# Advanced Thermodynamics and Molecular Simulations
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## Lecture - 54
## Thermodynamic Integration (Continued); Widom's Particle Insertion; Overlapping Distribution Method

Hello all of you so in the last lecture we started discussing the thermodynamic integration method for the free energy calculation and the way we have defined is we need to know a reference state for which the free energy is known to us and, I will call that the state 1 and then the system under consideration is my state 2 and then I assume some path between the two states which is characterized by the variable λ such that U2 and U1 are basically the energies that we get for λ equal to 1 and λ equal to 0 and in general we can define Uλ as-

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

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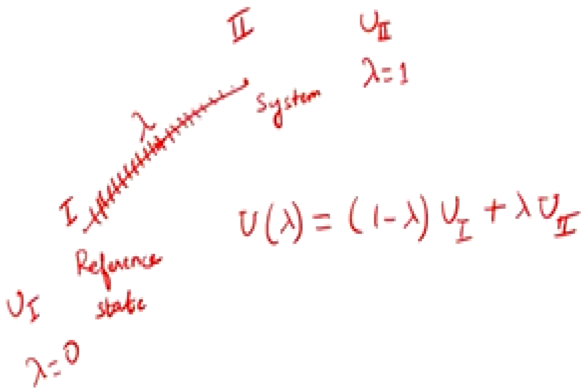

And, then we have discussed that we can also have other forms of this Uλ and we have to perform it for many, many lambda values between 0 to 1. So, now let us look at the partition function for this particular case where I have introduced an artificial variable λ. So, for any particular value of λ I can define the partition function as the following where the Boltzmann factor will have the U value for that particular λ-

$$Q(N,V,T,\lambda) = \frac{1}{\Lambda^{3N} N!}\int dr^N \exp[-\beta U(\lambda)]$$

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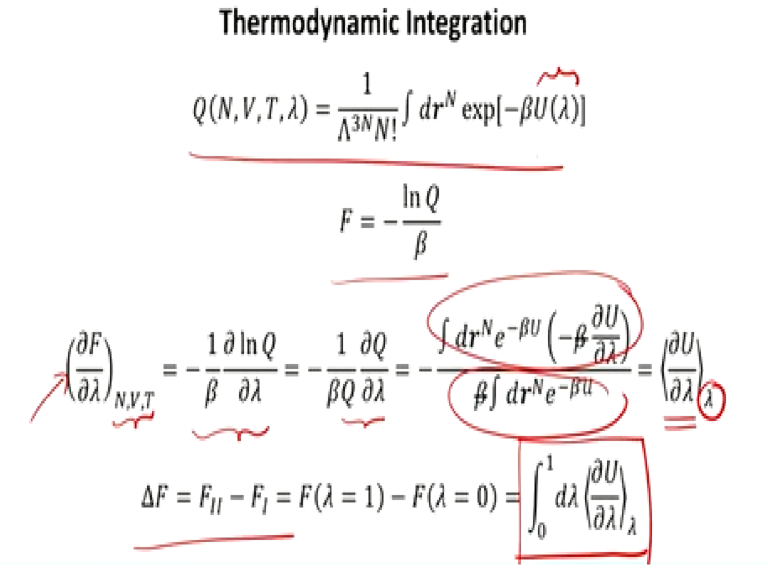

## Thermodynamic Integration

$$Q(N,V,T,\lambda) = \frac{1}{\Lambda^{3N}N!}\int dr^N \exp[-\beta U(\lambda)]$$

$$F = -\frac{\ln Q}{\beta}$$

$$\left(\frac{\partial F}{\partial \lambda}\right)_{N,V,T} = -\frac{1}{\beta}\frac{\partial \ln Q}{\partial \lambda} = -\frac{1}{\beta Q}\frac{\partial Q}{\partial \lambda} = -\frac{\int dr^N e^{-\beta U}\left(-\beta\frac{\partial U}{\partial \lambda}\right)}{\beta\int dr^N e^{-\beta U}} = \left\langle\frac{\partial U}{\partial \lambda}\right\rangle_\lambda$$

$$\Delta F = F_{II} - F_I = F(\lambda = 1) - F(\lambda = 0) = \boxed{\int_0^1 d\lambda \left\langle\frac{\partial U}{\partial \lambda}\right\rangle_\lambda}$$

and using the partition function I can then evaluate the free energy that is-

$$F = -\frac{\ln Q}{\beta}$$

when I say, I can evaluate that is conditional to the fact that we have to evaluate Q and, we have discussed that Q is very difficult to evaluate in molecular simulations and therefore we work with derivatives of Q or derivatives of the free energy which is something that is easier to prove.

So, in this case we can look at the derivative of free energy with respect to λ. So, now this is for constant value of N V and T because we are imagining along an arbitrary path defined by the variable λ and, along the path the N V T are constant that means all the other variables control variables that we have they are constant only the λ is something that we are looking the free energy derivative with. So, this gives me something like this using the definition of F-

$$\left(\frac{\partial F}{\partial \lambda}\right)_{N,V,T} = -\frac{1}{\beta}\frac{\partial \ln Q}{\partial \lambda} = -\frac{1}{\beta Q}\frac{\partial Q}{\partial \lambda} = -\frac{\int dr^N e^{-\beta U}\left(-\beta\frac{\partial U}{\partial \lambda}\right)}{\beta\int dr^N e^{-\beta U}} = \langle\frac{\partial U}{\partial \lambda}\rangle_\lambda$$

Now, I put in the expression of Q from here in the denominator and then if I take the derivative of Q with respect to λ what we have is the Boltzmann factor multiplied with minus beta dou U by douλ in this expression the β cancels out and essentially what we have is the canonical average of douU by douλ where the averaging is done for a fixed value of λ that is where we are computing the derivative and clearly we can do it for different λ windows or different λ points that we have in the simulation.

Now, I can find the free energy difference by simply integrating the dau F by dau λ with respect to λ in the interval 0 to 1 because λ is going from 0 to 1 and that gives me the free energy difference from the reference state that is λ equal to 0 and this is precisely what we do in here and now you can see why I was telling you that we have to do it for many lambda values intermediate between 0 to 1.The reason is we have to actually evaluate this particular integral.

$$\Delta F = F_{II} - F_I = F(\lambda = 1) - F(\lambda = 0) = \int_0^1 d\lambda \ \langle \frac{\partial U}{\partial \lambda} \rangle_\lambda$$

So, to get the better approximation of the integral we have to do it for many, many intermediate points where I perform a simulation, I compute the canonical evidence dou U by dou λ and then basically we do the same procedure for different values of λ and then once I look at the integral actually approximation of the integral that gives me the free energy difference.

Although, it is not possibly the most efficient method for computation of the free energy, it is actually the most simplest method that is typically used in most software’s because there is a whole liberty in which how I can choose the reference state all that we have to do is simply turn on one of the interactions slowly and as I was talking about the Lennard Jones system and Lennard Jones plus coulomb system and so on we can pretty much do it sequentially over many, many interactions that are present in the system.

At any given integration simulation we can slowly turn on one of those interactions that I am working with and then we have a reference state without that interaction and the final state with that interaction and all the intermediate values where you have intermediate or partial values of the interaction that is present and that can be done over all the possible interactions very simple straightforward way of getting the free energy.

Once we have the free energy we can also find the chemical potentials from there but in principle there can be other ways of finding the chemical potentials as well and one of the methods is the Widom’s method and the way it starts from is again the starting point is my canonical partition function and the partition function of the ideal gas this is something that we have already discussed that we can write the Helmholtz free energy as an ideal gas contribution and the excess energy that is coming from apart from the ideal gas contribution. So, now I can define my chemical potential as the derivatives of the Helmholtz free energy with respect to N keeping the volume and temperature constant and since F is - $k_BT$ ln Q, this pretty much looks like this and now in here, if you look at it; so $k_BT$ comes out and then we have dou ln Q by douN.

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} = -\frac{\partial}{\partial N}(k_BT\ln Q) = -k_BT\ln\left(\frac{Q(N+1,V,T)}{Q(N,V,T)}\right)$$

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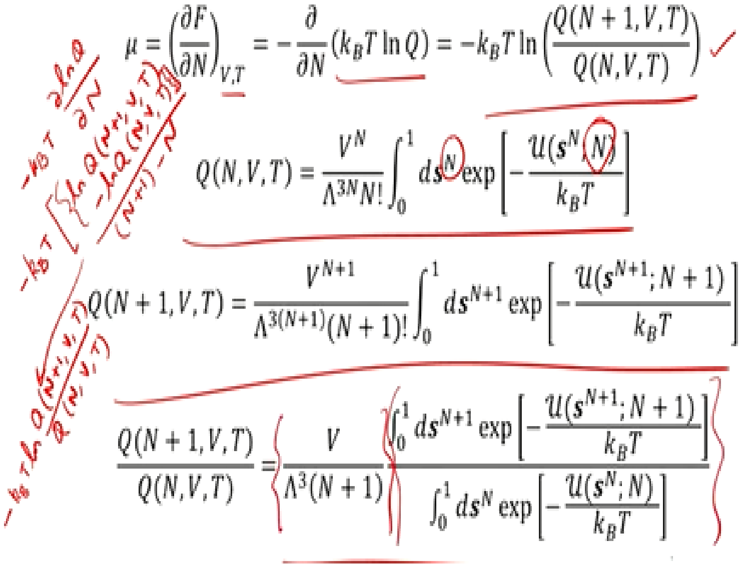

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} = -\frac{\partial}{\partial N}(k_BT\ln Q) = -k_BT\ln\left(\frac{Q(N+1,V,T)}{Q(N,V,T)}\right) \checkmark$$

$$-k_BT\frac{\partial \ln Q}{\partial N}$$

$$-k_BT\left[\frac{\ln Q(N+1,V,T) - \ln Q(N,V,T)}{(N+1)-N}\right]$$

$$-k_BT\ln\frac{Q(N+1,V,T)}{Q(N,V,T)}$$

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

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

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

Now in this case, I could have done something like 1 by Q douQ by douN that is what we have done in the earlier examples but what you also can notice here that N is always changed in the increments of 1, we can either insert a molecule or we can remove a part molecule. So, n is a discrete variable. So, instead of doing the differentiation using the way that we have done earlier, in this case what we do is we write the derivative in the difference form that is I can write; the dou lnQ by douN as the ln Q value for N + 1 case keeping the volume and temperature constant minus the ln Q value for the N case keeping the volume and temperature the same as earlier and this has to be divided by the difference N + 1 - N and that is clearly equal to 1. So, therefore what we have is $k_BT$ ln Q for N + 1 V T divided by Q N V T and there was a minus sign in front of that and this is what we have in here.

So, we have used the difference form for dou lnQ by douN because N is a discrete variable. So, then we can find the partition function of system containing N particles and the system containing N + 1 particles everything remains the same but wherever we have N in there I will replace with N + 1-

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

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

and therefore you may recall that I have chosen to represent N in the function of U because N is a variable in this case and, that is the reason why I was representing $dS^N$ as the integration variable because that will change to N + 1.

So, now if I take the ratio of these two that is required in here we get something like this-

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

this that is basically having a pre factor multiplied with the ratio of two integrals one for the case of N + 1 and one for the case of N. So, now we can further simplify this-

$$\mu = -k_B T \ln \frac{V}{\Lambda^3 (N+1)} - k_B T \ln \frac{\int_0^1 ds^{N+1} \exp\left[-\frac{U(s^{N+1}; N+1}{k_B T}\right]}{\int_0^1 ds^N \exp\left[-\frac{U(s^N; N)}{k_B T}\right]}$$

$$\mu = \mu^{id}(\rho^{id}) + \mu^{ex}$$

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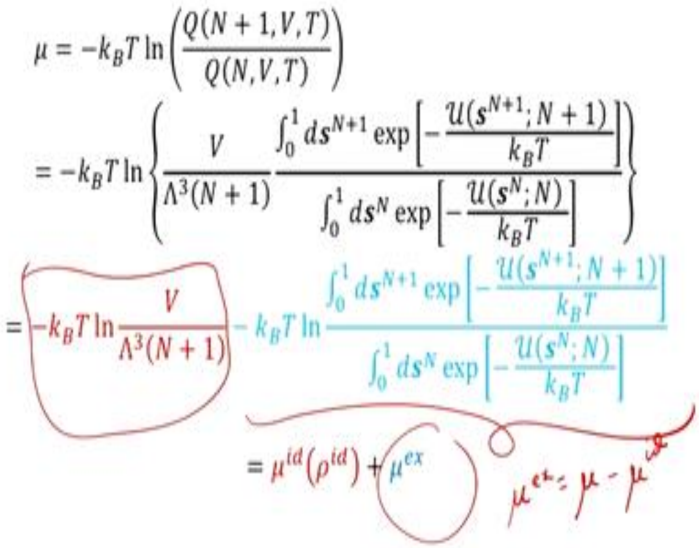

$$\mu = -k_B T \ln\left(\frac{Q(N+1,V,T)}{Q(N,V,T)}\right)$$

$$= -k_B T \ln\left\{\frac{V}{\Lambda^3(N+1)} \frac{\int_0^1 ds^{N+1} \exp\left[-\frac{\mathcal{U}(s^{N+1};N+1)}{k_B T}\right]}{\int_0^1 ds^N \exp\left[-\frac{\mathcal{U}(s^N;N)}{k_B T}\right]}\right\}$$

$$= \boxed{-k_B T \ln \frac{V}{\Lambda^3(N+1)}} \underbrace{- k_B T \ln \frac{\int_0^1 ds^{N+1} \exp\left[-\frac{\mathcal{U}(s^{N+1};N+1)}{k_B T}\right]}{\int_0^1 ds^N \exp\left[-\frac{\mathcal{U}(s^N;N)}{k_B T}\right]}}$$

$$= \mu^{id}(\rho^{id}) + \boxed{\mu^{ex}} \qquad \mu^{ex} = \mu - \mu^{id}$$

So, the first part of this as you may expect that is coming from the pre factor becomes the chemical potential of the ideal gas and the second bit of it that is the part containing the energies become the excess chemical potential just like what you had for the excess free energy. Now, we have an excess chemical potential that is defined as the difference between the chemical potential and the chemical potential of an ideal gas under the same conditions.

$$\mu^{ex} = \mu - \mu^{id}$$

So, the first part of this as you may expect that is coming from the pre factor becomes the chemical potential of the ideal gas and the second bit of it that is the part containing the energies become the excess chemical potential just like what you had for the excess free energy. Now, we have an excess chemical potential that is defined as the difference between the chemical potential and the chemical potential of an ideal gas under the same conditions.

Now, clearly chemical potential of an ideal gas is a function of it is density and therefore I am writing it as a function of the density and clearly there are analytical expressions available for the chemical potential of an ideal gas.

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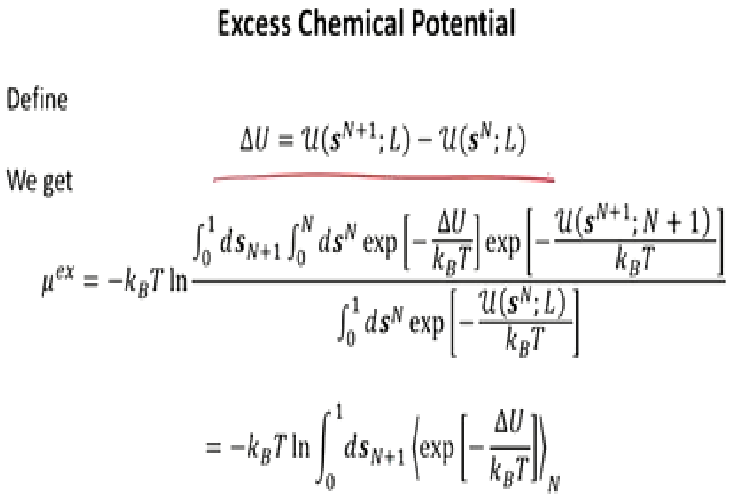

## Excess Chemical Potential

Define

$$\Delta U = \mathcal{U}(\mathbf{s}^{N+1}; L) - \mathcal{U}(\mathbf{s}^{N}; L)$$

We get

$$\mu^{ex} = -k_BT \ln \frac{\int_0^1 ds_{N+1} \int_0^N ds^N \exp\left[-\frac{\Delta U}{k_BT}\right] \exp\left[-\frac{\mathcal{U}(s^{N+1}; N+1)}{k_BT}\right]}{\int_0^1 ds^N \exp\left[-\frac{\mathcal{U}(s^N; L)}{k_BT}\right]}$$

$$= -k_BT \ln \int_0^1 ds_{N+1} \left\langle \exp\left[-\frac{\Delta U}{k_BT}\right]\right\rangle_N$$

So, now we can let us we can focus only on the excess chemical potential and for doing that I will define the free energy change ΔU as the energy of the system containing N + 1 molecules minus the energy of the system containing N molecules-

$$\Delta U = U(s^{N+1}; L) - U(s^N; L)$$

and then I can basically rewrite this particular expression in a slightly different form because we note that this guy is essentially U ($S^N$, N) + ΔU and, once we do that then the first term in the numerator inside the integral becomes same as the denominator and then we have an extra term something like exponential of minus ΔU and when we do that then essentially what we get is a canonical average of exponential of minus ΔU by k B T and this is evaluated at a particular value of N and clearly there was one integration variable remaining because denominator is from for N particles and numerator is for N + 1 particles.

$$\mu^{ex} = -k_BT \ln \frac{\int_0^1 ds_{N+1} \int_0^N ds^N \exp\left[-\frac{\Delta U}{k_BT}\right] \exp\left[-\frac{U(s^{N+1}; N+1)}{k_BT}\right]}{\int_0^1 ds^N \exp\left[-\frac{U(s^N; L)}{k_BT}\right]}$$

$$= -k_BT \ln \int_0^1 ds_{N+1} \langle\left[-\frac{\Delta U}{k_BT}\right]\rangle_N$$

So, until the $N^{th}$ particle we have the same scaling coordinates for one for numerator we have one extra variable that is $S^{N+1}$ and that will appear in here. So, therefore we have a neat looking expression for the excess chemical potential. Now, how do we implement that in practice? So, the ultimate goal is to find the canonical average of exponential of minus ΔU by $k_BT$ and, the way we do that is we basically perform trial random insertions and we do not accept them that is we do not change the number of molecules in the system because if we change the number of molecules in the system first of all we will not remain in the canonical ensemble and secondly, now I would be looking at the canonical average of system containing N + 1 particles.

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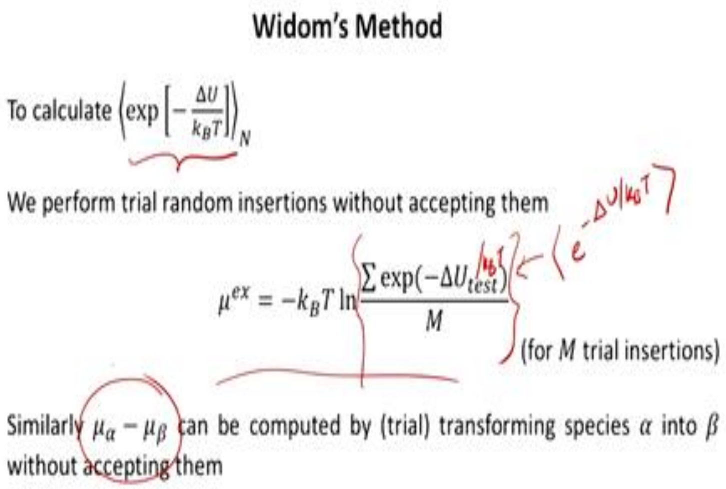

Widom's Method

To calculate $\underbrace{\left\langle \exp\left[-\frac{\Delta U}{k_B T}\right]\right\rangle_N}$

We perform trial random insertions without accepting them

$$\mu^{ex} = -k_B T \ln \underbrace{\left\{\frac{\sum \exp(-\Delta U_{test}/k_B T)}{M}\right\}}_{} \leftarrow \left\langle e^{-\Delta U/k_B T}\right\rangle \quad \text{(for } M \text{ trial insertions)}$$

Similarly $\mu_\alpha - \mu_\beta$ can be computed by (trial) transforming species $\alpha$ into $\beta$ without accepting them

In this case, I am interested in the canonical evidence of exponential of -ΔU by $k_B T$ for an N particle system when a new particle is being added or removed. So, clearly we want to do averaging over and particle system, so therefore we do not actually insert the particle we simply perform a trial insertion compute the energy changes but then we always reject all such Monte Carlo moves and by doing that a small trick what we can then evaluate is a quantity something like this. So, we can compute the arithmetic mean of the exponential of - ΔU by $k_B T$ for let us say M trial insertions and this is pretty much my average of exponential of - ΔU by $k_B$ T. Now, that $k_B T$ ln is appearing because it was appearing in the expression of μ, $\mu^{ex}$ that is excess chemical potential.

$$To\ calculate\ \langle \exp\left[-\frac{\Delta U}{k_B T}\right]\rangle$$

We perform trial random insertions without accepting them,

$$\mu^{ex} = -k_B T \ln \frac{\sum \exp(-\Delta U_{test})}{M}$$

So, we have pretty much evaluated the integrant that is the canonical average of exponential of - ΔU by $k_B$T this method is called the Widom's method and this method is again very popular because one of the advantage of this method is since we are not actually inserting the particles, we do not have to worry about acceptance rates because all the moves are pretty much being rejected.

So, we can always find the energy change of a move if we are not really interested in putting a particle inside the system computing the ΔU is a very easy affair, we can always find the energy change be it a small change or a large change unless we are really interested in increasing the number of molecules in the system we can pretty much have a simple job that we have simply a calculation of ΔU that can be easily conducted in fact, this method can be extended again to mixtures using an idea similar to the semi grand canonical ensemble that we discussed earlier in which case I will perform a trial transformation of species α into species β and we never accept that, so just like we are finding the excess chemical potential for one component in the earlier example that is right here if I am doing transformation of species α into β we would be computing the difference of the chemical potential between the α and β species and generally the ideal gas contribution will cancel out and therefore not only this method can be used for single component system but also can be extended very easily for a multi-component system. So, the next method along these lines is the method called the overlapping distribution method which is somewhat more efficient in comparison to the previous method that we have discussed. Again, the goal is to find the free energy differences and in this case what we do is we assume two systems- system 0 and system 1 and we defined the energy change between the two systems as basically the difference in energy between the two systems that is-

$$\Delta U = U_1(s^N) - U_0(s^N)$$

and both these systems are having the same value of N V T but they can have different interactions for example, because ultimately we are interested in the free energy difference that is the reason why we are defining two systems we should keep in mind that we never focus on computing the actual free energy but we are interested in always the free energy differences.

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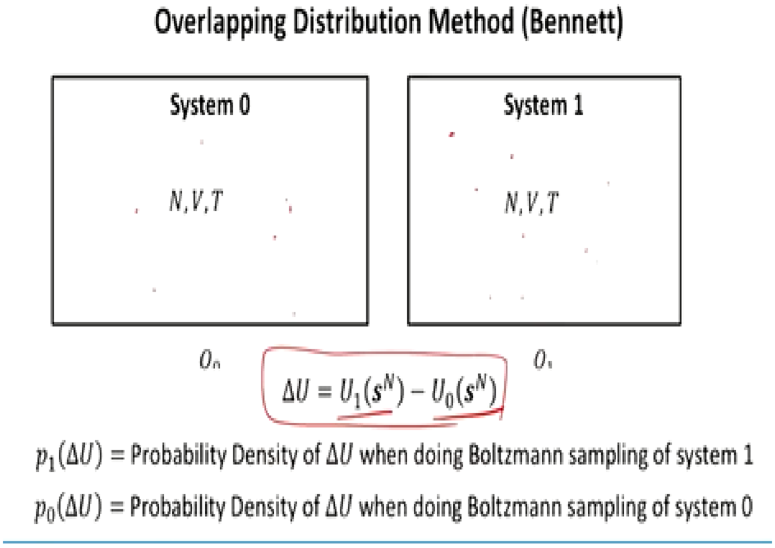

Overlapping Distribution Method (Bennett)

$$\boxed{\Delta U = U_1(s^N) - U_0(s^N)}$$

$p_1(\Delta U)$ = Probability Density of $\Delta U$ when doing Boltzmann sampling of system 1

$p_0(\Delta U)$ = Probability Density of $\Delta U$ when doing Boltzmann sampling of system 0

So, now once we have this particular variable representing the energy difference between system 0 and system 1, we can define two variables one that is the probability density of ΔU when we are doing the Boltzmann sampling of system 1 that is to say that we are doing my Monte Carlo simulation in system 1 and for every configuration that we get in my simulation I can pretty much map the same configuration in system 0 and compute the energy there and, therefore we can get a ΔU and this we can do it over all the steps of my simulation.

So, in this case we are doing Boltzmann sampling of system 1 and we are finding ΔU. Now, this will of course have some kind of probability density, so we can for example create a histogram and use that to find the probability density of ΔU.

Now, I can do the reverse I can perform the Monte Carlo simulation in system 0 again using the idea of Boltzmann sampling or by metropolis algorithm and, in this case for every configuration that we have in system 0, I pretty much map the same configuration that I copy the coordinates from system 0 to system 1 and compute ΔU for that and then I will get the probability density of ΔU when I am doing the Boltzmann sampling of system 0 and in fact we can do both of these.

So, I can find p 1(ΔU) and I can find p 0(ΔU) that is pretty much representing two different kinds of probabilities. One defined over system 1 and one defined over system 0, but in both these cases we are basically looking at the same quantity that is ΔU, only the averaging or the method to find probability density is different in one case we are averaging over system 1 configurations in one case, we are averaging over system 0 configurations.

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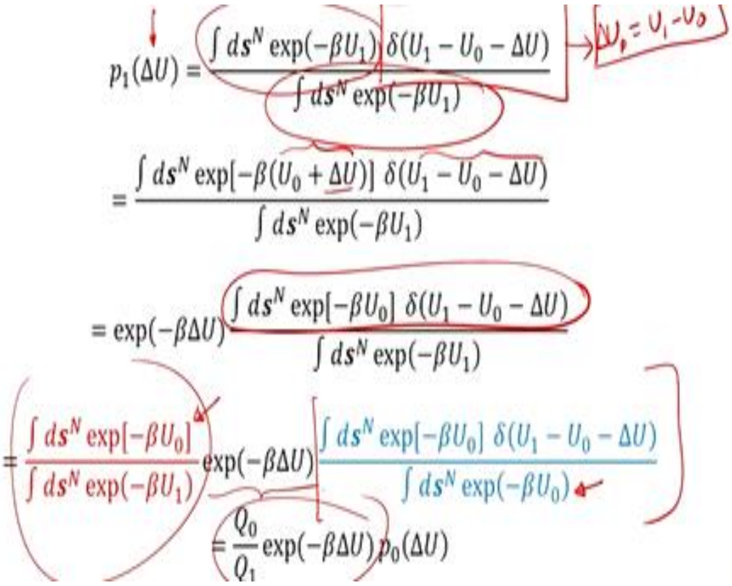

$$p_1(\Delta U) = \frac{\int ds^N \exp(-\beta U_1)\, \delta(U_1 - U_0 - \Delta U)}{\int ds^N \exp(-\beta U_1)} \rightarrow \boxed{\Delta U = U_1 - U_0}$$

$$= \frac{\int ds^N \exp[-\beta(U_0 + \Delta U)]\, \delta(U_1 - U_0 - \Delta U)}{\int ds^N \exp(-\beta U_1)}$$

$$= \exp(-\beta\Delta U) \frac{\int ds^N \exp[-\beta U_0]\, \delta(U_1 - U_0 - \Delta U)}{\int ds^N \exp(-\beta U_1)}$$

$$= \frac{\int ds^N \exp[-\beta U_0]}{\int ds^N \exp(-\beta U_1)} \exp(-\beta\Delta U) \frac{\int ds^N \exp[-\beta U_0]\, \delta(U_1 - U_0 - \Delta U)}{\int ds^N \exp(-\beta U_0)}$$

$$= \frac{Q_0}{Q_1} \exp(-\beta\Delta U)\, p_0(\Delta U)$$

So, now I can find the expression of p 1 ΔU for instance, which is basically having this particular partition function that is integration over the coordinates,

$$p_1(\Delta U) = \frac{\int ds^N \exp(-\beta U_1)\, \delta(U_1 - U_0 - \Delta U)}{\int ds^N \exp(-\beta U_1)}$$

$$= \frac{\int ds^N \exp[-\beta(U_0 + \Delta U)]\delta(U_1 - U_0 - \Delta U)}{\int ds^N \exp(-\beta U_1)}$$

$$= \exp(-\beta\Delta U) \frac{\int ds^N \exp[-\beta U_0]\, \delta(U_1 - U_0)}{\int ds^N \exp(-\beta U_1)}$$

$$= \frac{\int ds^N \exp(-\beta U_0)}{\int ds^N \exp(-\beta U_1)} \exp(-\beta U) \frac{\int ds^N \exp[-\beta U_0]\delta(U_1 - U_0 - \Delta U)}{\int ds^N \exp(-\beta U_0)}$$

$$= \frac{Q_0}{Q_1} \exp(-\beta\Delta U) p_0(\Delta U)$$

In this case we are using a scaled coordinates of course we have the volume term and the p factors but they will cancel out because we are looking at the ratio and then we have pretty much the same thing in the numerator but we have added a Δ function that pretty much tells me that ΔU is equal to $U_1$ - $U_0$. The Δ function will be meaningful only when ΔU is $U_1 – U_0$ or $U_1 – U_0$ is equal to ΔU, because we are basically interested in finding the probability density of ΔU.

So, now since the Δ function inherently is valid only when ΔU is equal to $U_1 – U_0$, I can replace U 1 in the integral here by $U_0$ + ΔU that is what I have done here and then the Δ function remains itself a simple rearrangement of equation, but now I can take the exponential of - βΔU outside because I was looking at p 1 which is a function of ΔU. So, delta U is known to me so I can pretty much factor out exponential of – β ΔU outside and now what we have is the numerator that we will get for $p_0$ of ΔU because, now the Δ function is being weighted by exponential of - $\beta U_0$ still in the denominator we have the partition function for the system 1.

So, we can slightly rearrange the equation again that is we multiply by the partition function of zero system and divide by the partition function of zero system and, by doing this small rearrangement what we see is that the blue guy in the expression it starts to represent the $p_0$ ΔU because the denominator is the partition function of the system 0 and the numerator is the Δ function but now weighted by the Boltzmann weights for the system zero.

So, clearly we will have exponential of – βΔU because it has factored out and this first term in red comes from the arithmetic rearrangement and, that essentially is the ratio of the partition functions in system 0 and system 1 and therefore what we have been able to relate is the probability density when I am sampling over system 1 with the probability density that I am, when I am sampling over system 0 both of these are related and since I can find both $p_1$ and $p_0$ in a simulation I can therefore find the quantity in between that is $Q_0$ by $Q_1$ exponential – β ΔU.

$$p_1(\Delta U) = \frac{Q_0}{Q_1}\exp(-\beta\Delta U)p_0(\Delta U)$$

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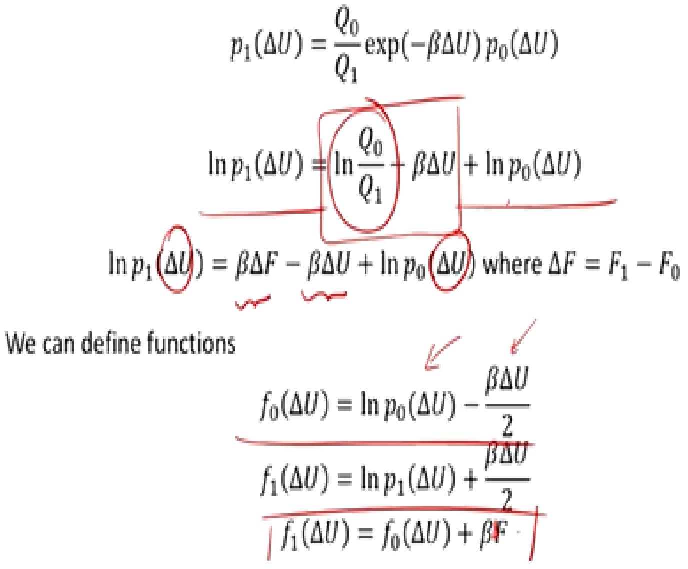

$$p_1(\Delta U) = \frac{Q_0}{Q_1}\exp(-\beta\Delta U)\,p_0(\Delta U)$$

$$\ln p_1(\Delta U) = \boxed{\ln\frac{Q_0}{Q_1} - \beta\Delta U} + \ln p_0(\Delta U)$$

$$\ln p_1(\Delta U) = \beta\Delta F - \beta\Delta U + \ln p_0(\Delta U) \text{ where } \Delta F = F_1 - F_0$$

We can define functions

$$f_0(\Delta U) = \ln p_0(\Delta U) - \frac{\beta\Delta U}{2}$$

$$f_1(\Delta U) = \ln p_1(\Delta U) + \frac{\beta\Delta U}{2}$$

$$f_1(\Delta U) = f_0(\Delta U) + \beta F$$

So, this is precisely what we do in the overlapping distribution method. So, I can rearrange that and I can write in the form and what we have in the middle is-

$$\ln p_1(\Delta U) = \ln \frac{Q_0}{Q_1} - \beta\Delta U + \ln p_0(\Delta U)$$

Now, the free energy is - ln Q by β or β multiplied by the free energy difference is the first term here and this is precisely what we write here and then you have -βΔU and clearly we are computing the probability densities as a function of ΔU.

$$\ln p_1(\Delta U) = \beta\Delta F - \beta\Delta U + \ln p_0(\Delta U) where\, \Delta F = F_1 - F_0$$

Now, we can slightly rearrange that so that it is somewhat neater. So, I can define two functions $f_0$ and $f_1$ defined over system zero and system one where I have slightly modified in a way that the final expression is simply $f_1$ is equal to $f_0$ plus β multiplied with the free energy difference between the two systems and, by doing that the problem would be to find $f_1$ and $f_0$ distributions and my free energy difference would be simply given by the difference between the two distributions divided by the value of β keep in mind it is β Δf in the final expression.

$$f_0(\Delta U) = \ln p_0(\Delta U) - \frac{\beta\Delta U}{2}$$

$$f_1(\Delta U) = \ln p_1(\Delta U) + \frac{\beta\Delta U}{2}$$

$$f_1(\Delta U) = f_0(\Delta U) + \beta F$$

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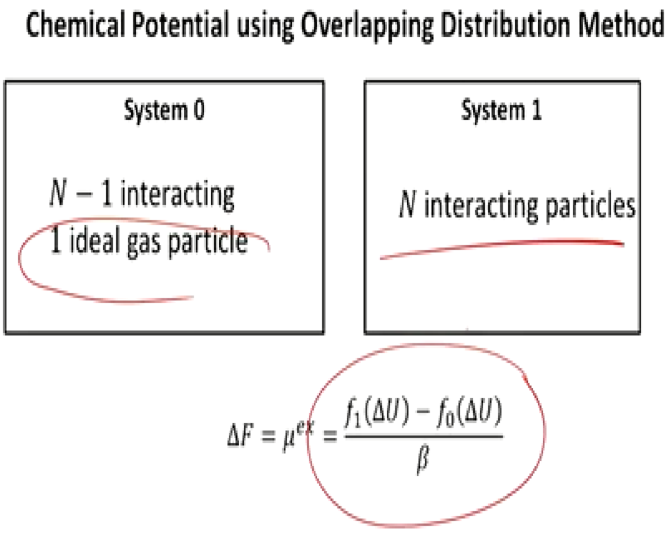

Chemical Potential using Overlapping Distribution Method

System 0

$N - 1$ interacting

1 ideal gas particle

System 1

$N$ interacting particles

$$\Delta F = \mu^{ex} = \frac{f_1(\Delta U) - f_0(\Delta U)}{\beta}$$

I can use this method to find the chemical potentials to do that what I can do is I will make my system 0 as containing N particles but N - 1 particles are interacting particles and one is an ideal gas particle. In system 1, we can have N interacting particles with the same interactions as system 0 and therefore when I take the difference in the free energy between them that should give me the excess chemical potential because excess chemical potential is the total chemical potential minus the ideal gas contribution.

So, in one case we have one ideal gas particle in other case we have none and therefore we pretty much will be looking at the chemical potential of one interacting particle minus chemical potential of one ideal gas particle, because all the other N - 1 particles are the same into the two systems and, therefore if I take my system definitions as above we can pretty much compute $f_1$ and $f_0$ for these two cases again as a function of $p_1$ and $p_0$ as we had defined and using that I can compute the free energy difference that will be in this case same as the axis chemical potential of the system.

$$\Delta F = \mu^{ex} = \frac{f_1(\Delta U) - f_0(\Delta U)}{\beta}$$

So, now one of the key problems in this method is when we find these two distributions $f_0$ and $f_1$ for the two systems this is these two distributions should somehow overlap because if they do not have an overlap region let us say, for example one of them let us say this in this case is like having a different range from the other one in that case there would be problems because ultimately we are computing the offset between the two graphs the two distributions the difference between these two is giving me a measure of $\beta\ \Delta f$.

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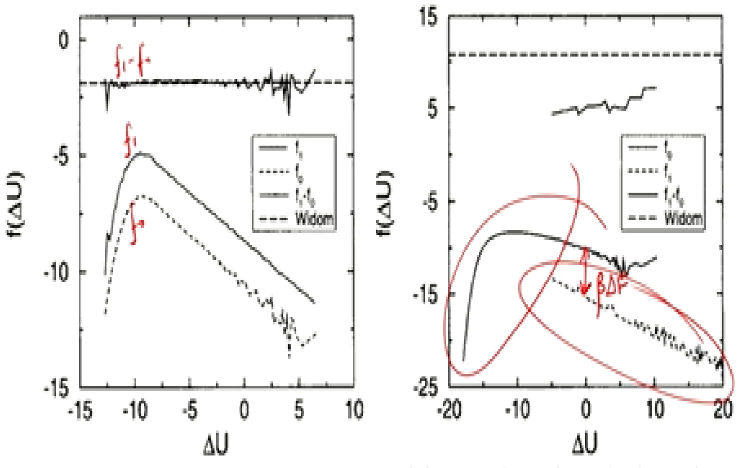
Distributions should overlap



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So, if they do not overlap or if they partially overlap clearly we can define offset over a smaller region or no region at all or if we have to define it we have to extrapolate one of those distributions that is again not really the correct way of doing it. So, this method will work ideally when you have a clear overlap between the two distributions that will be the case when system 0 and system 1 are not really very different from each other when they are closely located in terms of the model that we are using then in that case we may have an overlapping distribution but as soon as the two systems become different in terms of the behavior more and more parameters are different in that case clearly the distributions will no longer overlap.

So, the applicability of this method is only for the first case when there is a good overlap and as shown in this example here. So, in this case this is my $f_1$ this is my $f_0$ and $f_1 - f_0$ is the dotted line that you see here is the bold line that you see here and the dotted line is the estimate that we get from the Widoms method, just to compare the two methods and what you find is that both Widoms method and this method gives you pretty much the same answer except that this may be slightly more efficient in certain applications.

In this case however this is the result we get from the overlapping distribution method and this is what we get from the Widoms method. So, clearly there is a big difference assuming that the Widoms method was the correct result we can see that clearly our simulation is not giving me the correct answer and that has to be because the distributions are not significantly overlapping. This pretty much forms the basis for another class of methods that basically tries to match the two distributions by defining intermediate states between the two systems 0 and 1 where you always have some partial overlap between two adjacent steps in your sequence of steps and that is the basis of the method called the multiple histogram method which we will discuss in the next class.

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