Basic Statistical Mechanics
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Lecture – 20
Ideal Monoatomic Gas: Microscopic Expression of Translational Entropy Part 3

Till now, we have studied quite a bit of statistical mechanics, we started from the need to understand statistical mechanics and I try to impress upon you that the great multitude of natural phenomena that we experience in our everyday life and also in laboratory experiments can be explained only by the use of statistical mechanics, I emphasize that we essentially have 2 different branches of theoretical knowledge.

One is quantum mechanics, the other is statistical mechanics and they are complemented to each other, in fact, the information from quantum mechanics is translated to statistical mechanics and that is done routinely in every day in theoretical research. Remember that quantum mechanics came in order to explain spectroscopy, similarly statistical mechanics came to explain thermodynamic properties.

So, I will briefly recapitulate some of the things and then go over the derivations of monatomic gas once again and with certain more insight and certain repetitions but I think they are important because the working of statistical mechanics is based understood in case of ideal gas in monatomic ideal gas, so it all began with Maxwell in mid-19th century, when Maxwell wrote down the famous distribution law; velocity distribution law.

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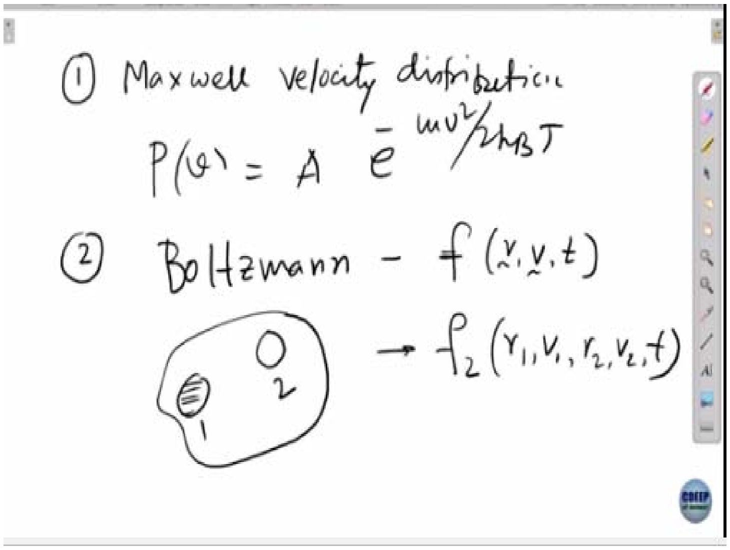

① Maxwell velocity distribution

$P(v) = A\, e^{-mv^2/2k_BT}$

② Boltzmann - $f(\underset{\sim}{r}, \underset{\sim}{v}, t)$

$\rightarrow f_2(r_1, v_1, r_2, v_2, t)$

So, the very first point that we need to think about is the Maxwell velocity distribution, so this was the quite a unique departure because Maxwell introduce the concept of distribution and the probability distribution; probability that the velocity of a particle can be within volume V and (V+dV) and that we all know is the famous distribution, where A is the normalization constant.

Now as I told you and the story goes that Boltzmann was completely taken you know bowled over by this paper of Maxwell and he carried that one paper which has the velocity distribution rest of his life, then there are certain problems in Maxwell velocity distribution, the molecules do not interact with each other or interaction between molecules giving rise to their distribution was not very clear.

So, Boltzmann took upon himself to develop a theory where these intermolecular interactions collisions between them can lead to a time evolution of the system and where the equilibrium distribution will be Maxwell distribution, so Boltzmann then tried to write down; he try to write down a distribution function that a particle at position R will have a volume v and t, r and v are 3 dimensional vectors in 3 dimensional space.

So, then he tried to derive an equation for this f, r, v, t and then he found that if you wants to describe between f, r, v, t that means if one particle, this is my tagged particle, if you want to do that, then undergoes a collision with another particle 2, so in order to describe the time evolution of singular distribution, the single particles probability of having velocity v at position r at time t gets coupled to that of the second particle.

So, then that in order to describe this process, one gets into then the second distribution now, the f, r, v, t itself, the first one already very complicated and this one is even more complicated, so Boltzmann tried to make certain approximations and that led to some advances but he was not fully successful to accomplish what he wanted to accomplish that means develop a theory of the kinetic properties like kinetic theory of gas of liquid and ultimately also get some idea of the thermodynamics.

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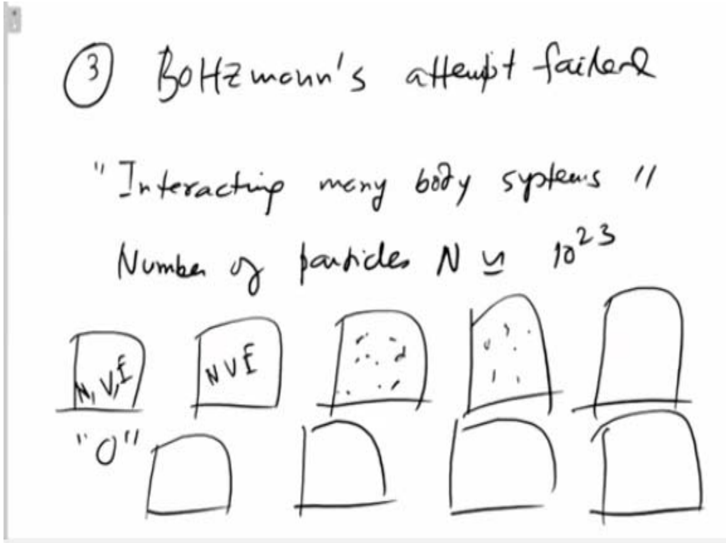

③ Boltzmann's attempt failed

"Interacting many body systems"

Number of particles $N \simeq 10^{23}$

Remember that Maxwell's distribution gives rise to the equipartition theorem that 1/2 MV square 2 kVT and so Boltzmann's attempt did not work; so let me put out that Boltzmann failed or Boltzmann's attempt failed, he derived many beautiful things, one of them is entropy and but he did not; he has got successful in accomplishing basically what he wanted to do.

So, he wanted to describe, he wanted to have it develop theory of interacting systems that molecules moving, they are interacting, they are colliding with among themselves and with the wall; they have given rise to the pressure, the effect of interactions that would give us that why carbon monoxide carbon dioxide is different from water or methanol, those kind of really; goal was not accomplished.

We do not know to what extent Boltzmann really had this goal in mind but when one looks back then we understand if Boltzmann would have been successful then that would have been a complete theory and in fact that is still a very active area of research that people are still trying and working along that line and to do a many body distribution function.

Now, when Boltzmann was trying all these things and trying to develop and did not work out, then on the other across the other side of the as I also mentioned before, the other side of the Atlantic one very, very smart person was watching the efforts of Maxwell and Boltzmann and his name is Willard Gibbs; Josiah Willard Gibbs and Willard Gibbs was interested to develop a theory of phase equilibrium and phase transition.

And he was interested not in dynamics but in equilibrium properties, Willard Gibbs knew very well, the beautiful work of Van der Waals, the equation of state but one thing that Maxwell, Boltzmann and Willard Gibbs was quite aware the thermodynamics however, beautiful and the most successful theory as Einstein pointed out this is a self-contained in the sense that you can predict the changes of entropy enthalpy free energy.

Or you can if you choose to be integrate it from 0 kelvin to get certain absolute values but they do not have any expression that means other than G = H - TS or A is Helmoltz free energy ie A = E - TS, E is energy, TS is the internal energy enthalpy, I do not have any expression, I do not have any method starting with intermolecular interactions to calculate the properties, to calculate the thermodynamic properties, to calculate the free energy, this is a serious limitation of thermodynamics.

However, beautiful and self-contained and self-consistent thermodynamics is, it does not provide us any microscopic picture or microscopy inside, so Willard Gibbs was interested also in the same thing that Maxwell and Boltzmann was interested to develop a theory of matter starting from kinetic theory of gases but where molecules interact with each other not like in ideal gas where molecules do not interact with each other.

So, then Willard Gibbs realized one thing that the reason that Boltzmann failed or Boltzmann's approach failed was that it was just wanted to achieve too much that means, it wanted to describe the time evolution of this large number of particles. Now, when the large number of particles interacts with each other like in real gas like in this room, the nitrogen and oxygen and they are interacting with each other and we are breathing, our life going on.

So, this when the particles interact with each other with a potential, then we call that interacting many body system, it is a jargon that we use that interacting many body system. So, it just means that there are very large number particles typically we are fond of saying that there are number of particles, N is typically a Avogadro number.

So, now such a huge number of particles and if we try to do Boltzmann's approach then what we means; means we would like to have a single particle motion coupled to 2 particle motion, then 2 particle motions coupled to 3 particle motion, 4, 5 like that there is a hierarchy and it is the never ending thing and we do not know how to truncate it, we do not know how to stop it without making a serious approximation and not only serious approximation, uncontrolled approximation.

But Boltzmann; Willard Gibbs realized one thing that he was interested in equilibrium properties, he was interested in the relation between pressure and density and between the you wanted to understand Vander Waals equation of state, how could he do that so, but Willard Gibbs realise one thing that if there is a glass of; I have a glass of water that the thermodynamic properties is the state of that properties of the water at a given thermodynamic state does not really need, we do not really does not seem that we need to know the details motion of the each of the water molecules.

Then, he realise something and visualise the following thing what happens if I have a very large number of my glass of water molecules, identical, identically free now, all these water molecules have the same thermodynamic property, they have the same density, they have the same specific heat but at a given time, the individual water molecules and there is this large number of water molecules in one glass and in different glasses, the water molecules are in different positions, they are not in the same positions.

And if I tag a water molecule and then I said okay, I tag water molecules and each of them I give number 1, 2, 3, 4 like that and even they start the same time then after some time, these velocities and positions of the water molecules will be different but that does not matter, the fact that the dynamical evolution or dynamical motion of water molecules different from one glass to another glass does not affect its thermodynamic properties that made Willard Gibbs realized one very important point.

And this is a brilliant observation, of the most brilliant observation that a theoretical scientist ever made that is why Einstein went over to tell about Willard Gibbs the most brilliant mind of America now, Willard Gibbs realized that then if I could now think in a of my system, my embody system, my original glass of water and I can make a mental replica of many, many, many of such water molecules many, many mental replica glass of full of water molecules.

Then, what happens my; in my mental replica in each system, the water molecules are differently moving, now that could be now then a way to describe what Boltzmann tried to do; Boltzmann tried to do take one system and try to map out the evolution of the distribution of velocity and position of the water molecules instead now, I constructed an ensemble where each microscopic state of each system is different from the other.

And microscopic state is defined by the positions and velocities of the water molecules of the Avogadro number of water molecules, now what Boltzmann tried to do; Boltzmann try to; the goal was to derive a distribution function then properties can be obtained by averaging over the distribution function. Now at equilibrium, my system this ensemble or my mental replica billions of billions of glasses are full of water molecules, billions of billions of mental replica of my original system or each in a different microscopic state.

So, instead of doing Boltzmann's approach of following the motion which is called a trajectory of each water molecule and averaging over the trajectory of the system, I can now talk of averaging over the instantaneous state of my mental replica of by ensemble of systems.

These are little tricky and these are the translation of picture from very straightforward Boltzmann’s view where you want to follow the time evolution of water molecules, each of the water molecules to a view where you now do not have time evolution, instead you have these billions and billions my ensemble of the original system each in a different microscopic state.

And now I am going to take average over the properties of the system of my ensemble, so I can go on talking about it but you need to think about it that this is my system, original system let me call it 0, then I constructed many of the mental replica, all in the same thermodynamic state, same number of molecules each of them, total volume V and may be total energy E, all of them are the same but they are in different.

They are same macroscopic state, same thermodynamic state but each of them the molecules are positioned differently, the microscopic states are different. Now, this is wonderful but what did Gibbs achieved by introducing; what did Willard Gibbs achieved by doing this thing, doing such a kind of a very abstract logic, what he achieved is something just very, very far-reaching.

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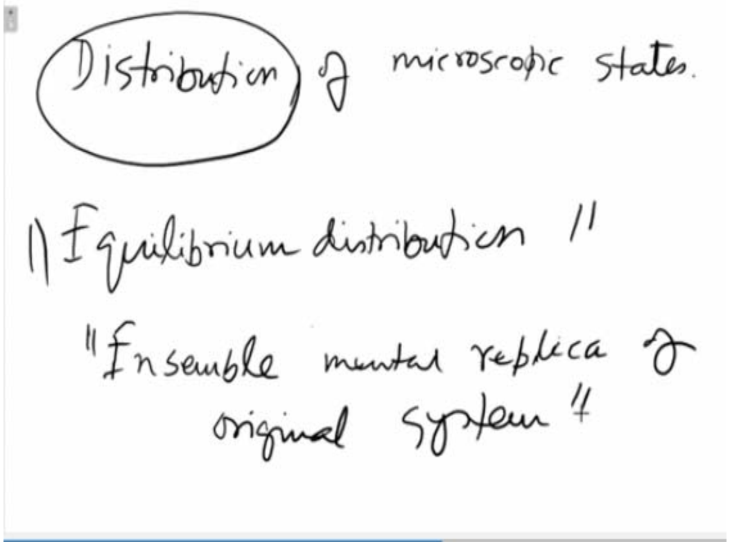

Distribution of microscopic states.

1) Equilibrium distribution "

"Ensemble mental replica of original system"

He now said okay, I will now follow more or less what Boltzmann did, I will say now, I have all these systems in different, each of my system in different microscopic state but now I can start talking of a distribution of microscopic states. So, from a trajectory dynamical evolution I go to a distribution for example, I can now even in NVE, I can say what is the; for example temperature of a system or I can talk of what is the pressure of one of my system.

So, I can now go from; I can start talking about distribution of different properties because microscopic state of each of the system is different, so the basic idea then that we go over to a distribution, we go over from a very; these distribution that we are talking of now because every system is in different microscopic state but they are at equilibrium, that is the beauty of it they are in equilibrium.

I do not have to talk of dynamics, I do not have to talk of time evolution, I do not have to talk of predicting, I do not have to solve Newton's equations or I do not have to solve these very difficult equations that Boltzmann to develop, so the distribution so what I achieved that is by constructing of the ensemble is that I can now talk of equilibrium distribution okay that is a wonderful thing.

Because suddenly again these concept of probability that is what Boltzmann was criticized so much for but it was also introduced by Maxwell, so concept of probability distribution comes back and it now Gibbs could take it much further. So, Gibbs gives introduced the concept of ensemble which is the mental replica of original system and now one comes to this beautiful; okay now how will construct the distribution?

And remember what experimentally one does is an averaging but that is we get the property of a system like the pressure by a temperature by at equilibrium by measuring it over certain time, so the experimental things are at the time averaging but here we do not have time anymore, we got rid of time, we say time is not important for equilibrium properties, we construct it ensemble and we are going to average over all these members of the ensemble which are identical thermodynamic systems.

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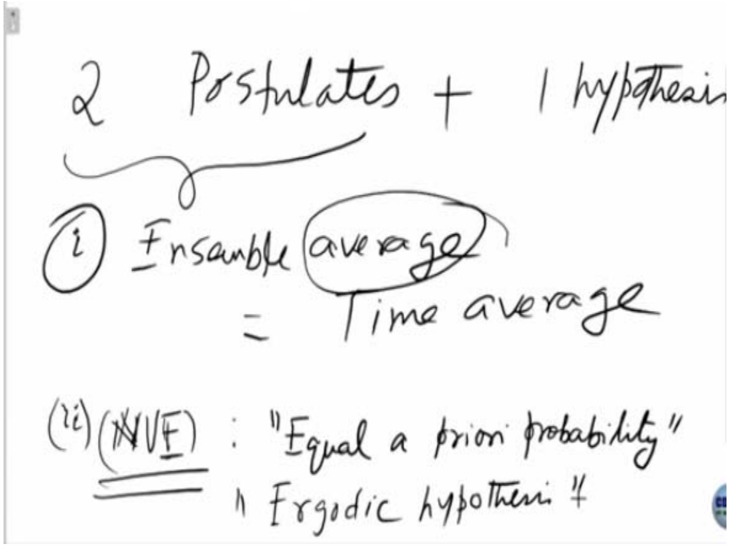

2 Postulates + 1 hypothesi

(i) Ensamble average
= Time average

(ii) (NVE) : "Equal a priori probability"
" Ergodic hypothesis "

So, now given that condition how do you go about, first thing that Willard Gibbs ends, these are now we have discussed 2 postulates, we will not spend too much time on that anymore and 1 hypothesis, the Ergodic hypothesis and these 2 postulates we have discussed and this also given in the book you know fairly detailed form is that one is the ensemble average that the average over the ensemble is ensemble average equal to time average and that is the first postulate.

Second postulate is kind of interesting that ensemble average allows you to go through over a large number of microscopic states of the system because each system of my ensemble is in a different microscopic state now, this is something you should think a little bit about why, why should you, you should not believe what I am saying, why should it be that the different these billions and trillions and trillions of mental replica my systems which constitute the ensemble, why they should be in a different microscopic state.

The reason is that in a large system, the number of microscopic states accessible to the system is huge, they are not just trillions, the trillions of trillions like a one cc water molecules that means it is something like 10 to the power 22 water molecules, their microscopic states is huge 10 to the power 100 or so, so there will be there are much more many more microscopic states than the number of systems that you need in ensemble.

So, naturally all these system for the microscopic states of the system are distributed into different microscopic states, so that part is okay, that part is actually these are the things we know much later we know through computer simulations and many other information that filled in from the last more than 100 years. So, ensemble average equal to time average is the first postulate.

But then what is the probability, now I need to talk of probability because I am trying to talk of averaging, so I need a probability distribution. What is the probability; that a system is in a given microscopic state that is where now Willard Gibbs made another brilliant observation, he said okay, let me construct the following every system as a constant number of molecules N, volume V and energy E.

And then all the systems of my ensemble at the same energy, same number of particles and same volume V, now since they have the same energy, he could now postulate, he had no other option but 2 postulate they turned out to be correct is equal a priori probability all the states are every microscopic state is equally probable, they are all have the same energy, so this was wonderful.

So, now I have equal measure of all the microscopy states that now allows me to calculate on some level average because I have huge number of microscopic states, all are equally probable, if I can get a thermodynamic property in each of the system in a different microscopic states, I add them up and divide by the total number of systems in my ensemble I get the ensemble average that we discussed before, if I not discuss that I am discussing it now, well and good.

But now things got a little murky because ensemble average is the time independent but I am telling it is equal to time average so, if I have to make it an experimental time then I have to make sure that in my time averaging of my original system that one system which I started with in my original system, I must wait long enough but all the microscopic states or a good number of the, fraction of the microscopic states is explored.

So not only that what happens if I want to go from one microscopic state to another microscopic state in my original system, there is a large barrier and there are some states I cannot access, then of course if I do ensemble averaging my system is in that state but in my time averaging that state might not be that easily accessible, so then there; so I in order to implement one in order to ensemble average, time average in order to implement ensemble average, I needed equilibrium probability.

But now my time average is in danger, so then it was started Boltzmann and I think it was Gibbs that the hypothesis was introduced is called Ergodic hypothesis, so the statistical mechanics is the 2 postulates and 1 hypothesis, ensemble average and time averaged and equilibrium probability and then your; the Ergodic hypothesis okay, so that is essentially that after doing that, what did you do?

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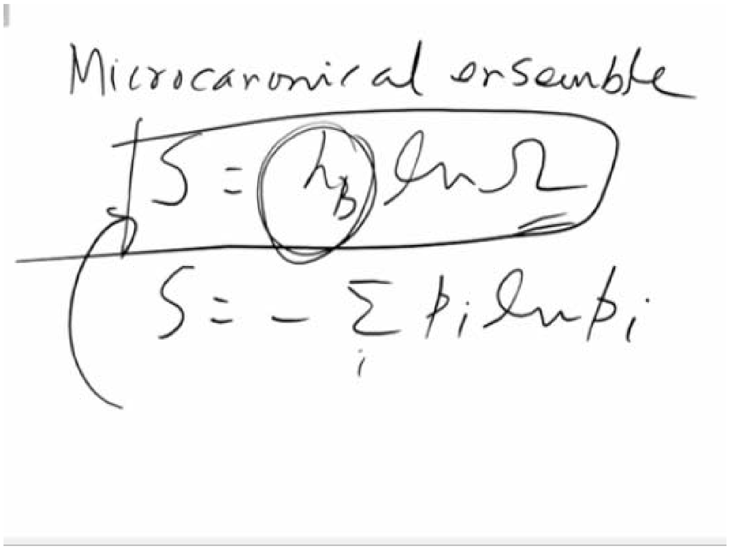

Microcanonical ensemble

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

$$S = -\sum_i p_i \ln p_i$$

After doing that we went on to develop with the postulates when to develop the different ensembles; microcanonical ensemble, canonical ensemble and canonical ensemble and some others we will do later as I said, microcanonical ensemble that we had omega is number of microscopic states in the system and remember that this is that is the reason this k_B is the Boltzmann constant okay and Ω is the total number of microscopic states.

And this is a beautiful relation or the most fundamental relation in the; of statistical mechanics and one you can derive it by some simple derivations that we have done that by writing $S = P_i \ln P_i$ in probability distribution but they are identical because if all the states are equally probable, then Pi is 1 over omega and then you from here you get to that one, you can as well take these in the equilibrium statistical mechanics you can take it as a postulate also or a starting assumption.

Now and this of course, originally it was derived by Boltzmann in kinetic theory approach, then we go into do this omega Ω can be calculated in some cases that we did not do too much, we will do some later.

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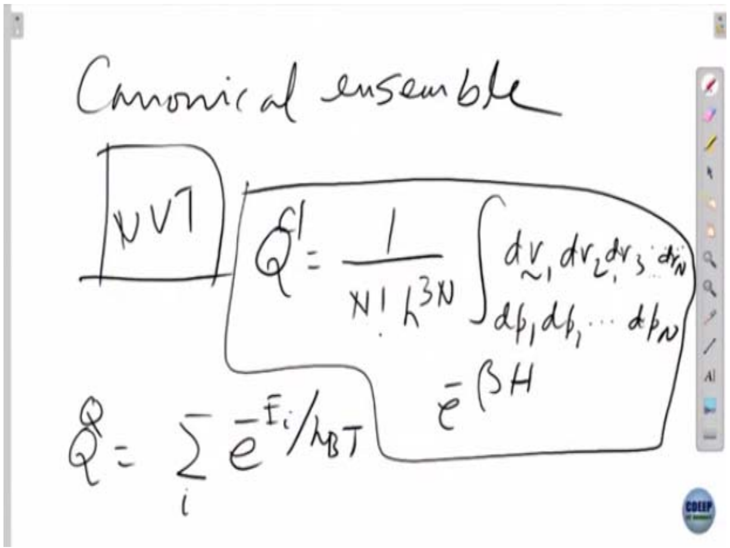

Canonical ensemble

$\boxed{NVT}$

$$Q' = \frac{1}{N!\,h^{3N}} \int d\underset{\sim}{r}_1\, dr_2\, dr_3 \cdots dr_N \; dp_1\, dp_1 \cdots dp_N \; e^{-\beta H}$$

$$Q = \sum_i e^{-E_i/k_BT}$$

Then we went to canonical ensemble where we separated the; now we allowed the systems to exchange energy well for me there is a masterful construction again done by Gibbs who put these different canonical ensemble energy is exchanged touch with each other, allowed the energy to exchange and then put it then insulated it and put it in a bath, so that the one gets a temperature, it reaches an equilibrium with a temperature T with a temperature bath, then you put an insulation around it.

So, this each member of the system interacting energy with the other but the temperature is kept constant in equilibrium and then one goes on to develop a theory of this partition function and other things, so the partition function that we derived is the following, this and in if I write in terms of quantum system energy levels, so I is sum over all the energy levels, so this is the classical and this is the quantum.

They are identical as you can see that these can be written in terms of the e to the power minus beta V put in a wave function here and putting a wave function on the two sides and then integration over these things and then this becomes e to the power minus Ei by k_BT and when you do quantum, beta stat mech, we will get back to that, little bit more seriously but right now I think we do not need to worry about it.

So, we can take these as the partition function of the classical partition function of the system, now what we will do now; what we have done before but I want to revise little bit after this preliminary division and starting with this equation, these classical expression of the partition function and we have already done that the partition; how the partition function is related to free energy and all those stuff but I want to go through the 2 important things.

Because that is where working of statistical mechanics becomes very clear and I want to go through the derivation of the ideal monatomic gas where we can get the partition function exactly done and then we can get from there the entropy, we can get the free energy, we can get the entropy, we can get the equation of state, so many other things and some of these things are extremely useful new things.

And in the process, we get an expression for entropy, microscopic expression for entropy even for ideal gas law which thermodynamics could not give us, thermodynamics has no way to give the absolute value of entropy, so what we got here in the process is enormously important and it is very important that even though it is the ideal gas monatomic and diatomic and polyatomic that we understand them well because from there starts the understanding of the rest of the system.