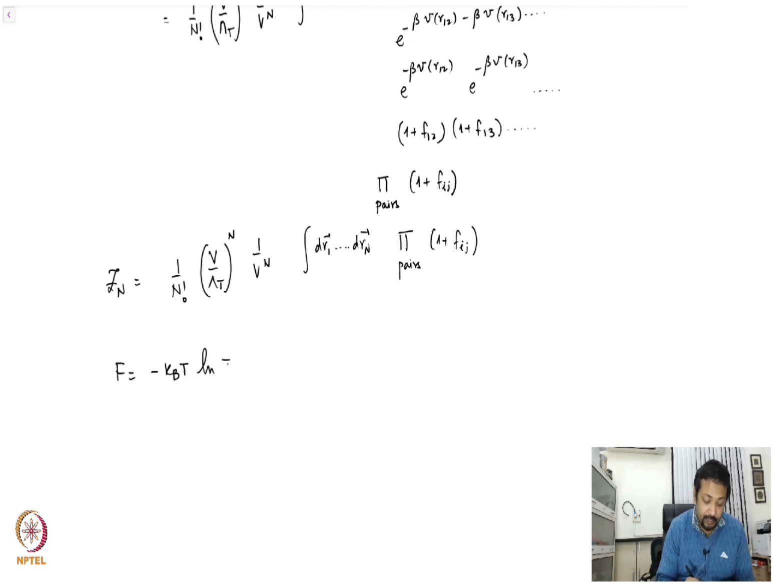
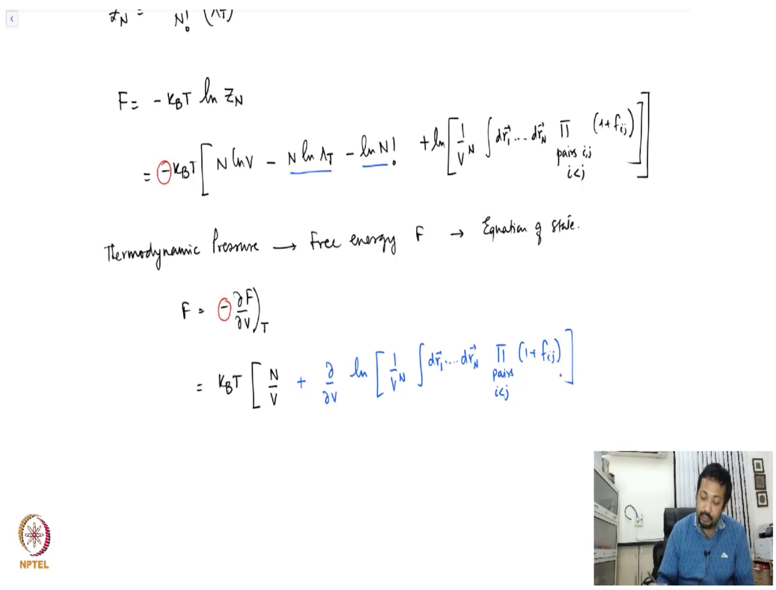
Statistical Mechanics
Prof. Dipanjan Chakraborty
Department of Physical Sciences
Indian Institute of Science Education and Research, Mohali

Lecture - 39
Interacting System – Part II

(Refer Slide Time: 00:15)



(Refer Slide Time: 00:22)



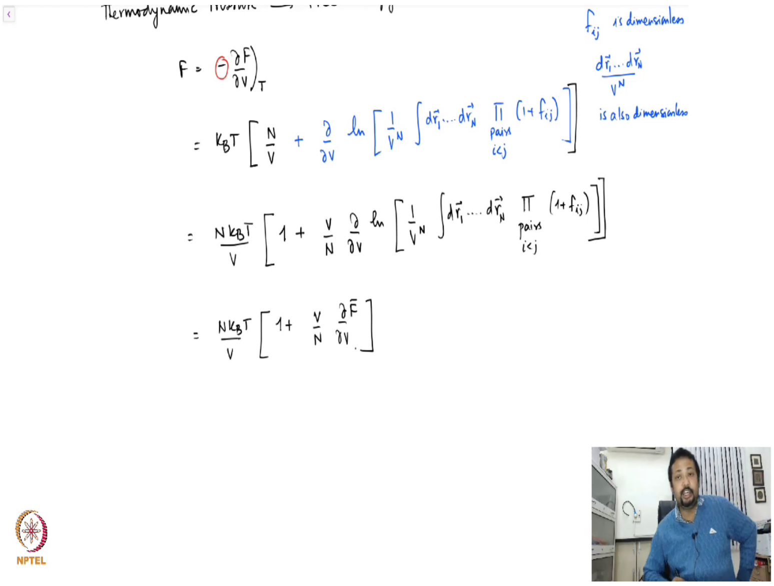
The free energy, therefore, it follows as minus K B T ln which is minus K B T N ln V minus N ln lambda T minus ln N factorial plus 1 over V to the power N logarithm of dr 1 dr N product over pairs i j 1 plus f i j with it is understood that i is less than j, and then we close this bracket for this.

Thermodynamic pressure, first interest is to look at the thermodynamic pressure. If you know how is the derivative related to the Helmotz, so how this thermodynamic. So, our first interest is to calculate the thermodynamic pressure from the free energy F because this gives me the equation of state and that is what I am after. So, this equation of state is what I am after. So, I know the relation is minus del F del V temperature held constant.

So, let us do that. So, thus this minus that you see over here and the overall minus that is contained in the free energy makes with a plus, so that I have K B T N by V. The second term does not have any volume factor, so you do not have to worry about it.

The third term also does not have any volume factor it also does not come into the picture. But the last term does have this, so this has to be del del V of ln 1 over V to the power N dr 1 dr N product over pairs i less than j 1 plus f i j.

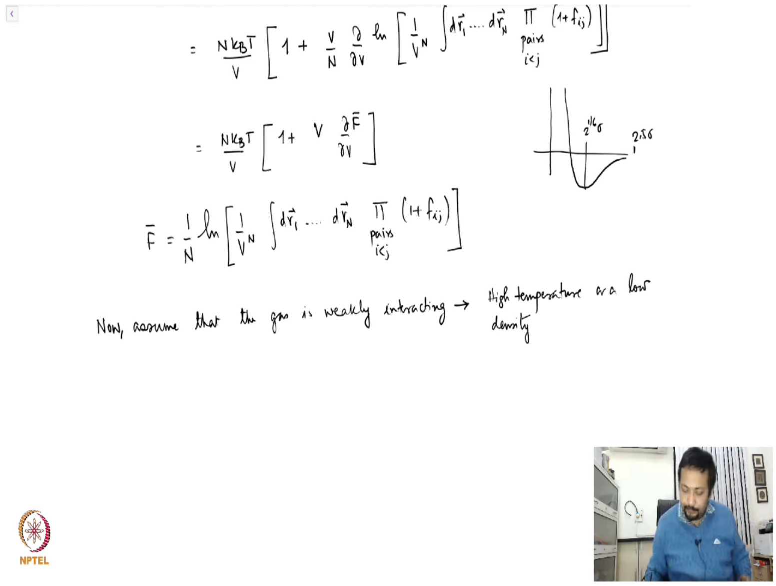
(Refer Slide Time: 03:12)



Now, it also you have to note one thing that f i j is dimensionless and d r 1 d r m divided by V to the power N is also dimensionless. So, this makes the picture very consistent, one does not have to worry about dimensions at every step of your calculation. N K B T over V, if I take this outside, this becomes V over N del del V of ln of 1 over V to the power N dr 1 all the way up to d of r N and I have product over pairs i less than j 1 plus f of i j and then we close the bracket.

We did not close the bracket here; so we close the bracket over here. To shorten the notation and to make our life little bit more convenient, what we will write over here is that this is going to be del del V of some free energy F bar.

(Refer Slide Time: 04:38)

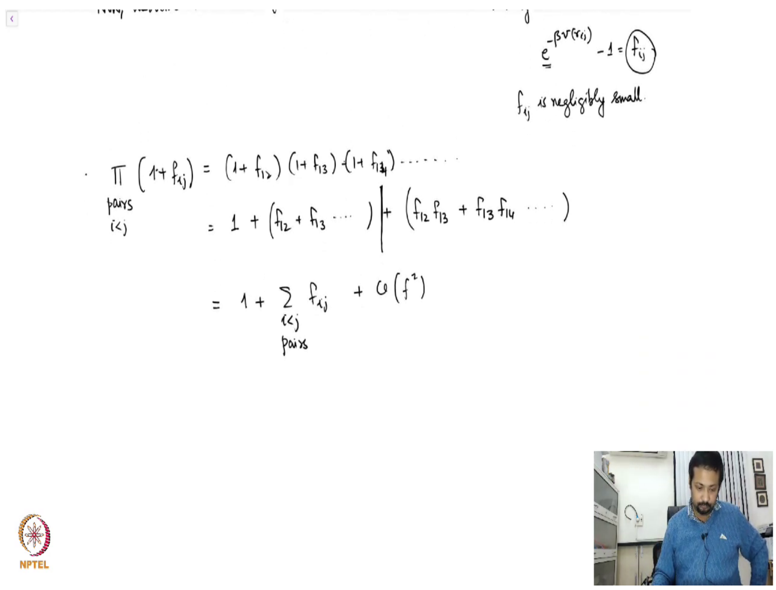


Where F bar is now ln 1 over V to the power N dr 1 dr N product over pairs i less then j 1 plus f i j. So, let us see. Did we do anything stupid over here? It means something N factorial. I think this is fine. In fact, what additionally we can do here is to take the N, keep this V, and absorb the N in F bar.

Now, assume that the gas is weakly interactive which means that it could be at a high temperature or a low density. In either of these situations, if it is a low density system, then the two particles rarely see each other right. So, most of the time, it is like almost of free particle system, but sometimes they have to collide when they come within the interaction reach.

So, if you recall that the potential that we are looking at the soft coal potential have something like this, and this one was 2 to the power 1, 6 sigma. And if you see this to be 2 sigma or even 2.5 sigma, the potential is already vanishing. It is small. So, for no density system, most of the particles are far away only when they come within a distance of 2.5 sigma, 3 sigma, they feel some kind of any bits of interaction; otherwise, it is vanishing; otherwise, it is also 0. Similarly, in the high temperature limit also you have the same situation.

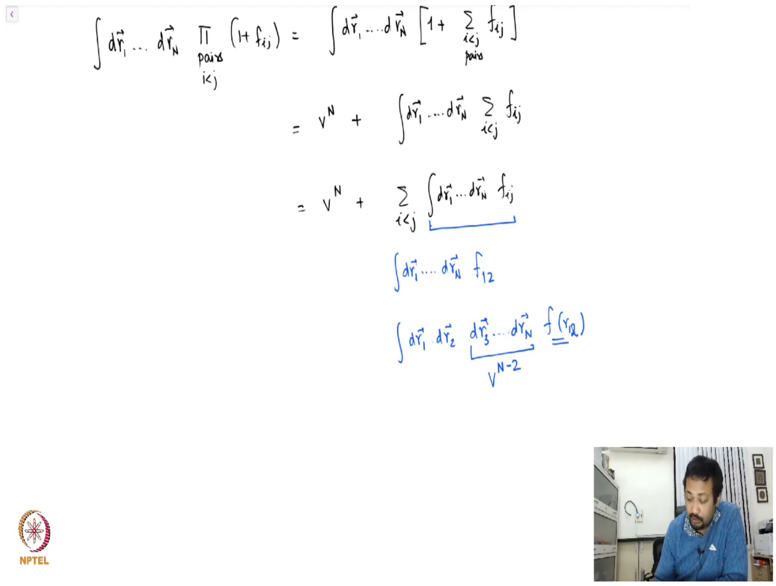
(Refer Slide Time: 07:26)



So, what happens? It means in such a situation that this quantity beta v of r i j because you have a high temperature beta is very low minus 1 is equal to f of i j right. So, this factor is almost one. So, that f i j is very, very tiny tiny. So, f i j is negligibly small. Under such a circumstances we can write down this product over pairs with i less than j 1 plus f i j, if you now see that this if I write down explicitly f 12 1 plus f 13 1 plus f 1 sorry 1 f 14 so and so forth.

If I expand, then the first term obviously, is going to be unit, the second term is f 12 plus f 13 so on and so forth all possible pairs you have, and then you have f 12, f 13 plus f 13 f 14 so on and so forth. So, we will truncate our series over here because f is so small. We have 1 plus sum over i less than j all pairs f i j plus order of f square which we ignore.

(Refer Slide Time: 09:20)

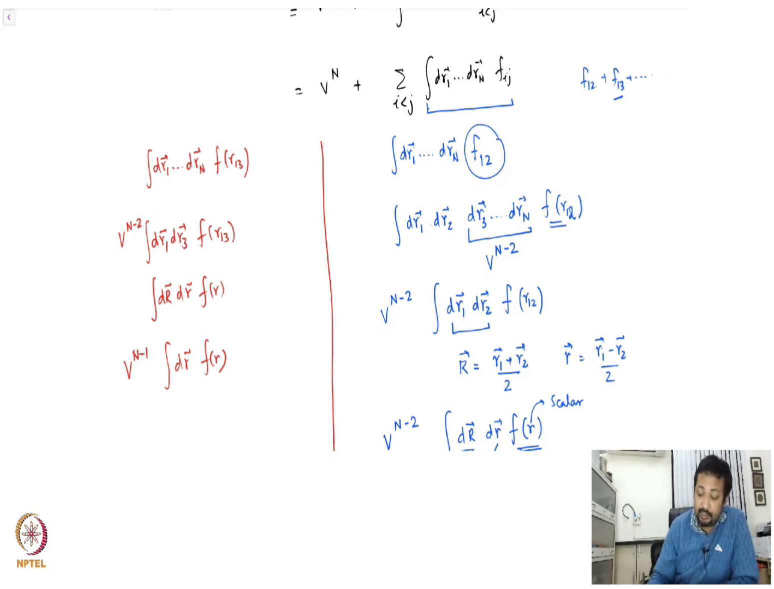


Now, let us look at the integral of this quantity dr 1 dr N product over pairs with i less than j 1 plus f i j is going to be integral dr 1 dr N 1 plus i less than j all the pairs you are considering f of i j plus something which is of higher order which we ignore. The first one is very trivial to do. The first one is nothing but V to the power N. The second one is integral dr 1 all the way up to dr N sum over i less than j f i j. So, clearly I can rewrite this as i less than j dr 1 dr N f i j.

Let us pick up one term we have seen this right we have expanded this. Let us say I am just looking at the term f 12 so that this integral now. Just look at if I write down the sum explicitly and I pick up only one term this means let us say I have dr 1 dr N f of 1 2. So, you are looking at r 1 and r 2; particle number 1, interaction between particle number 1 and interaction and particle number 2.

Here I can clearly separate out dr 1 dr 2, the rest of the integral dr 3, all the way up to dr N f of r 12. This f function does not depend on the other coordinates 3 4 all the way to n. So, this can be integrated out. And all of this is going to give you a volume V. So, this is going to give you V to the power N minus 2. There are N minus 2 term integrals over here.

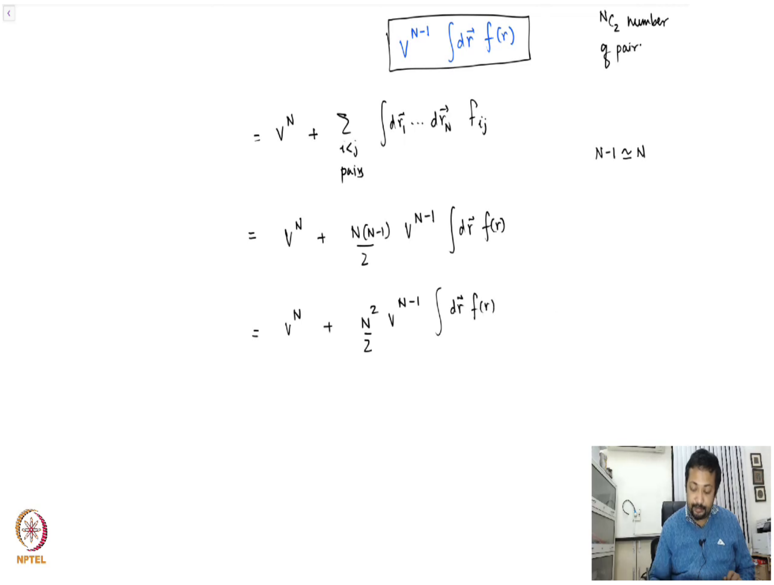
(Refer Slide Time: 11:42)



So, this comes out N minus 2 integral dr 1 dr 2 f of r 12. But now I know how to handle such a measure. I will go to the center of mass coordinate which is r 1 plus r 2 divided by 2, assuming they have the same mass. And the separation r which is going to be r 1 minus r 2 divided by 2. The Jacobin of the transformation is unity and you are going to get V to the power N minus 2 integral d of R d of r small r f of r.

This is a scalar r. Please note that, whereas, this is an integral over a vector. This part I can easily integrate because the integrant does not depend on the center of mass coordinates. So, this center of mass coordinate is also allowed to have the whole of the volume, and so you take out another factor of volume.

(Refer Slide Time: 12:47)



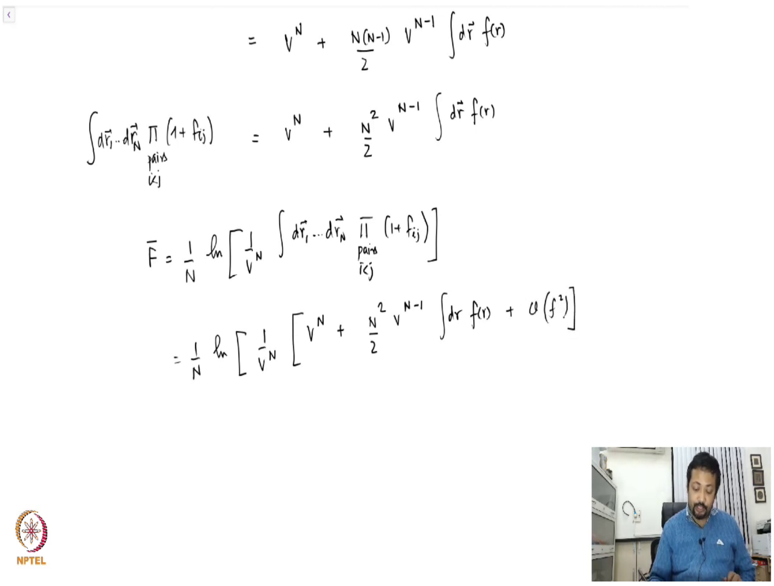
And this becomes V to the power N minus 1 integral dr f of r correct. Now, this we did with one f 1 such things. So, if I write down this open up this sum, I will have f 12 plus f 13 so on and so forth. I could have chosen f 13 here.

If I choose f 13 just very briefly I want to write down over here if I choose f 13 I can carry forward the same argument that I did f of r 13 and again you will see that I will have dr 1 dr 3 f of r 13, the integral over the rest of the coordinates is going to give you N minus 2.

And this again is going to give you dr dr f of r, so that you are going to have V to the power N minus 1 d of r f of r. So, what does it mean? It essentially means that if I look at this structure which was V to the power N plus sum over i less than j pairs integral d r 1 d r N 1 plus sorry not 1, 1 has already integrated over, I will have f of i j. This effectively means that I can just pick up one such integral and how many possible pairs can I have N C 2, N C 2 number of pairs I can pick up from the system from these N particles.

So, that I can just replace this sum by N into N minus 1 by 2 which is essentially your N C 2 integral V to the power N minus 1. And so I replace the sum by this and just pick up one of the typical integrals that I have by choosing one pair. So, I have V to the power N minus 1 integral dr f of r, V to the power N. So, that in the thermodynamic limit N minus 1 is approximately N, and this becomes V to the power N plus N square V to the power N minus 1 dr f of r.

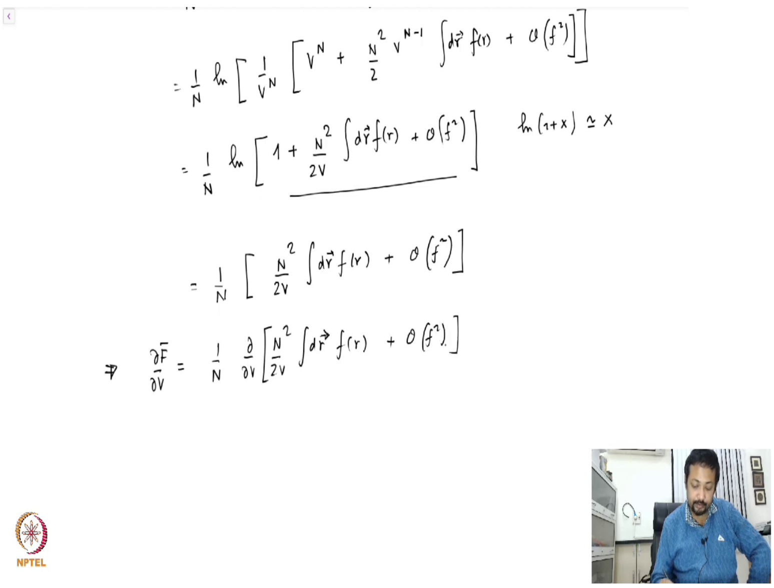
(Refer Slide Time: 15:34)



Let us see. So, this integral is therefore integration product dr 1 dr N product over 1 plus f of i j pairs with i less than j is going to be this, then this means I am interested in this quantity. So, let us write down f bar. I am interested in f bar which is going to be 1 over N, and then I have log of 1 over V to the power N integral dr 1 dr N product of pairs i less than j 1 plus f i j.

This was the quantity that we had defined is exactly over here. And I know that now integral has now evaluated to be only in the low density or high temperature limit as 1 over V to the power N times V to the power N plus N square over 2 V to the power N minus 1 dr f of r plus whatever you will have is going to be order of f square, and then you close the bracket.

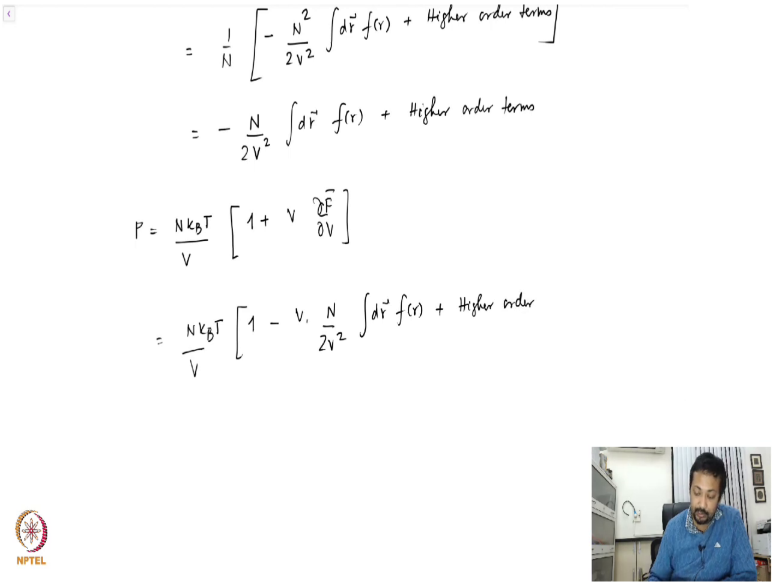
(Refer Slide Time: 16:59)



So, this is 1 by N ln 1 plus V to the power N is N square over twice p integral dr vector r f of r plus order of f square. Again since f is very very tine so that and we are looking in the low density limit, I can just keep take this expansion l use ln 1 plus x is approximately equal to x to write down this as 1 over N, so I am going to have 1 over N N square over twice V dr f of r plus order of f square right.

So, that this implies del F bar over del V is going to be 1 over N del del V of N square over twice V d of r f of r plus order f square.

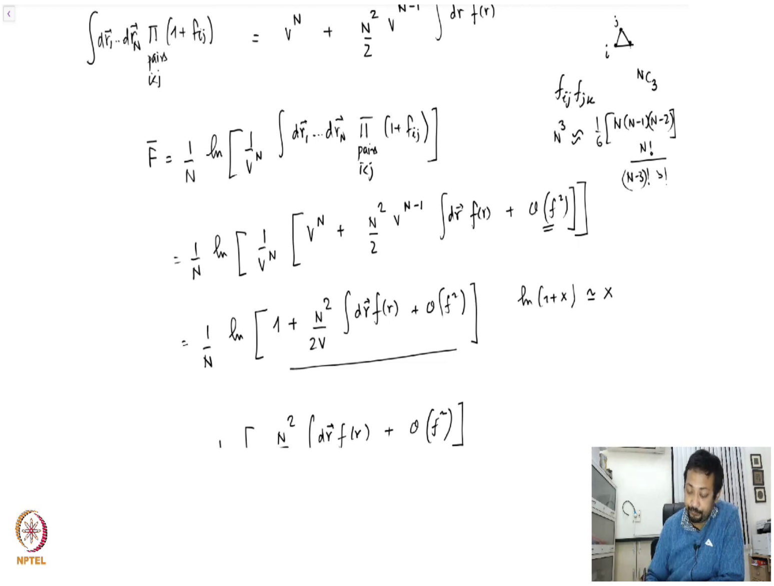
(Refer Slide Time: 18:59)



And this gives me 1 over N minus N square over twice V square integral dr f r plus higher order terms. I can simplify this further to write down this as N over 2 V square integral dr f r plus higher order terms. But I also so with this it is understood that I am only looking at the low density limit or high temperature right, good.

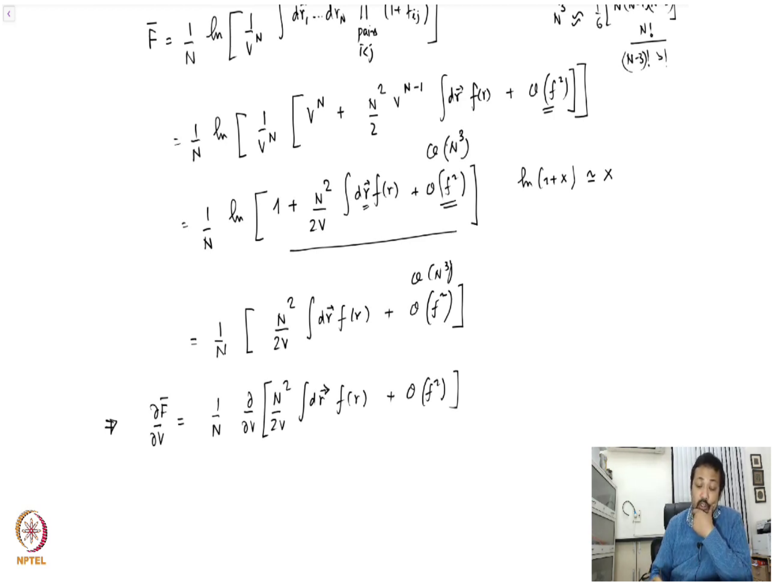
So, now, let us go back to the expression for the pressure. The expression for the pressure was very simply this. So, the thermodynamic pressure was N K B T divided by V. Now, before we do that, let us just be a little bit more careful. What we have done over here is essentially we have taken order of f square, but in reality this is not the case what one has to look at is.

(Refer Slide Time: 20:39)



If I keep the term which is f i j, the next or f j k which means that you are not only choosing pairs, but i j, and j and k, and i and k, so three of them are being chosen which is going to be N C 3. So, N into N minus 1 into N minus 2, this is N factorial N minus 3 factorial divided by 3 factorial and you have one-sixth of this. Now, clearly you see that this is going to be of the order of N cube.

(Refer Slide Time: 21:20)



So, when you see that you ignore this f square term essentially you are looking at a term which is of the order of N cube. So, even though I have written it of the order of f square just to emphasize the fact that I am ignoring terms which are of the order of m f square at in reality that translates because after you have to integrated over f, we are want to integrated over this coordinate. So, in reality it essentially means that there is an order in N cube term which you have neglected.

So, these all would mean that I have neglected an order N cube term. So, then P V P equal to N K B T 1 plus V del F bar over del V which is going to be N K B T over V 1 minus let us substitute V times N over 2 V square integral dr f r plus higher order terms. Let us go back a step, and you see that I have a 1 by N.

(Refer Slide Time: 22:35)

$$\Rightarrow \frac{\partial \bar{F}}{\partial V} = \frac{1}{N}\frac{\partial}{\partial V}\left[\frac{N}{2V}\int d\vec{r}\, f(r) + O(\ldots)\right]$$

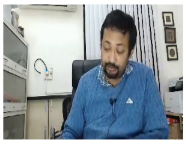
$$= \frac{1}{N}\left[-\frac{N^2}{2V^2}\int d\vec{r}\, f(r) + \text{Higher order terms}\right]$$

$$O(N^2)$$

$$= -\frac{N}{2V^2}\int d\vec{r}\, f(r) + \text{Higher order terms}$$

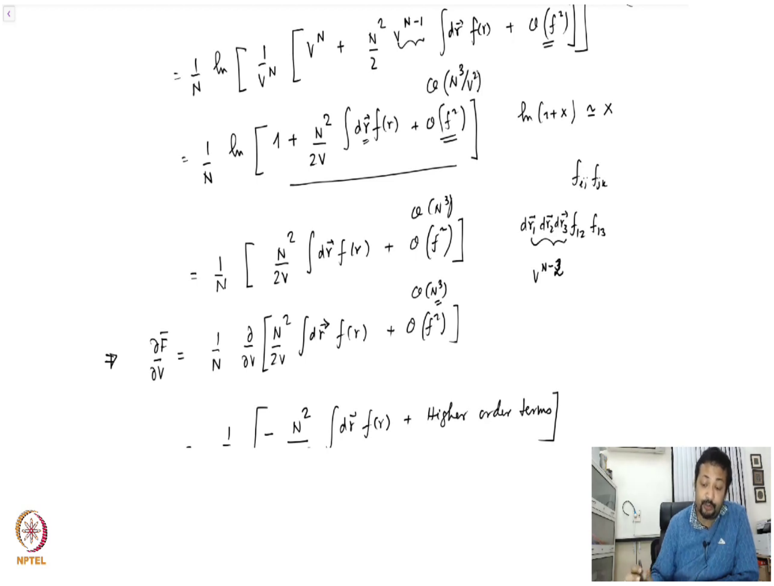
$$P = \frac{Nk_BT}{V}\left[1 + V\frac{\partial \bar{F}}{\partial V}\right]$$

$$= \frac{Nk_BT}{V}\left[1 - V.\frac{N}{2V^2}\int d\vec{r}\, f(r) + \text{Higher order}\right.$$



So, if this was of the order of N cube, then we realize that this is of the order of N square right.

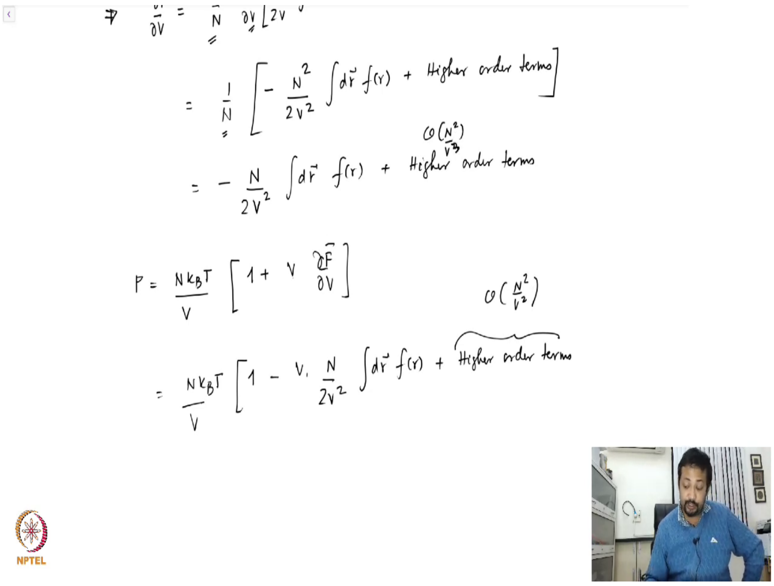
(Refer Slide Time: 22:49)



Now, one can also refine the argument a little bit more by saying look I will have an integral which is f i j, f j k. For example, this term will give me f 12, f 13, and I will have dr 1, dr 2 and dr 3, rest of the in coordinates I can integrate over to give me N minus 3. And one of them just as you will have V to the power N minus 1, you are also going to get a volume from here. So, this is finally going to be V to the power N minus 2.

The next order term is going to be V to the power N minus 2. If you now take V to the power N common, then this is going to be of the order of N cube, the first term was of the order of N square over V, this becomes N cube over V square.

(Refer Slide Time: 23:45)

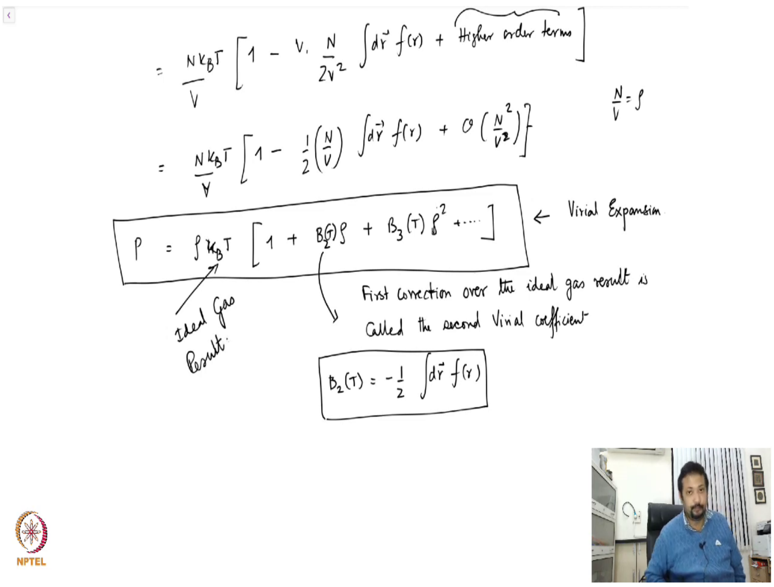


So, that you are going to have a term which is going to be N square over V square. And when you write higher order terms essentially means mean a term which is of the order of N square over V square.

I think it should be V cube. So, let us see where did we made the mistake? Correct. So, this is going to be N cube over V square, but then there is a derivative with respect to V which is going to give you N square over V square because you not only have divided by 1 over N, but you have also taken a derivative with respect to the volume.

Now, this is going to be N square over V cube, not this one, this is going to be N square over V square, since you multi V cube of. So, this higher order term is going to be an order of N square over V square. Up to here, it is going to be a order of N square over V cube. And once you multiply with V, you are going to get order of N square over V square and we can close this.

(Refer Slide Time: 25:23)



So, then we have N K B T over V 1 minus half N by V times dr f of r plus N by V whole square plus terms which of order of N square over V square. Now, identifying N by V as the density I have this as rho of K B T 1 plus B 2 rho remember f r has a temperature dependence f r has a beta factor. So, this is going to be B 2 times T times rho plus B 3 times T time rho square plus. So, the equation of state takes this particular this is what is called the virial expansion.

And this quantity the first correction over the ideal gas result is called the second virial coefficient B 2 of T as minus half integral dr f of r. Given in the form of the potential, you can evaluate the this coefficient. The first is always the ideal gas result.