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

Lecture - 13
Energy Distribution in Molecular System Revisited; Introduction to Thermodynamic Ensembles

Hello, all of you. So in the last lecture, we have been discussing the Lagrange multipliers that is for maximization with constraints, and we discussed the drunkard walk example. So in today's lecture, we will take the idea to distribution of quanta in molecular systems and later on we will discuss the idea of thermodynamic ensembles.

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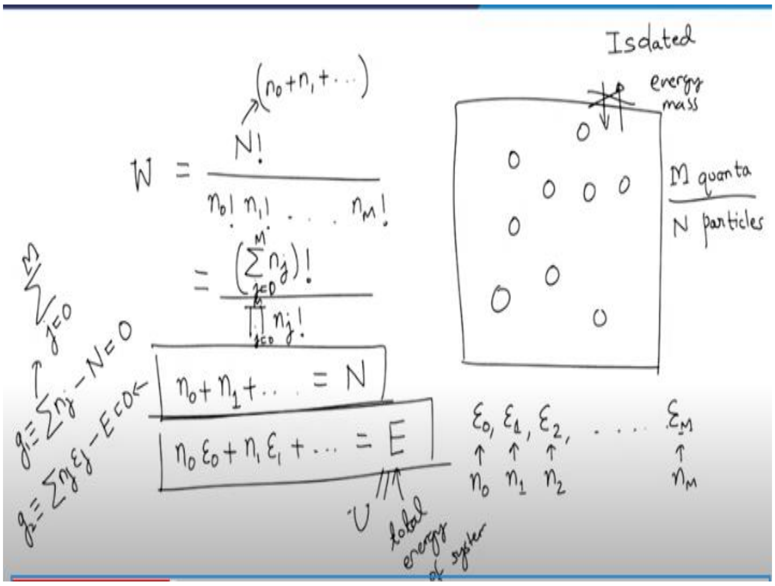

So to begin with, let us just go back to the example that we have done couple of times in this course already. So if you have some quanta of energy to be distributed amongst some particles, let us say you have M quanta among N particles. And again I will emphasize that the particles can be atoms or molecules whatever is appropriate for the context and the quanta need not be equally spaced that means we can in general say that we have energy levels ϵ_0, ϵ_1, ϵ_2 to some ϵ_M. If they were uniformly spaced then it was like in multiples of epsilon, but this need not be generally true. So then for this particular problem, we have already established that the number of ways for a particular distribution in which n_0 particles have energy ϵ_0, n_1 has energy ϵ_1, n_2 has energy ϵ_2 and so on. Let us say n_M has energy ϵ_M then the number of ways for this particular distribution is given as-

$$W = \frac{N!}{n_0!\, n_1! \ldots \ldots \ldots \ldots \ldots \ldots n_M!}$$

Now we have two constraints in this problem. The first constraint is-

$$n_0 + n_1 \ldots \ldots \ldots \ldots n_M = N$$

And then if I assume the system to be isolated that means the energy of the system is constant, there is no exchange of energy with the surrounding. And there is no exchange of mass as well, which in this case is the number of molecules. So in that particular case, there is also a condition for energy and that is-

$$n_0\epsilon_0 + n_1\epsilon_1 + \cdots \ldots \ldots \ldots \ldots \ldots \ldots . = E$$

Energy E that is the total energy of the system.

Now in fact, this corresponds to the internal energy, but we will use the word E instead of U that we used earlier. So E is same as U in our earlier description. And I am doing that because most textbooks on statistical mechanics use E as the representation for the internal energy.

So then, we can write this in the shortcut notation and also keeping in mind that these two constraints have to be met in a shortcut way and since we do not want to include the constraint in the expression itself of W, we will represent this N as the sum over of n_0, n_1 and so on, right. So the fact that the sum is equal to n is taken care of by the constraint. So in the equation or the expression for W, we will simply write as sum over the n_0, n_1 and so on. So we can write this in the shortcut notation then as-

$$W = \frac{(\sum_{j=0}^{M} n_j)!}{\Pi_{j=0}^{M} n_j!}$$

Keep in mind that this Π symbol is for products over the n_j values. In this case n_0 factorial multiplied with n_1 factorial and so on. And both these things are going from j equal to 0 to M.

And then I can also write this constraint in the shortcut notation as let us say g_1 is the name of the constraint. Then g_1 is-

$$g_1 = \sum n_j - N = 0$$

$$g_2 = \sum n_j\epsilon_j - E = 0$$

Although I am not putting in any index in the summation keep in mind that whenever I put a summation symbol sigma, it means that we are doing a summation over all possible values of j that is j equal to 0 to M in this case. Just for simplicity, I will simply use summation symbol, but we always mean summation over all possible values of j or whatever index we have in the problem.

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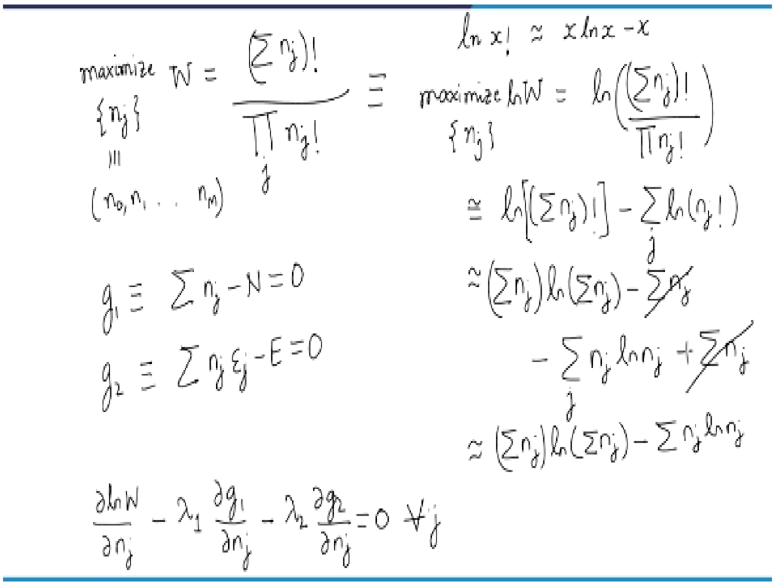

$$\underset{\{n_j\}}{\text{maximize}}\ W = \frac{(\sum n_j)!}{\prod_j n_j!} \equiv \underset{\{n_j\}}{\text{maximize}}\ \ln W = \ln\left(\frac{(\sum n_j)!}{\prod n_j!}\right)$$

$$\{n_j\} \equiv (n_0, n_1, \ldots n_M)$$

$$\ln x! \approx x \ln x - x$$

$$\cong \ln[(\sum n_j)!] - \sum_j \ln(n_j!)$$

$$\approx (\sum n_j)\ln(\sum n_j) - \cancel{\sum n_j} - \sum_j n_j \ln n_j + \cancel{\sum n_j}$$

$$\approx (\sum n_j)\ln(\sum n_j) - \sum n_j \ln n_j$$

$$g_1 \equiv \sum n_j - N = 0$$

$$g_2 \equiv \sum n_j \epsilon_j - E = 0$$

$$\frac{\partial \ln W}{\partial n_j} - \lambda_1 \frac{\partial g_1}{\partial n_j} - \lambda_2 \frac{\partial g_2}{\partial n_j} = 0 \ \forall j$$

So essentially in this shortcut notation the formula is W is-

$$W\{n_j\} = \frac{(\sum n_j)!}{\prod_j n_j!}$$

And we have to maximize this. So we have to find the values of n_j for which this function is maximized whenever I put a curly bracket, this is a shortcut for n_0, n_1 to n_M, okay. And this subject to two constraints –

$$g_1 = \sum n_j - N = 0$$

$$g_2 = \sum n_j \epsilon_j - E = 0$$

Now as we have noted earlier, we will use the Stirling formula for large N that says-

$$\ln x! \approx x \ln x - x$$

and since the maxima of W is going to be the same as maxima of ln of W, because, ln of W increases in the same way as W. So therefore, wherever we have maxima of W we also have maxima of ln W. So therefore, I can write the problem instead of this as-

$$maximise\ \{n_j\} \ln W = \ln(\frac{(\sum n_j)!}{\prod n_j!})$$

$$\cong \ln[(\sum n_j)!] - \sum \ln(n_j!)$$

$$\approx (\sum n_j)\ln(\sum n_j) - \sum n_j - \sum_j n_j \ln n_j + \sum n_j$$

$$\approx \left(\sum n_j\right)\ln\left(\sum n_j\right) - \sum n_j \ln n_j$$

and since the maxima of W is going to be the same as maxima of ln of W, because, ln of W increases in the same way as W. So therefore, wherever we have maxima of W we also have maxima of ln W. So therefore, I can write the problem instead of this as-

$$\frac{\partial lnW}{\partial n_j} - \lambda_1 \frac{\partial g_1}{\partial n_j} - \lambda_2 \frac{\partial g_2}{\partial n_j} = 0$$

And this has to be true for all j.

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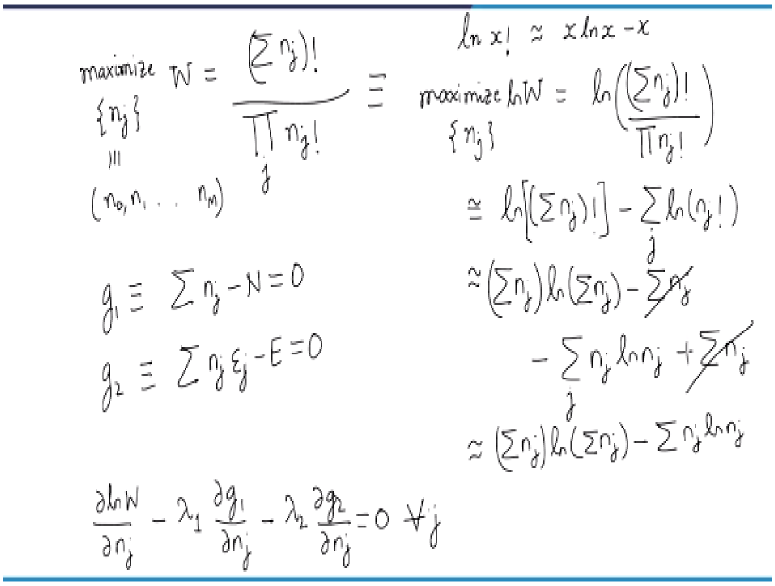

$$\underset{\{n_j\}}{\text{maximize}}\ W = \frac{\left(\sum n_j\right)!}{\prod_j n_j!} \equiv \underset{\{n_j\}}{\text{maximize}}\ \ln W = \ln\left(\frac{\left(\sum n_j\right)!}{\prod n_j!}\right)$$

$$\{n_j\} \equiv (n_0, n_1, \ldots n_M)$$

$$\ln x! \approx x\ln x - x$$

$$\approx \ln\left[\left(\sum n_j\right)!\right] - \sum_j \ln(n_j!)$$

$$\approx \left(\sum n_j\right)\ln\left(\sum n_j\right) - \cancel{\sum n_j} - \sum_j n_j \ln n_j + \cancel{\sum n_j}$$

$$\approx \left(\sum n_j\right)\ln\left(\sum n_j\right) - \sum n_j \ln n_j$$

$$g_1 \equiv \sum n_j - N = 0$$

$$g_2 \equiv \sum n_j \varepsilon_j - E = 0$$

$$\frac{\partial \ln W}{\partial n_j} - \lambda_1 \frac{\partial g_1}{\partial n_j} - \lambda_2 \frac{\partial g_2}{\partial n_j} = 0 \ \forall j$$

So let us write this expression and since we know-

$$lnW = \left(\sum n_j\right)\ln\left(\sum n_j\right) - \sum n_j \ln n_j$$

We have then-

$$\frac{\partial lnW}{\partial n_j} = \frac{\sum n_j}{\sum n_j}\,.1 + \ln\left(\sum n_j\right).1 - \frac{n_j}{n_j} - \ln n_j$$

So for all the values of j not equal to the j with which I am finding derivative, the derivative is going to be zero only for that particular value of j at which I am finding derivative, it will be equal to 1, right. So this is the derivative of summation with respect to n j. Just for example sake, let us say if you have the summation written like this, and if I want to find derivative with respect to n_2 that is I am doing for j equal to 2. So in that case the derivative of n_0 with respect to n2 is 0, derivative of n_1 with respect to n_2 is 0 only the derivative of n_2 with respect to n_2 = 1 and therefore, we have a 1 there. So I hope that is clear. So then these two cancels out and what we have is essentially-

$$\frac{\partial lnW}{\partial n_j} = -\ln(\frac{n_j}{\sum n_j})$$

Now there are two other derivatives here that is-

$$\frac{\partial g_1}{\partial n_j} = 1$$

As since we know-

$$g_1 = \sum n_j - N = 0$$

Similarly,

$$\frac{\partial g_2}{\partial n_j} = \epsilon_j$$

And as we know

$$g_2 = \sum n_j \epsilon_j - E = 0$$

So therefore, the minimization expression that we have-

$$\frac{\partial lnW}{\partial n_j} - \lambda_1 \frac{\partial g_1}{\partial n_j} - \lambda_2 \frac{\partial g_2}{\partial n_j} = 0$$

$$-\ln\left(\frac{n_j}{\sum n_j}\right) - \lambda_1 - \lambda_2 \epsilon_j = 0$$

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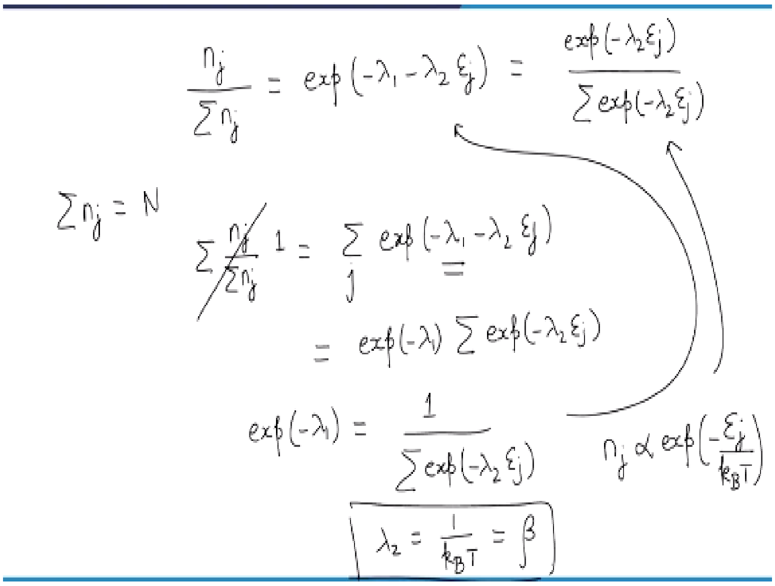

$$\frac{n_j}{\sum n_j} = exp(-\lambda_1 - \lambda_2 \xi_j) = \frac{exp(-\lambda_2 \xi_j)}{\sum exp(-\lambda_2 \xi_j)}$$

$$\sum n_j = N$$

$$\cancel{\sum \frac{n_j}{\sum n_j}}\ 1 = \sum_j exp(-\lambda_1 - \lambda_2 \xi_j)$$

$$= exp(-\lambda_1) \sum exp(-\lambda_2 \xi_j)$$

$$exp(-\lambda_1) = \frac{1}{\sum exp(-\lambda_2 \xi_j)}$$

$$n_j \propto exp\left(-\frac{\xi_j}{k_B T}\right)$$

$$\boxed{\lambda_2 = \frac{1}{k_B T} = \beta}$$

Now this expression I can write as an exponential because I can move ln to the other side. And therefore, what we get is-

$$\frac{n_j}{\sum n_j} = \exp(-\lambda_1 - \lambda_2 \epsilon_j)$$

That is the most probable distribution in this case for which the ln W is maximized. Now we can use the constraints again to find the Lagrange multiplier λ1 and that is since we know that summation of nj = to n what we can do I can apply summation on the both left hand side and to the right hand side. So what we then have is-

$$\frac{n_j}{\sum n_j} = \exp(-\lambda_1) \sum \exp(-\lambda_2 \epsilon_j)$$

$$\exp(-\lambda_1) = \frac{1}{\sum \exp\left(-\lambda_2 \epsilon_j\right)}$$

. And therefore, what we have is-

$$\frac{n_j}{\sum n_j} = \frac{\exp(-\lambda_2 \epsilon_j)}{\sum \exp(-\lambda_2 \epsilon_j)}$$

So the result that we have got is actually similar to the Boltzmann distribution that we have obtained earlier. So what we have found earlier or what we have used earlier is that, I said that the number of the molecules in a state j or having energy ϵj is-

$$n_j \propto \exp\left(-\frac{\epsilon_j}{k_B T}\right)$$

So if I compare this expression with that expression, so the denominator is a summation. So whatever we have here should apply to the numerator. And what we should find then is-

$$\lambda_2 = \frac{1}{k_B T} = \beta$$

in statistical mechanics.

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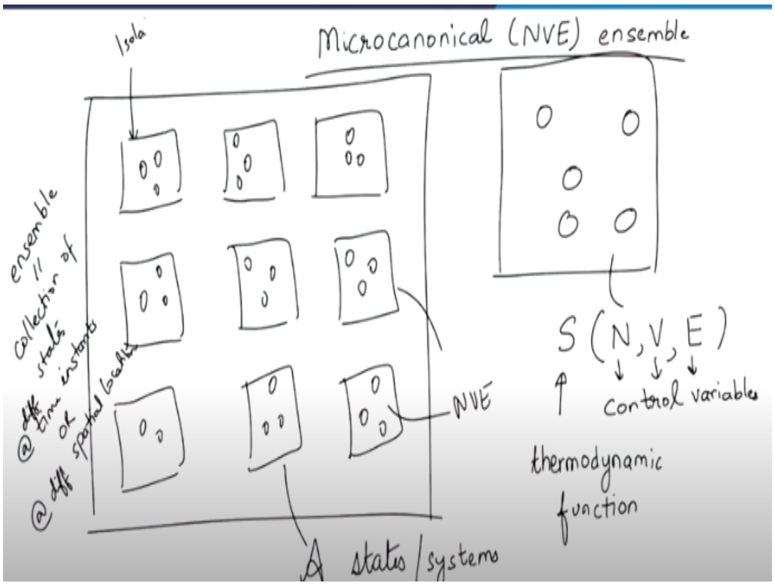

So it turns out that the example that I have taken where the system is isolated and it has some number of molecules and since I was not doing any work as well although I did not state that the volume is also constant and in fact, at most probable distribution the entropy is also constant right but the other way to say that is that the energy is constant. So I can write energy as a function of entropy or I can write entropy as a function of energy. So what we can say then here is that, for this particular case, entropy can be thought of as a thermodynamic function and N that is the number of molecules, V that is the volume and E that is the internal energy of the entire system are the control variables.

Now if I think of a system that has a constant number of molecules, constant volume and constant energy, then there is not only one system that is possible for this particular scenario. So you can have various distribution of quanta of energy that will still give you the same total energy. So whenever we are talking about a system in thermodynamics, actually we are not talking about one particular configuration or one particular distribution of energy, we are talking about a whole ensemble of distribution, right. So essentially, we can imagine that we have many systems that are present which are having same N, V and E. So all of them can have same N, V, E, but they can have different energy distribution or even the position of molecules among there and all of them will refer to the same system at N, V, E.

The other way to think about it is let us say if I specify that this room is an equilibrium, and we have certain properties. Now the molecules in the room are not frozen, the molecules keep on moving. So therefore, when I specify the thermodynamics of this room, I am not interested in a particular configuration that is like a snapshot taken at a particular instant but an average over many conformations that is going to be realized over a period of time. The other way to look at it is that if the room is in equilibrium, I can think of like small volumes of the room, which are having same property at every other volume because the property of the room, property of the air in the room should not change if I go from here to there. If it does, then the room is not in equilibrium. When we are in equilibrium, then the properties of every particular small volume remains the same.

So when we think of an ensemble, we can think of it as a collection of states either at different time instance or at different spatial locations and whenever we talk about any property in the in thermodynamics, it is always an average over many possible states of the system having the same value of control variables, in this case N, V and E, but different possible configuration and different possible distribution of energies, right that is a very important point that we will build on and in this particular case, where I am keeping the N, V, and E constant is referred as a micro canonical (NVE) ensemble and the ensemble will comprise of some A states and any property A states or A systems to be more precise. So now I am not talking about the state of a molecule, I am talking about the state of the entire system. So you can have multiple configurations of the system, which are present at this NVE we can think in terms of different time instants or we can think in terms of different spatial locations but nonetheless, whenever we are doing thermodynamics, we are essentially interested in the average over all those possible states and systems.

Now you can clearly imagine that the number of possible states are going to be huge. So it may go for large molecules something like infinity, right. So this may be more like a theoretical construct than being like a complete enumeration of all possible states. So A in theoretically speaking should represent all possible states of system, but we need to make certain approximations if I want to represent the system with fewer number of states, right so because we cannot do like infinite possible states and compute the average, that is not quite possible and therefore, we will enumerate some of these states. So we can approximate the ensemble for some possible state or systems but in reality, the number of systems or number of states can be huge. So A can be really a very huge number.

And then what we are also assuming is that all these systems are isolated. So although they are present in a box that I am showing, there is no interaction between systems there is no exchange of mass or exchange of energy between different systems in this case, because we are doing a NVE ensemble, which refers to an isolated system as we discussed.

So this is it turns out that this is not a very useful ensemble for many applications. And the reasons we have stated earlier that it is not always possible to control entropy or the volume. Sometimes it is more appropriate, actually experimentally it is always more appropriate to control temperature as opposed to entropy but sometimes it can be also appropriate to control pressure instead of volume. And therefore, we can have a variety of ensembles and the ensembles are defined on the basis of what is the control variable in the particular case.

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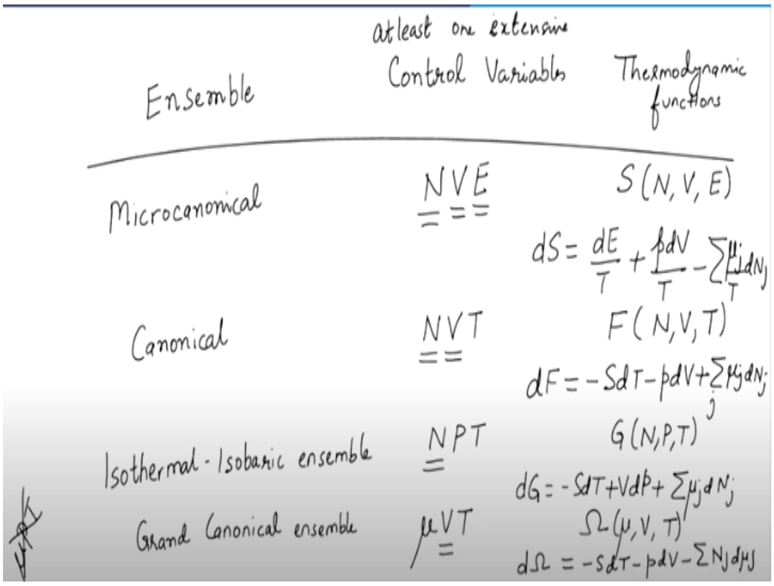

Ensemble	atleast one extensive Control Variables	Thermodynamic functions
Microcanonical	$\underline{\underline{N}}\,\underline{\underline{V}}\,\underline{\underline{E}}$	$S(N, V, E)$ $dS = \frac{dE}{T} + \frac{p dV}{T} - \sum \frac{\mu_j}{T} dN_j$
Canonical	$\underline{\underline{N}}\,\underline{\underline{V}}\,T$	$F(N, V, T)$ $dF = -SdT - pdV + \sum_j \mu_j dN_j$
Isothermal - Isobaric ensemble	$\underline{\underline{N}}\,P\,T$	$G(N, P, T)$ $dG = -SdT + VdP + \sum \mu_j dN_j$
Grand Canonical ensemble	$\mu\,\underline{\underline{V}}\,T$	$\Omega(\mu, V, T)$ $d\Omega = -SdT - pdV - \sum N_j d\mu_j$

So we will discuss in this course four different ensembles, which are most commonly used which will have different set of control variables and therefore, different thermodynamic functions representing them and these are the one that we already have discussed, the micro canonical ensemble and in this case the control variables are number of molecules, volume and the energy.

So we will discuss in this course four different ensembles, which are most commonly used which will have different set of control variables and therefore, different thermodynamic functions representing them and these are the one that we already have discussed, the micro canonical ensemble and in this case the control variables are number of molecules, volume and the energy and thermodynamic function is S (N, V, E). We can write in differential form as-

$$dS = \frac{dE}{T} + \frac{pdV}{T} - \sum \frac{\mu_j dN_j}{T}$$

We can also have something called a canonical ensemble. In that case the control variables are N, V and T, number of molecules, volume and temperature and in this case the thermodynamic function is called the Helmholtz free energy, that is a function of N, V and T and the differential form is-

$$dF = -SdT - pdV + \sum_j \mu_j dN_j$$

By the way we are doing for multi component systems in this case. If it is a one component system the last term with chemical potentials will not appear.

And then we can have something called an isothermal isobaric ensemble and in this case NPT is constant; the number of molecules, pressure and temperature. And in that case the thermodynamic function we are interested in is the Gibbs free energy N, P, T. In differential form it is-

$$dG = -SdT + VdP + \sum \mu_j dN_j$$

And the last one is the grand canonical ensemble and in that case, the control variables are mu V T that is the chemical potential volume and temperature and we can define a grand canonical potential that is a function of μ, V, T that is-

$$d\Omega = -SdT - pdV - \sum N_j d\mu_j$$

One thing to note here is that in all these cases I have kept at least one extensive variable, right. In this case, both N and V and E all of them are extensive. There is nothing called a μP T ensemble because then all the variables become intensive and we have earlier said using the Gibbs-Duhem theorem that, that does not give me a meaningful differential form, it becomes zero you must have at least one extensive variable because something in the system something about the system should specify the size of the system.

So with that I conclude the discussion of thermodynamic ensembles. In the next few lectures, we will show that how can we find thermodynamic properties for all these ensembles by first defining the ensembles, then defining the function that we have to maximize and then or minimize and then finally, using the method of Lagrange multipliers, we can determine the average properties for the ensemble and whenever we talk about an average it is average over all the systems present in the ensemble.

So with this I conclude the discussion here. Thank you.