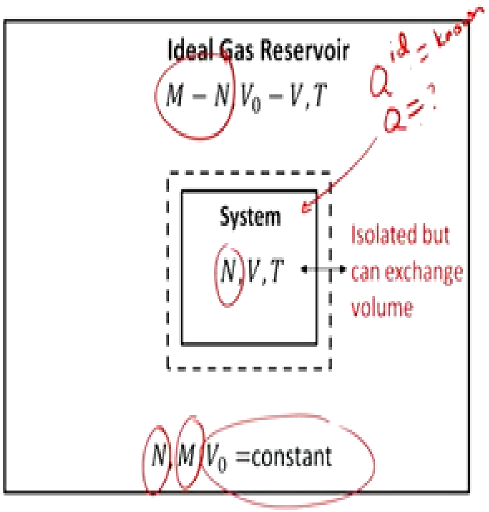
Advanced Thermodynamics and Molecular Simulations
Prof. Prateek Kumar Jha
Department of Chemical Engineering
Indian Institute of Technology, Roorkee

Lecture - 52
Extension of Canonical Ensemble Monte Carlo to Other Ensembles (Continued)

Hello all of you. So, in the last lecture we have been looking at how can we extend the NVT ensemble Monte Carlo to an NPT ensemble Monte Carlo. And where we have been in the last class where we ended is, we were assuming that the system is in placed in a reservoir that is an ideal gas and the system can exchange volume with the reservoir.

(Refer Slide Time: 00:52)

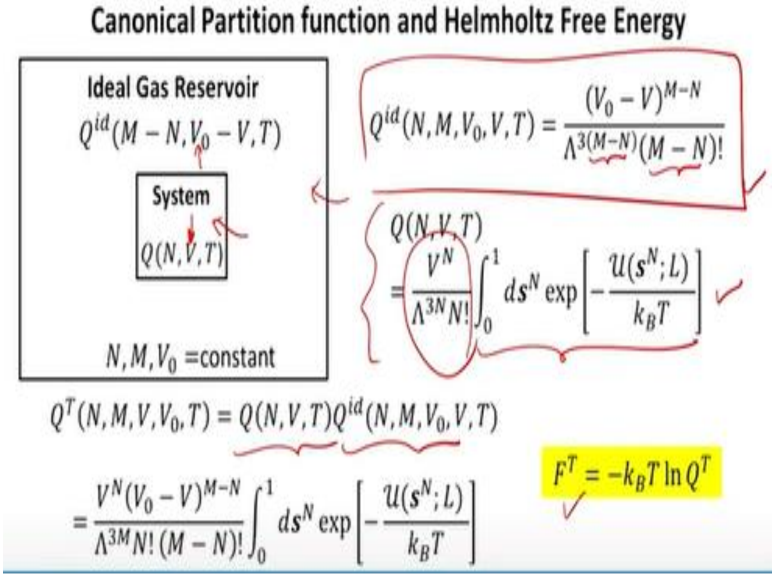
Extending to Constant Pressure



So, in total the volume of the system plus reservoir is constant that is the V_0 in here and the number of molecules in the system and the reservoir are also constant that is the N and M - N here or N and M are constant but the volume of the system can change. And the reason why we started with this kind of prescription is because in the NPT ensemble the volume of the system can change the N and T are constant anyway and we know the partition function for the ideal gas we do not know the partition function for the system but we know the partition function for the ideal gas so that means that we do not have to actually simulate the ideal gas reservoir we can analytically evaluate the partition function and the free energy whenever is needed and we will only simulate the system and that will give me the behavior of interest in the NPT ensemble so it is one easy way to extend the NVT ensemble to and NPT ensemble.

I would like to remind you that when we were doing the pressure control in the molecular dynamics the idea was very different from what we are doing here. So, in that case we placed a Barrostat that was controlling the pressure of the system. In the Monte Carlo the pressure control is done in a completely different way and the reason is that in a Monte Carlo simulation we can pretty much simulate the volume changes in a way we like to because our goal is not to simulate the true dynamics of system, our goal is to capture the equilibrium behavior.

(Refer Slide Time: 02:50)



Canonical Partition function and Helmholtz Free Energy

Ideal Gas Reservoir

$Q^{id}(M-N, V_0-V, T)$

System

$Q(N,V,T)$

N, M, V_0 =constant

$$Q^{id}(N,M,V_0,V,T) = \frac{(V_0-V)^{M-N}}{\Lambda^{3(M-N)}(M-N)!}$$

$$Q(N,V,T) = \frac{V^N}{\Lambda^{3N}N!}\int_0^1 ds^N \exp\left[-\frac{\mathcal{U}(s^N;L)}{k_BT}\right]$$

$$Q^T(N,M,V,V_0,T) = Q(N,V,T)Q^{id}(N,M,V_0,V,T)$$

$$= \frac{V^N(V_0-V)^{M-N}}{\Lambda^{3M}N!(M-N)!}\int_0^1 ds^N \exp\left[-\frac{\mathcal{U}(s^N;L)}{k_BT}\right]$$

$$F^T = -k_BT\ln Q^T$$

So, the volume changes that we are introducing in a Monte Carlo simulation are completely artificial. As long as they give me the equilibrium behavior it is fine, we do not care about the actual or true dynamics of the equilibrium behavior. So to get the partition function for this particular ensemble in the NPT case. Let us first look at the canonical partition function of the system plus reservoir where I am not looking at the volume change in the system. So, I am looking at a particular value of the system volume and a particular value of the reservoir volume. So, in this kind of canonical kind of a case we can write the partition function in the canonical way for both the system and the reservoir once we write that then we worry about how to account for the volume changes but for this case we are assuming that the volume of system is also constant.

So, we already have derived the ideal gas partition function and in this case the volume of the ideal gas either where is V_0 - V in what we discussed in the last lecture it was V. That is the only difference the formula is pretty much same as earlier and the number of molecules are M

- N in the last class it was N or something the formula itself is pretty much same as earlier and then for the system it is something like this-

$$Q(N,V,T) = \frac{V^N}{\Lambda^{3N}N!}\int_0^1 ds^N \exp\left[-\frac{U(s^N;L)}{k_BT}\right]$$

So, the system also contains an ideal gas part but for the system and some access part that contains the effect of the interactions. Now I can define the total partition function of the system plus the reservoir as the product of the partition function of the system and the partition functions of the reservoir. So, partition function refers to the number of ways and therefore, they are always multiplied whenever we look at a composite system. On the other hand, the energies are added up. So, free energy in this case will add up because free energy goes like ln of the partition function. So, let us say if Q is for system and Q id for outside when I take a ln of that they will add up so free energy will add up. But the partition function themselves will we have to take a product to get the total partition function. So, this is what we do here so we take a product of whatever we have obtained for the system and for the reservoir.

$$\begin{aligned} Q^T(N,M,V,V_0,T) &= Q(N,V,T)Q^{id}(N,M,V_0,V,T) \\ &= \frac{V^N(V-V_0)^{M-N}}{\Lambda^{3M}N!\,(M-N)!}\int_0^1 ds^N \exp\left[-\frac{U(s^N;L)}{k_BT}\right] \end{aligned}$$

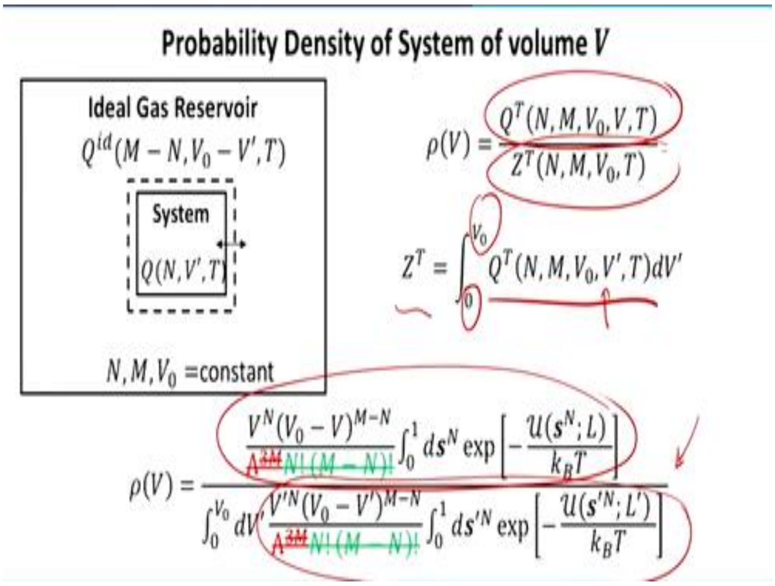
And once we have that then for the entire system plus reservoir thing here. I can find the Helmholtz free energy as - k_B T ln of that partition function for the total thing that is system plus reservoir.

$$F^T = -k_BT\ln Q^T$$

So, now I want to allow the volumes to change because ultimately, we want to extend to the NPT ensemble. So, the only change that is going to happen is that now instead of the V being constant for the system we have some volume V prime that is changing at different states of the system. So, if I want to find the partition function for the new case the partition function always refers to sum over all the possible states so in that case whatever canonical partition function we had for a constant volume we have to integrate over all the possible volume of the system and this is what is given by Z^T there that is-

$$Z^T = \int_0^{V_0} Q^T(N,M,V_0,V',T)dV'$$

(Refer Slide Time: 06:17)



Probability Density of System of volume V

$$\rho(V) = \frac{Q^T(N, M, V_0, V, T)}{Z^T(N, M, V_0, T)}$$

$$Z^T = \int_0^{V_0} Q^T(N, M, V_0, V', T)\,dV'$$

$$\rho(V) = \frac{\dfrac{V^N(V_0-V)^{M-N}}{\cancel{\Lambda^{3M} N!(M-N)!}}\int_0^1 ds^N \exp\left[-\dfrac{\mathcal{U}(s^N; L)}{k_B T}\right]}{\int_0^{V_0} dV' \dfrac{V'^N(V_0-V')^{M-N}}{\cancel{\Lambda^{3M} N!(M-N)!}}\int_0^1 ds'^N \exp\left[-\dfrac{\mathcal{U}(s'^N; L')}{k_B T}\right]}$$

I can imagine any volume V prime for the system in the range 0 to V_0 because V_0 is the total volume of system plus reservoir. So, minimum volume of system is 0 and the maximum is V_0. So, I can find the canonical partition function Q^T for all the V prime value in the interval 0 to V_0 and then integrate that over the V prime variable and that will give me the partition function for the case where volume is allowed to change or for the NPT ensemble case.

Now once we have that we can also find the probability density of the system having a volume V and that is given as the canonical partition function we have obtained for the case when the volume was V by the total partition function now that is basically an integral of the Q T over all possible volume.

So, I am simply dividing if you have to think about it dividing the number of ways in which I am getting the volume V by total number of ways. The number of ways in which I am getting volume V is basically given by the partition function and the total number of ways is given by the integral of the canonical partition function over all the possible value of volume and this is what we are doing in here.

So, now if I do the math then my ρ of V that is the probability density for volume V can be written like this. So, Z^T is simply an integral of whatever Q^T we have obtained earlier the canonical partition function of the system plus reservoir. But for V replaced with V prime and now we are integrating over all the possible value of volume.

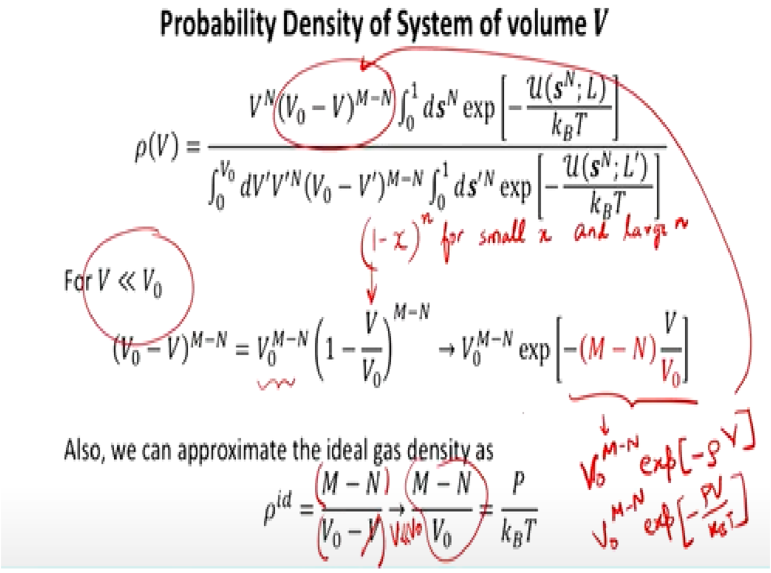
$$\rho(V)=\frac{\dfrac{V^N(V_0-V)^{M-N}}{\Lambda^{3N}N!\,(M-N)!}\int_0^1 ds^N \exp\left[-\dfrac{U(s^N;L)}{k_BT}\right]}{\int_0^{V_0} dV'\,\dfrac{V'N(V_0-V')^{M-N}}{\Lambda^{3N}N!\,(M-N)!}\int_0^1 ds'^N \exp\left[-\dfrac{U(s'^N;L)}{k_BT}\right]}$$

So, with this I can then define using an idea that the reservoir is very large in comparison to the system and that can always be assumed because we are not worried about the reservoir because we are not simulating it. So, we can always choose a larger volume than compared to the system.

$For\ V \ll V_0$

$$(V-V_0)^{M-N}=V_0^{M-N}\left(1-\frac{V}{V_0}\right)^{M-N}\rightarrow V_0^{M-N}\exp\left[-(M-N)\,\frac{V}{V_0}\right]$$

(Refer Slide Time: 09:04)



Probability Density of System of volume V

$$\rho(V)=\frac{V^N(V_0-V)^{M-N}\int_0^1 ds^N \exp\left[-\dfrac{\mathcal{U}(s^N;L)}{k_BT}\right]}{\int_0^{V_0} dV' V'^N(V_0-V')^{M-N}\int_0^1 ds'^N \exp\left[-\dfrac{\mathcal{U}(s^N;L')}{k_BT}\right]}$$

$(1-x)^n$ for small x and large n

For $V \ll V_0$

$$(V_0-V)^{M-N}=V_0^{M-N}\left(1-\frac{V}{V_0}\right)^{M-N}\rightarrow V_0^{M-N}\exp\left[\underbrace{-(M-N)\frac{V}{V_0}}\right]$$

$V_0^{M-N}\exp[-\rho V]$

$V_0^{M-N}\exp\left[-\frac{PV}{k_BT}\right]$

Also, we can approximate the ideal gas density as

$$\rho^{id}=\frac{M-N}{V_0-V}\xrightarrow[V\ll V_0]{}\frac{M-N}{V_0}=\frac{P}{k_BT}$$

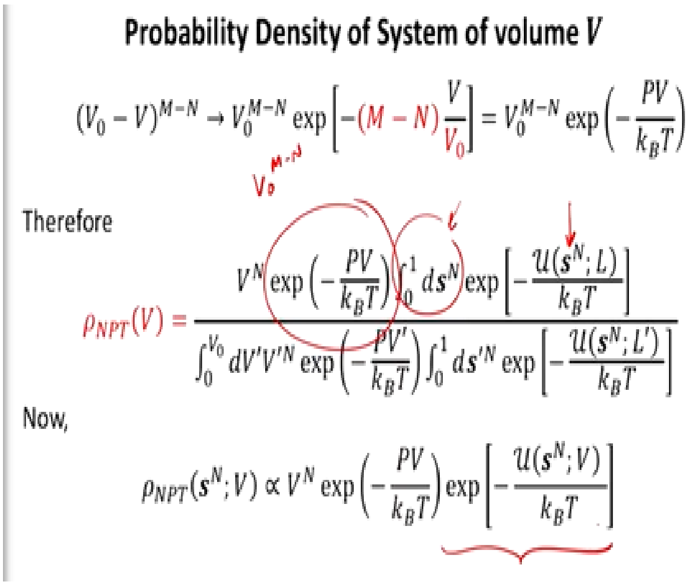
So, where for V much smaller than V$_0$ what we can see is that whatever factor we are having (V$_0$ – V)$^{M - N}$. That I can approximate by taking V$_0$ common and then we have (1 - V by V$_0$)$^{M - N}$. V by V$_0$ is a small number so I use the rule for an approximation of something like this for small x and M minus N is large number because M - N is the number of the molecules in the ideal gas reservoir so this is for small x and large n and we can approximate that by an exponential function. So, this is what we get here. And then we can approximate simply the ideal gas density. And it is not really an approximation so as to speak. The density is given by the number of molecules per unit volume. So, it is M - N is the number of molecules in the reservoir divided by the volume of reservoir that is V$_0$ – V but then I use V less than much less than V$_0$ here. That is the approximation in the expression and that is M - N by V$_0$ because I can drop V here because V is pretty small. And then we know the ideal gas density is given by P by k B T from the ideal gas low. So, M - N by V_0 can therefore be replaced by the P by k_BT.

$$\rho^{id} = \frac{(M-N)}{(V-V_0)} \to \frac{M-N}{V_0} = \frac{P}{k_BT}$$

So, that I will put in there so what you will have then is something like V_0 to the power M - N exponential of minus ρV and I can replace the ρ by P by k_BT. So, this can be V_0 M - N exponential of minus PV by k_B T

$$V_0^{M-N}\exp[-\rho V] = V_0^{M-N}\exp\left[-\frac{PV}{k_BT}\right]$$

(Refer Slide Time: 11:26)



Probability Density of System of volume V

$$(V_0 - V)^{M-N} \to V_0^{M-N}\exp\left[-(M-N)\frac{V}{V_0}\right] = V_0^{M-N}\exp\left(-\frac{PV}{k_BT}\right)$$

V_0^{M-N}

Therefore

$$\rho_{NPT}(V) = \frac{V^N\exp\left(-\frac{PV}{k_BT}\right)\int_0^1 ds^N \exp\left[-\frac{\mathcal{U}(s^N;L)}{k_BT}\right]}{\int_0^{V_0} dV' V'^N \exp\left(-\frac{PV'}{k_BT}\right)\int_0^1 ds'^N \exp\left[-\frac{\mathcal{U}(s^N;L')}{k_BT}\right]}$$

Now,

$$\rho_{NPT}(s^N;V) \propto V^N \exp\left(-\frac{PV}{k_BT}\right)\underbrace{\exp\left[-\frac{\mathcal{U}(s^N;V)}{k_BT}\right]}$$

So, therefore I can now define the probability density now for the NPT ensemble because now I am basically counting the number of ways in relation to total number of ways where total number of ways is for all possible values of volume and the number of ways is for a particular value of volume. So, basically, we are allowing volume to change. So, we are looking at the probability density of the NPT ensemble and this is pretty much given by the expression where the only change that we have done from earlier is we have replaced that factor $(V_0 – V)^{M-N}$ with the exponential of minus PV by k_BT.

$$(V-V_0)^{M-N} \to V_0^{M-N}\exp\left[-(M-N)\frac{V}{V_0}\right] = V_0^{M-N}\exp\left(-\frac{PV}{k_BT}\right)$$

And there was a V_0 to the power M minus N here that got multiplied with another volume there and got cancelled. So, this is what you get after simplification and therefore for a particular configuration. So, now a particular configuration is given by a particular value of S^N that is the scaled coordinates of all the n particles and in here we are integrating over all configuration.

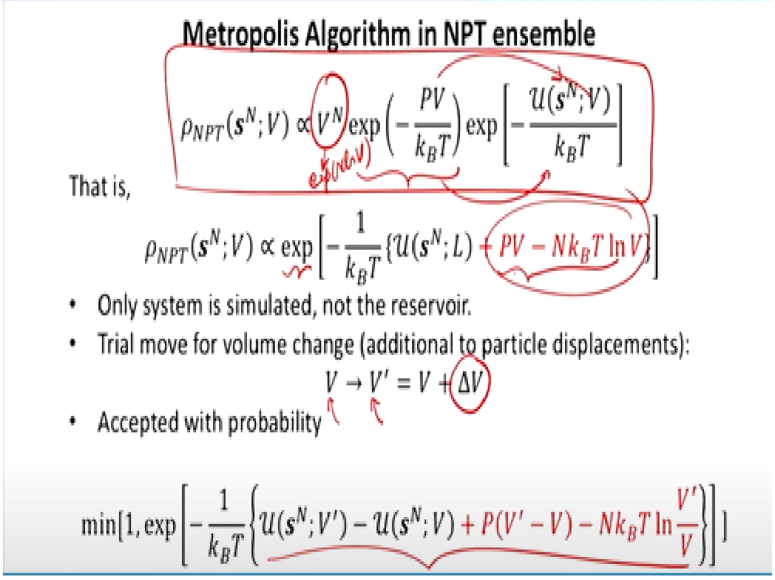
$$\rho_{NPT}(V) = \frac{V^N \exp\left(-\frac{PV}{k_B T}\right) \int_0^1 ds^N \exp\left[-\frac{U(s^N;L)}{k_B T}\right]}{\int_0^{V_0} dV'V'N \exp\left(-\frac{PV'}{k_B T}\right) \int_0^1 ds'^N \exp\left[-\frac{U(s^N;L')}{k_B T}\right]}$$

So, if I now ask what is the probability density of a particular configuration at volume V in that case we are interested in the term inside the integral not the integral because this is integrated over all the configuration. If I ask the question that what is the probability density of having a volume V then we have to integrate over all the possible configurations having volume V.

On the other hand, if I am looking at any particular configuration at volume V I can only look at the term inside the exponential and this is what we have done here. So, I simply look at the term inside that. And then denominator is any way a normalizing factor. So, the probability density is basically given by the numerator where we have dropped the integral over ds.

$$\rho_{NPT}(s^N;V) \propto V^N \exp\left(-\frac{PV}{k_B T}\right) \exp\left[-\frac{U(s^N;V)}{k_B T}\right]$$

(Refer Slide Time: 13:41)



Metropolis Algorithm in NPT ensemble

$$\rho_{NPT}(\mathbf{s}^N;V) \propto \boxed{V^N} \exp\left(-\frac{PV}{k_B T}\right) \exp\left[-\frac{\mathcal{U}(\mathbf{s}^N;V)}{k_B T}\right]$$

exp(N ln V)

That is,

$$\rho_{NPT}(\mathbf{s}^N;V) \propto \exp\left[-\frac{1}{k_B T}\{\mathcal{U}(\mathbf{s}^N;L) + PV - Nk_B T \ln V\}\right]$$

- Only system is simulated, not the reservoir.
- Trial move for volume change (additional to particle displacements):

$$V \rightarrow V' = V + \Delta V$$

- Accepted with probability

$$\min\left[1, \exp\left[-\frac{1}{k_B T}\left\{\underbrace{\mathcal{U}(\mathbf{s}^N;V') - \mathcal{U}(\mathbf{s}^N;V) + P(V'-V) - Nk_B T \ln\frac{V'}{V}}\right\}\right]\right]$$

So, therefore we have got the expression of the probability density of having a configuration at volume V and now we can use the arithmetic of the metropolis algorithm. The reason why we can do that is because the probabilities or transition probabilities in the metropolis algorithm was basically represented in terms of the probability density of configurations and we have already obtained that so simply these will become the transition probability once it gets in there.

And this is what we have done. So, before we do that what we can see here is that this and this can be coupled together. So, PV by k_BT can be placed inside the other exponential. And this can also be written as something like exponential of N ln V and therefore, both these terms can be added to a single exponential that already had minus U by k_BT.

$$\rho_{NPT}(s^N;V) \propto \exp\left[-\frac{1}{k_B T}\{U(s^N;L) + PV - Nk_B T \ln V\}\right]$$

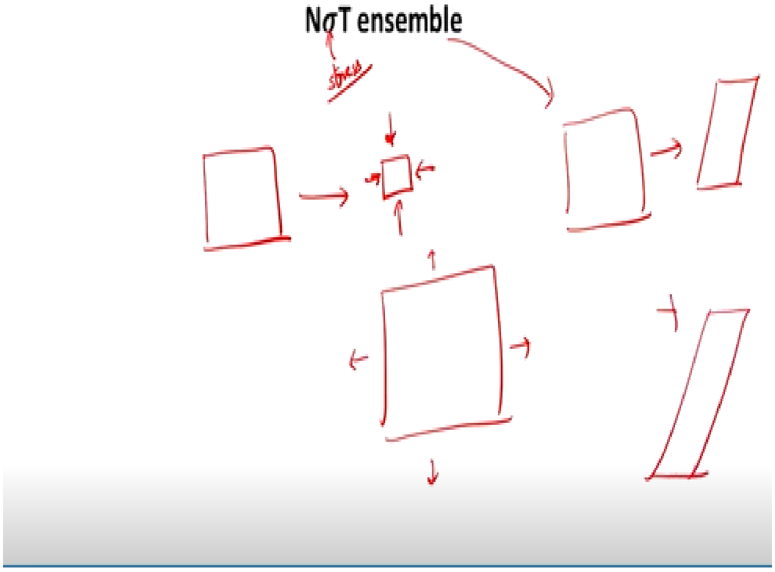
Now when we are doing in the NPT ensemble, we have to worry about I would say two other contributions that is, one is PV and other is N k_BT ln V but other than that, the basic scheme of the Monte Carlo is unchanged only the acceptance criteria or the transition probability has slightly changed. So, in this case what we do is we still keep on doing the particle displacements as we would in the canonical ensemble but also, intermittently we will try some volume changes. So, let us say I want to go from the original volume V to some new volume V prime. Or let us say we are doing some volume change delta V. So, that is accepted now with a modified probability for the NPT ensemble it is given by the difference of the energy of the new state minus the old state plus the difference that will come in the two new contributions we have that is PV and N k_B T ln V.

$$min\left[1, \exp\left[-\frac{1}{k_B T}\left\{U(s^N;V') - U(s^N;V) + P(V'-V) - Nk_B T \ln\frac{V'}{V}\right\}\right]\right]$$

So, we get P multiplied with V prime - V and - N k_BT ln V - N k_B T ln V prime and that basically will be minus N k_B T ln V prime by V. That is the last term here in here and everything else in the Monte Carlo will remain pretty much similar to earlier we generate the system randomly or whatever way we are doing that the only change from the NVT Monte Carlo is now we are doing also trial moves of volume changes in addition to particle displacement. They may not happen in conjunction with particle displacement. For example, there can be two types of move let us say hundred times you try particle displacement and every so often you try a volume change may be after 100 you try a volume change or something of that sort and whenever we are doing a volume change the only difference is we now compute with a modified transition probability that contains two new terms when I compare with the canonical ensemble Monte Carlo simulation so this is about it.

Keep in mind that what we have discussed is assuming that we are having some kind of an isotropic deformation of the simulation box. So, in our case since the pressure is kind of like constant the box will deform pretty much like this or like this in other words, it can deform in a manner that preserves its shape because pressure is same in every direction.

(Refer Slide Time: 17:35)



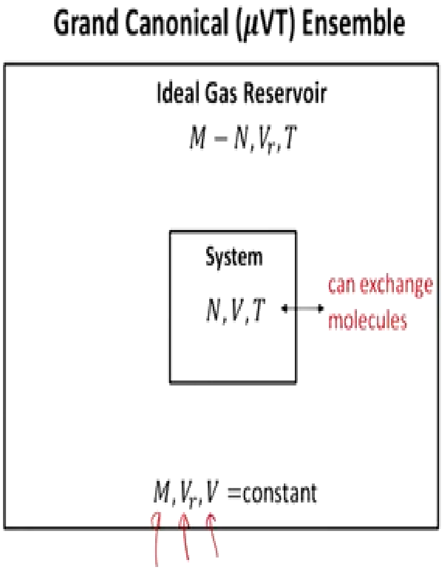
NσT ensemble

In general, we can think of working in some kind of an N sigma T ensemble where sigma is the stress that is being held controlled or that is being held fixed and in that case the stress can be different along different phases in fact, stress will have 9 components when I look in the three dimensions. So, we can have variable stresses along different boundaries of the simulation box and that will pretty much allow change in the shape of the simulation box. So, now the simulation box will not only change in the volume but they can also change in the shape because the stresses can be different along different phases.

Now there are more mathematical details of doing that I will not get to that but basic idea remains the same. So, the NPT ensemble is valid whenever we are having some kind of an isotropic kind of a fluid when we have the same pressure in every direction. On the other hand, if there is significantly different stresses among different directions then in that case we can use a constant stress ensemble that is also useful for certain applications especially in the context of solids because they are in the system itself is not isotropic. So, the stresses existing along different crystalline planes happen to be different and therefore, we are worried about the deformation of crystalline unit cells and that has to be done in somewhat different manner then compared to for liquids and gases where pressure can be assumed to be pretty much isotropic and the simulation box can deform while keeping its shape as cubic.

So, next I want to generalize to the grand canonical ensemble that is the µV T ensemble. So, in this case the number of molecules can undergo a change unlike in the NPT case where the volume could change now the number of molecules can change again, we can start with the canonical partition function and again we can use the prescription of the system in an ideal gas reservoir. Now the only difference is that the system can exchange molecule so it is no longer isolated with the reservoir so in this case there is some molecule exchange that has to be taken care of but this volume itself is constant.

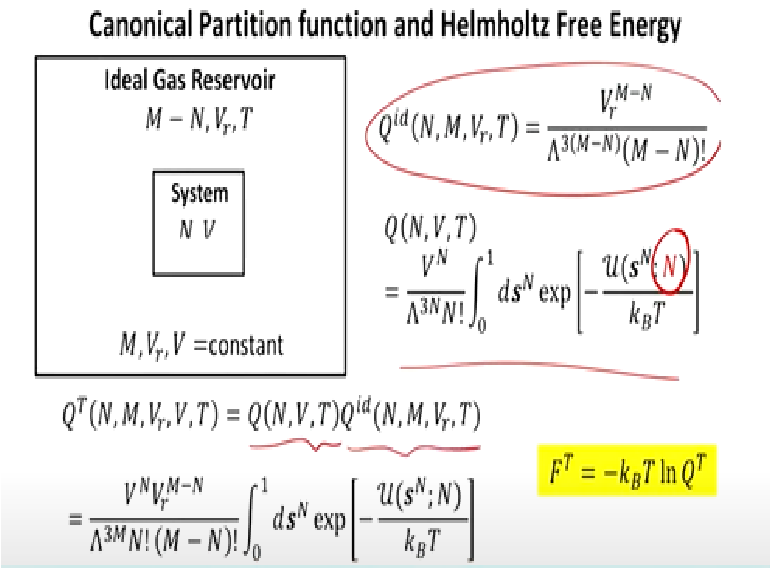
(Refer Slide Time: 20:39)



Grand Canonical (μVT) Ensemble

So, in this case the volume of the system is fixed the volume of the reservoir is fixed and the total number of molecules counting the system and the reservoir is fixed that means whenever there is a molecule leaving the system it enters the reservoir and there is an increase in the number of molecules of reservoir whenever a system gains a molecule there is a decrease in the number of molecules of a reservoir. So, pretty much overall system is assumed to be having a constant number of molecules.

(Refer Slide Time: 21:16)



Canonical Partition function and Helmholtz Free Energy

Ideal Gas Reservoir

$M-N, V_r, T$

System

$N\ V$

$M, V_r, V =$ constant

$$Q^{id}(N,M,V_r,T)=\frac{V_r^{M-N}}{\Lambda^{3(M-N)}(M-N)!}$$

$$Q(N,V,T)=\frac{V^N}{\Lambda^{3N}N!}\int_0^1 ds^N \exp\left[-\frac{\mathcal{U}(s^N;N)}{k_BT}\right]$$

$$Q^T(N,M,V_r,V,T)=Q(N,V,T)Q^{id}(N,M,V_r,T)$$

$$=\frac{V^N V_r^{M-N}}{\Lambda^{3M}N!\,(M-N)!}\int_0^1 ds^N \exp\left[-\frac{\mathcal{U}(s^N;N)}{k_BT}\right]$$

$$F^T=-k_BT\ln Q^T$$

So, again I will start with the canonical partition function. Now the only difference that we have to keep in mind is that now when I look at the energies now, they are changing when N is changing. So, whenever we look at u, we have to be careful what is the N value that I am putting in there and therefore, I have put an N there the box size in this case is constant. When I was doing the NPT ensemble, I put an l here to signify the fact that the box size may change. Now I have put an N here this is also good whenever we are doing this kind of math to make sure that we; make no mistakes in writing the expressions.

But still I can get the ideal gas partition function pretty much similar to earlier. Earlier I was representing the volume of reservoir as V_0 - V. Now I am writing as V_R. But other than that, the functional form is pretty much same and I can write the partition function of the system.

$$Q(N,V,T)=\frac{V^N}{\Lambda^{3N}N!}\int_0^1 ds^N \exp\left[-\frac{U(s^N;N)}{k_BT}\right]$$

And again, I can define the total canonical partition function and when I am doing that, I am keeping the number of molecules of system fixed. So, I am writing in the canonical ensemble only. So, this is product of the system partition function with the reservoir partition function and again we got an expression for the total partition function.

$$Q^T(N,M,V_r,V,T)=Q(N,V,T)\,Q^{id}(N,M,V_r,T)$$

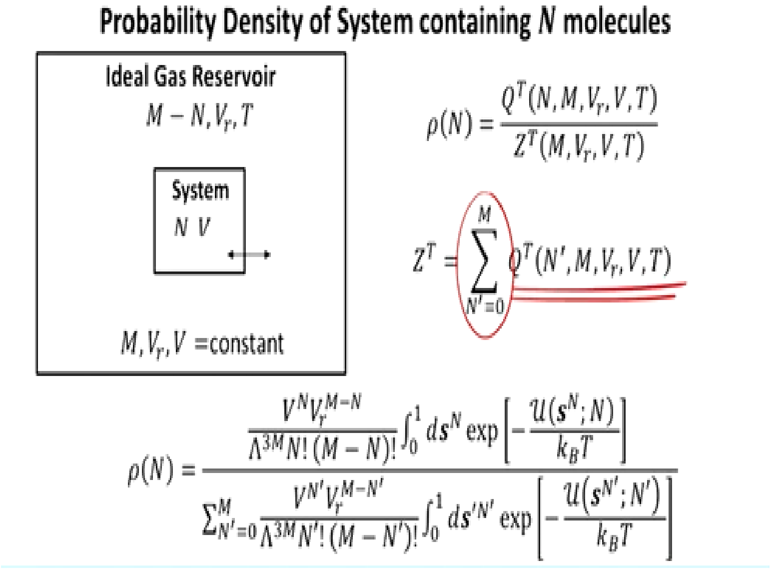
$$=\frac{V^N V_r^{M-N}}{\Lambda^{3N}N!\,(M-N)!}\int_0^1 ds^N \exp\left[-\frac{U(s^N;N)}{k_BT}\right]$$

And again, we can evaluate the Helmholtz free energy of the system plus reservoir as minus k_BT ln of this total partition function.

$$F^T = -k_B T \ln Q^T$$

Now however; when I want to look at the partition function for the case where N is a variable. Now in this case I have to basically sum over all the possibilities of N value. So, now when I was doing it in the volume space I was basically integrating over the volume but in this case, I prefer to do a summation over all possible number of molecules because the, number of molecules are discretely defined in the way we are representing the system. So, therefore we should basically sum over all the possible number of molecules as opposed to doing an integration because N is and M are discretely defined.

(Refer Slide Time: 23:32)



Probability Density of System containing N molecules

Ideal Gas Reservoir

$M-N, V_r, T$

System

$N\ V$

M, V_r, V =constant

$$\rho(N) = \frac{Q^T(N,M,V_r,V,T)}{Z^T(M,V_r,V,T)}$$

$$Z^T = \sum_{N'=0}^{M} Q^T(N',M,V_r,V,T)$$

$$\rho(N) = \frac{\frac{V^N V_r^{M-N}}{\Lambda^{3M} N!\,(M-N)!}\int_0^1 ds^N \exp\left[-\frac{\mathcal{U}(s^N;N)}{k_B T}\right]}{\sum_{N'=0}^{M} \frac{V^{N'} V_r^{M-N'}}{\Lambda^{3M} N'!\,(M-N')!}\int_0^1 ds'^{N'} \exp\left[-\frac{\mathcal{U}(s^{N'};N')}{k_B T}\right]}$$

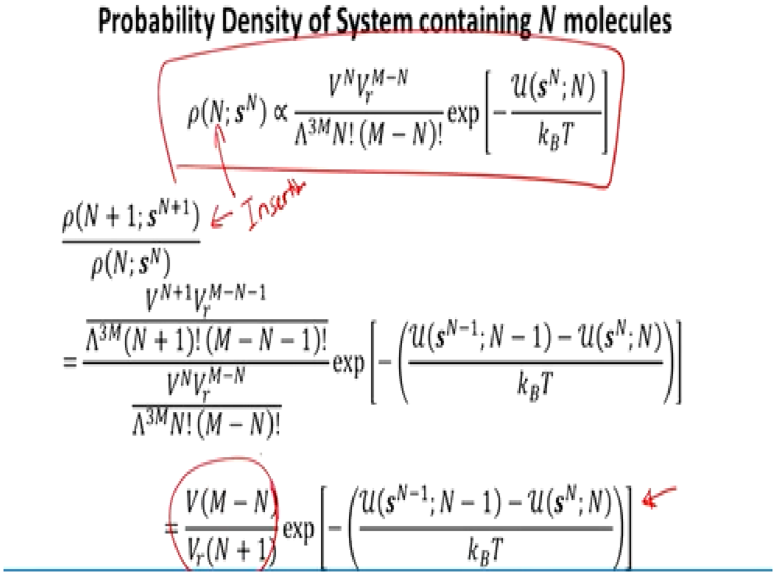
So, therefore the partition function when I allow for the number of molecules to change is given by all the possible value of N. And the N can range from pretty much zero that means system vanishes to and equal to M where the system fills the entire reservoir. So, all the possible molecules in the reservoir they come and become part of a system. So, this is the integration for and this is the again the canonical partition functions for the cases when the number of molecules is N prime the only difference is I am summing over N prime equal to 0 to M.

$$Z^T = \sum_{N'=0}^{M} Q^T(N', M, V_r, V, T)$$

Again, I can define the probability density now for a system containing N molecules unlike ρV we had in the NPT ensemble case. Now I write ρN for this case which is pretty much similar to the way we wrote. It is the ratio of the canonical partition function of given number of molecules and divided by the total partition function that is sum over all the possible values of N prime.

$$\rho(N) = \frac{\frac{V^N V_r^{M-N}}{\Lambda^{3N} N!\,(M-N)!} \int_0^1 ds^N \exp\left[-\frac{U(s^N;N)}{k_B T}\right]}{\sum_{N'=0}^{M} \frac{V^{N'} V_r^{M-N}}{\Lambda^{3N} N'!\,(M-N')!} \int_0^1 ds'^{N'} \exp\left[-\frac{U(s^{N'};N')}{k_B T}\right]}$$

(Refer Slide Time: 24:47)



Probability Density of System containing N molecules

$$\boxed{\rho(N;s^N) \propto \frac{V^N V_r^{M-N}}{\Lambda^{3M} N!\,(M-N)!} \exp\left[-\frac{\mathcal{U}(s^N;N)}{k_B T}\right]}$$

$$\frac{\rho(N+1;s^{N+1})}{\rho(N;s^N)} \leftarrow \text{Insertn}$$

$$= \frac{\frac{V^{N+1} V_r^{M-N-1}}{\Lambda^{3M}(N+1)!\,(M-N-1)!}}{\frac{V^N V_r^{M-N}}{\Lambda^{3M} N!\,(M-N)!}} \exp\left[-\left(\frac{\mathcal{U}(s^{N-1};N-1)-\mathcal{U}(s^N;N)}{k_B T}\right)\right]$$

$$= \frac{V(M-N)}{V_r(N+1)} \exp\left[-\left(\frac{\mathcal{U}(s^{N-1};N-1)-\mathcal{U}(s^N;N)}{k_B T}\right)\right] \leftarrow$$

And therefore, I can also write the probability density of a given configuration as N and that is basically the numerator here without the integral over all, the configuration. This is what we did in the last case as well. Now we are doing it for ρ (N, S^N) as opposed to ρ (V; S^N) that we did for the isothermal isobaric ensemble.

$$\rho(N;S^N) \propto \frac{V^N V_r^{M-N}}{\Lambda^{3N} N!\,(M-N)!} \exp\left[-\frac{U(s^N;N)}{k_B T}\right]$$

Now when I am doing the Monte Carlo simulation for this case we can imagine that we will have moves where molecules are going to be added or removed and the probability density is ultimately should be divided by the new configuration or the old configuration as appropriate. And therefore, we should be interested in the ratio of the probability density for N + 1 with respect to N whenever I am doing an insertion of molecule and N - 1 with respect to N whenever I am doing a removal of molecule.

So, when I am doing insertion in that case, I am interested in the ratio of the probability density of the new state that has N + 1 molecule relative to the old state that has N molecules. And it is their ratio that will dictate our transition because metropolis basically goes towards or favors more the states which are having higher probability. This is what basically what is there in the metropolis and therefore you should compute this particular ratio unlike in the NVT and NPT ensemble case, in this case the changes in the system configurations are discrete whenever we talk in terms of the number of molecules, they can only increase by units of one. So, when I do that and I do the math what I get is something like this. So, again we have a pre factor to worry about which we can approximate using the ideal gas.

$$\frac{\rho(N+1; s^{N+1})}{\rho(N; s^N)} = \frac{V(M-N)}{V_r(N+1)} \exp\left[-\left(\frac{U(s^{N-1}; N-1) - U(s^N; N)}{k_B T}\right)\right]$$

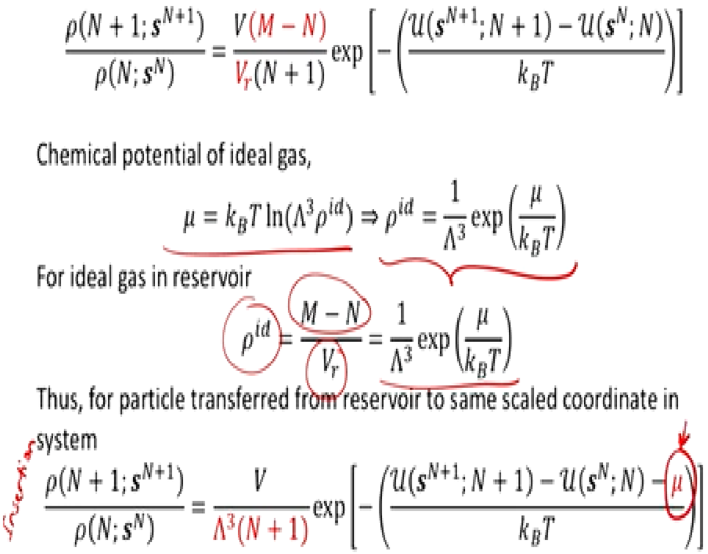
And similarly, I can do it for the removal where the new configuration will have one molecule less that is N - 1 molecule and the old one has N molecule. So, again we have slightly different ratio of the old to new configuration so with that I can basically use the expression of the chemical potential of ideal gas that is given by this-

$$Chemical\ potential\ of\ gas, \mu = k_B T \ln(\Lambda^3 \rho^{id})$$

Therefore,

$$\rho^{id} = \frac{1}{\Lambda^3} \exp\left(\frac{\mu}{k_B T}\right)$$

(Refer Slide Time: 27:28)



$$\frac{\rho(N+1;\mathbf{s}^{N+1})}{\rho(N;\mathbf{s}^{N})}=\frac{V(M-N)}{V_r(N+1)}\exp\left[-\left(\frac{\mathcal{U}(\mathbf{s}^{N+1};N+1)-\mathcal{U}(\mathbf{s}^{N};N)}{k_BT}\right)\right]$$

Chemical potential of ideal gas,

$$\underline{\mu=k_BT\ln(\Lambda^3\rho^{id})}\Rightarrow\underbrace{\rho^{id}=\frac{1}{\Lambda^3}\exp\left(\frac{\mu}{k_BT}\right)}$$

For ideal gas in reservoir

$$\rho^{id}=\frac{M-N}{V_r}=\frac{1}{\Lambda^3}\exp\left(\frac{\mu}{k_BT}\right)$$

Thus, for particle transferred from reservoir to same scaled coordinate in system

Insertion

$$\frac{\rho(N+1;\mathbf{s}^{N+1})}{\rho(N;\mathbf{s}^{N})}=\frac{V}{\Lambda^3(N+1)}\exp\left[-\left(\frac{\mathcal{U}(\mathbf{s}^{N+1};N+1)-\mathcal{U}(\mathbf{s}^{N};N)-\mu}{k_BT}\right)\right]$$

And using that; I know that the density of an ideal gas is basically a function of its chemical potential. And therefore, for the ideal gas in reservoir that is the number of molecules per unit volume that is M minus N in our model divided by V r that is equal to whatever expression that we have for the ideal gas.

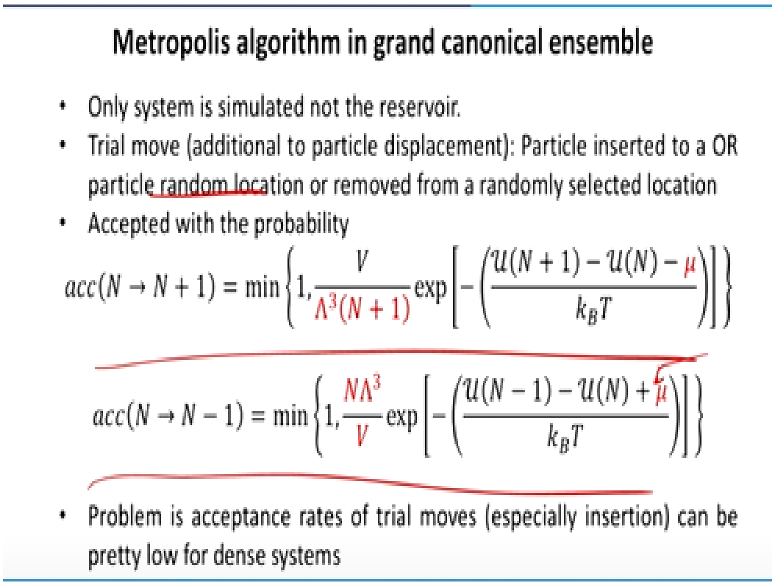
$$\rho^{id}=\frac{M-N}{V_r}=\frac{1}{\Lambda^3}\exp\left(\frac{\mu}{k_BT}\right)$$

Again, I want to remind you that we are not simulating the ideal gas in the reservoir because we know the expressions and therefore, we can then write the expression for the ratio of probability densities. In this case for insertion using the formula for the ideal gas and therefore, there would be a mu coming there if I do the arithmetic in this particular problem.

$$\frac{\rho(N+1;s^{N+1})}{\rho(N;s^{N})}=\frac{V}{\Lambda^3(N+1)}\exp\left[-\left(\frac{U(s^{N+1};N+1)-U(s^{N};N)-\mu}{k_BT}\right)\right]$$

Now the same thing has to be done for the removal case as well so this is purely arithmetic manipulations I will not derive that. So, basically what the Monte Carlo simulation will work will do in this case what the metropolis algorithm will do in this case is we will make trial moves which will be insertion or removal keep in mind that in a given time we are only inserting one molecule or removing one molecule. Now that molecule that is being inserted or removed is done at any arbitrary random location inside the system and that point is very important because if it is not put in a random location; then if for example, we fix the location where we insert the particle in that case the criteria of detailed balance will not be satisfied.

(Refer Slide Time: 29:14)



Metropolis algorithm in grand canonical ensemble

- Only system is simulated not the reservoir.
- Trial move (additional to particle displacement): Particle inserted to a OR particle random location or removed from a randomly selected location
- Accepted with the probability

$$acc(N \rightarrow N+1) = \min\left\{1, \frac{V}{\Lambda^3(N+1)} \exp\left[-\left(\frac{\mathcal{U}(N+1) - \mathcal{U}(N) - \mu}{k_B T}\right)\right]\right\}$$

$$acc(N \rightarrow N-1) = \min\left\{1, \frac{N\Lambda^3}{V} \exp\left[-\left(\frac{\mathcal{U}(N-1) - \mathcal{U}(N) + \mu}{k_B T}\right)\right]\right\}$$

- Problem is acceptance rates of trial moves (especially insertion) can be pretty low for dense systems

So, we really have to insert at a random location and for that we will have certain probability of acceptance or for example we can remove from a random location whatever particle is there. And in that case, we will have slightly modified criteria that, the reason why the criteria are different is because the ratio of probability densities are different.

So, for the insertion case we had V over N plus 1 multiplied with lambda cube. And for removal case we had Vr multiplied with N divided by V multiplied with M - N + 1. And therefore, only the pre factor is changing in these cases and therefore, when I include the pre factor effect by approximating using the idea of ideal gas or using the expression of ideal gas basically, we get slightly modified forms of the transition probability in these two cases.

And then basically we can keep on going again we are still doing the particle displacement as we were doing in the canonical ensemble intermittently or after every step as convenient to us or as required for the problem. We will also try some insertion and removal. Both must be done to satisfy the detailed balance condition. We should try both insertion and removal but having said that the; acceptance rates of the insertion removal can be very small because you may imagine that if the system is pretty dense in that case it will be very difficult to place a particle inside the system.

There will be no room for the particle particularly when I randomly choose a location. Removal is somewhat easier to think about but then that may also have lower probability of acceptance in certain cases because the removal may come at a large energetic penalty.

So, it turns out that grand chronicle ensemble is not generally the most convenient way to simulate any phase equilibrium kind of a problem because the acceptance rates happen to be pretty low. And therefore, it takes forever to actually get the statistics that is required to get the coexistence behavior. However, there are cases for example looking at adsorption processes or for example for simple systems like Lennard Jones systems the grand canonical ensembles have been shown to be like very efficient but particularly for atomic systems it turns out that acceptance rates for grand canonical Monte Carlo is pretty low and in those cases, we have to think of something else apart from doing this kind of simulations.

So, with this I want to conclude the lecture today. In the next lecture we will discuss a method called the Gibbs ensemble method that is an alternate strategy for studying the phase equilibrium where we simulate both the system and the reservoir in contact. So, in the two methods that we have discussed the reservoir was not being simulated. So, there was only system being simulated in the Gibbs ensemble method we parallelly simulate or simultaneously simulate two boxes which can exchange particles between them and therefore, it is found to be extremely useful when we are studying the phase equilibria of liquids and all that.

So, with that I want to conclude here and we continue from this point in next lecture.