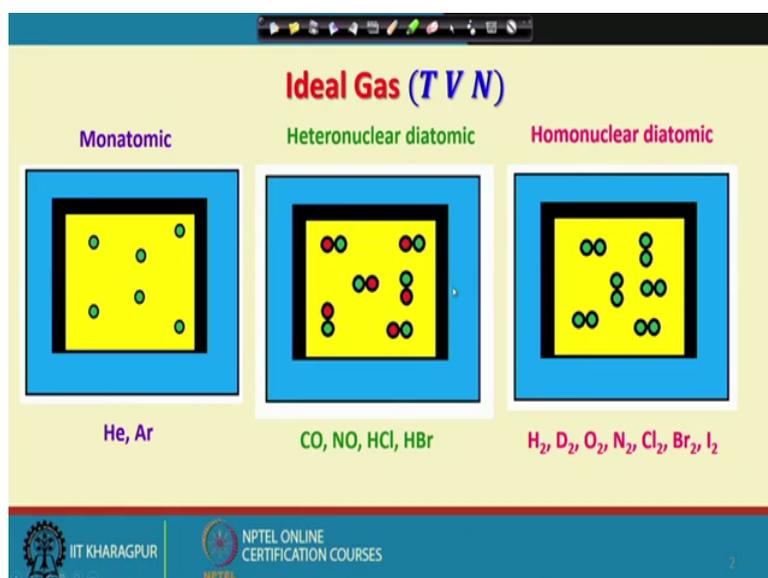


Introduction to Molecular Thermodynamics
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Lecture – 35
Introduction to Classical Statistical Mechanics

Welcome back. In today's lecture we are going to learn the principles of classical statistical mechanics. So, let me start by explaining what I mean by classical statistical mechanics.

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As you would know that we have been discussing how to deal with the statistical mechanics or molecule thermodynamics of ideal gases, when the ideal gas in the microscopic level is explicitly considered to be comprised of atoms or molecules and these molecules may be of different types like the hetero nuclear diatomic molecule or the homo nuclear diatomic molecule and each.

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Effect of Structure on Thermodynamics : An ideal Gas

$$q = q_{COM} q_{int}$$
$$F = F_{COM} + F_{int}$$
$$U = U_{COM} + U_{int}$$
$$C_v = C_{v,COM} + C_{v,int}$$

The slide features a yellow background with a blue header and footer. The equations are written in black and green text. The terms q_{COM} , F_{COM} , U_{COM} , and $C_{v,COM}$ are underlined in green. The terms q_{int} , F_{int} , U_{int} , and $C_{v,int}$ are underlined in black. A red hand-drawn circle encloses the three equations below the first one. The footer contains the IIT Kharagpur and NPTEL Online Certification Courses logos.

In each of these cases, we saw that there was a specific effect of the underlying microscopic structure of these constituent particles on the measured thermodynamic property of the system and that was because we could show that the single particle partition function is comprised of a contribution coming from the motion of a structure less particle which may be an atom, molecule or molecule and the internal structure of the ah this particle, which is moving in the volume v at a temperature t for the single particle. Now, the consequence was that for all the thermodynamic properties we could see that there were contributions coming from the properties of that structure less particle and the contributions coming from the internal structure of each of these particles.

Now, when I talk about classical mechanical description; obviously, I cannot distinguish between an atom or a homo nuclear or a hetero nuclear diatomic molecule. It has to be a structure less particle like a billiard ball. So, then in classical statistical mechanics, what we are looking at is essentially neglecting this structural part and trying to formulate this single particle partition function entirely in terms of a structure less ball like particle and how it can be related to the to the thermodynamic properties like f u and C_v . (Refer Slide Time: 02:53)

Contribution of structural correction at ordinary temperatures

$U = U_{trans} + U_{elec}$

$U_{trans} = \frac{3}{2} Nk_B T$

$U_{elec} = \frac{N\omega_{e,2} \Delta\epsilon_{12} \exp(-\beta\Delta\epsilon_{12})}{\omega_{e,1} + \omega_{e,2} \exp(-\beta\Delta\epsilon_{12})}$

For He, $\omega_{e,1} = 1$, $\omega_{e,2} = 3$ and $\Delta\epsilon_{12} = 19.82 \text{ eV}$

Temperature (K)	$k_B T$ (eV)	$\Delta\epsilon_{12}/k_B T$	$\exp(-\Delta\epsilon_{12}/k_B T)$	U_{trans}/N (eV)	U_{elec}/N (eV)
10	8.62×10^{-4}	2.3×10^4	0	1.3×10^{-3}	0
50	4.31×10^{-3}	4.62×10^3	0	6.5×10^{-3}	0
300	0.02586	7.66×10^2	0	3.9×10^{-2}	0
1000	8.61	2.30	0.012	12.92	0.69

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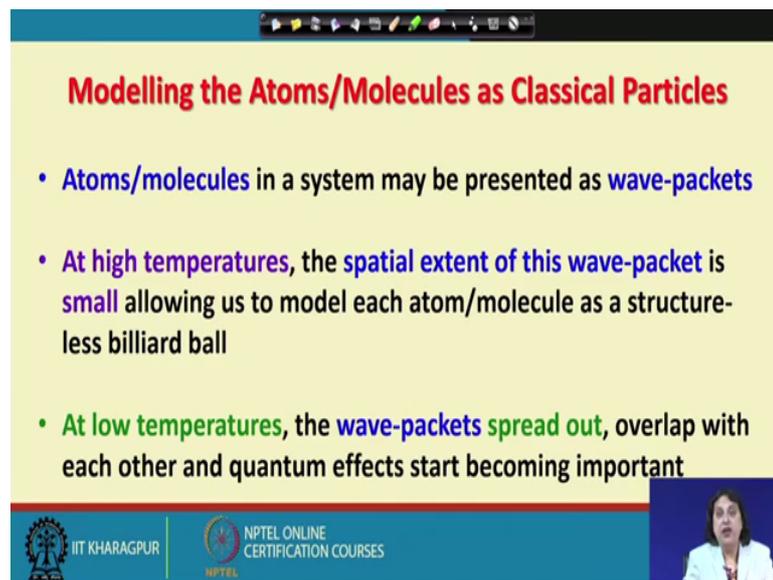
Now, if you remember that we actually looked at the relative contributions of these underlying structure for an monatomic ideal gas in the case of internal energy of a monatomic ideal gas. We found that if I think of the system as being comprised of a structure less ball then corresponding contribution of its translational motion would come from U_{trans} and this U_{trans} is nothing, but the energy at a temperature T that comes from the equipartition theorem and you can also prove that this indeed is so. And the correction term because of the underlying microscopic structure of the atom is also given by this expression and this is dependent on the temperature and the microscopic energy states of the electronic energy levels of the system.

Now, what we have done in this ah discussion earlier, we looked at the relative contributions of U_{trans} and U_{elec} part atom and we found that it was only around 1000 Kelvin that some nonzero contribution started becoming important as far as U_{elec} is concerned.

Therefore, if I am looking at behavior of particles at say 300 Kelvin, what I find is the entire the total energy, internal energy of the system is dominated by the translation energy of the structure less particle and the relative contributions of the underlying electronic structure is very small. So, that gives us the first clue that if we are looking at calculating thermodynamic properties of a system at temperatures very close to the room temperature, I can probably neglect the effect of underlying microscopic structure and instead focus on understanding the properties of the microscopic states of this system in terms of only the ah structure less particle itself ok.

So, with this idea in mind, let us next go and try and understand how I can model atoms and molecules as classical particles. Sounds totally counterintuitive, in the sense that we already know from quantum mechanics, that this is not an accurate description, but as I said at finite temperature, where you are measuring the bulk properties like thermodynamic properties this kind of approximate description may still be good enough for our practical purposes.

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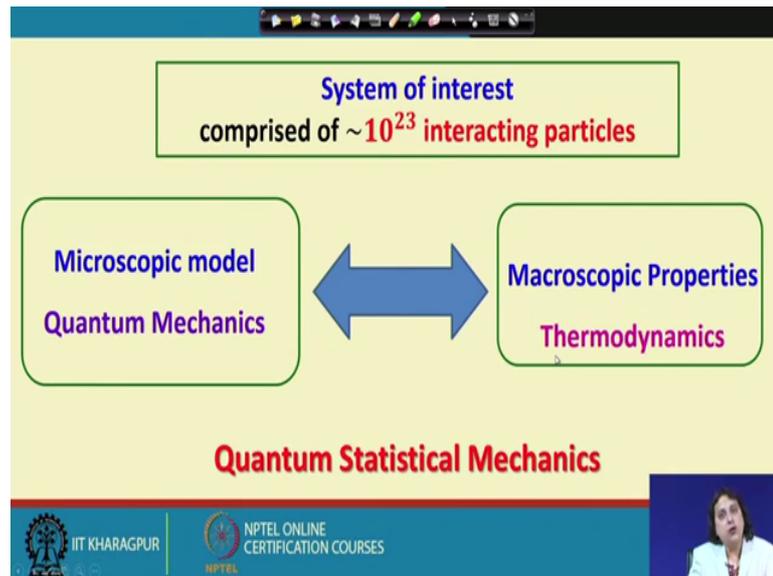
Modelling the Atoms/Molecules as Classical Particles

- **Atoms/molecules** in a system may be presented as **wave-packets**
- **At high temperatures**, the **spatial extent of this wave-packet is small** allowing us to model each atom/molecule as a structure-less billiard ball
- **At low temperatures**, the **wave-packets spread out**, overlap with each other and quantum effects start becoming important

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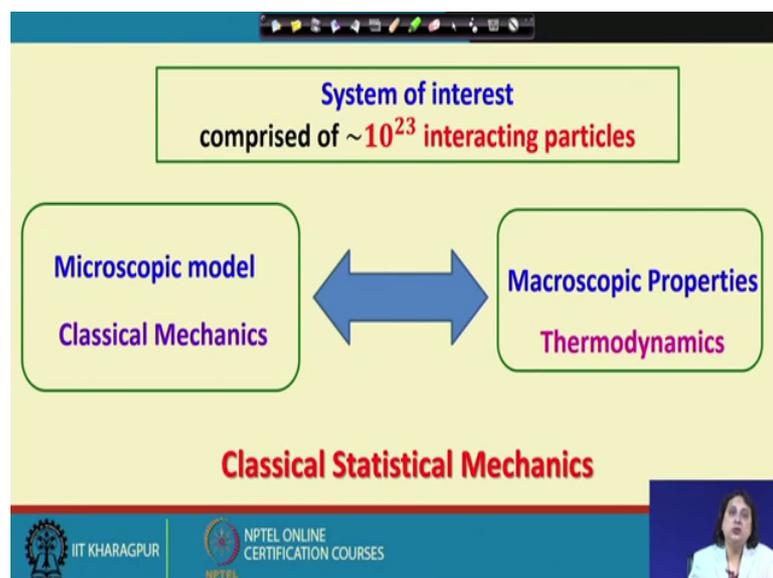
Now, we already know that atoms and molecules in a system may be presented as wave packets. Now, when you are at high temperatures like 300 Kelvin ah. So, in that case the special extent of this wave packet is small and this allows us to model each atom or molecule as a structure less billiard ball. On the other hand, there may be problems which are inherently quantum in nature and in those cases especially at low temperatures the wave packets are spread out, they overlap with each other and the quantum effects start become very important. As a result of which we cannot adopt the description of the atoms and molecules as a structure less billiard ball, but we have to resort to the description taught to us by the language of quantum mechanics.

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So, in today's lecture once again let me remind you that I am going to talk about the properties of a system, which is a bulk system which is comprised of 10 to the power of 23 interacting particles and for which we have already developed the necessary framework for describing the microscopic model in terms of quantum mechanics and the macroscopic properties in terms of thermodynamics and we have seen how the principles of quantum statistical mechanics connects these two extreme limits.

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In today's lecture, although I am going to retain the same kind of description of the macroscopic properties of thermodynamics what I am going to do is, I am going to describe my microscopic model in terms of classical mechanics. So, all the constituent

particles at the microscopic level in today's discussion, they obey the principles of classical mechanics instead of quantum mechanics; obviously, this is an approximate description, but these are useful to predict thermodynamic properties of systems when we are interested in temperatures such as room temperature and so, that gives me the purpose of classical statistical mechanics.

Now, the for very first question, when you formulate the principles of such theoretical description, you have to start from the definition of the microscopic state of a system. So, if I have a system comprised of classical particles at the microscopic level, the question is how do I describe the microscopic state of a system like this.

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

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So, let us say that I have capital N particles in a 3 dimensional system. So, in that case its microstate is completely defined in terms of its position coordinates and momenta coordinates. Now, particle 1 has how many a position coordinates? 3 in 3 dimension, particle 2 also has 3 in 3 dimensions. So, for capital N particles I have a total of $3N$ position coordinates. Similarly for each particle I have 3 momenta coordinates, the x component of the momentum, y component of the momentum and the z component of the momentum. Therefore, if I consider all that N particles together in 3 dimension I will be having $3N$ momenta coordinates and therefore, the basic idea is that when I have a system like this, then the microstate, each microstate is specified by attaching a value to

each of these $3N$ position coordinates and $3N$ momenta coordinates. For another microscopic state they will be having some different values of these $3N$ position coordinates and $3N$ momenta coordinates. Therefore, in general we can say that each microstate is a point in the $6N$ dimensional space that is spanned $3N$ positions and $3N$ momenta coordinates. So, this basically introduces to us the very important concept of phase space and it is best to use a pictorial description of the phase space to understand what it is, but before I go into that let me now explain the next concept that we had associated with microstates and that is the concept of an ensemble.

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The slide is titled "Microstates of a classical system" in red text. Below the title, it states "An ensemble is then defined as" followed by two bullet points: "a collection of state points in the phase space and" and "all these state points correspond to the same macroscopic state". The second bullet point is underlined in red. At the bottom of the slide, there are logos for IIT Kharagpur and NPTEL Online Certification Courses, along with a small video inset of a speaker.

So, in this picture an ensemble is defined as a collection of state points in the phase space and I would expect that for a given, which is defined by a given condition of macroscopic states like a constant volume, a constant number of particles and constant energy, in the case of a micro canonical ensemble. All the state points that I have as the collection of points in the phase space, they must correspond to the same condition of the macroscopic state. So, this is basically an extension of whatever we have learnt in the previous part of our discussion in this course.

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A classical, one dimensional simple harmonic oscillator

Microstate: position coordinate, x momentum coordinate, p

Phase space:

A two-dimensional space
spanned by (x, p)

The slide features a 2D coordinate system with a vertical axis labeled 'p' and a horizontal axis labeled 'x'. A single red dot is plotted in the upper-left quadrant, with a red arrow pointing to it from the right. The background is light yellow with a blue header and footer. The footer contains the IIT Kharagpur logo and the text 'NPTEL ONLINE CERTIFICATION COURSES'.

So, now let me take this very simple example of a classical 1 dimensional simple harmonic oscillator and try to understand how I am going to define its microstate. So, it is pretty obvious that my 1 dimensional simple harmonic oscillator has only 1 positional degree of freedom, which is given by this position coordinate x and associated with it there is only 1 momentum coordinate p , which is defined as mass into \dot{x} that is the rate of change of x with time.

Now, once I understand this then; obviously, I would ask the question, what is the phase space of this single 1 dimensional simple harmonic oscillator? You have 2 variables, position coordinate that is the first variable and the momentum coordinate that is the second variable. So, the phase space is going to be a 2 dimensional, which is spanned by this single position coordinate x and the single momentum coordinate p and therefore, I would say that this microstate that I see here, which is characterized by this position coordinate x and momentum coordinate p , in this 2 dimensional plane this is going to be a point in this 2 dimensional plane as shown by this red dot here.

Of course, this is the simplest possible visualization of the phase space of the single classical 1 dimensional simple harmonic oscillator, but of course, as you understand in an ensemble, we are going to have not only a single point, but it is possible that we are going to have many microstates obeying the same conditions of the macroscopic thermodynamic state.

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A classical, one dimensional simple harmonic oscillator

Microstate: position coordinate, x momentum coordinate, p

Macrostate: Total energy, E is a constant

Equation of motion

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

$U(x) = \frac{1}{2} k x^2$

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So, let us next see what happens for this particular system, when I solve its equation of motion and under the condition that in the macroscopic level its total energy E is a constant. So, basically then how do I visualize the different microscopic states of the system? In this animation each position of this mass m is one of the microscopic states of the system and this movie is showing you that this mass is moving and having different values of x at different times.

So, this is a representation of the system populating different microstates with different values of x and different values of y . Now, here I know that by my definition the this particular mass is under the influence of a potential energy function which is given as $U(x) = \frac{1}{2} k x^2$. As a result of which, here x is the displacement in its position coordinate from its mean position at $x = 0$. Then, I would say that there will be a restoring force acting on this particular system which when the system undergoes a large displacement takes it back to its equilibrium position.

Then what we can say is here I have a representation of the different values of x , that can describe the microscopic state of the system with associated momentum coordinate p . Now, once I understand this, then I will try and see this motion in the phase space.

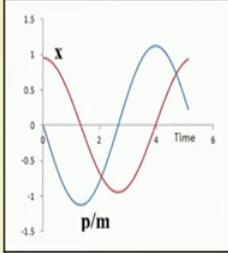
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A classical, one dimensional simple harmonic oscillator

Microstate: position coordinate, x momentum coordinate, p

Macrostate: Total energy, E is a constant

Equation of motion Solution

$$\frac{d^2x}{dt^2} = -kx$$
$$x(t) = x_0 \sin(\omega t + b)$$
$$p(t) = m\omega x_0 \cos(\omega t + b)$$


The constants of integration x_0 and b are determined by initial conditions.

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Before I do that, I do understand that if I solve this equation of motion, I get the values of x and p as a function of t and here basically x and p both of them are oscillating functions and I have introduced to constants of integration x_0 and b and ω is the intrinsic angular frequency of the simple harmonic oscillator. Now, what is this telling me? It is telling me that starting from an initial condition which defines my x_0 and b , then I can calculate the values of x and p for this system at any given time right

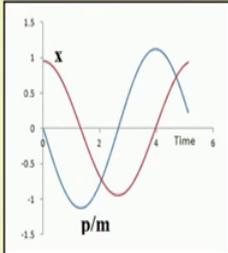
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A classical, one dimensional simple harmonic oscillator

Microstate: position coordinate, x momentum coordinate, p

Macrostate: Total energy, E is a constant

Equation of motion Solution

$$\frac{d^2x}{dt^2} = -kx$$
$$x(t) = x_0 \sin(\omega t + b)$$
$$p(t) = m\omega x_0 \cos(\omega t + b)$$


obeying the condition $E = \frac{1}{2} k x_0^2$

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So, this basically for a micro canonical ensemble where the total energy is fixed, will have to obey the condition that I must look at only those values of x and p which obey this condition that $\frac{1}{2} k x^2$ is equal to the given value E and therefore, x is defined by the given value of E which in turn goes and defines what I am going to have as the values of x and p at a given time starting with some x_0 and p_0 as the initial condition.

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A classical, one dimensional simple harmonic oscillator

Microstate: position coordinate, x momentum coordinate, p

Macrostate: Total energy, E is a constant

A microcanonical ensemble ($E, V, N = 1$)

All microscopic states correspond to those values of x and p that obey the condition

$$E = \frac{p^2}{2m} + \frac{1}{2} k x^2 \quad \text{or} \quad \frac{x^2}{x_0^2} + \frac{p^2}{m^2 \omega^2 x_0^2} = 1$$

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So, what we are going to do next is, we are going to see this collection of microscopic states x and p for a micro canonical ensemble where I have a total energy E fixed and this simple harmonic oscillator is present in a constant volume and N is equal to 1 by the construction of the very simple system. Then all the microscopic states which correspond to those values of x and p in this micro canonical ensemble are accessible which obey this condition. So, what I have done is instead of writing it in terms of k , I have identified the k is nothing, but $m \omega^2$, if m is the mass of the oscillating body, which is oscillating with an angular frequency ω .

In that case this condition can be rewritten using this expression. Now, in this expression as you see that x_0 is the initial condition and x and p are the microscopic state information at a given time. Now, if I look at what happens to the phase space, I understand that all these microscopic states in the phase space 2 dimensional phase space x and versus p , they all the values of x and p which obey this relation will show me the

accessible microscopic states of this system. So, that is what we are going to have a look at next.

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Microcanonical ensemble of 1d classical simple harmonic oscillator

Microstate: position coordinate, x momentum coordinate, p

Macrostate: $E, V, N = 1$

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

$$\frac{x^2}{a^2} + \frac{p^2}{b^2} = 1$$

ellipse with axes
 $a = x_0$ and $b = m\omega x_0$

The slide contains two phase space plots. The left plot shows a red ellipse centered at the origin (0,0) with a horizontal axis labeled 'a = x_0' and a vertical axis labeled 'b = m\omega x_0'. The right plot shows a taller red ellipse centered at the origin (0,0) with a horizontal axis labeled 'a = x_0' and a vertical axis labeled 'b = m\omega x_0'. The origin is marked as (0,0) in both plots.

So, please have a look at this expression, I understand that this expression is telling me what are the possible values of x and p that obey this constant condition of E , where E , is a constant therefore, x_0 is a constant for a given system of m and ω . Now, this has a form of x^2 by a^2 plus p^2 by b^2 equal to 1 and this of course, is the equation of an ellipse and therefore, I understand that I am going to have a plot of an ellipse with axis a equal to x_0 and b equal to $m\omega x_0$, when I look at the microscopic states obeying this constant energy condition in the phase space.

So, depending on what these values of a and b are I am going to have an ellipse like this and I am or I am going to have an ellipse like this representing this condition that has been highlighted over here. Now what does this tell me? It tells me that let us say that these are the points of origin in the phase space which is a 2 dimensional space in x and p .

Now, this is a which is nothing, but x_0 which is dependent on the initial condition and then I would say that b is this height, which tells me that this is $m\omega x_0$ and for any point x and p which lies on this red curve representing the constant energy

surface in this 2 dimensional space is a representation of a microscopic state which obeys the condition that the total energy is fixed it is present in a constant volume and the number of particles is equal to 1.

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**Microcanonical ensemble
of a classical 1d simple harmonic oscillator**

$$E = \frac{1}{2} m \omega^2 x_0^2$$
$$x(t) = x_0 \sin(\omega t + b) \quad p(t) = m \omega x_0 \cos(\omega t + b)$$

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

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Now, in this case what we can also say that well all points on this red curve are the possible microstates for this given ensemble. So, what is the number of these possible microstates? So, the number of these possible microstates is equal to the number of points present on this ellipse and; obviously, that is a very large number for all practical purposes, there is a in finite number of points which are dimensionless quantities that can be populated over this red curve. So, that gives back this idea that we had that associated with a given macro state, there is a very large number of microscopic states possible for a system, even if it is a simple system like a classical like a simple harmonic oscillator ok.

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**Microcanonical ensemble
of a classical 1d simple harmonic oscillator**

$E = \frac{1}{2} m \omega x_0^2$ $x(t) = x_0 \sin(\omega t + b)$ $p(t) = m \omega x_0 \cos(\omega t + b)$

p

x

- For a given value of energy E , x_0 is fixed.
- There is no reason why any value of b would be preferred over others
- All solutions (x, p) are **randomly and uniformly distributed over the fixed ellipse**

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Now, let us go further ahead and see that for a given value of energy, let me remind you that x_0 is fixed. If that is so, then we can ask the question that if I start from some value of b , I mean let me have a look at this particular point, this particular point is x , x is equal to x_0 and b is equal to 0, that will correspond to this particular point ok.

Now, there is no reason why any solution x and p of this equation of motion would prefer some particular value of b or the other. As a result as you see there is no bias in any of these solutions regarding where your solution $x(t), p(t)$ is or in other words I would say that all solutions x, p of the equation of motion are randomly and uniformly distributed over the fixed ellipse which has been shown using this red curve in the 2 dimensional phase space of this simple harmonic oscillator.

So, what is the consequence, which means that let me look at these 2 points, now in these 2 points they differ only by the phase. They have the identical x_0 values and you would say that is there any reason why this solution will be preferred over this solution. I know the solutions x and p at these 2 points and I find that then it is no reason why plus b will be preferred over minus b and this tells me that each of the points present in this over this ellipse they are equally probable and therefore, they have a completely random and uniform distribution over this red curve.

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Averaging over microstates to obtain thermodynamic properties

- The equilibrium value of any thermodynamic property A is

$$A_{eq} = \sum_{i=1}^N A_i P_i \quad A_i \equiv A_i[x_i, p_i] \quad P_i = \frac{1}{N} \Big|_E$$

$$A_{eq} \propto \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dp A(x, p) P(x, p|E)$$

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




Now, when I understand this then; obviously, once you know what the microstates are. So, basic idea is I will average over these microstates and obtain the thermodynamic properties. Now, let us say a is a measurable equilibrium property of my system, then let me remind you, how did we calculate the equilibrium value of this property equilibrium will be $A_i P_i$ where I have measured A_i for all microstates i with a probability and I sum them all up and this probability is the equilibrium probability for the given ensemble.

And so, if in my case if it is a simple 1 dimensional system having only 1 position coordinate x_i and only 1 momentum coordinate P_i A_i is going to be a function the value of A_i is going to be a function of X_i and P_i and then I can measure these values, let us say for capital n points over that constant energy contour in the system, but here as you see that all the x and p values if t varies continuously they can also vary continuously. As a result we find that it is easier to replace the summation in the classical case by this integration. So, essentially I am doing the same thing for a given microscopic state I am looking at this x, p ok.

Now, for a given microscopic state that is characterized by the coordinate x and P I calculate what the value of a is. Then I multiply it with the probability of observing the system in that microscopic state when it obeys the constant energy condition and then I sum over all possible values of x and p and since x and p are nearly continuously

distributed instead of the summation I do the integration, but as you see that here when I am evaluating E equilibrium instead of having a sum over dimensional of the microscopic states, I am now having an integration over the phase space.

So, while this equilibrium value was dependent only on the dimensional dimensionless quantity P_i , now I have introduced in my discussion the dimensions corresponding to d_x and d_p . So; obviously, when I normalize this value I normalize this probability, then there will be some normalization constant appearing here, that I have indicated as $1/c$. I have not defined what these things are rather I would like to highlight that for any such system.

A equilibrium is going to be given by estimated value of A at a given microscopic state and then under the condition that you have only those microscopic states which satisfy this condition that the corresponding value of energy of the system is equal to the equilibrium energy value, that is given to you and then I integrate over the entire phase space and normalize the summation this integrated value suitably with a constant and that will give me A equilibrium.

So, once I know this, then; obviously, I would understand that if I have information regarding the microscopic states of the system I should be able to find out the equilibrium properties just as I have done in the case of the quantum systems, starting from the quantum mechanical model of the microscopic state we could obtain the thermodynamic properties. So, in the next part of the lecture we will see how to use this kind of concept of having an integration over the phase space to find out the thermodynamic properties in a given ensemble using classical microscopic states.

Thank you.