Basic Statistical Mechanics
Prof. Biman Bagchi
Department of Chemistry
Indian Institute of Technology, Bombay
Indian Institute of Science, Bangalore

Lecture - 09
Relation with Thermodynamics in Microcanonical Ensemble Part - 1

We will start briefly revising. What is this course about? So, the whole goal of statistical mechanics came into with this phenomenal paper of Maxwell to propose the velocity distribution. Now why Maxwell propose the velocity distribution? Because that was the time if you remember, around the same time the equation of state was being formulated.

You remember the name of Berthelot, Dieterici; all these names but of course the successful one was by Van Der Waals. So there was, with the kinetic theory of gases it is fair to say the atomistic view of nature put forwarded by Dalton, but the atomistic view of nature came into being with the kinetic theory gases. So I think that is the time people started thinking. You are not understood the perspective that the time when people are doing classical mechanics. People are doing hydrodynamic which was almost fully developed.

So things were mostly continuum and based on the theory of classical mechanics. That is what made quantum mechanics such a huge impact. So the kinetic theory was growing and where people like Maxwell must have realized that almost much of what we know today. That way to describe the gases starting with the simplest model as particles which are moving and colliding among themselves is the way pressure comes into being. That is the way heat is being conducted.

So Maxwell went out to develop the theory of these kind of phenomena, viscosity and he then realized that it is not possible to calculate the voltage but he realized one thing if I have a distribution of velocity probability that there is the number of particles with the velocity between v and v + d v which is called p(v) dv.

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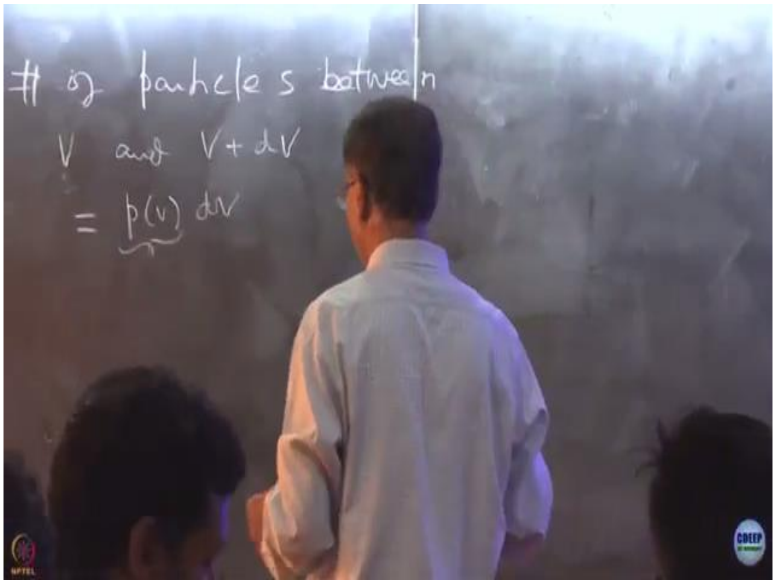

So the number of particles between v and v + d v, was p(v)d v, that was the basic. So p(v) is the probability, that was the first time in this game we are playing the probability distribution was introduced and he could calculate as we know the equation of state viz $PV= n RT$, you could calculate pressure equal to $P=1/3\ mnc^2$ and the average speed of light or a particle which is c square is I think $\sqrt{\frac{k_B T}{m}}$.

All this relations that you read in your undergraduate, follow from that particular answers that a probability distribution. I told you that it was difficult to take into account the collisions in equilibrium system, equilibrium means, which is time in variant.

That means state of the system is not changing, the macroscopic state of the system is not changing with the time, but microscopic state of the system is changing its time. The basic understanding that already was evolving at that time and so what Boltzmann tried to do. Boltzmann tried to put that into far more concrete, expressively taking into interaction between atoms and molecules.

And there is a term in his theory called collision cross section. When the two particles are approaching towards each other with the velocity v_1 and v_2 then probability is the collisional cross section, which is determined by the intermolecular interaction. He could not go very far as we discussed.

And that is a subject of time dependent statistical mechanics which we are not going to discuss in this course but it has a very paramount importance because it gave rise to a function which essentially became the entropy. So basic idea then was is the following that, people face with the problem of describing, such questions as; why Ice melts with the latent heat of 80 calories per gram.

Why argon like systems or iron goes into FCC lattice while sodium goes into BCC while water crystallizes to this hexagonal ice? And the hue or protein folds into the native state and why it folds into state that it folds so or the, how in your body when you living Delhi, you know, you are all the pollution so you can imagine the kind of damage your DNA being made.

But we still survive. The reason of surviving is because of we have a efficient, I accept the young children and old people immunity in our body that all these DNA that are being or getting all oxidized or the particles getting deposited on lungs are getting removed. So the way a DNA gets continuously rectified because there are certain proteins that move around DNA and correct the mutation.

So these are the process you need to understand so this name of all these processes that I am talking; freezing, melting, boiling or these protein folding, protein DNA interaction, they are called large amplitude phenomena. These are involving many particles as I discussed several times that we cannot even solve with a simple potential as an interaction potential with three body problems.

The reason Boltzmann failed beyond a point because of that, there is no way even this time and hundred more than a hundred years now. Substantially more than 100 years people have tried and there are certain advances but not a great deal of advances of understanding starting from the required corpuscular nature of matter, then go to calculate the thing. So faced with the difficulties that what Boltzmann failed, Willard Gibbs decided that the other way of doing this things.

We must be abundant these ambitious project of doing from fully atomistic description following the trajectory and collisions of every atoms and molecules. And by the trajectory I mean that you have the two followings. In the first one tagged particles positions in the three dimensions of space and its momentum with time and then the same for the all other n particles so it is a 6N-dimensional coordinate space which we call phase space.

So the system is executing the motion in this 6N dimensional space even if we neglect rotation in this huge dimension space. This is called trajectory. So the concept of trajectory is very essential that I describe before. That will come again and again in the discussions so.

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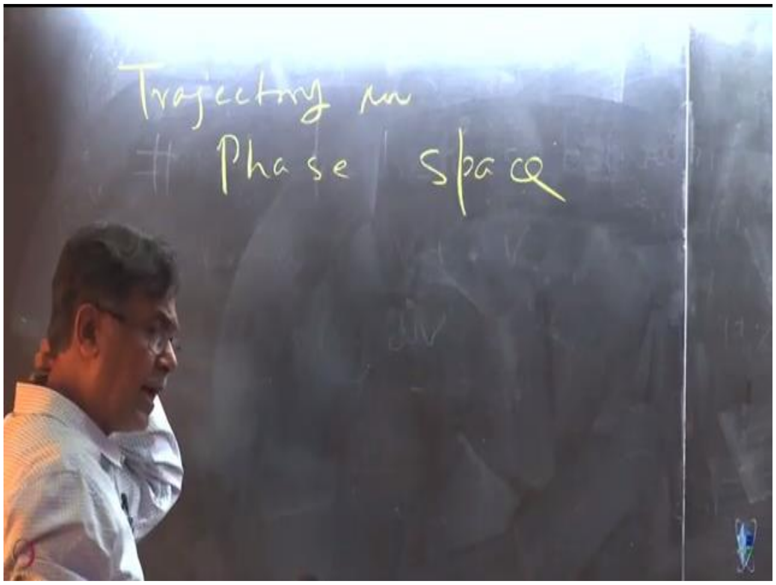

So this hugely complicated thing which is the, motion in phase space which is the trajectory and so trajectory in phase space that is not possible to get. Now you think of that say we solved the trajectory, we do that in computer simulation trajectory of these number certain number of much smaller number. Many of the time what you do with that information yes, you know the position of atoms.

And molecules are in very free space for a second and hours and what do you do with that information? You know, that is a huge amount of information, and much of that is just impossible to analyze. It is of course, correct and getting the velocity correlation function for few particles that we know, that is very helpful these days not at the time of Gibbs. But we know can do that now.

But this is a huge amount of information that it trajectory has in it for equilibrium properties of this system. But this information is not meaningful. We need a method for the kind of synthesis of a system and use this information in a much more succinct, more clever and intelligent way. And that was done by Willard Gibbs, this brilliant construction of ensemble.

He said as I give the example that there are 10 glasses of water and you know all the 10 glasses have the same properties like same density, same specific heat, same conductivity at the room temperature. However few Avogadro number of water molecules or a few hundred Avogadro number of water molecules present in the 10 glasses are in different state.

At any time the microscopic state of water is changing. I want to get idea of the microscopic state, then I need to construct mentally huge number of this glasses. Now each of them at a given time is in a different microscopic state. So now I can construct as like Maxwell and Boltzmann did.

So ensemble picture allowed you this transition from a trajectory-based description to probability-based description that was the whole idea of ensembles. Ensembles allowed you to go to probability. And once you go to probability then you start discussing these things in a certain quantity, analytical way which Gibbs develops.

So that was the goal to make the transition to probability and you know Boltzmann was heavily criticized for his description of probability, but on the other side Willard Gibbs alone, sitting in the Sterling laboratory in Yale University, single-handedly did all these theories of statistical mechanics.

There is a beautiful quotation by Mulliken and other people that how he single-handedly did that. I have the ensemble and now I want to relate the total number of microscopic states to the thermodynamic property.

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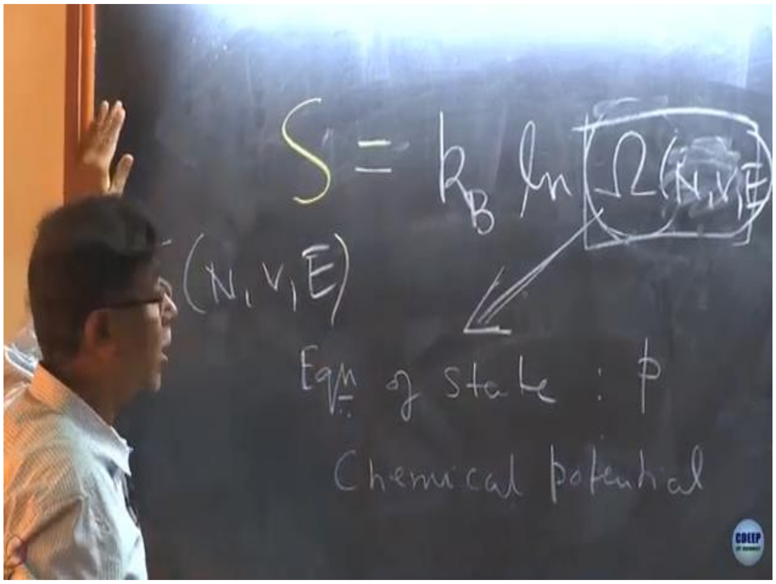

This is what we discussed in yesterday's lecture. This is the important thing that in certain form came from Boltzmann and as I told you that this could be considered very much as one of the postulates of statistical mechanics.

This is the equation from which entire equilibrium statistical mechanics develops. So now how do you go from here to the next step? I should be able to derive an equation of states that means I should be able to get pressure as a function. I should be able to get, for example the chemical potential or free energy.

So this, if I know these, and I know these equation, this is the equation which gives the relation between the microscopic states, which is the real microscopic area of the system, we discussed in the last class that the energy level diagrams in my arrows as particles occupying different energy levels and giving rise to different arrangement or microscopic states and total number of microscopic states, we worked out with the energy equal weight that four states allowed.

If I have four energy levels; 0, 1, 2, 3. Now with that information, all of them have the same energy. And I have these like in particle in a box, remember if you have what, a particle in a box and it is done in the context of the solid state physics that you go to density of states i.e. Ω(E). We know Ω(E) grows exponentially. And that is a very important thing.

So this is a very important relation but here we are saying a very fundamental thing that, the number of microscopic states uniquely determines thermodynamic function entropy. So now given that, I have to now discuss that from the total number of microscopic states, how other macroscopic properties like pressure, chemical potential can be determined.

One important thing about micro canonical ensembles is that we are talking everything in terms of NVE, so this S is a function which is NVE. And Ω is a function that is NVE. So there is no concept of temperature in this framework micro canonical ensemble, no concept of pressure, no concept of chemical potential, nothing is there in micro canonical ensemble. So now our task is to evolve these relations to show how this thing hangs together.

How the micro canonical ensemble leads us to thermodynamics. That is the next call and there are lots of equations and so I am not writing to them. Now we can start these from the book of Statistical Mechanics.

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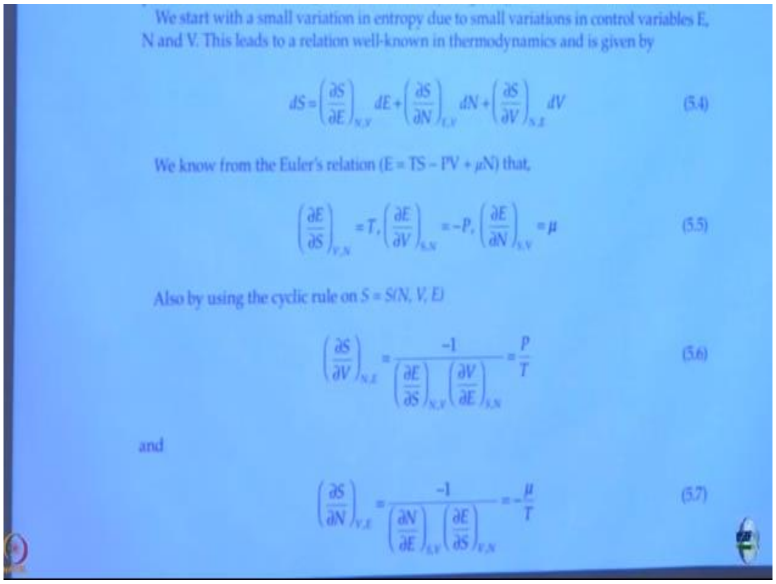

We start with a small variation in entropy due to small variations in control variables E, N and V. This leads to a relation well-known in thermodynamics and is given by

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

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

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

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

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

and

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

So the way we now think of these equations here, that will give a small fluctuation in the variables in NVE. Now let us see what would happen if I increase the energy then Ω will increase because for any particle in a box if we increase the volume V keeping other things constant, then again the number of states will increase. Can you explain why if I keep everything the same and then increase volume V, then the number of states will increase?

So one best way to think of a lattice is in terms of different grids and each molecular size you give it is a grids and then you make it larger, keep it fixed then there are more grids and more places to place the body. And this is a dicey thing because it is not always a monatomic function, it could be very large density, it could actually start decreasing. But V and E; it will be monatomic functions. So now we consider a small variation of fluctuation and then my variation in entropy from Boltzmann formula, I can write like that. There are two ways of doing it and I do both the two ways. ‘dS’ is a variation so I take it as any partial derivative.

Because it is a function of three variables that I have three terms dS/dE, dS/dV, dS/dN. Now we know this is what I call the differential form of this function, that means, $dE = TdS - PdV + \mu\, dN$ as the fundamental equation or fundamental relations of thermodynamics, I think following Castellan and these people.

You bring the TdS on this side, then you have dS equal to divide everything by T. Then what you realize now that, dE/dS becomes T, dE/dV will become -P, dE/dN becomes chemical potential, μ. By using the cyclic rule which essentially; dS/dV into dE/dS, dV/dE, these three products equal to -1. That we use in thermodynamics constantly. Now I know that dE/dS = T, I know dE/dV = P, then I know now combining this thing, dS/dV = P/ T.

My system depends on three variables, that three variables are E, V and N, so they are independent variables.

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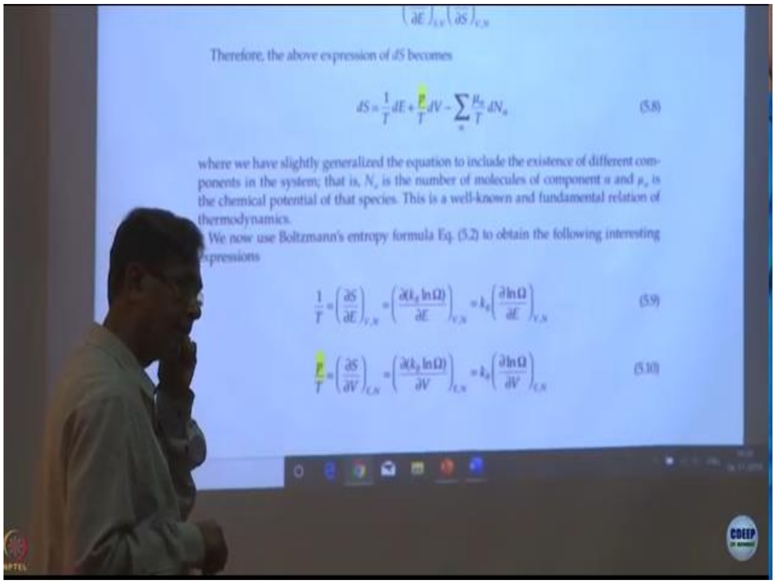

Therefore, the above expression of dS becomes

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

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

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

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

All the three P are dependent on N,V,E. All three, see all these are the things, so only there are three independent variables, the system is fully determined by all three, everything else comes out from these three. These are questions always ask, because these one comes, if we do, it will come again to the question of the first time I had this confusion, when we do the stability conditions in thermodynamics.

There we expand the free energy in a similar form involvement temperature then the way we prove that specific heat is positive. There is one proof to fluctuations, but another proof is through thermodynamics. For a system to be thermally stable, we have to say specific heat is positive and mechanically stable, we have to show pressure is dV/dP that is negative, so these are the stability conditions.

So there you expand your free energy exactly in terms of these variables. But you think a little. You have to keep track of only the independent variable, dependent variables do not matter. So then I have, this is the equation that I am saying essentially what is called fundamental relation of thermodynamics.

Now, if I go back to my earlier equation, there are two things going parallelly, please note one thing that is this equation from there, so one is this and then all the other thermodynamic relations we are using. However, we know $S = k_B \ln \Omega$, So that it immediately tells me the relationship like $\frac{\partial \ln \Omega}{\partial E} = \frac{1}{k_B T}$, $\frac{\partial \ln \Omega}{\partial V} = \frac{p}{k_B T}$ and $\frac{\partial \ln \Omega}{\partial N} = -\frac{\mu}{k_B T}$.

Now, these are equations of very kind of profound importance because you are getting a microscopic definition of temperature of a system in terms of the density of states. Now kinetic theory gives you a much simpler and exact relation between temperatures, what is that? Equipartition theorem that, $1/2MV^2$ = KE. That is the one we use in competition all the time.

So but you see those things you developed in the kinetic theory of gas that, let us see is a canonical ensemble where temperatures are given from outside. I have a system at a fixed temperature of gas for a certain number or number density and a given volume. That is why calling NVT and there I know temperature is driven through outside, for particles are undergoing collisions and exchanging energy.

But they are exchanging energy in the path and there is a temperature maintained, in under that condition $1/2MV^2 = k_B T$. So it is supplied from outside but here I do not know the temperature at all, I have an isolated system because my micro canonical ensemble is purely isolated, it is constant N, V and E. This is something I did not emphasize yesterday. So this is the epitome of an isolated system, it is not allowed to exchange particles N is fixed.

It is not allowed to exchange volume. And it is completely isolated and not allowed to exchange energy. So since it is conveniently isolated, we do not know the temperature of this system. We have no control of the temperature of the system. That is why in computer stimulations they will do all calculations in NVE.

But will start with the NPT ensemble and to get a constant pressure then we need to put Barostat. Then you will start with the canonical ensemble NVT and then they will remove the thermal bath, Noose Hoover whatever the thermostat and all the things and then you get simulate in the NVE, the conditions that we use and essentially these conditions. So we use the fluctuation formula but that is different here.

This again the same question he asked, this is a huge country, so this is what if you do classical mechanics **by** Goldstein, you will see. So I have this system NVE then I take a small variation, I make the volume slightly variant, very small amount but then I start the response. Then I saw this small energy I changed and I study the response.

What I am telling my small variation executed mathematically, gives me a variation of Ω and that variation is the almost fundamental important. This is a mathematical construction; we are doing purely analytical work at the highest level because you are thinking you have to be like that. So with their isolated system I mentally take little change of volume and I say how is Ω changing, I say ok, that gives me the pressure.

So how much the $\log\Omega$ will change with energy determines the temperature. This is what we call the conjugate variables, energy and temperature is the conjugate variable. They are connected in a mechanical NVE ensemble. Similarly, pressure and volume are conjugate variables. And that exactly works out, I take the derivative of $\ln\Omega$ with this dV, I get the pressure.

And similarly, energy and number of particles, they are conjugate variables and they give you chemical potential, so this is the one.

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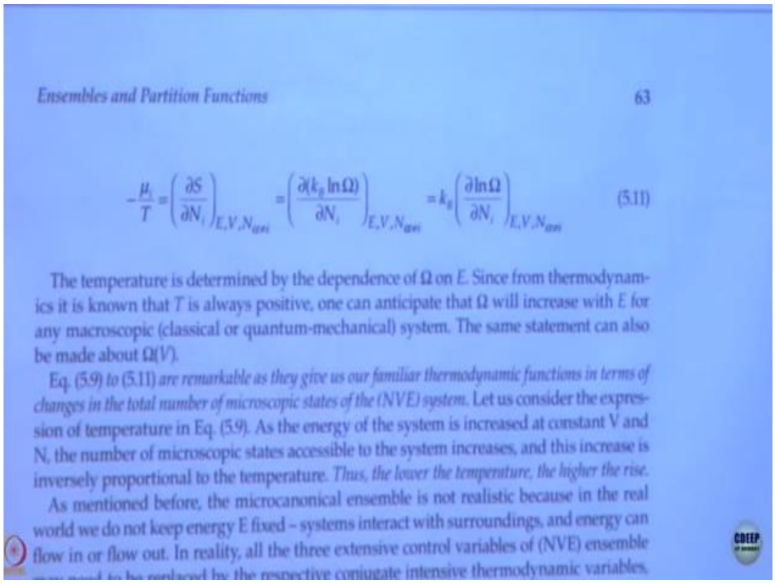

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$$-\frac{\mu_i}{T} = \left(\frac{\partial S}{\partial N_i}\right)_{E,V,N_{a\neq i}} = \left(\frac{\partial (k_B \ln\Omega)}{\partial N_i}\right)_{E,V,N_{a\neq i}} = k_B\left(\frac{\partial \ln\Omega}{\partial N_i}\right)_{E,V,N_{a\neq i}} \quad (5.11)$$

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 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 be replaced by the respective conjugate intensive thermodynamic variables.

Then, if you want in your micro canonical ensemble to calculate these things, we do not do it this way, but this is the way we use these three relations. We use it extremely and will use now in a canonical ensemble this equations, to get the subsequent and developments. So these are remarkable because they give the familiar thermodynamic function in terms of changes in the total number of microscopic states of the NVE system.

So this is the things I told you can write that, the micro canonical ensemble is not realistic because none of the real system is NVE, real systems typically are in chemistry is μ,P,T or NPT, if the number of particles change then we do the μ PT means the chemical potential, P pressure to the temperature and many other things like phase transition, many of the times we do NPT that means pressure temperature, quite far from NVE. So Gibbs went on to beautifully construct and this was I think the Marvelous thing that he did.