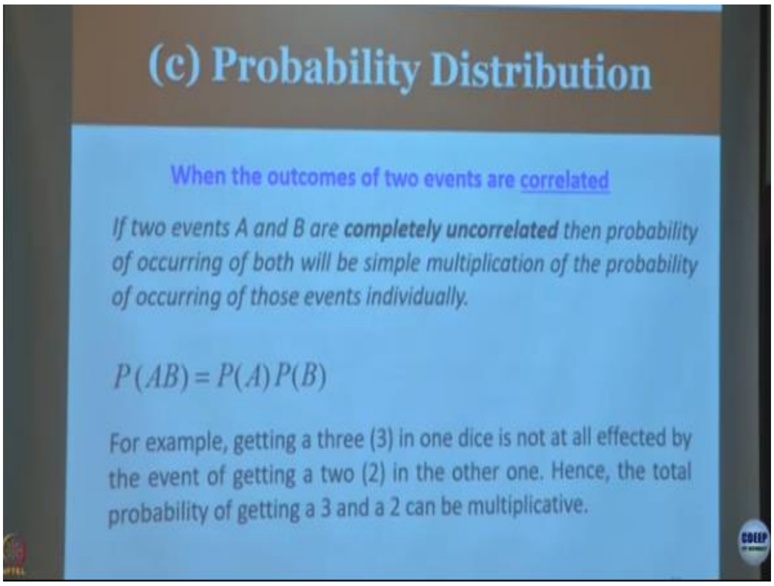
Basic Statistical Mechanics
Prof. Biman Bagchi
Department of Chemistry
Indian Institute of Technology, Bombay
Indian Institute of Science, Bangalore

Lecture - 04
Probability Theory Part - 2

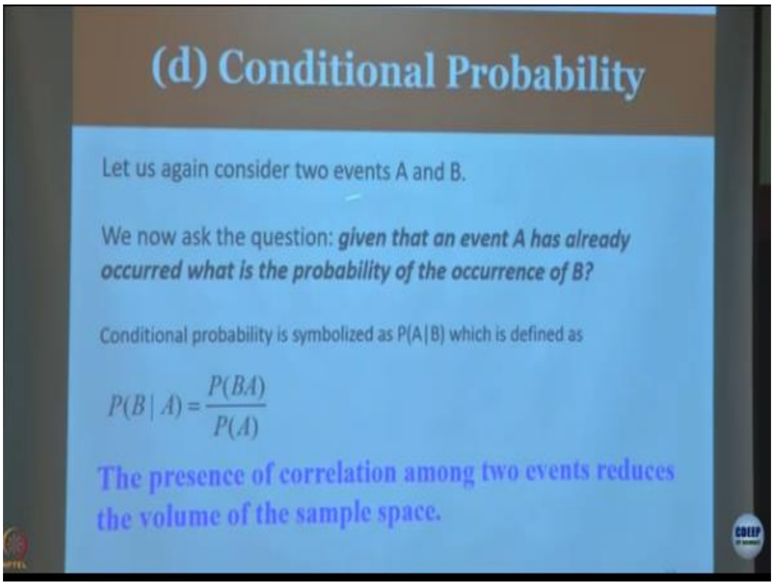
(Refer Slide Time: 00:15)



Now, what is very important is that what if two events are correlated? Now if two events for example I am tossing dice, I throw dice twice once I get 5, another time I get 3 are they correlated? If they are independent in my experiment then probability of happening two independent event will be just P(A) times P(B). So if it is in case of throwing a dice, then probability will be 1/6 * 1/6.

That becomes 1/36, like if I have 1 and 5 then I also get 1/36 for that independent probability distribution function. This is very important because in real world in many cases this independence theorem you can say independence is not valid. So not at all affected by one getting 1,3 of dice is not important by the 2, hence the all probability as I said is multiplicative.

(Refer Slide Time: 01:26)



Again consider two events A and B now we want to know what happen in this case they are not correlated at all; One outcome of second experiment does not depend any outcome of the first experiment. However, as I keep saying in the most of the case in the world these two are indeed correlated, that is what is interesting? What is important when there is a correlation? You have a phase transition when there is a correlation.

You know, we live in the world because things are correlated, if they are independent ideal gas then we would not survive. So now if we can ask the question given an event A, what is the probability of the occurrence B? This is called the conditional probability. That I give you information now. If A has already occurred then probability of B depends that A has occurred.

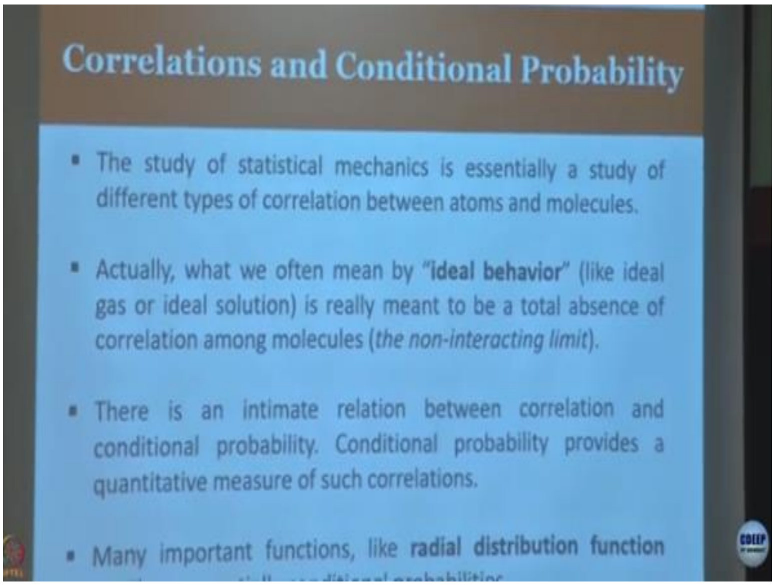
I give an example, I take a liquid molecule and around the equivalent molecule there are 10 neighbours. I tell you that there is a 10 neighbours now, now next time about say one pico second later or 100 femtoseconds later I ask you what are the probability the number of molecules will be 10 or 11 or 12 and you will know now it is within that number that means either 10,11 or 12.

So conditional probability says knowing an information of an experiment when you know that, before even you do the next experiment you have an idea of what would be the outcome. So this is the, what is the presence of correlation or correlated events is a very common term, we used in probability theory or physics or chemistry that the two events can be correlated by many different ways.

But in the examples I am giving you they are correlated by inter molecular interaction. So the study of statistical mechanics, so we have now talked about random variable, we have talked of sample space, we have talked when the two events are not correlated like throwing a dice or tossing coin. However in real world as I said, things are interesting only when they are correlated.

And so study of statistical mechanics is that is what Boltzmann tried to do all his life. This correlation between two particles in a binary system ideal gas does not have a correlation but you can see when ideal gas has such rich, rich predictive power. When you take binary thing into account you again go very far, but you have to work much harder now. So study of statistical mechanics is a study of different types of correlations between atoms and molecules whether liquid or gas or solid.

(Refer Slide Time: 04:35)

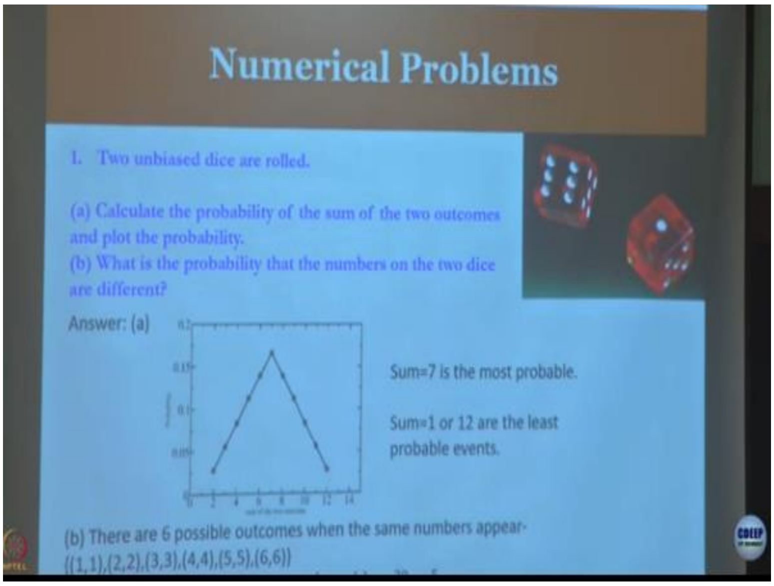


Superconductivity or whatever you do this is essentially studies of these correlations in different form or other. So this we call our ideal behaviour when total absence of correlation of molecules that we call very important term non-interacting limit. So this non-interacting limit is the limit that I said we will do later, then as I already said that the correlation is essentially conditional probability.

So when you talk of conditional probability the two events one happening and what is the probability then the next experiment will have this outcome that is essentially is our beginning of the correlation. So this is a quantitative measure, so conditional probability provides a quantitative measure of such correlation that is how we construct for example, radial distribution function or other things.

As I said this is one of the central quantity in many body systems whether colloids or liquids or, your Ostwald ripening all these things essentially depends on this kind of things.

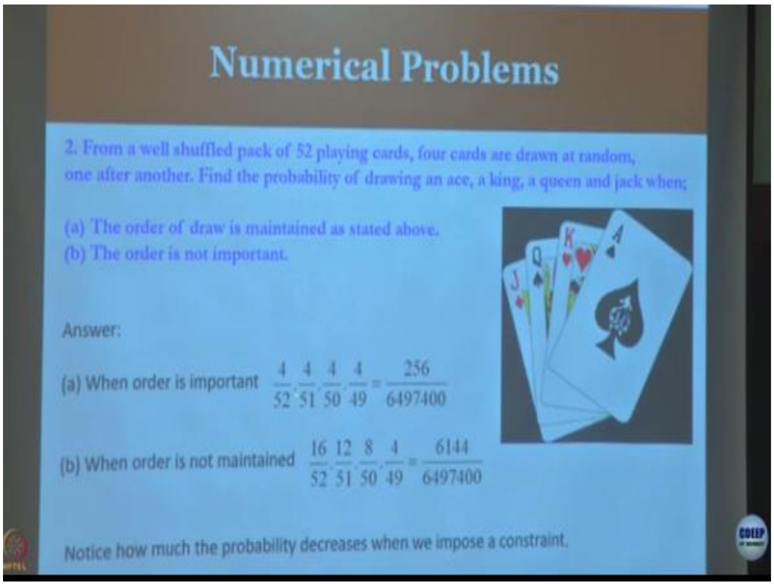
(Refer Slide Time: 05:52)



So I have some problems for you to do, that two unbiased dice are rolled. Calculate the probability that you already did, what is the probability of the number, this is simple thing. Now, I will give you an interesting result that the, what is the probability that numbers of the two dice are different? And you can see that, if I sum of the two outcomes and plot the probability of course nothing can be below 2, nothing can be above 12.

But this is this interesting structure, because the one that is here is the maximum way it can happen, 2 is 1+1, 12 is 6+6, this. So as you have for example 8, 8 can be 5+ 3, 3+5, 4+4, Okay? So this is 6 possible outcomes and you can get the answer.

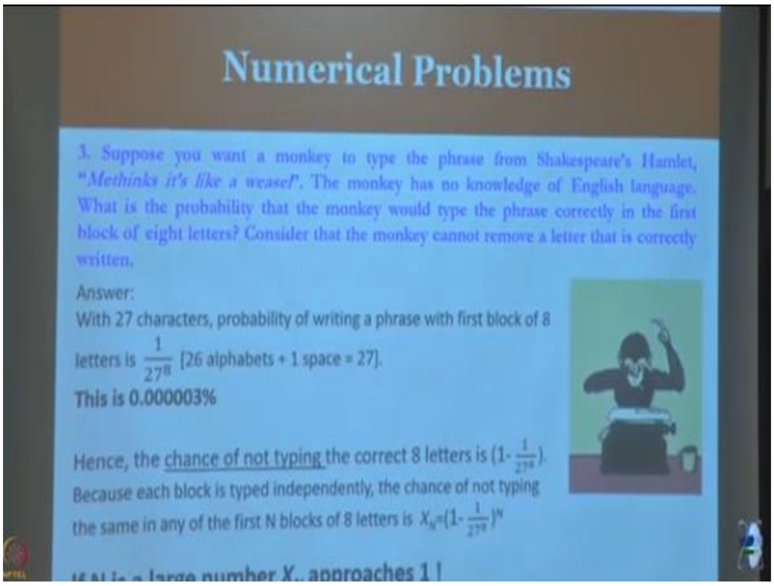
(Refer Slide Time: 06:54)



Another thing is that from a well shuffled pack of 52 playing cards, find the probability of drawing an ace, a king and a queen: the order of draw is maintained, you know you are doing the combinatory and permutation the order is not important, now this is again when order is important then of course you have many more outcome, when order is not important when order is not maintained.

When order is important, yes you have a less number but order is not maintained, every time you have lot more outcomes.

(Refer Slide Time: 07:36)

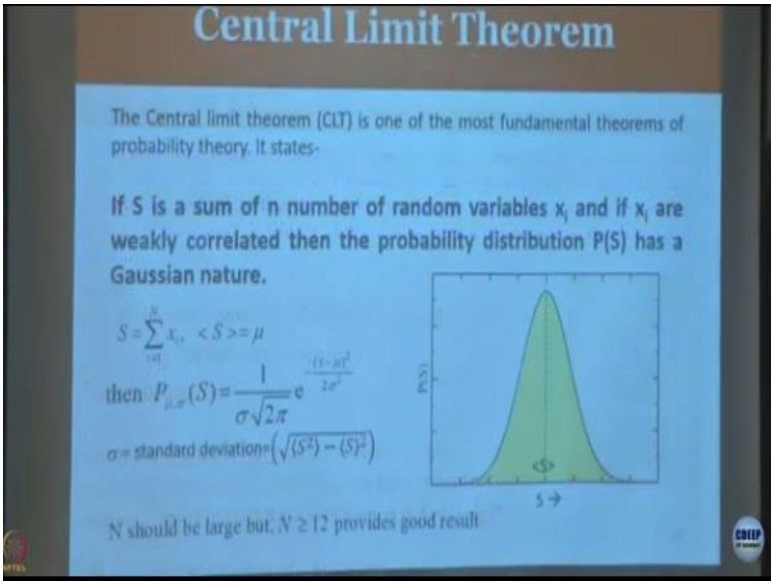


And next is, this is my favourite. I have talked about it there and let us see a monkey typing a line from Shakespeare's Hamlet "Me thinks it is like a weasel", then you have 27 characters probability of writing, so very interesting is that suddenly from this kind of rather, in a course textbook or you know your high school math, suddenly graduated to a front line research problem.

This happens in statistical mechanics, this is protein folding and most important paper of protein folding is on the Levinthal paradox. So this is the beauty of the probability theory, that everywhere you have to construct the elementary model and the basic idea again that if you do, if the monkey has no like it typed randomly then it takes if how long it will take it will have 10^{33} attempts. But anyway you can do it yourself and it is a little bit more complicated that would be block of the correct 8 letters this is a little bit simpler. You know this block of 8 letters made simple.

But if you do this will be blank here me thinks it is like a weasel then you will have 27, 28 including blank 28 spaces, so to do you have to have 27^{28} that many, that is your sample space. 27 to 28 and that is what I said 10^{33}, here it makes a little bit simpler there is a block of eight letters, but whatever so this is a Levinthal paradox. That Levinthal paradox is in terms of protein folding. Now, so this is the elementary probability theory.

(Refer Slide Time: 10:09)



Now I am going to do something extremely important and that is the Central Limit Theorem. Now, as I told you that you know mathematicians are not given to use this kind of terminologies, that they have one thing they call fundamental theorem of algebra. Now what is the fundamental theorem of algebra? Anybody remembers? You read it many, many times in your past high school and your BSc.

I told you mathematicians do not at all, nothing is interesting for them, when they use a language like that it is very important. What is the fundamental theorem of algebra? Guys you should read up your algebra a little bit, no doubt people do not respect chemists. So that is the theorem is that you have a polynomial of degree N, how many roots it has ?

N roots, and now if this depending on the values of a, b, c you can have all real or you have complex conjugate in pairs. Why it is so important? All your numerical work whenever you are finding a solution by method of roots. Now this Central Limit Theorem is an amazing theorem.

This is the most fundamental theory of, not one of the most fundamental theorem of probability theory, saying that it is very important in chemistry is a sum of N number of variables which can take random numbers within a sample space. N number of random variables, now let me do I am tossing the coin N number of times, dies N number of times.

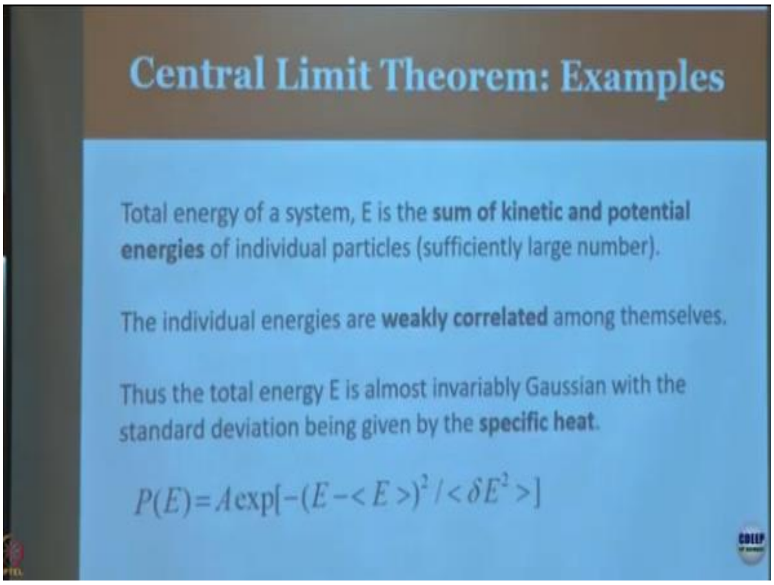
Now I define S as a sum of the random variables, I give you the average number, then the Central Limit Theorem this comes from nowhere it tells you the probability that the sum has value S, is this thing. But it is magical theorem. I think in my book I have probably three times discussed Central Limit Theorem. That is really magical. I have gone to many comprehensive you know in physics.

I do not have to ask they will always ask in Stat Mach comprehensive or cumulative exam. What is Central Limit Theorem and explain Central Limit Theorem? So this is now why your energy of the system is Gaussian and this full width at half of energy distribution, what is the full width at half in energy distribution? Specific heat this is $\left\langle \delta E^2 \right\rangle = k_B T^2 C_V$.

But you have to consider fluctuation of the empty space, that is also then Gaussian and that gives isothermal compressibility and the way we when we used to do we did not always trust the computer program to give us random variables. So we used to sample from Gaussian distribution, you know if you are simulating a Lagrangian dynamics then your force has to be Gaussian distributed.

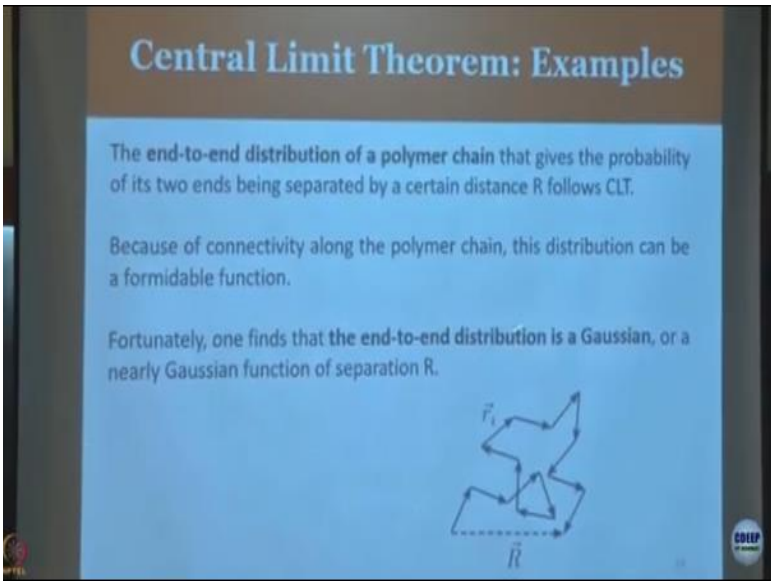
And then we used to form this from, I seemed we form the Gaussian distribution then we sample from the distribution, so this is what we use everywhere. It is something we are routinely using in time dependent statistical mechanics or equilibrium statistical mechanics or anywhere.

(Refer Slide Time: 14:51)



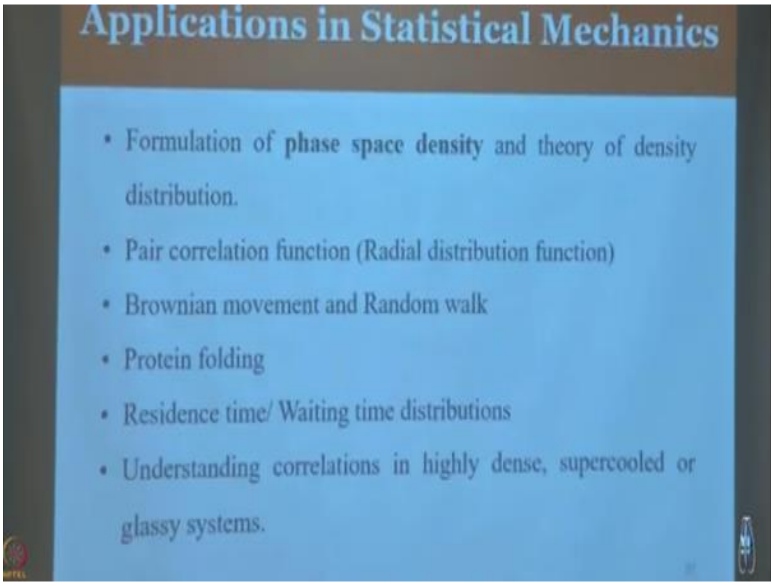
So total energy of the system then weakly correlated, they have to be correlated among themselves. There is a very strong theorem actually and so this is the specific heat as I just described invariably Gaussian with the standard deviation.

(Refer Slide Time: 15:03)



Then the other thing that you know end to end distribution in a polymer chain, and where the total end to end distribution is some over these things and then this end to end is Gaussian distribution and that is again follows trivially, you do not have to do anything, it simply follows from Central Limit Theorem.

(Refer Slide Time: 15:28)



And then many, many other cases, now in Statistical Mechanics we have the phase space density and all the probabilistic description goes there, Pair correlation function as I described, Brownian motion I described, Protein folding Lavinthal paradox, The monkey typing Shakespeare sonnet. So these are the things they are all essentially of probability theory**.**

So to summarize this part of the probability theory is that it is something essential and you have to know. You never know when you will need but you better develop a good understanding of the correlations and sample space and the probability that would really stand you in good, when you are doing these things. No, basic idea is to following you have a random variable x.

Let’s say position and you now do an experiment to find out what is the position, now you have to do more. So whenever you think of random variables you have to think what is the outcome? What are the values it can have, that define the sample space. Now first I do the experiments to find all the sample space. Now if I do an experiment I get a value say 10, now I am repeating the experiment.

If it is not correlated next value can be anywhere in the sample space. However, if they are correlated then it will be a constraint on that, it will be near about that 10, something like that. Now this is anything else, any other question? Yes, sure, it is a very good question. See this is just a very well defined discrete experiment our outcome is discrete, we are tossing we are doing a dice and that is the reason of cusp like thing.

But if your outcome is a continuous, within again a sample space then you have no problem then you have your smooth thing that you are looking for. That is what is important even when you do computer simulations, you know we always tell students to look at individual values what is your outcome and have a many times one or two results go out of bounds, then something is wrong and ultimately many times the program becomes unstable.

So an idea of, for example in a many body simulation energy has to be conserved. What do you mean energy has to be conserved? It is fluctuating of course, but it has to fluctuate within a given bound volume if you do NPT simulation then volume is fluctuating. So, but you need to know when it fluctuates too much we discard it, because then we say, my sample space is not what it should be.

So, instead of blindly going and using a computer program is very important to realize, what is going on inside the, not inside the program but in the problem what are the kind of things. Because like one of my students now simulating the old problem I did long time ago the diffusion you know 30 years ago diffusion in a triangular potential, which is a very interesting trapping incident.

And once, one professor from Cambridge was an African actually came to me and was very excited about that work, he heard of that work and how do I mean Bangalore he wanted to do a study of chaos. And I was least interested, you know in my young age I do what I want to do. I just not interested anybody coming and telling me that let us do this problem. I would not take that, I should have done that.

But that problem now my student is doing. I told him just to simulate it and find out so what happened there is a trapping, it is not trapping in local in within region it is trapping in a trajectory space. So then it goes like this in a along a line then after some time it goes off, it becomes diffusive in a very long time. So how it goes from one trap trajectory to another trap trajectory and how the diffusion sets seem?

When you publish that, we did some work but we did not have this kind of computer power, so we could do only up to for example elementary steps of 1 million or so, to do this you

need to run it many billions, so I am asking I tell this student look into it carefully as a problem of mechanics. Now will, anything else?
If you do just the binary coin then 1/N comes in and so basic idea, of course one gets from other than Centre Limit Theorem the you want a physical insight 1 over root N, is that what you question? So one of the thing is that you know the statistical mechanics that when we get delta E square and we divide delta E square by N, and a system is stable if it goes is N going to infinity the relative fluctuation has to go to 0.

So we get root over N by N of you know and over 1 by root N that goes to 0 and that saves our day and we become with that. Now what precisely 1 over root over N comes from? In the tossing of coin that I believe comes from our application of Stalling's theorem. But physical inside of that I have to think about it. It is a very good question probably I knew, but now I do not remember it.

Why it is $1/\sqrt{N}$ why not 1/N to the one third. Yeah, that is different, that is very different thing that is when you have instability or you have things going out of bound. Yeah, you get always 1 over root over N, Central Limit Theorem gives you 1 over root over N and many of the times we are happy with the Central Limit Theorem giving 1 over root N.

Is there anything deeper into that, that means why 1 over root N why not a little different? Probably there is a very simple explanation of that, but I have to think about it and I will get back to you about that. Right now, I am more into probably getting into the next phase.