

**Statistical Thermodynamics for Engineers**  
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**Indian Institute of Science, Bangalore**  
**Lecture 05**  
**Basic Concepts**

Okay, welcome to lecture five of the statistical thermodynamics for engineers course. So, we have seen the different ways the different combinatorial analysis of the systems, we know a little bit about probability and statistics right now. So, let us now delve a little bit deeper into the statistical thermodynamics.

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The screenshot shows a digital notebook interface with the following content:

- Handwritten text in red: "All laws learnt so far do not provide insight into the microscopic level".
- A diagram showing a box labeled "System" with an arrow pointing to "3 energy levels".
- Three horizontal lines representing energy levels, labeled on the left as  $E_1$ ,  $E_2$ , and  $E_3$ , and on the right as  $E_1=1$ ,  $E_2=2$ , and  $E_3=3$ .

So, as we already said earlier that all laws that you have learned so far, learned so far do not provide, do not provide you know sufficient insight and insight into the into the microscopic level. When I say the, a particular system has this much energy you have absolutely no idea that how that energy is distributed for example, or what is the composition of that energy. So, let us consider a system which has got.

So, there is a system which has basically say three energy levels as we know already in quantum mechanics the energy levels are discretized. So, three energy levels and we named them as  $E_1$   $E_2$   $E_3$ . So,  $E_1$  as not an energy of say unit 1  $E_2$  is 2,  $E_3$  is 3 just for the sake of convenience and the total energy of this particular system is actually say 6.

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The screenshot shows a digital notebook with the following content:

- Energy levels:  $\epsilon_1$  with energy 0,  $\epsilon_2$  with energy 0, and  $\epsilon_3$  with energy 0.
- Energy values:  $\epsilon_1 = 1$ ,  $\epsilon_2 = 2$ , and  $\epsilon_3 = 3$ .
- Text: "Total energy of this system is 6" (circled in red).
- Text: "there are 3 particles" (circled in red).
- Text: "Only arrangement" (written in red).

Let us put some numbers total energy of this system let us say six arbitrary units and then there say three particles very simple arrangement, three particles. So, now, if we have this kind of, if I say that the total energy of the system is 6 and then there are only 3 particles, there is only one arrangement that is possible because I have said the total energy of the system is 6 and there are only 3 particles at your disposal. So, this is the only arrangement that is possible. So, this is only arrangement. So, this is the only arrangement that is possible.

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The screenshot shows a digital notebook with the following content:

- Text: "Total energy is 6 and # of particles is 4" (written in red).
- Energy levels:  $\epsilon_1$  with energy 0,  $\epsilon_2$  with energy 0, and  $\epsilon_3$  with energy 0.
- Energy values:  $\epsilon_1 = 0$ ,  $\epsilon_2 = 0$ , and  $\epsilon_3 = 0$ .
- Text: "or" (written in blue).
- Text: "00" (written in blue).
- Text: "X" (written in blue).
- Text: "00" (written in blue).

Now, if I say that the total energy is say 8. Let us assume that the total energy of the system, energy is 8 and number of particles is 4, particles is say 4. So, what will be the different types of arrangements that we can think of. So, let us again put  $E_1 E_2 E_3$  because there are only three energy levels.

So, you can have one particular at energy level 1 two particular energy level 2 and one particular dimension 3, so this will give rise to a total energy of 8, but this is not on the arrangement that is possible. Let us take the other arrangement, in which you can have two particles in energy level 3, no particle in energy level 2 and 2 particle in energy level 1. So, this is like no particles here.

(Refer Slide Time: 03:43)

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Two possible arrangements

So these  $E_1, E_2, E_3$  are called energy levels

Probability of finding particles at different energy levels is different

So, therefore, as you can see there are two possible arrangements now, two possible arrangements. So, you can see this energy levels and particles that we are talking about these are essentially like your containers and the objects that we covered in the previous lecture. So, these are therefore called energy levels and the probability of finding at particles or different energy levels is therefore different. So, these  $E_1 E_2 E_3$  etc are called energy levels.

So, the probability of finding particles at different energy levels is different. So, you have got a very clear idea of what we are trying to say that there are these energy level goes and there is a probability of finding particles at these energy levels and these are different.

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9:41 AM Tue 9 Jan  
Untitled Notebook (31)

Probability of finding particles at different energy levels is different

Introducing degeneracy

$E_1$   $\overline{\text{U U U U}}$  } ( $E_j, g_j$ )  
 $E_2$   $\overline{\text{U U U}}$  }  $g_j$ : degeneracy  
 $E_3$   $\overline{\text{U U U U}}$

So, therefore, we introduce now introducing a concept called degeneracy let us mark this word degeneracy. So, what is degeneracy? So, say for example, you take energy level  $E_1$ , now inside  $E_1$  you can imagine that these are the 4 boxes, containers, let us consider an  $E_2$  which instead of 4 now has got 3 containers, so 3 boxes and energy level 3 which just say 1, 2, 3, 4 boxes. So, you designate this is  $E_j$  are the energy levels  $g_j$  are the number of boxes in each of these energy level where  $g_j$  is called to degeneracy.

So, it is almost like energy levels are the floors of our house. For example, we may have a 4 storey house, so, each of the floor is something like an energy level and each of these floor has got different rooms like you have a bedroom, you have a living room, dining room etc. So, those rooms can be considered to be some kind of a degeneracy, if there is a number of rooms at each particular energy level is what is called degeneracy, like each floor may not have the same number of rooms.

Similarly, the degeneracy need not be the same for all energy levels. So, each energy level has got its own degeneracy to begin with. So, I think the concept is pretty clear, this is like the further subdivision within an energy level. So, they have the same energy, but their degeneracies are different.

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The image shows a digital notebook interface with a dark blue header. The title bar reads "Untitled Notebook (31)". The notebook page is yellow with horizontal lines. At the top, there is a red scribble and the text "E<sub>3</sub>". Below this, the text "No. of available energy states per energy level" is written in blue ink, followed by an arrow pointing to the word "degeneracy". Below that, the text "I. Energy states are equally probable" is written. On the left side of the notebook, there is a vertical black bar with the text "Statistical Thermodynamics for Engineers Lec5". In the bottom right corner, there is a small video feed showing a person's face.

So, this is almost like saying if I want to put it in a nice little word is like the number of available energy states per energy level is basically what is called the degeneracy, this energy states is called degeneracy. So, it is almost like how I possess that energy, say I have 4 units of energy, because I am at energy level 4. Now, how I actually possess this 4 level of, 4 units of energy is determined by the energy state that  $(\ )$ (8:03). I can even see these are related to the different quantum states that are there.

So, this is the basic concept. So, these are thermal partitions within an energy level. So, all of them have the same energy, but the energy states are actually different. So, now, let us get a few things out of the way number 1, energy states are equally probable. Energy states are equally probable, energy levels are not by the way.

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The image shows a digital notebook interface with handwritten notes in blue ink. The notes are organized into two sections. The top section contains two numbered points: '1. Energy states are equally probable' and '2. 1 particle  $\rightarrow$  per energy state'. The bottom section contains a flowchart starting with 'fermion', which points to 'protons & electrons', and then 'multiple particles per box (Bosons)  $\rightarrow$  photo'. The notebook interface includes a top toolbar with various editing tools and a sidebar on the left with the text 'Statistical Thermodynamics for Engineers Lec5'. A small video feed of a person is visible in the bottom right corner of the notebook window.

And 2 if there is one particle per energy state for energy state then we call that fermions. Examples of fermions, protons and electrons. And when there are multiple particles, multiple particles per box or per energy state, these are called bosons they named after S.N Bose, once such example is photons, light. So, you can understand the concept. So, degeneracy is a further sub refining within an energy level. The room example is more or less perfect in this regard, you can keep it in your mind. And when there is only, so these are rules when a single particle alone recites in a room. That is called fermion. If there are a lot of particles in a room. That is called bosons. It is almost like a joint family versus a singleton family kind of a structure. So, that is the broad level or very crude subdivision that we are talking about.

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The screenshot shows a digital notebook interface with a dark blue header. The title bar reads "Untitled Notebook (31)". The notebook page is yellow with blue horizontal lines. At the top, "Maxwell-Boltzmann" is written in blue ink and underlined. Below it, "Two basic postulates of Stat Thermodynamics" is written and underlined. The first postulate is numbered "1." and reads: "Time average of a system thermodynamic variable is equal to its ensemble average." A small video feed of a person is visible in the bottom right corner of the notebook window. On the left side of the screen, there is a vertical black bar with the text "Statistical Thermodynamics for Engineers Lec5" in white.

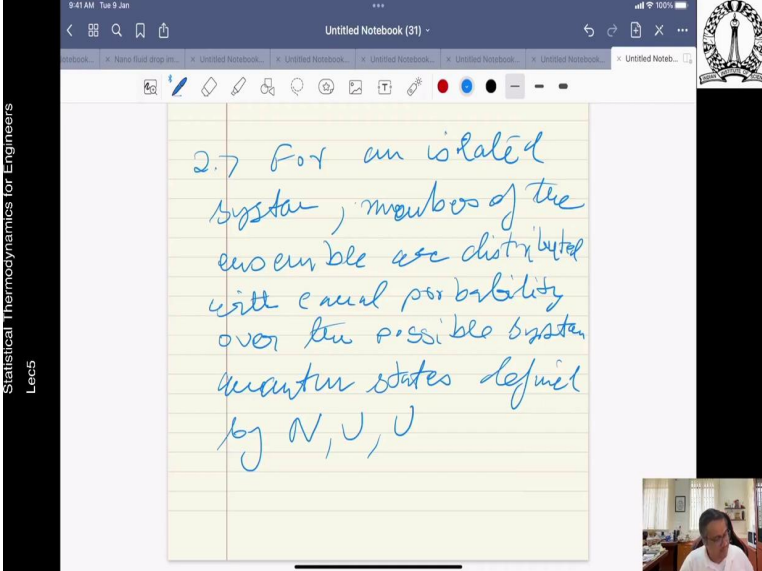
Now, let us talk about something now the Maxwell Boltzmann distribution we will come to that in a little bit, before we delve into this, let us take a look at the two basic postulates, two basic postulates of statistical thermodynamics of stat thermos two basic postulates. So, the first postulate or postulate one is that the time average, we will write it the properly, time average of the system thermos dynamic variable is equal to its ensemble average and what is that ensemble average. This ensemble average is nothing but.

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This screenshot shows the same digital notebook interface as the previous one. The text "system thermodynamic variable is equal to its ensemble average." is visible at the top. Below it, a blue arrow points to the right, followed by the text: "average over the instantaneous values of the variable in each member of the ensemble as  $n \rightarrow \infty$ ". The same video feed and vertical bar are present as in the previous screenshot.

So, this ensemble average is nothing but the average over the instantaneous values of the variable in each member of ensemble as  $n$  approaches infinity was the first one.

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The screenshot shows a digital notebook interface with a dark blue header. The header includes the time '9:41 AM', the date 'Tue 9 Jan', and the title 'Untitled Notebook (31)'. Below the header is a toolbar with various drawing and editing tools. The main content area is a yellowed page with handwritten text in blue ink. The text reads: '2.7 For an isolated system, members of the ensemble are distributed with equal probability over the possible system quantum states defined by  $N, U, U$ '. On the left side of the notebook, there is a vertical black bar with the text 'Statistical Thermodynamics for Engineers Lec5'. On the right side, there is a small circular logo featuring a figure. In the bottom right corner, there is a small video feed showing a person's face.

Then the second one is that, for an isolated system we all know what an isolated system is, isolated system, numbers or other members, so members of the ensemble are distributed with equal probability, over the possible system quantum states defined by  $N$  total number of particles ( $N$ )(13:19) and the total energy. So, this is, these are the two postulates of the dynamics, of statistical thermodynamics. So, the new insights new insights in three basic concepts are important to classical thermodynamics.





(Refer Slide Time: 14:53)

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statistically average  
over sufficiently #  
of particles ( $10^1 - 10^{25}$ )  
↳ one can calculate  
typical thermodynamic  
properties of an assembly  
like  $C_p$ ,  $U$ ,  $H$ ,  $S$  etc

9:41 AM Tue 9 Jan  
Untitled Notebook (31)  
100%

So, what it essentially again translates to that if you statistically average over sufficiently large number, sufficiently large number of particles, which can range from 10 to the power 10 to 10 to the power 25 basically, one can get, you do that one can calculate typical thermodynamic properties, typically properties, a kind of a assembly and what are those properties like the  $C_p$   $U$   $h$ ,  $S$  etc. So,  $C_p$ , specific heat, internal energy and enthalpy and entropy. So, you can estimate all of these.

(Refer Slide Time: 16:05)

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typical thermodynamic  
properties of an assembly  
like  $C_p$ ,  $U$ ,  $H$ ,  $S$  etc

→ Energy of molecules  
atoms  
are always quantized

→ Energy levels that  
are available they  
are not equally possible

30 of 30

9:41 AM Tue 9 Jan  
Untitled Notebook (31)  
100%

So, and of course, to reiterate, before we go to the Maxwell Boltzmann distribution, energy of the molecules are always quantized molecules or atoms cannot stop reemphasizing this are always quantized that is they are discretized that is they have discrete values. Energy levels are not equally probable, energy levels that are available, that are available as I said it cannot have in all possible energies, but whatever energy levels are available, they are not equally probable, they are not equally probable.

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always quantized

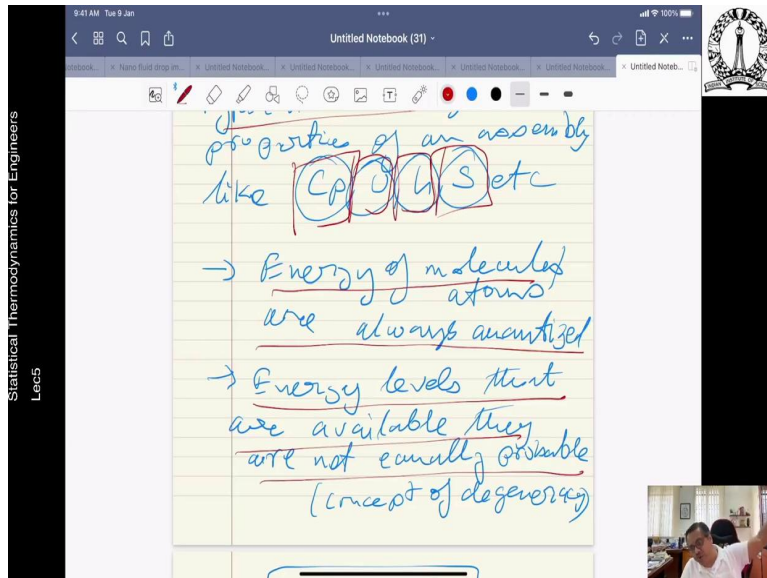
→ Energy levels that are available they are not equally probable  
(concept of degeneracy)

→ most particles are indistinguishable

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statistically average over sufficiently # of particles ( $10^{11} - 10^{25}$ )

↳ one can calculate typical thermodynamic properties of an assembly like  $C_p, U, H, S$  etc

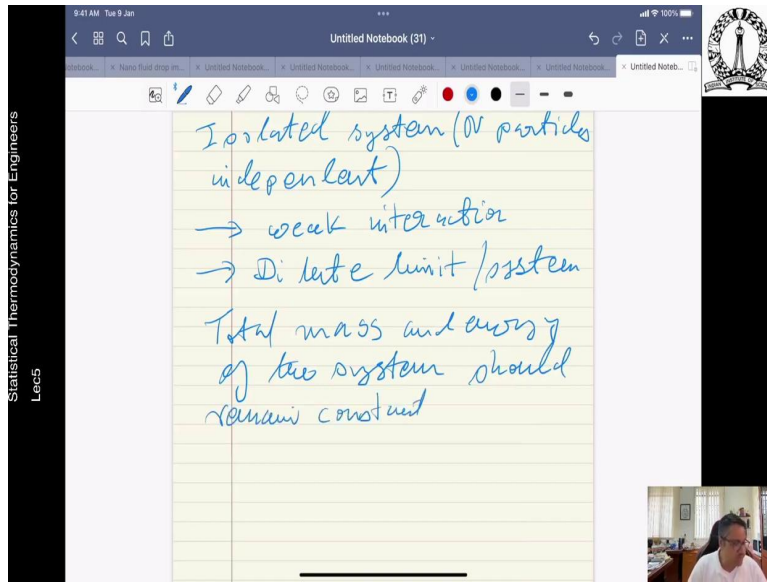


And we now know the concept of degeneracy. And most particles and this is important, most particles are indistinguishable. This is good. So, most particles that you're going to encounter they are indistinguishable, from Tom and Harry you cannot determine who is which. So, they are indistinguishable to begin with. So, just to recap, so, you feel statistically average over a sufficiently large number of particles, you can calculate typical thermodynamic properties of an assembly like your  $C_p$ ,  $U$ ,  $h$  and  $S$ . And we know that the energy of the atoms and the molecules are always quantized. They are these discrete energy levels, energy levels that are available are not equally probable. That means it is not like that energy level 2 and level 4 will be equally probable.

But the energy states are equally probable. And we introduce the concept of degeneracy which he said it's a number of compartments within a particular floor. And then of course, most particles that you are going to encounter are indistinguishable to begin with.

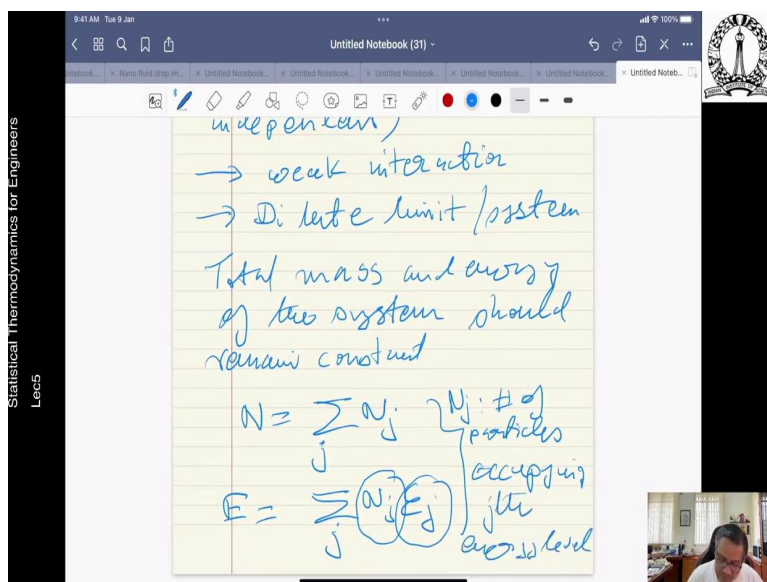
So, in addition to that, we have also iterated the basic postulates of statistical thermodynamics. And we have also said that when there is one particle per energy state, in one particle that is called fermions. And when there are multiple particles per energy state, those are examples of bosons, examples of fermions are protons and electrons, examples of bosons are photons, there is light. So, that takes care of the first part of this.

(Refer Slide Time: 19:02)



Now, we go to the case where let's look at it an isolated system. Let us take a look at an isolated system, where there are  $N$  particles, they are independent. So, that means, that these two assumptions means that is unique interaction. And we also assume it is dilute limit, and a dilute system that means the particles do not interact with each other, remember the lecture 1, where we actually say that. Now, the total mass, total mass the particles, of the total mass and energy of the particles of this other system element ( $i$ )(20:00) particles of the system should remain constant, like a conservation principle essentially .

(Refer Slide Time: 20:11)



So,  $N$  is the total number, but it is the sum total of all the particles at different energy levels and  $E$  is the total energy which is basically the summation over  $j$   $N_j E_j$ . So, that means, each energy level multiplied by the total number of particles in that energy level will give you the total energy level summed across it will give you the total energy level. So,  $N_j$  is therefore, number of particles occupying that  $j$ th energy level the number of particles occupying  $j$ th energy level.

(Refer Slide Time: 21:10)

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9:41 AM Tue 9 Jun  
Untitled Notebook (31)

$$E = \sum_j N_j E_j$$

with energy  $E_j$

$E$  (Total energy) is equivalent to the macroscopic internal energy  $U$

With energy  $E_j$ , so the  $E$  which is basically nothing but the total energy is equivalent is equivalent to the microscopic rate, to the microscopic variable which is internal energy, microscopic internal energy  $U$ . So,  $U$  somewhat connected to that.

(Refer Slide Time: 21:50)

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Energy  $U$

Ratio  $\frac{N_j}{N}$  → fraction of particles in  $j$ th energy level

↳ probability that a single particle will be in  $j$ th energy level

→ many distributions are possible

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$E = \sum_j (N_j E_j)$  over all levels

with energy  $E_j$

$E$  (Total energy) is equivalent to the macroscopic internal energy  $U$

Energy  $U$

Ratio  $\frac{N_j}{N}$  → fraction of particles in  $j$ th energy level

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9:41 AM Tue 9 Jan

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Total mass and energy of the system should remain constant

$$N = \sum_j N_j$$

$N_j$ : # of particles occupying jth energy level

$$E = \sum_j N_j E_j$$

with energy  $E_j$

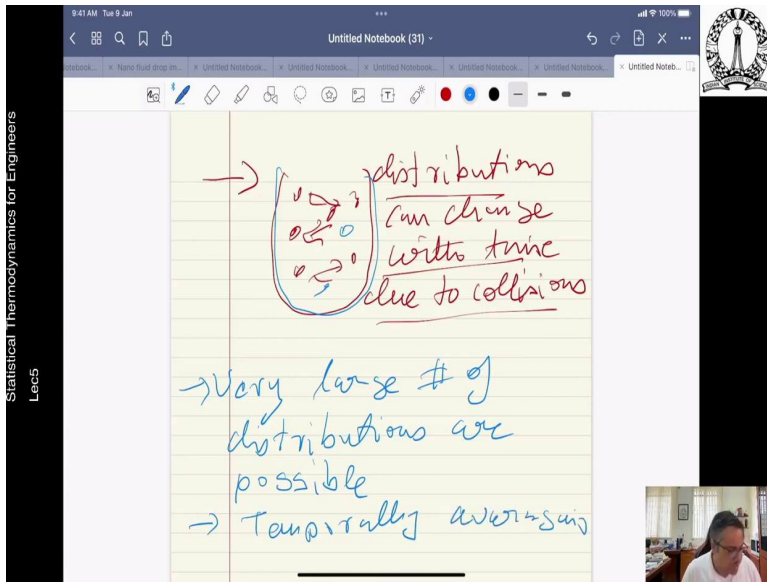
E (Total energy) is

Now also if you look at the ratio  $N_j$  by  $N$ , this particular ratio is the fraction of particles, fraction of particles in  $j$ th energy level and it is also can be interpreted as the probability, that a single particle, that a single particle will be in  $j$ th energy level. So, that ratio  $N_j$  by  $N$  which is also can be the fraction, the fraction of the particles that are residing in the  $j$ th energy level you can also interpret it as a probability that a probability of a single particle being in the  $j$ th energy level, so these two are the two basic things,  $E$  the total energy which you can see it is equivalent to the microscopic internal energy variable and the total number of particles is of course conserved. So, is the energy, so up to this point it should be fairly commonplace that what you are going to get So, because of this now, many distributions are possible, we saw that earlier many distributions are possible you can have the same energy in a variety of ways and this distribution.



(Refer Slide Time: 23:40)

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→ distributions can change with time due to collisions

→ Very large # of distributions are possible

→ Temporally averaging

9:41 AM Tue 9 Jan  
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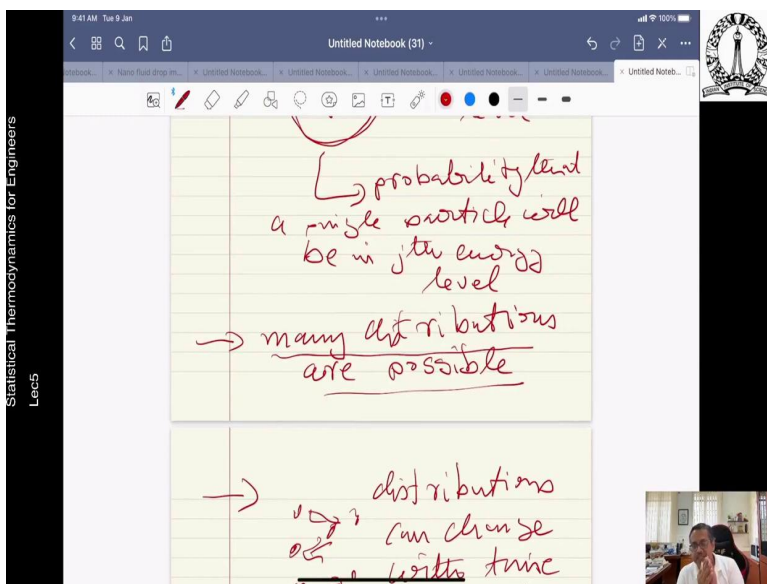
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9:41 AM Tue 9 Jan  
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Nano fluid drop in...  
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↳ probability level a single particle will be in its energy level

→ many distributions are possible

→ distributions can change with time

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of the system should remain constant

$$N = \sum_j N_j$$

$N_j$ : # of particles occupying the  $j$ th energy level

$$E = \sum_j N_j E_j$$

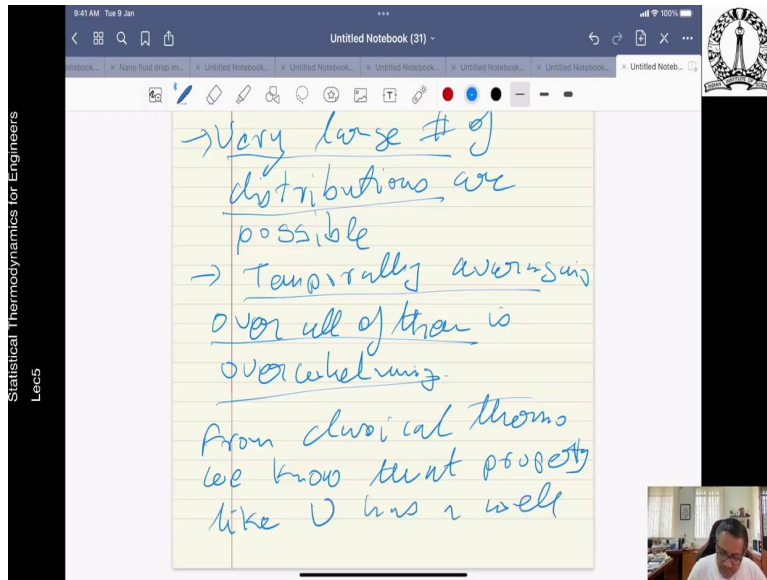
with energy  $E_j$

$E$  (Total energy) is equivalent to the

Now, if you look at the particles they will you know these are particles in the system, they will collide with each other, okay. And so, this distributions can change with time, can change with time due to collisions with the molecules and the atoms they are very large numbers, so they will collide with each other. So, you can see that many distributions are possible that means, the same energy if you look at the energy content the same energy content which is the total energy  $E$ , is total energy  $E$  can be attained by different combinations of  $E_j N_j$  that we already saw more the number of particles many arrangements are possible. So, that is the first thing, second thing is that, not only that they are possible that distributions can change with time due to collisions.

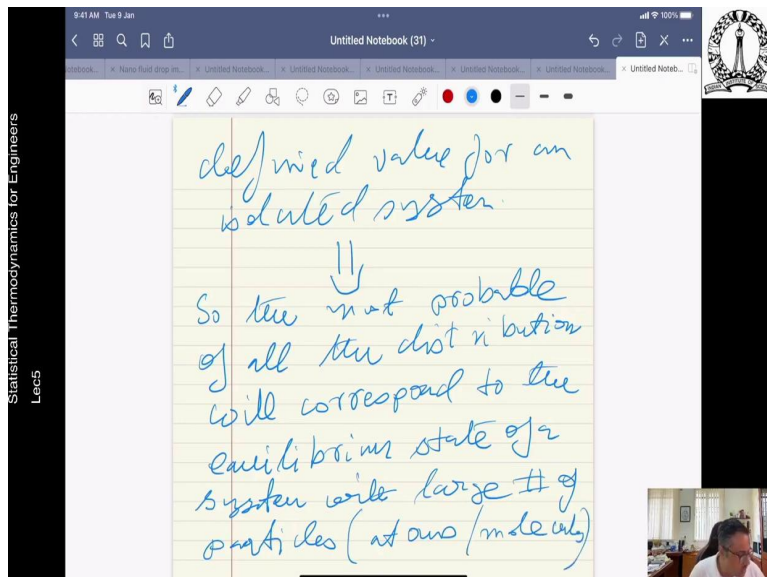
If you look at this box, this particles collide with each other and the energies can change the distribution can actually change, not the total energy, the distributions can actually change. The catch is that, the catch to all these things are that very large number of distributions are possible, large number of distributions are possible, because there are a lot of particles, lot of energy levels and if you want to temporarily average, temporarily tempo means on a time basis, if you want to average them, averaging.

(Refer Slide Time: 25:31)



Over all of them all of them is overwhelming, but we also know so, you can see that there is a lot of, looks like mountainous (())(25:51), but from classical thermodynamics, we know one thing for sure that the property like  $U$  has got a well-defined value for an isolated system from classical thermodynamics.

(Refer Slide Time: 26:30)



We know that property like  $U$ , you has a well-defined, has a well-defined value for an isolated system. So, the idea is that you might have a large number of distributions, so the most probable of all the distributions which will correspond to that equilibrium state of a system with very large

number of particles. So, the idea that we are going to infer before we end this class is essentially, so the most probable because there will be large number of combinations with different probabilities of all the distributions, all the distributions, all the distributions will correspond, will correspond to the equilibrium state system with large number of particles, atoms or molecules.

(Refer Slide Time: 27:53)

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isolated system

So the most probable of all the distributions will correspond to the equilibrium state of a system with large # of particles (atoms/molecules)

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9:41 AM Tue 9 Jan  
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From classical thermo we know that property like  $U$  has a well

defined value for an isolated system

So the most probable of all the distributions is correspond to the

33 of 34

So, this is the most important catch that you might have a large number of possibilities, but out of those possibilities, one possibility should be the most probable that is implied. So, the most probable distribution will actually correspond to the macroscopic equilibrium state of the system

specially systems with large number of particles such that you know your property like  $U$  or internal energy will have a very well-defined value and not a fluctuating value, it will have a well-defined value for an isolated system. So, this particular thing you drill in your mind like that is what it is. So, the next class we are going to see what our macro states and micro states and we will evolve this concept further. Thank you so much