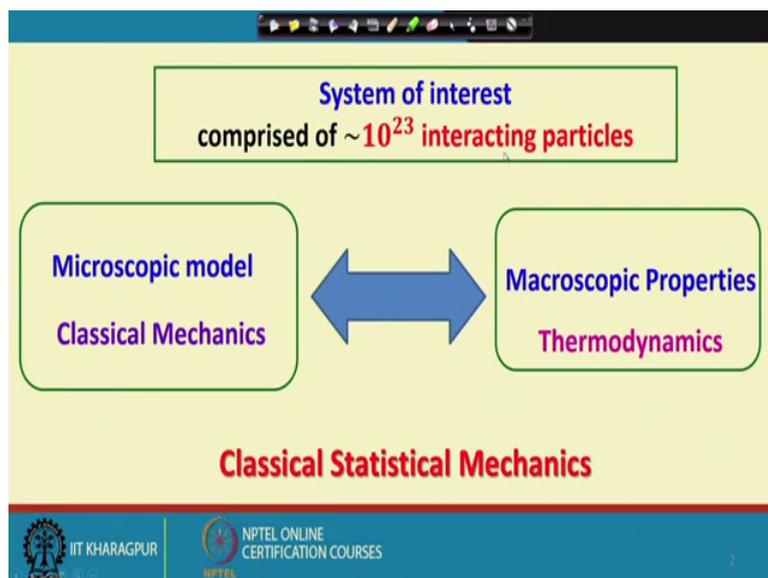


**Introduction to Molecular Thermodynamics**  
**Prof. Srabani Taraphder**  
**Department of Chemistry**  
**Indian Institute of Technology, Kharagpur**

**Lecture – 36**  
**Introduction to Classical Statistical Mechanics (Contd.)**

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Welcome back. Let us continue our discussion on classical statistical mechanics where we have already mentioned that our system of interest is comprised of  $10^{23}$  interacting particles and for such systems we are interested in describing the microscopic model in terms of classical mechanics and then connect them to the macroscopic properties through the formulation of classical statistical mechanics.

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**Microstates of a classical system**

For a system comprised of  $N$  particles in 3 dimensions, its **microstate** is completely defined in terms of

$3N$ position coordinates	$3N$ momenta coordinates
---------------------------	--------------------------

Each microstate is a point in the  $6N$ -dimensional space spanned by  $3N$  position and  $3N$  momenta coordinates

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And in this connection we defined the microstates of the system in terms of  $3N$  position coordinates in  $3N$  momenta coordinates and introduced the concept of a phase space.

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**Microstates of a classical system**

An ensemble is then defined as

- a collection of state points in the phase space and
- all these state points correspond to the same macroscopic state

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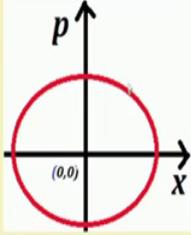
So, when you say that you know the microstates of a classical system, then an ensemble is defined as a collection of state points in the phase space and all these state points correspond to the same macroscopic state.

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**Microcanonical ensemble of a classical 1d SHO**

$$E = \frac{1}{2} m \omega x_0^2$$

$$\frac{x^2}{x_0^2} + \frac{p^2}{m^2 \omega^2 x_0^2} = 1$$



- All points  $(x, p)$  on the ellipse represent possible microstates.
- Number of possible microstates is very very large!
- All microstates are uniformly distributed over the ellipse



So, we took an example of a classical 1 dimensional simple harmonic oscillator, for which the total energy is fixed at a given value and its microstates are given by those values of  $x$  and  $p$  which obey this relationship where the given value of  $E$  is half of  $m \omega x_0^2$ . So, in this case we understand that the ensemble is this particular red elliptic curve in the phase space, in the 2 dimensional phase space spanned by the position coordinate  $x$  and the momentum coordinate  $p$ .

We also said that any point  $x$  and  $p$  on this ellipse would represent a possible microstate corresponding to that constant value of energy  $E$ . We also mentioned that; obviously, there is no limit to the number of points that can reside on this red ellipse and therefore, the number of possible microstates for the given value of  $E$  is very large and also we have said that if we look at all possible values of  $x$  and  $p$ , there is no reason why at some point here the values of  $x$  and  $p$  will be more preferred over some other  $x, p$  combination, for example, a point like here and therefore, we have no option, but to assume that all the microstates are uniformly distributed over the ellipse.

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**Averaging over microstates to obtain thermodynamic properties**

- The equilibrium value of any thermodynamic property  $A$  is

$$A_{eq} = \frac{1}{C} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dp A(x,p) \delta [E(x,p) - E_{eq}]$$

Estimation of  $A_{eq}$  requires the values of  $A(x,p)$  at all microstates  $(x,p)$  on the ellipse defining the constant energy value

**How do we sample all the microstates  $(x,p)$  for the given value of  $E$  ?**

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And with this framework in mind, then the equilibrium value of any thermodynamic property  $A$ , would be given by an expression like this where  $x$  and  $p$  correspond to a given microscopic state in that ensemble,  $A$  is the value of that property when you measure its property at that particular microstate and I have put in the restriction that only those values of  $x$  and  $p$  are allowed, where this the corresponding energy equals the given total energy of the system.

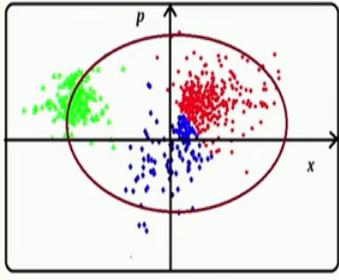
And here  $c$  takes care of the fact that I am integrating over the phase space and the average value should depend should not have any additional dimensions arising from this averaging procedure. As a result the normalization constant takes care of that. Now, as you understand that any estimation of the equilibrium value of  $A$ , would require us to obtain the value of  $A$  at different microscopic states, which are characterized by a given value of  $x$  and a given value of  $p$ .

Therefore, this estimation relies very much on, if we can do this estimate the value of  $A$  at these different microscopic states for the constant energy value. Therefore, the question that we ask is how do we sample all the microstates  $x$  and  $p$  for the given value of  $E$ ? Once we know all possible  $x$  and  $p$  combinations, I can find out  $A$  and correspondingly find out a equilibrium.

Now, there are at least 2 alternative ways of doing this.

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**Thermodynamics of a classical 1d simple harmonic oscillator**



- Generate as many points  $(x, p)$  for a given value of  $E$  keeping the distribution uniform
- Measure  $A$  for each  $(x, p)$  thus sampled
- Compute the equilibrium value of  $A$  as an ensemble average  $\langle A \rangle$

$$\langle A \rangle = \frac{1}{c} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dp A(x, p) \delta [H(x, p) - E]$$

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So, let me first tell you that well in this case, I am given that the total energy is fixed and therefore, I have a fixed ellipse. So, I can adopt some procedure to generate all the points on this ellipse and thereby obtain all kinds of combinations of  $x$  and  $p$  which obeys this general condition that I have a single particle whose energy is a point on the in the phase space as given by a point on the red ellipse. Now, if I do that, then I have to make several atoms.

Maybe I can use a random number generator and try and see if my  $x$  values fall between this and the  $p$  values fall between this and then whether I am exactly on this red curve. Now, once I understand that I am on the red curve I can calculate  $A$  for each of these points present on the red curve and then compute the equilibrium value of  $A$ . So, here I am not using any time dependent propagation or anything. All I am doing is I am using a random number generator and trying to guess those values of  $x$  and  $p$  which will lie on the curve as shown here and once I know that I have hit that condition I will measure  $A$  and then average over all those measured values and the average obtained this way is known as the ensemble average.

So, what you have done is you have looked at all possible microstates in the ensemble weighted each microstate with its average probability, which in this case is a  $1$  by  $N$ , if you have met capital  $N$  observations corresponding to the constant energy curve  $E$ . So, if that happens, then I will represent my average value of  $A$  with this bracket. So, this

angular bracket represents an equilibrium value of  $A$  as obtained through an ensemble averaging or by obtained by adding up the values of  $A$  at different microstates at the different allowed regions of the phase space.

Now, there is an alternative route to this and that is the one that we have seen by generation of those  $x$  and  $p$  values of this system by solving its equation of motion. (Refer Slide Time: 07:27)

**Thermodynamics of a classical 1d simple harmonic oscillator**

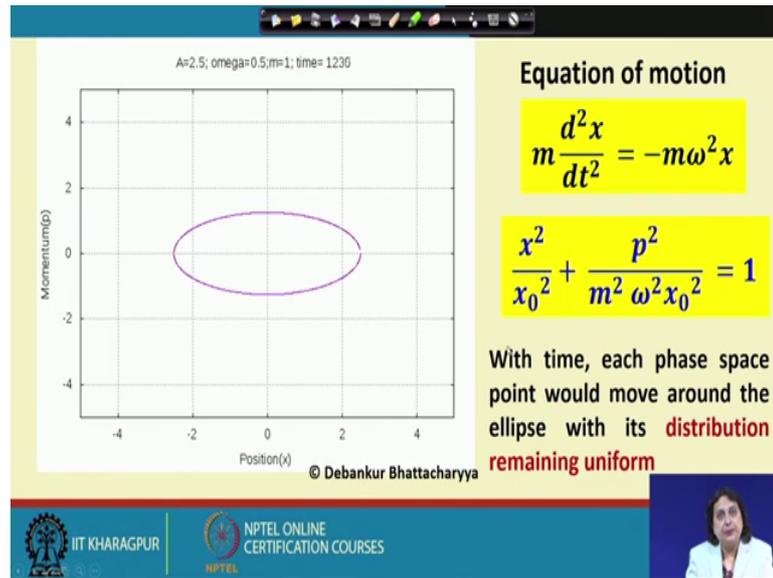
**An alternative route**

- Solve the **equation of motion** to obtain  $x(t), p(t)$
- The solution at different times  $t$  would take the system from an initial point  $(x_0, p_0)$  to other accessible phase space points  $(x, p)$  for a given value of  $E$
- Compute  $A$  at each point  $x(t), p(t)$  at a given time  $t$
- Compute the equilibrium value of  $A$  as a **time average**  $\bar{A}$

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So, let us solve the equation of motion and obtain  $x$  and  $p$ . Now, what do I expect the solution at different times to do? If I start from some initial state,  $x$  naught and  $p$  naught, the solution  $x$   $t$  and  $p$   $t$  will show me how the system will evolve from the initial point to the through some other point  $x$   $t$   $p$   $t$  in time for a given value of  $E$  and then for each such point  $x$   $t$  and  $p$   $t$  accessed by the system at a given time  $t$ , I will compute the value of  $A$  and in that case what will happen is once I collect a very large number of such values of  $A$ , I will calculate take an average, but in this case it is going to be a time average ok.

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So, let us see how this can be done for the 1 dimensional simple harmonic oscillator. So, I have here this equation of motion and I am going to solve it to get all possible values of  $x$  and  $p$  which obey this equation and this equation is set in such a way that  $x$  naught is fixed and hence  $E$ , the total energy is also fixed and I am going to show see the result of  $x$  and  $p$  that I access in this system as a function of time in the phase space.

So, this is where I start and this is how under this equation of motion, the system is evolving and tracing out a trajectory that is a succession of  $x$   $t$  and  $p$   $t$  values in the phase space. So, as you see the system is moving from an initial point to another point here, but it is tracing out its path along an ellipse. So, basically with time each phase space point is found to move around the ellipse and its distribution remains uniform ok. So, by the initial condition we asked you to move in this direction. So, it is moving in this direction and it uniformly samples all the points that are present on this particular ellipse and then what happens.

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A=2.5; omega=0.5; m=1; time= 1215

Momentum(p)

Position(x)

Equation of motion

$$m \frac{d^2x}{dt^2} = -m\omega^2x$$

$$\frac{x^2}{x_0^2} + \frac{p^2}{m^2 \omega^2 x_0^2} = 1$$

If one waits for a long time, the system will visit all the accessible microstates  $(x, p)$  for the given  $E$

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We also note that if I wait for a long time, then the system in turn will visit all these my accessible microstates for the given energy. So, here I am showing you a movie which is a finite time movie and stops at after some time, but if you allowed it to go on and on and on then it would have done something like this.

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Thermodynamic property as a time average along a trajectory in the phase space

$\bar{A} = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^{\tau} dt A[x(t), p(t)]$

$\bar{A} \neq \langle A \rangle$   
NON-ERGODIC

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So, I would have started from this point and then when I allowed the system to move as you have seen in the movie, it went through many different intermediate points on the ellipse to arrive at this point and if I wait for a long time the succession of these

microscopic states is called a trajectory in time, which tells me how the system moves from this initial point to another point in time  $t$  through a succession of many intermediate points in the on the ellipse in the phase space and if I went waited for a long time. What would have happened is this system would have traced out this path again and again and again and again. So, in the long run, what I would have a is the system tracing out this red curve this red ellipse again and again.

And therefore, if I look at the time dependent kind of property of this, what I will find is at every time  $t$ , it is a point the system the microscopic state of the system is represented by a point like this, at which I can calculate the value of  $A$  which depends on  $x$  and  $p$ ; obviously, and then I do this measurement for a time  $\tau$ , up to a time  $\tau$  and for every intermediate stage we calculate  $A$  and then integrate over  $\tau$  and then I divide it by  $1$  by  $\tau$ , to take the time average and this time average; obviously, is accurate in the limit where you have waited for a very long time.

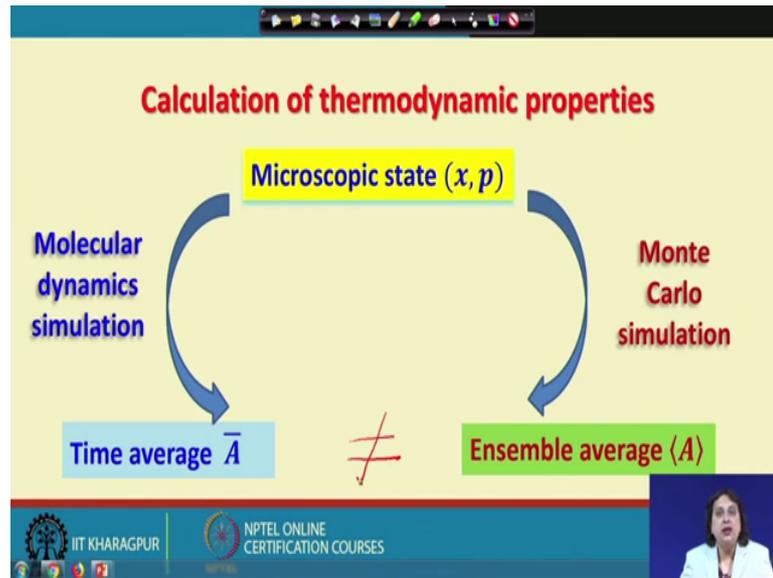
So, that the system had a chance to explore all the points that are accessible to it on this ellipse. If I for example, stopped here in that case this part of the phase space would have remained unexplored. As a result of it I would not have obtained contribution of those values of  $A$  which are coming into the average when I sampled this part. Therefore, our time averaged obtained starting from here up to here is not going to be a good estimate of the average, rather if I can collect all such points all over the phase space which is this ellipse in this case, then of the constant energy surface which is this ellipse in this case by waiting for an very large time I will have an accurate representation of  $\bar{A}$  or the time averaged property of the system.

Now, at this point you would; obviously, argue that by waiting for a very long time, what essentially you are doing is you are allowing the system to access all possible values of the all possible microscope states of the system. So,  $\bar{A}$  must be the same as  $A$  obtained as angular average or  $\bar{A}$  as must in that case be equal to the  $A$  angular or the  $A$  ensemble average. So, there are systems where  $\bar{A}$  is equal to  $A$  average and those systems are known as Argodic systems.

So, we are not going to discuss this in much detail, but as you understand that if you have an ergodic system, then what will happen is for some reason the system will sample only say this part of the phase space and will never go to points like this and therefore, I

will not have in those cases therefore, non ergodic systems, time average of  $A$  is going to be not equal to the ensemble average of  $A$ . So, in the case of ergodic system, the time average is the same as the ensemble average. For a non ergodic system I have the time average is not equal to the ensemble average, simply because the system has not been able to sample a large part of the phase space under the given condition.

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Now, once we know this, then we can go ahead further and try and summarize what I have said so far in this lecture. We started by pointing out that the microscopic state of a system which obeys the laws of classical mechanics can be completely specified in terms of its position coordinate  $x$  and the momentum coordinates  $p$  ok. I cannot do this simultaneously in a quantum system because in that case the Heisenberg uncertainty principle would make it impossible for me to define precisely both the position coordinate and the momentum coordinate accurately simultaneously. So, now, in the classical systems, once I have the microscopic state then I can find out the thermodynamic property like the average property  $A$  by carrying out an ensemble average.

In the literature, this kind of ensemble averaging by generating different microstates following random number generator is usually carried out in terms of Monte carlo simulation. So, what is a simulation? A simulation is the model mimic of how the system would have many different microscopic state. So, that is a numerical procedure that you

can use there is a specific algorithm, which says that I start from a known point and then I put on the system a little at random, then generate the bottom structure. If this part of structure has not changed much, I will examine if it still belongs to a point on the ellipse and then I will say that, if this condition is met I have a second representation of the microstate and I will go on generating as many microstates as possible and then calculate the ensemble average of  $A$ .

On the other hand I could have the time average by solving the equation of motion and this way we would monitor the different microscopic states of the system through the prescriptions of molecular dynamics simulation. So, what do we do in molecular dynamics simulation? We have a suitable equation of motion which can be solved starting from a given initial , which will then in turn take me from 1 initial microscopic state to another one as time progresses therefore, any quantity any property that I calculate at each of these time slices gives me the time average  $\bar{A}$  and as I have already said for ergodic systems, I do have these 2 averages equal to each other, but there are systems which are non ergodic, then in that case that the time average is not going to be equal to the ensemble average.

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**Classical Description of Canonical Ensemble**  
 Macrostate:  $T, V, N$   
 One must include ellipses corresponding to **all accessible values of  $E$**

The slide contains several diagrams:
 

- Harmonic Oscillator:** A plot of energy levels (vertical lines) with a blue dot representing a microstate. Below it is a bar chart with two bars labeled 'U+K' and 'H'.
- Phase Space:** A plot of position  $x$  versus momentum  $p$  showing several concentric ellipses representing different energy levels.
- Energy vs. Phase Space:** A small plot showing a black dot representing a microstate in phase space.

 A watermark <http://i.imgur.com> is visible at the bottom of the diagrams.

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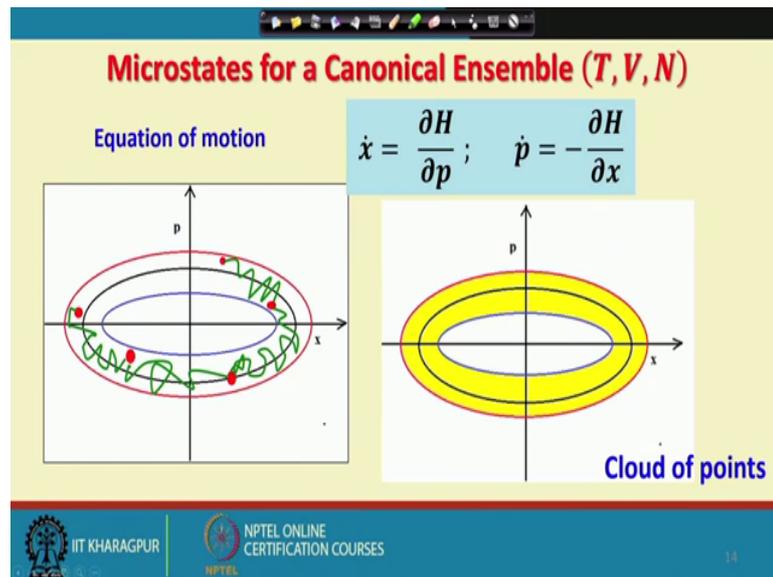
Now, once we have learnt all that, then let us go back and try to see if the same kind of description can be adopted to generalize our observations in the canonical ensemble. So,

once again let me remind you that a canonical ensemble is characterized by the macro state for a given value of temperature, volume and number of particles. So, here I if I talk still talk about the simple harmonic system, a 1 dimensional simple harmonic oscillator, I understand that this oscillator now is connected to a temperature reservoir and therefore, its energies are now represented not only as 1 single energy, but to keep the temperature constant it has certain range of energy values accessible to the system

Therefore, in this picture I would say that let us say that this black line this is the constant the ellipse corresponding to the average time dependent energy of the system, when it has equilibrated at a given temperature, but since it is interacting with the thermal reservoir in order to keep the temperature constant it will either absorb energy whereby its energy will go to a higher value or it will give out energy to the reservoir whereby its energy will go to a lower value.

So, I understand that then it is not only the microstates on this black curve, but the system will have access to all the points on this red curve as well as all the points in the blue curve. This is what I mean by saying that in the phase space now, I must include all the ellipses corresponding to the accessible values of  $E$  and in that case what I am looking for is all the values of  $x$  and  $p$  which are corresponding to the  $x$   $p$  values of this harmonic oscillator, oscillating in equilibrium with a thermal reservoir and what I find is in that case the total energy is going to fluctuate around an average value and as a result the phase space once again is going to be traced out by an ellipse.

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But here it is going to be a thick ellipse, not a single ellipse, but a family of ellipses representing the range of energy values that are accessible to the system now in order to keep the temperature constant.

So, in this case if you want to go through the molecular dynamics route and try to find out what are the different values of  $x$  and  $p$  that represent the microscopic states of this system, you will have to solve this equation of state which is the Hamiltonian equation of state and they are going to give you solutions like this. So, initially you started from here, then the trajectory which is a succession of different time intermediate time positions, after certain time will bring you here and then it probably brings you farther and as you see that the system is essentially moving about through this region in the ellipse.

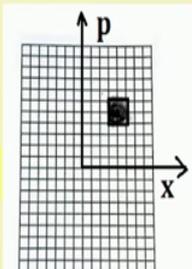
And if I wait for a long time, you understand that my trajectory will be sampling each and every point in this region highlighted by the yellow color and therefore, if I try to see how the system moves here, I will see that this system will now move like a cloud of points with time in this yellow region ok. So, it is very important to understand the representation of the dynamical evolution of the system as a cloud of points in the phase space.

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### System in Equilibrium – Canonical Ensemble

Probability density of states in the phase space  $\rho(x, p, t) \propto \exp[-\beta H(x, p)]$

Number of phase space points in the volume  $\rho(x, p, t) dx dp$   
 $dv = dx dp$







There is an interesting consequence of this. As I said that whenever we think about all the microscopic systems, that all the microscopic states of the system which belong to the overall systematic equilibrium, then I understand that what I am seeing is, if I make a measurement on the system, then the system may be either in 1 given microstate I will measure that value or it may be in some other microstates. So, that the corresponding value of A is given by that microstate. So, basically then I am looking at a very large number of microstates and they are continuously distributed in the phase space as shown by the cloud of points accessed by the family of ellipses in the case of the canonical ensemble. Then it becomes pertinent to talk in terms of the probability of density of states in the probability density of states in the phase space.

So, let us look at this small cloud of points in the phase space are shown here and I would say that the probability density of states here is given by a term like this which is rho. Rho is the probability density not the number density of the mass density. So, rho is given by this particular expression  $E$  to the power of minus beta  $h$ , where  $h$  is a function of the phase space variables  $x$  and  $p$  and  $h$  is a classical Hamiltonian of the system.

So, basically it follows from this definition that, if I want to know what is the number of phase spaced points in the volume  $d v$ , correspond to corresponding to  $d x$  and  $d p$ ; obviously, I will have to take this number which is the number of phase space points per unit volume and multiply it by the volume in which I am interested.

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**System in Equilibrium – Canonical Ensemble**

Probability density of states in the phase space  $\rho(x, p, t) \propto \exp[-\beta H(x, p)]$

Even though the cloud of state points may move or change shape,

at equilibrium, the probability density remains unchanged

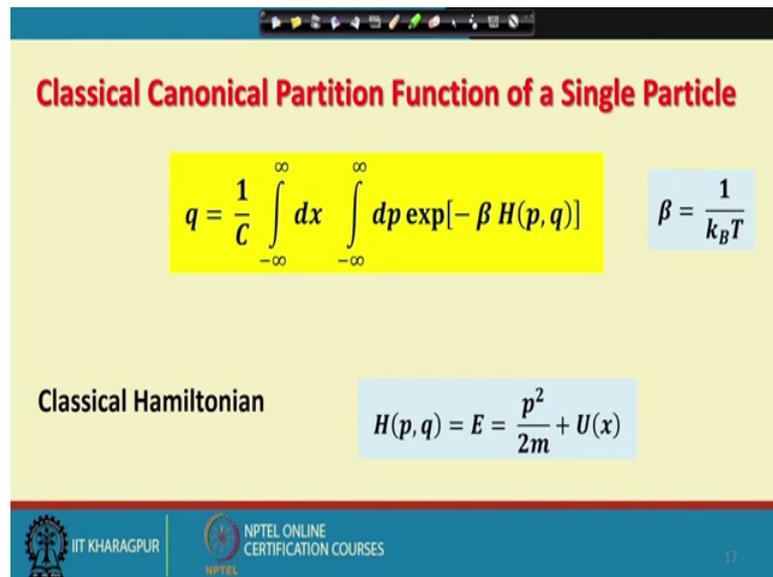
$$\frac{d}{dt} \rho(x, p, t) = 0$$

The slide features a yellow background with a blue header and footer. The header contains the title 'System in Equilibrium – Canonical Ensemble'. The main text describes the probability density of states in phase space, followed by a phase space diagram with axes labeled 'x' and 'p'. The diagram shows a grid with several black dots representing state points. The footer includes the IIT Kharagpur logo and the NPTEL Online Certification Courses logo. A small video inset of a woman is visible in the bottom right corner.

And next what I say is as the system moves with time as I as a solution of my equation of state, this cloud may move here or it may move here, as time goes on and while moving it may even change its shape ok. So, the cloud they not only change their positions, but in the phase space as the system evolves through the many possible points that is accessible to them, that are accessible to them, but it can also change shape. Then, since something is changing at the microscopic level, how do I say that the property A that I measured at these microscopic states on averaging is going to give me a time independent value, that is what I expect when I say that system is at equilibrium and therefore, comes this very important result that when the system is at equilibrium, the probability density remains unchanged. So, which means that  $\rho(x, p, t)$  its explicit time dependence is equal to 0.

Therefore, if you look at this region where I have the yellow band within the ellipsis, then this is a small volume space where I am focusing and this for a small volume will evolve in time and occupy moved to different areas of the accessible portion of the phase space and it may not only change its position, but it may also change its shape as shown here, but the point is if the system is at equilibrium, the probability density in this case will remain unchanged with time. So, correspondingly when I calculate the values of A are different when the system is a different position will give me an estimate of the property of A as evaluated and weighted by an equilibrium probability distribution.

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**Classical Canonical Partition Function of a Single Particle**

$$q = \frac{1}{C} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dp \exp[-\beta H(p, q)] \quad \beta = \frac{1}{k_B T}$$

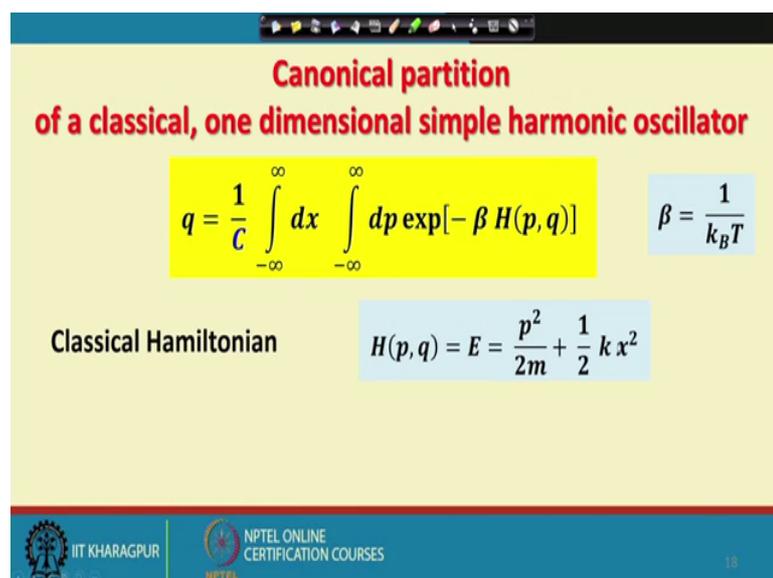
**Classical Hamiltonian**

$$H(p, q) = E = \frac{p^2}{2m} + U(x)$$

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So, this brings us to the expression for a classical partition function of a single particle, which we have already discussed and here let me remind you that I am using beta as the inverse of  $k_B T$  and the classical Hamiltonian as the total energy kinetic energy plus the potential energy which in the case of a simple harmonic oscillator, we already know how to write it down.

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**Canonical partition of a classical, one dimensional simple harmonic oscillator**

$$q = \frac{1}{C} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dp \exp[-\beta H(p, q)] \quad \beta = \frac{1}{k_B T}$$

**Classical Hamiltonian**

$$H(p, q) = E = \frac{p^2}{2m} + \frac{1}{2} k x^2$$

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Now; obviously, in this case I have still left discussed the determination of the constant C.

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**Determination of the constant  $C$**

For a one dimensional, classical simple harmonic oscillator  
 $C$  = area between two ellipses in the phase space with energies

$$E_1 = \left(n + \frac{1}{2}\right) \hbar\omega \text{ and } E_2 = \left(n + 1 + \frac{1}{2}\right) \hbar\omega$$

Area of an ellipse with axes  $a$  and  $b$   $A = \pi ab$

Area of an ellipse with axes  $a = x_0$  and  $b = m\omega x_0$   $A = \pi m\omega x_0^2$

Area of an ellipse with axes  $a = x_0$  and  $b = m\omega x_0$   
corresponding to an energy  $E = \frac{1}{2} k x_0^2 = \frac{1}{2} m\omega^2 x_0^2$   $A_E = \frac{2E}{\omega}$

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If you want to understand, what the constant  $C$  is the  $C$  is nothing, but the area of the phase space that belongs to 1 discrete quantum state and therefore, this area between the 2 ellipses in the phase space with these 2 energies  $E_1$ , which is  $n$  plus half  $\hbar$  cross  $\omega$  and  $E_2$ , which is  $n$  plus 1 plus half  $\hbar$  cross  $\omega$  is what will give me a measure of the constant  $C$ . In order to understand this what we know is we go back to our preliminary knowledge of coordinate geometry and say that if I have an ellipse with axes  $a$  and  $b$ , what is the area of that ellipse that is given by  $\pi$  into  $a$  into  $b$ .

Now, if I have then an area an ellipse with  $a$  equal to  $x_0$  and  $b$  equal to  $m\omega x_0$ , then what is its area; obviously, I put the values of  $a$  and  $b$ , I get it is  $\pi m\omega x_0^2$ . Now, if I say that this is an ellipse under such a condition that the total energy  $E$  is given by this condition, then I can use all the relations that I have here and say that well  $A_E$ , the area or under the ellipse in the phase space with energy  $E$  is  $2E$  by  $\omega$  right. If I do that then I can very easily find out  $C$  because  $C$  is the area between the 2 ellipses in the phase space with energies  $E_1$  and  $E_2$  and I know for a given energy  $E$  the area is  $2E$  by  $\omega$ .

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**Determination of the constant  $C$**

For a one dimensional, classical simple harmonic oscillator

$C$  = area between two ellipses in the phase space with energies

$$E_1 = \left(n + \frac{1}{2}\right) \hbar\omega \text{ and } E_2 = \left(n + 1 + \frac{1}{2}\right) \hbar\omega$$

Area of an ellipse with axes  $a = x_0$  and  $b = m\omega x_0$   
corresponding to an energy  $E = \frac{1}{2} k x_0^2 = \frac{1}{2} m\omega^2 x_0^2$

$$A_E = \frac{2E}{\omega}$$
$$C = A_{E_2} - A_{E_1} = 2\pi\hbar$$
$$C = h$$

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So, when I Do this I find that  $E$  is nothing, but the plank constant. So, here is that universal constant, that gives us the connection between the classical description and the quantum description of the microscopic state of the system.

So, let us quickly then look up the specific form of the classical canonical partition function for a single particle, where now we have explicitly written down  $h$  as the normalization constant, which takes care of the fact that in the phase space each quantum state is corresponding to that  $dx dp$  small square and if now I can write down I try to evaluate the canonical partition function for the simple harmonic motion oscillator.

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**Classical Canonical Partition Function  
of a Single One Dimensional Simple Harmonic Oscillator**

$$q = \frac{1}{h} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dp \exp[-\beta H(p, q)] \quad \beta = \frac{1}{k_B T}$$

**Classical Hamiltonian**  
 $H(p, q) = E = \frac{p^2}{2m} + \frac{1}{2} k x^2$

Handwritten notes:  
 $q_{cl} = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}$   
 $q = \frac{1}{\beta\hbar\omega}$   
 $\int_{-\infty}^{\infty} dx e^{-\alpha x^2}$   
 $\int_{-\infty}^{\infty} dp e^{-\gamma p^2}$

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So, I put E is equal to p square by 2m plus half k x square. When you put this in you find that you have 2 integrals which are like this. So, I have 1 integral which is of the form minus infinity to plus infinity d x into the power of minus alpha x square and I have another integration minus infinity to plus infinity d p into E to the power of minus some gamma v square. Now, these are 2 integrations that we have already done in this course. So, if you do these 2 integrations and put them back, this is the expression that you are going to get.

And here I see that this is q equal to beta h cross omega, but you already know what the expression for a simple single simple harmonic oscillator quantum mechanical simple harmonic oscillator would be, that is going to be equal to minus E to the power of minus half beta h cross omega divided by 1 minus E to the power of minus beta h cross omega. So, the requirement is that in the limit where the quantum effects are the same quantum effects can be neglected, this expression must go over to this expression and I leave it as an exercise to you to show that when beta in a limiting value of beta this expression indeed goes to the classical expression ok. So, that tells me that yes what I am doing is not wrong it is certainly a feasible exercise.

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**Classical Canonical Partition Function  
of a N-Particle System**

$$Q(T, V, N) = \frac{1}{h^{3N}} \int \underbrace{dq_1 dq_2 \dots dq_{3N}}_{6N} \underbrace{dp_1 dp_2 \dots dp_N}_{6N} \exp[-\beta H(\{p_i\}, \{q_i\})]$$

$$Q(T, V, N) = \frac{1}{h^{3N}} \int \underbrace{d\vec{r}_1 d\vec{r}_2 \dots d\vec{r}_N}_{6N} \underbrace{d\vec{p}_1 d\vec{p}_2 \dots d\vec{p}_N}_{6N} \exp[-\beta H(\{p_i\}, \{q_i\})]$$

$$Q(T, V, N) = \frac{1}{h^{3N}} \int \underline{d\vec{r}^N} \underline{d\vec{p}^N} \exp[-\beta H(\vec{r}^N, \vec{p}^N)]$$

$e^{\beta H}$   
 $1 \ q_1 \ q_2 \ q_3$   
 $\vec{r}$

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And I can extend this discussion to an n particle system, where the phase space is going to be much more complicated. I will still have this kind of expression for the canonical partition function which is nothing, but  $E$  to the power of minus beta h, but here h is a function of all the  $3N$  position coordinates and all the q all the p coordinates which are the momentum coordinates and all the q coordinates which are the position coordinates and therefore, the integration over the error phase space is now a  $6N$  dimensional integral, corresponding to  $3N$  position coordinates and  $3N$  momenta coordinates.

We actually use in many cases a condensed notation whereby, let us say for particle 1,  $q_1, q_2$  and  $q_3$  are the 3 x y z coordinates of the particle 1. I condense it using a rotation  $r_1$  ok. So, instead of the  $q_1$  to  $q_2$  d,  $q_3$ , I will write the yard 1, similarly for each of the particles. So, I will have this part representing the integration over all possible position coordinates of the capital N particle,s similarly I can use a condensed notation for the integration over all the capital N p vectors in the phase space,and even more condensed representation is used when all these are represented as this ok.

So, this is nothing, but this  $3N$  dimensional integral in a condensed rotation. Similarly this is nothing, but this  $3N$  dimensional integral in a condensed rotation. You can use any of these notations and try and find out what happens when I use the classical description you as you see that we have been able to show how to obtain an expression for the canonical partition function for a single particle and also for  $3N$  are also for capital n non

interacting particle capital  $N$  particles, I have not mentioned interacting or non interacting in the 3 dimensional space. In the next lecture we will take up application of these concepts in the case of ideal gases imperfect gases as well as simple liquids.

Thank you.