Basic Statistical Mechanics

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Lecture - 03
Probability Theory Part - 1

We will briefly recap what we did last time with extra things here and there. So basic idea is that, you know, statistical mechanics has two parts - one is equilibrium statistical mechanics that addresses problems like phase transition and properties of matter and then you have the time dependent statistical mechanics which addresses things like chemical kinetics, details of protein folding, then dynamic of protein folding and things like that these are very complex systems.

And as I tried to explain that there is a huge amount of work that gone into in Chemistry, theoretical Chemistry, only quantum we really do not do quantum in any kind of sophisticated way. We do density functional theory and that kind of thing nothing against it because we will develop them over physicists and they are very smart people. In statistical mechanics, however, starting with many people like Onsager, Kirkwood, Zwanzig and others there is a considerable contribution that has gone in from chemists, physical chemists of course physical chemistry as you know was born essentially 1900 or 1901 around that with the hand of Arrhenius and Ostwald and what they did essentially was some form of other is this statistical mechanics. However, there is a history which I will recap again but before that let me tell you;

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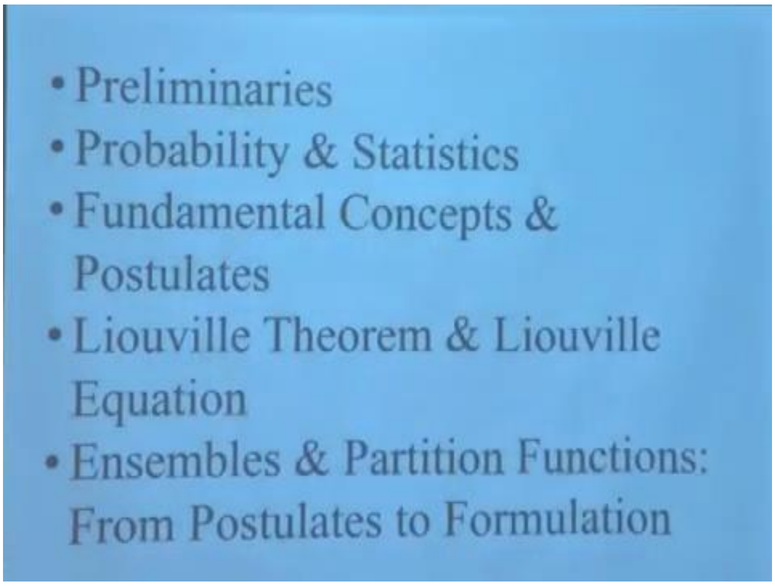

- Preliminaries
- Probability & Statistics
- Fundamental Concepts & Postulates
- Liouville Theorem & Liouville Equation
- Ensembles & Partition Functions: From Postulates to Formulation

What would be the first few things that preliminary we did in last class. I will just do 5 minutes recap of that, because I want to, I like to put really heat on the head again and again on few points that I think important to these students and I get very upset when they do not understand. Now what I will do today probability and statistics, then I will explain why we need to know some amount of very elementary to what you have learned by and large in your class 11 or 12.

And fundamental concepts actually what we will do here something like phase space trajectory and then I will try to motivate and explain to you why this time dependent statistical mechanics needed these things. So I hope to finish this today. So Liouville theorem and Liouville equation we will do these things and these will be next, not in this thing.

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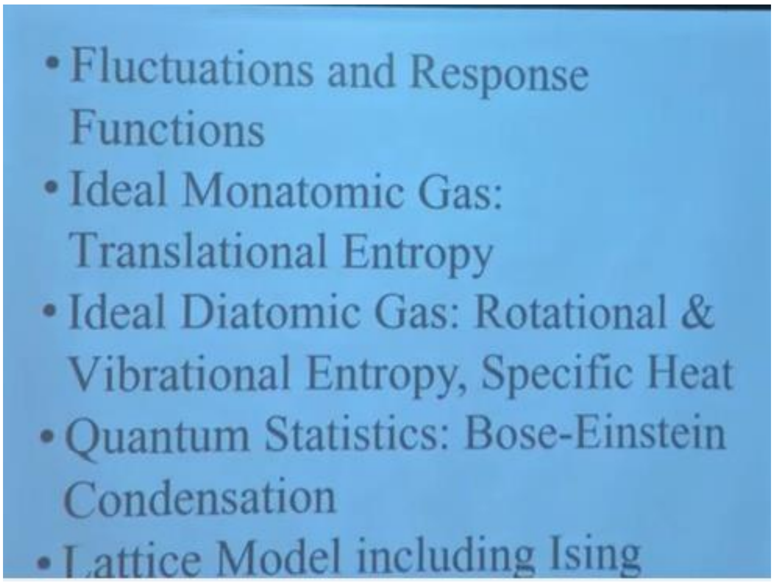

- Fluctuations and Response Functions
- Ideal Monatomic Gas: Translational Entropy
- Ideal Diatomic Gas: Rotational & Vibrational Entropy, Specific Heat
- Quantum Statistics: Bose-Einstein Condensation
- Lattice Model including Ising

Then we will go on my very favourite and one of the most favourites is the fluctuations and response function. Then we will do this is amazing the ideal Monatomic gas but even the translation entropy is used almost every day in the drug discovery or drug DNA interaction because that gives you the entropy of a drug going into DNA and the entropy is losing which is the Sackur-Tetrode equation.

Then of course here we have all the things that we need you know rotational, vibrational entropy, things essential for chemical kinetics. We use them without knowing where they came from but they came from a very elementary statistical mechanics. So, we will do that and then we will do bit of quantum statistics. I am not to greatly fond of doing this thing but there are some nice points here.

That I think students should know and they are not taught and or not covered in books very simple things. Then we will go to Ising model which I think is one of the simplest model. The first and perhaps the only solvable model of interacting systems and one must know Ising model and this is the chronology of my doing now what I briefly tell the hierarchy the way things happen in statistical mechanics, though it was involved as I did.

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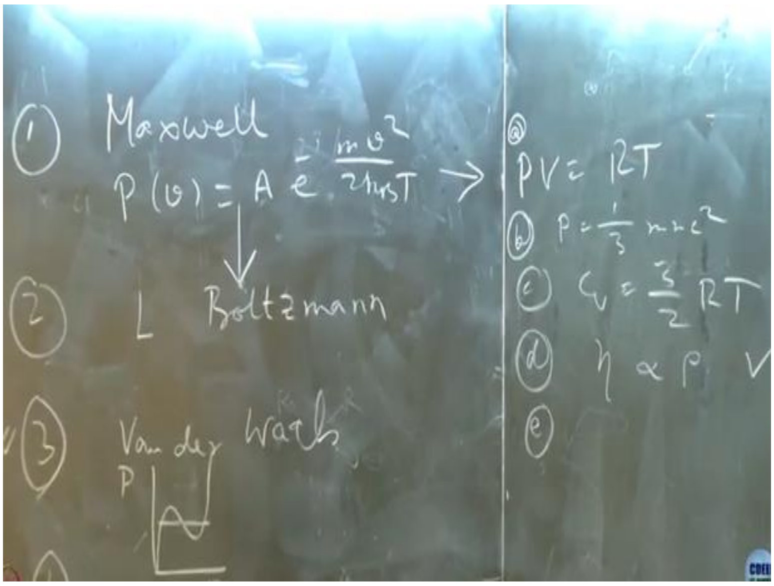

It is started with Maxwell who did the derivation of the velocity distribution that was the first step and then Ludwig Boltzmann who was as I told you so impressed that rest of his life he carried this paper of Maxwell with him. So this is the chronology. He is the one who started very seriously introducing concepts for probability theory, which was enormously criticized.

Because those days everybody believed the mechanical law of motion will be able to explain everything. And Boltzmann introduced many things one of them is the, you know, Boltzmann kinetic equation where he tried to develop. So Maxwell gave these Maxwell and then a little bit of Boltzmann was able to this one, all these things came out from then your $P = 1/3\ mnc^2$, $C_V = 3/2\ RT$.

Then expression for viscosity that, I forgot but something to do with density and other thing is σ^3. So, all these things, huge numbers, in few are these equations. So in the beginning the birth of kinetic theory of gases started with Maxwell and that was also the start of the statistical mechanics but Maxwell and Boltzmann could connect to Thermodynamics, but at this same time get the expressions like this, which are transport properties.

And as you know, this approach also gave the universal gas constant which ultimately also used by many people including Einstein to get the estimate of Avogadro number, one of the landmark of Einstein's 1905 paper. Boltzmann wanted to go beyond this ideal gas, collision less ideal gas. He introduced then these binary collision and binary collision operator which even today is used.

But in the process he had to introduce essentially many-body distribution function because the probability of a particle at r_1,v_1 colliding with a guy another particle at r_2,v_2 and then going off r_1',v_1' and r_2',v_2', this is hugely complicated thing, because these are 3 dimensional vectors.

So he made an approximation that if $r_1,v_1,\ r_2,v_2$ if that is F_2 that becomes $F_1(r_1,v_1,\ r_2,v_2)$ that is called the approximation of molecular chaos by and large for which he was criticized; but then what came out of Boltzmann rigorous work is the definition of entropy that is $S = k_B \ln \Omega$ and that ultimately lead to the you know very heavily used by Gibbs. So then around the time we had Van Der Waals and as I told you last day the Van Der Waals had this famous Van Der Waals equation of state.

And which has this kind of unphysical shape but P versus density and Maxwell did the Maxwell tie line construction. This work and this work motivated the earth person across the Atlantic, Willard Gibbs who made this important he could observation that you look of course knew all of Boltzmann. He knew this the difficulty Boltzmann suffered in order to do a Newtonian description.

That means everything obeys laws of conservation, Newton's laws of mechanics and then of course as I told you we cannot solve three body problems. Willard Gibbs then realize that there could be a time independent because if we have to solve this Avogadro number because you know we are interested in one cc at least or two cc then those many molecules we cannot solve in three body and even for spheres and forget about water or ice when I try.

So he realized very early the time-dependent approach of Boltzmann he is not going to go very far if I am doing the equilibrium properties because for equilibrium properties, it should not be that difficult; after all as I told you yesterday that we have millions of glasses of water, they are all the same properties. Then he realized one very important thing which I forgot to tell last time, he realized that if such a system Avogadro number of there were huge number of microscopic states.

And if I have billions and billions of my glass having full of water then each of them will be in different microscopic states and since each of them in different microscopic states, at any given instant and exploring other microscopic states, it makes sense to talk of a distribution and distribution that is why they introduced the concept of ensemble which I will elaborate little bit more because these things are in no other than the book of Tolman.

And I have not seen anybody doing a really good job on describing these things but Tolman of course goes a little old-fashioned and goes different things. So then the Willard Gibbs, we do not need anything beyond Willard Gibbs as of now. Willard Gibbs explained how to think of Van Der Waals, he explained the phase equilibrium, the famous book of thermodynamics of heterogeneous system.

And they extremely impressed Maxwell; of course Boltzmann was going his time-dependent venture and when Maxwell died at very young age, everybody made a joke which was Willard Gibbs was unmarried, lived the Sterling laboratory at Yale and he used to only thing he used to take is to journey from his home to the second floor; but of course before that three years he spent in Europe after that where he learned all these things.

And then Maxwell died, then the joke at Yale was that there was only one man who understood Gibbs and he is dead. So, but he alone kind of went on doing and did many, many things. Now coming back, then he introduced all these and the concept of probability.

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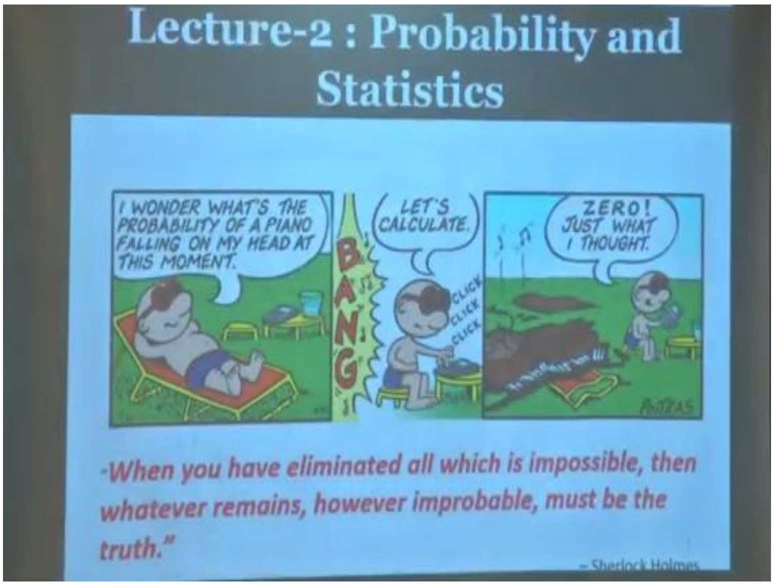

Lecture-2 : Probability and Statistics

-When you have eliminated all which is impossible, then whatever remains, however improbable, must be the truth."

– Sherlock Holmes

And now I will briefly go through to all the questions too much time to what and you know there is enormous number of jokes about probability theory and many, many poetries and poems of probability and this is my favourite of Sherlock Holmes.

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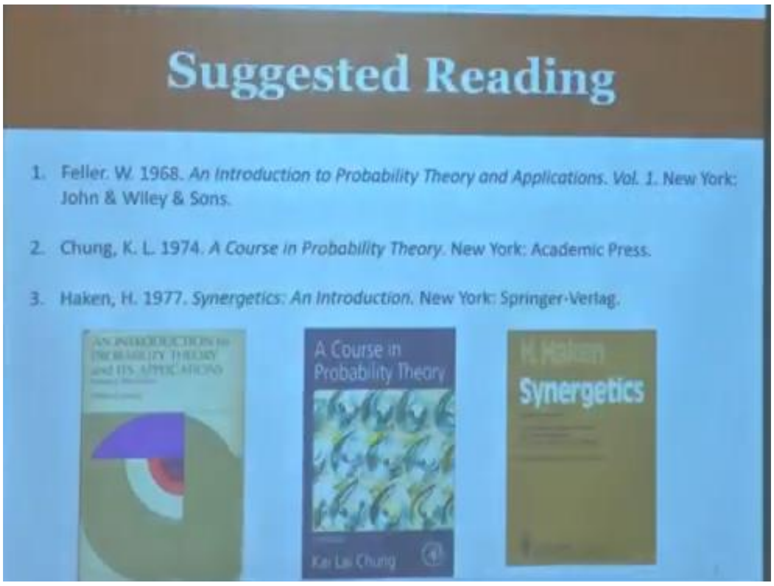

Suggested Reading

1. Feller. W. 1968. *An Introduction to Probability Theory and Applications. Vol. 1.* New York: John & Wiley & Sons.
2. Chung, K. L. 1974. *A Course in Probability Theory.* New York: Academic Press.
3. Haken, H. 1977. *Synergetics: An Introduction.* New York: Springer-Verlag.

So now I will go through but before that let me tell that we have this is my favourite book. This is not the book I have in my mind and I told my student to put this together. And an introduction to probability theory by Kai Lai Chung was famous in mathematics department by KLC. So they have two KLC, KLC 1 introduction to probability theory that is a wonderful book which I studied when they took a course on probability theory.

And this is the one absolutely fantastic which mainly helped me. I got this when I solved the barrier less reaction, which is really quite significant and is classic now I could do that because I knew how to solve method of images. By method of images and repeated reflections all this technique I knew that I could solve and there is another beautiful book which is an introduction.

This I think all of them are available free on the internet and but this is beautiful because these are things of talks of probability, determinism, then probability and deterministic together, goes on deriving beautiful equations. So these are highly recommended; so these three books for the probability theory that I recommend to everybody.

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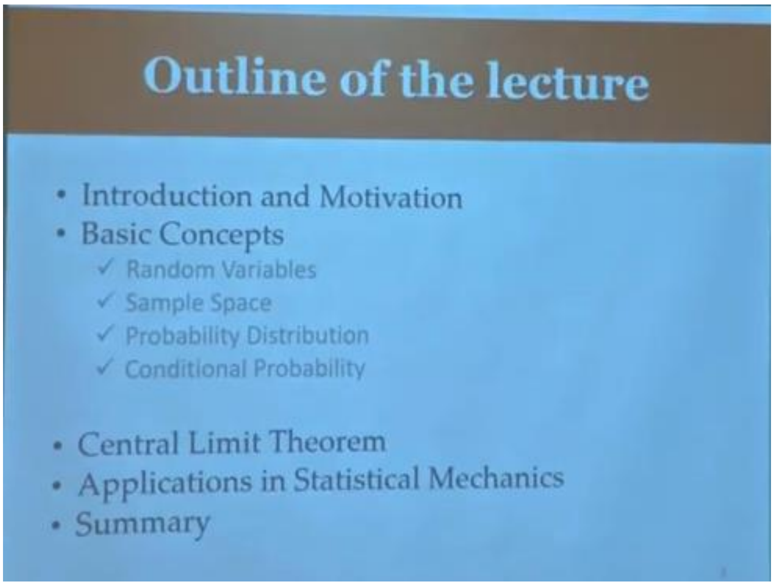

Outline of the lecture

- Introduction and Motivation
- Basic Concepts
    - ✓ Random Variables
    - ✓ Sample Space
    - ✓ Probability Distribution
    - ✓ Conditional Probability
- Central Limit Theorem
- Applications in Statistical Mechanics
- Summary

So this particular part of the lecture will now be on motivation I have already done a little bit more, then I will go through what is a random variable, how do we define sample space which is so important in when you do the statistical mechanics, then probability distribution and the conditional probability. This is extremely important because conditional probability is the one that goes what to become the radial distribution function.

So this conditional probability you have heard and read in I think and Bayesian’s theorem things like that in your undergraduate in your class 12, but that is the same thing we again and again we come across. Then we will do central limit theorem; as the name says mathematicians are not given to adjectives, not like chemists. We do say everything very interesting. They hardly say anything interesting; they say it is trivial. Feynman has a wonderful joke about mathematicians.

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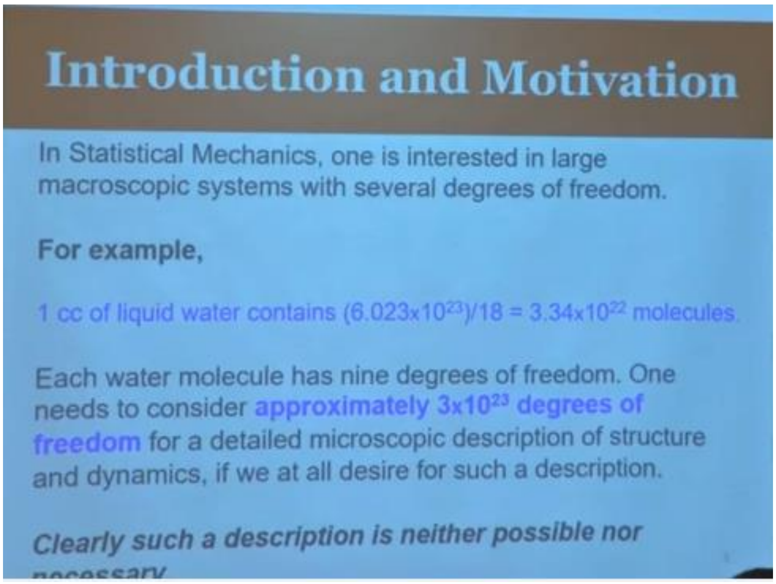

Introduction and Motivation

In Statistical Mechanics, one is interested in large macroscopic systems with several degrees of freedom.

For example,

1 cc of liquid water contains $(6.023 \times 10^{23})/18 = 3.34 \times 10^{22}$ molecules.

Each water molecule has nine degrees of freedom. One needs to consider **approximately 3×10^{23} degrees of freedom** for a detailed microscopic description of structure and dynamics, if we at all desire for such a description.

Clearly such a description is neither possible nor necessary

So as I said, what the motivation is in statistical mechanics, what is the interest in large macroscopic systems; many, many degrees of freedom not several degrees of freedom. 1 cc of liquid water contains these many molecules and each has 9 degrees of freedom. So we are dealing with huge number. So if we want to have a Newtonian description of solving positions and momentum of each particle not only that you will not be able to do it even in computers.

We are doing about it now probably few thousand; even then we need these same concepts that we will be using also, if we have all those things we have no need for that. It is not necessary to have all this huge aim. When we have started doing that we could hardly simulate few hundred water molecules or few hundred Lennard Jones. So we had little bit more elaborate in describing but now computer simulations come along way.

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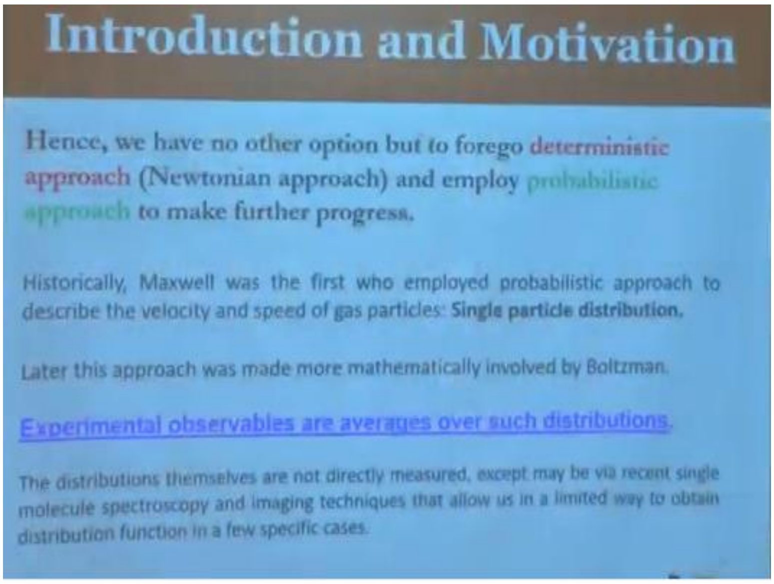

Introduction and Motivation

Hence, we have no other option but to forego deterministic approach (Newtonian approach) and employ probabilistic approach to make further progress.

Historically, Maxwell was the first who employed probabilistic approach to describe the velocity and speed of gas particles: **Single particle distribution.**

Later this approach was made more mathematically involved by Boltzman.

Experimental observables are averages over such distributions.

The distributions themselves are not directly measured, except may be via recent single molecule spectroscopy and imaging techniques that allow us in a limited way to obtain distribution function in a few specific cases.

So now these are very important and very loaded statement and that we no longer can afford and no longer it is realistic practical to take a deterministic approach, which is Newtonian approach instead we have to go to probabilistic approach, which was already initiated by Maxwell was the first thing who did the single particle distribution. Now there is a very, very important point that comes now, that what the experimental observables that we do.

For example, specific heat or the density they are all averages over a random variables. If you look, for example the standard Castellan book, if you remember, it has this nice picture that how to get the pressure of a liquid and what Castellan did was that.

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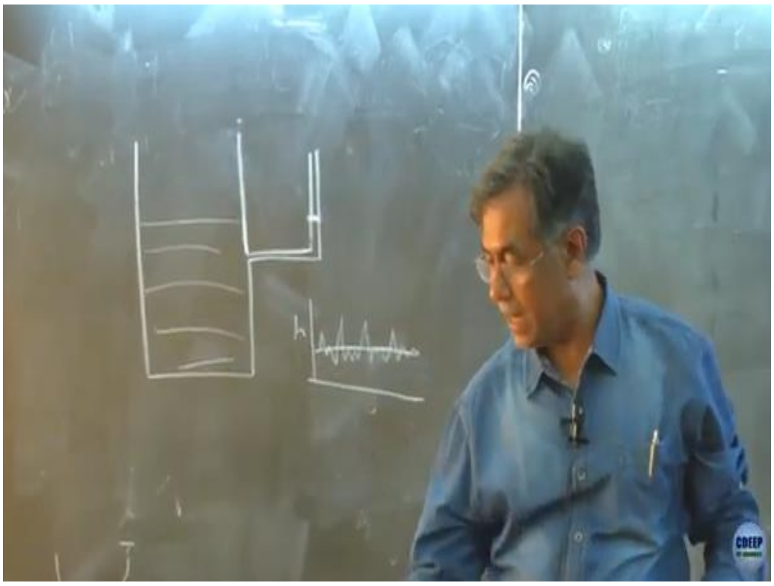

He had the colour thing and you know it is full of water. Now, so water up to this and then water up to this, there is a colour liquid. What is now given that if you now with a microscope, the optical microscope, ordinary microscope also can do that. We have it in our undergraduate laboratories, you will find that height is continuously fluctuating; so there is nothing really a constant pressure and the pressure that we mean is we do an average over that and it is a time average. So these are very important point in understanding that experimental observables are themselves a random number.

And of course when you do spectroscopy you get a broad distribution that because the probe which say dye molecule you put in a liquid and then this diabolical phases , when you put a dye molecules of 0.1 molar about 0.01 molar so there is a 10^{20} of dye molecules, each of them facing a different environment. So what you see in spectroscopy is an average again over all these molecules.

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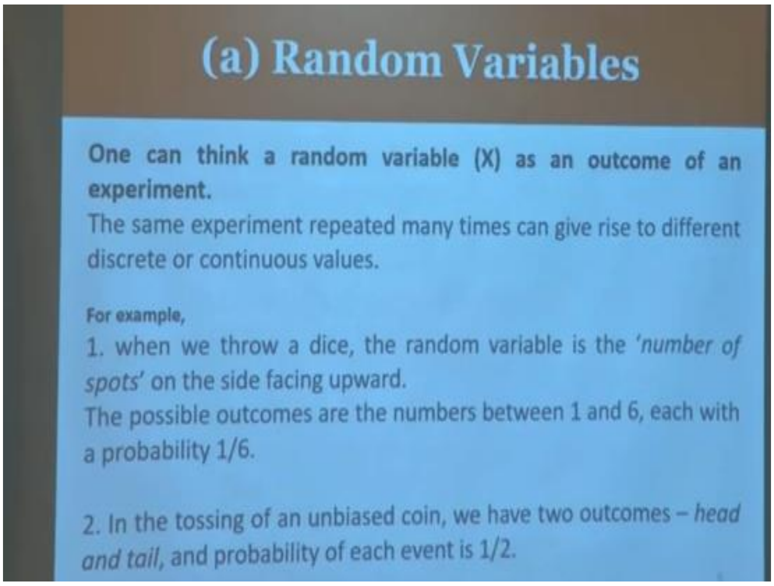

(a) Random Variables

One can think a random variable (X) as an outcome of an experiment.

The same experiment repeated many times can give rise to different discrete or continuous values.

For example,

1. when we throw a dice, the random variable is the *'number of spots'* on the side facing upward.
The possible outcomes are the numbers between 1 and 6, each with a probability 1/6.

2. In the tossing of an unbiased coin, we have two outcomes – *head and tail*, and probability of each event is 1/2.

Now I will quickly go through something. I am just using this slide I do not need to use that but it is a little bit it saves time and it a little bit more precise. So now we have to think when I start discussing the going towards the statistical mechanics, so we are till now we have argued that we give out the deterministic approach of Newtonian dynamics, Newtonian approach and we are trying to go to a probabilistic approach.

And the reason is that a deterministic approach is not feasible approach because as I say that they are all fluctuating, so then the central quantity in statistical mechanics is a random variable X. For example, X here is a random variable. Energy of a system in environment or in equilibrium with a path is a random system.

So random variable means we do not know and we will never know the exact instantaneous value of this quantity, but we know its average, we will know its second moment if necessary, we will know its fourth moment but this quantity is a central quantity in our descriptional statistical mechanics. For example, you realize that this random variable or set of random variable I want the liquids and position of a water molecule in liquid; they need to in a position (r_1) and orientation (ω_1).

Then I would like to know how far another water molecule with orientation ω_2 at position r_2. So in statistical mechanics, in chemistry, physics all the time whether doing conductivity all the time we are talking with these quantity, so these are very general thing. X can take the quantity of our interest. Some examples of random variable, when you throw a die, then possible outcomes are 1 to 6, each of them having 1/6 probability. Similarly, in the case of tossing coin where each side head or tail will be half.

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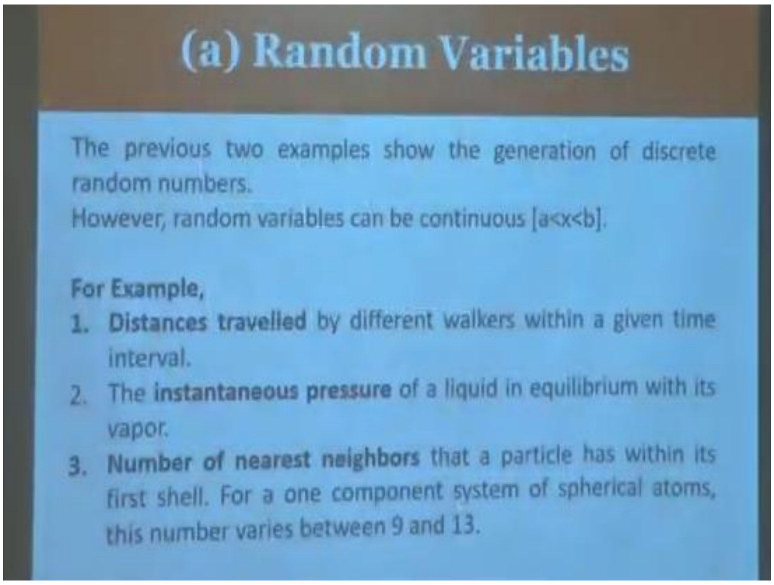

(a) Random Variables

The previous two examples show the generation of discrete random numbers.
However, random variables can be continuous [a<x<b].

For Example,

1. **Distances travelled** by different walkers within a given time interval.
2. The **instantaneous pressure** of a liquid in equilibrium with its vapor.
3. **Number of nearest neighbors** that a particle has within its first shell. For a one component system of spherical atoms, this number varies between 9 and 13.

Now there are some things which immediately comes to our mind that things like the way we do random walk, left or right. If you want random walk in one dimension is equivalent to the throwing of a die.

So these are very important quantities; you want to discover random walk, you want to describe a walker, you how far it is moving, how fast it is moving, which is diffusion, what the pressure, everywhere we are doing with this kind of random, which is the same as essentially throwing of the die or the coin.

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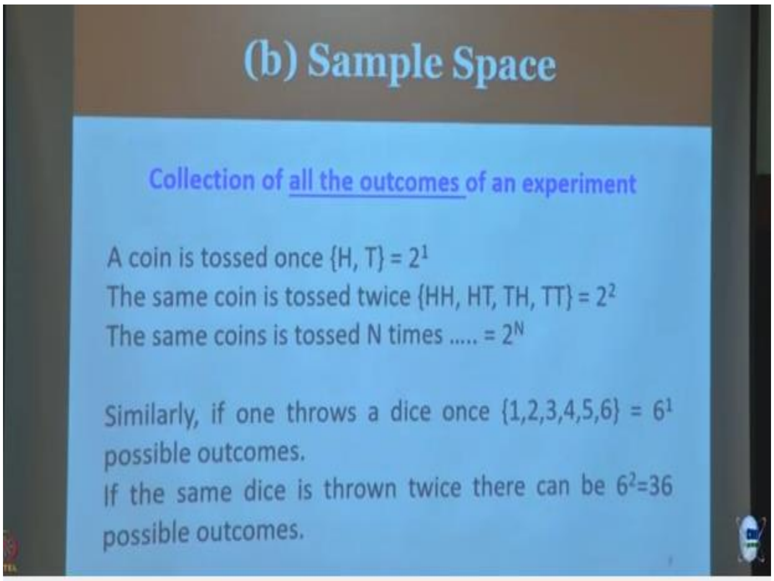

(b) Sample Space

Collection of all the outcomes of an experiment

A coin is tossed once {H, T} = 2^1
The same coin is tossed twice {HH, HT, TH, TT} = 2^2
The same coins is tossed N times ..... = 2^N

Similarly, if one throws a dice once {1,2,3,4,5,6} = 6^1 possible outcomes.
If the same dice is thrown twice there can be 6^2=36 possible outcomes.

So random variable, then let me summarize, is a quantity of interest which can take a number of values which are not predetermined but which follows a distribution, as we go through. Now the collection of all the outcomes of the experiment is the sample space, this is very important. So when we do in statistical mechanics, we integrate over some dx or something we integrate over all the possible values and all the possible values together define the sample space.

Like sample space of a tossing coin is 2, then you got twice coins the sample space become 4 because it can be head, head, head, tail, tail, head, tail, tail. Similarly, dice if we so many times then we have if twice we have the 36 possibilities. So then sample space which you have done in your school like Venn diagram and similar things, it just the collection of possible events.

We need to know the collection of all the events because we would need to know the total sample space in order to define probability of a given event. So we need all the events to know once.

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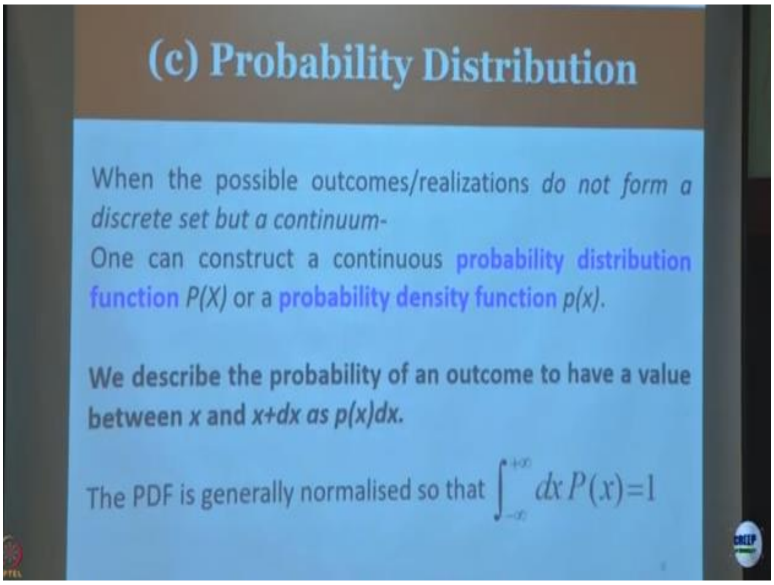

(c) Probability Distribution

When the possible outcomes/realizations *do not form a discrete set but a continuum*-
One can construct a continuous probability distribution function *P(X)* or a probability density function *p(x)*.

We describe the probability of an outcome to have a value between *x* and *x+dx as p(x)dx.*

The PDF is generally normalised so that $\int_{-\infty}^{+\infty} dx\, P(x) = 1$

we have all the events then now we can say.

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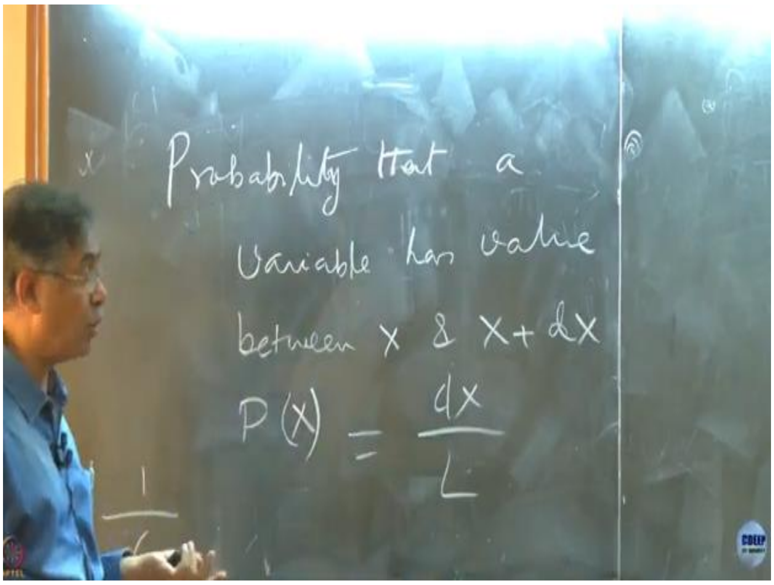

Probability that a
variable has value
between X & X+dX
$P(X) = \frac{dX}{L}$

If we have a value of the probability of a random variable in the continuous case between X and X + dX, now in a discrete it is easy as we say in case of throwing dice it will be 1/6 that what is the probability. If has value 1, then also it is 1/6. In a continuum you need to measure between X and dX using uniform distribution.

And the length will be normalized because when you integrate you would get $\int dX = L$. So these are fairly trivial things, straightforward things. We describe the probability of an outcome to have a value between X to X+dX by Px dX. The probability is normalized, so that it has to be somewhere and that is now again the distribution it will be you can do –L to +L.

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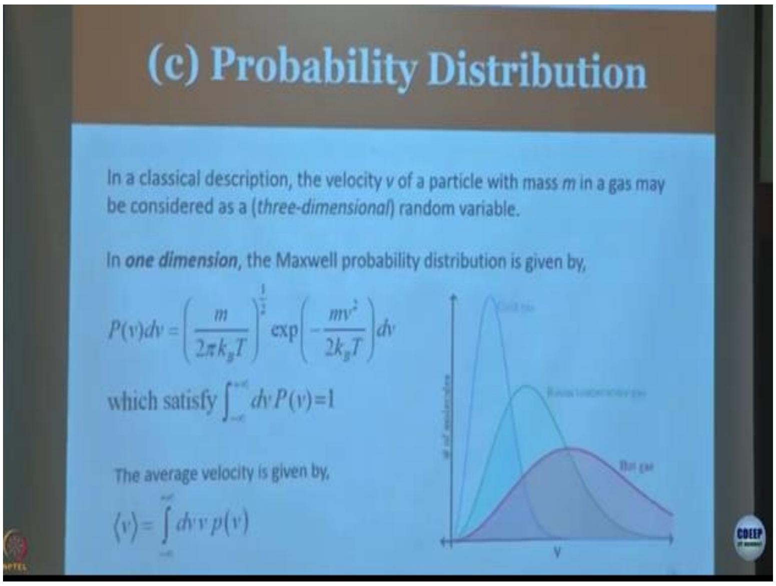

(c) Probability Distribution

In a classical description, the velocity *v* of a particle with mass *m* in a gas may be considered as a (*three-dimensional*) random variable.

In ***one dimension***, the Maxwell probability distribution is given by,

$$P(v)dv = \left(\frac{m}{2\pi k_B T}\right)^{\frac{1}{2}} \exp\left(-\frac{mv^2}{2k_B T}\right)dv$$

which satisfy $\int_{-\infty}^{+\infty} dv\, P(v) = 1$

The average velocity is given by,

$$\langle v \rangle = \int_{-\infty}^{+\infty} dv\, v\, p(v)$$

There are many, many examples of that as I told you; very first one was given by Maxwell and you have to realize that it came from nowhere, that means at that time nobody in 1950 or 1960, 1850 or 1860 nobody talked about distribution except mathematicians but they are not applied to physics or chemistry. So this was done by and he derived it and the derivation is you have done in your undergraduate textbook how you get this particular form.

This is normalized because in 1d, for example, you have velocity can go to $-\infty$ to $+\infty$. This is the average velocity we know will go to zero but the $\langle v^2 \rangle$ which gives the width which again is related to temperature and the derivation of many things of kinetic theory of gases almost everything in the elementary kinetic theory of gases for flows from this equation.