Basic Statistical Mechanics
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Lecture - 15
Thermodynamic Potentials for Grand Canonical and Isothermal- Isobaric Ensembles

So in the last lecture we did discuss the microcanonical ensemble and the canonical ensemble. We started, we discussed and I want to repeat that. Statistical mechanics starts with the two postulates and one hypothesis. The postulates are time averaged equal to ensemble average. Time averaged is the experimental quantity that goes on and we let Gibbs at the main brilliant construction of the ensemble.

So, they had to put these two together that the first postulate time averaged equal to ensemble average. Second postulate in order to ensure that quality that every state visited in time averaging is equally probable or every state picked up in our ensemble is equally probable. However, one has to assure that the system explores to all different states and that is the Ergodic hypothesis.

That every state is visited and that is the one that has evoked a lot of research over the years particularly in from mathematicians and the statistical mechanics starts at the level of construction of this formidable theoretical framework, the most important role is played by.

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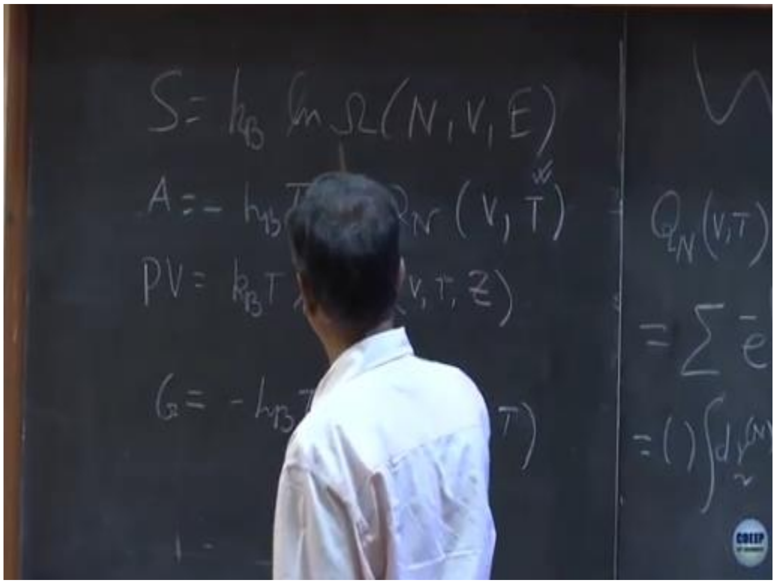

This relation of Boltzmann formula $S = k_B \ln \Omega$ which is often not realized that the entire statistical mechanics, the microcanonical, canonical grand one and all the ensembles everything relation between statistical thermodynamics is right from Boltzmann formula. So a variant of Boltzmann formula which is here by the number of microscopic states available to the system which is kept first at volume V, energy E, within the number of particles.

If a variant of that is used to derive the second equation which is free energy, Helmholtz free energy $A = -k_B T \ln Q$ and canonical partition function is given by this quantum version was sum over energy levels or classical that is integration over the phase space position and momentum. What we will do today we will go from Canonical ensemble to grand canonical then ultimately to isothermal isobaric ensemble.

So, the whole derivation what we did from microcanonical to canonical we had the following mental construction you put all the systems in canonical ensemble together and we allow them to exchange energy and we put them in a temperature bath and when they achieve constant temperature then we remove the bath and put an insulation around it.

So that ensemble the canonical ensemble becomes a super system in the microcanonical ensemble. Then we do a super ensemble and with this construction then we repeat the calculations that we did in the microcanonical and that allows us to get to the result free energy is equal $-k_B T \ln Q$. So today we will first briefly review the canonical ensemble and then we will go to do the grand canonical.

And we would like to finish today and discuss the isothermal isobaric ensemble which is the NPT ensemble and the NPT ensemble is the one which is most commonly used in computer simulations are also very close to experimental results one who can start this essentially as a derivation as a definition of grand canonical ensemble.

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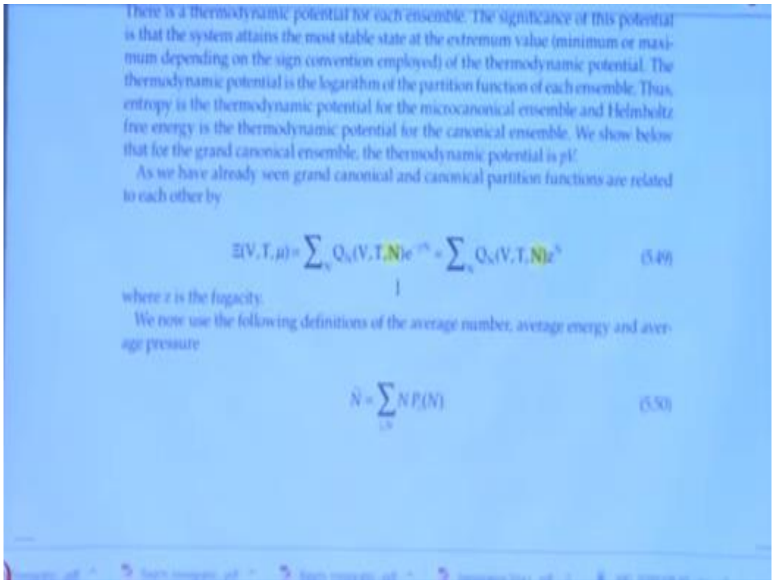

There is a thermodynamic potential for each ensemble. The significance of this potential is that the system attains the most stable state at the extremum value (minimum or maximum depending on the sign convention employed) of the thermodynamic potential. The thermodynamic potential is the logarithm of 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

$$\Xi(V,T,\mu) = \sum_N Q_N(V,T,N) e^{\beta\mu N} = \sum_N Q_N(V,T,N) z^N \qquad (5.49)$$

where *z* is the fugacity.

We now use the following definitions of the average number, average energy and average pressure

$$\bar{N} = \sum N P(N) \qquad (5.50)$$

Here, μ is the chemical potential. And this is partly my doing because I usually use these notations. So this was in between putting because many of the things were edited by my students. Now what we now have to do?

We have to have in these putting in the constraint which is the how we define not the constant how I define the average number which we have, which will define density average volume and what the volume is fixed. So average if I get the average number then I divide by the volume which is given from supplied from our strike and external constraint, I will get the density.

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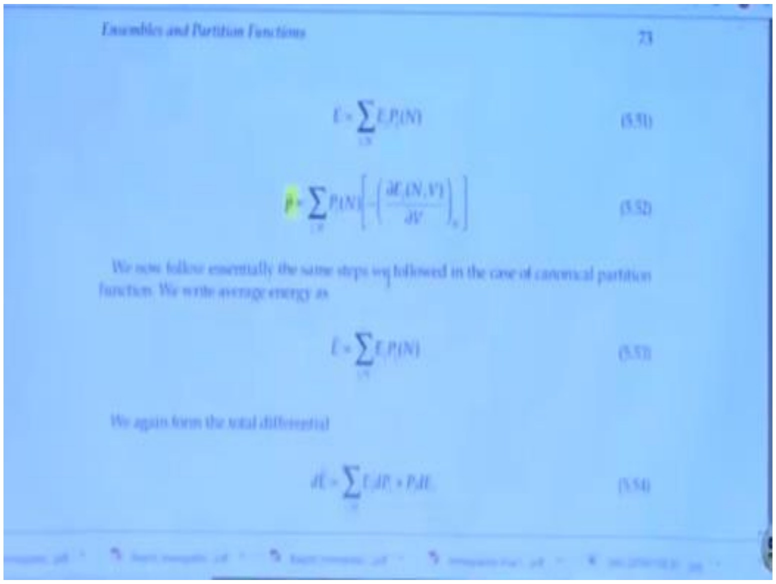

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$$E = \sum_{j,N} E_j P_j(N) \qquad (5.51)$$

$$p = \sum_{j,N} P_j(N)\left[-\left(\frac{\partial E_j(N,V)}{\partial V}\right)_N\right] \qquad (5.52)$$

We now follow essentially the same steps we followed in the case of canonical partition function. We write average energy as

$$E = \sum_{j,N} E_j P_j(N) \qquad (5.53)$$

We again form the total differential

$$dE = \sum_{j,N} E_j dP_j + P_j dE_j \qquad (5.54)$$

And because it is a large number of particles still there at much of the time, interestingly in the grand canonical ensemble these. So this is the average energy as I was saying that they note that they are a double sum. Now very interestingly the same definition we used of the pressure in the canonical ensemble. We do the same thing but again sum were Ej,N,V and one thing that I was going to say is very, very interesting property you have to look into the limiting properties of this quantity this grand canonical ensemble.

Because you know when you do these kind of sums that calls the generating function. Whenever I put a polynomial like there is a genetic function. So grand canonical is the genetic function of the canonical series. These are all positive that is very important and these are all positive because it is nothing but the sum of boltzmann factors and boltzmann is an exponential of an entire function.

That is a completely analytical function these are very important properties the since it is completely analytical function that means this should is another analytical function. You know, if you know a little bit of mathematics one of the things now mathematicians are not given to the talk of very, very big language. But there is a thing which is called fundamental theorem of algebra.

Now mathematicians are not all, superlative they are very reserve people. So what is the fundamental theorem of algebra? There is a beautiful loop by Liouville, I loved it. Where is that fundamental theorem of algebra you are as the rational approach that is the rational function and that is a way to develop a proper summation.

We have our basal function and all these things we have the rational approximation. But what is the fundamental theorem in algebra is there a polynomial order in then you have n roots and depending. If all these are positive then you will have roots in a complex conjugate that means one will be Z, another will be Z*.

The one of the reasons many people do not use Z here is that you want to keep this Z as a complex number. You know, that is why many times that is the result of the confusion that two schools are there. So it is extremely important to realize two or three properties one of them it starts from n = 0, second at all of them, are positive and when all of them positive then you have these roots which are complex conjugate.

And that plays very important role and without that property anyone will not be able to describe any phase transition or any property. Now, so then energy goes like that PJ and the pressure is also. So I have now, definition of pressure, I have definition of energy, and I have definition of all that.

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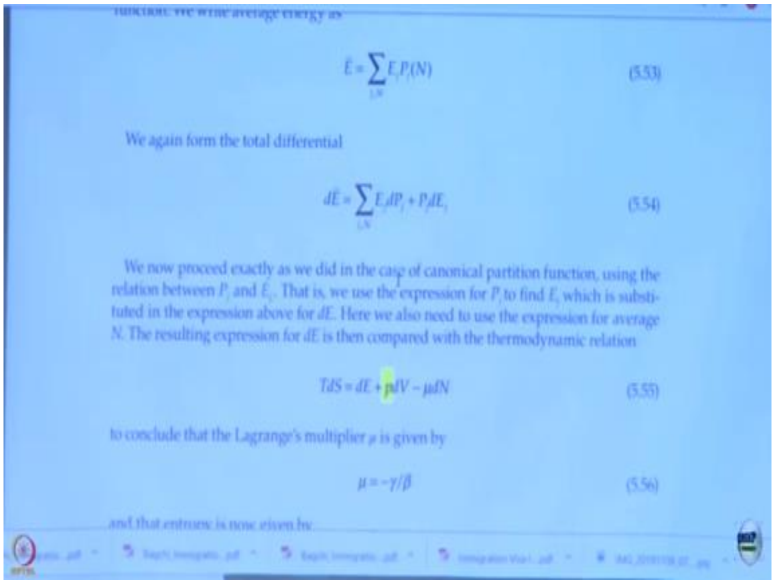

function. We write average energy as

$$\bar{E} = \sum_{j,N} E_j P_j(N) \qquad (5.53)$$

We again form the total differential

$$d\bar{E} = \sum_{j,N} E_j dP_j + P_j dE_j \qquad (5.54)$$

We now proceed exactly as we did in the case of canonical partition function, using the relation between P_j and E_j. That is, we use the expression for P_j to find E_j which is substituted in the expression above for dE. Here we also need to use the expression for average N. The resulting expression for dE is then compared with the thermodynamic relation

$$TdS = dE + pdV - \mu dN \qquad (5.55)$$

to conclude that the Lagrange's multiplier μ is given by

$$\mu = -\gamma/\beta \qquad (5.56)$$

and that entropy is now given by

Then we play the game exactly we played from going to canonical from micro canonical to canonical. Exactly we do the same thing it is the dPj, exactly the same equation we did before but now everything is sum over j and n. There I had sum only over j, now then we would compare that with the thermodynamics.

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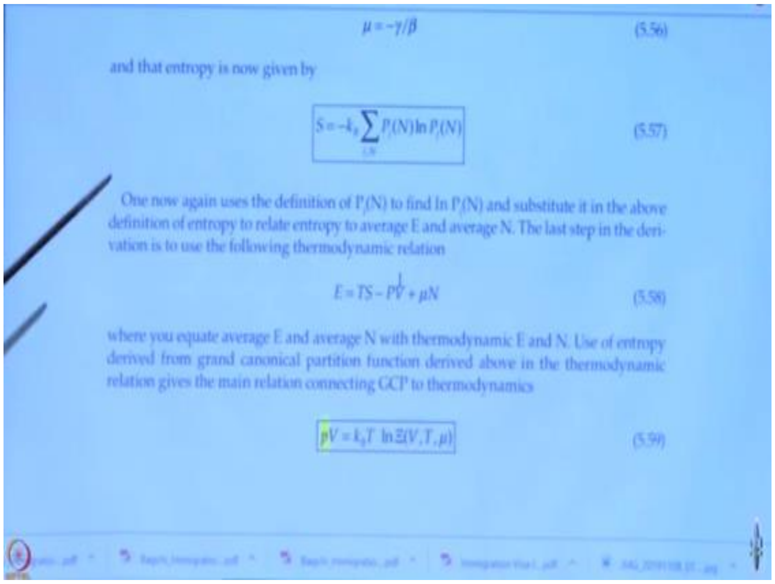

$$\mu = -\gamma/\beta \qquad (5.56)$$

and that entropy is now given by

$$\boxed{S = -k_B \sum_{j,N} P_j(N) \ln P_j(N)} \qquad (5.57)$$

One now again uses the definition of $P_j(N)$ to find ln $P_j(N)$ and substitute it in the above definition of entropy to relate entropy to average E and average N. The last step in the derivation is to use the following thermodynamic relation

$$E = TS - PV + \mu N \qquad (5.58)$$

where you equate average E and average N with thermodynamic E and N. Use of entropy derived from grand canonical partition function derived above in the thermodynamic relation gives the main relation connecting GCP to thermodynamics

$$\boxed{pV = k_B T \ln \Xi(V,T,\mu)} \qquad (5.59)$$

Now realize one thing while in a micro canonical I maximize entropy to find the stable equilibrium system. In canonical ensemble I will minimize the free energy or if I do - A that is the better way to write actually. I will maximize - A which means everywhere I maximize the partition function. So here we maximize the quantity PV. So PV also has the dimension of energy.

So in grand canonical applications in phase transition all the things we impose equality of chemical potential to derive our equations then we put to calculate the pressure

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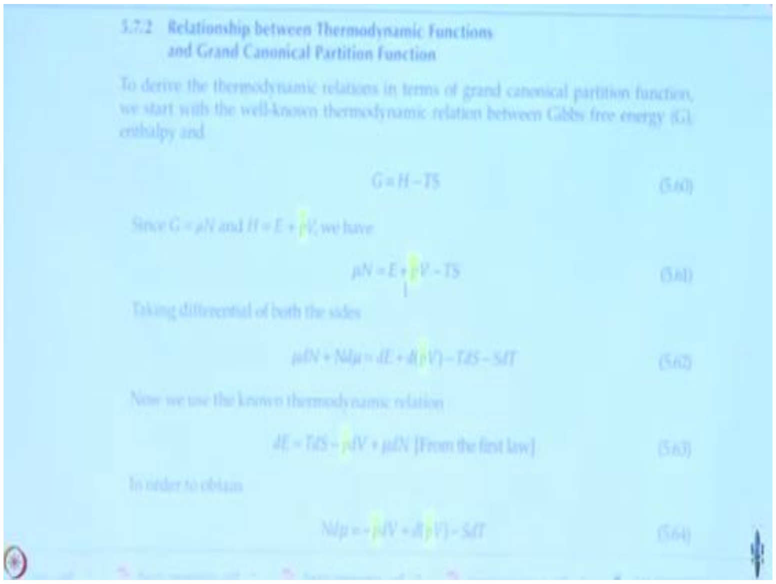

5.7.2 Relationship between Thermodynamic Functions and Grand Canonical Partition Function

To derive the thermodynamic relations in terms of grand canonical partition function, we start with the well-known thermodynamic relation between Gibbs free energy (G), enthalpy and

$$G = H - TS \quad (5.60)$$

Since $G = \mu N$ and $H = E + pV$, we have

$$\mu N = E + pV - TS \quad (5.61)$$

Taking differential of both the sides

$$\mu dN + N d\mu = dE + d(pV) - TdS - SdT \quad (5.62)$$

Now we use the known thermodynamic relation

$$dE = TdS - pdV + \mu dN \text{ [From the first law]} \quad (5.63)$$

In order to obtain

$$N d\mu = -pdV + d(pV) - SdT \quad (5.64)$$

So then we still go on doing the relationship you can partition functions that we just again do the same thing we have to go to G = H - TS + µ N - PV. So the kind of things we did in the thing is again done here.

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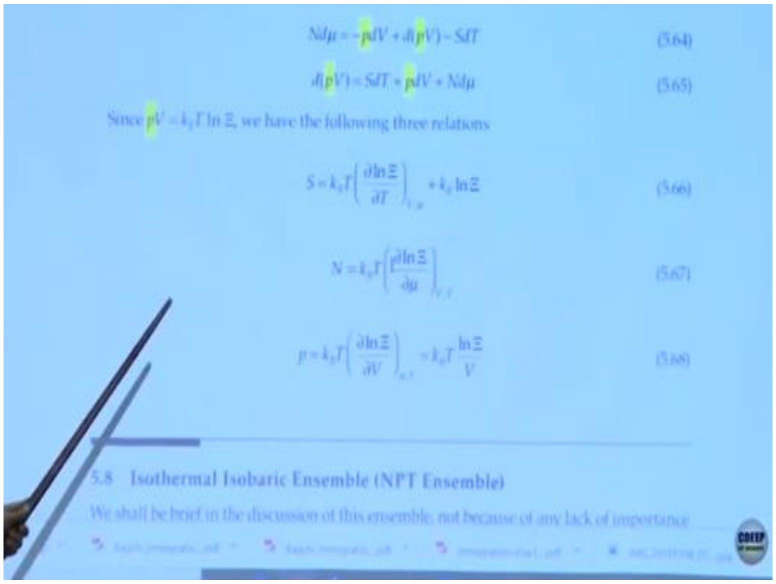

$$N d\mu = -pdV + d(pV) - SdT \quad (5.64)$$

$$d(pV) = SdT + pdV + N d\mu \quad (5.65)$$

Since $pV = k_B T \ln \Xi$, we have the following three relations

$$S = k_B T \left(\frac{\partial \ln \Xi}{\partial T} \right)_{V,\mu} + k_B \ln \Xi \quad (5.66)$$

$$N = k_B T \left(\frac{\partial \ln \Xi}{\partial \mu} \right)_{V,T} \quad (5.67)$$

$$p = k_B T \left(\frac{\partial \ln \Xi}{\partial V} \right)_{\mu,T} = k_B T \frac{\ln \Xi}{V} \quad (5.68)$$

5.8 Isothermal Isobaric Ensemble (NPT Ensemble)

We shall be brief in the discussion of this ensemble, not because of any lack of importance

And one gets the beautiful relations of entropy. So we have the grand partition function, you have this is the entropy then this is the number this should be the average number and this is the pressure. So that finishes this part now I will spend some time because this is the one that is used most extensively in computer simulations isothermal isobaric. It was done, it was created because Gibbs when Willard Gibbs was doing statistical mechanics.

Willard Gibbs carried it out the whole development of statistical mechanics. We take aim to understand Van Der Waals equation of state, so there are in those days two major approaches. One was Boltzmann trying to understand Maxwell distribution and the phenomena and contribution was made by Van Der Waals.

Actually Van Der Waals is one of the underrated scientists of the era. So Van Der Waal said whatever equation we state he also had a beautiful equation of interface and so that Willard Gibbs was trying to develop a theory of interface particularly gas liquid interface and so as soon as it developed the ensemble thing one of his first goal or was the beginning goal was to understand Van Der Waals equation of steam.

The story is that when he did these things Maxwell, so the Willard Gibbs, nobody knew what Willard Gibbs was doing you know far ahead of time. So he was doing this ensemble, canonical ensemble, microcanonical grand one even terms were new, nobody understood. However, on the other side of Atlantic Maxwell was keenly following the development of Willard Gibbs and Maxwell sent or the other around.

I think but they never made, but sent a solid kind of not marble, but this kind of cement-based with a solid array of loop of equation of state and Gibbs always used to go to class with the one that was sent by Maxwell. However Maxwell died very young, Maxwell died at the age of I think 37 or 39 and within that time Maxwell not only did his kinetic theory of gases he did a whole of electromagnetic theory.

So it is amazing how much he did in such a short time as i remember he died at 37. So when he died there is a common joke in Yale or in America that if in the entire world one person used to understand what Gibbs does and that person is dead.

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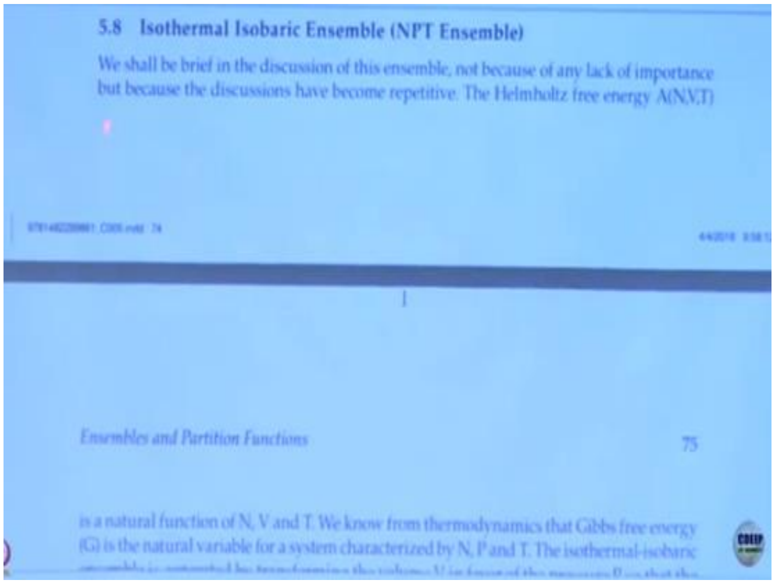

5.8 **Isothermal Isobaric Ensemble (NPT Ensemble)**

We shall be brief in the discussion of this ensemble, not because of any lack of importance but because the discussions have become repetitive. The Helmholtz free energy A(N,V,T)

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is a natural function of N, V and T. We know from thermodynamics that Gibbs free energy (G) is the natural variable for a system characterized by N, P and T. The isothermal-isobaric

So nobody, so now naturally comes isothermal isobaric ensemble, which we need to spend a little time trying to understand this ensemble. So, now in this ensemble we are not allowing number fluctuations and it is a very important computer simulation because as I told you this is the most suitable in many cases. We allow fluctuations in volume so long we have not allowed fluctuations in volume.

So this is the time when the fluctuation problem is done and that one of the reasons is that if you are studying a system where say liquid is going to crystal, you can simulate with n number of particles but volume must change. Like what I am going to ice, volume has to increase 10-11 %. That is why this is an important thing in the study of his condition as I said we let Willard Gibbs did almost the entire thing with an aim..

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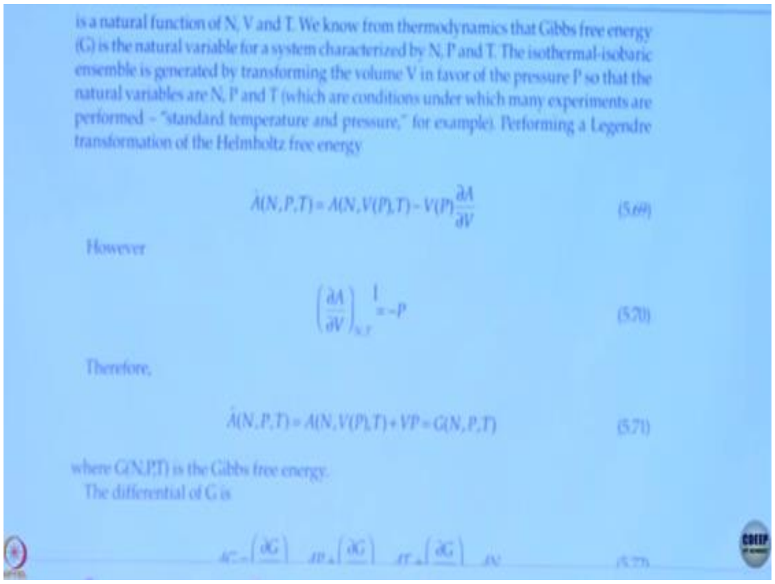

is a natural function of N, V and T. We know from thermodynamics that Gibbs free energy (G) is the natural variable for a system characterized by N, P and T. The isothermal-isobaric ensemble is generated by transforming the volume V in favor of the pressure P so that the natural variables are N, P and T (which are conditions under which many experiments are performed – "standard temperature and pressure," for example). Performing a Legendre transformation of the Helmholtz free energy

$$\tilde{A}(N,P,T) = A(N,V(P),T) - V(P)\frac{\partial A}{\partial V} \qquad (5.69)$$

However

$$\left(\frac{\partial A}{\partial V}\right)_{N,T} = -P \qquad (5.70)$$

Therefore,

$$\tilde{A}(N,P,T) = A(N,V(P),T) + VP = G(N,P,T) \qquad (5.71)$$

where G(N,P,T) is the Gibbs free energy.

The differential of G is

We will follow a little trick of going through by introducing a Lagrangian transformation and this relation alone leads to a definition of Gibbs that I want to analyze here.

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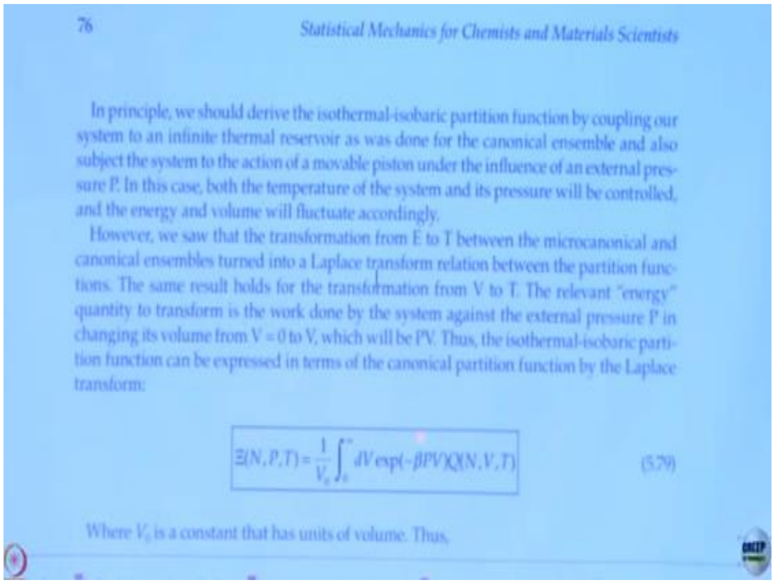

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In principle, we should derive the isothermal-isobaric partition function by coupling our system to an infinite thermal reservoir as was done for the canonical ensemble and also subject the system to the action of a movable piston under the influence of an external pressure P. In this case, both the temperature of the system and its pressure will be controlled, and the energy and volume will fluctuate accordingly.

However, we saw that the transformation from E to T between the microcanonical and canonical ensembles turned into a Laplace transform relation between the partition functions. The same result holds for the transformation from V to T. The relevant "energy" quantity to transform is the work done by the system against the external pressure P in changing its volume from V = 0 to V, which will be PV. Thus, the isothermal-isobaric partition function can be expressed in terms of the canonical partition function by the Laplace transform:

$$\boxed{\Xi(N,P,T) = \frac{1}{V_0}\int_0^{\infty} dV \exp(-\beta PV)Q(N,V,T)} \qquad (5.79)$$

Where V_0 is a constant that has units of volume. Thus,

But one important relation that one finds useful in analytical work is that you can consider the partition function as a Laplace transformation of the, these are accustomed. Then you see that one is a Laplace transformation other and that is very, very important consequence because then I can get Q as a Laplace inversion of the grand canonical partition function.

Now the A is that so what we are using one thing that, see the other notation that I use this chapter I think I think probably a big chapter will come through.

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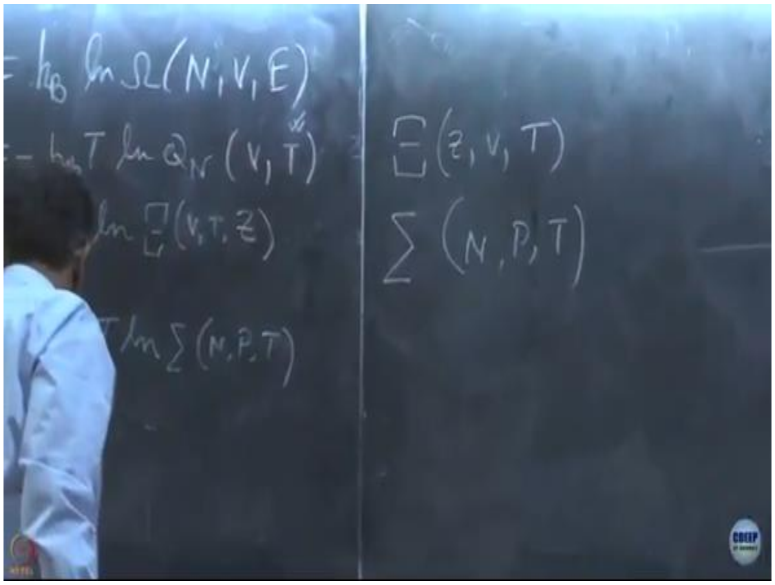

So this is the notation we are using for both one is N V T that is the canonical and for isothermal isobaric NPT.

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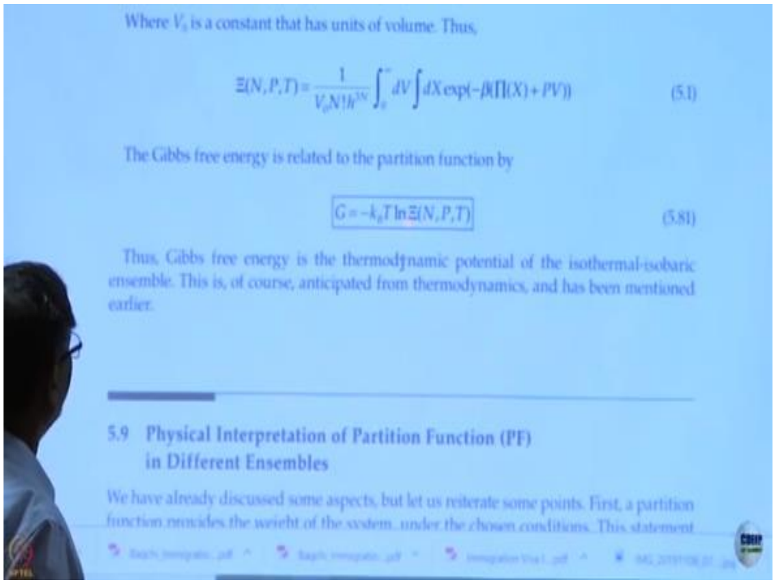

Where V_0 is a constant that has units of volume. Thus,

$$\Xi(N,P,T) = \frac{1}{V_0 N! h^{3N}} \int_0^\infty dV \int dX \exp(-\beta(\Gamma(X) + PV)) \qquad (5.1)$$

The Gibbs free energy is related to the partition function by

$$\boxed{G = -k_B T \ln \Xi(N,P,T)} \qquad (5.81)$$

Thus, Gibbs free energy is the thermodynamic potential of the isothermal-isobaric ensemble. This is, of course, anticipated from thermodynamics, and has been mentioned earlier.

5.9 Physical Interpretation of Partition Function (PF) in Different Ensembles

We have already discussed some aspects, but let us reiterate some points. First, a partition function provides the weight of the system, under the chosen conditions. This statement

So what one can do by doing analysis very similar to the one that we are doing all through that going then you have to do what is the average number and what is the average volume and average pressure and then you need to go through.

So this is the final expression for the isothermal isobaric ensemble. So the advantage of isothermal isobaric particularly in chemistry is that we get the Gibbs free energy. This plays an extremely important role in phase transition. So this is known as thermodynamic potential in grand canonical ensemble.

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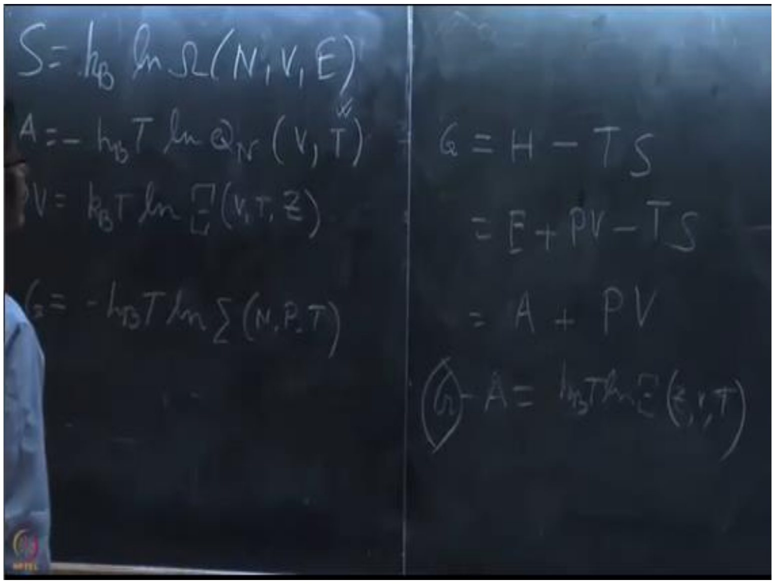

$S = k_B \ln \Omega(N,V,E)$

$A = -k_B T \ln Q_N(V,T)$

$PV = k_B T \ln \Xi(V,T,z)$

$G = -k_B T \ln \Sigma(N,P,T)$

$G = H - TS$

$= E + PV - TS$

$= A + PV$

$G - A = k_B T \ln \Xi(z,V,T)$

So if I do remember G equal to E+ PV - TS and E - TS is homogeneity, then + PV. So G - A is PV. What I am trying to say that we have a relation at the level of log and we make of all the partition functions this is then comes in isothermal isobaric this is the canonical and this is a grand canonical and this is an amazing relation that is often given in a slightly advanced courses of statistical mechanics that show that this relationship.

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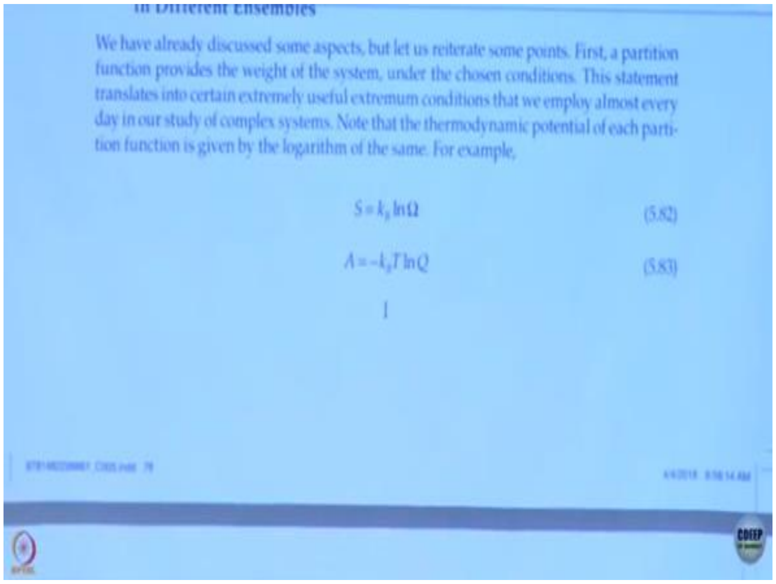

in Different Ensembles

We have already discussed some aspects, but let us reiterate some points. First, a partition function provides the weight of the system, under the chosen conditions. This statement translates into certain extremely useful extremum conditions that we employ almost every day in our study of complex systems. Note that the thermodynamic potential of each partition function is given by the logarithm of the same. For example,

$$S = k_B \ln \Omega \qquad (5.82)$$

$$A = -k_B T \ln Q \qquad (5.83)$$

Now I have discussed here the physical interpretation of the partition function. I have already discussed different ensembles coming with different partition function. So the state that is selected or the state that is thermally stable is the one that has the maximum partition function.

Now you can understand that physical insight from canonical ensemble.

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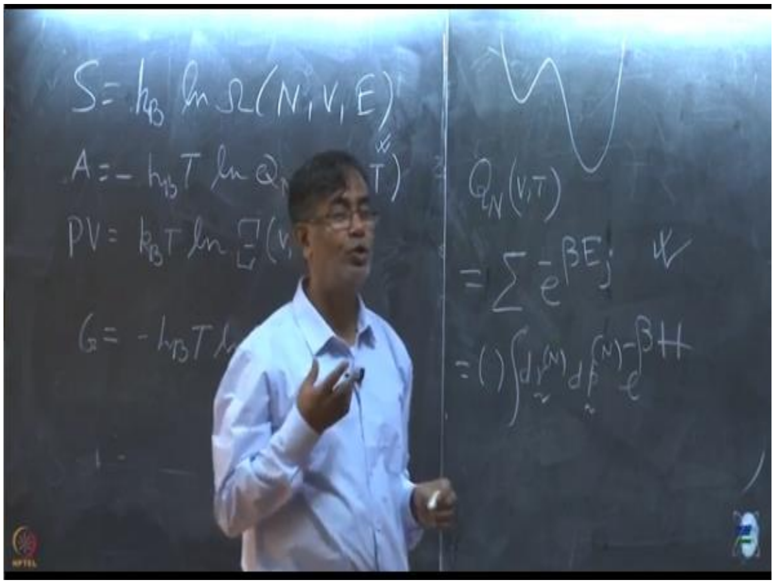

So partition function I can write, I can also write normalization constant which I am not going to talk now. I do not remember giving these equations to you we did microcanonical ensemble. So we start with grand canonical ensemble which allows number fluctuation.

Now I am asking you a question that it is intuitively clear in any of this definition, this most clear in this ensemble not even in micro canonical. Why a partition function maximum or partition function selects the macroscopic state, not that I am asking something very simple it is it trivially simple but you need to think that a macroscopic state which defines the equilibrium or the stable state is that supposed to be stable for time T goes to infinity. Why that is partition function is maximum?

Now, I give you a simple example and now you should be able to tell. If I have just 2 state like that then this still has certain contribution but I have to say infinite number of particles in my system microscopic each particle is little stabilized then this just disappears. This is selected and that comes from this expression.

That is the energetic criteria which we intuitively understand from our Boltzmann distribution which is included in the partition function and that is exactly very important that I am telling because that is how selection is done. Particularly in computer simulation that is extremely difficult even in computer simulation of 1000 particles this is what I am telling here becomes very important.

So let us continue. These are very intuitive and very nice, so you have to understand I remember when I taught and gave exams we should do some problems so now that what I have been telling.

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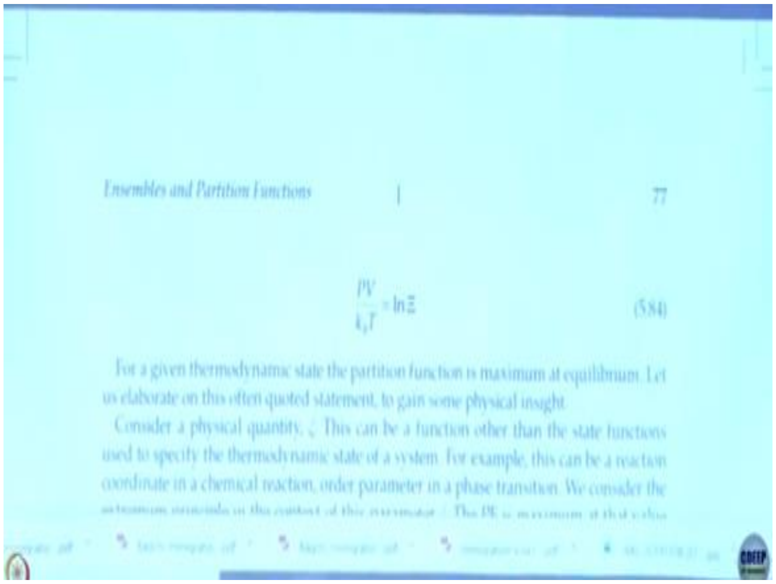

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$$\frac{PV}{k_BT} = \ln \Xi \qquad (5.84)$$

For a given thermodynamic state the partition function is maximum at equilibrium. Let us elaborate on this often quoted statement, to gain some physical insight.

Consider a physical quantity, ζ. This can be a function other than the state functions used to specify the thermodynamic state of a system. For example, this can be a reaction coordinate in a chemical reaction, order parameter in a phase transition. We consider the

So the partition function is maximum at equilibrium this is a very important thing that notes that my book tells you. Let us elaborate this and we will obtain a statement to gain some physical insight then I describe consider physical quantity it can be function.

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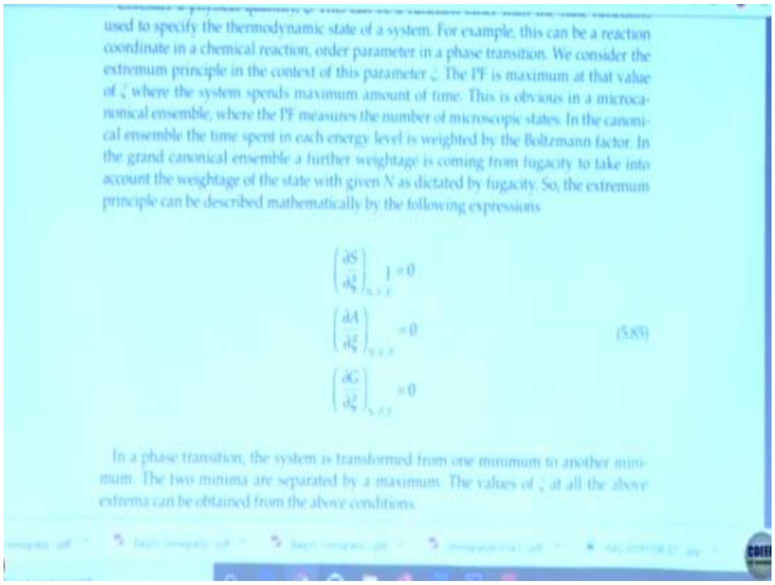

used to specify the thermodynamic state of a system. For example, this can be a reaction coordinate in a chemical reaction, order parameter in a phase transition. We consider the extremum principle in the context of this parameter ξ. The PF is maximum at that value of ξ where the system spends maximum amount of time. This is obvious in a microcanonical ensemble, where the PF measures the number of microscopic states. In the canonical ensemble the time spent in each energy level is weighted by the Boltzmann factor. In the grand canonical ensemble a further weightage is coming from fugacity to take into account the weightage of the state with given N as dictated by fugacity. So, the extremum principle can be described mathematically by the following expressions

$$\left(\frac{\partial S}{\partial \xi}\right)_{N,V,E} = 0$$
$$\left(\frac{\partial A}{\partial \xi}\right)_{N,V,T} = 0 \qquad (5.85)$$
$$\left(\frac{\partial G}{\partial \xi}\right)_{N,P,T} = 0$$

In a phase transition, the system is transformed from one minimum to another minimum. The two minima are separated by a maximum. The values of ξ at all the above extrema can be obtained from the above conditions.

Very important because when you try to expand the free energy like Taylors' theorem or any kind of thing that we the first derivative so the order parameter theta is the order parameter in the parameter that distinguishes between old and new. That we will discuss in detail this condition is very important so the first term and if there is a symmetry then third order term also not there.

So that is why this is the reason why the free energy function for small displacement is harmonic with an extremely important quantity because the coefficient of the harmonic the force constant are what we call the response function. The specific heat thermal compressibility all these things are the second derivative of this quantities and that is the reason in a phase transition these quantity will become the harmonic frequency goes to 0 because these Springs we call the a small functions of the springs and they soften up.

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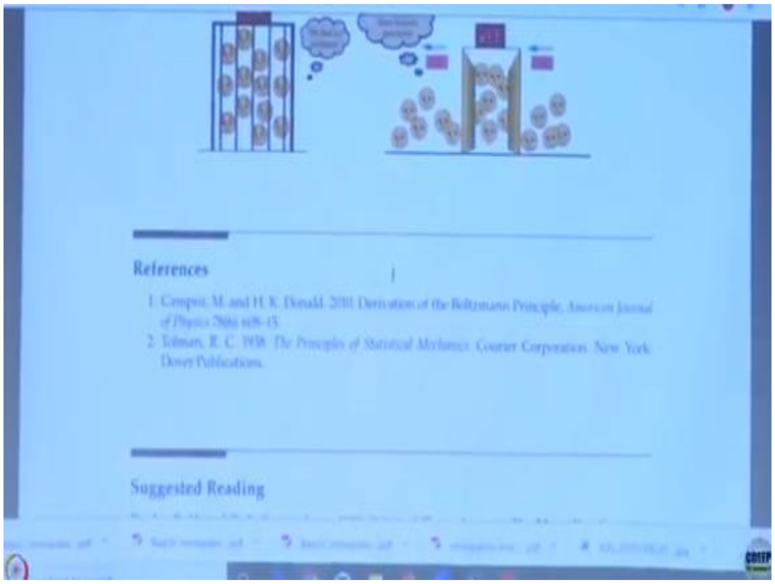

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1. Campisi, M. and H. K. Donald. 2010. Derivation of the Boltzmann Principle. *American Journal of Physics* 78(6): 608–15.
2. Tolman, R. C. 1938. *The Principles of Statistical Mechanics*. Courier Corporation. New York Dover Publications.

Suggested Reading

This very beautiful thing that going on there so then as I am telling you that there are, so these are the cartoons microcanonical then canonical and grand canonical that kind of thing my students I found are very good in cartoons and so these problems that I have imagined somebody has to do the problem set. So these complete the answer on canonical partition functions. Next what you are going to do is to start on the next chapter.

We have two ways to go from here but I would like to really jump the boat a little bit and do something very interesting which this is the response functions that you have been discussing. So the response functions are second derivative of the free energy like specific heat and compressibility but their real meaning is that they are the quantities which are the standard deviations or mean square fluctuation of the relevant quantity.

So it is not correct to say absolutely not fluctuating but it is fluctuating very small amount, the one that is fluctuating is the volume. Volume is fluctuating in a big way, but you can still define a volume and the mean square volume fluctuation that gives you the compressibility. Absolutely the thermodynamic properties calculated in ensemble.

In every ensemble all the thermal properties are the same because one can show that. We will do little bit in the energy fluctuations today afternoon will do that. The fluctuations or mean square fluctuation. See what we need to talk of the quantity and then you know how relative fluctuation goes as one over $1/\sqrt{N}$.

So you start with the microcanonical ensemble where no fluctuation is allowed in E,N and V. Now I go to canonical ensemble I allow fluctuation energy now I calculated how the fluctuation of energy goes? It will go as $1/\sqrt{N}$, now I go to grand canonical I allow fluctuation of N now, I calculate the how the fluctuation? So the result that you get at the fixed in the microcanonical ensemble becomes the same at canonical ensemble the same at grand canonical ensemble, calculation of properties in micro canonical ensemble is essentially impossible.

It is extremely difficult. They would become progressively easier and that we will discuss. That because these I think you got to, you know you need to lab mathematics to do stat mech, because stat mech is a mathematical subject that I was going to tell and I forgot because I usually do a random walk in my teaching. So I tried to tell that is where I came to tell you the fundamental theorem of algebra, that grand partition function is infinite series is a polynomial but it is the series because up to infinity. However you can pack only certain number of particles because of RCI kind of interaction shorter interaction when you touch them. So n equal to never infinity it becomes a maximum value.

But you know this was also one of their phenomenal contribution. It has to be, think of putting a marble ball in a jar you can put only a certain number because after that you cannot pack. So we will come back.