Advanced Thermodynamics and Molecular Simulations
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Lecture - 12
Solution of Drunkard Walk; Lagrange Multipliers

Hello, all of you. So in the last lecture, we have discussed how a binomial distribution approaches a Gaussian distribution. We first did the coin toss example, and basically reestablished the central limit theorem and then towards the end of it, I introduced the problem of a drunkard walk. So today we will complete the drunkard's walk example and then I will also introduce the idea of Lagrange multipliers that is as I said, is a more systematic way of including constraints in the minimization or maximization. So just to quickly recap the drunkard walk problem.

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$$n_+ \rightarrow \text{right}, \quad n_- \rightarrow \text{left}$$

$$d = n_+ - n_-$$

$$n_+ = \frac{N+d}{2}, \quad n_- = \frac{N-d}{2}$$

$$W = \frac{N!}{n_+!\, n_-!} = \frac{N!}{\left(\frac{N+d}{2}\right)!\left(\frac{N-d}{2}\right)!}$$

So a drunkard starts from bar and he is fully unconscious. So he is totally forgotten where his home is. So he is making steps to the right or to the left randomly, but with equal probability to the right and left. So let us say he moves to the right in the first step, then he can come back to the left, again to the right, again to the right he can come back and there are a large number of possible ways in which this can happen and then I said, let us say if he makes N steps in total, and out of this n+ are to the right, and n- are to the left. Then the net displacement after

N steps is n+ - n- and therefore, if his home is say d steps to the right, he can get there in n steps for this particular value of n+ and n-.

And so the idea is that even though the average displacement may appear to be zero because the going to the right and left are having the same probability, he is undergoing a displacement in certain number of steps and therefore, he is likely to get to his home.

So now we are interested in getting the most probable distribution for this case and then to find what is the probability that he can get to his home more specifically, we want to find the width of the distribution in this case that will characterize how much he is able to move from his position from the bar. So W was equal to-

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

And we have found-

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

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

And therefore-

$$W = \frac{N!}{\left(\frac{N+d}{2}\right)!\left(\frac{N-d}{2}\right)!}$$

And the objective for us is to maximize ln of W by using the Stirling approximation that we already have stated because capital N is very large.

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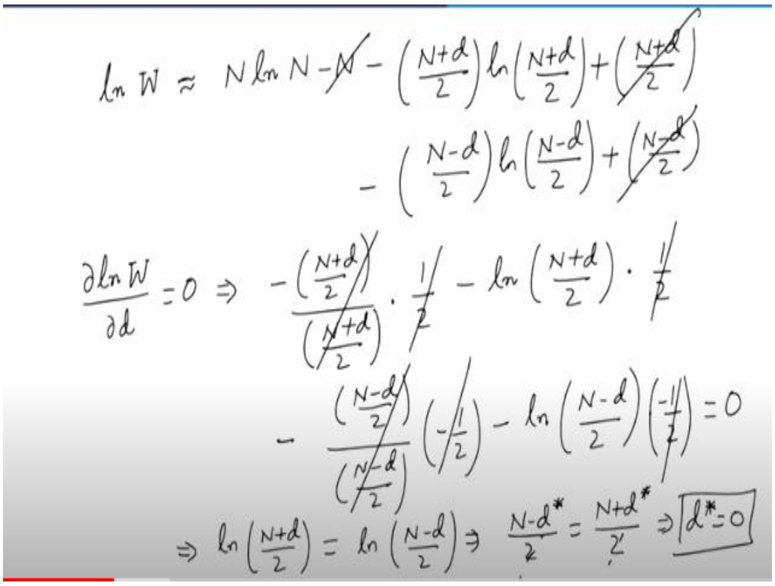
Thus,



So essentially what we have is ln of the W can be approximated as-

$$\ln W \approx N \ln N - N - \frac{N+d}{2} \ln \frac{N+d}{2} - \left(\frac{N+d}{2}\right) - \left(\frac{N-d}{2}\right) \ln \left(\frac{N-d}{2}\right) - \left(\frac{N-d}{2}\right)$$

So therefore-

$$\frac{\partial lnW}{\partial d} = 0$$

When I want to minimize this we are ultimately interested in d. I want to maximize this in this case extremum. So now this equals to-

$$\frac{-\frac{N+d}{2}}{\frac{N+d}{2}} . \left(\frac{1}{2}\right) - \ln\left(\frac{N+d}{2}\right) . \left(\frac{1}{2}\right) - \frac{-\left(\frac{N-d}{2}\right)}{\left(\frac{N-d}{2}\right)} . \left(-\frac{1}{2}\right) - \ln\left(\frac{N-d}{2}\right)\left(-\frac{1}{2}\right) = 0$$

Again there are certain cancellations. So what we see first is that we have a plus minus half here and a plus half here, these two cancel out and then half cancels out because it is being equated to zero. So what I essentially have is-

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

And therefore,

$$\frac{N-d^*}{2} = \frac{N+d^*}{2}$$

Thus,

$$d^* = 0$$

Which should not come as a big news, because the probability of going to the right is same as probability of going to the left. So the most probable displacement is equal to zero but just like what we did for the coin toss example, we are actually interested in the distribution of ln W around this particular point d* or this particular displacement d*. So for doing that, I again use the idea of Taylor series.

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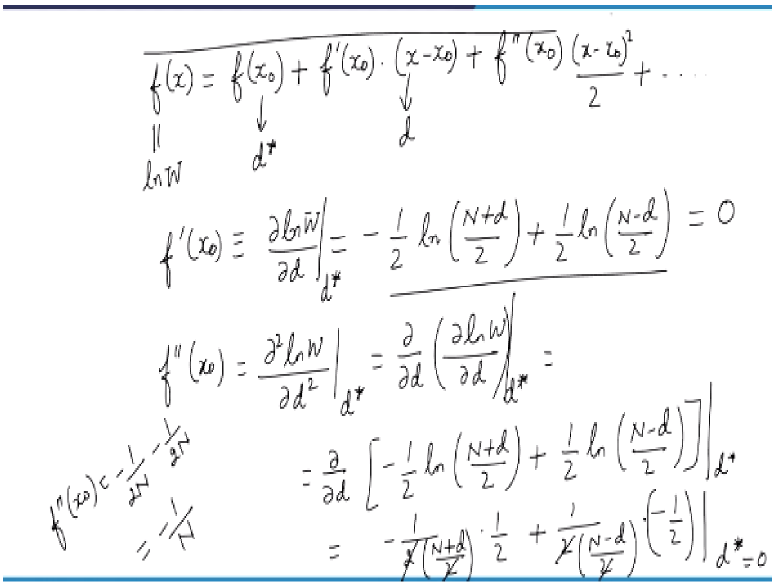

So I want to expand the function f (x) around x_0 and the way to do that is this-

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

In this case again, f is same as my ln of W and x_0 is same as my d* and x is some value d for the displacement. So then again we have f prime of x_0 that is a equivalent to-

$$f'(x_0) \equiv \frac{\partial lnW}{\partial d}\bigg]_{d^*} = -\frac{1}{2}\ln\left(\frac{N+d}{2}\right) + \frac{1}{2}\ln\left(\frac{N-d}{2}\right) = 0$$

That is what we have found in the previous example. And this is equal to zero clearly because that is the condition we used for the extremum anyway, right. So what is of more interest is to find the second derivative. So second derivative is going to be-

$$f''(x_0) = \frac{\partial^2 lnW}{\partial d^2}\bigg]_{d^*} = \frac{\partial}{\partial d}\frac{\partial lnW}{\partial d}\bigg]_{d^*} = \frac{\partial}{\partial d}\left[-\frac{1}{2}\ln\left(\frac{N+d}{2}\right) + \frac{1}{2}\ln\left(\frac{N-d}{2}\right)\right]\bigg|_{d^*}$$

$$-\frac{\frac{1}{2(N+d)}}{2}\cdot\frac{1}{2}+\frac{\frac{1}{2(N-d)}}{2}\cdot\left(-\frac{1}{2}\right)$$

And essentially, since I am evaluating around d* and d* equal to 0, you can see what do we get from here what we get is something like this-

$$f''(x_0)=-\frac{1}{2N}-\frac{1}{2N}=-\frac{1}{N}$$

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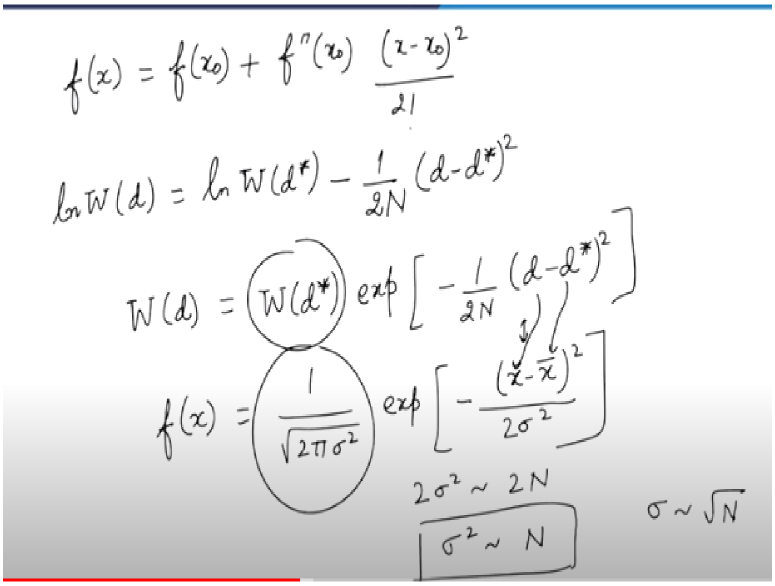

So now if I put this back in the expression that is right here, what we see is-

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

$$\ln W(d)=\ln W(d^*)-\frac{1}{2N}(d-d^*)^2$$

So this we can write as-

$$W(d)=W(d^*)\exp\left\{-\frac{1}{2N}(d-d^*)^2\right]$$

And if I again compare with the expression of the Gaussian distribution-

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

It is important to mention here that whenever we compare this I am only comparing the term inside the exponential, not the pre-factor, right and the reason for this is the following. So if you recall, if I am looking at a probability distribution function, if I integrate that over the entire range that must be equal to 1, right. So the pre-factor essentially is a normalization factor that will apply there and that factor should be such that the probability integrates to 1, right. So of course, the pre-factor need not be the same between the binomial distribution and the Gaussian distribution, or whenever I go from a discrete to a continuous distribution, the pre-factor may change, but the term inside the exponential is the one, that is what we have to compare. The pre-factor has to come from the condition that the probability is normalized or it integrates to 1.

So now if I compare this then d is analogous to x and d star is analogous to x bar. And so we have $2\sigma^2$ going like 2N. And therefore, σ^2 goes like N. It basically get the same result as we had for the coin toss example that is my standard deviation goes like square root of N that is the number of steps I am making in the earlier case it was number of tosses now it is the number of steps, right because this is also a binomial distribution just like what we had for the coin toss example.

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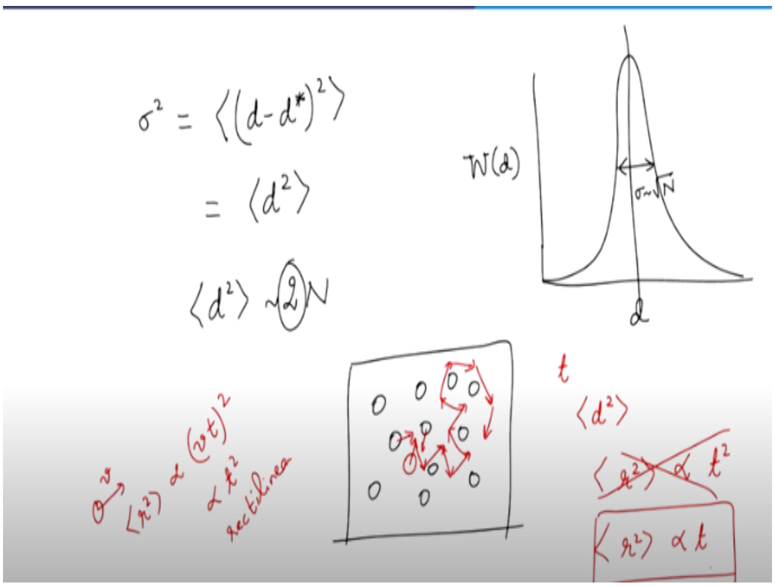

If I now look at my W (d) versus d, this is going to be a Gaussian distribution and the width of that corresponds to σ and σ is going like square root of N, right. Now we already have said that σ is also the square root of variance or σ^2 is the variance, right. And what is variance? Variance is the characterization of the deviation from the mean, right. So we can also write as-

$$\sigma^2 =< (d - d^*) >= d^2 \ and \ d^2 \sim N$$

So therefore, the square in this case goes like N because σ^2 is going like N. We have to be slightly careful here because the plus displacement and the minus displacement, the + d and -

d give the same value of d^2 and therefore, there will be a factor of 2 that will come in here, but that is beside the point. The main point is that my mean square displacement is going like the number of steps that I am making. So even though the average displacement of the drunkard walker or a random walker in one dimension is zero, the mean square displacement is quite significant and in fact, it is linear in the number of steps that the random walker is making and this has a very strong analogy with the diffusion process or the molecular movements inside a thermodynamic system or a room.

So let us say for example, if I look at molecules present in a room, the molecules are undergoing collisions with other molecules every time they undergo a collision, their direction of motion changes, because now the other particle may be coming at a different velocity at a different direction than the particle in question. So once they collide, then the original direction of the particle will change and the original velocity will change. So what may appear like is that any particle is undergoing many collisions as it is going along and that is similar to a random walk if I focus on a particular particle in the system.

So let us say for example, you have a system of molecules and I define the motion of a particular molecule here. Now as it starts moving with the velocity that is moving, this will undergo collisions from the other molecules. As soon as they collide, the direction and the velocity of the molecule changes and this keeps happening throughout time that it is moving inside that system because the collisions are so frequent and since the particles may come from any particular direction, the collisions can be in any particular direction. So for us it may appear like it is undergoing a random walk, right and this essentially is the idea of a diffusion process, whenever we talk about a diffusion process, it essentially refers to motion of molecules as a result of the collisions they experience from every other molecule. And what is special about diffusion process is that at any given time t, the mean square displacement or typically it is called r^2, it does not go like t^2, but it goes like t. And why it shouldn't go like t^2 because let us say for example, the same guy was moving and it does not undergo any collision. Then it will move with certain velocity v. So at any given time, the mean square displacement from the original position will go like v t^2 and provided the velocity is constant, this should go like t^2. That is the whole idea of rectilinear motion, when it is moving at a constant velocity.

We will come back to this example although we have done for a one dimensional case. The same result one can get also for a walk in two dimension or three dimension actually, this can be generalized to pretty much continuous space just like what molecules have they can move in any particular direction, not really in along x or along y. They can move in any particular direction in three dimensions but the basic result that we have obtained that the square displacement proportional to N is generally valid irrespective of what dimension that we are solving the problem in. So with this particular idea, I now move to the description of Lagrange multipliers.

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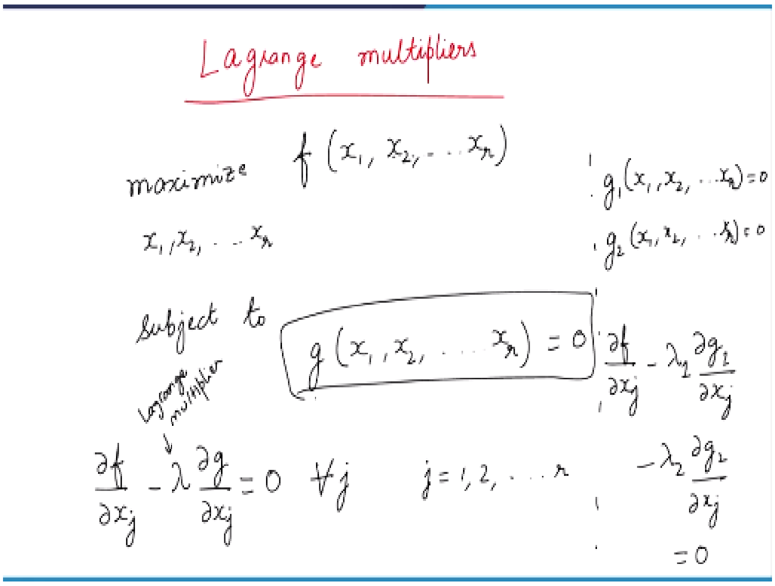

We already have introduced, why it is an important concept. It helps when we are interested in minimizations with respect to certain constraints. So let us say for example, I want to maximize or for example minimize since we already did first derivatives, whether it is a maxima or minima can only be established by looking at second derivative. So we are actually doing an extremization problem.

A function that is a function of variables x_1, x_2 to some x_r. So I want to find the values x_1, x_2, x_r that maximizes this function but this is subject to certain constraints and that is some function g of these variables that is equal to 0. So in this particular case, the maximization problem can be stated like the following. So what we do is-

$$\frac{\partial f}{\partial x_j} - \lambda \frac{\partial g}{\partial x_j} = 0$$

Here,

$$j = 1,2,3 \dots \dots \dots \dots \dots \dots . r$$

$$\lambda = lagrange\ multiplier$$

And this is for all values of j. So for all values of j the λ variable remains the same. Of course, the derivatives are going to change.

If you have more than 1 constraint, let us say we have instead of one, let us say we have two constraints, g_1 and g_2 which can be any function. The functional form is not very important here. Then we have two Lagrange multipliers i.e.-

$$g_1(x_1, x_2 \dots \dots \dots \dots \dots x_r) = 0$$

$$g_2(x_1, x_2 \dots \dots \dots \dots \dots x_r) = 0$$

Then,

$$\frac{\partial f}{\partial x_j} - \lambda_1 \frac{\partial g_1}{\partial x_j} - \lambda_2 \frac{\partial g_2}{\partial x_j} = 0$$

In fact, for every constraint I will add, I will basically add one Lagrange multiplier in the picture and the number of Lagrange multipliers are equal to the number of constraints that we have in the problem. So let us see how it works in practice.

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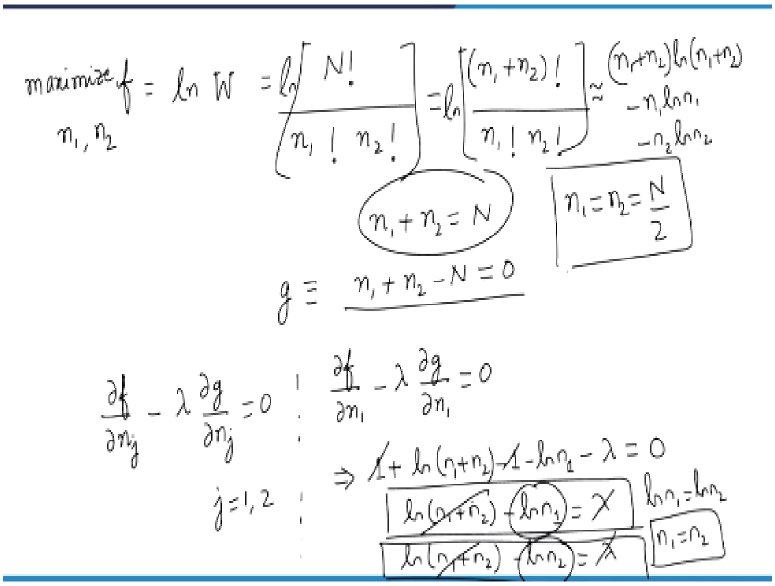

So let us say I go back to the example that we have been doing of binomial distribution so we have N tosses which can result in n1 heads or n2 tails or I am distributing N entities into two baskets and n1 and n2 or it is a random walker making N steps. Whatever is happening, the key point is that it is a binomial distribution. And we had a constraint n 1 + n 2 = N. So I can also write this as-

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

Here,

$$n_1 + n_2 = N$$

The reason why I am doing this is that now I am separating the equation from the constraint when we did the example earlier I replaced N2 with n – n 1. So I eliminated one variable because of the constraint. Now we no longer eliminate that variable, because we separately account for the constraint. This approach becomes more useful when we have more than one variable or we have a multinomial distribution but the idea is generally valid.

So then, the way we handle this is that this becomes my function f. actually we are interested in ln of that. So f can be ln of this-

$$f = \ln W = \ln\left[\frac{N!}{n_1!\,n_2!}\right] = \ln\left[\frac{(n_1 + n_2)!}{n_1!\,n_2!}\right]$$

And I want to maximize f with respect to n1 and n2, where n1 and n2 must satisfy this constraint.

Now if you recall, the constraint was written in the form that the right hand side was equal to zero, which we can do in this case as well. So I can write my g as n 1 + n 2 – N = 0.

So if I state the problem in this way, I reemphasize I am no longer using the constraint to eliminate any variable in the problem and every time we had capital N, we can replace with n1 + n2 because the fact that n1 + n2 = N is taken care of in the constraint equation that really makes it much more systematic than what we have been doing earlier.

So now the maximization problem reads-

$$\frac{\partial f}{\partial n_j} - \lambda \frac{\partial g}{\partial n_j} = 0$$

In this case j is equal to 1 and 2. So let us say if I want to do for j = 1, then we have-

$$\frac{\partial f}{\partial n_1} - \lambda \frac{\partial g}{\partial n_1} = 0$$

And this becomes we can already use the Stirling approximation. And this will be-

$$maximise\ n_1, n_2\ f = \ln W \approx (n_1 + n_2)\ln(n_1 + n_2) - n_1 \ln n_1 - n_2 \ln n_2$$

And,

$$\frac{\partial f}{\partial n_1} - \lambda \frac{\partial g}{\partial n_1} = 0$$

Therefore, it becomes-

$$1 + \ln(n_1 + n_2) - 1 - \ln^{n_1} - \lambda = 0$$

$$\ln(n_1 + n_2) - \ln n_1 = \lambda$$

And now if I do the same thing for n 2, what do we get-

$$\ln(n_1 + n_2) - \ln n_2 = \lambda$$

If I compare these two equation, or you can subtract it, what you notice is that-

$$\ln n_1 = \ln n_2$$

And we already had this particular constraint. So if n1 = n2 we can clearly see that n 1 = n 2 = N/2 because only then it will satisfy this particular constraint.

So it is the same minimization problem that we have done earlier with a small twist that we no longer eliminate any variable when we write the function we take care of the constraint separately by including a Lagrange multiplier. And you will see later that how it becomes extremely useful when we apply it to the in the context of the thermodynamic functions that we will do later.

So with that, I conclude the discussion for today's lecture. Thank you.