Advanced Thermodynamics and Molecular Simulations
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Lecture - 11
Binomial Distribution Approaches Gaussian distribution for large N; Definition of Drunkard Walk

Hello, all of you. So in the last lecture, we have been discussing the Stirling approximation for large numbers and we particularly discussed how can we go from a discrete distribution to a continuous distribution.

$$\ln N! \approx N \ln N - N$$

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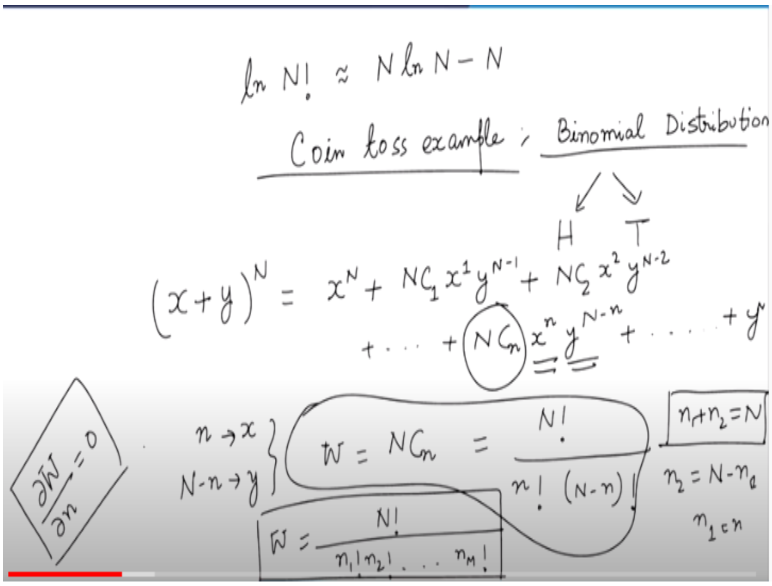

And today we will see like how does it apply for example, for the case of a binomial distribution, again going back to the coin toss example and then I will do very interesting theory in the statistical mechanics called the drunkard walk.

So let us first go back to the coin toss example. We have already done it several times in this course, but the point now is to mathematically derive the notion of central limit theorem that we already have discussed earlier that the fluctuations decay as the number of molecules increases. So mathematically speaking, the coin toss example, is an example of a binomial distribution and the reason why it is called a binomial is because there are two possible outcomes in every experiment, it is head or tail. If it were like multiple outcomes, let us say three or four, we call it a multinomial distribution in general and the other reason why it is called a binomial distribution is, if I am interested in finding how many heads will I have in N experiments, one way is to use this particular expression-

$$(x+y)^N = x^N + NC_1 x^1 y^{N-1} + NC_2 x^2 y^{N-1} + \cdots \ldots .. + \cdots \ldots .. + N\,C_n x^n y^{N-n} + \cdots \ldots . + \cdots \ldots + y$$

So essentially, if I want to find the number of ways in which you have 'n' times you get the output x automatically '(N – n)' times you get the output y. So the number of ways of doing that is given by the coefficient of the N^{th} term here, because in here x is coming small n power and y is coming N - n power.

The other way of saying that is we are multiplying x small n times and we are multiplying y capital N minus small n times and therefore, the number of ways of doing that is $N\,C_n$ which is same as the formula that we have obtained earlier but written slightly differently i.e. –

$$W = NC_n = \frac{N!}{(n! - (N-n)!)}$$

So in general, if I have to find the ways of dividing capital N things into n_1 things of particular type, n_2 things of another type, and so on this is the number of ways. For a binomial distribution since $n_1 + n_2 = N$, we can replace the n_2 with $N - n_1$. And in this case, I am using $n_1 = n$. so therefore-

$$W = \frac{N!}{n_1!\,n_2! \ldots \ldots .. n_M!}$$

So now if I am interested in finding what the most probable fraction of heads is or what is the most probable number of heads, essentially the problem is to maximize this number of ways. So the value that will give me the maximum of W will give me the maximum of the number of heads and if I say small n is the number of heads, then we want to find the value of n for which the partial derivative of W with respect to n is equal to zero, which is the condition of extremum. Now this can be a maxima or a minima. For a maxima, we also go for the second derivative typically, but in this case it turns out that the extremum is always a maxima. So let us try to do that.

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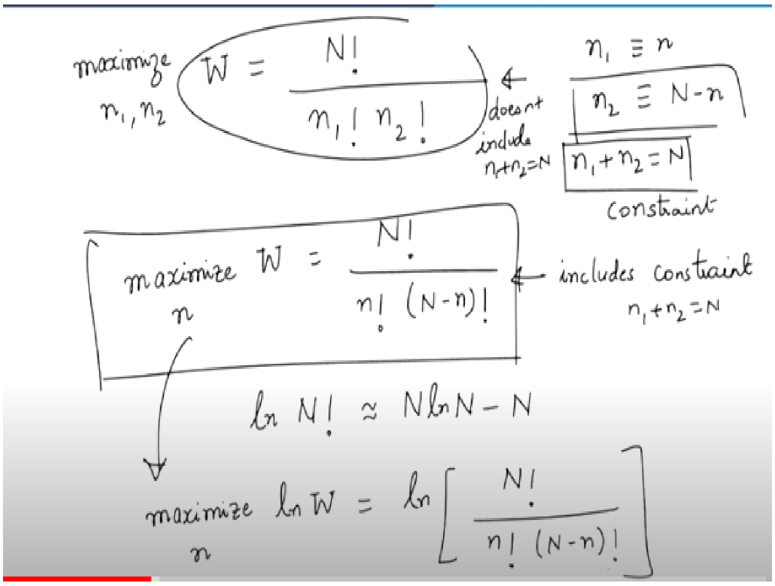

So I want to maximize W that is-

$$W = \frac{N!}{n_1!\,n_2!}$$

Here,

$$n_1 \equiv N$$

$$n_2 \equiv N - n$$

And essentially, the problem is to find the value of n_1 and n_2 for which W is being maximized, right. However, it is very important to note that n_1 and n_2 are not quite independent of each other. Essentially, you have a constraint that $n_1 + n_2 = N$. In the next class, we will see how can we include the effect of constraint in the maximization problem by use of something called Lagrange multipliers but in today's lecture, we will incorporate the constraint in the definition of W itself and the way we will do it is simply eliminate n_2 from the expression by using the definition that I just used but keep in mind that the maximization problem has to include the effect of constraint. And the way we are doing it is by eliminating the variable n_2 using the equation N - n.

So if I now write this, then the problem can be written as maximize for the value of n-

$$maximise\ n = W = \frac{N!}{n!\,(N-n)!}$$

So the one way to look at it is let us say for example, if I maximize the first function, that is the function that is right here-

$$W = \frac{N!}{n_1!\,n_2!}$$

Then if I maximize it, I will get some value of n_1 and n_2 for which W is maximum. Now that particular value may or may not satisfy that constraint and if it does not satisfy the constraint, then even though W is being maximized for the particular value of n_1 and n_2 those values are not correct, because $n_1 + n_2$ must be equal to N that is a constraint that is given in the problem, right.

So whenever we are doing maximization, we need to have a way to include the constraint. When I write the problem in the way like this-

$$maximise\ n = W = \frac{N!}{n!\,(N-n)!}$$

in that case, we have included the effect of constraint by eliminating the variable n_2 and we eliminated using the constraint.

In the next class we will see a better way or a more systematic way of doing it is the use of something called Lagrange multipliers but let us stick with this for the moment. So then, we discussed in the last class that n factorial become very large for large value of n and it is better to use Stirling approximation, if I want to approximate the value of n factorial, right. And the approximate approximation is-

$$\ln N! \approx N \ln N - N$$

And then instead of maximizing W, we can maximize the-

$$\ln W = \ln\left[\frac{N!}{n!\,(N-n)!}\right]$$

So let us try to maximize this.

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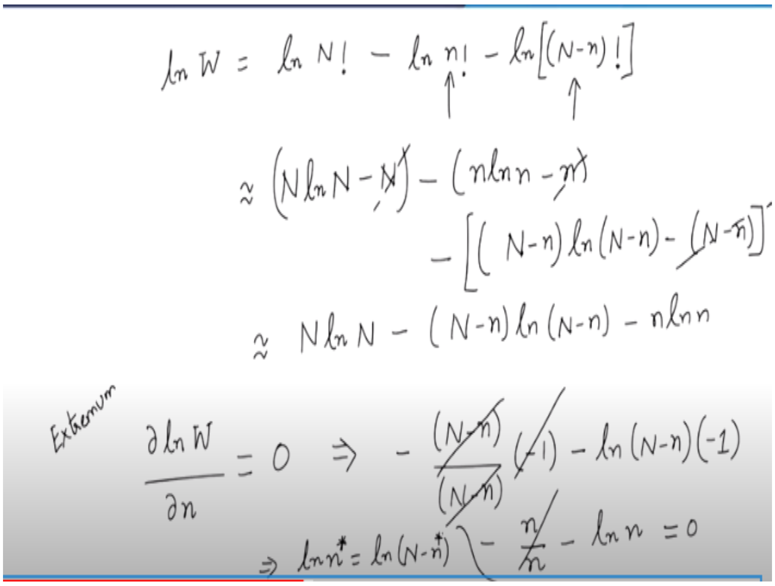

So essentially, this is equal to-

$$\ln W = \ln N! - \ln n! - \ln[(N-n)!]$$

So now if I use the Stirling approximation, I am also assuming that Stirling approximation applies to this and this as well right. So clearly capital N can be large, but the small n and (N – n) need not be large, right and the reason is like for every large value of capital N you always start the count from small n equal to 1 but the point is that the number of ways for small values of small n are anyway going to be small, because of the logic we made earlier that the system will go towards the most probable distribution and for large value of capital N this will be very narrow distribution, right. So even though small n equal to 1 that is having one head in large number of experiments is possible the probability of that to happen is very small. So therefore, we are looking at the value of small n in the vicinity of the most probable distribution, where the probability is high and for those values, we may assume that a small n is also large and N - n is also large that is a very important point and we will see that happening when we look at the distribution. So now I can approximate this as-

$$\ln W \approx (N\ln N - N) - (n\ln n - n) - [(N-n)\ln(N-n) - (N-n)]$$

Now you can see there is some cancellation here so ln W is therefore, approximated as-

$$\ln W \approx N\ln N - (N-n)\ln(N-n) - n\ln n$$

And therefore, the problem of maxima can be solved by the formula for the extremum-

$$\frac{\partial \ln W}{\partial n} = 0 = -\frac{N-n}{N-n}(-1) - \ln(N-n)(-1)$$

So again we have certain cancellations. So we have 1, 1 that gets cancelled. And therefore, what you have is-

$$\ln n = \ln(N - n) - \frac{n}{n} - \ln n = 0$$

That is the condition of extremum.

Let me call that value where this happen as n*.

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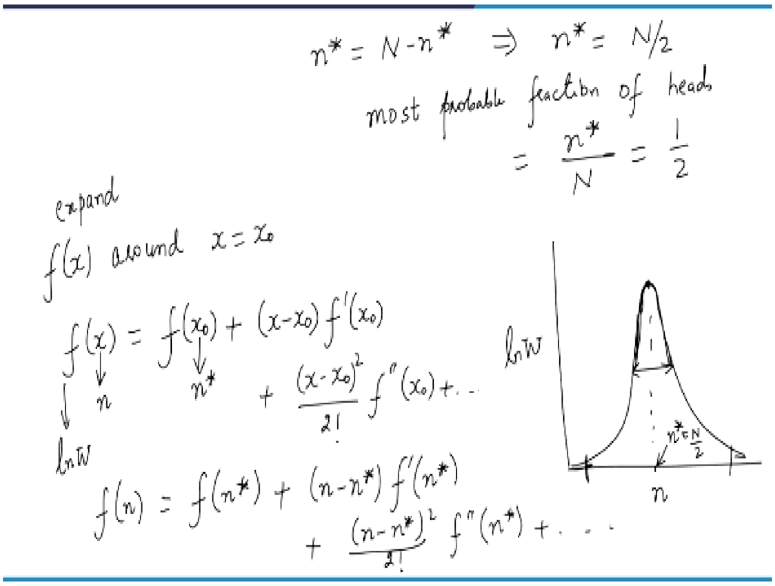

So therefore, we can say that my n* is equal to N – n* which gives me n* is equal to capital N by 2, which is the most probable number of heads that we can possibly have. So if I want to find the most probable fraction of heads, it is clearly going to be the number of heads by the number of tosses that is equal to 1 by 2, something that we have already obtained earlier.

So now that gives me what is the most probable number, but it is not still giving me the distribution of the probability or the number of ways as a function of n. So what we are interested in is how this ln W is changing with n. We know that it is maximum for n* is equal to N by 2 but we do not yet know the shape of the curve or what is the width of this particular distribution and more importantly, what is the form of this distribution, right. So for doing that, what we can do is we can use the idea of Taylor series, right. So what Taylor series say is that if I want to expand a function around some value of x that is equal to x_0, then that expansion is given by-

$$f(x)\ around\ x = x_0$$

$$f(x) = f(x_0) + (x - x_0) f'(x_0) + \frac{(x - x_0)^2}{2!} f''(x_0) \ldots \ldots \ldots$$

So now in this case, my x is the n value that we have, and my x_0 is the n*. So I want to do expansion of ln W. So my f is ln W around the most probable distribution, because only near to this is the part where probability is high. So let us focus on near that distribution, because anyway, for large value of n, we have seen that the probability for smaller or very large value of n is going to be small the distribution will be narrowed around the n* or the most probable fraction of heads or the most probable number of heads. So if I do that, so then I can write-

$$f(n) = f(n^*) + (n - n^*)f'(n^*) + \frac{(n - n^*)^2}{2!} f''(n^*) + \cdots \ldots ..$$

Now let us find this expansion, these terms in the expansion.

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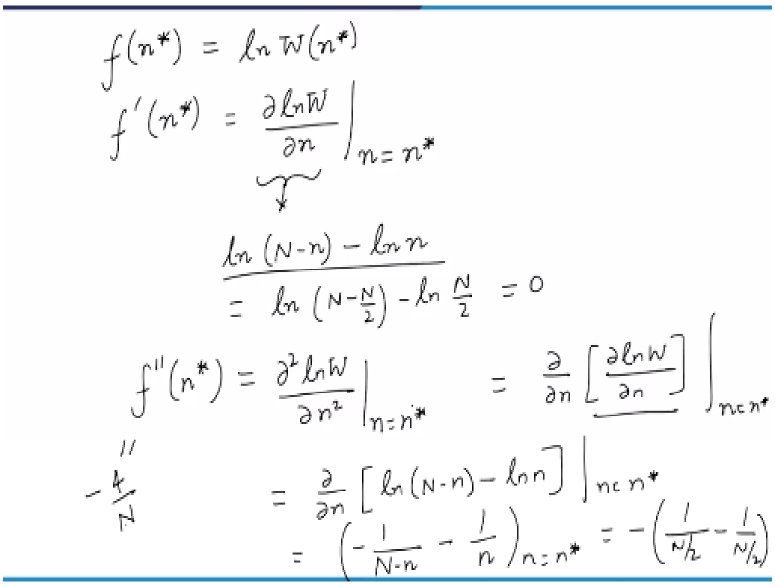

So clearly,-

$$f(n^*) = \ln W(n^*)$$

$$f'(n^*) = \frac{\partial \ln W}{\partial n}\bigg]_{n=n^*}$$

As we know from earlier derivation-

$$\frac{\partial \ln W}{\partial n} = \ln(N - n) - \ln n$$

$$= \ln\left(N - \frac{N}{2}\right) - \ln\frac{N}{2} = 0$$

which can be surprising because this is the condition we used to find the extremum in the first place.

So the second derivative is then given as-

$$f''(n^*) = \frac{\partial^2 \ln W}{\partial n^2}\bigg]_{n=n^*} = \frac{\partial}{\partial N}\left|\frac{\partial lnW}{\partial n}\right]_{n=n^*} = \frac{\partial}{\partial n}[\ln(N-n) - \ln n]_{n=n^*}$$

$$= \left(-\frac{1}{N.n} - \frac{1}{n}\right)_{n=n^*} = -\left(\frac{1}{\frac{N}{2}} - \frac{1}{\frac{N}{2}}\right) = -\frac{4''}{N}$$

So if I now put this expression back in what I have written earlier, that is right here the first term is going to be zero, but the second term we are going to replace with -4 by N, i.e.-

$$f(n) = f(n^*) - \frac{(n-n^*)^2}{2} x \left(\frac{4}{N}\right)$$

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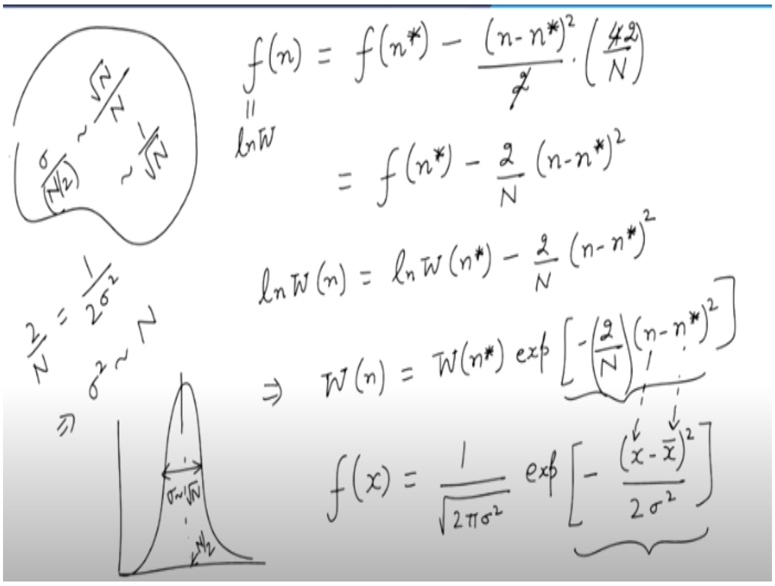

So we have this and this gives me-

$$= f(n^*) - \frac{2}{N}(n-n^*)^2$$

so this I can now put f is equal to ln W. So what we have is-

$$\ln W(n) = \ln W(n^*) - \frac{2}{N}(n-n^*)^2$$

And therefore, we can write W of n as-

$$W(n) = W(n^*) \exp[-\frac{2}{N}(n-n^*)^2$$

Now this turns out to be similar in form as what is known as the Gaussian distribution, right. So the Gaussian distribution is defined as the following-

$$f(x) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp[-\frac{(x-\bar{x})^2}{2\sigma^2}$$

So if I compare now n is analogous to my x, n* is the mean value of my number of heads, that is equal to n* that is where the, we have most probable number of heads and then we are left with 2 by N that is equal to 1 by 2 σ^2 and that tells me that my σ^2 goes like N, right that is the key point that I want to make from here that my σ^2 goes like N and the σ is the standard deviation or the width of the Gaussian distribution, right.

So essentially what I now know is that we have a maxima at N by 2 and the width of the distribution is characterized by σ that is going like square root of N. So now if I look at the fraction of heads, or if I look at the ratio between the standard deviation or the width with the mean value, what I will have is σ by N by 2, which is going like square root of N divided by N. And that is going like 1 over square root of N. So therefore, going back to our earlier statement, when we said that the fluctuation decreases with n, that is indeed true except that now we know the functional form that the width is decaying with 1 over square root of N. So as we increase capital N, as we increase the number of tosses, we are having a narrowing of distribution, right.

And the way to look at it is to look at the ratio of standard deviation to the mean because ultimately we are interested in the fraction of head not the number of heads clearly as we increase the large N number of tosses, we will have more heads but what is more important that characterizes the width of distribution or narrowness of distribution that is the width divided by the mean value or the standard deviation divided by the mean value and that is going like 1 over square root of N. And so as we increase n, we are going to a narrower and narrower distribution in the limit when N goes to infinity, we will have basically a delta function.

That is true for a binomial distribution that is what we have showed here, that binomial distribution is approaching a Gaussian distribution for large N and why we say that, because we have already made use of the Stirling approximation that is only valid for large N value but the result itself is true for any distribution, even a multinomial distribution, we will not derive it but take it for granted that if I take any stochastic distribution, and if I take the limit of large N, it always gives me the fact that fluctuation is decaying with 1 over square root of the number of experiments that you conduct or in our case of thermodynamics, the number of molecules we have and so on.

So this particular idea can be applied in many different contexts. One of the examples that I will now do is the example of a drunkard walk. I will introduce the problem in today's lecture and then in the next lecture, we will actually show that significance of that particular problem and how to get the mathematical results of that.

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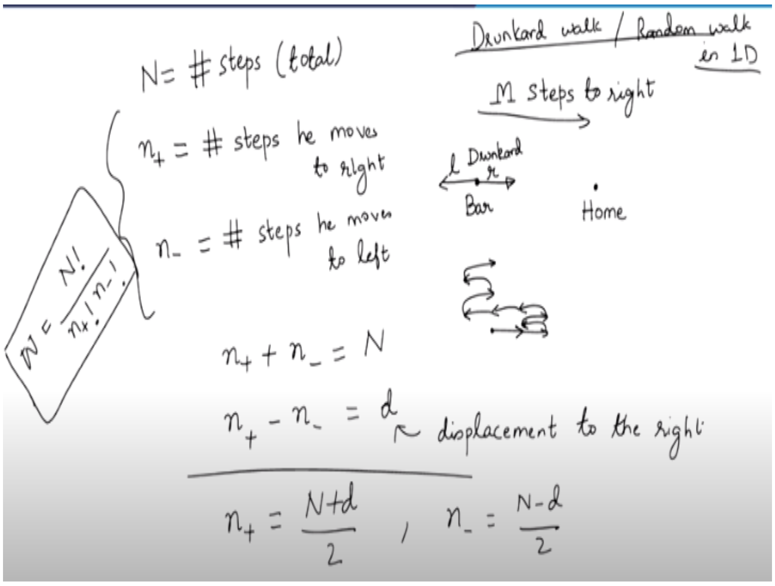

So the problem goes like this. Let us say for example, you think of a drunkard who is heavily drunk once he leaves the bar and he is so much drunk that he has completely forgotten all his senses and he does not know where his home is, whether it is the left or to the right. So what he is doing then is that at every given time or within every small time interval delta t, he is making a step either to the left or to the right, with equal probability. So at any given time, he can move to the right or move to the left, right and this he is doing for every small time interval or every step that he is making.

So for example, he may start from the bar. First step he makes to the right. Second, he makes to the right. The third, he comes back to the left. Fourth, he comes back to the right. Fifth, again to the left. Sixth, again to the left. Seventh, again to the left. Eight, again to right. Nine, again to left. Ten, again to right and this keeps on happening just like a coin toss problem every two steps are completely uncorrelated. It does not matter whether he has moved to the right in the previous step that will not determine the direction he will move but if he is making in total a large number of steps, then it is most probable to have the probability that half of them will be to the right and half will be to the left, because every step is made with a probability of half to the right and half to the left.

And now the question is like, let us say, for example, his home is located here. That can be for example some m steps to the right. The question is that, can he get to his home? Now if you think about this problem, since he is moving with right and left with equal probability, on an average his displacement for the bar is going to be zero. So if I look at the average distance he travels over a large number of steps, that should be equal to zero because he can go to the right or to the left with equal probability. Let us say if he makes 500 steps to the right, he would have made roughly 500 steps to the left as well and as the number of steps increases, this becomes closer and closer he will move towards a most probable distribution, will have a narrowing of distribution.

However, that does not dictate whether he can get home or not, because if he makes 500 steps, it is quite likely that at one of the points during the 500 steps, he was 10 or 20 steps to the right. So even though the average says that he will remain at the bar, in reality we have to look at the trajectory of this drunkard walker that is called a drunkard walk or a random walk in one dimension.

So what is important here is that we are assuming that he can only move to the right and left. So maybe his home is on the same road where the bar is located, just for simplification of the problem what we will see later is that it does not matter even for a two dimension or a three dimension, the results are quite similar.

So now for this particular problem, what we can notice is again we have a binomial distribution, because there are only two outcomes for every step that he is taking. He can either move to the left or to the right. So let us say for example, n+ is the number of steps he moves to right and n- is the number of steps he moves to left. And let us say capital N is the number of steps, the total value of that. So clearly the sum of n+ and n- is equal to capital N. And the net displacement from the bar is n+ - n-. This is like how much to the right he is located from the bar.

$$n_+ + n_N = N \ (total\ distance)$$

$$n_+ - n_- = d \ (total\ displacement)$$

If it is a negative number, then he is towards the left and let us say this is my d that is the displacement to the right. So we can easily solve these two equations. And what we obtain is-

$$n_+ = \frac{(N+d)}{2}$$

$$n_- = \frac{N-d}{2}$$

And this particular choice of n+ and n- can be done in certain number of ways. In the same way we have found for heads that is-

$$W = \frac{N!}{n_+!\,n_-!}$$

So in the next lecture, we will see how starting from this particular value of W, we can again get a Gaussian distribution because this is again a binomial distribution, and then I will relate it to the idea of diffusion, because what I want to say is that this random walks are very similar to how molecules move inside any room or anywhere in the system in a thermodynamic system.

So with that I stop here.

Thank you.