Statistical Mechanics
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Lecture - 33
Grand Canonical Ensemble

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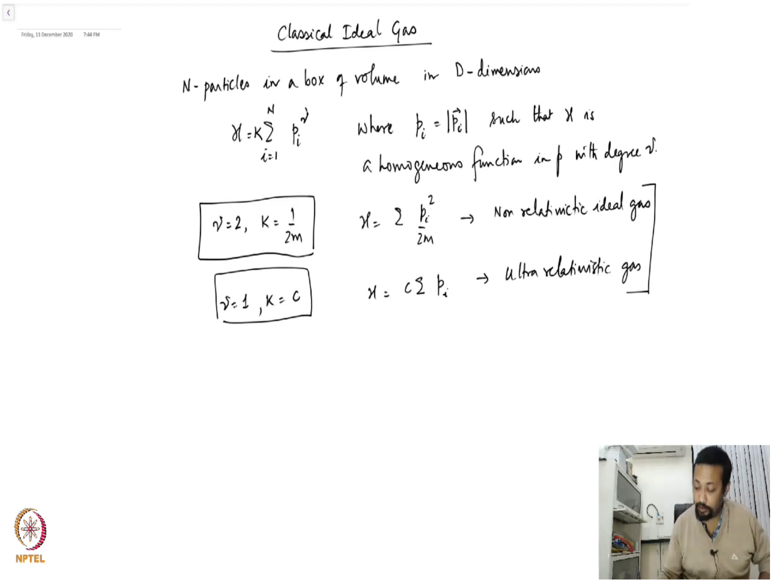

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Classical Ideal Gas

N-particles in a box of volume in D-dimensions

$\mathcal{H} = K\sum_{i=1}^{N} p_i^{\nu}$ where $p_i = |\vec{p}_i|$ such that $\mathcal{H}$ is a homogeneous function in p with degree ν.

$\boxed{\nu = 2,\ K = \frac{1}{2m}}$ $\mathcal{H} = \sum \frac{p_i^2}{2m}$ → Non relativistic ideal gas

$\boxed{\nu = 1,\ K = c}$ $\mathcal{H} = c\sum p_i$ → Ultra relativistic gas

Welcome back. So, we will take our final example, that of the classical ideal gas and treated canonically. So, our system is N-particles in a box of volume V in D-dimensions. So, the Hamiltonian of this system is sum over i equal to 1 to N p i raise to the power nu. Where so there is a sorry there is a k outside or kappa outside where p i is mod p i right, such that h is a homogeneous function in p with degree nu right. So, given this Hamiltonian two cases are of particular interest for us.

One is nu is equal to 2, and k is equal to 1 over twice M. In that case, the Hamiltonian becomes p i square over twice M which is a non-relativistic ideal gas. The second case of interest is nu is equal to 1, and k is equal to c in which case this is sum over p i times c and this is an ultra relativistic gas. We will come back to this special cases later right.

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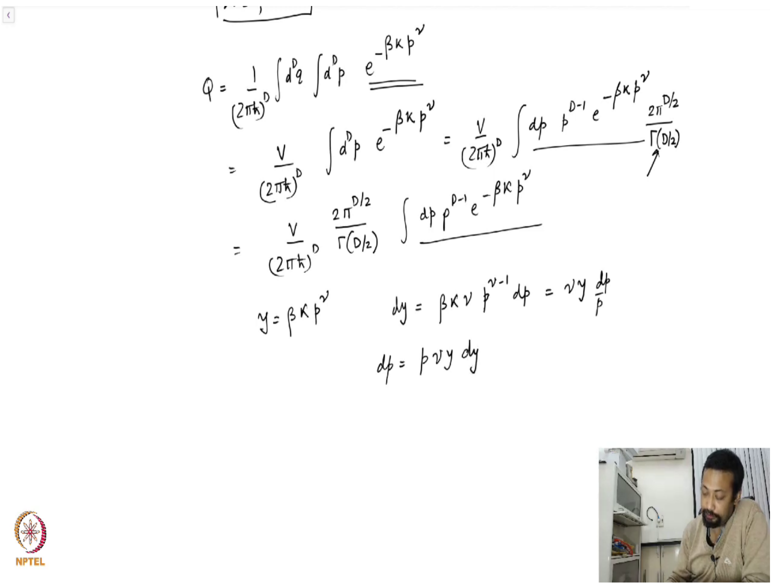

$$Q = \frac{1}{(2\pi\hbar)^D} \int d^D q \int d^D p \; \underline{\underline{e^{-\beta \kappa p^\nu}}}$$

$$= \frac{V}{(2\pi\hbar)^D} \int d^D p \; e^{-\beta \kappa p^\nu} = \frac{V}{(2\pi\hbar)^D} \int \underline{dp \; p^{D-1} e^{-\beta\kappa p^\nu}} \; \frac{2\pi^{D/2}}{\Gamma(D/2)} \nearrow$$

$$= \frac{V}{(2\pi\hbar)^D} \frac{2\pi^{D/2}}{\Gamma(D/2)} \int \underline{dp \, p^{D-1} e^{-\beta\kappa p^\nu}}$$

$$y = \beta\kappa p^\nu \qquad dy = \beta\kappa\nu p^{\nu-1} dp = \nu y \frac{dp}{p}$$

$$dp = p \nu y \, dy$$

So, given this Hamiltonian, we write down the single particle partition function as d D q d D p, since, is a d-dimensional e to the power minus beta k p i raised to the power nu. Now, you notice that this quantity still dimension full, because it has a dimension of q times p which is the dimension of action. And therefore, you divide this 1 by 2 pi h bar raised to the power D right.

This exponential integrals, this part does not depend on the coordinates. And therefore, we can straight forward write down this as 2 pi h bar raised to the power D integral of d D p e to the power minus beta k p i, sorry, we will not put the index i over here anymore, because it is just a single particle now, p to the power nu, which is v over 2 pi h bar raised to the power D d p p to the power D minus 1 e to the power minus beta kappa p to the power nu, but this is not all of it, because we have still have to take care of the factor a 3 N that we did for.

And that answer is sorry, D by 2 gamma D by 2. So, this quantity is v over 2 pi h bar raised to the power D. So, this is the part which is comes from the angular integral 2 pi D by 2 gamma D by 2. And then I have the integral d p p to d power D minus 1 e to the power minus beta kappa p to the power nu, good. Once I have this, then I now want to evaluate this integral.

But for that, let me substitute y as beta k p to the power nu right, so that d y is beta k nu p to the power nu minus 1 d p which is equal to nu times y d p over p. So, the d p the change of variable gives me p nu y dy.

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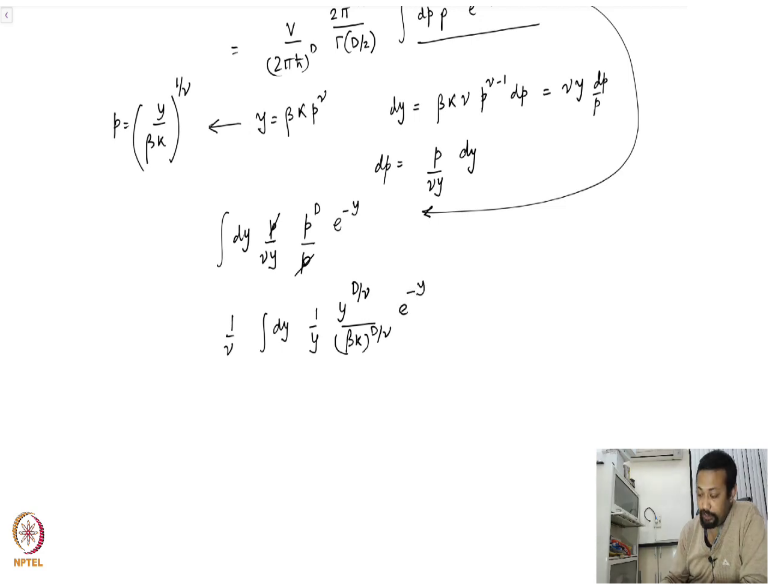

$$= \frac{V}{(2\pi\hbar)^D} \frac{2\pi}{\Gamma(D/2)} \int dp\, p\ e$$

$$p = \left(\frac{y}{\beta\kappa}\right)^{1/\nu} \leftarrow y = \beta\kappa p^{\nu} \qquad dy = \beta\kappa\nu p^{\nu-1} dp = \nu y \frac{dp}{p}$$

$$dp = \frac{p}{\nu y} dy$$

$$\int dy \frac{\cancel{p}}{\nu y} \frac{p^D}{\cancel{p}} e^{-y}$$

$$\frac{1}{\nu} \int dy \frac{1}{y} \frac{y^{D/\nu}}{(\beta\kappa)^{D/\nu}} e^{-y}$$

And this integral if I calculate now, this becomes d y p nu y; I have p to the power D minus 1 which is p to the power d by p. So, that this p and this p is going to cancel out that is why I wrote this differential in terms of p and I have e to the power minus 1.

So, this, this gets cancelled out. I think there is something wrong over here. So, I can see that this is going to be d p is going to be p over nu y. So, I will have p over nu times y. And this p, this p cancels out. So, you will be left off with d y 1 over nu 1 over y. And from this p is y over beta k raised to the power 1 over nu, so, y over D by nu beta k D by nu e to the power minus 1 as e to the power minus y.

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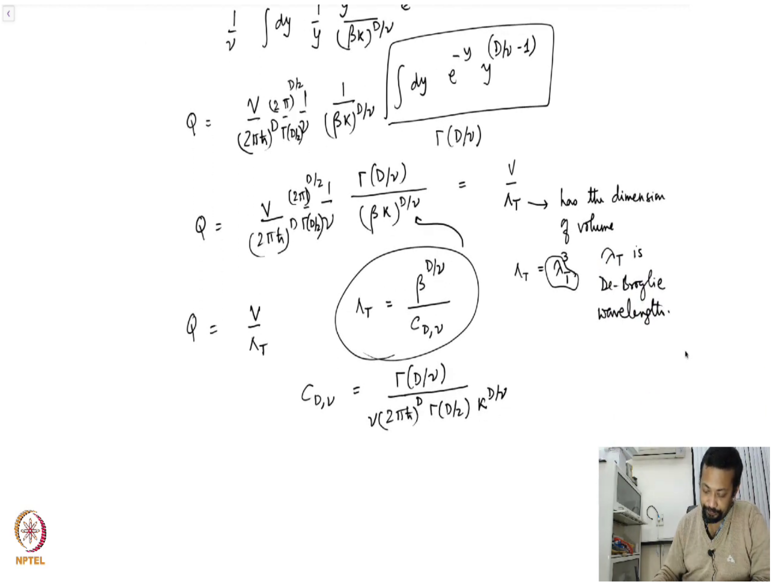

$$\frac{1}{\nu}\int dy\,\frac{1}{y}\,\frac{y}{(\beta K)^{D/\nu}}\,e$$

$$Q = \frac{V}{(2\pi\hbar)^D}\frac{(2\pi)^{D/2}}{\Gamma(D/2)}\frac{1}{\nu}\frac{1}{(\beta K)^{D/\nu}}\underbrace{\boxed{\int dy\, e^{-y}\, y^{(D/\nu-1)}}}_{\Gamma(D/\nu)}$$

$$Q = \frac{V}{(2\pi\hbar)^D}\frac{(2\pi)^{D/2}}{\Gamma(D/2)}\frac{1}{\nu}\frac{\Gamma(D/\nu)}{(\beta K)^{D/\nu}} = \frac{V}{\Lambda_T} \rightarrow \text{has the dimension of volume}$$

$$\Lambda_T = \boxed{\lambda_T^3}$$

λ_T is De-Broglie wavelength.

$$Q = \frac{V}{\Lambda_T} \qquad \Lambda_T = \frac{\beta^{D/\nu}}{C_{D,\nu}}$$

$$C_{D,\nu} = \frac{\Gamma(D/\nu)}{\nu(2\pi\hbar)^D\,\Gamma(D/2)\,K^{D/\nu}}$$

So, your single particle partition function is V over 2 pi h bar d do not be afraid, because with this call r p symbolic integration like k d an all this, I am sure you would have done it somewhere and 1 over nu 1 over beta k raised to the power D over nu d y eta power minus y y to the power D by nu minus 1. This integral is a gamma function gamma D over nu.

So, now, you see that I have a all solved the problem, I have 1 by nu gamma of D by nu beta kappa D over nu. There is one mistake, I think I have forgotten a gamma D by 2 factor, 1 over gamma D by 2 1 of over gamma D by 2 right. Let me write this as V over lambda T. Well, lambda T you see has the dimension of volume. So, lambda T, I can write down in terms of lambda cube T. And this quantity it lambda T is call the De-Broglie wavelength right ok.

So, Q then becomes V over lambda T. And then lambda T is beta to the power D over nu divided by a constant C D, nu. And this C D, nu if you just read of, if you just put it over here, you can immediately read of what this is going to be, this is going to be 1 over 2 pi h bar D gamma D by 2 nu gamma D over nu. And then there is going to be kappa D over nu. So, let us see whether we have the right expression or everything.

So, this is the term which is the angular integral. And I think we have missed out 2 pi raised to the power D by 2.

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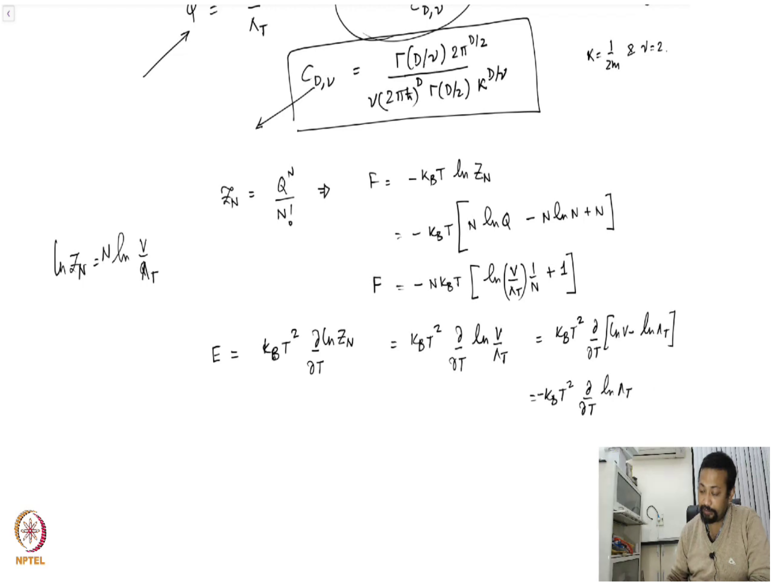

$$\varphi = \frac{\quad}{\Lambda_T}$$

$$C_{D,\nu}$$

$$\boxed{C_{D,\nu} = \frac{\Gamma(D/\nu)\, 2\pi^{D/2}}{\nu (2\pi\hbar)^D\, \Gamma(D/2)\, K^{D/\nu}}}$$

$K = \frac{1}{2m}$ & $\nu = 2.$

$$Z_N = \frac{Q^N}{N!} \Rightarrow F = -k_B T \ln Z_N$$

$$= -k_B T \left[N \ln Q - N \ln N + N \right]$$

$$F = -N k_B T \left[\ln\left(\frac{V}{\Lambda_T}\right) \frac{1}{N} + 1 \right]$$

$$\ln Z_N = N \ln \frac{V}{\Lambda_T}$$

$$E = k_B T^2 \frac{\partial \ln Z_N}{\partial T} = k_B T^2 \frac{\partial}{\partial T} \ln \frac{V}{\Lambda_T} = k_B T^2 \frac{\partial}{\partial T} \left[\ln V - \ln \Lambda_T \right]$$

$$= -k_B T^2 \frac{\partial}{\partial T} \ln \Lambda_T$$

So, 2 pi raised to the power D by 2 over here, so that there is a 2 pi raised to power D by 2 setting over here. So, this is the expression for given any arbitrary dimension d and a value nu, one can construct the De-Broglie wavelength from here. We will come back to this; we will explicitly derive this expression particularly for the case of k equal to 1 over 2 M, and nu is equal to 2.

But right now, let us continue with this calculation, the N-particle partition function is Q to the power N, and now, we bring in the factor N factorial, because the particles of this gas are indistinguishable. You cannot distinguish one from the other and therefore, you are over counting your micro states. So, the total possible permutations, total possible T of over counting permutations is N factorial with which you divide this, which implies the free energy which is minus K B T ln of Z N is going to be minus K B T N.

We will put that in a bracket ln Q minus N ln N plus N. And this becomes minus N K B T ln V over lambda T 1 by N plus 1 right. So, this is your free energy. Therefore, the energy E is k b K B T square del del T of ln of Z N. And if I look at ln of Z N, ln of Z N is ln of V over Q T sorry, V over lambda T N which is K B T square del del T of ln V over lambda T, which is K B T square del del T of ln of V minus ln of lambda T.

And therefore, you have K B T square minus del del T of ln of lambda T right good.

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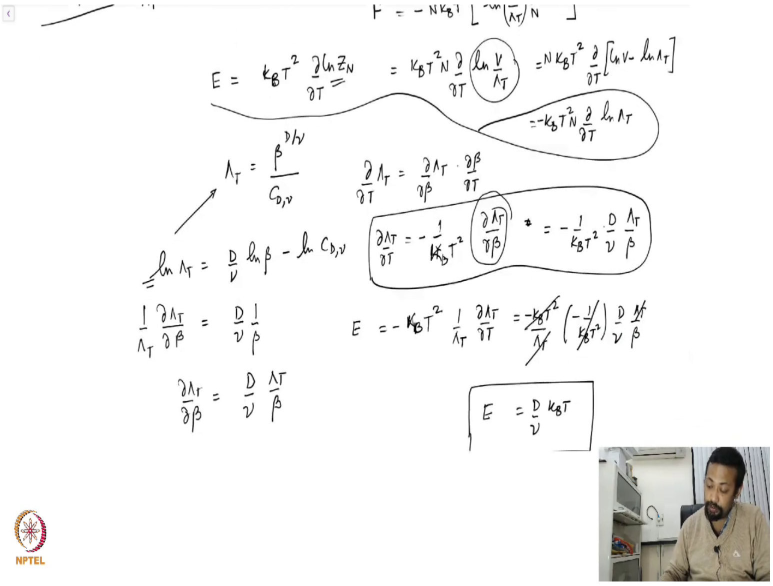

$$E = k_B T^2 \frac{\partial \ln Z_N}{\partial T} = k_B T^2 N \frac{\partial}{\partial T}\left(\ln \frac{V}{\Lambda_T}\right) = N k_B T^2 \frac{\partial}{\partial T}\left[\ln V - \ln \Lambda_T\right]$$

$$= -k_B T^2 N \frac{\partial}{\partial T} \ln \Lambda_T$$

$$\Lambda_T = \frac{\beta^{D/\nu}}{C_{D,\nu}}$$

$$\frac{\partial}{\partial T} \Lambda_T = \frac{\partial \Lambda_T}{\partial \beta} \cdot \frac{\partial \beta}{\partial T}$$

$$\ln \Lambda_T = \frac{D}{\nu} \ln \beta - \ln C_{D,\nu}$$

$$\frac{\partial \Lambda_T}{\partial T} = -\frac{1}{k_B T^2} \frac{\partial \Lambda_T}{\partial \beta} = -\frac{1}{k_B T^2} \cdot \frac{D}{\nu} \frac{\Lambda_T}{\beta}$$

$$\frac{1}{\Lambda_T} \frac{\partial \Lambda_T}{\partial \beta} = \frac{D}{\nu} \frac{1}{\beta}$$

$$E = -k_B T^2 \frac{1}{\Lambda_T} \frac{\partial \Lambda_T}{\partial T} = \frac{-\cancel{k_B T^2}}{\cancel{\Lambda_T}} \left(-\frac{1}{\cancel{k_B T^2}}\right) \frac{D}{\nu} \frac{\cancel{\Lambda_T}}{\beta}$$

$$\frac{\partial \Lambda_T}{\partial \beta} = \frac{D}{\nu} \frac{\Lambda_T}{\beta}$$

$$\boxed{E = \frac{D}{\nu} k_B T}$$

Lambda T by our definition was beta to the power D over nu divided by C of D comma nu. So, del del T of lambda T, del del T of lambda T is del del beta of lambda T into del beta del T. del beta del T is minus 1 over k b K B T square del lambda T del beta. So, I just have to evaluate this. But let us take a log of this expression ln lambda T is d over nu ln beta minus ln C D comma nu the constant over here.

So, del lambda del T beta let us say so, 1 by lambda T if I now take a derivative with respect to beta, then D over nu 1 over beta, am I right? So, del lambda del T del beta is equal to D over nu lambda T over beta. And therefore, I have minus 1 over K B T square times D over nu say this is D over nu lambda T over beta. We will keep it like this way. So, this becomes your del lambda T del T right.

Let us go back to the energy expression which we had over here. And the final form was this is minus K B T square del del T of ln lambda T is 1 by lambda T del lambda T del T. Actually, we could have avoided all this a exercise just taken a derivative of T with respect to just this one, then life would have been simpler. Anyway, since, we have done it let us go just go ahead with this K B T square over lambda T del lambda del T I know is minus 1 over K B T square D over nu lambda T over beta.

So, this means this, this cancels out; this, this cancels out. And I have the nice expression D over nu K B T right.

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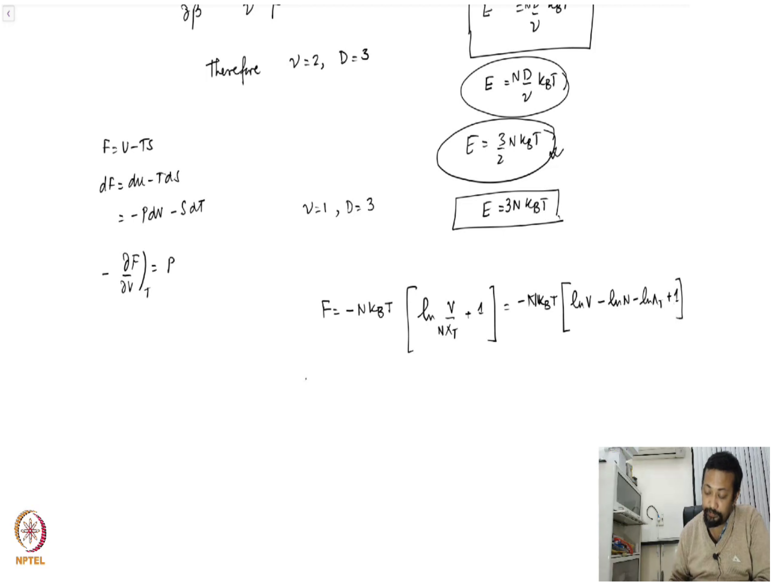

Therefore $\nu = 2, \; D = 3$

$$E = N \frac{D}{\nu} k_B T$$

$$E = \frac{3}{2} N k_B T$$

$$F = U - TS$$

$$dF = dU - TdS$$

$$= -PdV - SdT$$

$$-\left.\frac{\partial F}{\partial V}\right)_T = P$$

$\nu = 1 , \; D = 3$

$$\boxed{E = 3N k_B T}$$

$$F = -N k_B T \left[\ln \frac{V}{N \lambda_T} + 1 \right] = -N k_B T \left[\ln V - \ln N - \ln \lambda_T + 1 \right]$$

Therefore, for a non-relativistic gas when nu is equal to 2 in three dimension D is equal to 3, you see E is equal to D over nu I am sorry, there has to be an N which I have missed somewhere D over nu K B T. But you see there is a problem over here, and the problem rests in this part.

Now, when I do not turn around this, this had ln Z N is N ln V over lambda T and I missed out a factor N over here, so, that factor has to be carried all throughout. And once you do that calculation, you are going to come up with an N over here. If you did not have an m; that means, energy was not extensive. So, there is something wrong seriously, wrong with the calculation. So, one has to be very, very mindful of all of these right. So, if nu is equal to D two and D is equal to 3.

I have E is equal to 3 by 2 N K B T. And this is the classical ideal gas that we have seen. When nu is equal to 1 and D is equal to 3, E is equal to just N K B T strikingly different then sorry, 3 N K B T it is strikingly different from the result that we have seen for this case. Now, recall that F was U minus T S and unlike the magnetic system that we are this is not the Gibbs free energy, there is no external pressure imposed.

So, therefore, d F is dU minus T dS. And one can work this out; this is going to be minus T P dV minus S dT. So, that del F del V is going to be minus of del F del V is going to be the thermodynamic pressure.

Let us look at the expression for F. F had this very nice expression minus N K B T ln V over lambda T N lambda T plus 1 which means I can just explicitly, write it down as ln V minus ln N minus ln lambda T plus 1.

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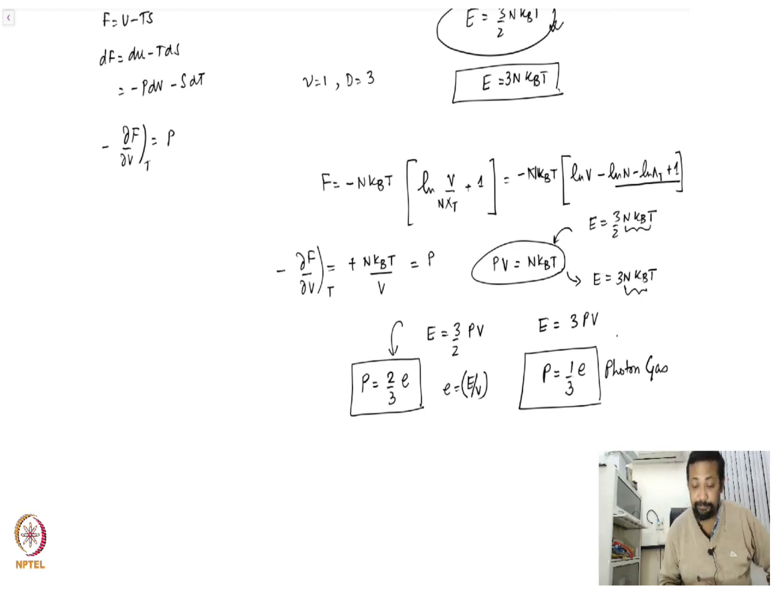

$F = U - TS$

$dF = dU - TdS$

$= -PdV - SdT$

$-\frac{\partial F}{\partial V}\Big)_T = P$

$\nu = 1,\ D = 3$

$E = \frac{3}{2} N k_B T$

$\boxed{E = 3N k_B T}$

$F = -N k_B T \left[\ln \frac{V}{N \lambda_T} + 1 \right] = -N k_B T \left[\ln V - \underline{\ln N - \ln \lambda_T + 1} \right]$

$-\frac{\partial F}{\partial V}\Big)_T = + \frac{N k_B T}{V} = P$

$PV = N k_B T$

$E = \frac{3}{2} N k_B T$

$E = 3N k_B T$

$E = \frac{3}{2} PV$

$E = 3PV$

$\boxed{P = \frac{2}{3} e}$ $e = (E/V)$

$\boxed{P = \frac{1}{3} e}$ Photon Gas

And if I take a derivative of the free energy with respect to the volume, these two three terms will not matter temperature held constant is minus N K B T over V. So, that minus of del F del V temperature constant is just plus this and therefore, this is the pressure. So, you have P V is equal to N K B T. Remarkably, it does not depend on whether it is an unrelativistic gas or whether it is a non-relativistic gas. So, it does not depend on nu, it does not depend on K, it does not depend on T.

It is just the pressure times volume is equal to N K B T. Where does the difference coming? For a non-relativistic gas, this is going to be 3 by 2 N K B T, whereas, for a relativistic gas the energy relation is different right. So, N K B T is P V, so, I will just replace this 3 by 2 P V for a non-relativistic gas. And for an ultra relativistic gas, this is equal to 3 P V.

Immediately, you see that the pressure is 2 3rd the energy density which we will write as small e for a non-relativistic gas. For a relativistic gas, the pressure is 1 3rd the energy density. So, this is the case for a photon gas; and this is the case for a normal ideal non relativistic ideal gas. For non-relativistic ideal gas, the pressure is always two-third the energy density; your small e is capital E over V. And for a ultra relativistic gas such as a photon gas, your pressure is always 1 3rd of the energy density.

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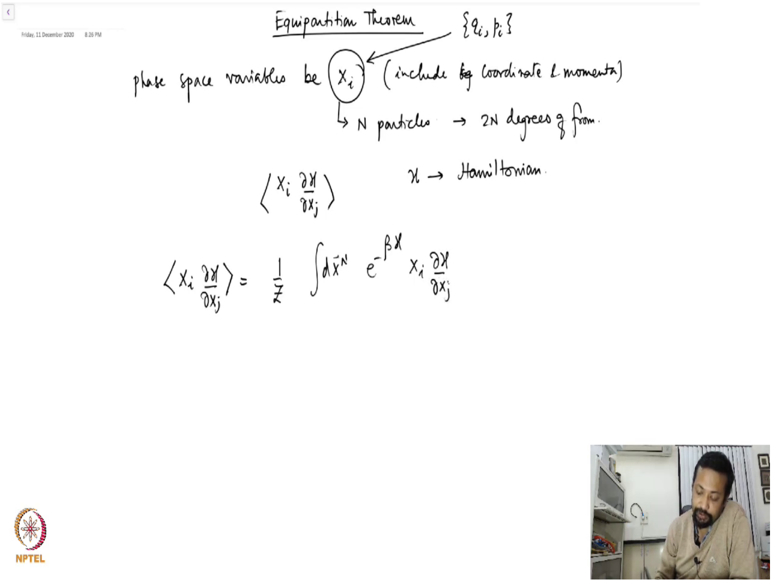

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Equipartition Theorem

$\{q_i, p_i\}$

phase space variables be $\boxed{x_i}$ (include ~~bg~~ coordinate & momenta)

$\hookrightarrow$ N particles → 2N degrees of from.

$\mathcal{H} \rightarrow$ Hamiltonian.

$$\left\langle x_i \frac{\partial \mathcal{H}}{\partial x_j} \right\rangle$$

$$\left\langle x_i \frac{\partial \mathcal{H}}{\partial x_j} \right\rangle = \frac{1}{Z} \int d\vec{x}^N e^{-\beta \mathcal{H}} x_i \frac{\partial \mathcal{H}}{\partial x_j}$$

So, what we now, want to discuss is what is called the equipartition theorem. It is a very very useful theorem as you will see in the following discussion. So, let us denote the phase space variable. So, that the phase space variables be X i, and this include my coordinate and momenta. So, for N particle for a system with N degrees of freedom sorry, for a system with N particles, there are 2 N degrees of freedom in 1 D right.

So, if there it is in three dimension, then it is a 6 N, anyway that is not the concern over here. So, X i the set q i p i is denoted by the X i right. So, now I want to determine the average of this quantity del H del X j, where H is the Hamiltonian.

So, by definition X i del H del X j is equal to 1 over Z D of X N which means X 1, X 2 all these thing e to the power minus beta H X i del H del X j right. Now, let us just focus from this expression in the right hand side just let us just focus on the integral over X j.

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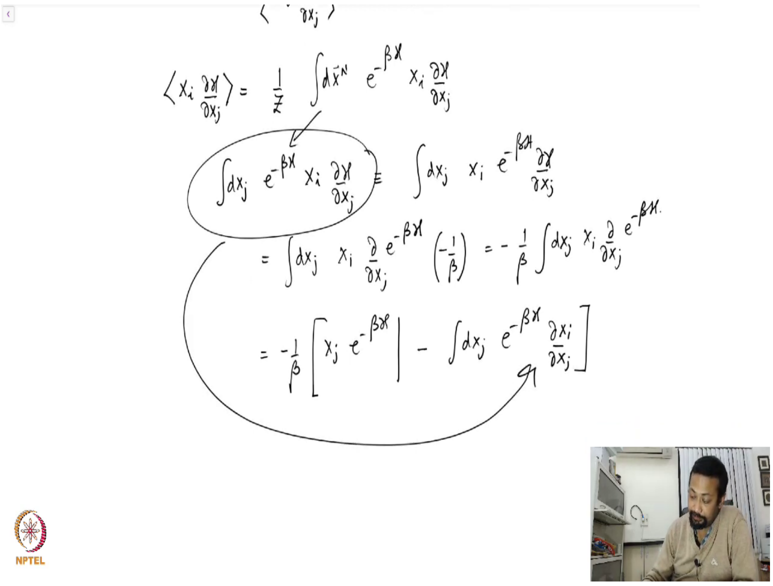

$$\left\langle x_i \frac{\partial \mathcal{H}}{\partial x_j} \right\rangle = \frac{1}{Z} \int d\vec{x}^N \, e^{-\beta \mathcal{H}} \, x_i \frac{\partial \mathcal{H}}{\partial x_j}$$

$$\boxed{\int dx_j \, e^{-\beta \mathcal{H}} \, x_i \frac{\partial \mathcal{H}}{\partial x_j}} \equiv \int dx_j \, x_i \, e^{-\beta \mathcal{H}} \frac{\partial \mathcal{H}}{\partial x_j}$$

$$= \int dx_j \, x_i \frac{\partial}{\partial x_j} e^{-\beta \mathcal{H}} \left(-\frac{1}{\beta} \right) = -\frac{1}{\beta} \int dx_j \, x_i \frac{\partial}{\partial x_j} e^{-\beta \mathcal{H}}.$$

$$= -\frac{1}{\beta} \left[x_j \, e^{-\beta \mathcal{H}} \Big| - \int dx_j \, e^{-\beta \mathcal{H}} \frac{\partial x_i}{\partial x_j} \right]$$

So, from this I just extract the term which is minus beta H X i del H del X j which I manipulate or rather first rearrange as X i e to the power minus beta H del H del X j. This is going to be d of X j X i del del X j of e to the power minus beta H. If you do that you are going to get a minus beta H. So, I have to divide by minus 1 over beta. So, this becomes minus 1 over beta d X j X i del del X j e to the power minus beta H.

If I now, integrate by parts, then essentially I have 1 over beta X i e to the power minus beta H the boundary terms minus d of X j e to the power minus beta H del X i del X j.

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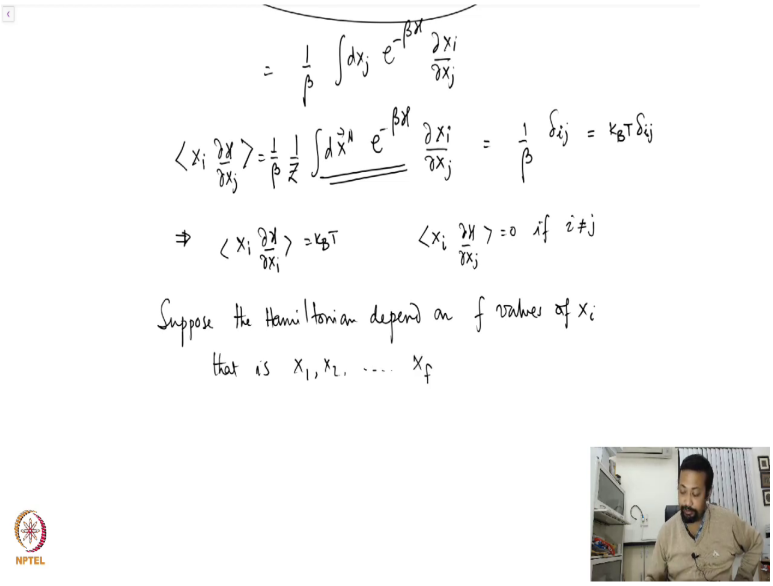

$$= \frac{1}{\beta} \int dx_j \, e^{-\beta\mathcal{H}} \frac{\partial x_i}{\partial x_j}$$

$$\left\langle x_i \frac{\partial \mathcal{H}}{\partial x_j} \right\rangle = \frac{1}{\beta} \frac{1}{Z} \underline{\underline{\int d\vec{x}^N \, e^{-\beta\mathcal{H}}}} \frac{\partial x_i}{\partial x_j} = \frac{1}{\beta} \delta_{ij} = k_B T \delta_{ij}$$

$$\Rightarrow \left\langle x_i \frac{\partial \mathcal{H}}{\partial x_i} \right\rangle = k_B T \qquad \left\langle x_i \frac{\partial \mathcal{H}}{\partial x_j} \right\rangle = 0 \text{ if } i \neq j$$

Suppose the Hamiltonian depend on f values of x_i

that is $x_1, x_2, \ldots x_f$

So, just this part of the integral has now come to this, but these are the boundary terms. The first term vanishes, because it is a boundary term. And therefore, you are left out with 1 over beta integral d X j e to the power minus beta H del X i del X j. Which means this average X i del H del X j is 1 over Z d X N minus beta H del X i del X j and a 1 over beta outside.

Therefore, this expression becomes 1 over beta the del X i del X j is delta i j. So, we will put a delta i j, and then the rest of the expression is nothing but the partition function. So, this becomes K B T times delta i j right. So, this would imply that X i del X i average is K B T, X i del H del X j is 0 if i is not equal to j.

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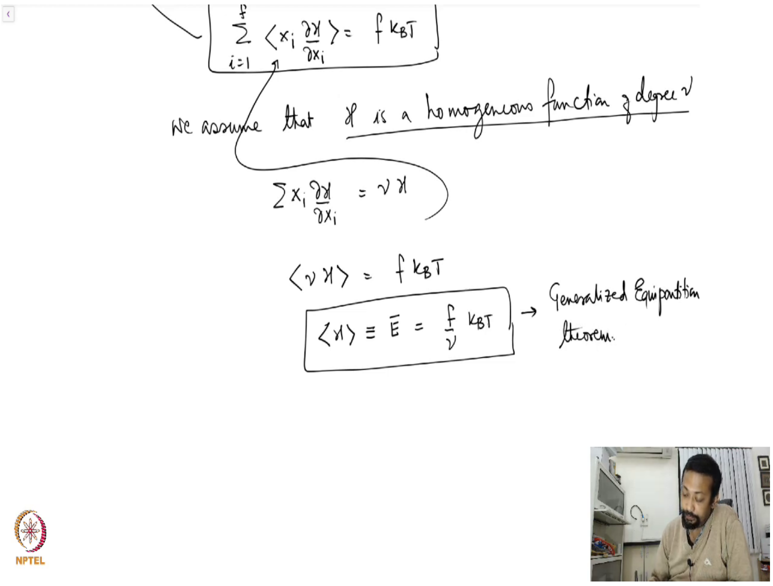

$$\boxed{\sum_{i=1}^{f} \left\langle x_i \frac{\partial \mathcal{H}}{\partial x_i} \right\rangle = f k_B T}$$

We assume that $\mathcal{H}$ is a homogeneous function of degree ν

$$\sum x_i \frac{\partial \mathcal{H}}{\partial x_i} = \nu \mathcal{H}$$

$$\langle \nu \mathcal{H} \rangle = f k_B T$$

$$\boxed{\langle \mathcal{H} \rangle \equiv \bar{E} = \frac{f}{\nu} k_B T} \rightarrow \text{Generalized Equipartition theorem.}$$

Now, suppose the Hamiltonian depends on f such values. Suppose, the Hamiltonian depends on f values of X i that is X 1, X 2 all the way up to X f right. Then it means that sum over i equal to 1 to f X i del H del X i is equal to f times K B T. This particular expression follows from the one that we have written down over here good.

Further, we take it now one more step we assume that H is a homogeneous function of degree nu right. So, normally, for the ideal gas we also have this to be homogeneous function. We just did it for this a little while ago or in the earlier class, so H is a homogeneous function of degrees.

Then I can apply, my Euler theorem to write own this as nu times H right, sorry, not this and this theorem we have done earlier. Once we substitute this over here, this essentially means that nu times H is f over times K B T. So, that the average of the Hamiltonian which is equivalent to the average energy is going to be f over nu K B T and this is the generalized equipartition theorem right.

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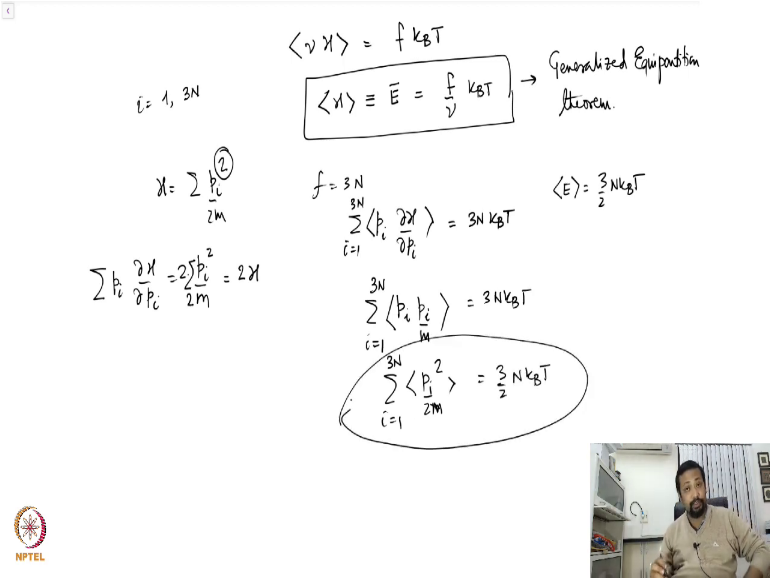

$$\langle \nu \mathcal{H} \rangle = f k_B T$$

$$\boxed{\langle \mathcal{H} \rangle \equiv \bar{E} = \frac{f}{\nu} k_B T} \rightarrow$$ Generalized Equipartition theorem.

$i = 1, 3N$

$$\mathcal{H} = \sum \frac{p_i^{②}}{2m}$$

$$\sum p_i \frac{\partial \mathcal{H}}{\partial p_i} = 2\sum \frac{p_i^2}{2m} = 2\mathcal{H}$$

$f = 3N$

$$\sum_{i=1}^{3N} \left\langle p_i \frac{\partial \mathcal{H}}{\partial p_i} \right\rangle = 3N k_B T$$

$$\sum_{i=1}^{3N} \left\langle p_i \frac{p_i}{m} \right\rangle = 3N k_B T$$

$$\sum_{i=1}^{3N} \left\langle \frac{p_i^2}{2m} \right\rangle = \frac{3}{2} N k_B T$$

$$\langle E \rangle = \frac{3}{2} N k_B T$$

For a non-relativistic gas, I have p i square over twice M right. Now, so i runs from 1 to 3N, therefore, your f is equal to 3 N which means sum over p i del H del p i average i is equal to 1 to 3N is going to be 3 N K B T. But del H del p i is just p i over m. So, therefore, this is sum over i equal to 1 to N. And you can easily see that p i times del H del p i is p y square over m, we can multiply it by 2 divided by 2 take the sum over here, take the sum over here is just two times H.

So, it is a homogeneous function of degree 2, but nevertheless this would mean that the average energy in this case is going to be 3 by 2 N K B T. More explicitly, if I this is p i p i over m average is 3 by sorry, it is 3 N K B T for average p i square over 2 M sum over i equal to 1 to 3 N is going to be 3 half N K B T.

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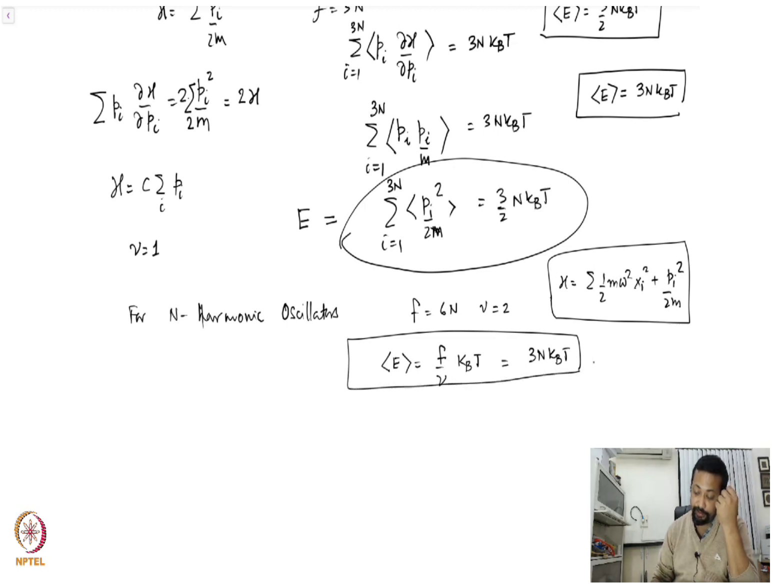

$\sum p_i \frac{\partial \mathcal{H}}{\partial p_i} = 2\sum \frac{p_i^2}{2m} = 2\mathcal{H}$

$\sum_{i=1}^{3N} \langle p_i \frac{\partial \mathcal{H}}{\partial p_i} \rangle = 3N k_B T$

$\boxed{\langle E \rangle = 3N k_B T}$

$\sum_{i=1}^{3N} \langle p_i \frac{p_i}{m} \rangle = 3N k_B T$

$\mathcal{H} = C \sum_i p_i$

$E = \sum_{i=1}^{3N} \langle \frac{p_i^2}{2m} \rangle = \frac{3}{2} N k_B T$

$\nu = 1$

$\boxed{\mathcal{H} = \sum \frac{1}{2} m\omega^2 x_i^2 + \frac{p_i^2}{2m}}$

For N- Harmonic Oscillators $f = 6N$ $\nu = 2$

$\boxed{\langle E \rangle = \frac{f}{\nu} k_B T = 3N k_B T}$.

So, the total kinetic energy of the system which in this case is also the total energy of the system is 3 half N K B T. And this immediately follows from the equipartition theorem. If I had H as sum over i C p i, then you see your average energy your nu is equal to 1. It is a homogeneous function of d p 1 its going to be 3 N K B T, the result that we divide, so laboriously, a little earlier right.

For N-harmonic oscillators in three dimension, your degree of freedom your f is 6 N. It depends your Hamiltonian is sum over half M omega square X i square plus p i square over twice m, where i runs from 1 to 3, and X i i also runs from 1 to 3 m. So, you have 6 N degrees of freedom and nu is 2. This Hamiltonian is a homogeneous function of degree 2. So, that the average energy in this case is f over nu N K B T sorry, f over nu K B T which is going to be 3 N K B T.

And this is exactly the result we derived, when we treated such a system in a metro canonical assemble right.

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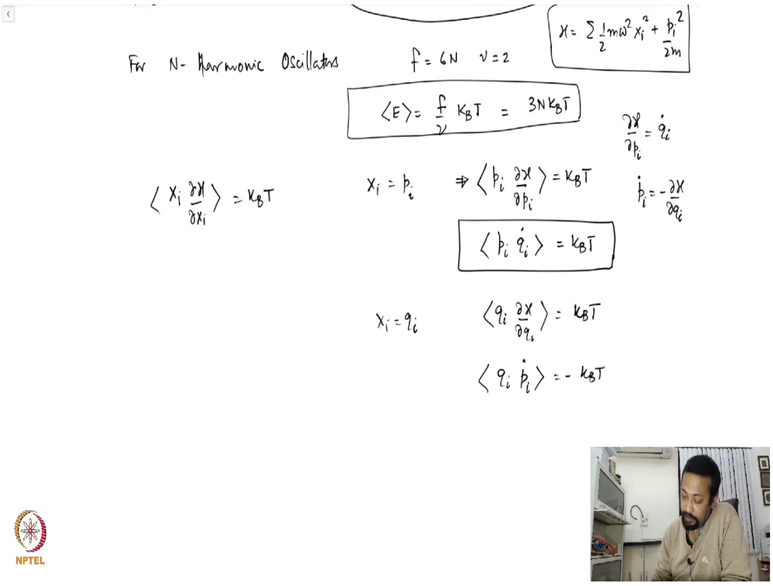

$$\boxed{\mathcal{H} = \sum \frac{1}{2} m\omega^2 x_i^2 + \frac{p_i^2}{2m}}$$

For N- Harmonic Oscillators $f = 6N \quad \nu = 2$

$$\boxed{\langle E \rangle = \frac{f}{\nu} k_B T = 3N k_B T}$$

$$\frac{\partial \mathcal{H}}{\partial p_i} = \dot{q}_i$$

$$\left\langle x_i \frac{\partial \mathcal{H}}{\partial x_i} \right\rangle = k_B T \qquad x_i = p_i \Rightarrow \left\langle p_i \frac{\partial \mathcal{H}}{\partial p_i} \right\rangle = k_B T \qquad \dot{p}_i = -\frac{\partial \mathcal{H}}{\partial q_i}$$

$$\boxed{\langle p_i \dot{q}_i \rangle = k_B T}$$

$$x_i = q_i \qquad \left\langle q_i \frac{\partial \mathcal{H}}{\partial q_i} \right\rangle = k_B T$$

$$\langle q_i \dot{p}_i \rangle = -k_B T$$

Our last point to note in this particular discussion is let us say, I have del H del X i is K B T. So, if I choose X i is equal to p i which will imply that p i del H del p i average is equal to K B T. But del H del p i, if you recall your Hamiltonian equation of motion del H del p i is q i dot. So, p i q i dot is equal to K B T right.

Similarly, if you choose your X i as q i, then this is q i del H del q i which is going to be K B T by the equipartition theorem. And del H del q i is minus so, p i dot is minus del H del q i. And therefore, you have del H p i dot as minus K B T right.

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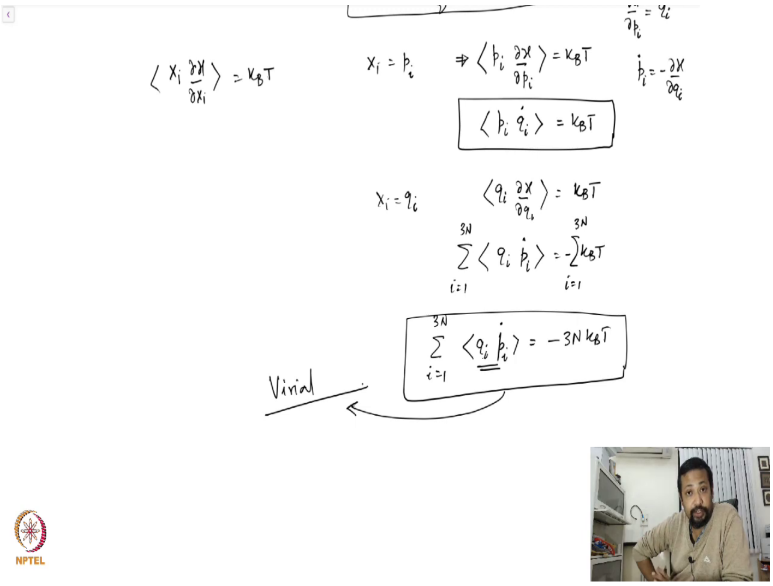

$$\left\langle x_i \frac{\partial \mathcal{H}}{\partial x_i} \right\rangle = k_B T$$

$$x_i = p_i \quad \Rightarrow \left\langle p_i \frac{\partial \mathcal{H}}{\partial p_i} \right\rangle = k_B T \qquad \dot{p}_i = -\frac{\partial \mathcal{H}}{\partial q_i}$$

$$\boxed{\langle p_i \dot{q}_i \rangle = k_B T}$$

$$x_i = q_i \qquad \left\langle q_i \frac{\partial \mathcal{H}}{\partial q_i} \right\rangle = k_B T$$

$$\sum_{i=1}^{3N} \langle q_i \dot{p}_i \rangle = -\sum_{i=1}^{3N} k_B T$$

$$\boxed{\sum_{i=1}^{3N} \langle \underline{\underline{q_i \dot{p}_i}} \rangle = -3N k_B T}$$

Virial

So, now, if you sum it over i equal to 1 to 3N, then essentially this becomes i equal to 1 to 3N. So, that sum over i is equal to 1 to 3 N q i p i dot is equal to minus 3 N K B T.

Now, this particular expression has very significant relation, significance in statistical mechanics. If you look at the dimension of this, this is r dot f. And therefore, this is the work done. In statistical mechanics this is called the virial and the work done in a hydrostatic system particularly is related to the pressure. So, if you want to calculate the equilibrium pressure, one has to evaluate this virial together with the kinetic energy or kinetic contribution, one gets the thermodynamic pressure from the microscopic quantities.