Foundations of Computational Materials Modelling
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Introduction to phase space
Lecture 22

So, what we were discussing in the last time we meet was concerning the solution of the equations of motion or setting up the equations of motion so that we can obtain the position and the momenta of a particle or all the particles constituted... constituting the system as a function of time.

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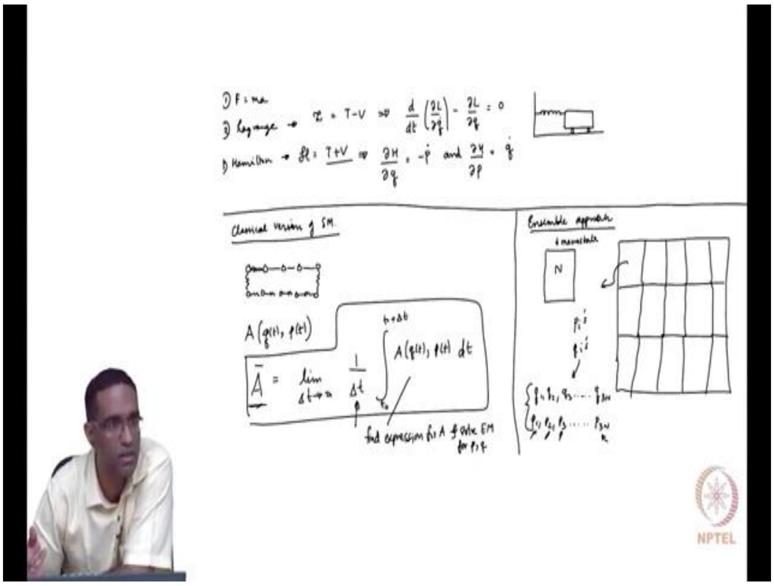

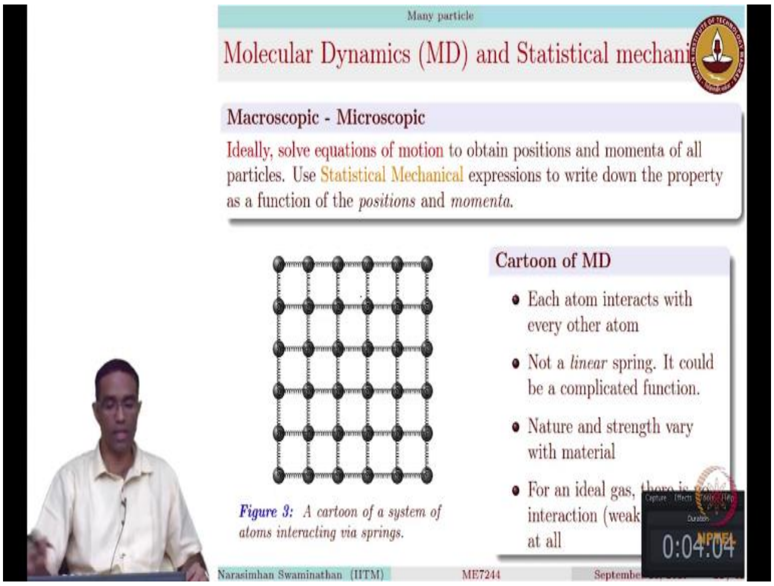
Many particle

Molecular Dynamics (MD) and Statistical mechani

Macroscopic - Microscopic

Ideally, solve equations of motion to obtain positions and momenta of all particles. Use Statistical Mechanical expressions to write down the property as a function of the *positions* and *momenta*.

Figure 3: A cartoon of a system of atoms interacting via springs.

Cartoon of MD

- Each atom interacts with every other atom
- Not a *linear* spring. It could be a complicated function.
- Nature and strength vary with material
- For an ideal gas, there is interaction (weak at all

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So, we saw 3 different methodologies, one is the normal F equal to ma kind of method. The other one was the Lagrange method. And third one was the Hamilton method, right. In this, you define this L which is equal to T minus V and then you are able to do something like d by dt of dou L by dou q dot minus dou L by dou q must be equal to 0.

Performing this essentially gave you the equations of motion for a simple problem which we studied. I hope, you remember that, right. We studied something like that. And for this problem, we had to derive the equations of motions. This is these by the equations that we could use in order to write down the equations of motions.

There, in the Hamilton’s method, we define what is referred to as the Hamilton which turned out to be that kinetic plus the potential energy in case of conservative systems. Ofcourse, there are a couple of steps that you have to follow in order to write down. There are couple of steps that you have to use in order to write down the Hamilton so, I hope you can find that in the slides.

And for conservative systems, it turns out to be the sum of the kinetic and the potential energy and then, once you have that, you can write down what are referred to as the canonical equations of motions as follows.

$$\frac{\partial H}{\partial q} = -\dot{p} \quad \text{and} \quad \frac{\partial H}{\partial p} = \dot{q}$$

These gave us the equations of motion. So, now the whole idea is we are looking at what is referred to as the classical version of statistical mechanics, right?

Statistical Mechanics, so for this in order to motivate the idea behind this, what we say is, let us consider a system of... a crystal okay, which where, all the atoms are connected by some springs. I think I have a better picture in my slides right here. We consider a system like that where you have a large number of atoms, a very large number of atoms and all of them are interacting with each other through some sort of non-linear springs.

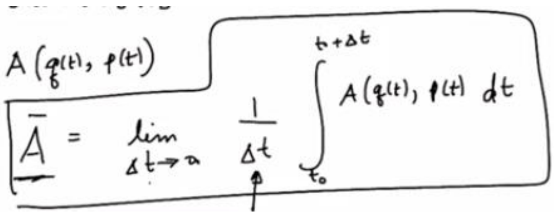
So, at a finite temperature, at a finite temperature, each of these atoms are going to be vibrating about their mean positions. So, keeps vibrating about their mean positions. Now, the question is, firstly I would like to mention that, it is not necessary that these springs or the interaction between these atoms are always you know linear springs. There are some complicated interactions that exists between all the atoms in the system.

And at a finite temperature, they are moving. That means, at every instant of time, there is a position and a velocity that is associated with all the particles of the system. So, the idea of statistical mechanics, in statistical mechanics, the basic idea is that, you are able to say that, there is some property of the system which is actually a function of the position.

Okay let us use let us use q for position, the generalised position and the momentum of all the particles in the system. And if you knew this function A, whatever may be A, let some property of the system, then you can find some average A. so, let us use time averaging. So, let us use a different symbol for time averaging.

So, A bar is the time averaged value. So, what did I say here? I think I wrote this expression down as well. So, it was, limit some delta t tends to infinity, very large value of delta t integrate from 0 to say t naught to t naught plus delta t, A of q of t comma p of t times dq dp. So, or rather, not dq dp, maybe dt because A becomes a function of time when you write it like this.

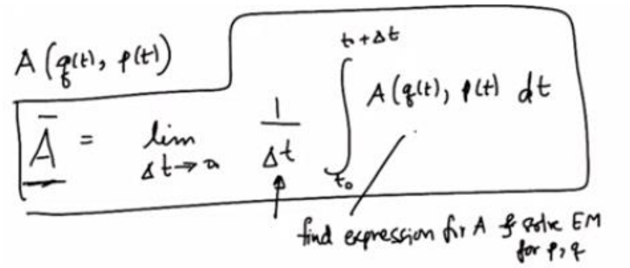
Now, what are the problems? So you are, you now have some average value for A and I told you in the last class that, when you are trying to measure the physical quantity, then you are actually measuring this time averaged quantity in reality. So, the atoms are basically vibrating very fast and they have some temperature that is oscillating about some mean value.



But when you put a thermometer there and remove it, the time period for you for this to actually reach the particular value is very large when compared to the time it actually takes for you to see the mean value, right. So, that is essentially the whole idea. So, basically this delta t also while I told you that it tends to infinity. This infinity is actually not very large unit comes to materials like solids and it also depends upon the property that you are basically looking at.

So, now what are the problems that one can see when you look at an expression like this? So, firstly you have to know what this A? So, for example, if I say I want the elastic constants of the systems, then I have to have an expression for the elastic constants of the systems as a function of p and q, right? And then I have to be able to evolve this p and q by solving the equations of motions.

I need to know how p and q change continuously as a function of time. So, that I can then plug it into this expression and find the expression for A as a function of time and then integrate it over time, and then obtain this average equilibrium value. Now, the whole problem is so, there are two issues. So, find the expression for A and then solve equations of motion for this p and q.



So, remember this p and q are just what are p and q? They are the momenta and the positions of all the atoms that is comprising the system. It is just a huge, when there are huge number of atoms, then it becomes extremely difficult for you to solve and calculate how p and q are moving in reality. When you have the atoms in the order of 6.023 into 10 to power 23, right, it is very hard for you to solve the equations of motion when you have such large number of atoms.

However, in the in the topic that we will be addressing next which is basically addressing you know finding on the material properties using molecular dynamics stimulations that is exactly what we do. So, we construct our crystal structure based on the methods that I just taught you and then we solve the equations of motion and trace the positions in the momenta of all the particles comprising the system.

And then once we known this function A, then we can perform some sort of time averaging to calculate the averaged, average property, average thermodynamic property of the system that we are trying to look at. But practically, when we talk about statistical mechanics, we do generally talk about this time average. Simply, because of the fact that, it is not theoretically possible for us to evolve the p and q for a system comprising of 6.023 into 10 to the power 23 atoms in the order of.

So, statistical mechanics now takes a slightly different approach. Takes a slightly different approach and that approach is referred to what is known as the Ensemble approach, okay Ensemble approach. What happens here, is the following. So, instead of actually assuming that you have to track the positions and the momenta of all the particles in the system continuously with time, you imagine several snapshots of the system each of which is in a different micro state. So, but in the same macro state.

For example, if you have a crystal with N number of atoms. Then you imagine several mental copies of the system, of the same system okay, a large number of them and each of these systems have certain p i’s and q i's that means the so, q i is what? q i is q i in extends from q1, q2, q3 and so on till q3n. P i is nothing but p1, p2, p3 and so on till p3n.

That means q1 is basically the x coordinate for example, of a particle 1. q2 is the y coordinate of particle 1, q3 is the z coordinate of particle 1 and so on and q3 n should would be the z coordinate of the Nth coordinate. Similarly, these things are the x coordinate x momentum, y momentum and z momentum of first particle and this one is the z direction momentum of the nth particle.

Now, what I am trying to say is, if a macroscopic state is imposed on the system, is imposed on the system. The values of q’s and p’s that the system can take can be different but the macro state that they all process will still be the same. So, there are so many different ways that the same micro states can be macro state can be reached through different values of p’s and q’s, right? So, is this aspect clear, right?

So, basically each element of the ensemble is basically in a different micro state corresponding to the same macro state. That means, the p, the positions of all the atoms and the momentum of all the atoms are changing, are different from one ensemble to the other. However, they all have the same macro state. That is, whatever we imposed on that. So, we talk now, what is referred to as the phase space of the system.

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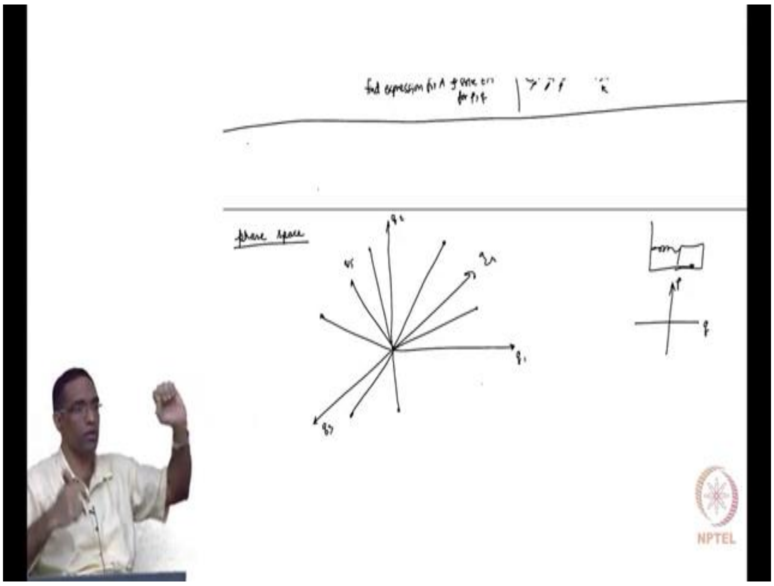

So, what you do? You construct a 6 n dimensional space. So, 6 n dimensional space. So, this would be for example, q1, q1 means just the q2, q3, q4, q5 and so on p1, p2, p3, p4, p5 and so on, 6 n dimensional space okay, just imagine it. Hard to imagine but you can give it a shot, okay. If you or if you want to if you want to simplify stuff in a one dimensional system of this one, then there is only one position and one momentum, so, you have a q, you have a p, right this is easy to imagine. But if you have 3, if you have n particles, then I want you to imagine a space where you have axis running for each and every p and q that the system can actually possess. Now, any point on that space is representing a micro state for a given macro state. Any given point in that space is actually representing a micro state for a given macro state of the system.

Now, each of these ensembles have different points in the phase space, right? and all of them are now moving because p and q are getting evolved with time, each of these things that are getting evolved with time. So, you can imagine for a system with a large number of particles this entire phase space is going to be a swam of a large number of particles. Each particle representing a micro state incommensurate which or matches the macro state of the system.

They are not any arbitrary points that micro state should be such that, it satisfies the imposed micro state. So, what happens now is, several properties of this particular phase becomes useful in defining or in helping us formulate this statistical mechanics. So, let me just highlight a few things.

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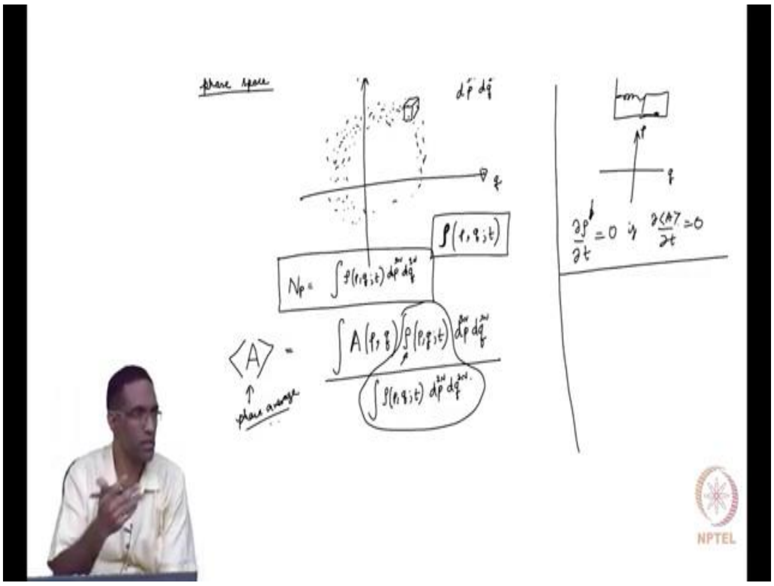


phase space

$d\vec{p}\,d\vec{q}$

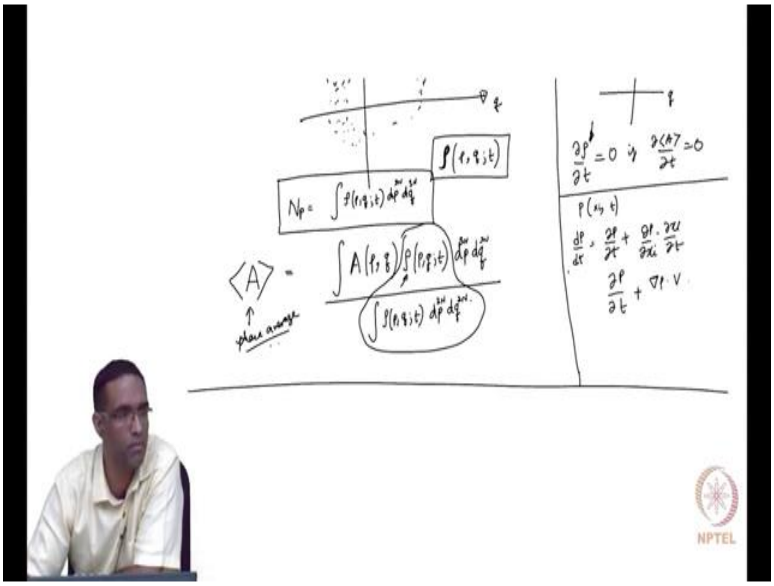
$\boxed{\rho(p,q;t)}$

$$\boxed{N_p = \int \rho(p,q;t)\,d\vec{p}^{\,3N} d\vec{q}^{\,3N}}$$

$$\langle A \rangle = \frac{\int A(p,q)\,\rho(p,q;t)\,d\vec{p}^{\,3N} d\vec{q}^{\,3N}}{\int \rho(p,q;t)\,d\vec{p}^{\,3N} d\vec{q}^{\,3N}}$$

phase average

$\frac{\partial\rho}{\partial t} = 0$ iff $\frac{\partial\langle A\rangle}{\partial t} = 0$



$\boxed{\rho(p,q;t)}$

$$\boxed{N_p = \int \rho(p,q;t)\,d\vec{p}^{\,3N} d\vec{q}^{\,3N}}$$

$$\langle A \rangle = \frac{\int A(p,q)\,\rho(p,q;t)\,d\vec{p}^{\,3N} d\vec{q}^{\,3N}}{\int \rho(p,q;t)\,d\vec{p}^{\,3N} d\vec{q}^{\,3N}}$$

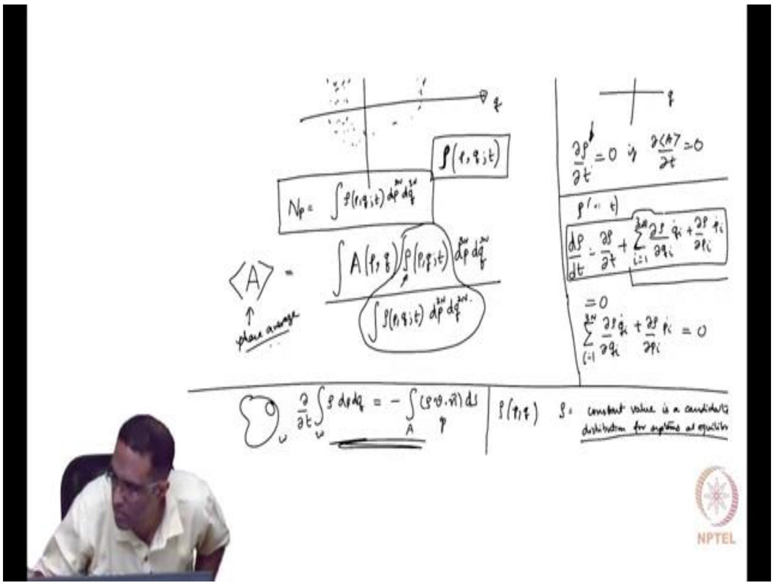
phase average

$\frac{\partial\rho}{\partial t} = 0$ iff $\frac{\partial\langle A\rangle}{\partial t} = 0$

$\rho(x_i, t)$

$$\frac{d\rho}{dt} = \frac{\partial\rho}{\partial t} + \frac{\partial\rho}{\partial x_i}\cdot\frac{\partial x_i}{\partial t}$$

$$\frac{\partial\rho}{\partial t} + \nabla\rho\cdot V$$



I am just going to put p and q but it does not mean this is just one particle. I am just this is there are many-many particles and there is just a swam of so many different particles here. Because these particles are huge in number, a very large in number, and they are so close together. This is going to be little bit hand waving but you will see that, there is a meaning to this in a little bit either this class or in the next class.

It becomes useful for us to define and infinite decimal volume element in this phase space okay. And the dimensions of each are obviously dp power 3n, dq power 3n. A small volume element, right. Therefore, the total number of points so if, so we can also define what is referred to as a density rho. So, imagine continuous mechanics, so you are able to define a density which is mass per unit volume. Whereas in phase space in statistical mechanics I will call this density as number of points per unit volume of the phase space at any given instant of time. So, this basically rho is basically telling you how these points are basically distributed in the phase space. So, this is going to play very important role in statistical mechanics.

So, you have clearly the total number of points in the phase space is obviously integral over the entire phase space, rho p comma q t dp dq, okay? Is this okay, so far? Are there any anything that is, any doubts before we proceed? Okay fine, very good. So, now instead of saying that I am going to take a time average of the quantity that I am interested in. I am going to tell you that I am going to take a phase average of the system that I am of the quantity that I am interested in.

So, for example, the same quantity A if I want to take the phase average, what I would essentially do is, the following. I will say it is A but now A is only a function of p comma q. p and q maybe functions of time, rho p comma q. So, this actually gives me the phase average of the quantity A, correct?

$$\langle A \rangle = \frac{\int A(p,q)\, \rho(p,q;t)\, d^{3N}p\, d^{3N}q}{\int \rho(p,q;t)\, d^{3N}p\, d^{3N}q}.$$

So, this tells me, so this quantity if you look at it, it is telling me what is it, what does that tell me? This is the total, this is the density at that particular point p comma q divide by probability per unit volume that I can find a point at p comma q right, that is what it is telling, correct? Probability per unit volume.

So, this entire quantity is basically telling you what is refer to as phase average of the quantity. So, this and this are different. This is time averaging. This is phase averaging. Now, the whole point is, in writing the expression this way, that is a functional dependence of this rho on t that means, t could explicitly, could explicitly depend on time. The total number of points that is present per unit volume in that phase space could actually vary with time is what that expression is telling you.

So, this average quantity could also vary with time, right? Yes or no? This average quantity could also vary with time. Now, if I am talking about the system which is in equilibrium, do you think this average quantity should vary with time? No, alright, if a system is (my goodness previously the AC was not there but can we increase it to) okay, so this average quantity A cannot vary with time, If we are talking about the system which is in equilibrium. So, the only thing here, that actually depends on time explicitly in the way I have written it is this rho. So, if rho does not explicitly depend on time, that is, number of points per unit volume in the phase space is such that it does not explicitly depend on time, then that rho is a good candidate to describe systems in equilibrium, right.

That distribution is a good distribution, is a valid distribution describes the systems at equilibrium. Is this okay? The average does not change with time. If this has to be true, if dou A by t must be 0. Is not it? That is different. Let us not talk about non-equilibrium thermodynamics, that is now complicated, right. We will talk about equilibrium systems. Systems at equilibrium.

So, rho being not being explicitly dependent on time, is a valid distribution the system can have. If you want to describe systems at you know when we talk about systems which are at equilibrium, right? A few properties of the phase space. So, rho is a functional of p q t in general and what is the material derivative of rho with t? Students who have studied advanced mechanics of solids, transport phenomena, so what is it? Dou rho by dou t plus something you said grad something. Grad? Correct-correct, tell me.

Student: ....

Professor: Rho divergence of rho, correct? But V is what here? Okay, we remember this, we remember this, okay let us start with a little bit of P. P is a function of this. Then you had dp by dt is equal to dou p by dou t plus dou p by dou xi times dou xi by dou t.

Student: Dou p by dou t dou p by dou xi ...

Professor: Okay, that is fine too. Dou p by dou t dou p by dou xi because p is a function of this xi which is nothing but gradient of p dotted with the velocity, right? You studied this before this you seen this before, right? So, I am going to write it down for this rho that is it. There are more, there may be better derivations to do but that is not needed for what I am trying to get at so, d ...

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N} \frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i$$

is that right?

D rho dou t is nothing but do rho by dou t plus summation i equal to 1 to 3 n because now. I am not talking about rho as a function of x y and z, rho is a function of q, p and t, right? So, I have do rho by dou q i into qi dot plus dou rho by dou pi inot pi dot, is that right? Yeah, okay. good. Anybody who has not seen this before at all. You are not seen it? Transfer phenomena, continue mechanics, material derivative you have not seen? Okay, fine.

So, you will eventually learn this. This is actually very simple stuff. You learn it. Well, it is not simple. You learn it. There is lot of, lot of things that goes into actually writing this down, but look at it from this perspective, I am taking a total derivative but involves a partial derivative plus partial derivative with respect to time plus you know partial derivative with respect to q and then the derivative of q with respective to time plus partial derivative of rho with respect to p and then again p with respect to time.

Somewhat intuitive, but it cannot be derived so easily, okay. So, the thing is what does this physically represent? If you are taken again continue mechanics. How this number of points is changing with respect to time for an observer that is travelling along with that point. If you are talking about if you have derived mass balance in transport phenomena or in continue mechanics.

That is essentially what it means is, if you are sitting on a volume element and what is that in Eulerian and Lagrangian and all those thing is so, you can derive that based on that. So, if you are if a person is sitting on a particular volume element in a phase space and travelling with it, it is telling you how many the rate at which the total number of points inside that volume element are changing with respect to time.

Now these are the, the points that are there in the phase space are all coming from the Hamilton's equations. There are no new points which are going to be generated all of a sudden or the existing points are not going to vanish from the system. There is no reason for us to believe that that is going to happen.

Therefore the total number of points that is there with the person who is actually travelling with that volume element is going to remain the same, okay. Therefore, this quantity is 0. It is similar to your mass balance idea. Basically, the points in the phase space moves like an incompressible fluid okay. This is different from this obviously, d rho by dt is equal to 0, is the fundamental property of the phase spacew whereas, d rho, dou rho by dou t is equal to 0 may or may not be true. If you are talking about systems in equilibrium then, dou rho by dou t is actually equal to 0. Otherwise, it need not be zero. Now, if dou rho by dou t and d rho by dt have to be 0 if d rho by dt is 0 any ways okay and dou rho by dou t has to be 0, has to vanish, then this quantity here has to be 0, right. Yes.

Student: Over the volume rho agerage ?

Professor: Rho average, which one? This one?

Student: Yeah, for a particular volume element.

Professor: Particular point, it is at a point. It is the incompressible fluid flow. So, if d rho by dt is zero anyways and dou rho by dou t has to be zero for our system at equilibrium, then the only condition that rho has to satisfied is the fact that this quantity here must actually be equal to zero. So, what there is nothing we can do to q and qi dot because they are just the positions of the velocities of all the atoms in the system.

But what about, what can you say about rho? When will this be zero? Under what condition can this be zero? What can rho be, so that this is zero, right? Now rho is the function of p q. What if it is a constant? If rho is a constant it does not depend on p and q. At every point it does not really depend on p or q then it is zero. So, rho equal to constant value is a candidate distribution for systems at equilibrium.

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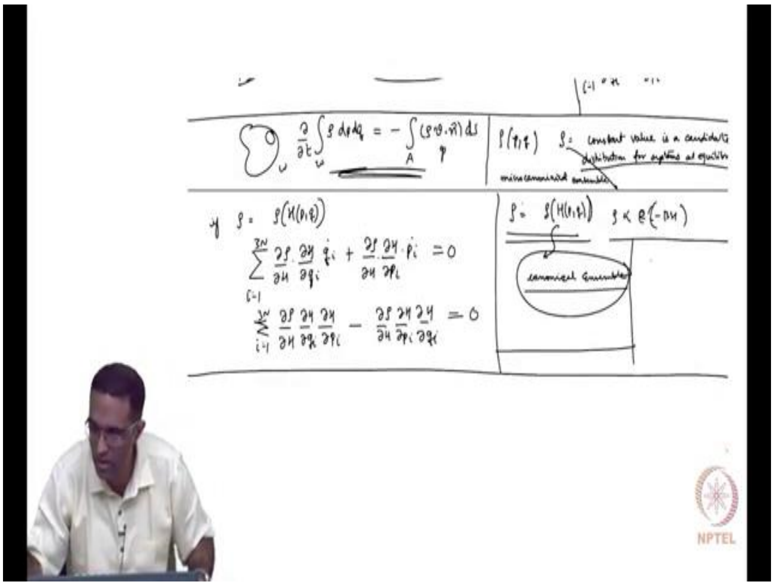

$$\frac{\partial}{\partial t}\int_V \rho \, dp\, dq = -\int_A (\rho \vec{v}\cdot\hat{n})\, dS$$

$\rho(p,q)$ $\rho =$ constant value is a candidate distribution for systems at equilib

microcanonical ensemble

if $\rho = \rho(H(p,q))$

$$\sum_{i=1}^{3N} \frac{\partial \rho}{\partial H}\frac{\partial H}{\partial q_i}\dot{q}_i + \frac{\partial \rho}{\partial H}\frac{\partial H}{\partial p_i}\dot{p}_i = 0$$

$$\sum_{i=1}^{3N} \frac{\partial \rho}{\partial H}\frac{\partial H}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial H}\frac{\partial H}{\partial p_i}\frac{\partial H}{\partial q_i} = 0$$

$\rho = \rho(H(p,q))$ $\rho \propto e^{(-\beta H)}$

canonical ensemble

And it is so happens that, if rho is a function of H explicitly H. Is a function of p and q only through H or the Hamiltonian, even then this quantity become zero. For example, if you take a look at this i is equal to 1 to 3n dou, rho by dou H multiplied by dou H by dou q i into q sorry q i dot plus dou rho by dou H into d o H (into Pi). I am saying this is zero which it is because if I,... qi dot is nothing but do H by dou pi according to the equations of motion.

And this one dou H by dou pi and pi dot is nothing but minus of dou H by qi equal to 0, right.

$$\sum_{i=1}^{3N} \frac{\partial \rho}{\partial H}\cdot\frac{\partial H}{\partial q_i}\dot{q}_i + \frac{\partial \rho}{\partial H}\cdot\frac{\partial H}{\partial p_i}\cdot\dot{p}_i = 0$$

$$\sum_{i=1}^{3N} \frac{\partial \rho}{\partial H}\frac{\partial H}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial H}\frac{\partial H}{\partial p_i}\frac{\partial H}{\partial q_i} = 0$$

If rho is a function of p and q only through H, through the Hamiltonian, even then this quantity became zero. It is so happens that this distribution describes the micro canonical ensemble. And this one describes the canonical ensemble. We will see how it turns out for this.

So, you will figure out that this rho is nothing but e to the power minus beta H by or beta H where beta is nothing but 1over kt we will or proportional to rho will be proportional to e to the power minus beta H or beta E.

E is nothing but the energy, H and energy are the same for the conservative systems. Okay. we will show this probably in the next class. So, what did I, quite a few things we have looked at.

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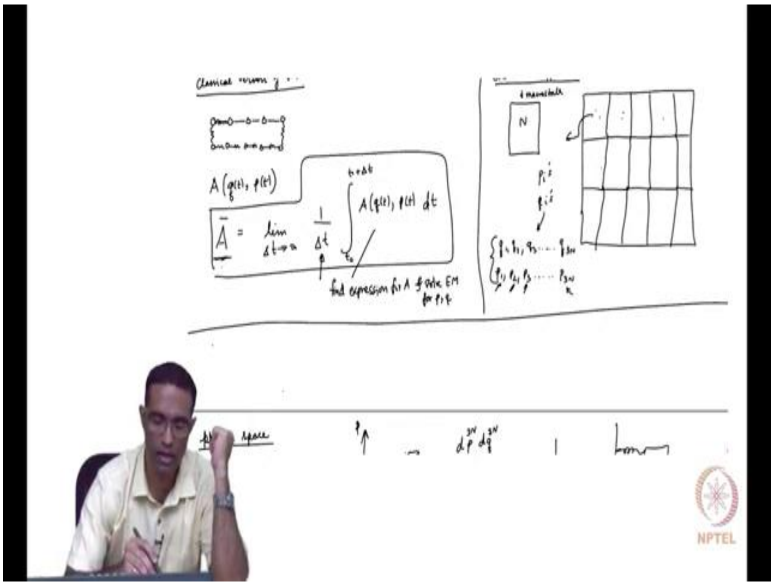

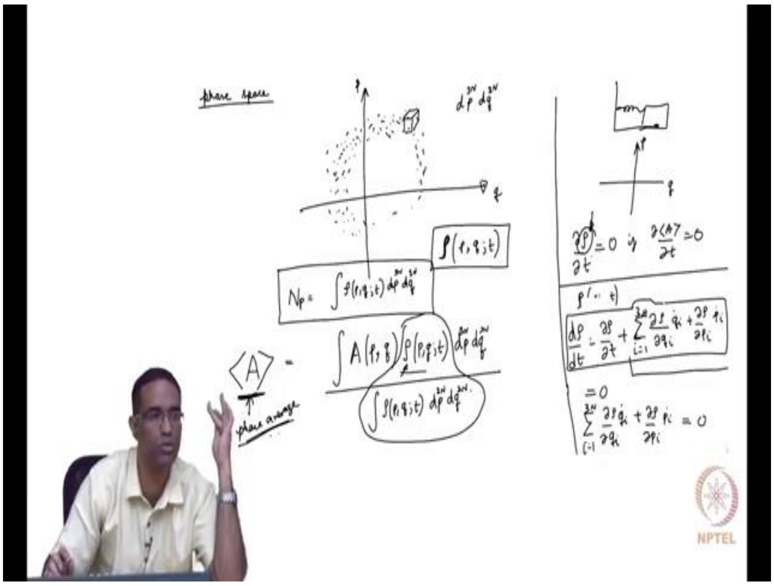

So, I just want to have a recap because some of these things seems, might seen a little bit unrelated to what we have been talking so far. The whole idea is to seen whether we can obtain this expressions A using statistical mechanics so that we can, once you obtain A as a function of p and q and then you will be able to use molecular dynamics simulations to calculate this quantities.

And in molecular dynamics you always use this time averaging in order to calculate these quantities. However in reality not in molecular dynamics in reality it becomes difficult to evolve p and q with time.

Therefore, we resort to what is refers to as phase space approach and phase space basically consists of a large number of points in the phase space which is consisting of this p and q.

And each point is representing as specific micro state okay. And the points are also close together and its so happens that at a particular point p comma q, you can define an infinite decimal volume element dp dp.

And then you can define a phase average like that and you can define a density like that, okay. And this phase, points in the phase space are all moving, they are all moving, because they are moving in accordance with Hamilton's equations of motion, right? So, dou rho by dou t sorry. ....

So, so, the value of the density may be varying with time, number of particles per unit volume may be varying with time. However we know that the phase average should physically at for systematic equilibrium the phase average should not change with time. So, we make the argument that, that is possible if this density function is also not explicitly dependent on time, right.

And we derived we derived this, we did not derive it we note down an expression to show that or suggesting that the particles in the phase space are moving like an incompressible fluid okay. And if which means d rho by dt is 0. If it, if we want our system to be representing at system at equilibrium then we are able to derive some simple properties that this rho should have that is the whole idea.

Rho should be a constant or rho should be explicitly a function of H. We can show through another analysis what this function is, for the canonical ensemble. And we will do that in the next class. But now since there is a little bit of time left I just want to talk about something, simple. So, let us consider an ideal gas, a system of ideal gas, right.

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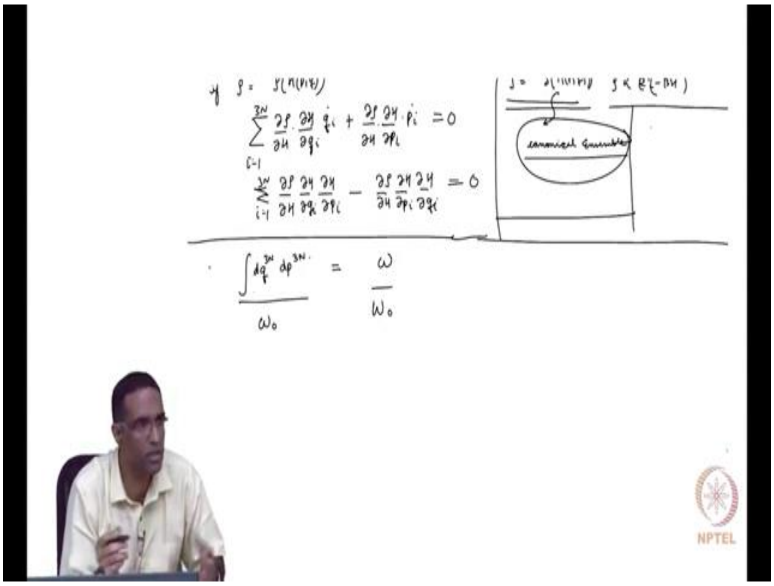

If $\rho = \rho(H(p,q))$

$$\sum_{i=1}^{3N} \frac{\partial \rho}{\partial H} \cdot \frac{\partial H}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial H} \cdot \frac{\partial H}{\partial p_i} \cdot \dot{p}_i = 0$$

$$\sum_{i=1}^{3N} \frac{\partial \rho}{\partial H} \frac{\partial H}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial H} \frac{\partial H}{\partial p_i} \frac{\partial H}{\partial q_i} = 0$$

$$\frac{\int dq^{3N}\, dp^{3N}}{\omega_0} = \frac{\omega}{\omega_0}$$

It contains may be n particles, okay. What will be the, what would be the total number of particles in the system? How would I calculate it? Total number of particle in the system is total number of microstates, right, that is okay with you? Total number of particles in the phase space is nothing but the total number of microstates, possible? Possible microstate right.

The system can take at equilibrium that omega that we saw from the quantum mechanics, this this number of particles should also give us that information. Because there is so many points but so many points but there may be gaps it is not going to form a lattice.

Student: So if there are gaps then how can we?

Professor: Which one? Because you do not integrate where there are, where rho is 0, that is it, you do not integrate where there is 0, with rho is equal to 0 there, in this there is no rho, in this you do not have to worry.

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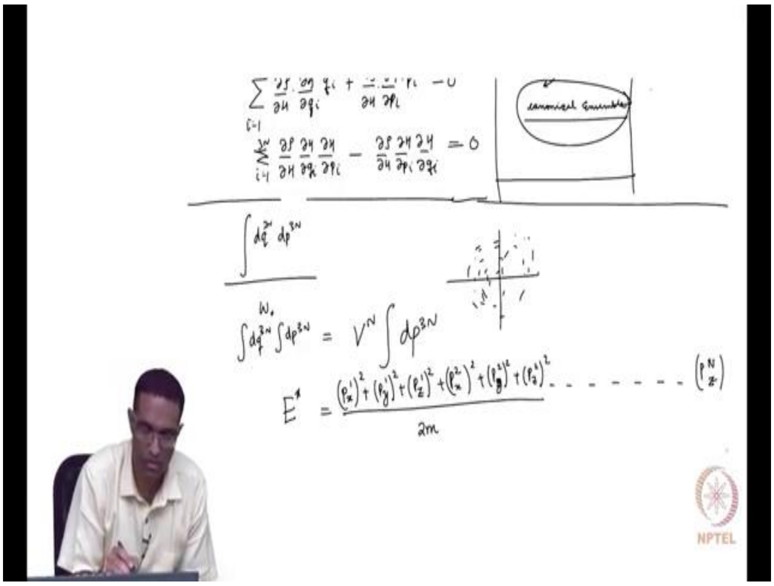

$$\sum_{i=1}^{3N} \frac{\partial f}{\partial H}\frac{\partial H}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial f}{\partial H}\frac{\partial H}{\partial p_i}\frac{\partial H}{\partial q_i} = 0$$

canonical ensemble

$$\int dq^{3N} dp^{3N}$$

$$\omega_0$$

$$\int dq^{3N}\int dp^{3N} = V^N\int dp^{3N}$$

$$E^* = \frac{(p_x^1)^2+(p_y^1)^2+(p_z^1)^2+(p_x^2)^2+(p_y^2)^2+(p_z^2)^2 \ldots\ldots\ldots (p_z^N)}{2m}$$

So, so you have a large number of points, d q over 3 d p. These are the possible what is this is going to you. Do you agree that this is going to give you the total number of points, sorry total volume of the all the phase space? And if I have omega naught which is actually a fundamental volume element that will give you a total number of points. Yes or no? Yes. So, now let us consider an ideal gas, the same thing that we actually looked at previously.

In that case, if you perform this integration, q is basically the positional coordinates, x coordinate, y coordinate and z coordinate of my particles, right? So, each dq1, dq2, dq3 if I integrate over the entire volume of the phase space, is going to give me the volume that gas is actually, can actually occupy. So, this thing is actually V to the power 3n because every 3 dq is contributing to one volume, right sorry V power N because every 3 dq is contributing to one volume.

$$\int dq^{3N}\int dp^{3N} = V^N$$

Is that right? I think I have lost most of you, this makes sense? Yes.

Now, this one I am supposed to integrate over all the possible p’s that it can have., right?However, the p’s are supposed to be such that, this must be equal to E star because we are talking about the ideal gas at the confirmed volume and at a specific energy, right, yes or no?

Student: How did we split the integral?

Professor: Which integral? This is not what to say what is the issue. So, let us let us take a simple system.

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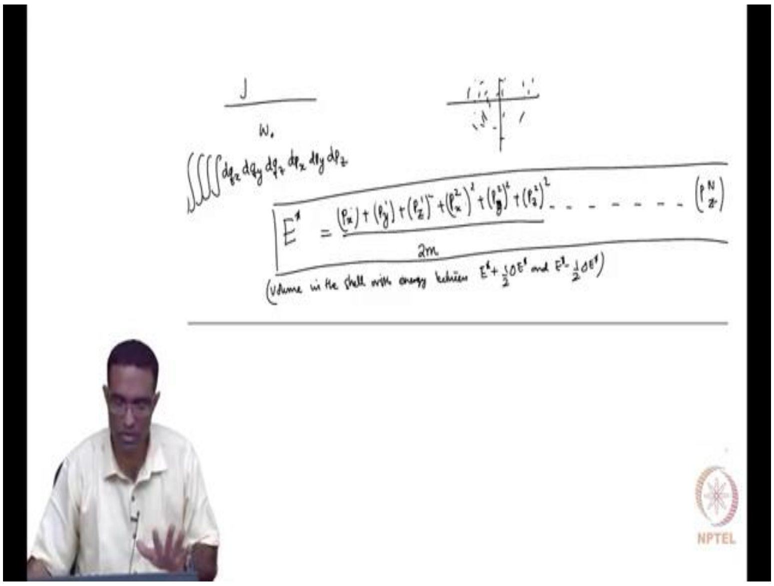

$\frac{J}{W_0}$

$\iiiint dq_x\, dq_y\, dq_z\, dp_x\, dp_y\, dp_z$

$$\boxed{E^* = \frac{(p_x^1)^2 + (p_y^1)^2 + (p_z^1)^2 + (p_x^2)^2 + (p_y^2)^2 + (p_z^2)^2 - - - - - - - (p_z^N)^2}{2m}}$$

(Volume in the shell with energy between $E^* + \frac{1}{2}\delta E^*$ and $E^* - \frac{1}{2}\delta E^*$)

So, if you have only one particular atom in your one particular atom of gas in your box, then you have dq x, dq y, dq z, dp x, dp y, dp z. This is only possible thing. And this is actually over the entire or overall all possible values of p and q. So, I can actually split it separately because there is no nothing else here, right? can I split it or not? You are not convinced that you can split it?

Student: Why is dp and dq integrated separately? dp x can be split it separately, x component can be....

Professor: Why? Why? Which one? No, now in Hamiltonian formulation, q and p are independent variables. That is our idea of the Hamiltonian formulation. You are saying that p is nothing but q dot, no, no, no. No, in Hamiltonian formulation, p and q are independent variables that you get right, they are not dependent on each other.

They need not be they need not be treated being dependent on each other, no, they are independent quantities. So, you can split, okay. Now, this, have you seen something like this before? You have seen this before? In schrodinger’s wave equation for n particle biased system instead of p x and p y, you had some nx, ny, nz, squares and so on and so on and so on right, and it was equal to some E star, right.

And this look like the equation of a hypersphere and you calculated the volume of the hypersphere, yes or no? All that you did. You can do the same analysis in this, okay. You can do it. You remember that or not? If you are not remembering then I cannot. You remember that, right you can do exactly the same analysis here to find out the volume in the shell with energy between E star plus half delta E star and E star minus half delta E star.

We did this analysis very in great detail when we were actually looking at the quantum mechanical system. So, this exercise, you should be able to do. So, this is not a very complicated thing. You can easily do it. What I wanted to show you is, the following interesting aspects.

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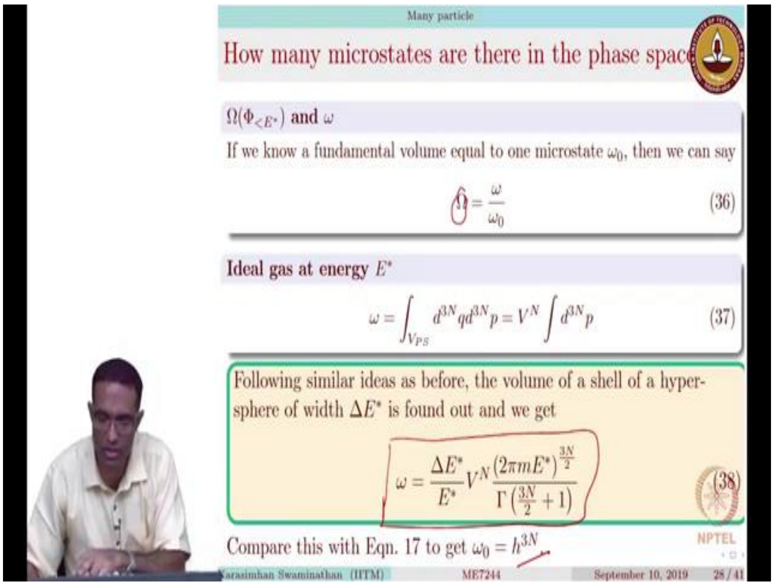

Many particle

How many microstates are there in the phase spac

$\Omega(\Phi_{<E^*})$ and ω

If we know a fundamental volume equal to one microstate ω_0, then we can say

$$\Omega = \frac{\omega}{\omega_0} \quad (36)$$

Ideal gas at energy E^*

$$\omega = \int_{V_{PS}} d^{3N}q d^{3N}p = V^N \int d^{3N}p \quad (37)$$

Following similar ideas as before, the volume of a shell of a hyper-sphere of width ΔE^* is found out and we get

$$\omega = \frac{\Delta E^*}{E^*} V^N \frac{(2\pi m E^*)^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2}+1\right)} \quad (38)$$

Compare this with Eqn. 17 to get $\omega_0 = h^{3N}$

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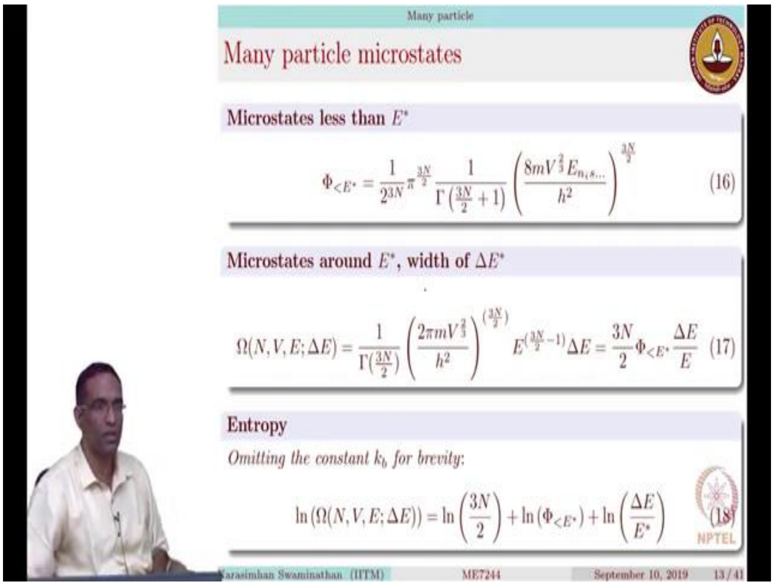

Many particle

Many particle microstates

Microstates less than E^*

$$\Phi_{<E^*} = \frac{1}{2^{3N}} \pi^{\frac{3N}{2}} \frac{1}{\Gamma\left(\frac{3N}{2}+1\right)} \left(\frac{8mV^{\frac{2}{3}}E_{n_i s \ldots}}{h^2}\right)^{\frac{3N}{2}} \quad (16)$$

Microstates around E^*, width of ΔE^*

$$\Omega(N,V,E;\Delta E) = \frac{1}{\Gamma(\frac{3N}{2})} \left(\frac{2\pi m V^{\frac{2}{3}}}{h^2}\right)^{\left(\frac{3N}{2}\right)} E^{\left(\frac{3N}{2}-1\right)} \Delta E = \frac{3N}{2} \Phi_{<E^*} \frac{\Delta E}{E} \quad (17)$$

Entropy

Omitting the constant k_b for brevity:

$$\ln\left(\Omega(N,V,E;\Delta E)\right) = \ln\left(\frac{3N}{2}\right) + \ln\left(\Phi_{<E^*}\right) + \ln\left(\frac{\Delta E}{E^*}\right) \quad (18)$$

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So, this omega is what I wrote down here. This omega is, sorry, is the total number of microstates available to the system and there is nothing but this small omega which is total volume under the phase space divided by omega naught which is a fundamental volume and this omega is can be written like that and then it happens to d to the power 3n and this.

And this d 3n p is that large expression that I just wrote. It is essentially calculating the volume in the spherical shell having energy between E star plus half delta E star and E star minus half delta E star. And that gives us the following omega.

$$\omega = \frac{\Delta E^*}{E^*} V^N \frac{(2\pi m E^*)^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2}+1\right)}$$

Do not worry about the derivation. If you are not able to do derivation, do not worry. It is not it is not important for this what I am going to highlight. But, this is what you will get, you will get that expression right there, Eq38, okay. The only difference between this omega and the capital omega or sorry, if you want this capital omega, the total number of microstates, then omega has to be divided by some quantity and that quantity turns out to be h to the power 3n.

The ratio omega by omega naught where omega is this and omega not is h power 3n gives us the actual quantum mechanical microstates. There is no other way you can actually derive the total number of microstates from a classical mechanical fluids because h is simply not there in classical mechanics.

Planks constant, the expression here, which is why this is interesting, so this expression 38 when you compare it to equation 17, differs by that h power 3n only. So, if you want to obtain the right number of microstates, you have to derive the classical mechanical volume by H power 3n.

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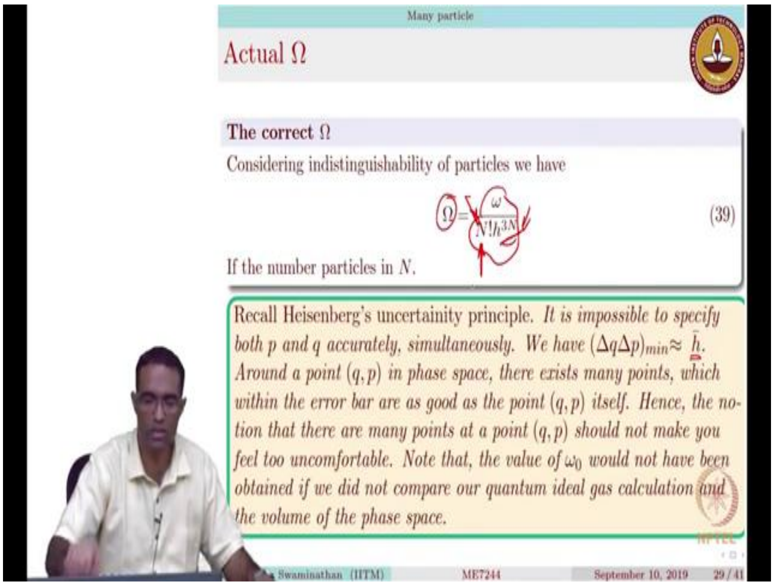

Many particle

Actual Ω

The correct Ω

Considering indistinguishability of particles we have

$$\Omega = \frac{\omega}{N! h^{3N}} \tag{39}$$

If the number particles in N.

Recall Heisenberg's uncertainity principle. *It is impossible to specify both p and q accurately, simultaneously. We have* $(\Delta q \Delta p)_{min} \approx \bar{h}$. *Around a point* (q, p) *in phase space, there exists many points, which within the error bar are as good as the point* (q, p) *itself. Hence, the notion that there are many points at a point* (q, p) *should not make you feel too uncomfortable. Note that, the value of* ω_0 *would not have been obtained if we did not compare our quantum ideal gas calculation and the volume of the phase space.*

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This is still even more interesting to me because what is this have you heard about Heisenberg's..., Heisenberg's Uncertainty Principle? You have heard of that. So, it says that it is impossible for you to specify both the position and momenta of a particle and the uncertainty will be in the order of Planks constant. But what did we do?

In the classical thing, we put up arrow mark and said, there is a point p comma q, we put a cubic volume element of size dp dq and did all these things. Our analysis is telling that, the error that we have made in actually identifying that point is actually in the order of H. so, the whole so, I know that during the beginning of the class, it was getting a little bit weird. I do not want you to understand those weird thing.

I just want you to keep in mind that, the d p dq that we did there is okay. Simply because of the fact that, you cannot specify both the position of the momenta or the particle beyond,... that is some uncertainty associated with it which is in the order of Planks constant and you get that here. so, the quantum mechanical microstate is related like this.

And you have the h power 3n. And of course, another factor called N factorial for taking care of the fact that, you want the particles to be in, to consider for the fact that the particles are actually indistinguishable. We did this also, right? For the classical, for the quantum system, right.

So, around point p q in phase space, you have to assume that, there are many-many points which actually can be treated as a same p q. simply because there is an uncertainty in specifying this p and q. So, even in classical statistical mechanical quantities, you will often encounter a denomination with h power 3n and this quantity with N factorial to take into account for the fact that, there is an uncertainty in specification of p and q and there is in-distribution in-distinguishability of the particles.

Just because it is classical, it does not mean this h will appear. There is no other way to get the correct value from classical statistical mechanics. You have to compare it with the quantum. So, this is what I wanted to tell. So, the basic, the goal of todays class was just to highlight this h power 3n and phase space.

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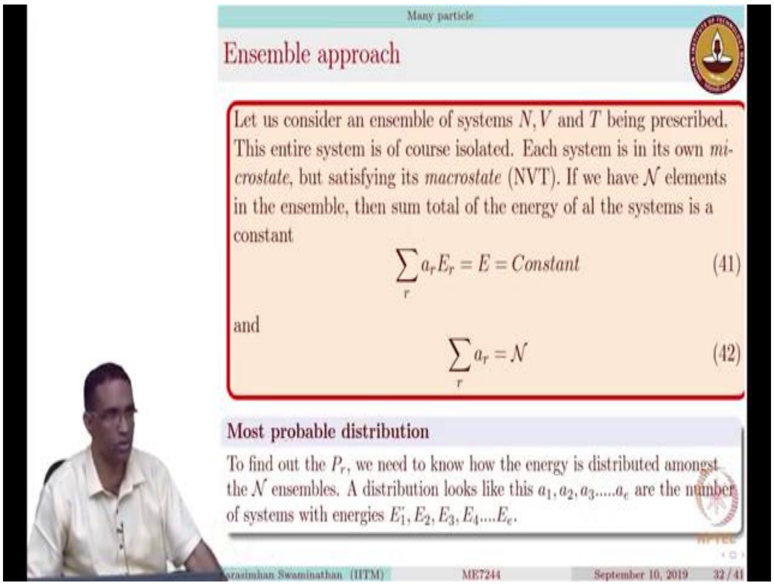

Many particle

Ensemble approach

Let us consider an ensemble of systems N, V and T being prescribed. This entire system is of course isolated. Each system is in its own *microstate*, but satisfying its *macrostate* (NVT). If we have $\mathcal{N}$ elements in the ensemble, then sum total of the energy of al the systems is a constant

$$\sum_r a_r E_r = E = Constant \qquad (41)$$

and

$$\sum_r a_r = \mathcal{N} \qquad (42)$$

Most probable distribution

To find out the P_r, we need to know how the energy is distributed amongst the $\mathcal{N}$ ensembles. A distribution looks like this $a_1, a_2, a_3.....a_e$ are the number of systems with energies $E_1', E_2, E_3, E_4....E_e$.

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Tomorrows class, we will show that this rho depends explicitly on h for the canonical ensemble. I will do some very simple derivations.

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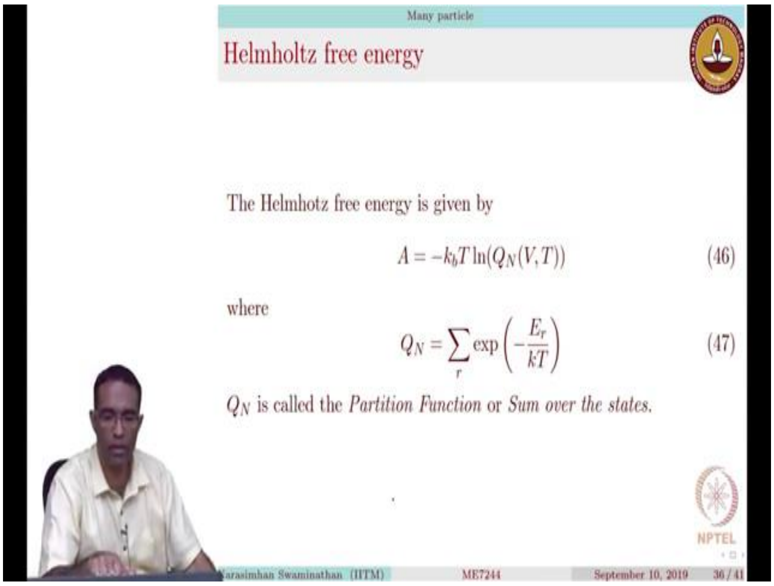

Many particle

Helmholtz free energy

The Helmhotz free energy is given by

$$A = -k_b T \ln(Q_N(V,T)) \qquad (46)$$

where

$$Q_N = \sum_r \exp\left(-\frac{E_r}{kT}\right) \qquad (47)$$

Q_N is called the *Partition Function* or *Sum over the states.*

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And then we will derive the Helmholtz free energy as a function of H for the system. And then I will leave you with the motivation that, if you know the Helmholtz free energy, you have basically done. Ofcourse, mathematically it can complicated you, for example, if know the Helmholtz free energy as a function of position and the velocities, if you know the strain as a function of position in velocities, then you can actually differentiate them.

How I do not know. You can actually theoretically differentiate the Helmholtz free energy with respect to the strain to get stress, you can differentiate it one more time to get the elastic constant and all that we can do. So, that is the spirit of this portion of the class. Just to bring it to the point, tell you that you know once you find this A as a function of p and q and you find your strains as a function of p and q, you can actually get all the thermodynamic properties of the system.

And then since we cannot do all the everything in statistical mechanics in this class, we will then start doing some molecular dynamic stimulations which I think many of you are awaiting to start learning, okay.