Advanced Thermodynamics and Molecular Simulations

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Lecture No -51

Free Energies and Phase Behaviour; Extension of Canonical Ensemble Monte Carlo to Other Ensembles

Hello all of you, so in the last few weeks, we have discussed the Monte Carlo and molecular dynamics method we have basically looked at what is the theory behind it and how do we implement that using codes in Python particularly for the Monte Carlo simulations and briefly we touched upon the software we can use for molecular dynamics.

So, in the remaining time of this course I will touch on some advanced topics such as the calculations of free energies. The calculations of coexistence and then how can we generalize the molecular dynamics or Monte Carlo methods at mesoscale that is at larger length scales and time scales and how can we possibly do a non-equilibrium simulations.

So, first I will begin with the idea of coexistence and phase behavior we already have discussed in the context of lattice model, how can we represent the phase behavior if we have the Helmholtz free energy density using a particular functional form of the Helmholtz free energy density we showed what should the form B in order to have a homogeneous system and in order to have a phase separating system and then using lattice model we derived the functional form of that.

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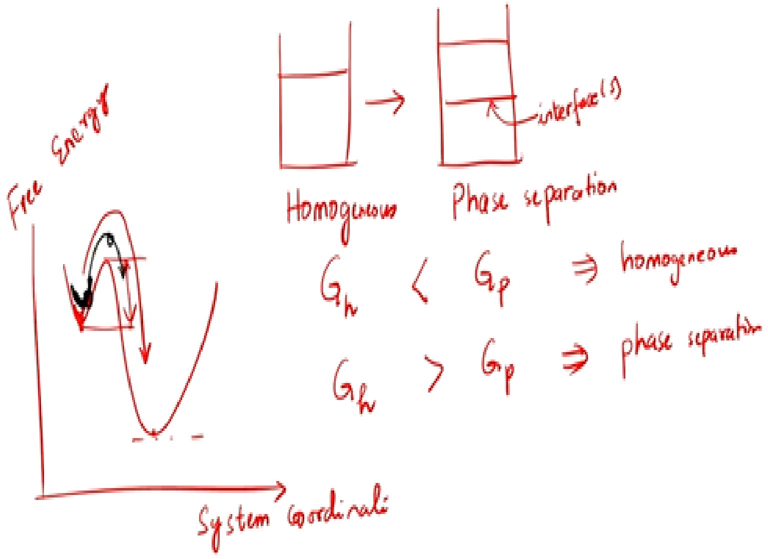

So just to quickly recap what I was telling you is that let us say for example, I am interested in the phase separation then I am going to compare the free energy in the two cases one is a homogeneous solution and one is the phase separating case and whichever will happen will be dictated by the corresponding free energy.

If for example, the free energy in this case happens to be less than the free energy in this case then in that case we are going to have a homogeneous solution or no phase separation.

$$G_n < G_p => homogenous\ solution$$

On the other hand, if G_h happens to be higher than G_p in that case we are going to have a phase separation.

$$G_h > G_p => phase\ seperation$$

Now, if I want to track these things in a molecular simulation there are couple of problems. The first problem is in whatever we have discussed we have not discussed the evaluation of free energies. We discussed how can we compute temperature? How can we compute pressure? How can we compute evidence energies and so on. But if we have not quite discussed how can we compute the free energy? It turns out that calculating free energy is quite difficult in molecular simulation it is possible and we discussed some techniques in this lecture and later on but it is not a part of the standard arithmetic of Monte Carlo or molecular dynamics that is the first problem.

The second problem is that whenever a phase separation happens in reality that is somewhat macroscopic in nature that is to say that, you clearly have formation of interface or interfaces that separate the two phases or the more phases. Now, that interface itself is realized when you have a very large number of molecules being simulated for simulations containing smaller number of molecules that we typically can do using Monte Carlo or molecular dynamics that is somewhat difficult to do.

The second problem is if we think about the homogeneous state and a phase separation state both are somewhere like near minima of the free energy. In other words, there is a free energy barrier between the homogeneous state and a phase separation state, what this means is that even if in a given conditions my system should phase separate thermodynamically if I start with a homogeneous solution in my simulation I will remain in homogeneous solution because the free energy barrier for reaching the phase separation state is not achieved. In other words, let say for example, my system is somewhere here in my free energy landscape and let us do it with reference to some arbitrary system coordinate which can be for example, a thermodynamic variable like temperature or volume fraction or whatever.

Now clearly in this case let us say this state has a lower free energy but if I start my system from here I will tend to be close to this minima because that is the local minima and it is easily accessible to me. So, with a few Monte Carlo steps or molecular dynamic system or a series of Monte Carlo steps that you perform we can get to that local minima but to come to the actual global minima we need to cross a free energy barrier or some sort of activation energy well do we do not talk about chemical reactions but even to go from two physical states which are simply different in terms of the their phase separation behavior there may be some kind of activation energy some barrier that we have to cross to make it happen and it turns out that although, the barriers can in principle be crossed they are not crossed in the time scales we simulate, if we think about the how the barriers will be crossed in reality the way it is going to happen is let say For example, if I start my system in here whether I am doing a Monte Carlo or molecular dynamics I am going to undergo fluctuations around this particular state.

Now, only when the fluctuations are large enough we can pretty much cross the barrier if the fluctuations are small then we will not cross the barrier. For example, we can talk about density as an order parameter. So, in the homogeneous state we are at certain density. So to go to a phase separation state we need to undergo density fluctuations such that we form a denser state and a dilute state separated by an interface not only the interface is difficult to simulate but such large density fluctuations also do not happen in the typical MD or Monte Carlo simulation because we are probing only small length and time scales.

There is one more problem and that is really physical in nature. Let us say for example, we are looking at a crystallization process then to form a crystal the molecules of a liquid or a gas should first come together and, then they have to reorient to form a unit cell of the crystal to form an ordered arrangement. Now, while the molecules coming together is really a fast process this can happen over the time scales of simulations they are reorientation to form a crystalline arrangement can take forever even when looking at from a physical point of view let us say in an experiment.

So even though a crystal is state can be a minima state in terms of free energy even experimentally it can be very difficult to realize and therefore we have to do some tricks in experiments as well to cross the free energy barrier to reach the crystalline state and the same kind of technique or something else need to be adopted also in simulations in order to cross the free energy barriers and fortunately there are many methods that have been developed over the last couple of decades which can basically address this particular challenge or in general that can pretty much explore the free energy landscape of systems and this is the kind of focus of this lecture and what I will discuss in the following lectures.

But before we do that let us first begin with a quick recap on what do I mean by phase transition and what do I mean by phase behavior and what can conventional Monte Carlo or molecular dynamics that we have already discussed can give us or how does it approach this particular problem. So, let us say for example, I want to simulate the phase behavior of water.

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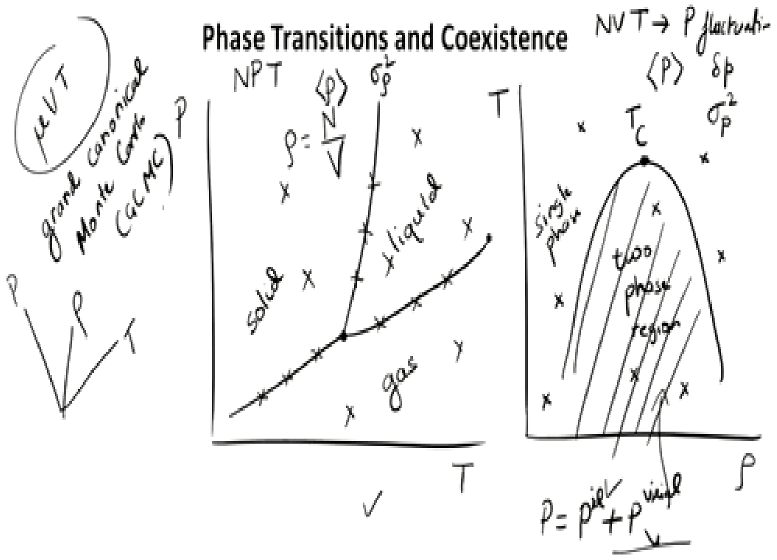
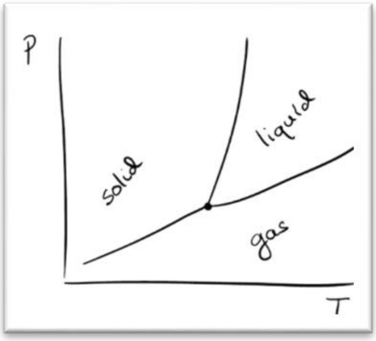


Phase Transitions and Coexistence

So, I can look at the pressure temperature diagram and it looks something like this-



In here this is my triple point in here you have a solid state, in here you have a liquid state and in here you have a gas state.

I can also draw a temperature density diagram where in you will have basically a two phase reason of liquid and gas forming somewhere over here and then you have a single phase region outside it and this is my critical point in here and this is my critical point in here.

So, in reality pressure, temperature and volume or pressure, temperature and density are basically the variables that we are track the thermodynamic variable. So, whenever we are interested in the equation of a state, the equation of a state gives me a pressure, volume, temperature relation, so in reality this is going to be having three axis pressure, temperature and volume and replacing the volume by density and, what I am showing you in the next two plots in here the pressure, temperature or temperature volume is a 2D cross section or a cut on this particular diagram.

So, therefore let us say for example, I am doing an NVT simulation so I can when I do a NVT simulation the control variable that we have is ρ and the control variable is temperature. So, in this case we are pretty much somewhere in this diagram and I can pretty much lie anywhere in there. So, as long as I am in the single phase regime there is pretty much no problem because there is no interface I just mentioned that but when I am in the two phase regime then it depends where I start from if I start from the homogeneous phase then falls simulation to reach a phase separation state where you can see the two phases may take forever there will be a free energy barrier with that and this is a part that will be I would say difficult to get there but nonetheless if I am controlling the density and temperature and as long as we are in the single phase regime we can compute the value of the pressure in this particular case, I am working at a fixed value of density and temperature I can compute the pressure but the pressure in this case would be for NVT ensemble the pressure is going to be fluctuating.

So, there is no meaning to say that the pressure value is this we should talk about the average value of pressure and the fluctuation in the pressure that I can represent for example, by the variance in the pressure it turns out that since our system sizes are pretty small in what we can simulate these fluctuations are pretty large and therefore the pressure value that we get from the NVT simulations are not very reliable and this is really coming from the fact that we are simulating a small system that is main reason.

The other reason is pressure is computed using the virial equation of a state and that equation of a state itself has certain assumptions built into it basically, we represent the pressure as an ideal term plus an excess term that we come from the virial which in turn depends on the positions and the forces acting on the particles and it turns out that this is really an approximation there can be more terms in there and therefore the pressure estimates although we can obtain that they are not very reliable.

In the other hand what we can do is we can do an NPT simulation now in the NPT simulation we can be anywhere on the pressure - temperature diagram. Again, as long as I am in the single phase regime there is pretty much no problem but once I come to the coexistence now the coexistence part are these lines in the diagram. So, in the temperature density curve it was a region in the graph and in the pressure - temperature diagram it is like along the three lines we have for different coexistence.

Now, it turns out that whatever problem we mentioned regarding NVT ensemble for the two phase regime it same problem will also happen for two phase regime in the NPT ensemble because when I am trying to simulate at a pressure and temperature value near the coexistence we will have large free energy barriers to cross. But again when we are in the single phase regime for pressure and temperature value given or being controlled we can find the corresponding density of the system or the volume the n is constant, so the density can be obtained and by v and those density estimates again are going to fluctuate.

So, you will have again some average value of density and some fluctuation in the density that we can represent using some variance there. It turns out that the estimates of density are quite reliable then in comparison to the pressure estimates in the NVT simulations and the reason is because density is rather well defined quantity there is no approximation when we define it density is simply given by the number of molecules by V or we can represent in terms of volume fraction if we need to and that quantity is well defined there is no approximation in there and, it turns out that the density fluctuations are not as serious in comparison to the pressure fluctuations.

So typically when I am interested in the phase behavior if I have to pick one of these two we should go for the NPT simulations not only because the pressure and temperature is usually specified in the experiments and therefore NPT ensemble makes more physical sense but also because the density fluctuations are less serious than compared to the pressure fluctuations or measurements are more reliable than compared to the pressure measurements.

Now, we can do something else here instead of working with NPT or NVT variables we could have worked with μVT and that is the grand canonical ensemble. In this case, now we are pretty much simulating an open system where the number of molecules can also change and it turns out that the grand canonical ensemble therefore is more convenient in terms of the description of the phase transitions because first of all we are working for an open system.

So, in that case the number of molecules can change and secondly we are working with the variables that we can easily control in also simulation. Let us say the chemical potential dictates the phase equilibrium so if we are working at different chemical potentials we can eventually reach a condition where the chemical potentials in the two phases are equal and that will represent the condition of phase equilibrium.

So, in that sense working with the μVT ensemble in some cases is more convenient and this is the grant canonical ensemble. So, first of all we will discuss how can we generalize our Monte Carlo scheme that we discussed in the NVT ensemble to the NPT ensemble and then more importantly we will discuss how can we generalize the grand canonical ensemble and the particular scheme that we are aiming at is called the grand canonical Monte Carlo or GCMC.

Later on, I will show that and do we can develop a scheme for doing that is not very convenient in win many cases, particularly this cannot be applied in the context of molecular dynamics for sure and therefore we need to think of some other schemes for analyzing the phase behavior and one of the ways is to compute the free energies because free energy computations can provide I would say an alternate way to look at the phase transitions using the kind of math that we have discussed earlier that we can find the free energy of the two possible states and whichever gives me the lower free energy is the state that we should go for so, in that case we can imagine doing two different simulations and computing the free energy for that or as we will discuss we are interested in the free energy difference between the two states and therefore we will have a clear sense of when will we have a phase separation or when will we have a phase transition not only that this can also help me explore the coexistence reason in somewhat better way that in comparison to the conventional Monte Carlo or molecular dynamics.

So, the way to go about it is I first will discuss how can I extend the canonical ensemble Monte Carlo to NPT Monte Carlo and therefore I will go back to the mathematical description of canonical ensemble and then how can we generalize to NPT ensemble and then how can we do that in practice. So, the canonical ensemble partition function is given by something like this-

$$Q(N,V,T) = c\int dP^N\, dr^N \exp\left[-\frac{H(p^N,r^N)}{k_B T}\right]$$

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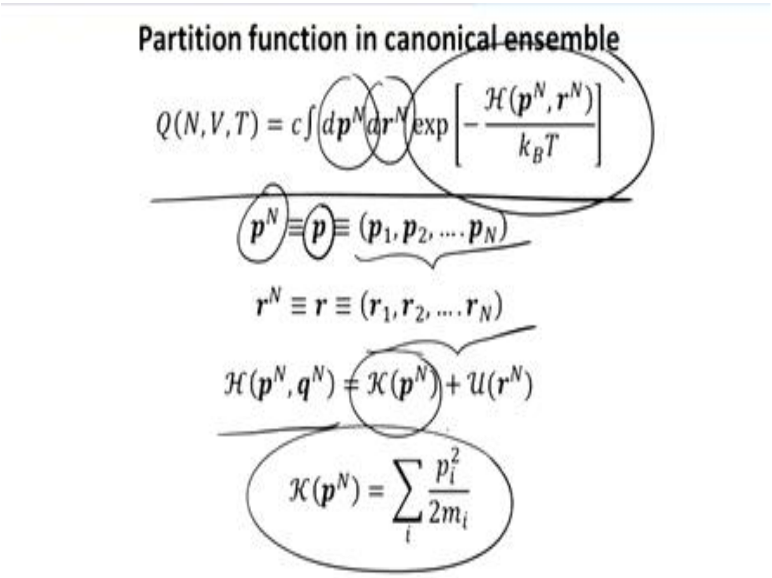

Partition function in canonical ensemble

$$Q(N,V,T) = c\int d\mathbf{p}^N d\mathbf{r}^N \exp\left[-\frac{\mathcal{H}(\mathbf{p}^N,\mathbf{r}^N)}{k_B T}\right]$$

$$\mathbf{p}^N \equiv \mathbf{p} \equiv (\mathbf{p}_1, \mathbf{p}_2, \ldots .\mathbf{p}_N)$$

$$\mathbf{r}^N \equiv \mathbf{r} \equiv (\mathbf{r}_1, \mathbf{r}_2, \ldots .\mathbf{r}_N)$$

$$\mathcal{H}(\mathbf{p}^N, \mathbf{q}^N) = \mathcal{K}(\mathbf{p}^N) + \mathcal{U}(\mathbf{r}^N)$$

$$\mathcal{K}(\mathbf{p}^N) = \sum_i \frac{p_i^2}{2m_i}$$

This is my Boltzmann factor H is my Hamiltonian I use slightly different representation for the momentum variables and the position variable. Earlier, I represented using P now I am representing using P power N to emphasize the fact that we will have N such variables and also because later on we want to do cases where N becomes a variable. So for from now on I will represent the dp by dp N and dr by dr N keep in mind that in both these cases it was representing the momentum and the coordinates of all the particles in the system.

$$p^N \equiv p \equiv (p_1, p_2 \ldots \ldots \ldots . p_N)$$
$$r^N \equiv r \equiv (r_1, r_2 \ldots \ldots . r_N)$$

Now, my Hamiltonian in most cases can be broken down into two distinct terms one that depends on momentum only and the second that depends on the positions only or the coordinates only.

$$H(p^N, q^N) = k(p^N) + U(r^N)$$

$$K(p^N) = \sum_i \frac{p_i^2}{2m_i}$$

The first term is the kinetic energy part that is given by something like sum over the kinetic energy of all the molecules and that is basically p square by 2 m summed over all the molecules and then you have a potential energy part that is coming from the inter particle interactions.

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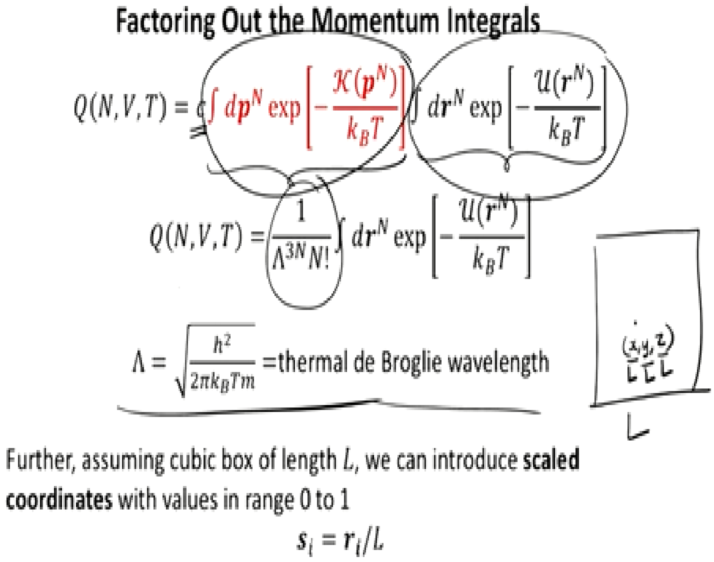

Factoring Out the Momentum Integrals

$$Q(N,V,T) = c\int dp^N \exp\left[-\frac{\mathcal{K}(p^N)}{k_BT}\right]\int dr^N \exp\left[-\frac{\mathcal{U}(r^N)}{k_BT}\right]$$

$$Q(N,V,T) = \frac{1}{\Lambda^{3N}N!}\int dr^N \exp\left[-\frac{\mathcal{U}(r^N)}{k_BT}\right]$$

$\Lambda = \sqrt{\frac{h^2}{2\pi k_B T m}}$ =thermal de Broglie wavelength

Further, assuming cubic box of length L, we can introduce **scaled coordinates** with values in range 0 to 1

$$s_i = r_i/L$$

Now it turns out that, if we can write the kinetic energy like that, and if my U does not depend on the movement are then we can factor out the P integral from the total integral and that is what we have done here.

$$Q(N,V,T) = c\int dp^N \exp\left[-\frac{k(p^N)}{k_BT}\right]\int dr^N \exp\left[-\frac{U(r^N)}{k_BT}\right]$$

So, I just wrote the kinetic energy part separately and the potential energy part separately, the first integral only depends on p and the second integral only depends on r and therefore we can pretty much factor out these two and this is how you may recall we got the expression of the partition function of an ideal gas.

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

So now it turns out that the first integral is something like this there is a small detail here there is a small constant that appears here that constant relates to the degeneracy of the energy states and therefore as we have discussed in the case of ideal gas partition function we get some particular term that I define as in this case as thermal de Broglie wavelength.

$$\Lambda = \sqrt{\frac{h^2}{2\pi k_B T_m}} = thermal\ de\ broglie\ wavelength$$

So, this is really a constant for a constant value of N. So, we have 1 over lambda to the power 3 N. where lambda is the thermal de Broglie wavelength and that will be constant for particles of constant mass and at a given temperature value, h is the Planck's constant. So, it is also a constant.

So, now we basically have the expression of the partition function where we have factored out the momentum integral and now for convenience in what we will discuss later I am going to introduce scaled coordinates instead of actual coordinates. So, in general the particles are in the box and the box is of length L. So pretty much every coordinate within the box can be normalized by the box size if it is a cubic box then the length is the same in every direction.

So, I can divide every coordinate by L and that particular scaled variable will now range from 0 to 1 because, we can say that the box is going from 0 to L or from like - 0.5 to + 0.5 in what we have discussed but we can also scale from 0 to 1. The main point is that we are pretty much removing the effect of box size by introducing the scaled coordinates.

$$scaled\ coordinates\ s_i = \frac{r_i}{L}$$

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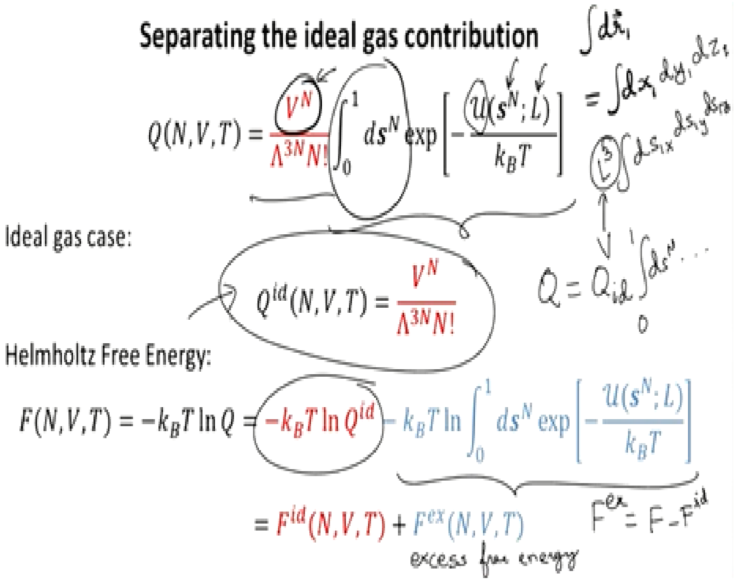

Separating the ideal gas contribution

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

Ideal gas case:

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

Helmholtz Free Energy:

$$F(N,V,T) = -k_B T \ln Q = -k_B T \ln Q^{id} \underbrace{- k_B T \ln \int_0^1 ds^N \exp\left[-\frac{\mathcal{U}(s^N;L)}{k_B T}\right]}$$

$$= F^{id}(N,V,T) + F^{ex}(N,V,T)$$

excess free energy

$$\int d\vec{r}_1 = \int dx_1 dy_1 dz_1$$

$$L^3 \int ds_{1x} ds_{1y} ds_{1z}$$

$$Q = Q_{id} \int_0^1 ds^N \ldots$$

$$F^{ex} = F - F^{id}$$

So then I can now write the drN integral by an integral over the scaled coordinates and therefore the volume to the power N factors out because we are basically integrating over the r in reality so but the r is factored by L and every r has three components. So for example, for one particle the dr one let say for particle one will be the dx_1, dy_1, dz_1 that is the x y z coordinates of that particle and, I am scaling all of them by s and therefore we will have something like ds_{1x}, ds_{1y}, ds_{1z} and L cube will factor out and that L cube is my volume and now we are doing it over all the particles and therefore we have V to the power N, factoring out of the integral. So, what we then have is under integral we are integrating from 0 to 1 in the scaled coordinates but now the U that is the potential energy depends clearly on the scaled coordinates but also depends on L because clearly, if L is different you will have different interval energy or potential energy in the system. So, therefore we have simply written in a manner that the integral goes from 0 to 1 but that does not mean that the U is changed in the representation it is simply a way to make the coordinates dimensionless there is no change otherwise in the result.

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

So then the advantage now is what you see in the red part in the first expression that becomes the partition function of an ideal gas. This we have derived earlier, but you can also see it from here because for the case of ideal gas U is going to be 0. So the term inside exponential will be 1 and since I am integrating from 0 to 1 for all the variables what we get is the entire integral will be 1 and therefore the result will be whatever is in the red in the expression here.

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

So, therefore I can now write my partition function as the ideal gas partition function multiplied by whatever we have under the integral and therefore I can define the Helmholtz free energy which is defined as - k_BT ln Q in terms of the partition function. So, the ideal gas part comes out and the second term is the contribution to the free energy apart from the ideal gas contribution which will I refer as the excess free energy. That is the free energy in excess of the ideal gas contribution the F excess is F - F_{id}.

$$\begin{aligned} F(N,V,T) &= -k_BT\ln Q \\ &= -k_BT\ln Q^{id} \\ &\quad - k_BT\ln\int_0^1 ds^N \exp\left[-\frac{U(s^N;L)}{k_BT}\right] = F^{id}(N.V,T) + F^{ex}(N,V,T) \end{aligned}$$

And,

$$F^{ex} = F - F^{id}$$

So, you already are talking about a free energy difference as opposed to the free energy in this case so I can look at the same system for the same N, V, T with the interactions turned off and that becomes the ideal gas counter part of the system, I can compute the free energy from for that and for the free energy of that we know the partition function analytically because for ideal gas case we can evaluate the partition function this is what is done here and therefore all that is important to us is to evaluate the excess part of the partition function or the excess part of the free energy and, this is the kind of term that we are actually most bothered about whenever we talk about the free energy calculation.

So, now I want to extend this N, V, T ensemble to an N, P, T ensemble and the way to do that is I assume that the system is placed in an ideal gas reservoir and the system can now exchange volume with the reservoir and it cannot exchange the any other thing like the molecules or energy it can only exchange the volume with the reservoir because for the N, P, T ensemble the volume can change so essentially what we want to do is we want to extend the N, V, T ensemble to the N, P, T ensemble, so the only variable that changes is the volume is replaced by the pressure and therefore volume can now change and therefore we are assuming that the system volume can change the number of molecules remain the same and therefore we basically assume some reservoir outside having certain number of molecules and certain volume and, whatever volume the system is expanding or compressing that is coming from the reservoir.

So, total volume of the system plus reservoir is constant total number of molecules is constant, the number of molecules of the system is a constant, the number of molecules of reservoir is constant.

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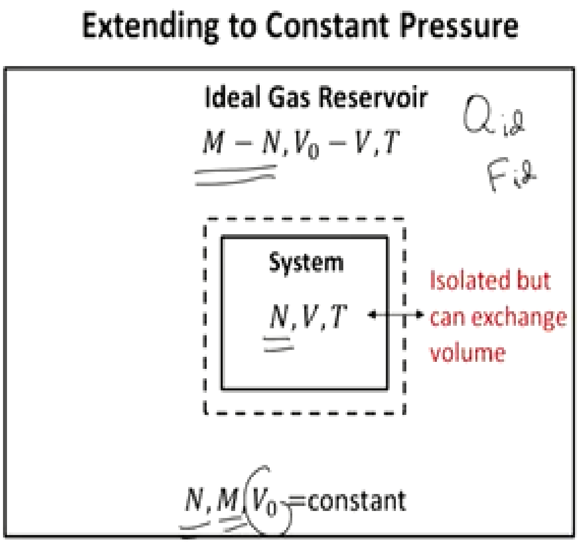
Extending to Constant Pressure

In this case M - N is constant and N is constant, so basically N and M are constant and V_0 that the total volume is constant but V is not constant and that would be an easier way to go form an N, V, T ensemble to N, P, T ensemble.

Keep in mind, that this prescription although is we are making it for the N, P, T ensemble does not mean that we are actually simulating the molecules in the reservoir what we will see in the next class is that just by doing the simulation of the system itself I can include the reservoir effect formally and the reason is I already know the partition function and the free energy of the ideal gas and therefore I do not need to simulate the ideal gas reservoir, I will only simulate the system but I will allow for the exchange of volume and that will provide me an extension to the N, P, T ensemble.

So, with that I want to conclude this lecture in the next lecture we will go through the math and derive the metropolis algorithm for the N, P, T ensemble, so I want to conclude with this.

Thank You.