Basic Statistical Mechanics
Prof. Biman Bagchi
Department of Chemistry
Indian Institute of Technology - Bombay

Lecture – 18
Ideal Monoatomic Gas: Microscopic Expression of Translational Entropy Part 1

Till now what we have done; we have first discussed that why one needs stat mech, one needs statistical mechanics because we put in bluntly we cannot even solved the 3 body interacting system that means, 3 layer zones of particles we cannot solve. Boltzmann solved in dynamics with great difficulty and lot of approximations the 2 body problem, in equilibrium stat mech, 2 body problem becomes equivalent to a quadrature which then be done in computer.

But in simple problems like Lennard-Jonnes we cannot even do that analytically, so this is one reason that one has to have statistical, there is a technical reason and there is a more profound conceptual reason is that even if we could solve Newton's equation for all the particles, avoid a number of particles, what do we do with that because that contains lots of irrelevant information.

This term in statistical mechanics; what is relevant and what is irrelevant is an extremely important concept, we have to extract from lot of things that are going on something which we observe in real world and also what is experimentally accessible okay. So, having said that, so that was the difficulty, Boltzmann who was motivated by Maxwell's velocity distribution to introduce the probabilistic description.

He took it a half way but he could not do very far as I said other side of the Atlantic our great Willard Gibbs realized that there could be a different way of doing the things, Willard Gibbs did completely equilibrium statistical mechanics, this has to be understood clearly while Boltzmann was trying to do transport properties, even today transport properties are time dependent statistical mechanic starts with Boltzmann’s kinetic equation.

So, this is a very important distinction one makes, so Willard Gibbs realized that you know that many different systems which observe they have same macroscopic properties, they must have been different microscopic states, so this is the different microscopic states of the system that belong to a given macroscopic state then there must be way to look into equilibrium distribution in terms of a probability.

So, the important breakthrough then came going from the trajectory or time dependent stat mech or time dependent distribution function which gives time averaging, from there one wants to go to an equilibrium distribution, so Willard Gibbs realized that the simplicity gets in doing the equilibrium distribution that could allow him to do a probabilistic description.

And by that time early 20th century his book was published, I think 1903 by that time probability theory was well developed; mathematics or probability theory central limit theorem and all other things were well developed. So, he had now then he could rely on that so he then said he if I want to describe a probability distribution then what are the probability distribution I want?

I want a quantity, which is if I could talk in terms of thermodynamics in terms of entropy, energy fluctuation, these kinds of quantities. He already had one result in front of me which is Boltzmann definition of a function entropy, to what extent that entropy already thermodynamics was rather well developed, entropy function or heat function was well known that correspondence had been had occurred to Boltzmann, I am not too sure about probably it was.

But suddenly Willard Gibbs realized it, so he had that formula $S = k_B \ln\Omega$ where k_B is Boltzmann constant, very appropriately put there and so now he had to find the omega and of course and rest of the thermodynamics, how did he go about it? So he said okay, let me construct an ensemble which is a huge collection of the systems, each system has characterized by same number of particles N, same volume V and same energy all are constant.

Now and then in this ensemble, he said okay, how can I describe now probability distribution, he then introduced 2 postulates; one is that he wanted to do the average, how do I do the average instead of a one way; of course time average follow one system for a very long time, the other one you follow many identical systems now, the idea is that many identical system billions and billions of identical systems of NVE, they are all in different microscopic states, why?

Because number of microscopic state is enormous, it is billion to the power billion, so all these systems will be in different microscopic states, so that is a very critical understanding that all my; I can construct an ensemble means the collection of identical particles all of them in different microscopic states, then if time averaging that I do by following in one system, a trajectory for infinitely long time or very long time that can be replaced by averaging of these different systems.

Low and behold, what is the advantage; instead of following the trajectory which is a time dependent quantity, I am going to talk of something which is time independent and that is the enormous simplification, I do not have to solve Newton's equation anymore which was the prescription of Boltzmann, then when he did that of course, he had these ensemble picture of systems in different microscopic states and averaging over them is what is today is Monte Carlo simulation.

Trajectory is molecular dynamics simulation however, in order for the trajectory to be equivalent to ensample; ensemble I have in all different microscopic states, you have to understand these are still at a conceptual level, things are assumed, these are postulates and the verification comes you know with the results and comparison of the experiments, then he said that okay my trajectory then must go to all the microscopic states that I am representing in ensemble.

Then comes the second postulate which is called equal a priori probability that means all microscopic states are equally probable to be visited by the system and in a long trajectory, there will be visiting equal number of times, these are limiting things, infinite number of states, infinite time, infinite number of systems, so everything asymptotic where things can be proven exactly.

Now, when I say things can be proven exactly that is of course happen only in 1981 one case, more than 100 years later almost, so these thing that a system equally probable but equally probable does not mean that it will be visited, so 2 things I jumbled together to separate it that comes under the hypothesis that all these states will be visited that is the Ergodic hypothesis that each state will be visited in the course of time.

That means, if system will not get stuck in a minimum that haunted us in molecular dynamics simulation that is why he cannot do phase transition just in NVE because it gets stuck in one minimum, then all the new techniques like umbrella sampling, meta dynamics that have been invented and created are essentially to take the system out.

So, the reason that one has to be conceptually clear and study these things even more now than before is because of the connection with the modern stat mech and which is so powerful now it has reaching the state of quantum chemistry in the sense, the packages are being available, I see my students or other students getting like one of my students without understanding too much got great results in a rotation of carbon monoxide, nitric oxide and cyanide ion in an aqueous binary mixture, something which was unthinkable, few years ago such complex system.

But that can be done now, I cannot claim that the student knows very great of the concept of statistical mechanics, can do Mode coupling theory and analytical work but the results at their hand and at the end of the day, results are that are important that is what everybody wants from you, so statistical mechanics has come to that level now.

So, we have to understand this little bit more detail to have a sophisticated, certain sophistication or understanding sophistication in our; so then from that microcanonical ensemble using S is equal to k ln omega, we derived the expression of pressure, expression of energy, dS/dT is energy, so everything is number of microscopic states omega. Well done, if that part was done but then NVE is a very artificial system.

Because it is a system which has same number of constant number of particles which is not change a constant volume, constant energy that is not the real system, real system which volume is fluctuating, the phase transition ice melting, density goes up by 10 percent, then you have the energy fluctuating because the systems are far more open in at least in chemistry and physics.

And in chemistry we have also systems, so a chemical reaction taking place, so N is changing, so NVE microcanonical is too restrictive, so the next stage Gibbs did construct a beautiful and brilliant monumental construction that he went over to constructing a super system out of NVT, where energy exchange allowed, we put all NVT together allowed interaction between them to flow of energy then put it whole thing in a bath, let it be equilibrate, then put an insulator around them.

So that the whole super system is an NVE, Italian size N is my N number of particle, then Italian size N by normal N, Italian size N by V, Italian size N by E are the number of particles volume and energy of my super system, now we formed a micro canonical ensemble of the super system and then show it by doing constant method of constant variation or Lagrangian multiplier we can get a quantity called partition function which is logarithmic Gibb's free energy and whose derivatives gives all the thermodynamic properties.

After doing that he was genius of highest degree, he did not waste his time in seeing movies or other things, he was single and he was always going coming back and forth from Sterling laboratory probably he had all the time but this is amazing what did he; he did a grand canonical ensemble where now number of particles also is allowed, the same thing was done and he got the beautiful, beautiful expression of equation of state $PV = k_BT$.

We remember all these are energy dimension PV equal to k_BT and grand canonical partition function, then we also discussed NPT which is used most in simulation and experiments. So, till now we have done all the groundwork still keeping things fairly simple, we have done 4 ensembles and we could have spent more time on NPT but okay that is I told you that it is essentially same construction.

But the thermodynamic potential of NPT is Gibbs free energy, so thermodynamic potential of microcanonical is entropy, thermodynamic potential of canonical is Helmoltz free energy thermodynamic potential of grand canonical is PV and thermodynamic potential of NPT is Gibbs free energy, that is what exactly thermodynamic tells us that exactly comes out to be true.

So, one of the major goal of statistical mechanics is to explain thermodynamics, remember one of the things that you read in thermodynamics, I do not know we had a great teacher

Professor Mihir Chowdhury who again and again told us one thing that a thermodynamics cannot give you anything a priori, it give the results, it gives certain relations, so thermodynamics does not give you what is the value of entropy, it cannot give a, unless of course you integrate over CPT.

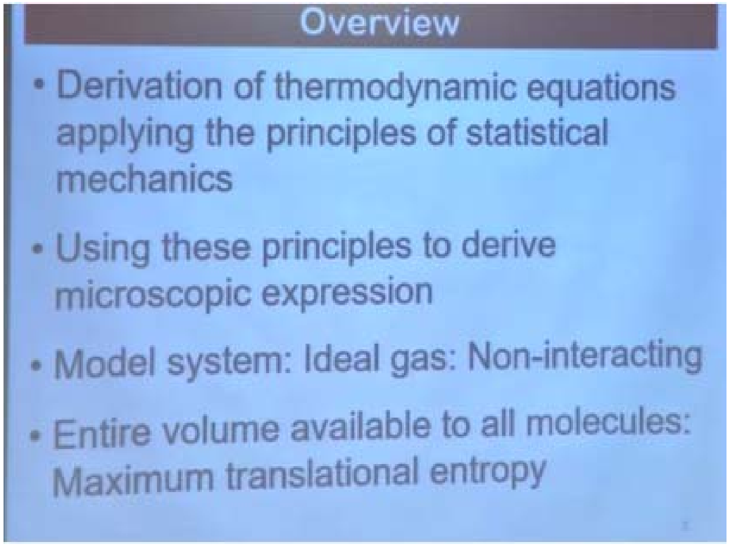
It does not give, so that means there is a; it is not a theoretical machinery that gives you anything from first principles that is the correct statement, it does not have first principles, it has certain working principles which equal laws of thermodynamics which will be fun to teach sometime the thermodynamics in a very deep and fundamental level because it is a wonderful subject.

However, here we do not have a for that time or course content for that but here thermodynamics then comes out of statistical mechanics, so one of the first idea of statistical mechanics was to explain thermodynamics and what it does; it does in a beautiful way; starting from microscopic principles, intermolecular interactions which gives you energy levels, they knew everything flows you get all the thermodynamics exactly. So, these are the theories we are going to do applications of statistical mechanics and we will do the simplest thing first which is monatomic ideal gas, ideal gas, monoatomic.

(Refer Slide Time: 14:10)

So, these two things are very important, so this is what we are going to do and it is an extremely less steady and very, very nice and I saying when we studied these things, we thought is useless when then later much, much later when I did postdoc on drug DNA intercalation, okay.

(Refer Slide Time: 14:38)



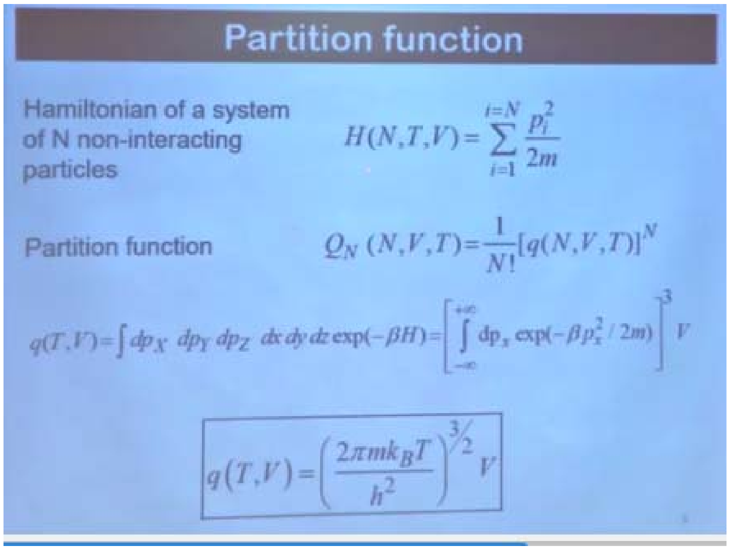
Overview

- Derivation of thermodynamic equations applying the principles of statistical mechanics
- Using these principles to derive microscopic expression
- Model system: Ideal gas: Non-interacting
- Entire volume available to all molecules: Maximum translational entropy

So, we will do the; this is the following thing what we will do today; derivation of the thermodynamic equations applying principles of statistical mechanics, these to derive microscopic expression, model system we will do now, entire volume available to all the molecules maximum translational entropy in ideal gas, these are very important thing again because just you know in BARC, I gave the lecture on where I had a path which is diffusion and entropy.

There is a very hot topic now even in active matter and everywhere diffusion and entropy, what is a role entropy place and okay, so what goes in there, the entropy called excess entropy, an excess entropy, entropy system minus the entropy of the ideal gas and diffusion is e to the power excess entropy, this is amazing how these things want you come back to get you the results. So, you know those of us who thought that ideal gas, mono atomic gas is not important we are using it every day now okay, so let us now do these things.

(Refer Slide Time: 15:42)



Partition function

Hamiltonian of a system of N non-interacting particles $H(N,T,V)=\sum_{i=1}^{i=N}\frac{p_i^2}{2m}$

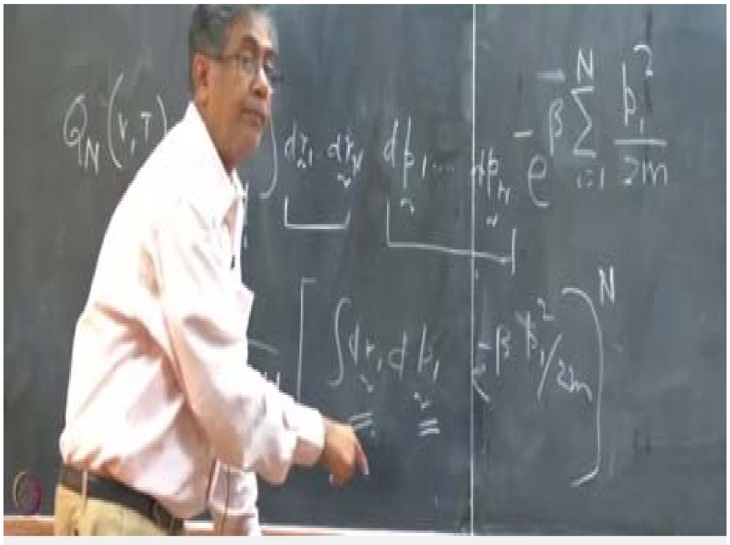
Partition function $Q_N\,(N,V,T)=\frac{1}{N!}[q(N,V,T)]^N$

$$q(T,V)=\int dp_X\ dp_Y\ dp_Z\ dx\,dy\,dz\exp(-\beta H)=\left[\int_{-\infty}^{+\infty}dp_x\exp(-\beta p_x^2/2m)\right]^3 V$$

$$\boxed{q(T,V)=\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V}$$

Hamiltonian of the system is N interacting particles is H NTV is equal to N number of particles, so Hamiltonian is just kinetic energy, there is non-interacting, so there is no potential energy i.e. $H(N,T,V)=\sum_{i=1}^{i=N}\frac{p_i^2}{2m}$. If they are not then, partition function is just N over integration over all the particles.

(Refer Slide Time: 16:07)



So, partition function of N number of particles, Chinese people did tell you know, nothing to worry about India because most of the Indians are sick, which I think is by and that is true, I myself got sick yesterday, so this is the configuration part and this is the momentum part and then these are function of all r^N that we will write like that and function of without rewriting, so this is the integration that we have to do.

So, N particle integration over N vector of 1 to N, momentum of N number of this and this is the Hamiltonian, then I hope you understand, this is very important because this will be repeated again and again, it will repeated today and it will be the important class that will starts on Wednesday morning with the Meyer's cluster expansion theory, we will use this again and again and again and again and again okay.

Momentum 3 and integral here, 3 and integral here and this is the Hamiltonian, in my case Hamiltonian is just kinetic energy and then you can see this will come out straight with a; since this is additive, I can have to the power N, I hope you understand additive means, it is just multiplication, this is the thing, is it clear this thing how it is happening because this will happen again and again that is what I am spending some time here.

$$Q_N\ (N,V,T)=\frac{h^{3N}}{N!}[q(N,V,T)]^N$$

$$q(T,V)=\int dp_X\ dp_Y\ dp_Z\ dx\,dy\,dz\exp(-\beta H)=\left[\int_{-\infty}^{+\infty}\mathrm{dp}_x\exp(-\beta p_x^2/2m)\right]^3 V$$

$$q(T,V)=\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V$$

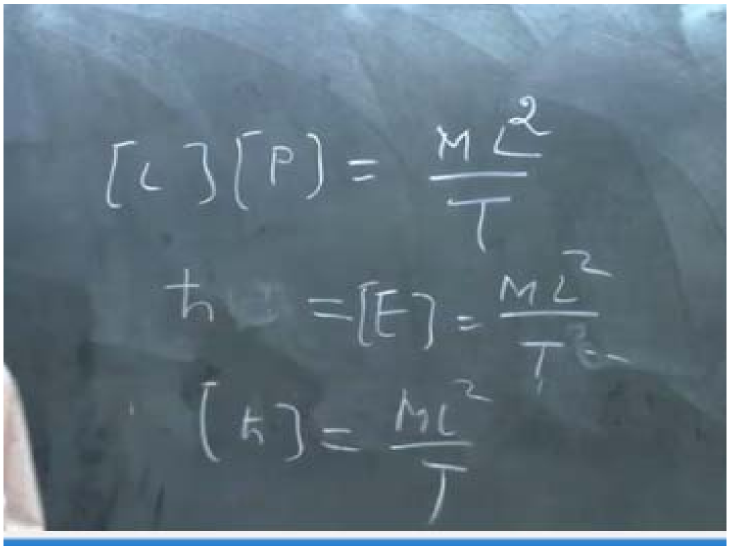
What we have done that since this is sum, all of them have the same mass, now I can write it as a product and then the product means, there is a N number of them okay, this is H to the power 3N here that has been missed we have to put that back, this indistinguishable thing called Boltzmann's factor he put it by hand, with then quantum mechanics came, it became okay. The basic idea is that you do not get an extra state but just by exchanging 2 particles in the by keeping everything identical.

So, permutation factor is this thong and we have H to the power 3N and there is a great new reason for H to the power 3N, anybody can tell why H to the power 3N should be there and must be there? A very nice and elegant, very simple explanation you guys did text stat mech course know, yeah absolutely, it is close to the answer.

Real answer that it has to be dimensionless quantity, see we put log in front of that, you cannot have a dimensional quantity after log or in exponential, there has to be dimensionless that the first thing, we usually ignored that fact very much. Second; that we actually normalize the volume integration by the volume in the cell and the following the cell is given by Planck's constant.

And if you do that this quantity that Q, Q is one of them, so let me say, so let me also put it here H 3N, N factorial then now, dr^1 dp^1 e to the power minus beta p1 square by 2 m the whole thing the exponent, this is to the power N because the N particles is here okay. Now, this is volume, this is momentum okay, now if I make now, this is L cube, this is momentum cube.

(Refer Slide Time: 20:58)

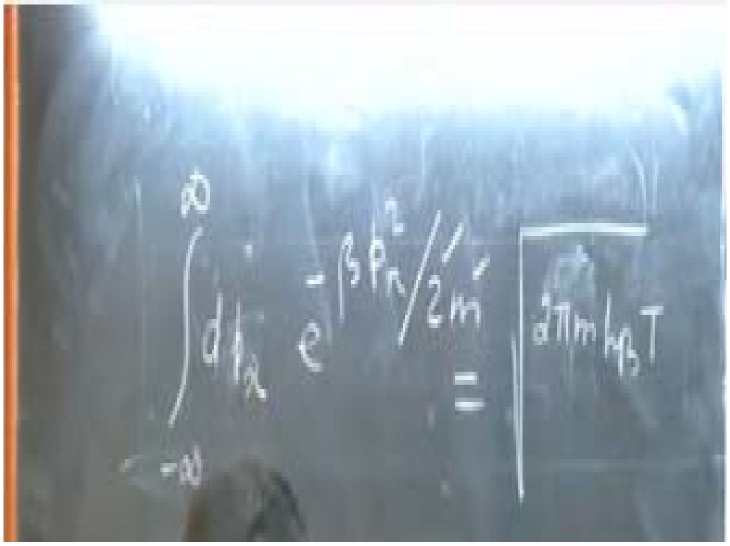


If I make length in momentum then what is the dimension of length momentum okay, so length and momentum, so dimension of length dimension of momentum is ML by T right, yes, so this is the dimension of; this is also the dimension of the Planck's constant, so momentum L by T; ML by T where energy is ML by T square, ML square right that is what I was seeing something is missing, I was mumbling ML square.

Now, in Planck’s constant remember H omega is energy that is ML square by T square okay, that means we are having that is why H, dimension of H bar, with this 1 T goes out right, you get ML square by T, this is also called the dimension of the action, so that is the volume in the phase space which is normalized, there should be H to the power 3N here okay. Now, we most of the time do not write it, I actually do not like to write that one but it is okay, this is the dimensionally correct one has to be.

So, now one does this integration of one particle, this is a single particle that decomposition is possible because this is non-interacting when you do that, then dp_x dp_y dp_z dx dy dz e to the power minus beta H, so one of them; this one gives volume, so that volume comes out then these integration is same integration because next decomposition comes p, p momentum square same as px square py square plus pz square, right.

(Refer Slide Time: 23:02)



And px square, py square pz square, so this integration is this one, what is this of this integration, value of this integration, rhp pi by A, yeah so root over pi by A means, this is 1 over k_BT, 2 here, m here, 2 pi m k_BT, right root over pi by A, both are A, this also comes in here yeah, $2\Pi m k_B T$, so this is the integration, that integration in its full glory comes here and since it is root over 3 of them; 1, 2, 3 of them becomes cube and since root become 3 by 2, I have to put Planck's constant H to the power 3N here that goes here at h square okay, so this is the q I have to; 1 over N factorial in front of the Q, this is the partition function of the monatomic gas.