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

Lecture - 40
Van-Der Waals Equation of State

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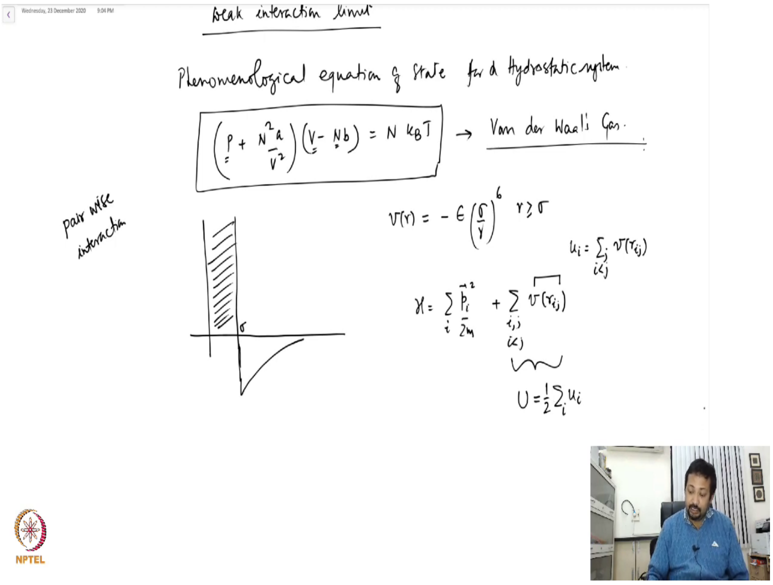

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Weak interaction limit

Phenomenological equation of state for a Hydrostatic system.

$$\boxed{\left(P + \frac{N^2 a}{V^2}\right)(V - Nb) = N k_B T} \rightarrow \text{Van der Waal's Gas.}$$

pair wise interaction

$$v(r) = -\epsilon\left(\frac{\sigma}{r}\right)^6 \quad r \geq \sigma$$

$$u_i = \sum_{\substack{j \\ i<j}} v(r_{ij})$$

$$\mathcal{H} = \sum_i \frac{\vec{p}_i^{\,2}}{2m} + \underbrace{\sum_{\substack{i,j \\ i<j}} v(r_{ij})}_{U = \frac{1}{2}\sum_i u_i}$$

So, now that we have looked at a interacting system how to handle such interacting system in weak limit of interaction, weak interaction limit, we want to see how really it does compare with real life examples of particular of particular interest is the phenomena phenomenological equation of state which is P plus N square a over V square V minus N times b is going to be NK B T. If you have not encounter such an equation, this is for a hydrostatic system which would be clear to you now because you are thermodynamic variables are P, V and N.

And this is called Van der Waal’s gas. But how does one arrive such an equation? Yeah. So, what we want to start off with the interaction. So, once again the starting point is the pair wise interaction. And here of course, we take that we say that there is a definite size sigma below which there is a hardcore repulsion, but there is a soft attractive part to this, so that V of r is minus epsilon sigma over r to the power 6 for r greater than equal to sigma something like this.

The Hamiltonian then is p square sum over i p square p i square over twice m plus sum over i u of i, where u i is the potential energy of the ith particle. So, one can write down u of i as sum over i less than j this is sum over j v of r ij. Now, one can take care of double counting, well, we will see. So, I can bring in a factor of half here, and the reason of bringing the factor half is going to be very clear.

So, but for the time being this is let us write down this explicitly and write this down as some over i, j i less than j v of r ij. So, this part is a potential energy, total potential energy. And we will describe it as sum over individual particles. But now this interaction is pair wise. So, I bring in a factor half.

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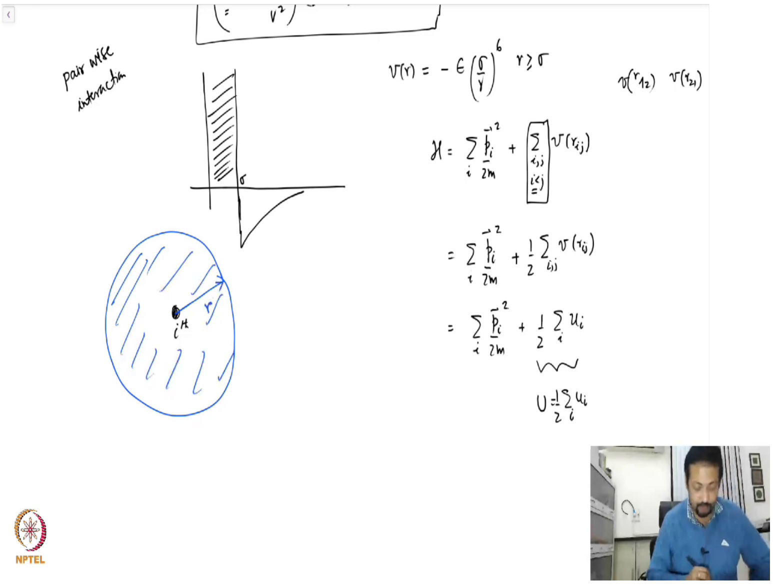

$$V(r) = -\epsilon\left(\frac{\sigma}{r}\right)^6 \quad r \geq \sigma$$

$$v(r_{12}) \quad v(r_{21})$$

$$\mathcal{H} = \sum_i \frac{\vec{p}_i^{\,2}}{2m} + \boxed{\sum_{\substack{i,j \\ i<j}}} v(r_{ij})$$

$$= \sum_i \frac{\vec{p}_i^{\,2}}{2m} + \frac{1}{2}\sum_{i,j} v(r_{ij})$$

$$= \sum_i \frac{\vec{p}_i^{\,2}}{2m} + \underbrace{\frac{1}{2}\sum_i u_i}_{U = \frac{1}{2}\sum_i u_i}$$

What I want to do now? No, let us start the Hamiltonian of the system is given by sum over i p i square over twice m plus sum over i comma j with i less than j v of r ij. Now, here this is one way of writing it down, but you have with the fact that you are taking into consideration that i must be less than j. And this restriction itself essentially ensures that there is no double counting of pair wise interaction, but no harm in double counting.

For example, I can consider v of r 12 and v of r 21 that is perfectly fine. Only thing I have to ensure that if i get this restriction out of the picture which we will do because of our interest in treating the problem in a kind of a mean field approach, we will write half v of r ij where there is an unrestricted sum over i and j. And essentially then this becomes p i square over twice m plus half sum over i u of i, where i is the small u of i is the interaction energy or the of the single of the ith particle.

This term U is sum over half sum over i u of i is a total internal energy of the system the first term is the total kinetic energy of the system. Now, the idea is we want to look at it in a slightly in a mean field way know a weakly interacting system a dilute system have. So, I have the ith particle and surrounding this particle let us say I consider a radius of r.

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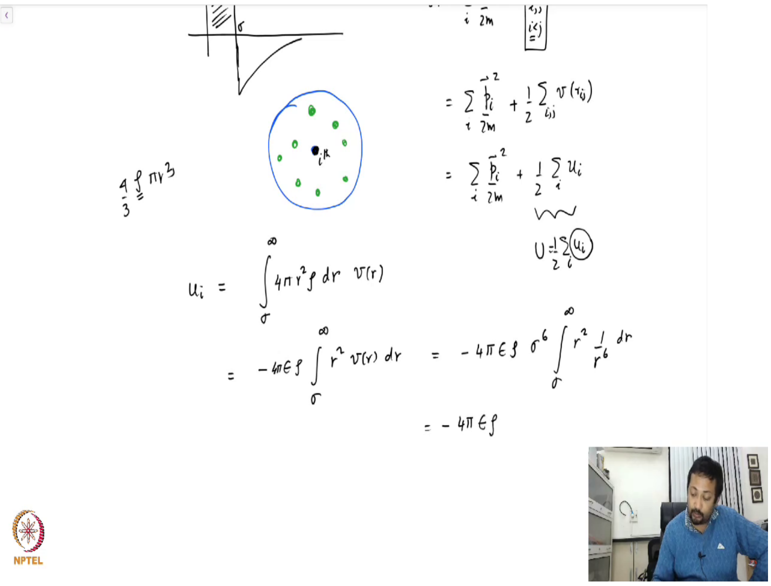

$$= \sum_i \frac{\vec{p}_i^{\,2}}{2m} + \frac{1}{2}\sum_{i,j} v(r_{ij})$$

$$= \sum_i \frac{\vec{p}_i^{\,2}}{2m} + \underbrace{\frac{1}{2}\sum_i u_i}$$

$$U = \frac{1}{2}\sum_i \boxed{u_i}$$

$$\frac{4}{3}\rho\pi r^3$$

$$u_i = \int_\sigma^\infty 4\pi r^2 \rho\, dr\, v(r)$$

$$= -4\pi\epsilon\rho \int_\sigma^\infty r^2 v(r)\, dr = -4\pi\epsilon\rho\,\sigma^6 \int_\sigma^\infty r^2 \frac{1}{r^6}\, dr$$

$$= -4\pi\epsilon\rho$$

So, if I have radius of r, this is a poor radius maybe one needs to draw a circle first. And at the center of this, I have the ith particle. And there are particles inside this which with which this ith particle is interacting. How many particles can it have? Rho times the volume right, pi 4 by 3 pi r cube.

So, the idea is that I want to replace this u of i by a mean field energy that this ith particle feels. And the way to do that is we can write down this phi or let us say we will just write u i now this is a function of r, but now I am going to make it independent of r. And I am going to say oh I have the density of the particle is rho therefore, the total number of particle that is contained in this volume is between 4 pi r square times rho dr. And each of the pair wise interaction that you take is of the form u i we had v of r.

So, this is going to be v of r. But the limits of integration are from sigma to infinity because that is where the potential how the potential behaves. So, this becomes minus epsilon 4 pi sigma. There is a rho there is sigma to infinity r square v of r dr which is minus 4 pi epsilon rho sigma to the power 6 sigma to infinity r square 1 over r to the power 6 dr that gives you minus 4 pi epsilon rho. 1 over r to the power 4 d r sigma to the infinity or to the power minus 4.

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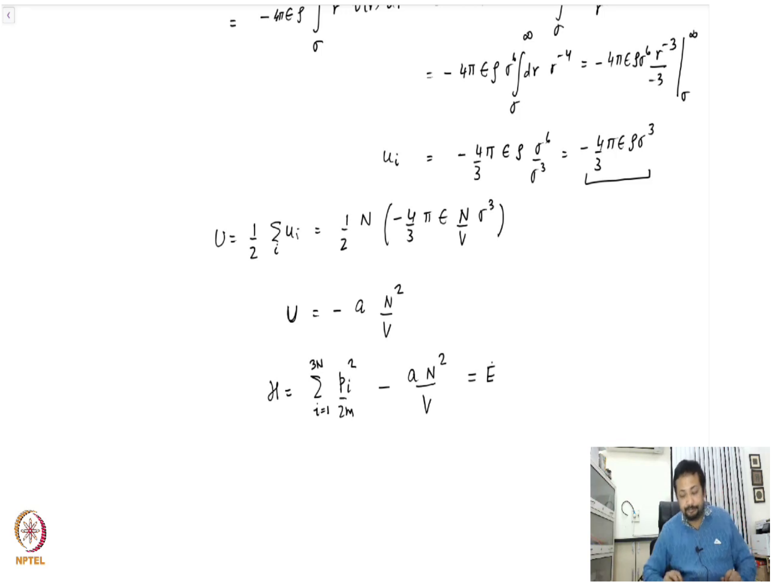

$$= -4\pi\epsilon\rho\sigma^6\int_\sigma^\infty dr\, r^{-4} = -4\pi\epsilon\rho\sigma^6\frac{r^{-3}}{-3}\Big|_\sigma^\infty$$

$$u_i = -\frac{4}{3}\pi\epsilon\rho\frac{\sigma^6}{\sigma^3} = \underbrace{-\frac{4\pi\epsilon\rho\sigma^3}{3}}$$

$$U = \frac{1}{2}\sum_i u_i = \frac{1}{2}N\left(-\frac{4}{3}\pi\epsilon\frac{N}{V}\sigma^3\right)$$

$$U = -a\frac{N^2}{V}$$

$$\mathcal{H} = \sum_{i=1}^{3N}\frac{p_i^2}{2m} - \frac{aN^2}{V} = E$$

There is a very trivial integral 4 pi epsilon rho r to the power minus 3 divided by minus 3 sigma to infinity. And when you put in the limits, you will see that this is going to give you minus 4 by pi 3 epsilon rho I miss a sigma 6 factor, sigma 6 over sigma cube which is minus 4 by pi 3 pi epsilon rho sigma cube.

Please note that this description is only valid when it is a weakly interacting gas with the density is very like dilute your at high temperatures. So, the particles rarely see each other. So, essentially what you do is look you kind of average out the interaction energy surrounding the particle.

So, if a particle separation is r how many particles if you consider this, how many particles are contained over here and then you integrate out the whole volume and essentially you find come up with this expression which is no longer dependent on or on the position.

So, that the total energy is now half some over u i which is half we will not N times this number minus 4 by 3 pi epsilon rho is density is N by V sigma cube. Now, you clearly see that this quantity is minus a times N square over V. This is your potential energy. So, the Hamiltonian which you started off with a many particle Hamiltonian now simplifies to p i square over twice m. Now, here I am going to change the level by saying that i goes from 1 to 3N.

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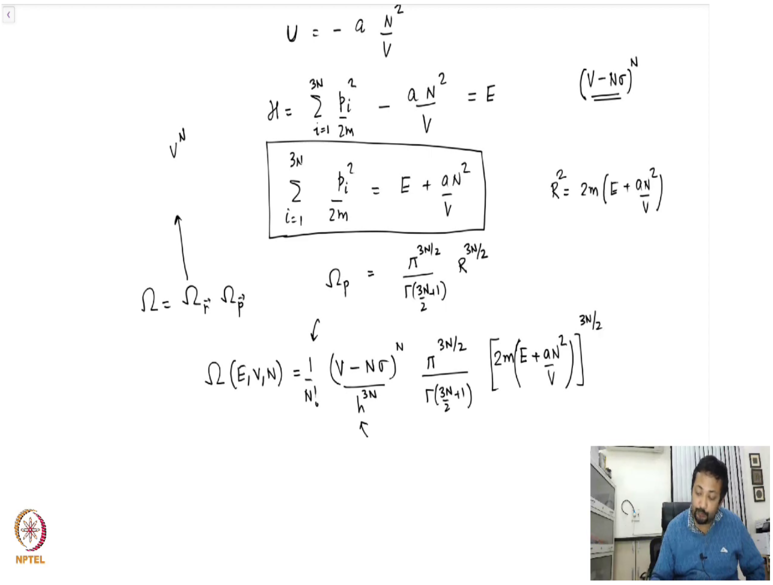

$$U = -a\frac{N^2}{V}$$

$$\mathcal{H} = \sum_{i=1}^{3N}\frac{p_i^2}{2m} - \frac{aN^2}{V} = E$$

$$\underline{(V - N\sigma)}^N$$

$$V^N$$

$$\boxed{\sum_{i=1}^{3N}\frac{p_i^2}{2m} = E + \frac{aN^2}{V}}$$

$$R^2 = 2m\left(E + \frac{aN^2}{V}\right)$$

$$\Omega = \Omega_{\vec{r}}\,\Omega_{\vec{p}}$$

$$\Omega_p = \frac{\pi^{3N/2}}{\Gamma\left(\frac{3N}{2}+1\right)}R^{3N/2}$$

$$\Omega(E,V,N) = \frac{1}{N!}\frac{(V-N\sigma)^N}{h^{3N}}\frac{\pi^{3N/2}}{\Gamma\left(\frac{3N}{2}+1\right)}\left[2m\left(E+\frac{aN^2}{V}\right)\right]^{3N/2}$$

Remove the vector sign on the momentum and the energy is N square over V and this must be equal to E. So, if you are considering this system to be isolated, if you are considering this system to be isolated, then essentially you are looking at the metro canonical formalism of this.

So, this becomes i equal to 1 to 3N p i square over twice m is going to be E plus a N square over V. So, this is a surface that you are considering. What is the total number of micro states? That before you calculate the total number of micro states, you must realize that I also have to figure out the volume accessible to this particles.

If they are point particles, no size, then of course, each of these particles can have at volume V. And therefore, the total number of micro states if I write down omega v, omega r, the coordinate space and the momentum space, omega r in the ideal gas case was V to the power N because they are not interacting.

Therefore, they could have been taken as point particles and each of these were allowed to take the volume V, but now they have this in our case they have a finite size they have interaction.

So, clearly you see that the total if sigma is the particle size. Total number the volume that is accessible to each of them is going to be this raise to the power N because this is the volume that is accessible to a single particle. Omega p is the volume contained within the hyper surface that is defined by this relation. And we have calculated that that was pi to the power 3N by 2 gamma 3N by 2 plus 1 R to the power 3N right, yeah, by 2 where R is R square is twice m E plus a N square over V.

Hence the total number of micro states that is accessible to the system is omega E, V, N is going to be V minus N times sigma raise to the power N 1 over N factorial h to the power 3N that is a standard indistinguishability criteria and that is non-dimensionalizing the phase the total number of micro states the ado introduction of this factor. And then I have this result which is pi to the power 3N by 2 gamma of 3N by 2 plus 1 twice m E plus a N square over V raise to the power 3N by 2.

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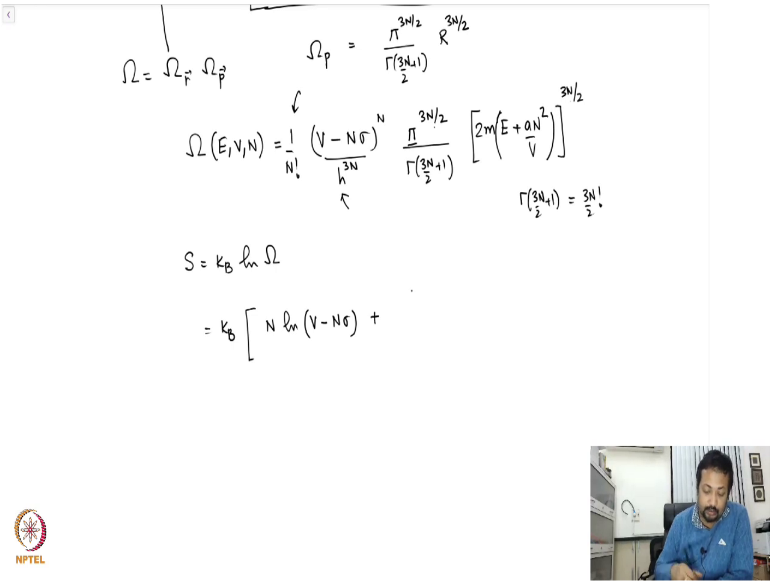

$$\Omega = \Omega_{\vec{r}}\,\Omega_{\vec{p}} \qquad \Omega_p = \frac{\pi^{3N/2}}{\Gamma\left(\frac{3N}{2}+1\right)} R^{3N/2}$$

$$\Omega(E,V,N) = \frac{1}{N!}\,\frac{(V-N\sigma)^N}{h^{3N}}\,\frac{\pi^{3N/2}}{\Gamma\left(\frac{3N}{2}+1\right)}\left[2m\left(E+\frac{aN^2}{V}\right)\right]^{3N/2}$$

$$\Gamma\left(\frac{3N}{2}+1\right) = \frac{3N}{2}!$$

$$S = k_B \ln \Omega$$

$$= k_B\left[N \ln(V-N\sigma) + \right.$$

Our job is almost done I know the total number of micro states, and the rest of the thermodynamic quantities I can easily calculate. We start off with the entropy which is k B ln of omega. The entropy now I can write down as K B N ln V minus N sigma plus this pi to the power 3N by 2 I can include let us ok.

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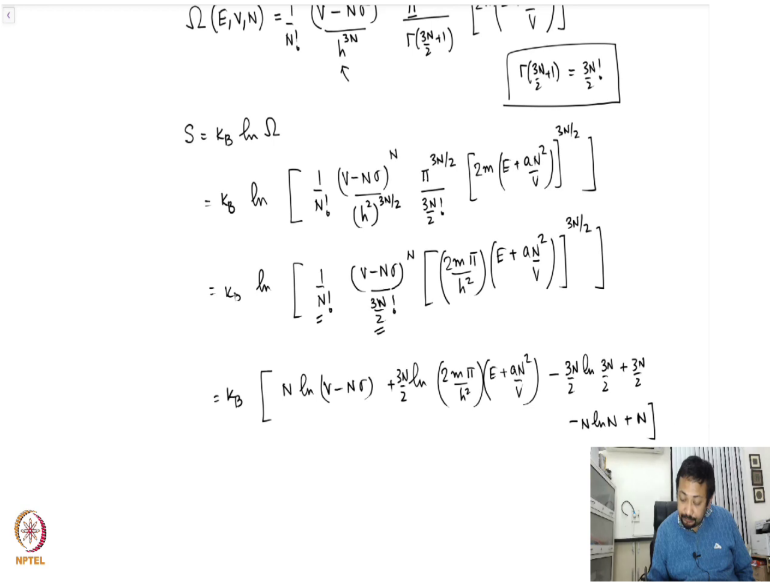

$$\Omega(E,V,N) = \frac{1}{N!}\,\frac{(V-N\sigma)}{\underset{\uparrow}{h^{3N}}}\,\frac{\pi}{\Gamma\left(\frac{3N}{2}+1\right)}\left[\quad\frac{}{V}\right)\Big]$$

$$\boxed{\Gamma\left(\frac{3N}{2}+1\right) = \frac{3N}{2}!}$$

$$S = k_B \ln \Omega$$

$$= k_B \ln \left[\frac{1}{N!}\,\frac{(V-N\sigma)^N}{(h^2)^{3N/2}}\,\frac{\pi^{3N/2}}{\frac{3N}{2}!}\left[2m\left(E+\frac{aN^2}{V}\right)\right]^{3N/2} \right]$$

$$= k_B \ln \left[\underset{=}{\frac{1}{N!}}\,\frac{(V-N\sigma)^N}{\underset{=}{\frac{3N}{2}!}}\left[\left(\frac{2m\pi}{h^2}\right)\left(E+\frac{aN^2}{V}\right)\right]^{3N/2} \right]$$

$$= k_B \left[N \ln (V-N\sigma) + \frac{3N}{2}\ln \left(\frac{2m\pi}{h^2}\right)\left(E+\frac{aN^2}{V}\right) - \frac{3N}{2}\ln\frac{3N}{2} + \frac{3N}{2} - N\ln N + N \right]$$

First let us simplify things and then we will expand the log. We will write it as ln of 1 over in factorial V minus N sigma raise to the power N. And then I see that the denominator is h square raise to the power 3N by 2 pi to the power 3N by 2 3N by 2 factorial gamma 3N by 2 plus 1 is 3N by 2 factorial.

I have twice m E plus a N square over V raise to the power 3N by 2. So, that I write this is K B ln 1 over N factorial V minus N sigma raise to the power N twice m pi over h square times E plus a N square V raise to the power 3N by 2, and then I have 3N by 2 factorial.

Now, let us take the law. So, that this b gives me K B N ln V minus N sigma plus ln twice m pi over h square E plus a N square over V raise to the power 3N by 2 gives me 3N by 2. And then I have minus 3N by 2 ln of 3N by 2, I have plus 3N by 2 that comes from this I have also an ln N factorial which is going to give me N ln N plus N.

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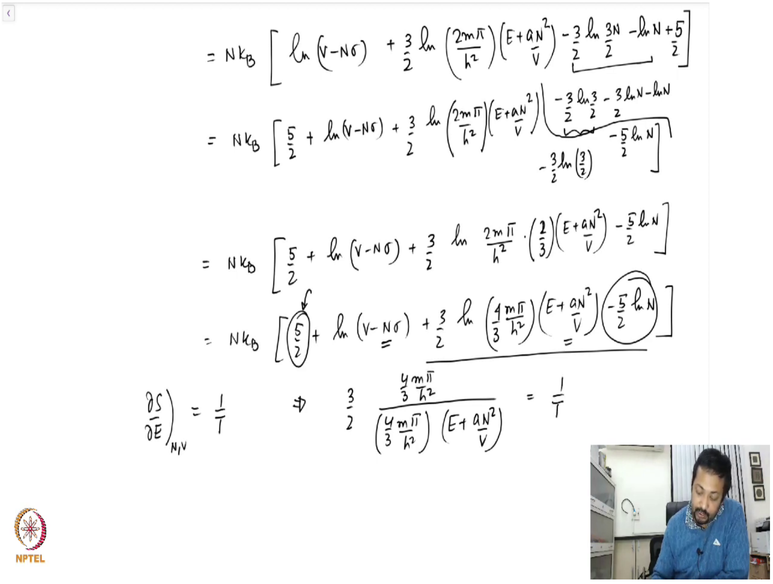

$$= Nk_B\left[\ln(V-N\sigma)+\frac{3}{2}\ln\left(\frac{2m\pi}{h^2}\right)\left(E+\frac{aN^2}{V}\right)\underbrace{-\frac{3}{2}\ln\frac{3N}{2}-\ln N}+\frac{5}{2}\right]$$

$$= Nk_B\left[\frac{5}{2}+\ln(V-N\sigma)+\frac{3}{2}\ln\left(\frac{2m\pi}{h^2}\right)\left(E+\frac{aN^2}{V}\right)\underbrace{-\frac{3}{2}\ln\frac{3}{2}-\frac{3}{2}\ln N-\ln N}-\frac{5}{2}\ln N\right]$$

$$-\frac{3}{2}\ln\left(\frac{3}{2}\right)$$

$$= Nk_B\left[\frac{5}{2}+\ln(V-N\sigma)+\frac{3}{2}\ln\frac{2m\pi}{h^2}\cdot\left(\frac{2}{3}\right)\left(E+\frac{aN^2}{V}\right)-\frac{5}{2}\ln N\right]$$

$$= Nk_B\left[\boxed{\frac{5}{2}}+\ln(V-N\sigma)+\underline{\frac{3}{2}\ln\left(\frac{4}{3}\frac{m\pi}{h^2}\right)\left(E+\frac{aN^2}{V}\right)}\boxed{-\frac{5}{2}\ln N}\right]$$

$$\left.\frac{\partial S}{\partial E}\right)_{N,V}=\frac{1}{T}\quad\Rightarrow\quad\frac{3}{2}\frac{\frac{4}{3}\frac{m\pi}{h^2}}{\left(\frac{4}{3}\frac{m\pi}{h^2}\right)\left(E+\frac{aN^2}{V}\right)}=\frac{1}{T}$$

Let us take N, N outside gives me N K B ln V minus N sigma plus 3 by 2 ln twice m pi over h square E plus a N square over V then I have minus 3 by 2 ln 3 by 2 N plus sorry it is also going to be N minus ln of N plus 5 by 2. So, the entropy now I can simplify this as 5 by 2 plus. What else can I do?

Let us see. I can take this part write down this as minus 3 by 2 ln 3 by 2 minus 3 by 2 ln of N minus ln of n. So, that this gives me minus 5 by 2 ln of N, and I have this term is going to be ln 3 by 2 raise to the power 3 by 2 right. So, this is just a constant term which is not very interesting to me, but anyway we will keep the 3 by 2 here minus ln 3 by 2. So, that I can combine it over here the is this going to be V minus N sigma plus 3 by 2 ln twice m pi over h square E plus a N square over V and then these two terms. ah

Please be careful with this. This is going to be minus 3 by 2 plus 3 by 2 ln minus ln. Is this correct? No, sorry this is minus correct, minus 5 by 2 5 by 2 ln of V minus N sigma. See all these details minute details are not very necessary because after all you have to take a derivative with V and E, but never the less ln twice m pi over h square.

Now, you have a 3 by 2, minus 3 by 2 ln 3 by 2, 3 by 2 gets is common. So, essentially you are going to have times 2 by 3 E plus a N square over V minus 5 by 2 ln of N. And this is the answer that you are looking for. So, we will finally write down this as 5 by 2 plus ln V minus a N sigma plus 3 by 2 ln of 4 by 3 m pi h square times E plus a N square over V minus 5 by 2 ln N. Remarkably, it has a very similar structure as for the ideal gas. The difference comes in here and here.

You have the residual part that is remainant of the ideal gas which is this term and this term. Del s del E is going to be 1 over t right N and V held constant. So, that means, if I take a derivative of E, I have 3 by 2 4 by 3 m pi over h square E plus a N square over V times 4 by 3 m pi over h square is continuing 1 by T.

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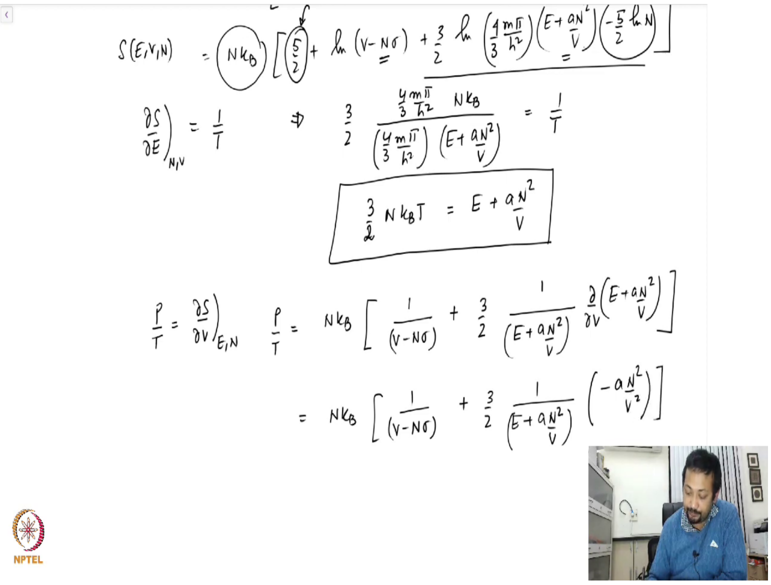

$$S(E,V,N) = NK_B\left[\frac{5}{2} + \ln\left(V - N\sigma\right) + \frac{3}{2}\ln\left(\frac{4}{3}\frac{m\pi}{h^2}\right)\left(E + \frac{aN^2}{V}\right)\left(-\frac{5}{2}\ln N\right)\right]$$

$$\left.\frac{\partial S}{\partial E}\right)_{N,V} = \frac{1}{T} \quad \Rightarrow \quad \frac{3}{2}\frac{\frac{4}{3}\frac{m\pi}{h^2} NK_B}{\left(\frac{4}{3}\frac{m\pi}{h^2}\right)\left(E + \frac{aN^2}{V}\right)} = \frac{1}{T}$$

$$\boxed{\frac{3}{2}NK_BT = E + \frac{aN^2}{V}}$$

$$\frac{P}{T} = \left.\frac{\partial S}{\partial V}\right)_{E,N} \quad \frac{P}{T} = NK_B\left[\frac{1}{(V - N\sigma)} + \frac{3}{2}\frac{1}{\left(E + \frac{aN^2}{V}\right)}\frac{\partial}{\partial V}\left(E + \frac{aN^2}{V}\right)\right]$$

$$= NK_B\left[\frac{1}{(V - N\sigma)} + \frac{3}{2}\frac{1}{\left(E + \frac{aN^2}{V}\right)}\left(-\frac{aN^2}{V^2}\right)\right]$$

So, that I missed out the NK B, which is sitting outside. So, I am going to have an NK B, so that 3 by 2 NK B T is E plus a N square over V right. What about the equation of state that is del s del V E and N held constant.

So, this by the way you should know that this is the desired fundamental relation of type one which we have already been which is kind of the holy (Refer Time: 21:53) thermodynamics right. So, when I have once I have P by T is equal to del s del V E and N and held constant.

Let us calculate the derivative the volume only appears over here also here that I am ask you very careful. So, I have NK B, the first term is going to be V minus N sigma 1 plus 3 by 2 I am going to have E plus a N square over V 1 over this and then I am going to have del del v of E plus a N square over V, so that I have NK B 1 over V minus N sigma plus 3 by 2 1 over

E plus a N square divided by V, and this derivative gives me gives me minus a N square over V square.

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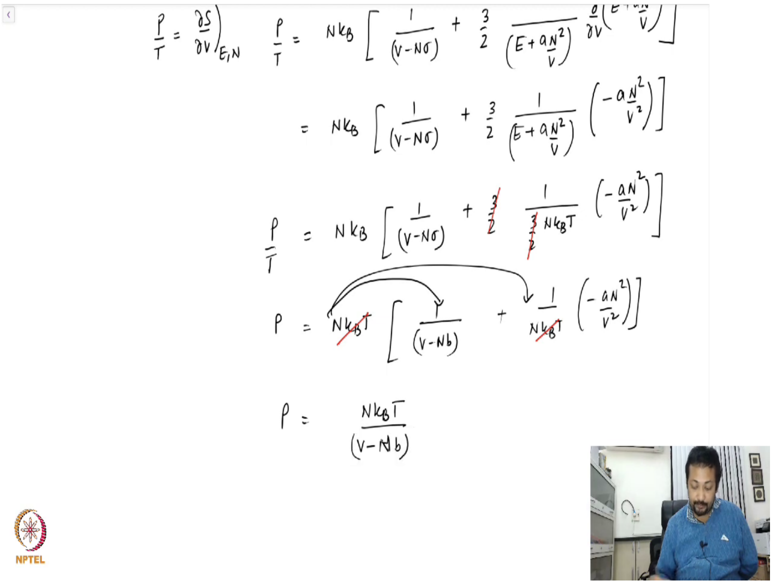

$$\frac{P}{T} = \left.\frac{\partial S}{\partial V}\right)_{E,N} \qquad \frac{P}{T} = Nk_B\left[\frac{1}{(V-N\sigma)} + \frac{3}{2}\,\frac{}{\left(E+\frac{aN^2}{V}\right)}\,\frac{\partial}{\partial V}\left(E+\frac{aN}{V}\right)\right]$$

$$= Nk_B\left[\frac{1}{(V-N\sigma)} + \frac{3}{2}\,\frac{1}{\left(E+\frac{aN^2}{V}\right)}\left(-\frac{aN^2}{V^2}\right)\right]$$

$$\frac{P}{T} = Nk_B\left[\frac{1}{(V-N\sigma)} + \cancel{\frac{3}{2}}\,\frac{1}{\cancel{\frac{3}{2}}Nk_BT}\left(-\frac{aN^2}{V^2}\right)\right]$$

$$P = \cancel{Nk_BT}\left[\frac{T}{(V-Nb)} + \frac{1}{\cancel{Nk_BT}}\left(-\frac{aN^2}{V^2}\right)\right]$$

$$P = \frac{Nk_BT}{(V-Nb)}$$

NK B 1 over V minus N sigma plus 3 by 2 let us use this relation, this is 3 by 2 NK B T right minus a N square over V square P by T. There are cancellations 3 by 2, 3 by 2 cancels out.

And I write pressure as NK B T 1 over V minus N b plus 1 over NK B T minus a N square over V square and close bracket this NK B T, I can take it inside over here and then over here. And you see that this is going to cancel with this, so that I am going to be left out with NK B T divided by V minus N times b minus a N square over V square.

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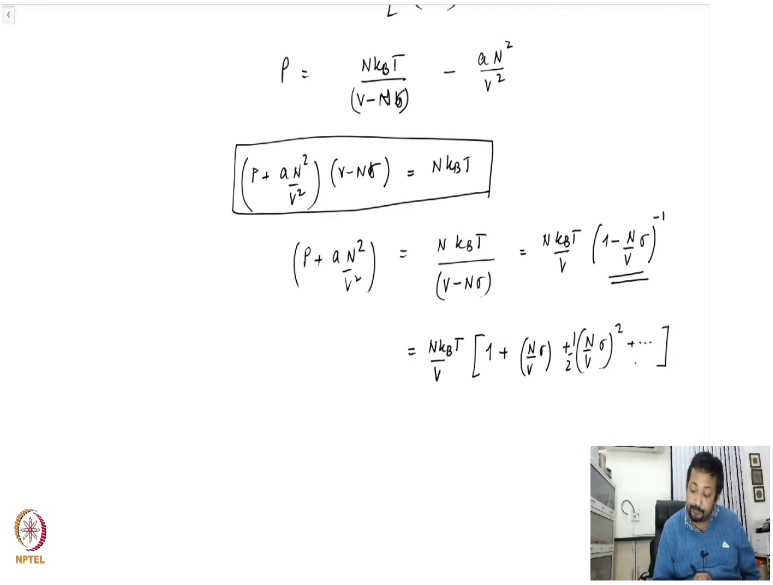

$$P = \frac{Nk_BT}{(V-N\sigma)} - \frac{aN^2}{V^2}$$

$$\boxed{\left(P + \frac{aN^2}{V^2}\right)(V-N\sigma) = Nk_BT}$$

$$\left(P + \frac{aN^2}{V^2}\right) = \frac{Nk_BT}{(V-N\sigma)} = \frac{Nk_BT}{V}\underline{\underline{\left(1-\frac{N\sigma}{V}\right)^{-1}}}$$

$$= \frac{Nk_BT}{V}\left[1 + \left(\frac{N\sigma}{V}\right) + \frac{1}{2}\left(\frac{N\sigma}{V}\right)^2 + \cdots\right]$$

So, that the equation of state becomes a N square over V square times V minus N sigma sorry not b this is going to be sigma and sigma is going to be NK B T. So, you nicely come up with the Van der Waals equation of state right.

As a purely phenomenological equation of state and can be derived within the mean field approach by we saying that you are looking at a very dilute system of a gas and you kind of replace the interaction energy by a mean field energy which you obtained by picking up the ith particle.

And looking at the contribution of all the jth particles surrounding that is all good. Now, I have P plus a this is the question we want to ask NK B T divided by V minus N sigma, so that I can write down this as NK B T over V 1 minus N by V sigma inverse. Now, you clearly see therefore this quantity is going to be NK B T over V I can expand for weak enough density for very low density. So, that this term is 1 plus N by V sigma plus N by V sigma square plus higher order terms.

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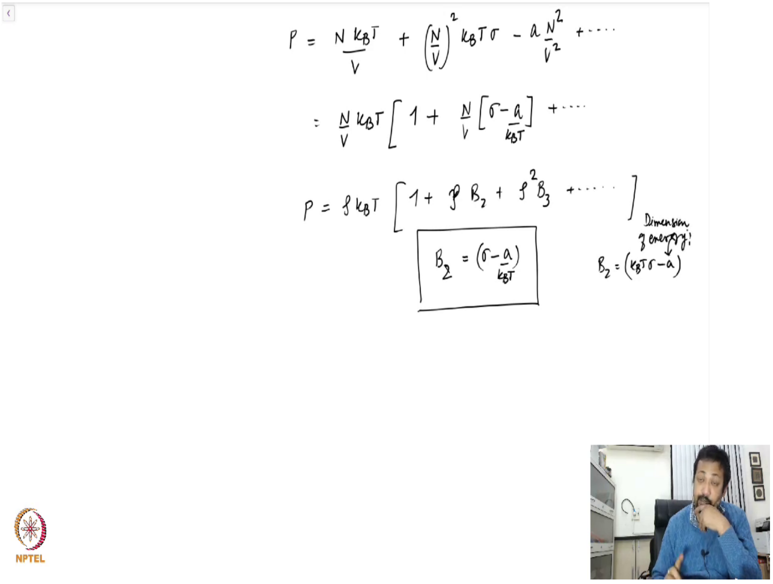

$$P = \frac{N k_B T}{V} + \left(\frac{N}{V}\right)^2 k_B T \sigma - a \frac{N^2}{V^2} + \cdots$$

$$= \frac{N}{V} k_B T \left[1 + \frac{N}{V} \left[\sigma - \frac{a}{k_B T} \right] + \cdots \right.$$

$$P = \rho k_B T \left[1 + \rho B_2 + \rho^2 B_3 + \cdots \right]$$

$$\boxed{B_2 = \left(\sigma - \frac{a}{k_B T} \right)}$$

Dimension of energy!

$$B_2 = \left(k_B T \sigma - a \right)$$

Therefore, pressure is a K B T over V plus N V whole square. If I open the bracket K B T times sigma minus a N square over V square plus higher order terms. And then I again take NK B T common which gives me 1 plus N by V sigma minus a plus higher order terms.

So, that your second virial coefficient you see that this expansion clearly has rho 1 rho times b 2 plus rho square times b 3 so and so forth. This is rho of K B T is equal to P. So, even this phenomenological equation which actually describes lots of gases actually can be written down in the same form that we have done.

We have arrived we had arrived that when we looked at the interacting system. And clearly here I think that B 2 the second virial coefficient is going to be sigma minus sorry one has to be careful if I have taken NK B T outside this has to be a over K B T a has a dimension of this thing right, yeah.

So, this is your second virial coefficient alternatively you can also absorb the K B T in the second virial coefficient. And defined B 2 as K B T sigma minus a; a has a dimension of energy please remember that.