Basic Statistical Mechanics

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Lecture - 10

Relation with Thermodynamics in Microcanonical Ensemble Part - 2

So what we these some I am telling that these are one of the most difficult part of statistical mechanics, which are usually not taught in courses and probably some of you who are here know the difficulty some are not there, so I will try to repeat about that.

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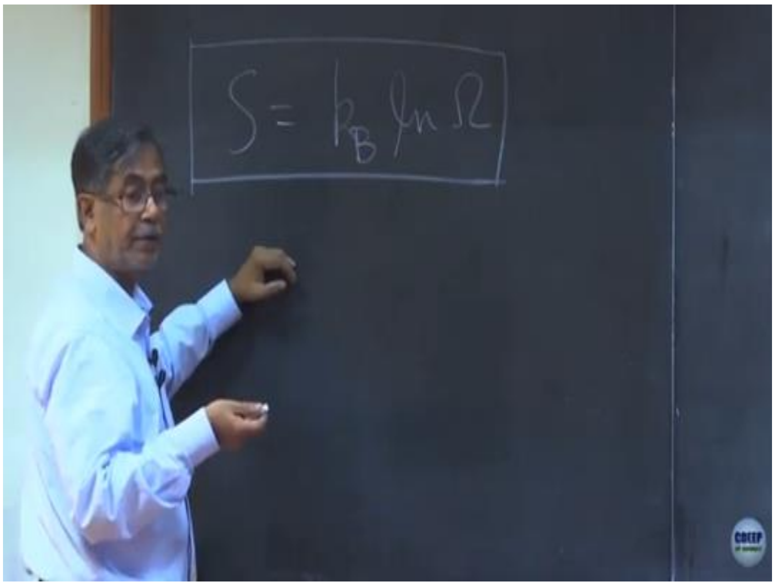

So, basic thing to remember which makes life really much, much simple in equilibrium statistical mechanics. Now equilibrium statistical mechanics is the discipline I explained at large we studied that we had learnt yesterday that this is the one we used to describe phase transition and all these things. So the say pressure of a system or energy, enthalpy what we do in terms of the radial distribution function… the thermodynamic properties.

And that a very important quantity is two-particle correlation function that will do probably somewhere to 10th lecture from now will come the radial distribution function which is the quantity which is observed experimentally in a many different ways. So at one side of this equilibrium statistical mechanics is this thermodynamic properties like entropy, other side is the information about microscopic arrangement.

How molecules are arranged around each other and as you can understand this microscopic arrangement play a very important role in chemical reaction. If two reactants A and B are going to react in a solvent which is the common scenario that we do, then that is done through these through the certain equation of motion, but the intermolecular arrangement plays a very important role.

All this information comes out of equilibrium statistical mechanics, and equilibrium statistical mechanics is a very major discipline not taught here, but in when I did PhD abroad then we had three courses in chemistry department on equilibrium stat-mech and going over to time-dependent in the last semester last a 201, 202, 203 from 20 the graduate level course used to start. So physics also had three courses.

So this was the kind of importance given to that and everybody was made to take 201. So then quantum used to start at that level somehow I like 206 or 7 quantum used to start. However in between there is a difficulty, but now again Stat-Mech is becoming very popular because we are having all these computer packages and we can calculate many things.

Another thing there is a much interest these days is the Nano material synthesis and the nucleation phenomena and phase transformation, currently kinetics of phase transition that is also comes under the essentially view of at the borderline between equilibrium and on statistical mechanics. So this is the preamble I will probably give you every class that why we need to study.

And what is the basic perception about everyday it will be different and different things I will bring in to motivate you and keep you focused in to this subject, which is I said a formidable theoretical discipline we do lot of quantum mechanics in chemistry particularly, but the advantage of quantum is that by the time you do quantum 1 or by the time you do not suddenly quantum 2 you are into Lutherans equation and all the perturbation theories are done and you go to numerics.

So it is fairly easy from there and there all the packages which are amazing packages. So huge number of people doing quantum and it is easy to publish papers because of the interface with organic chemistry or materials and they deal with molecules and chemists love molecules. In statistical mechanics we also deal with molecules but rather with molecules is taken in term of intermolecular interaction and also molecular shape and size. So there is always good to keep these two in mind.

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Now coming back so what we did yesterday was that, I said the most important relation in the entire statistical mechanics is this relation and as I said that this was derived in as a function which gives a measure of the state of the system by Boltzmann. However these in it was brought in equilibrium statistical mechanics used in his present by Josiah Willard Gibbs, J. W Gibbs and there is really no derivation of this expression as such.

So this is to be taken as a definition that is a very important point to remember this important thing from which role of equilibrium statistical mechanics follows entirely in its entirety is because of this Boltzmann formula. So that is why in his grave and also in his past in University of Vienna where he was they have just written this formula in is also wavier just this thing is written, you can do a Google, you can see them I saw the Vass in Vienna.

And of course there you know that about Vienna those days because of Austro-Hungarian Christian Empire. After Austro-Hungarian good Austro-Hungarian empire Vienna was the capital right, so it was a great, great people who had always all the including Mozart and many, many people who had in Vienna. It is much less crowded now actually population of Vienna is now less than what it was I think 50 years ago or hundred years ago. So how do we go from here and start?

So, I would prefer to consider this then we have two postulates connected by an Ergodic hypothesis that, we start this Statistical Mechanics, but two postulates granted by hypothesis is great to say that we really have ensembles and everything coming which is so much in the past microcanonical ensemble, but this also should be regarded actually more of a postulate, except that one can show unlike the two postulates.

Where you cannot move them apriori you put them you know posterior, that is similarly thing here also apriori motivation or there is motivation there is no a priori proof of that what is subsequently shown is that these function is the same function that we call entropy in thermodynamics, and entropy in thermodynamics you remember is given by the Clausius and it is dq reversible by G, Right?

So, that is the way if the connection between thermodynamics and statistical mechanics is very important comes.

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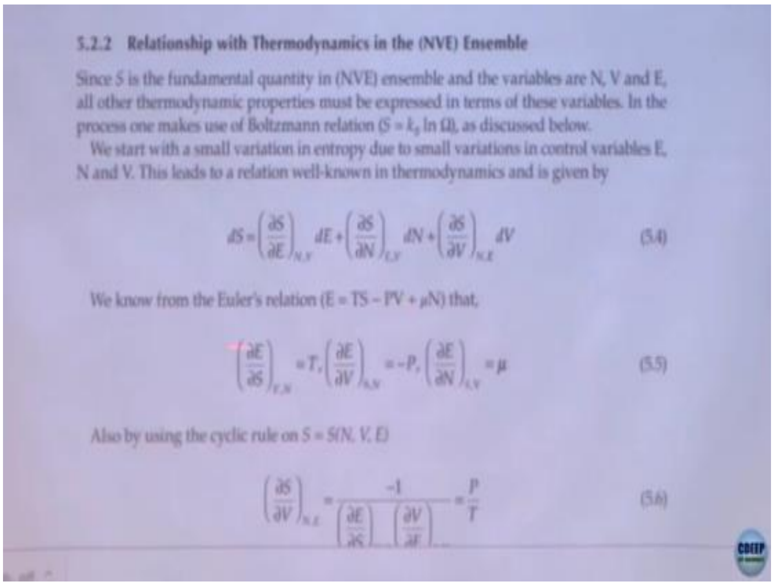

5.2.2 Relationship with Thermodynamics in the (NVE) Ensemble

Since S is the fundamental quantity in (NVE) ensemble and the variables are N, V and E, all other thermodynamic properties must be expressed in terms of these variables. In the process one makes use of Boltzmann relation ($S = k_B \ln \Omega$), as discussed below.

We start with a small variation in entropy due to small variations in control variables E, N and V. This leads to a relation well-known in thermodynamics and is given by

$$dS = \left(\frac{\partial S}{\partial E}\right)_{N,V} dE + \left(\frac{\partial S}{\partial N}\right)_{E,V} dN + \left(\frac{\partial S}{\partial V}\right)_{N,E} dV \quad (5.4)$$

We know from the Euler's relation ($E = TS - PV + \mu N$) that,

$$\left(\frac{\partial E}{\partial S}\right)_{V,N} = T, \left(\frac{\partial E}{\partial V}\right)_{S,N} = -P, \left(\frac{\partial E}{\partial N}\right)_{S,V} = \mu \quad (5.5)$$

Also by using the cyclic rule on $S = S(N, V, E)$

$$\left(\frac{\partial S}{\partial V}\right)_{N,E} = \frac{-1}{\left(\frac{\partial E}{\partial S}\right)\left(\frac{\partial V}{\partial E}\right)} = \frac{P}{T} \quad (5.6)$$

So as I go and then I think one of you had a question, so please ask the question. So now the basic idea then was that we start with, consider a small variation in micro canonical ensemble this is a system is characterized by total number of particles volume V and energy which are fixed, but I can always consider that I can change the number by little or volume by little, or I can change the energy by little.

So what is so this as a result of these variations that I do there is nothing wrong in this and nothing obscure about this, Ok? So I gave the variation of entropy as dS. However, these are already beginning to tell you something very interesting, that because you have seen these kind of things dS/dE, dS/dV these because this is we routinely use it as the temperature in our derivation, but even aside from that you have this Euler's equation, Euler's relation.

You know Euler was a mathematician who started doing his study at the age of 24 and for mathematics 24 is really, really quite old and then he needs some mathematics for a few years not very long time, but he had done huge amount of work in a relatively short period, I think he died young also. But his in thermodynamics, every field you go to hydrodynamics there a lot of contribution from Euler.

So, essentially, to Euler they were certain combinations and a very interesting combination that, temperature is the conjugate of entropy or entropy is the conjugate of temperature, pressure is the conjugate of volume, Right? And the chemical potential is conjugate of number, you know it in many different forms if I call it free energy, G; then I will bring it on this side E- TS, E-TS is E+PV, E+ PV is the enthalpy and then enthalpy minus TS, so free energy.

These things go over both in the G and A where Helmholtz free energy but it is the same. However this one now, can be used which started variation because we know it dE = TdS - PdV that condition we have these are the relations that follow from these things. Why you are doing that why you are doing Euler equation or all these things because we want to get a handle on these things and that then gives us the one that I want dS by dV from this relation I get dS by dV = P by T.

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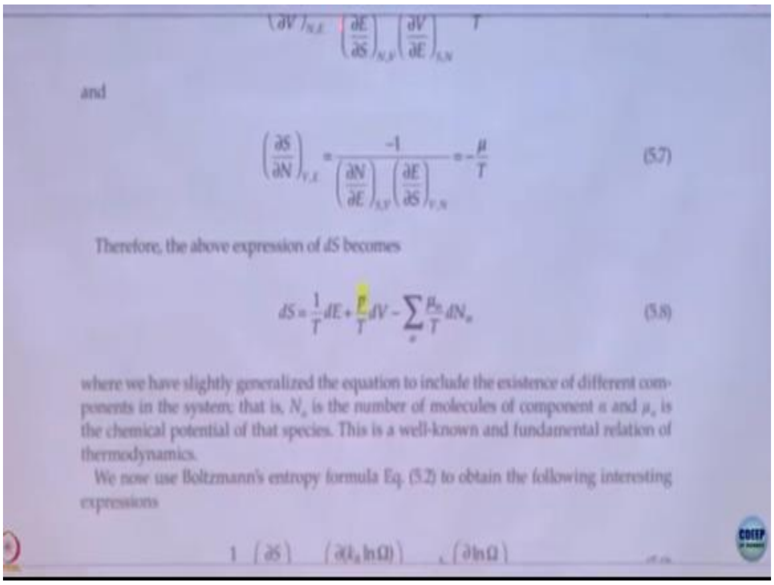

and

$$\left(\frac{\partial S}{\partial N}\right)_{V,E} = \frac{-1}{\left(\frac{\partial N}{\partial E}\right)_{S,V}\left(\frac{\partial E}{\partial S}\right)_{V,N}} = -\frac{\mu}{T} \quad (5.7)$$

Therefore, the above expression of dS becomes

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \sum_{\alpha}\frac{\mu_\alpha}{T}dN_\alpha \quad (5.8)$$

where we have slightly generalized the equation to include the existence of different components in the system; that is, N_α is the number of molecules of component α and μ_α is the chemical potential of that species. This is a well-known and fundamental relation of thermodynamics.

We now use Boltzmann's entropy formula Eq. (5.2) to obtain the following interesting expressions

And you have to understand just like in the Newton's equation of Schrodinger equation we write down things. They are a very strong possibility argument, we write them down you know as you know very well there is a derivation of Schrodinger equation, it was written down by transformation. So here also one writes down things and then see that whether they work or not like this most important equation.

Then this is of course we know very well is a multi-component not necessary for multi-component but this is very your familiar equation. So now you can call that you know it very well that this is then indeed is the entropy. The advantage of that now, if I make these identification the advantage now is the following.

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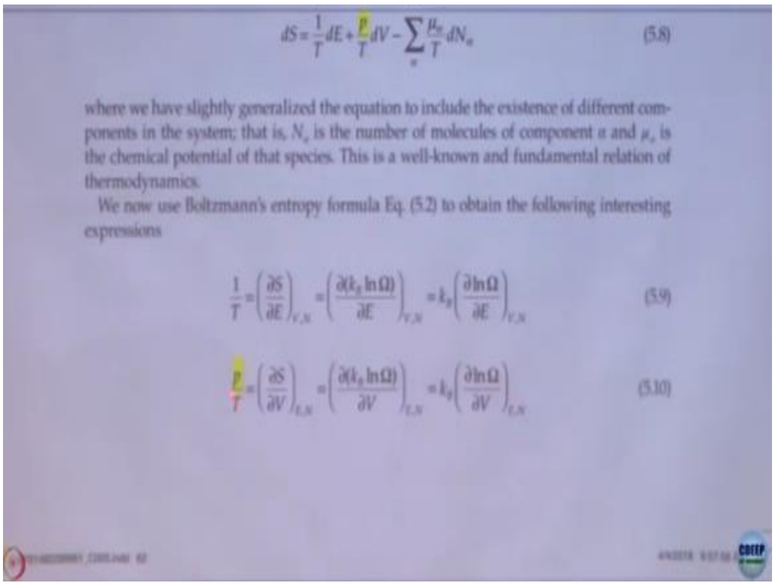

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$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} = \left(\frac{\partial (k_B \ln \Omega)}{\partial E}\right)_{V,N} = k_B \left(\frac{\partial \ln \Omega}{\partial E}\right)_{V,N} \quad (5.9)$$

$$\frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N} = \left(\frac{\partial (k_B \ln \Omega)}{\partial V}\right)_{E,N} = k_B \left(\frac{\partial \ln \Omega}{\partial V}\right)_{E,N} \quad (5.10)$$

I can know from micro canonical ensemble. This is the condition that means temperature is the derivative of log Omega with respect to energy which intuitively makes sense because Omega is the total number of microscopic states of a system belong to a system in the microcanonical ensemble characterized by NVE, then if I change a little energy then the number of microscopic states that increases by this quantity 1 by T. Now, similarly you can have definition appreciate in terms of microcanonical ensemble.

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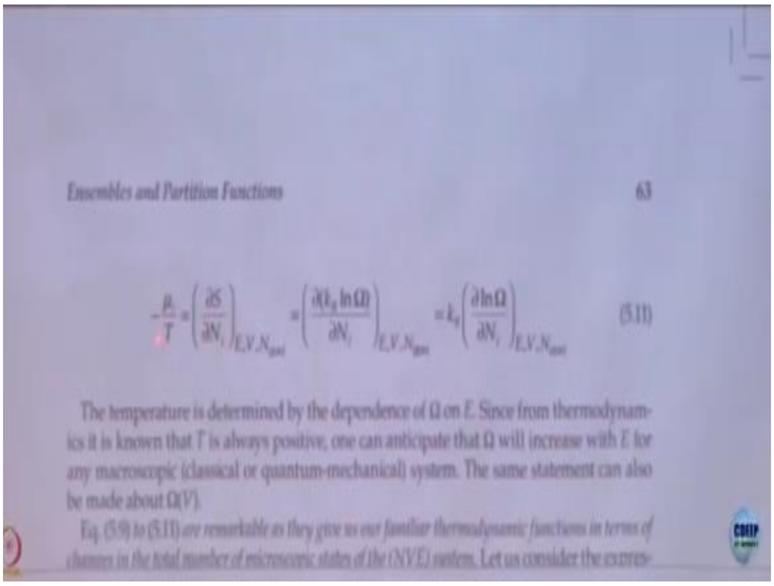

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$$-\frac{\mu_i}{T} = \left(\frac{\partial S}{\partial N_i}\right)_{E,V,N_{j\neq i}} = \left(\frac{\partial (k_B \ln \Omega)}{\partial N_i}\right)_{E,V,N_{j\neq i}} = k_B \left(\frac{\partial \ln \Omega}{\partial N_i}\right)_{E,V,N_{j\neq i}} \quad (5.11)$$

The temperature is determined by the dependence of Ω on E. Since from thermodynamics it is known that T is always positive, one can anticipate that Ω will increase with E for any macroscopic (classical or quantum-mechanical) system. The same statement can also be made about $\Omega(V)$.

Eq. (5.9) to (5.11) *are remarkable as they give us our familiar thermodynamic functions in terms of changes in the total number of microscopic states of the (NVE) system.* Let us consider the expres-

Then you can have chemical potential in terms of d Omega V. Now this has a very, very interesting one corollary, which I will discuss a little later if I come;

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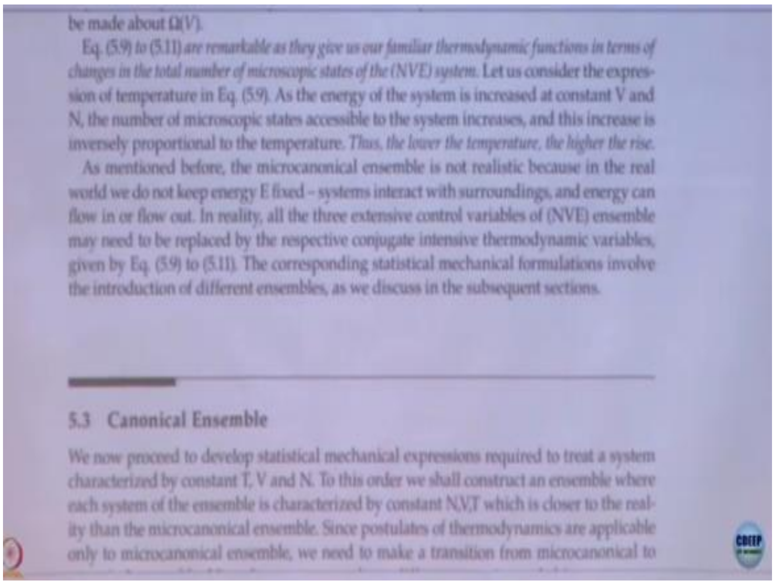

be made about $\Omega(V)$.

Eq. (5.9) to (5.11) *are remarkable as they give us our familiar thermodynamic functions in terms of changes in the total number of microscopic states of the (NVE) system.* Let us consider the expression of temperature in Eq. (5.9). As the energy of the system is increased at constant V and N, the number of microscopic states accessible to the system increases, and this increase is inversely proportional to the temperature. *Thus, the lower the temperature, the higher the rise.*

As mentioned before, the microcanonical ensemble is not realistic because in the real world we do not keep energy E fixed – systems interact with surroundings, and energy can flow in or flow out. In reality, all the three extensive control variables of (NVE) ensemble may need to be replaced by the respective conjugate intensive thermodynamic variables, given by Eq. (5.9) to (5.11). The corresponding statistical mechanical formulations involve the introduction of different ensembles, as we discuss in the subsequent sections.

5.3 Canonical Ensemble

We now proceed to develop statistical mechanical expressions required to treat a system characterized by constant T, V and N. To this order we shall construct an ensemble where each system of the ensemble is characterized by constant N,V,T which is closer to the reality than the microcanonical ensemble. Since postulates of thermodynamics are applicable only to microcanonical ensemble, we need to make a transition from microcanonical to

So this is what the thing that I wanted to review of the microcanonical ensemble then you may continue to do canonical ensemble. Now you have one of you had a question, yeah please tell me, in micro canonical, in MD very good question, oh yeah excellent question. So, when you do these calculations V is like phase transitions and this like this creates enormous problem and I give you problem we do NPT.

Like I give an example; right now, we are doing and also do we give the Gibbs ensemble that is because number of particles exchanged and that is new PT, that means what is the Gibbs ensemble NPT is isobaric. So all these things, all these different ensembles are brought in but at certain cost and ideal the cost. Right now we have been trying very hard to study ice - water interface other people have studied you can see several papers are there.

So two things we are trying to do one of them is that why, yes it is very interesting question well just write in the paper that, if you take like argon which are characterized by very energy potential then the FCC lattice and the liquid interface is another broad it is about 4 to 6 mono layers or molecular layers but water interface is sharp. So we tried to understand why water interface is sharp.

And it is a huge importance ice water interfaces in many, many different context and we came to that from there is a class of proteins called antifreeze protein which is a lot of threonine, in hydrogen bonding. So this antifreeze protein with the large number of threonine, they stop ice floats called ice remains static. So you want not just to growth we also so from there we went, let us just study the interface first.

And I knew this problem because it is a very difficult problem because when something an interface is 4 to 6 or 8 mono layers then you cannot study them by any experimental techniques. You know like, I cannot do neutron scattering on that that leads micrometer or millimetre length I can do imaging but the spectroscopic imaging cannot study that length scale.

I can do TEM, but TEM means is static it is not dynamic, I wanted to do the fluctuations at the interface, and then when we try to my student is trying, two - students are trying to stabilize NPT it is a hell of a problem because they just either the ice melts back or the ice forms, that because there is a barostat and idiotic barostat is giving forces into the system and then output is a thermostat.

So the people who are continuously studying in NPT or Gibbs Ensemble they have this difficulty, and you are right there is no way I can do NVE in that system, because if I do NVE then I will not be able to remove the latent heat. Say latent heat has to be removed you know otherwise I can stabilize them to you everything and same say it is NVE then that will stay in that system, unless I can have such a large system.

And humongous system then NVE will be able to capture, because this growth of crystal or melting will be captured as the fluctuations in the system, but what is not possible here. So but the kind of systems we do we have maybe five thousand water molecules and people are doing those who have done successful simulation they were very long a there with crystal slab and then liquid on the two sides and different people ask different questions.

So he absolutely right that there is this huge problem and that is why there are two kinds of simulation people; one are the people like us who are application and not expect it, and there are people who were developers would develop potential develop methods like these guys in Italy, what is his name? Parrinello, those who then toady and value who did umbrella sampling. The perinatal group did many things like Ab Initio plus metadynamics.

So the way to come around these things with phase transition then use this specific sampling you know that means you, which are called method of constraints, which are like our Lagrangian multiplier, which a method of constrain, you move things around in the direction you want it to go and we equilibrate along that, what is the way you do dissolution. So there is a huge problem one probably should at the, I have two chapters at the end of my book on computer simulation.

I want certainly to do the chapter 31 which is on computer simulations, where I have devised new ways of doing periodic images minimum-image convention I did not answer Ising model and it is so easy to see what is the method of minimum- image convention, periodic boundary convention, but what is in the chapter 31 of my book it is very simple. I was not happy with the conventions given, the explanation given by Allen and Tildesley or other books.

Because it seems to complicate, it is so simple a method but then you play the one-dimensional Ising model and the all these explanations and all these statistical mechanics becomes much simpler. So does that explain partly your question it is a difficult question and difficult to answer at the same time, because that is not done. Now so we now from then on we went so what will happen?

I am, so I will be spending more time on this because I want you to be comfortable, is because this is intimately connected with all our simulations and all the interpretation of our results that how we do statistical mechanics and once you become familiar with this is really very, very, very nice things and you can, you see when you for example you are doing lattice calculations very recently all this effect and work on the lipid Bilayer work.

We are done start by saying how many ways I can pack things and then how many ways do practicing from there you get Omega, and then you go on from there. So this is the partition function so in microcanonical ensemble Omega is the partition function or sometimes it is also called; so in micro organic ensemble this is the partition function and this is the thermodynamic potential.

Thermodynamic potential is the quantity that takes an extreme value. Actually if you think of that you always maximize the thermodynamic potential, so free energy we write as K_BT but way you write at a - K_BT. So that is the one that follows from Boltzmann's arrow of time which was Stephen Hawking and all these people wrote so much book on do that, that the arrow of time is because we entropy is a system left by itself goes to a state which has maximum entropy.

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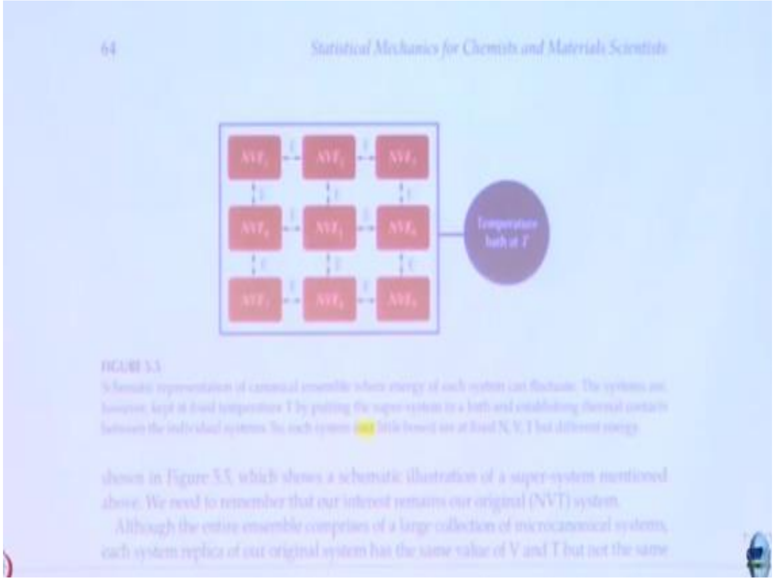

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FIGURE 5.5

shown in Figure 5.5, which shows a schematic illustration of a super-system mentioned above. We need to remember that our interest remains our original (NVT) system.

Although the entire ensemble comprises of a large collection of microcanonical systems, each system replica of our original system has the same value of V and T but not the same

That is the Boltzmann's principle. So then from but as we know micro canonical, answer please ask questions; Micro canonical ensemble is not very useful, so there are several issues one issue is system add equilibrium but away from phase transition, the properties of water, properties of ice break time or dynamical sulphur oxide or properties of a block of iron or whatever or solid there is one thing like that.

Another thing is phase transition and the many other aspects that we study, so when the system is at equilibrium in this stable state away from phase transition then if I were to describe that then NVE is not the greatest of this system because we are too much constrained real-world NVE is not there. So we have to go to with now we start relaxing we go to in the NVT then we go to NPT one by one will do that.