be there to be able to use the thermodynamic integration. The path can be completely arbitrary as long as it is mathematically valid and that is indeed true in this particular case.

We can assume other kinds of function apart from a linear function, but in this case we are assuming a linear function of U with respect to λ and we will change the interactions. You can imagine that I can slowly turn on the interaction in the system so if my system is Lennard Jones, we slowly turn on the Lennard Jones interactions, if Lennard Jones system is my reference state. If Lennard Jones system is my reference state, I can have some other interaction on top of it, let us say a Coulomb interaction then I will slowly turn on the Coulomb interaction by multiplying the Coulomb interaction by λ.

So, I can pretty much work in steps. So, let us say for example, I want to simulate a system where we have both Lennard Jones and Coulomb interaction. Now in the example I did previously I was doing a Lennard Jones only, so ideal gas was the reference state and I was slowly turning on the Lennard Jones interactions. Now the Lennard Jones system can be the reference state for λ equal to 0 there is no Coulomb interaction and as I change λ and I finally become λ equal to 1 then in that case we have the full Coulomb interactions and we can imagine many, many simulations being done at different λ values along these paths.

So, clearly this means that the method is quite time consuming, because we do not have to do just one simulations we have to do many, many simulations at the intermediate λ values along the path.

With that particular introduction I want to conclude here, in the next lecture I will go through the numerical implementation of the thermodynamic integration scheme and then we discuss other methods of free energy calculations, thank you.