Chemical kinetics and transition state theory
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Lecture No. 04
Dance of atoms: from Newton to Hamilton

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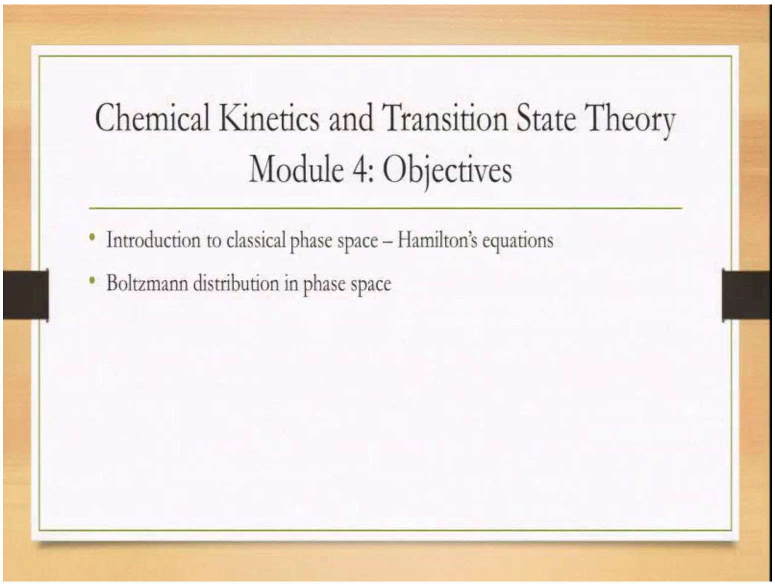

Hello and welcome to module 4 of chemical kinetics and transition state theory. So far, we have covered the prerequisites of this course. We will move on with some very basic fundamentals. We will today think on how dynamics happens on the most fundamental level on atomic scales. So, we will introduce the density of states today. And finally conclude with how to calculate the density at thermal equilibrium which is called the Boltzmann distribution. So, last module we ended with the most fundamental equation in chemical kinetics which is called the Arrhenius equation.

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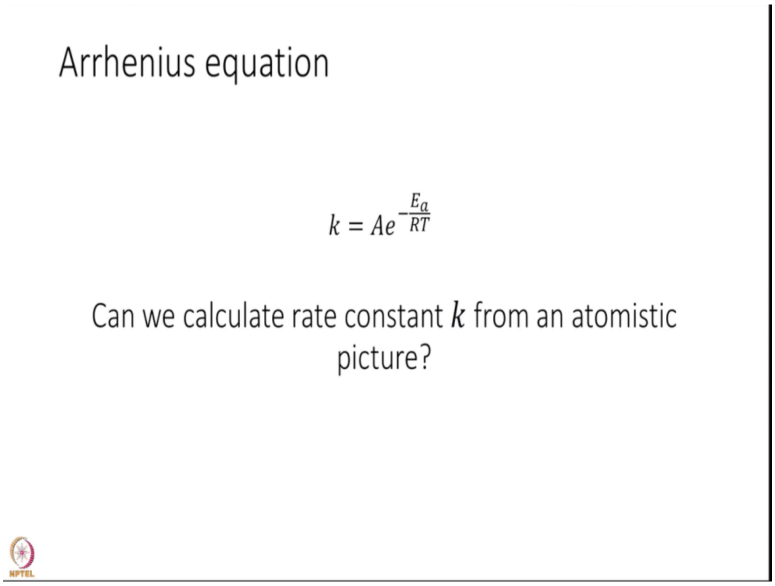

$k = Ae^{\frac{-Ea}{RT}}$. We motivated this equation via the Van't Hoff's analysis and ended with a analysis by Arrhenius on the physical interpretation of this equation. What we are going to focus from now on throughout this course is how do we calculate this k? So, if a new reaction is proposed to you and experimentally tell you that I want to do this reaction and the experimentally say this is not done the experiment but wants to know how, what will be the rate constant, is it feasible or not? So, what theories you can do to calculate this rate constant k.

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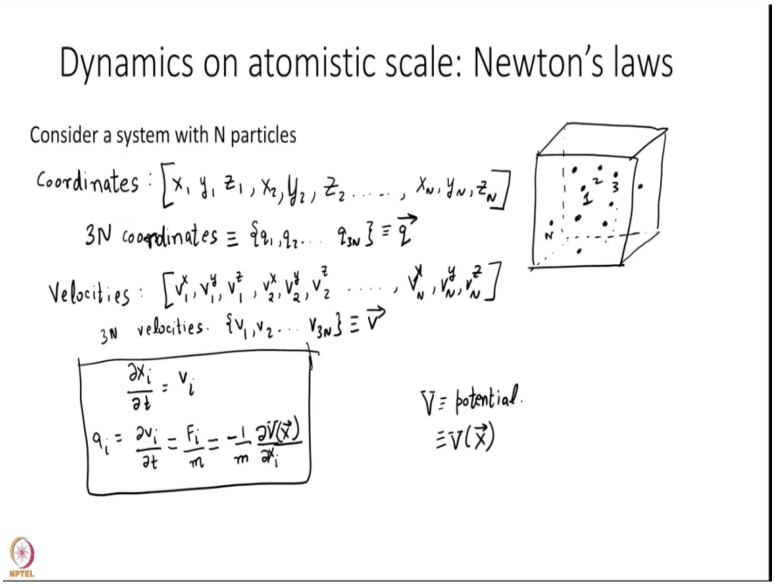

So, to do that we will have to 1st understand the dynamics on atomistic scale. Well, the dynamics on atomistic scale is governed by what is called as Schodengers equation by quantum mechanics. However, a we very well know that for massive particles Newton's laws is well applicable. So, what we will approximate in this course specifically is that the dynamics of the nuclear is governed by Newton's laws.

ok So, let us start a formally with defining a box of particles which has N particles and what's the formal definition of Newton's 2nd law for that. So, imagine I have a box and it has N particles in it, somewhere in this box. 1, 2, 3 so on till particle number N. So, for each particle I have an x, y and z. So, my coordinates are given by a lot of positions so it is x_1, y_1, z_1, xyz in of particle 1. x_2, y_2, z_2 so on till x_N, y_N, z_N.

So, can you tell me how many number of variables I have written here for N particles? It is 3N. So, I have written 3N coordinates, there are 3 coordinates for each particle x, y and z. So, for n particles I have 3N coordinates. Not only that I also have velocities of this n particles v_1^x, v_1^y, v_1^z, v_2^x, v_2^y, v_2^z, till v_N^x, v_N^y and v_N^z. So, I have 3N velocities as well. This becomes a lot of variables and writing them becomes a bit complicated. What we do instead is we define the 3N coordinates as simply q_1, q_2, till q_{3N} and this we call as the vector q.

So, I had 3N variables x_1, y_1 and z_1 till till x_N, y_N, z_N. I just want to simplify my notation and for that purpose only I start using q_1, q_2, q_3 till q_{3N} so you what you can imagine in your head is that q_1, is x_1, q_2 is y_1, q_3 is z_1 and so on and so forth. Yeah I will do the same thing for velocities, I will just simply call them as v_1, v_2, till v_{3N} and call this the vector v. So, what are the Newton's laws of motion?

The Newton's Laws of motion the I am particularly talking about of the 2nd law. The 1st one is my definition, that is how velocity is defined $\frac{\partial x_i}{\partial t}$ is v_i and acceleration is defined to be $\frac{\partial v_i}{\partial t}$ and this is equal to a well it is equal to acceleration is force/mass ok. Now, we also know that for all fundamental forces this Fi can be given as some function that looks like this ok.

So, we have a set of differential equations, differential of x is v and differential of v is given by some differential of potential function divided by mass. Also, V is potential and it is a function of only X and might in general depend on all X. So, these are called the Newton's 2nd Law, it is really the same as f = ma is what I have written for n particle system.

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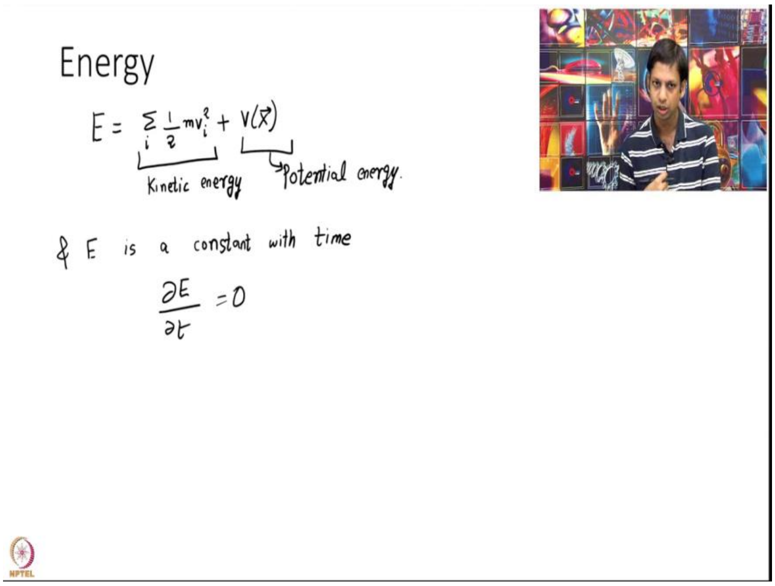

A 1 thing I just want to bring up for this such a system where potential is defined it tell how there is a constant of motion which is energy. So, I defined energy as a $\sum_i \frac{1}{2} m v_i^2$ this is kinetic energy and this is potential energy ok. And what 1 can show energy is a constant with time that is $\frac{\partial E}{\partial t} = 0$ okay. So, this is well known I am just highlighting it here for a specific reason we will see soon enough start. Looking at some functions which will look like this.

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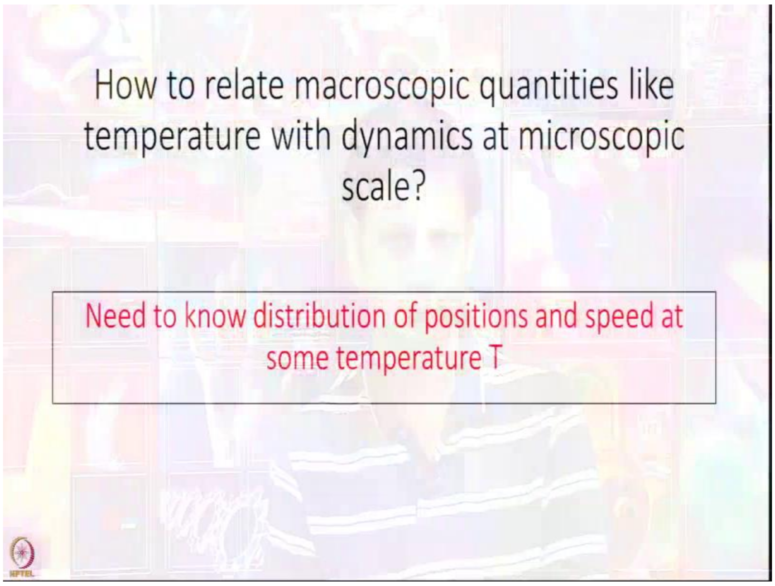

So, the question that we want to address why are they doing this is so that we can relate microscopic quantities let say like temperature or pressure with microscopic states which is given by this x and v's. And how do we do that? We do that basically what you think of when you think of temperature, you have a box with a lot of particles you have an Avogadro number of particles.

So, you do not want to find position and velocity of each particle that will be I mean 10^{23} positions and 10^{23} velocities I will go crazy. So, instead we transform to a different language that language is in this box how much is the density of particles at a given position okay.

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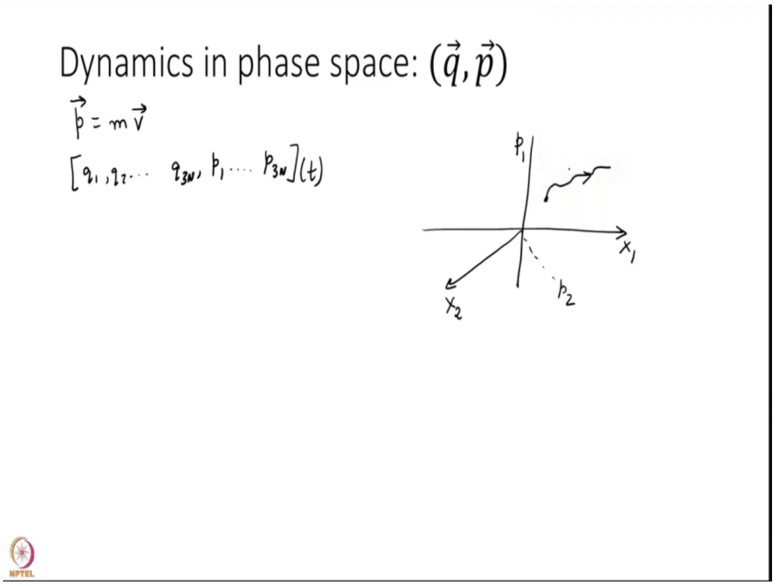

So, we transform to a different coordinate, different way of looking at things. So, to do that what we do is, 1st, so just bear with me for a couple of slides and then it should become very clear to you what I am doing. 1st, we transform from q, v to q, p where p is momentum. So, I define formally p to be m*v that is 1 way to define it. There are more rigours definitions.

So, what is going on? So, now we have 6N coordinates, we have q_1, q_2, till q_{3N} and we also have 3N momentum okay. And we are going to think of the dynamics of these 6N variables as a function of time. So, ah in effect what I have done mathematically is that my dynamics is happening in a 6N dimensional space well that just a little bit an extra for you just to get a little bit of flavour of what the mathematics is, you do not have to necessarily know this for this course.

But what we are doing really is we have let us say this is dimension x_1, this is dimension p_1, similarly I have much many more dimension that I cannot even draw. So, I have x_2 here and I have some fourth dimension p_2 and I have many many more such dimensions and I have a particle here in this 6N dimensional space moving around with time okay. So, that's the way to think about my system now in a mathematical language. Do not worry if this is not mathematically clear. We will continue on and hopefully this will keep on ingraining in. So, spend some time with it and think whether this gets to you or not.

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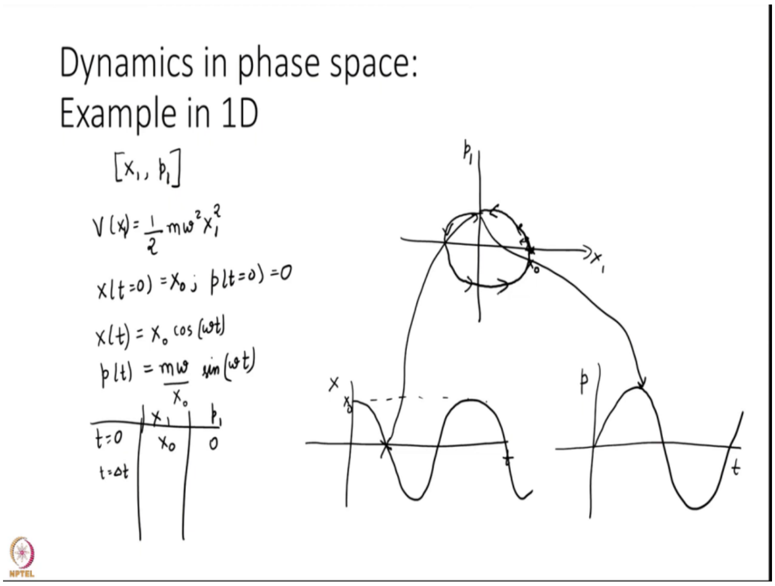

So, let me provide you an example in 1D just to understand this a little better. In 1D, let us say I have only x_1 and p_1, just saw that I am able to draw from figures, I do not know how to draw a 6N dimensional figure, nobody can really draw it on a piece of paper. So, what I am just to give you a sense, I also think the same way we are trying to build a knowledge you want 1D and we will be able to perhaps extrapolate it to 6N dimension.

So, I have only x_1 and p_1. So, these are my coordinates now okay. Let's imagine my potential is that of a harmonic oscillator okay that is how my potential is given, for harmonic oscillator its $\frac{1}{2}m\omega^2x_1^2$, where ω_1 one is, ω is the frequency of the harmonic oscillator. Alright Well, I actually know the solution of this. Let's say at xt = 0 is some x_0 and let us say for just for example p (t = 0) is 0 okay.

So, this problem is exactly solvable and you can quickly do the math for yourself and this will come out to be, so you can verify whether this is true or not. What I want to highlight is not really the details of the solution. I have some solution, okay just take it for now. I want to understand how this looks in phase space. So, think of it as follows, at t = 0, let me just draw a table, exponent p_1. I had x_0 and I had 0 here. So, let me mark this point in phase space. p_1 is 0, so I get a point here okay. I am assuming x_0 to be greater than 0 for example.

Now, as time progresses some Δt, well x_0 is going to decrease and momentum is going to increase. Yes So, if I plot a simpler plot, X looks like this. So, this is x_0. So, you see as time progresses X is decreasing. So, my particle is going to move in this direction, but you see on the same point my momentum will increase, so I am moving actually in this direction. So, my next point will be somewhere here okay. So, I get a trajectory that will look like this.

I continue this along till momentum becomes some positive number and X become 0, so that is this point. After that X will become negative, it will reach here, it will come back and will take a full ellipse back to where it started okay. So, you start at $X_0, 0$, you make some trajectory and you come back. So, this is for a simple harmonic oscillator. For a different potential, the trajectory will be different okay. So, that is what is meant by dynamics in phase space.

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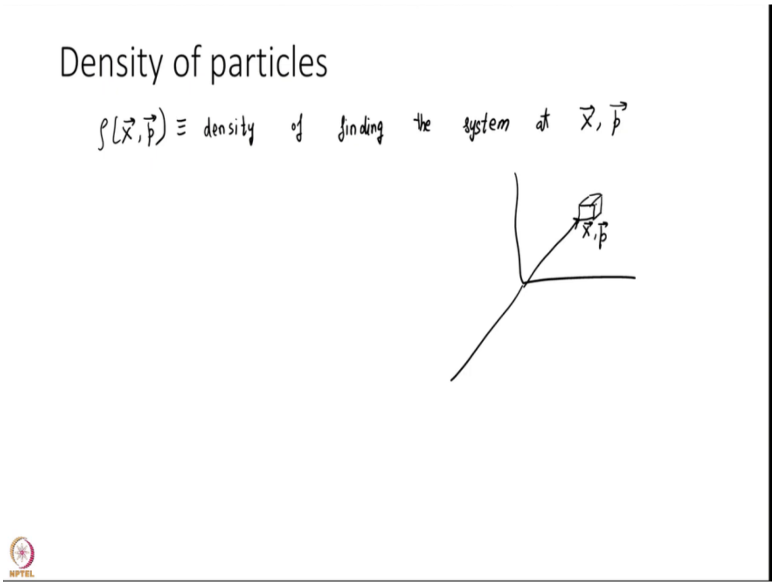

So, now we will come to our central question which is the density of particles. I am not interested in finding position and momentum of each particle of an Avogadro number of particles. So, I define a density of particles, which is the density of finding the system at x, p. So, the idea is that I am in some high dimensional space, I am drawing only 3dimension because that is what my limitation is, it is truly in 6N dimension though.

I have some point here which is x, p and I basically consider a small box here in 6N dimensions again and I find what is the probability that my system is found in that little box of dimensions dx* dt. So, I want to, before moving forward, I want to just highlight some of the property for phase space.

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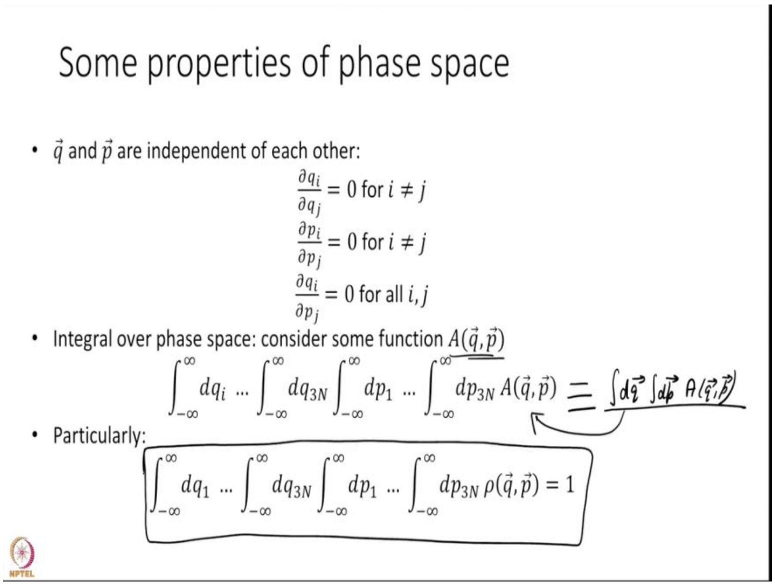

I am not going to prove all of this, but simply take these properties from classical mechanics. So, by the way little bit of history, this was basically developed by Hamilton. He was actually an abstract mathematician and mathematicians live in a world of their own, they don't really live in a real world. And he was trying to figure out properties of some equations and he got interested in the differential equation which is the Newton's laws of motion. That's the way he thought about it. And he was able to identify some very key features of Newton's laws which are much more general than how Newton originally had written.

So, a few things that we specify, 1st that q and p are all independent of each other, so I can vary each variable q or p completely independent of what other variable is doing. Mathematically this means the $\frac{\partial q_i}{\partial q_j}$ is 0. What it means is the $\frac{\partial q_i}{\partial q_j}$ is 0 for all $i \neq j$. The same applies for pi's and pj's, all the momentums are independent of each other, but what might come is a little bit of surprise to you is the $\frac{\partial q_i}{\partial p_j}$ is 0 for all I, j.

So, you this initially if you have never seen this comes as a bit of a surprise because you might think of p_i as mq_i dot. So, it looks like p_i's and q_i's share some relationship, but they really don't, p_i and q_i dot share a relationship, not p_i and q_i. So, what I am really saying is at a given position, the particles momentum can be anything. If I tell you the position of the particle, you still have no knowledge of the momentum of the particle. So, that is what it means that saying that $\frac{\partial q_i}{\partial p_j}$ is 0 for all I and j okay.

The 2nd property that we will look at is an integral over phase space, how do I integrate if I have to do some, I have some let us say variable A as a function of q, p and I want to integrate this function over all phase space, and we are going to do this integral soon enough. Basically, what we do is, we integrate over each variable 1 by 1 over entire range which is -∞ to +∞ okay.

So, in short, the shorthand notation on this we will use is like this. So, when I write this, this big integral is what I mean okay. So, that's just a shorthand notation, nothing more. 1 property of density matrix that I want to really highlight, if I integrate density matrix over all coordinates and momentum, what should I get? I should get 1. Because remember, what is density?

Density, is this δ is the density of finding the system in a given point x, p. If I integrate over all x and p, the system has to be somewhere. So, the whole integral must come out to be 1 okay. It is important to note, it does not come out to be 3N, it is comes out to be 1. Its, you can think of that as a matter of convention. So, this properties is a very important property of density matrices.

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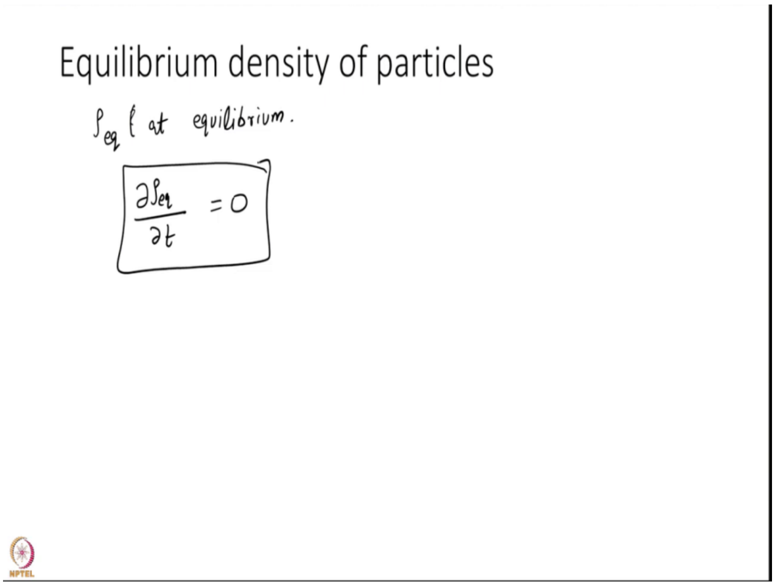

What we are interested in this course, this density of matrices are interesting and there is a lot of research on this on how to understand these density matrices, we are interested in the equilibrium density matrix. Equilibrium density matrix is essentially the density matrix at equilibrium. At equilibrium 1 very important property is that the density matrix will be independent of time, that is what equilibrium really means. So, I will have $\frac{\partial \delta_{eq}}{\partial t}$ must be = 0. So, that is what we are trying to find out. That is what today's aim is, what is δ_{eq}?

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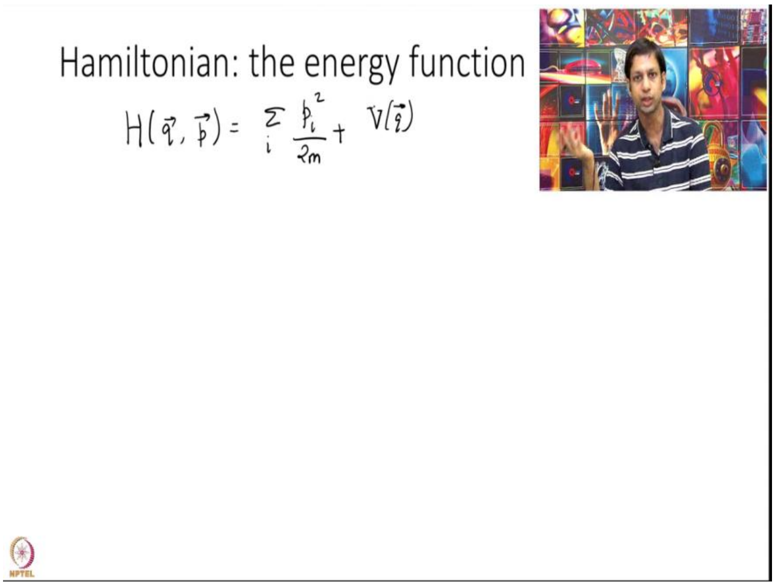

So, how do we find this? We know the Newton's laws. But we have q, p is slightly more complex dynamics occurring in the 6N dimensional phase space. So, how do we make progress? So, we 1st define what is called the Hamiltonian of the system, its a function. This is defined to be the kinetic energy in momentum space where this q is potential okay. So, there is a little bit of difference of this Hamiltonian with energy, Hamiltonian is a function.

So, you give me a value of this 6N coordinates of all these 3N q's and 3N p's and I will return back to a number which is this $\sum_i \frac{p_i^2}{2m}$ + potential energy okay. So, it's simply a definition and as I turns out this Hamiltonian is as you can imagine is a constant of time for Newtonian mechanics.

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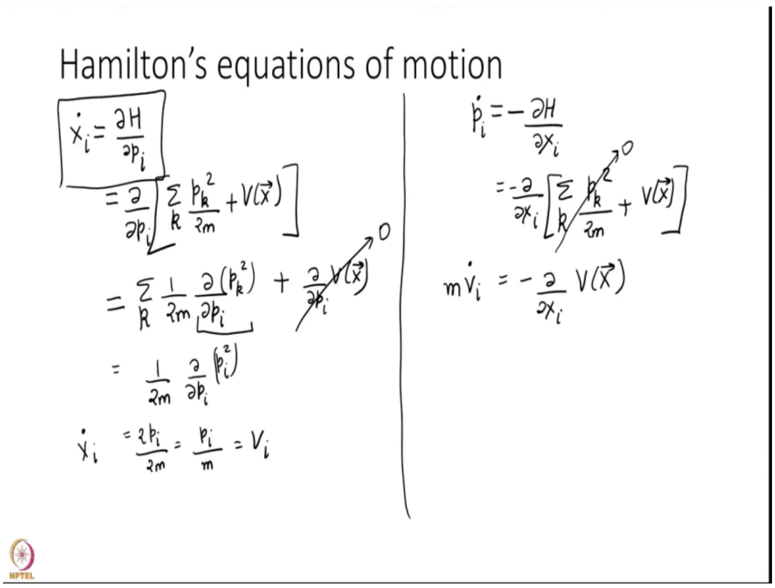

So, what we want to get to is what is called the Hamilton's equations of motion. So, again Hamilton was this abstract mathematician who derived all these. So, Hamilton basically derived that $x_i = \frac{\partial H}{\partial p_i}$ and p_i is $\frac{-\partial H}{\partial x_i}$. So, for the previous Hamiltonian that we had written, we are going to verify whether this is correct other not. so, we will insert that and find $\frac{\partial}{\partial p_i}$, we will just use a different summation index not to confuse ourselves, this is = $\sum_k \frac{1}{2m}\frac{\partial}{\partial p_i}$ (p_k^2)+ $\frac{\partial}{\partial p_i}$ $v(\vec{x})$.

The 1st thing to note is that positions are independent of momentum, remember that is 1 of the properties we mentioned. So, this term is 0, all positions are completely independent of momentum. Now, this term basically what I will get is simply $\frac{1}{2m}\frac{\partial}{\partial p_i}(p_i^2)$, all other momentums are also independent of p_i. So, at the end I get p_i, $\frac{2p_i}{2m}$ which is $\frac{p_i}{m}$ which is v_i. So, you note you get $x_i = v_i$ which is what you expected out of Newton's laws.

And we are going to consider the other point p_i as well. So, here we will have $\frac{-\partial}{\partial x_i}[\sum_k \frac{p_k^2}{2m} +$ $v(x)]$. Now, you will notice that the 1st term will vanish because all momentums are also independent of positions. So, this term vanishes, its derivative with respect to x_i vanishes and what I get is $\frac{\partial}{\partial x_i}V(\vec{x})$, sorry I forgot a arrow there. But this is exactly what we had defined is Newton's laws, yeah so p_i is nothing but mv_i. So, you get back Newton's laws from these Hamilton's equations of motion.

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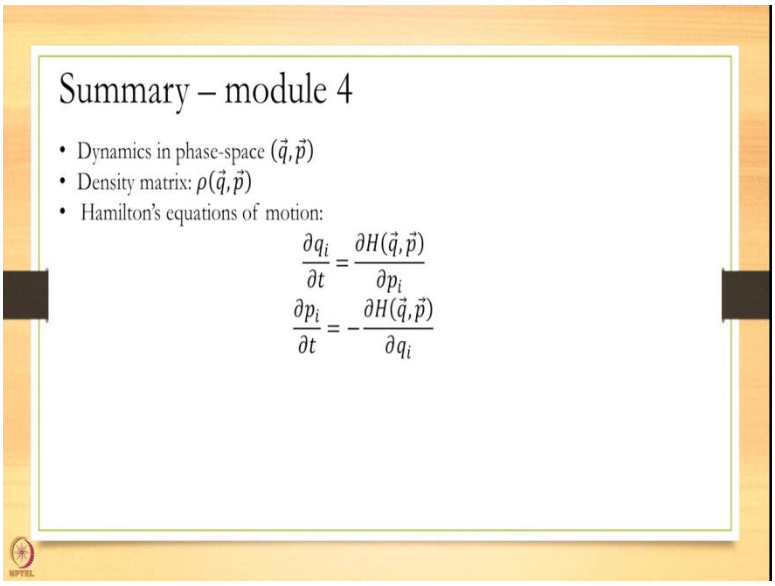

So, in summary, in this module number 4, what we have introduced are a few basic concepts. 1st is a notion of phase space which a comprises of positions and momentums that is important to note, it is momentum and not velocity. 2nd, we have looked at the density matrix in this phage space okay. And finally, we have looked at the dynamics in this phase space and the dynamics in this phase space is given by the Hamilton's equation of motion which are summarised here, $\frac{\partial q_i}{\partial t}$ is $\frac{\partial H}{\partial p_i}$ and $\frac{\partial p_i}{\partial t}$ is $\frac{-\partial H}{\partial q_i}$.

So, we have verified that this equation is true for the given Hamiltonian which is kinetic energy plus potential energy. In the next module we will use these ideas and derive the equilibrium density matrix and use this density, equilibrium density matrix to calculate useful properties. Thank you very much.