Basic Statistical Mechanics
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Lecture - 08
Microcanonical Ensemble

Now what we are going to do again (I do not need it but…), I will just start with this, Okay?

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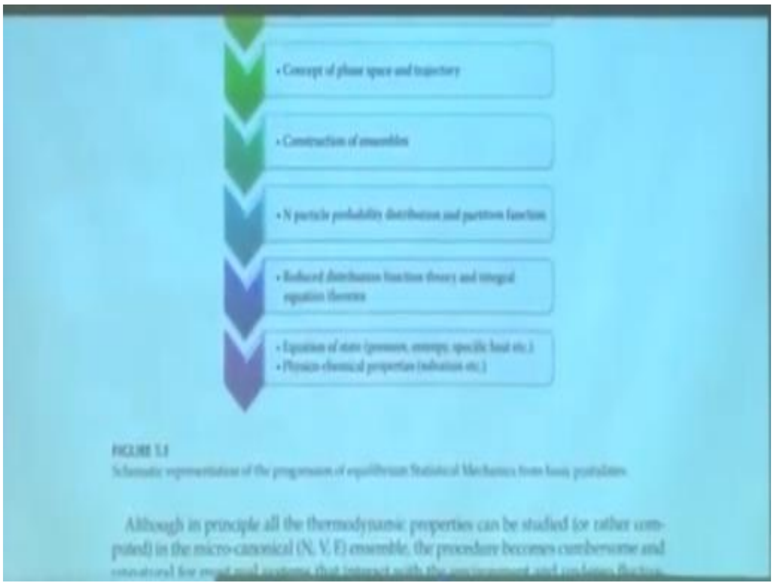

- Concept of phase space and trajectory
- Construction of ensembles
- N particle probability distribution and partition function
- Reduced distribution function theory and integral equation theories
- Equation of state (pressure, entropy, specific heat etc.)
- Physico-chemical properties (solvation etc.)

FIGURE 1.1
Schematic representation of the progression of equilibrium Statistical Mechanics from basic postulates

Although in principle all the thermodynamic properties can be studied (or rather computed) in the micro-canonical (N, V, E) ensemble, the procedure becomes cumbersome and unnatural for most real systems that interact with the environment and undergo fluctua-

So this flowchart kind of thing that I am going to follow, so Gibbs gave us this ensemble and Gibbs gave us the equivalent probability, Ergodic hypothesis. Ergodic hypothesis to an extent was already in Boltzmann, but this was all in this ensemble. That means every system has a constant number of particles N, constant volume V and all of them have the same energy. So you can immediately realize that this constant energy constraint is not practical.

Because your system is in interaction with surrounding media, the kind of example I gave, that if this is my huge my number with waters, glass they are in, I cannot keep them in NVE. I can keep them in NVT but, even NVT is difficult, I can keep them in NPT much more easily. That is what a chemist works, number of particles known, constant pressure, and temperature.

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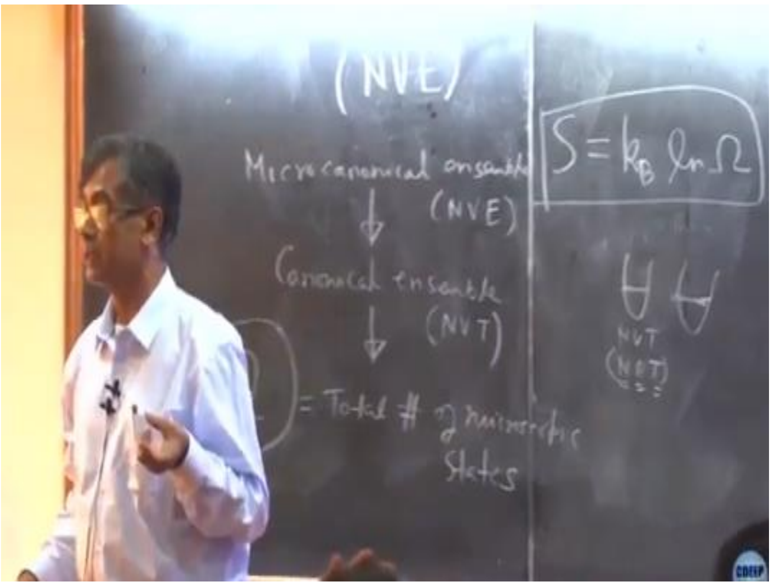

So this ensemble is called microcanonical ensemble. This is then graduated to or generalized to canonical ensemble and then goes to other things, right now do not need them. So this is NVE and this is NVT. For the time being two are enough because we now want to develop the concept of these things why we need them and how do you work with them.

Remember ensemble is a huge number of mental replica. And the whole idea of ensemble was that I can talk of a probability, that was introduced by Maxwell -Boltzmann. I already have my equal a priori probability. So I need to have now. How do I go ahead? How do I now calculate or construct a quantity which can lead me to thermodynamics?

The first attempt statistical mechanics lead to, you know it was immediately realized by all these great thinkers that the first demand on statistical mechanics is to derive thermodynamics. Because that is the one that is those days or even now explains everything all natural phenomena in terms of free energy, entropy, enthalpy all these things. So, statistical mechanics was geared from the beginning to describe thermodynamics.

So now the idea is, I have the NVE, I have a huge number of systems all have constant energy, all are volume V and all of total number of particles. So what is different from one system to another system in the ensemble? The difference from one system to another system is in the microscopic state. Each system is in a different microscopic state. That is the most critical realization.

Then you immediately realize that what could be and very important quantity. Some realized by Boltzmann's very critical quantity is the total number of microscopic states. Then what is the total number of microscopic states? How do I calculate the total number of microscopic states? And this is a pivotal quantity from which (what I am going to tell to you) which whole statistical mechanics came out that the total number of microscopic states.

How we calculate? It will come a little later. So if I know that is the system, now let us think this, in real world, there is one only one system, ensemble is my mental replica. Now these particles (in the systems) are moving, they are randomly moving, they are interacting with each other, they are changing positions, they are rotating and each of this tiny little movement is taking it from one microscopic state to another microscopic state.

Now it does not take too long to realize that if a system has a much more microscopic state then the system resides in that state longer time. Let me tell you something very important again I repeat these things if a system is in a given NVT condition, has a larger number of microscopic states then the system (they are all same energy) will spend the maximum amount of time there.

Now, what is then the measure that, that state that particular microscopic state that macroscopic state which has the maximum number, the maximum weight will dominate. So it is almost like the theory of evolution in certain sense. So that is where this came from Boltzmann and used by Gibbs is that this Ω has to be a property. I will give a derivation.

$$\Omega = \text{Total number of microstates}$$

It has to be a property that scales to the size of the system in a certain specific way. We all know that thermodynamic properties like entropy, enthalpy are extensive which means they are proportional to the number of particles in the system. Now, this thing is an enormously large quantity. So the Boltzmann introduced and this will become more this is the Boltzmann formula.

$$S = k_B \ln\Omega$$

I will motivate a little bit more but let me tell you also just like the postulates there is no absolutely convincing derivation of this and probably there is no need. Many of these things have been verified post facto but, before I motivate further let me tell you a little bit more about how this Ω comes about and as I tell you that this; As I talked let me repeat that this is that one formula is the most important formula of the statistical mechanics, whole statistical mechanics came from that.

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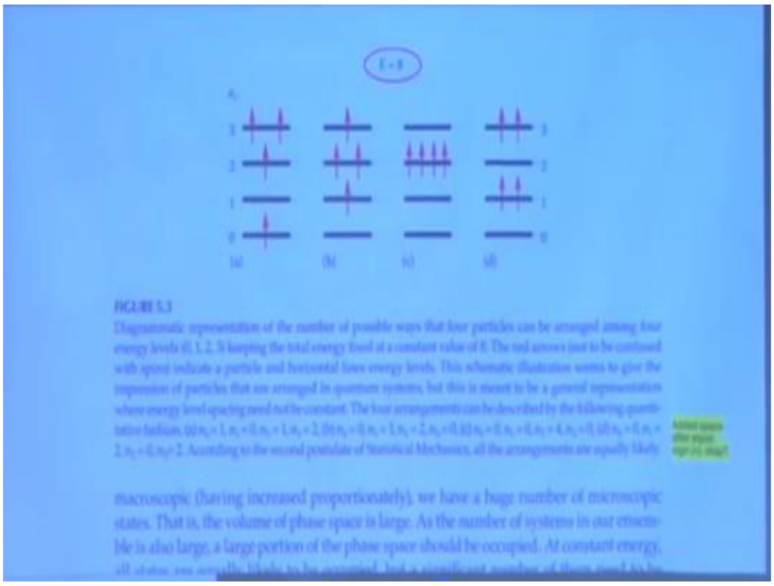

So this is a very simple picture, giving you an idea of the microcanonical ensemble, the number of microscopic states that you have. So I have these 4 energy levels and total energy is fixed 8. How many ways I can distribute that? So here you can distribute your system, so arrows are the systems. I am talking of ensemble.

And these are all distinct microscopic states. And I have taken care of distinguishability or indistinguishability. So, each of them is one state, now what happens if I increase the number of particles in the system. If I increase the number of particles in this, the number of random systems with energy E fixing 8 then there are many more ways to arrange it.

Similarly, if I can increase the number of energy levels then again many more ways to do it. Very soon in the real world when the atoms and molecules are moving there is a huge number of energy levels, a huge number of energy levels available to the system. One cc of gas at normal temperature, you can calculate (and McQuarrie book has given that we discussed it) as 10^{33} microscopic states.

That is the kind of huge number we are talking about. So that is also the difficulty of doing computer simulation because there is a huge number of microscopic states one has to sample. So the microscopic states increase what we call exponentially as the size of the system, size of the system by means that the energy level, so two things are coming, energy levels of the system are determined by the system itself by the interactions for example by Schrodinger equation.

So I am having a self-consistency here because I am going, taking a system then calculating its all the energy levels then I am doing an ensemble construction (is a very pretty very beautiful), then I am doing the ensemble construction (I am saying), I have the energy levels now. Now let me see, I have an infinite number or billions and billions of my systems which I am going to distribute with the constraint that energy is conserved.

This is NVE. I realize very quickly that the number of states that have a number of arrangements with my Ω is growing exponentially. You can do a simple calculation to show that it can a simple combinatory that it grows exponentially. As soon as that grows exponentially and I know my thermodynamic properties are dictated and determined by Ω. So in that case I am now having a beginning to have a certain insight that I want to describe thermodynamics and I want to have an extensivity.

Then I want to preserve the extensive property and I want to preserve what is this scaling. So now why it is entropy and that came from a much, much complicated and detailed derivation of Boltzmann. That is why $\ln\Omega$ was given to you at constant energy and volume is entropy .that is the way it turns out that this is the you can regard that this quantity $\ln \Omega$, Ω is more fundamental and $\ln\Omega$ is the quantity that we call entropy.

So this is essentially a definition of entropy. Do not consider it as, though it went like that entropy came first and then came Ω for statistical mechanics it is the other way around, Ω is the primary quantity and that determines entropy. So it is just exactly the other way around. Now there is a derivation that is given in many, many places and I will just sketch the derivation though as I told you better you can regard as well as a postulate.

And sometimes when I teach in class, I say statistical mechanics should actually be considered consist of three postulates and one hypothesis. One of them is this postulate. Because in many sense there is no realistic sense derivation of this but whatever so this is the $\ln\Omega$.

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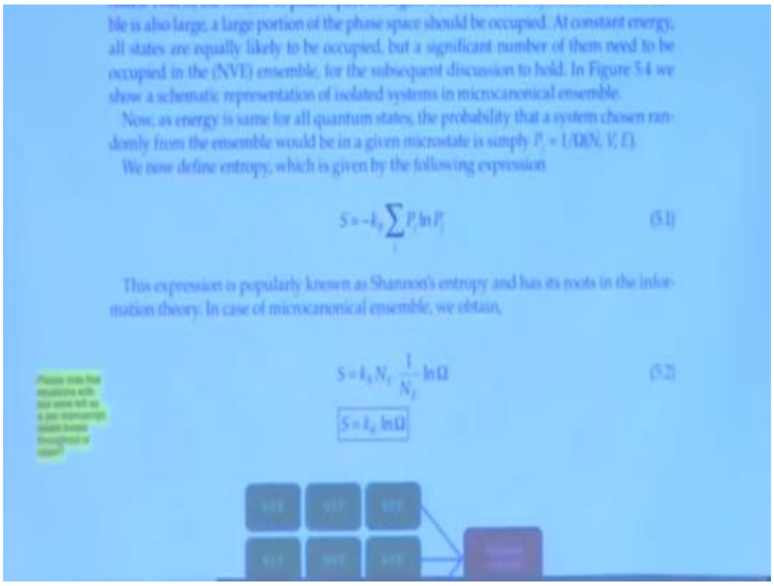

ble is also large, a large portion of the phase space should be occupied. At constant energy, all states are equally likely to be occupied, but a significant number of them need to be occupied in the (NVE) ensemble, for the subsequent discussion to hold. In Figure 5.4 we show a schematic representation of isolated systems in microcanonical ensemble.

Now, as energy is same for all quantum states, the probability that a system chosen randomly from the ensemble would be in a given microstate is simply $P_i = 1/\Omega(N, V, E)$.

We now define entropy, which is given by the following expression

$$S = -k_B \sum_j P_j \ln P_j \qquad (5.1)$$

This expression is popularly known as Shannon's entropy and has its roots in the information theory. In case of microcanonical ensemble, we obtain,

$$S = k_B N_E \cdot \frac{1}{N_E} \ln \Omega \qquad (5.2)$$

$$\boxed{S = k_B \ln \Omega}$$

The derivation is sketched here and this is derivation given in every textbook that you define an entropy function. So this is the derivation is given in my book (and the standard derivation in every textbook). You define your function entropy function in terms of probability. The energy levels that I discussed;

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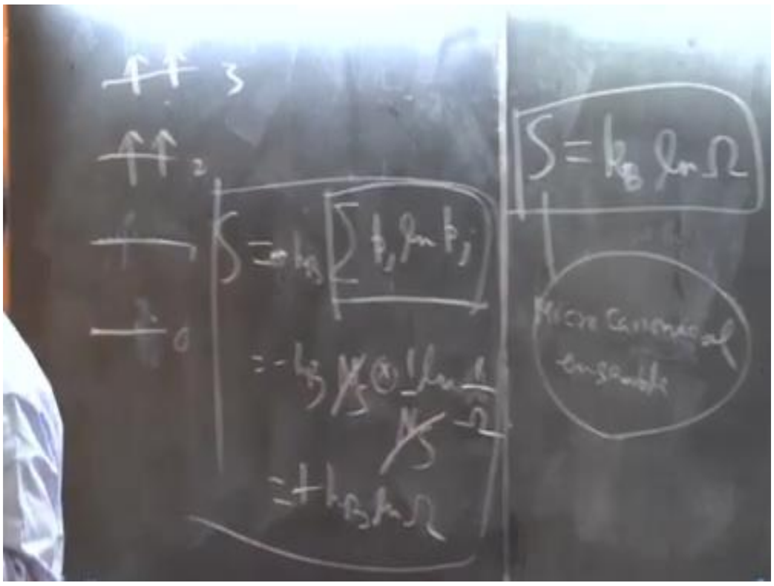

That and your my systems 0, 1, 2, 3; I think I remember that I have 2 here, 4 and 2 here, one just there are many like that one of them. Now so define this function, this what actually also came from Boltzmann, and I have some interesting tale to tell you that I will. So basic idea was that I define a function which is proportional to the probability it is occupied, it is the probability of the system in a j^{th} energy level because these are systems (arrows are systems), and they are systems for my ensemble.

$$S = -k_B \sum p_j \ln p_j$$

Again my energy levels are obtained by solving the Schrodinger equation or even classical mechanics by all the positions and moment available to the system which is called the phase space. We described a little bit of phase space in the last class and trajectory. So they are obtained from a given system. Now I construct my mental replica and put my systems, my arrows into different energy levels.

So once I do that since they are all equally probable I can find out what is the probability my system is in a given energy level J. Then I construct this quantity, so now the derivation says, they are all equally probable so pj is, so it is

$$S = -k_B N_s \frac{1}{N_s} \ln \frac{1}{\Omega} = k_B \ln \Omega$$

All the sums are the same probabilities the same, so if there are N_s number of total number of arrangements and probability is ln Ω and by p is one over N_S because each of the equal probable.

So this is the standard derivation that comes to the textbook that S equal to K_B ln Ω, even then in this derivation, which is heuristic, but it does bring in a little bit more Physics in the whole thing that you derive a function.

So this is the entropic function, this function defines entropy is the function that it defines microcanonical ensemble. This is the beginning of statistical mechanics actually or the relation between statistical mechanics or you know perhaps the most important relationship where everything flew from this one relation that $S = k_B \ln\Omega$

Because every state is equally probable, see what the reason I am a little bit fumbling because statistical mechanics was formulated by Boltzmann and then Gibbs. You have to understand that the theory of probability was almost entirely developed in mathematics. They were developed to a great extent by the 19th century already. So then the people had both Boltzmann and Gibbs had the understanding that they are going to look at an extensive property.

And their new probability is going to scale, probably to one over Ω but, Ω is going to scale as the something to the power n, so that brings the long term. So the whole motivation of introducing long term there and I am again and again saying this is a definition of entropy function. It remains to be shown this S is indeed thermodynamic entropy and that was done later.

So this was introduced as a function. Boltzmann definition this was H, it was not S. It was shown by Gibbs that this function is the S and we are using it as this, and I told you that I will say you something really interesting. The interesting thing is that S is proportional to ln Ω and the proportionality constant Kb is Boltzmann constant. Nobody yet knows why it is? Why K_B is 1.38 into 10 to the power minus 23 know, Good!

$S = k_B \ln \Omega$; this is introduced, I would like to tell as the primary postulate of statistical mechanics. But you can say no, this is a function defined by ln Ω and it has to be ln Ω. Because Ω is an exponential function of the total number of particle - size of the system.

So it must scale as it must be ln that brings in to the power n, n comes out and entropy is an extensive property and these as I said that the people very quickly realize that thing. But again I am not trying to justify that. The justification of that $S = K_B \ln \Omega$. S indeed describes the fundamental equation of state of thermodynamics and entropy, which is the detailed derivation of that exists in a transition from statistical mechanics to thermodynamics.

That thing will do in the next class where we will see how $S= K_B \ln \Omega$ can indeed describe thermodynamics. That is you know still unfinished agenda. That is the thing we need to do next to convince you that S is indeed the entropy. Once that is done and as I told you this only equation that you need, no other equation you need. From there you go to canonical ensemble, you go to grand canonical ensemble, isothermal-isomeric ensemble everything.

Because, you realize immediately that, the properties that will come to that microscopic properties that particular state of the system which will have a maximum Ω. Maximum Ω means maximum entropy. Stable state free energy is the minimum that also follows from this. So the whole thermodynamics follows from that one equation, entirely, which is amazing.

Now, these are all interactive, these are not what I said, when Maxwell did it, the ideal gas that is the whole kind of theory of gases that you read in an undergraduate is for an ideal gas. So in ideal gas means particles pass through each other but that was not allowed. So he derived PV = nRT, then he derived pressure(P)=1/3mNc^2. They are all ideal gas. But at the same time, he allows the exchange of momentum with the wall, which is the billiard ball.

So there is a mix of interaction and non-interaction which is fuzzy, very fuzzy. That is not the way but, that is way Maxwell did and got the right results. That is what led Boltzmann to remove the inconsistency in Maxwell and try to introduce interaction. If I ever teach time dependent statistical mechanics, then I always start with Boltzmann kinetic equation. That means you take a two-particle collision and f2 which is two-particle joint power distributions of r1, r2, p1, p2, and by the interaction that is changing.

But that then you explicitly have the collision and there is a term that comes in called collisional cross-section, which has a molecular diameter in it. See in the kinetic theory of gases you do not need pressure PV=nRT, PV=nRT does not have a molecular diameter. Then all these do not have except when you go to calculate the viscosity, and then you need the molecular diameter. Maxwell's kinetic theory of gases is many, many places internally inconsistent.

That was Boltzmann trying to do and he could do only partly. But these are very good issues and very fundamental issues that we bypass in our undergraduate physical chemistry but I always believe this interface between equilibrium and time-independent statistical mechanics is one of the most fundamental and most intellectually exciting and pleasing to think about these things. We stop here now.