Statistical Mechanics
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Lecture - 38
Interacting System – Part I

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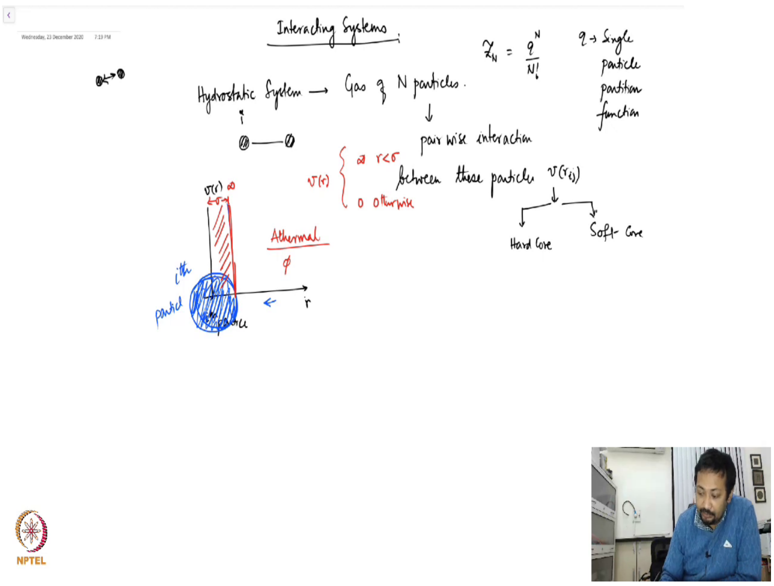

So, now, today, what we are going to talk about is Interacting Systems. It is in no means it is going to cover all possibles of possible interacting systems, but it is just to give you a flavor of how you treat interacting system, even to this extent we are going to consider weakly interacting.

Now, so far in all the systems that we have considered particularly in the canonical ensemble as well as in the micro canonical ensemble, we considered all our particles to be non-interacting, so that the advantage was in the canonical formalism. We could write down the particle partition function Z N is equal to q to the power N divided by N factorial, the N factorial essentially was because of the indistinguishability of the particles and q to the power q was the single particle partition function.

So, hopefully you will recall all these details, but in real life ideal gases and ideal things are really ideal. In the sense that they are just a model that we can do on pen and paper, it gives you a nice feeling that you have an analytical result but, in real life things are very difficult.

You have interacting systems with particles interacting with each other. So, the idea is how do we treat such things. So, we will take the example of a hydrostatic system for example, a gas of N particles and each of these particles interact there is a pair wise interaction between these particles.

We will call them let us call v of r ij. Now, usually mostly this pair wise interaction is typically either taken as a hard core which again gives you certain advantages or is a soft core. A hard core potential is if you plot the potential as a function. So, let us say you place this particle i-th particle and this is the distance from the center of the ith particle and you are plotting v of r you say that there is a certain size of this particle.

So, therefore, we will say so, there is a certain size of this i-th particle and no another particle can come and sit in this inside this volume. So, essentially we say that the potential is infinite. It is infinitely large, high so that you cannot have any kind of penetration in this part, right. Clearly so, v r is infinity for r less than sigma we will say that the size is sigma and is 0 otherwise.

This is one type of modeling and this is typically called a hard sphere system there is an advantage over here because your effectively your potential goes to infinity. Therefore, you see in the canonical ensemble we always used to write e to the power minus beta v of r, but then since v is infinity beta does not play a role.

So, such systems are typically a thermal which means all the properties that you see does not depend on the temperature, but rather it depends on the volume fraction of the particles.

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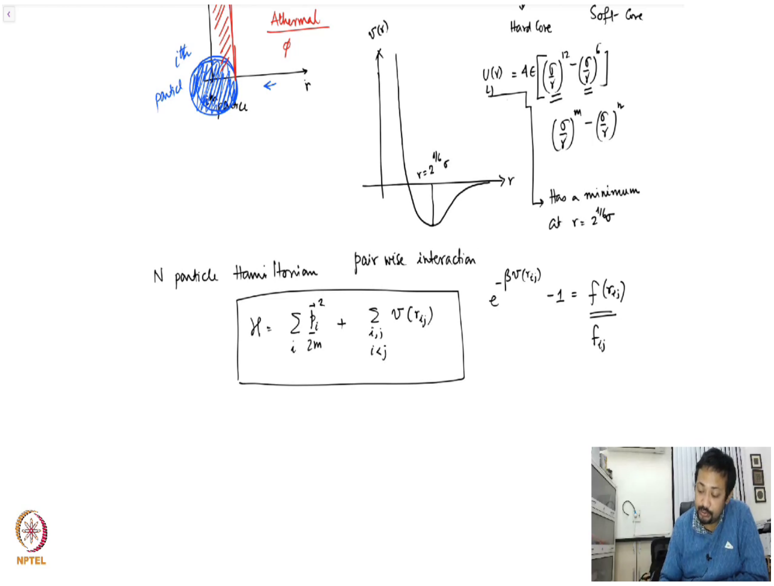

Now, the second type of interacting systems that people typically model are what are called soft core. For example, one of them is what is called Lennard-Jones potential and that is sigma over r to the power 12 minus sigma over r to the power 6. There are various modifications they are also called m n potential with this being m and the n being to m. So, this is the repulsive part and this is the attractive part.

So, the generalization can be this, but these are all generalizations of this, but the bottom line is if you plot now you see this part the potential has a minima this potential has a minimum at r is equal to 2 to the power 1 by 6 sigma not exactly sigma, but sigma. So, this potential is very steep, but it shows a attractive basin and then vanishes and this is where it is 2 to the power one sixth of the sigma.

Now, this is a soft potential, right here of course, your temperature will play a role you will have a phase transition or all the properties will depend on the temperature of the system unlike your hard sphere. So, the question now is how do you handle such a thing? So, let us start and our starting point again is the N particle Hamiltonian which is given by sum over i p i square over Z m plus i, j; i less than j, this is the interaction and we will call this as v of r ij.

Before we go further we define a function e to the power minus beta of v r ij minus 1 as f of r ij. The alternative notation that we are often going to use is instead of f of r ij we will write them as f of ij, but that comes later on good. So, we have this interaction and clearly you see that I am considering only pair wise interaction.

So, there is only pair wise interaction in the system I mean you can cook up any more complicated interactions which three particle, four particle interactions, but it suffices for us to consider such a simple system.

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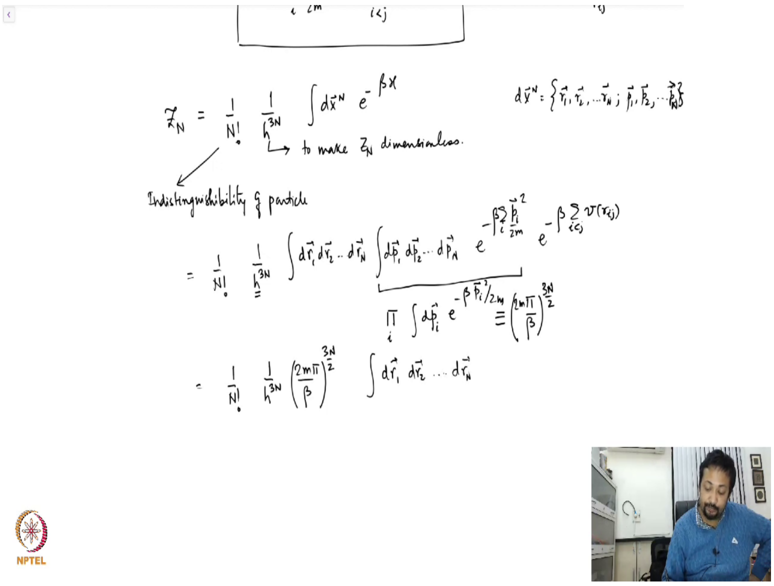

Let us calculate the N particle partition function. The N particle partition canonical partition function is 1 over N factorial 1 over h to the power 3N and if you have forgotten how this comes then factorial comes from the indistinguishability of particles.

This factor is essentially to make Z N dimensionless because after all k b t l n z n is going to give you the free energy and then of course, you have d of X N e to the power minus beta h where this vector is now the set r 1, r 2, r n, p 1, p 2, p N. If I work it out explicitly I have dr 1, dr 2, dr N integral dp 1, dp 2, dp N.

And, then the Hamiltonian is sum over i p i square over twice m minus beta and then you have minus beta i less than j v of r ij, right. Now, this is the part which is doable it is essentially product over i dp i e to the power minus beta p i square over twice m. So, it is three integrals and I know what is this is going to give.

So, I can immediately write down this as this h to the power 3N is going to. So, this is going to be 2 square root pi by a each of this integral is going to be pi and then a is going to be beta twice m pi 3 by 2; there are N such particles so, you are going to have 3N by 2. So, this integral is going to be 3N by 2.

So, I am going to have 1 over h to the power 3N twice m pi over beta raised to the power 3N by 2 integral dr 1, dr 2, dr N is e to the power minus.

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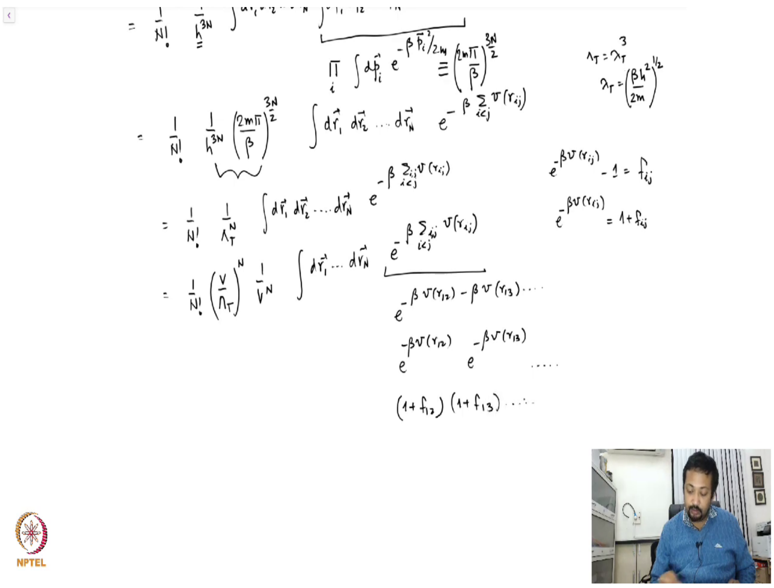

Then we continue with this ij v of r ij. This part we are already very familiar with and this takes the form 1 over N factorial 1 of a lambda T raised to the power N, where lambda T is the thermal de Broglie wavelength thermal de Broglie volume and I have dr 1, dr 2, d of r N e to the power minus beta sum of a i less than j v of r ij.

So, there is a double summation i comma j as well as i less than j. Now, lambda T is lambda T whole cube, where lambda T is beta is going to be beta h square over twice m raised to the power 5. We can recast this so that things are familiar with our ideal gas result we write this as V over lambda T raised to the power N and 1 over V to the power N dr 1, dr N e to the power minus beta sum over ij i less than j v of r ij.

If you expand this sum you see this becomes v of r 12 one particle number 1 interacting with particle number 2. Then you have beta of v r 13 so on and so forth and all of this factor out as beta v r 12 minus minus beta v r 13 so on and so forth. Now, recall we had defined the function beta of v r ij minus 1 is going to be f of ij.

So, clearly this means I can use this to rewrite e to the power minus beta v r ij as 1 plus f of ij. So, I have 1 plus f 12 1 plus f 13 all possibilities.

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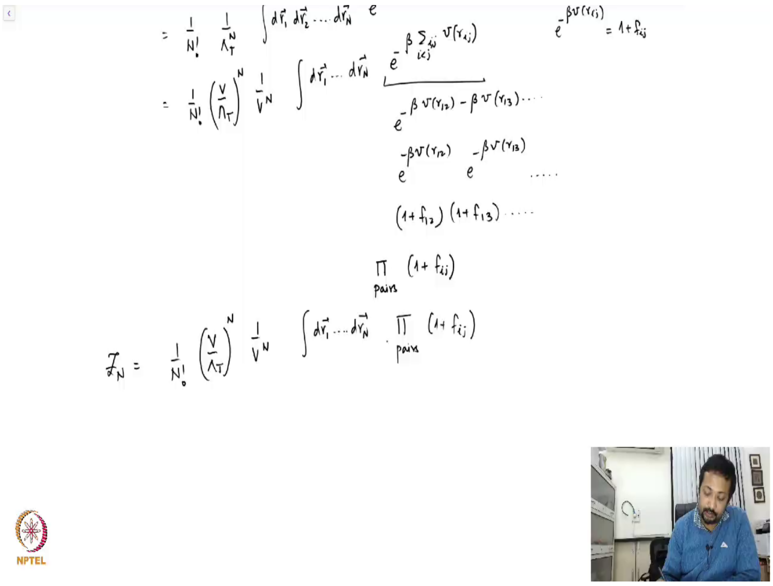

So, that this becomes product over pairs 1 plus f ij. So, the canonical partition function then takes the form 1 over N factorial V over lambda T raised to the power N 1 over V to the power m dr 1, dr N product over pairs 1 plus f of ij.