Basic Statistical Mechanics
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Lecture - 14
Grand Canonical Ensemble

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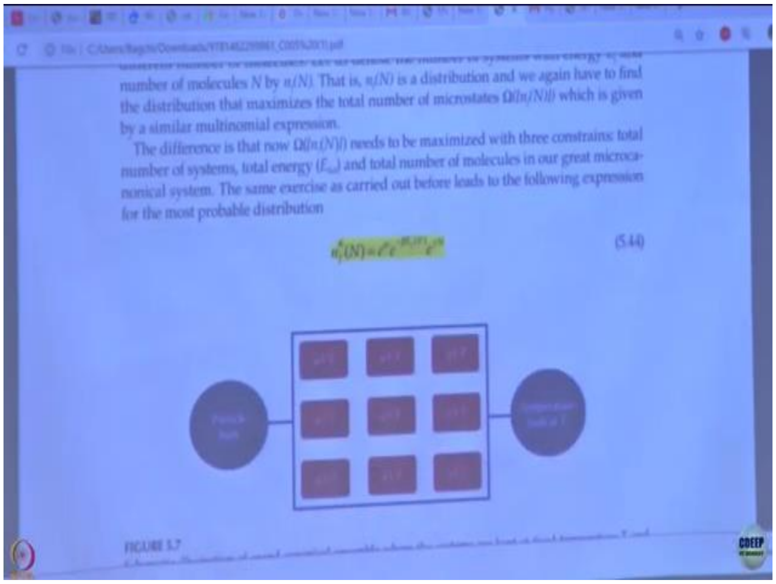

number of molecules N by $n_j(N)$. That is, $n_j(N)$ is a distribution and we again have to find the distribution that maximizes the total number of microstates $\Omega(\{n_j(N)\})$ which is given by a similar multinomial expression.

The difference is that now $\Omega(\{n_j(N)\})$ needs to be maximized with three constrains: total number of systems, total energy (E_{tot}) and total number of molecules in our great microcanonical system. The same exercise as carried out before leads to the following expression for the most probable distribution

(5.44)

FIGURE 5.7

Now, we are going to study the grand canonical ensemble. In grand canonical ensemble, I will not do in great detail. So now the way this is constructed is the following. I have tried to do a good job in explaining these things in my book but another person who has done a good job is Terrell Hill.

That is the second best place to look into other than my book. So now, what we did in doing the canonical partition function. We put the large number of systems characterized by NVT. But each of them has different energy levels because energy is not conserved or not constant in NVT. We put them together in contact with each other and then we put it in a bath and we let the temperature go to constantly.

When the temperature is equilibrated, we take it out and then we put insulation around this. So the whole microcanonical ensemble becomes a super system in a canonical ensemble.

The whole idea of going back from canonical to microcanonical is that I can use the principles of microcanonical ensemble, which is essentially $S = k_B \ln \Omega$. But now because of my construction of super ensemble and super system, I am now handpicked with two constraints one is the total number of systems that constitute my ensemble and other is the total energy.

So, I need to go to conservation of energy because I need to go back to microcanonical ensemble. If I do not go to microcanonical ensemble, I cannot use $S = k_B \ln \Omega$. So I go back and then I put Ω into distribution. Now each system has a different energy.

So it is this whole system that you are considering and the system has energy Ej. So nj, so with that the constraint and the combinatorics multinomial expression of the total Ω we go on and did the calculations. Going back and forth to the microcanonical ensemble and the canonical and we derived all that you derived and it is so fun. Next level, then I want to let, so I have allowed energy to fluctuate in view of the intensive variable temperature.

Now, I am going to let total number of particles fluctuate because that is very important in many applications. Like you have a gas at equilibrium then the molecules are exchanging between phases. Then that is the grand canonical ensemble. And so we do the again the same thing we put my grand canonical things and we now replace the wall like being in a canonical we let the system interact energetically. So the walls are for us to exchange energy but not number. Now, I make the walls such that that number of particles can also exchange. Then I do for my all this porous system putting them together in a kind of chemical potential path.

In addition, I have the thermal bath, so the system has now constant energy, constant chemical potential and constant temperature. So from grand canonical I passed in to canonical ensemble. Then from canonical I go to micro canonical.

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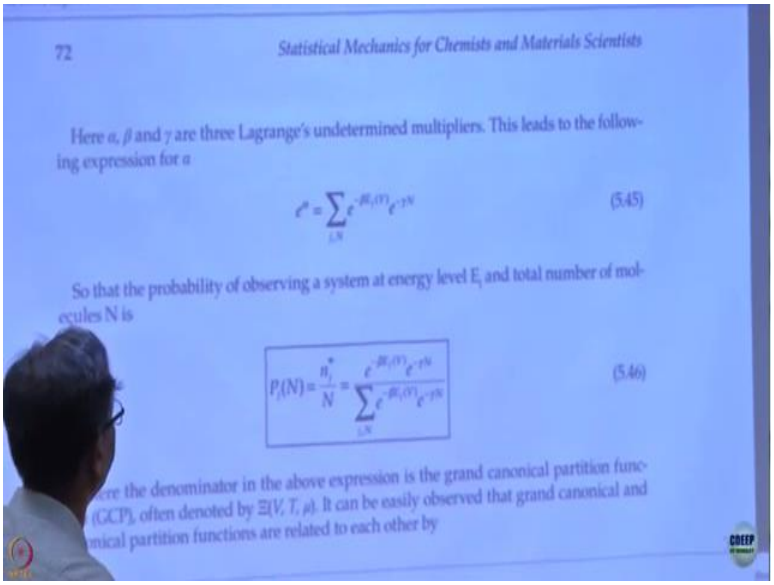

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Here α, β and γ are three Lagrange's undetermined multipliers. This leads to the following expression for α

$$e^{\alpha} = \sum_{j,N} e^{-\beta E_j(V)} e^{-\gamma N} \quad (5.45)$$

So that the probability of observing a system at energy level E_j and total number of molecules N is

$$\boxed{P_j(N) = \frac{n_j^*}{N} = \frac{e^{-\beta E_j(V)} e^{-\gamma N}}{\sum_{j,N} e^{-\beta E_j(V)} e^{-\gamma N}}} \quad (5.46)$$

re the denominator in the above expression is the grand canonical partition function (GCP), often denoted by $\Xi(V, T, \mu)$. It can be easily observed that grand canonical and nical partition functions are related to each other by

Previously, I had two constraints but now I have three constraints because not only the total number, I also have energy constraint. As a result of that, I will now have three undetermined multipliers one of them again becomes α , one is β and other is γ . And the form that comes in at the end of the day I have instead of having one sum, which is over energy levels sum over number of particles.

So I have some over N and this is the conservation condition that comes in. So now, I have the following double probability, probability that my system in energy level is j, so j is the index for the energy of the system and n is the index for the number of particles of the system.

So P_j is now defined by n_j by N. So when we have probability then I have to normalize it by summing over all these things and this comes from the undetermined multiplier. So this is the probability distribution in the grand canonical ensemble. So, there are many possible notations of this grand canonical partition function. I have used this one.

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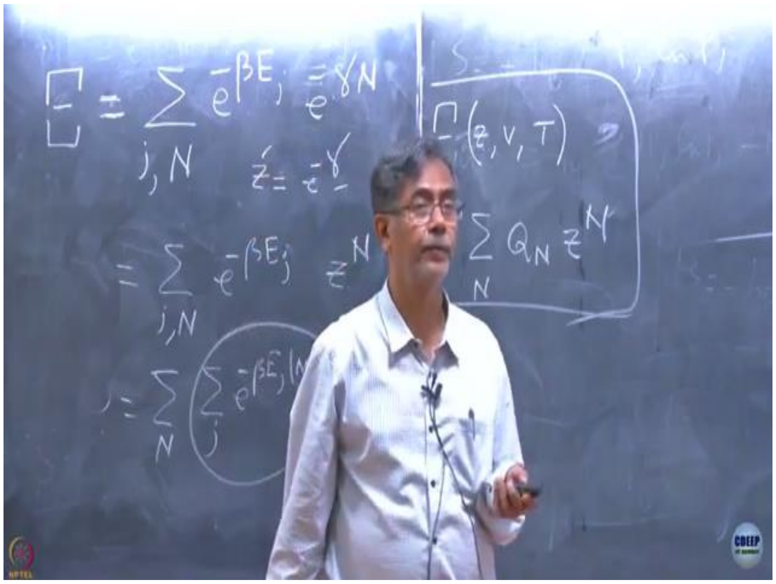

The reason is that Ξ is taken away. I will explain that why capital Ξ is taken away. So, this is now number of energy levels. Then this equal to the $e^{-\beta E-\gamma N}$ which is the less fugacity, this is the chemical potential.

So, we can identify canonical partition function in that expression. So this thing is really nice. So, this is the, definition of the grand canonical partition function. You know, I do not want to go through the detail because it is more elaborate but essentially repetition of what we did and it just bored you and will rob you of the beauty of the whole thing.

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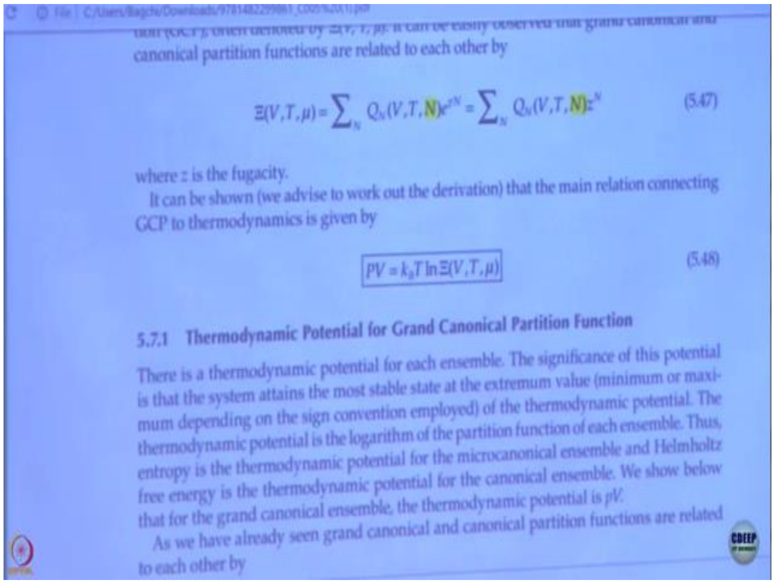

tion (GCP), often denoted by $\Xi(V,T,\mu)$. It can be easily observed that grand canonical and canonical partition functions are related to each other by

$$\Xi(V,T,\mu) = \sum_N Q_N(V,T,N) e^{\gamma N} = \sum_N Q_N(V,T,N) z^N \qquad (5.47)$$

where z is the fugacity.

It can be shown (we advise to work out the derivation) that the main relation connecting GCP to thermodynamics is given by

$$\boxed{PV = k_B T \ln \Xi(V,T,\mu)} \qquad (5.48)$$

5.7.1 Thermodynamic Potential for Grand Canonical Partition Function

There is a thermodynamic potential for each ensemble. The significance of this potential is that the system attains the most stable state at the extremum value (minimum or maximum depending on the sign convention employed) of the thermodynamic potential. The thermodynamic potential is the logarithm of the partition function of each ensemble. Thus, entropy is the thermodynamic potential for the microcanonical ensemble and Helmholtz free energy is the thermodynamic potential for the canonical ensemble. We show below that for the grand canonical ensemble, the thermodynamic potential is pV.

As we have already seen grand canonical and canonical partition functions are related to each other by

But this expression is just beautiful. These are notations I always use. And now, one can play the same game again, same thermodynamics that we played before. By going over all the way back and forth again, you have to write the entropy. And same thing you will do and then you come to this beautiful relation that in grand canonical ensemble.

So we call these term $-k_B T \ln \Xi$ is the thermodynamic potential. So let me write down all three you will see the beautiful symmetry and I meant, mention before that all these things was just done by one person.

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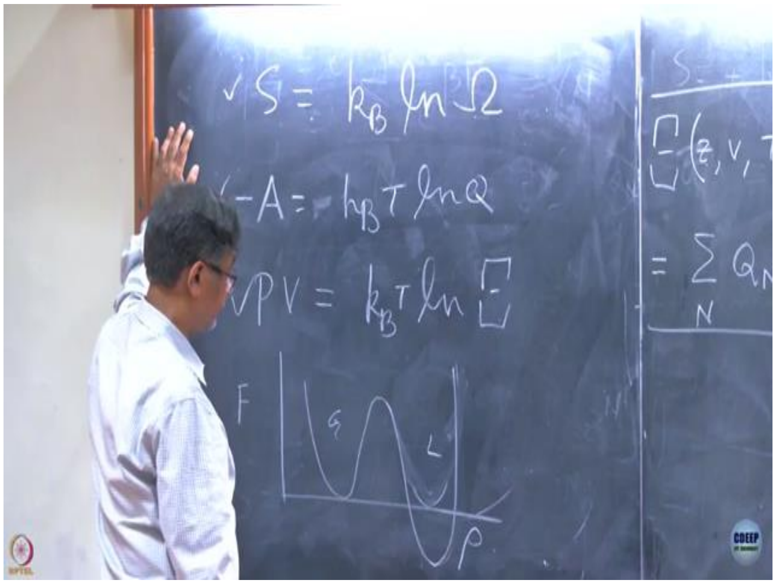

So $S = k_B \ln \Omega$ is actually said by many people, we put it like that. So this is micro canonical, this is canonical and this is grand canonical and everywhere you have to get the extreme of the quantity. So on the left hand side that I have written is the quantity that has to do maximize. Why? Because partition for the system is something quite remarkable, but that is that, you have to find the macroscopic state of the system.

And so, macroscopic state of the system many times, so when we try to study the crystal transition, you have to find out which state is most stable or you want to understand nucleation. The formations of the critical droplet or you want to do osmosis, all these phenomena that we study which are in equilibrium.

We treat them as equilibrium phenomena, because it is a dynamic part, but we will do that later. In that case, you have to find out, so why did I decrease the temperature? That state which is given by the density or other parameter or characteristics function these calculations will show that how it will select?

Because if I plot the free energy, then free energy against order parameter. Let us take a very simple gas liquid, so density, then at the coexistence point they have the same free energy. But when I go below so this is liquid, this is gas, but when I go to what temperature? The temperature is the control parameter, then this becomes like that. So when I go do my statistical mechanics and calculate the free energy and minimize the free energy.

If I am having grand canonical then I have to maximize PV. Then I will see this thing will, that maximum we will give you a solution which is, will give the low temperature, will be liquid state. So it is a principal of extremum that controls the thermodynamics and that is what we call the free energy has to be minimum which essentially we are saying that state will be selected which has the maximum partition function.

Yes sure! This is an extremely good question. I should talk about it tomorrow, so that is the answer to this question will be answered in many different ways. One of them is that when you go to grand canonical partition function, you are allowing number fluctuation. What can be sure that is number fluctuation decreases when N goes to infinity? So there is a very strong theorem essentially comes from probability theory that in the limit of infinite system predictions of all three becomes the same.

For example, if you try to do gas liquid equilibrium even in computer simulation in a canonical ensemble. You will never see the flat isotherm you always see a maximum, which is unrealistic maximum correctly. That because the fluctuations that are necessary are not captured in the canonical ensemble the number of fluctuations. You can of course get rid of the loop if you go to the limit of infinite system and you can see by increasing system size that artificial loop goes down because fluctuations are coming in so the answer to your question that as you go to infinite system size limit. All the systems in microcanonical, canonical, grand canonical and there is one isothermal isobaric ensemble, then there is a Gibbs ensemble, all these ensemble.

That has to be replaced by P. When you do µPT that is a Gibbs ensemble and isothermal isobaric is NPT, so there are two more ensembles that people use. So NPT is the one which is the most realistic.

All the ensemble produce identical results and that can be proven in a mathematical step. But this is really formidable and beautiful construction. That gives deep theoretically alone is one of the most powerful theoretical framework that we use. In grand canonical ensemble for molecular dynamic simulation one needs to introduce thermostat or Barostat.

Barostat takes care of the pressure; thermostat takes care of the temperature. So these are the kind of coupling to the bath you introduce. Remember how do you introduce thermostat? Whenever, velocity of your one particle whenever the temperature goes up you scale the velocity of every particle very artificially and when temperature goes down you upscale the velocity of every particle these is calling scaling.

Now if you come to ratio similarly whenever fluctuation pressure becomes less. You barostat you lower the volume and when the pressure becomes large, release the volume. That is the allowing volume fluctuation that is how your pressure barostat works. Just like a piston. So now you have to think of how to get the number of particles, so you need another like thermostat, barostat that was one number stat.

So the number stat will allow you to increase the fluctuation. Now, if I am doing a simulation in a grand canonical ensemble where number of particles can leave this system. Then you have to use a reservoir rule now barrow, you know the thermostat we use ball rule and some other rules. Pressure we use baring son and knows you whoever. There must be have been done but I do not know that in grand canonical.

What is happening when you do barostat? There are certain rules coming from conservation, which allows you to write an equation. So you need to write an equation that your pressure goes up. Then that, there is a systematic way to bring it back down certainly thermostat there is a systematic way to bring the temperature back, you know, it is not heuristic.

It has to obey certain rules those rules or equations, so that they have been done for grand canonical ensemble, but certainly it is done, but certainly not a popular. We have never in my entire life use thermodynamics and grand canonicals. It is because I think we do canonical then isothermal isobaric and then microcanonical. I have not seen but you can do it literatures, search if anybody has done.