

Chemical Principles II
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Thermodynamic Observables: It is all in the Average

Welcome to the next lecture, as I mentioned in the beginning of molecular thermodynamics lecture is that, that this particular subject can explain macroscopic observations because of averaging. It is all in the average as it is mentioned. We will explain to you in a moment.

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It is all in the average

Thermodynamic observables such as energy, pressure, volume are averages weighted by the probability

Thermodynamics energy $U = \langle E \rangle = \sum_i E_i P_i$
 Observed pressure $p = \langle p \rangle = \sum_i p_i P_i$
 Observed volume $V = \langle V \rangle = \sum_i V_i P_i$


$P_i = e^{-\beta E_i} = e^{-E_i/k_B T}$

Compare this with quantum mechanics where expectation value of an observable is also an weighted average. For a property p

$\langle a \rangle = \int \psi^* \hat{A} \psi d\tau$ where $\psi^* \psi$ is the probability density.

In statistical thermodynamics, we calculate similar averages weighted density: $\langle E \rangle = \int P(E) E dE$.

$\int \psi^* \psi d\tau$
 \downarrow
 $P_i \cdot E_i$



The thermodynamic observables such as energy, pressure, volume are averages weighted by the probability. You know by probability what we mean is that the probability is associated with a particular type of systems. We talked about three different kinds of probabilities, one associated with the classical systems, classical particles which gives rise to Boltzmann Distribution. We also talked about Bosons and Fermions giving rise to Bose–Einstein statistics and Fermi–Dirac statistics.

So these different statistics gives us probabilities of particles occupying a certain energy levels. And once we have the probabilities, then we can use these probabilities as weights in the average calculations. For example, I mentioned to you before that if I let us say calculate the average age of (1:30) students, then all that I can do, I can do that in two different ways. I can sum up the age of all students and divide by the number of all students. Or I can associate weights to each batch of students assuming that the first year batch has all age of 18 and I know their number.

Then I can use that information to write like this that 18 is the age multiplied by the number of students, plus let us say second year students may be 19, so 19 multiplied by the number of students for the second year. And then 20 multiplied by the number of students of third year and then I will divide by the all the weights. That means number of students from each year. So this is called weighted average. And in statistical thermodynamics we do weighted averaging in order to get the average property.

For example, when I talk about the average energy, it is $E_i P_i$, P_i is the weights and E_i is the energy. Now you know that E_i is basically Boltzmann Distribution. For example, we know that P_i is $e^{-\beta E_i}$ or $e^{-E_i / k_B T}$. β is $1 / k_B T$. Now if a particular state has lower energy, then this quantity will be, if it is lower energy, it will be small. No, if it is lower energy, let us say it is more negative, lower energy means let us say E_i becomes more negative, then this quantity will be larger.

If it is higher, a positive quantity, it will be smaller. And therefore, P_i for a low energy state will be higher and therefore it will contribute more to the system, which means that when we calculate the average property, the average will be governed by the systems which are of lower energy. I will give you an example. Let us say we talk about protein folding. You know the folded state is more stable, therefore it has lower energy. And unfolded state will be less stable and therefore it will have higher energy.

Now when you calculate the average property of the system, it will be governed by the folded state. Now done folded state, however there is a catch to that, you will see that folded states, there is only one possible ways of getting a perfect folded state, which you call as native state. However there are many many other ways of getting an unfolded state. So there although each term will contribute small amount, however there will be more number of them. So and that is essentially what we are talking about as an entropy contribution.

That means there are more possibilities for unfolded state to be present. Therefore the entropy of the unfolded state will be more and there is less possibilities for the folded state to be present, so entropy will be less. However energetically folded state will be more stable than the unfolded state. And this balance will lead to a smaller difference between the folded state and unfolded state. So idea behind that is that all that we calculate, all that we observe and they are nothing but the average properties associated with the weights.

And weights here is associated with the energy of the particular system. Similarly we can talk about pressure and volume as well. And this reminds us of what we have observed in the expectation value of the property one of chemistry. So you remember in Quantum Chemistry the expectation value which is nothing but the average value of any property A is given by this particular equation, $\langle A \rangle = \int \psi^* A \psi d\tau$ if I want to be more general. And then this A is an operator but once it operates on the ψ , let us say we get some value, it need not be again value. Let us say that we get as A, so then this one immediately will give us $\psi^* \psi d\tau$. Now $\psi^* \psi$ you know as a probability density, so it is almost like our P i.

And A is something like the property which is our E i and then this corresponds to the same as the above equation. So that is why and since this one the statistical thermodynamics came before Quantum Mechanics, so remember it started from 1872 by Boltzmann. And Quantum Mechanics came around 1925. So since the statistical thermodynamics came before, this probability is used to be called the new probability. The idea behind both of them essentially is the same that we only observe what is the average value.

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Using Particle in a box

So, partition function $Q = \sum_n e^{-\beta E_n} = \sum_{n=1}^{\infty} e^{-\frac{n^2 h^2}{8mL^2}} = \left(\frac{2\pi mk_B T}{h^2}\right)^{1/2} L$
 For 3D box, $E_i = \frac{h^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2)$. Since all x, y, z are independent,


$$Q = \left(\frac{2\pi mk_B T}{h^2}\right)^{3/2} V$$

$$\langle E \rangle = \sum_i E_i p_i$$

$$= \sum_i \left(\frac{E_i e^{-\frac{E_i}{k_B T}}}{e^{-\frac{E_i}{k_B T}}} \right) = k_B T^2 \frac{\partial \ln Q}{\partial T} = k_B T^2 \frac{\partial}{\partial T} \left[\ln \left\{ \left(\frac{2\pi mk_B T}{h^2}\right)^{3/2} V \right\} \right]$$

$$= k_B T^2 \left[\frac{\partial}{\partial T} (\ln T^{3/2}) + \frac{\partial}{\partial T} (\text{terms independent of } T) \right] = k_B T^2 \times T^{-3/2} \times \frac{3}{2} T^{1/2} =$$

So, average energy of a particle in 3D box is $3/2 k_B T$. For thus $3/2 nk_B T$.



So in order to give you an example, we are going to talk about particle in a box system. So this derivation I will show you in a moment. But before that let us just do the derivations ourselves.

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$$E_n = \frac{n^2 h^2}{8mL^2}, n = 1, 2, 3, \dots, \infty$$

$$Q = \sum_i e^{-E_i/k_B T}$$

$$= \sum_{n=1}^{\infty} e^{-E_n/k_B T}$$

$$= \sum_{n=1}^{\infty} e^{-\frac{n^2 h^2}{8mL^2 k_B T}}$$

$$\sum_{n=1}^{\infty} \rightarrow \int_{n=0}^{\infty} dn$$

So let us do the average energy calculation for a particle in a box system. So average energy or energy of a particle in a box system E_n is given by $n^2 h^2 / 8mL^2$ where n is 1, 2, 3, up to infinity. And when you draw that, we are seeing that how you actually normally represent it like that. So this is n equal to 1, and equal to 2, n equal to 3 and things like that. Now the partition function of the system Q is given by as you know, e to the power minus E_i by $k_B T$. Here i denotes the energy level. Since we are denoting energy levels by n we can write that as e to the power minus E_n by $k_B T$, where n goes from 1 to infinity.

So if we specify that, it will be minus $n^2 h^2 / 8mL^2 k_B T$. Now this is a sum and that sum is a discrete sum, it goes discretely from 1, 2 and different levels. However sometimes it is helpful to convert the sum to an integration. So for example, if I am summing n equal to 1 to infinity, and when there are so many values present, we can imagine that the differences are actually smaller and then we are integrating over all possibilities.

Although we are, in that we are taking all possible values of n , we can write that as an integration of dn that goes from all the way from 0 to infinity. We are adding more values in between but we are assuming that since we are doing like infinite number of points, that is why these differences will not matter so much. So it is called discrete to continuous approximation.

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$$\sum_{n=1}^{\infty} e^{-\frac{E_n}{k_B T}} = \sum_{n=1}^{\infty} e^{-\frac{n^2 h^2}{8mL^2 k_B T}}$$

$$\sum_{n=1}^{\infty} \rightarrow \int_{n=0}^{\infty} dn$$

$$\sum_{n=1}^{\infty} e^{-\frac{n^2 h^2}{8mL^2}} \rightarrow \int_{n=0}^{\infty} e^{-\frac{n^2 h^2}{8mL^2}} dn$$

$$\sum_{n=1}^{\infty} e^{-\frac{n^2 h^2}{8mL^2 k_B T}} = \sum_{n=1}^{\infty} e^{-\frac{n^2 h^2}{8mL^2}}$$

$$\sum_{n=1}^{\infty} \rightarrow \int_{n=0}^{\infty} dn$$

$$\sum_{n=1}^{\infty} e^{-\frac{n^2 h^2}{8mL^2}} \rightarrow \int_{n=0}^{\infty} e^{-\frac{n^2 h^2}{8mL^2}} dn$$

$$\hookrightarrow \int_0^{\infty} e^{-ax^2} dx \quad (\text{Gaussian integral})$$

Similarly so then in that case we can write the sum which is there on the left hand side as equal to 1 to infinity, e to the power minus n square h square by 8 m L square as integration of e to the power minus n square h square, 8 m L square d n going from n equal to 0 to infinity. Now in that we are talking about a fixed value of L which means that this quantity which is there on the right hand side, it resembles an integration going from 0 to infinity, e to the power minus a x square d x.

This type of integration is difficult to solve at least in the 12th std. level. However one can use some formula for standard integration in order to do this type of integration. This is called Gaussian integral and there is standard value available for that.

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The whiteboard contains the following handwritten mathematical expressions:

$$\sum_{n=1}^{\infty} e^{-\frac{n^2 h^2}{8mL^2}} \rightarrow \int_0^{\infty} e^{-\frac{n^2 h^2}{8mL^2}} dn$$

$$\hookrightarrow \sum_{n=0}^{\infty} e^{-\frac{n^2 h^2}{8mL^2}} \hookrightarrow \int_0^{\infty} e^{-ax^2} dx \quad (\text{Gaussian integral})$$

$$\int_0^{\infty} e^{-ax^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{a}}$$

$$\int_0^{\infty} e^{-\frac{n^2 h^2}{8mL^2}} dn$$

For example, the standard value for 0 to infinity, e to the power minus a x square d x is half root over pi by a. For minus infinity to plus infinity it is root over pi by a and for 0 to infinity, it is half root over pi by a. So we are taking the n equal to 0 because then it helps us in doing the integration and since we taking so many integers anyway, then adding one more is now going to matter so much, because n equal to 0 is going to add 0 value to that.

So when you are doing the integration, we are summing up all values, so there we add the zeroth value, 0 value also. That is not going to change the result because we are adding a zero value. If you put n equal to 0, you are going to get 0 energy and that is now going to change the partition function at all, which means that this sum I can also write as n equal to 0 to infinity, e to the power minus n square, h square 8 m L square. Because in a sum I can always add an extra zero, meaning of course here, of course I am adding not zero, I am adding value 1, I am adding 1 value.

But that is again not going to change the sum which is there for infinite number of steps. Now once we do that, then what is our a here? Now if I compare this equation with this equation, once I compare these two, I see that.

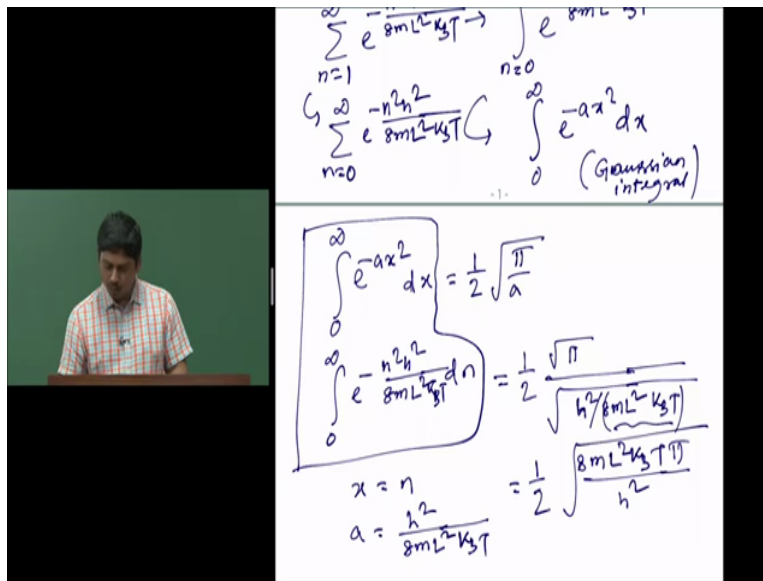
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My x is like n and my a is h square by 8 m L square. So therefore my result for this particular integration will be half root over pi by root over a which is root over of h square by 8m L square. Okay, I forgot to mention one thing. There is a k B T also down here. So here it will be k B T as well.

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So it is E square by k B T. So I will just correct that. Yes, as you can see this is there is k B T here. So there is a k B T there as well. And there is a k B T there as well. This is e by k B T, right? So I am going to write that.

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$$\sum_{n=1}^{\infty} e^{-\frac{n^2 h^2}{8mL^2 k_B T}} \rightarrow \int_{-\infty}^{\infty} e^{-ax^2} dx$$

$$\int_0^{\infty} e^{-ax^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{a}}$$

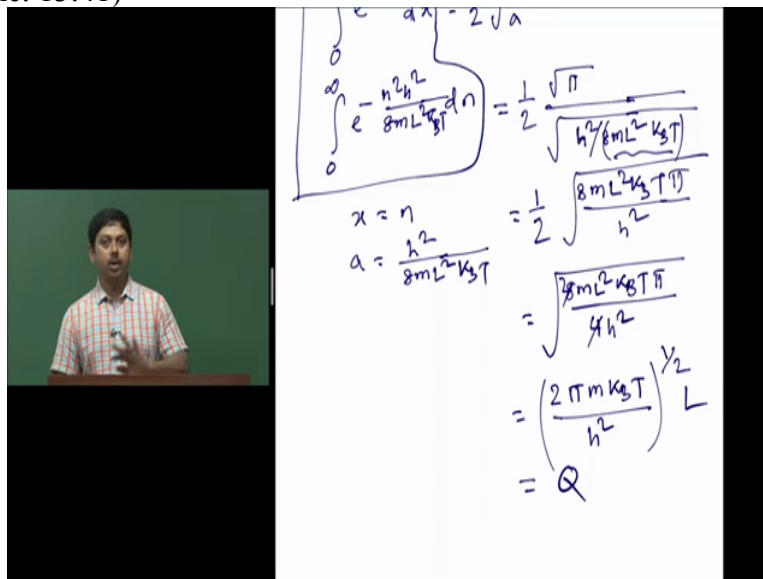
$$\int_0^{\infty} e^{-\frac{n^2 h^2}{8mL^2 k_B T}} dn = \frac{1}{2} \frac{\sqrt{\pi}}{\sqrt{\frac{h^2}{8mL^2 k_B T}}}$$

$$x = n \quad a = \frac{h^2}{8mL^2 k_B T}$$

$$= \frac{1}{2} \sqrt{\frac{8mL^2 k_B T \pi}{h^2}}$$

So in that case our this thing has $k_B T$ here as well. And that is what we get. Now which means that I get half, this term will go in the numerator, it will become $8mL^2 k_B T$ by π , no π will be under numerator itself. It will be h^2 square. Anything else I am missing? $8mL^2 k_B T \pi$ and the whole root will come.

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$$\int_0^{\infty} e^{-\frac{n^2 h^2}{8mL^2 k_B T}} dn = \frac{1}{2} \frac{\sqrt{\pi}}{\sqrt{\frac{h^2}{8mL^2 k_B T}}}$$

$$x = n \quad a = \frac{h^2}{8mL^2 k_B T}$$

$$= \frac{1}{2} \sqrt{\frac{8mL^2 k_B T \pi}{h^2}}$$

$$= \frac{\sqrt{8mL^2 k_B T \pi}}{2h^2}$$

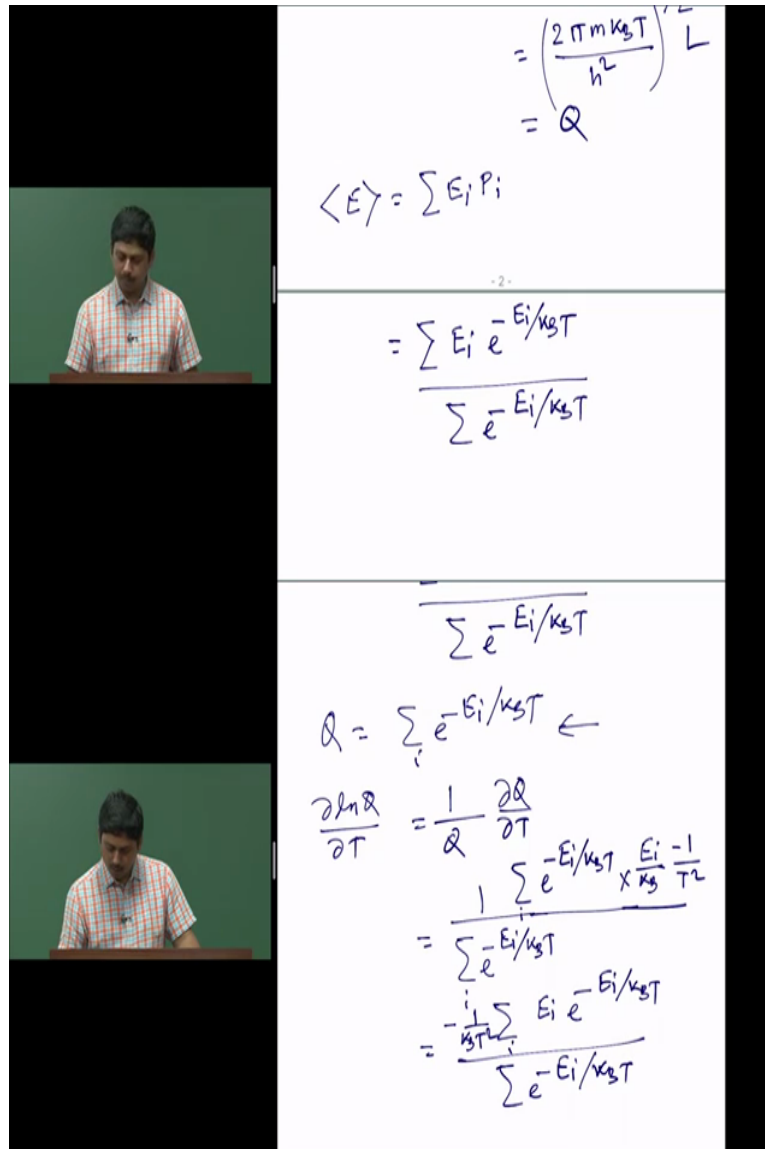
$$= \left(\frac{2\pi m k_B T}{h^2} \right)^{1/2} L$$

$$= Q$$

Now put the 2 inside, what I am going to get is $8mL^2 k_B T \pi$ by $4h^2$. I put 2 inside and it gives me 2, so I get $2\pi m k_B T$ by h^2 square to the power half into L . So that is the partition function that I got for particle in a 1-dimensional box. And you know what partition function is, it is just the sum of the exponential of the energy values. So this partition function I got as Q and now we have to see that how you are going to get the average energy. In order to calculate the average energy, we have to write as $E_i \pi$ and $E_i \pi$

is nothing but E_i to the power minus E_i by $k_B T$ divided by sum over e to the power minus E_i by $k_B T$.

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$$= \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} L^3$$

$$= Q$$

$$\langle E \rangle = \sum E_i P_i$$

$$= \frac{\sum E_i e^{-E_i/k_B T}}{\sum e^{-E_i/k_B T}}$$

$$Q = \sum_i e^{-E_i/k_B T}$$

$$\frac{\partial \ln Q}{\partial T} = \frac{1}{Q} \frac{\partial Q}{\partial T}$$

$$= \frac{1}{\sum_i e^{-E_i/k_B T}} \sum_i e^{-E_i/k_B T} \times \frac{E_i}{k_B T^2}$$

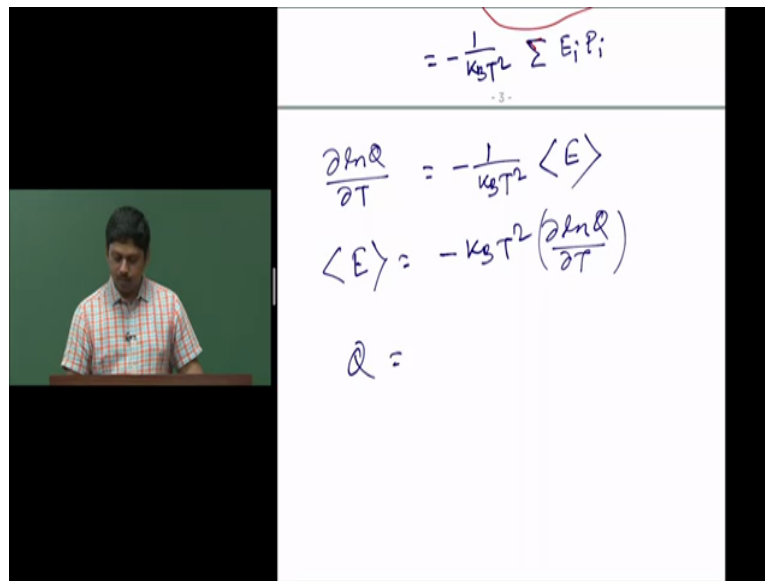
$$= \frac{\sum_i E_i e^{-E_i/k_B T}}{\sum_i e^{-E_i/k_B T}}$$

$$\begin{aligned}
 \frac{\partial \ln Q}{\partial T} &= \frac{1}{Q} \frac{\partial Q}{\partial T} \\
 &= \frac{1}{\sum_i e^{-E_i/k_B T}} \sum_i \left(-\frac{E_i}{k_B T^2} \right) e^{-E_i/k_B T} \\
 &= -\frac{1}{k_B T^2} \frac{\sum_i E_i e^{-E_i/k_B T}}{\sum_i e^{-E_i/k_B T}} \\
 &= -\frac{1}{k_B T^2} \sum_i E_i P_i
 \end{aligned}$$

So in order to obtain this particular relation, we need to use a trick. I will tell you what track is. So if my Q is this, then if I take $\partial \ln Q$ by ∂T , what I am going to get? Let us see, if I do that, then I am going to get $\partial \ln Q$ by ∂T is $1/Q$ ∂Q by ∂T . So Q is this one, so I am going to get $1/Q$ into ∂Q by ∂T . Now let us differentiate this quantity and if I do that, I am going to get e to the power minus E_i and there is a sum there. Sum over i e to the power minus E_i by $k_B T$ and then I have to take the differentiation of E_i by $k_B T$ with respect to T , so I will get E_i by k_B and then $-1/T^2$ is there, so I will get $-1/T^2$.

So let us simplify that, I get E_i , e to the power minus E_i by $k_B T$. Outside I will get $-1/k_B T^2$ divided by e to the power minus E_i by $k_B T$. So once that happens, so what I am doing now, $\partial \ln Q$ by ∂T , so $-1/k_B T^2$. On the right hand this particular quantity, this quantity will resemble as you can see exactly $\sum E_i P_i$, which means my $\partial \ln Q$ by ∂T is nothing but $-1/k_B T^2$ and average energy.

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$$= -\frac{1}{k_B T^2} \sum E_i P_i$$

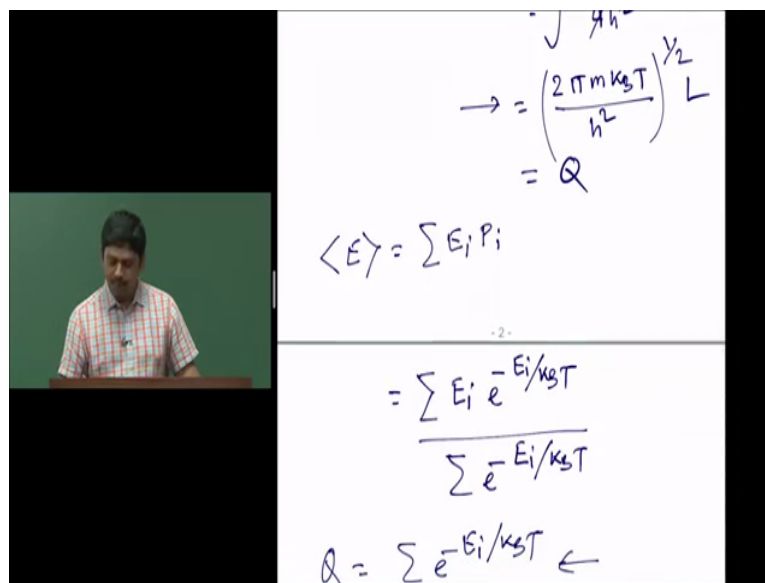
$$\frac{\partial \ln Q}{\partial T} = -\frac{1}{k_B T^2} \langle E \rangle$$

$$\langle E \rangle = -k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)$$

$$Q =$$

So average energy therefore is minus $k_B T^2$ del ln Q by del T. Why I do that? Because I have my Q already written. What was the Q? I will show you.

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$$\rightarrow = \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} L$$

$$= Q$$

$$\langle E \rangle = \sum E_i P_i$$

$$= \frac{\sum E_i e^{-E_i/k_B T}}{\sum e^{-E_i/k_B T}}$$

$$Q = \sum e^{-E_i/k_B T} \leftarrow$$

My Q is this quantity. This is my Q, $2\pi m k_B T$ by h^2 to the power half into L.

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The slide contains two panels of handwritten equations. The top panel shows the derivation of the average energy $\langle E \rangle$ from the partition function Q . The bottom panel shows the same derivation with more detailed steps, including the differentiation of Q with respect to T .

Top panel equations:

$$\frac{\partial \ln Q}{\partial T} = -\frac{1}{k_B T^2} \langle E \rangle$$

$$\langle E \rangle = -k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)$$

$$Q = \left(\frac{2\pi m k_B T}{h^2} \right)^{1/2} L$$

$$\langle E \rangle = (-k_B T^2) \times \frac{1}{Q} \times \left(\frac{2\pi m k_B}{h^2} \right)^{1/2} L \frac{1}{2} T^{-1/2}$$

Bottom panel equations:

$$\langle E \rangle = -k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)$$

$$Q = \left(\frac{2\pi m k_B T}{h^2} \right)^{1/2} L$$

$$\langle E \rangle = (-k_B T^2) \times \frac{1}{Q} \times \left(\frac{2\pi m k_B}{h^2} \right)^{1/2} L \frac{1}{2} T^{-1/2}$$

$$= \frac{(-k_B T^2)}{2} \times \left(\frac{h^2}{2\pi m k_B T} \right)^{1/2} \times \frac{1}{4} \times \left(\frac{2\pi m k_B}{h^2} \right)^{1/2} L T^{-1/2}$$

$$= \frac{-k_B T^2}{2} \times \frac{1}{T^{1/2}} \times \frac{1}{T^{1/2}}$$

Okay, so that means I have to do del ln, so now if I want to get the average value, I have to do del ln Q by del T which is del ln Q by del T of this particular quantity. So let us do that. So this quantity is del ln Q by del T into minus k B T square I have to do, so let us do that. Minus k B T square first I will write it, multiplied by I will do the differentiation of Q, so del ln Q by del T is 1 by Q, del Q by del T, 1 by Q into del Q by del T which means I have to take the differentiation of this guy. Now in that 2 pi m k B h square, they are all constant. Half and L, this is all constant. So I have to basically do T to the power half derivation. T to the power half is half T to the power minus half. That is now, our thing is now almost done.

Now let us see what it gives us. Minus k B T square into 1 by Q will be h square divided by 2 pi m k B T to the power half and there will be an L there, 1 by L, multiplied by 2 pi m k B by h square to the power half into L is there. And there is half here which I am writing here and

T to the power minus half which I am writing here. Now let us see what are the things that are going to cancel, h square, h square going to cancel. 2 pi m, 2 pi m going to cancel, k B also going to cancel, L is going to cancel, giving us minus k B T square by 2.

And then I have 1 by T to the power half and I have here also 1 by T to the power half. I am missing some quantity, let me see. So minus k B T square is fine, 1 by Q del Q by del T, now when I do del Q by del T, I have this constant quantity, 2 pi m k B. So there also there is a T there. No, not T, so 2 pi m k B by h square to the power half L is there. T to the power half is there. So T to the power half is half, minus half, that is also there. So now I have minus k B T square by 2. This is fine, but I am getting minus. Minus, there is a minus missing somewhere.

Student: Sir, in differentiation, sir there you have done the del ln Q by del T, that will be the plus k B T.


Correct. So let me see that. So del ln Q by del T let us review that.

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$$\begin{aligned} \frac{\partial \ln Q}{\partial T} &= \frac{1}{Q} \frac{\partial Q}{\partial T} \\ &= \frac{1}{\sum_i e^{-E_i/k_B T} \times \frac{E_i + 1}{k_B T}} \\ &= \frac{\sum_i e^{-E_i/k_B T}}{\sum_i e^{-E_i/k_B T}} \\ &= + \frac{1}{k_B T} \frac{\sum_i E_i e^{-E_i/k_B T}}{\sum_i e^{-E_i/k_B T}} \\ &= + \frac{1}{k_B T} \sum_i E_i P_i \\ &= - \frac{1}{k_B T^2} \langle E \rangle \end{aligned}$$

1 by Q del Q by del T, so 1 by Q is given in the first step, 1 by Q and then I have to differentiate del Q by del T, so e to the power minus E by k B T and then I have E i by k B and then I have a minus there and there is minus already is there. And then minus, minus becomes plus. So I have plus and I have plus here.

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$$\frac{\partial \ln Q}{\partial T} = + \frac{1}{k_B T^2} \langle E \rangle$$


$$\langle E \rangle = + k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)$$

$$Q = \left(\frac{2\pi m k_B T}{h^2} \right)^{1/2} L$$

$$\langle E \rangle = (+ k_B T^2) \times \frac{1}{Q} \times \left(\frac{2\pi m k_B}{h^2} \right)^{1/2} L^{1-1/2}$$

$$= \frac{(+ k_B T^2)}{2} \times \left(\frac{h^2}{2\pi m k_B T} \right)^{1/2} \times \frac{1}{4} \times \left(\frac{2\pi m k_B}{h^2} \right)^{1/2} T^{-1/2}$$

$$= \frac{-k_B T^2}{2} \times \frac{1}{T^{1/2}} \times \frac{1}{T^{1/2}}$$



$$Q = \left(\frac{2\pi m k_B T}{h^2} \right)^{1/2} L$$

$$\langle E \rangle = (+ k_B T^2) \times \frac{1}{Q} \times \left(\frac{2\pi m k_B}{h^2} \right)^{1/2} L^{1-1/2}$$

$$= \frac{(+ k_B T^2)}{2} \times \left(\frac{h^2}{2\pi m k_B T} \right)^{1/2} \times \frac{1}{4} \times \left(\frac{2\pi m k_B}{h^2} \right)^{1/2} T^{-1/2}$$

$$= \frac{+ k_B T^2}{2} \times \frac{1}{T^{1/2}} \times \frac{1}{T^{1/2}}$$

$$= \frac{k_B T^2}{2} \times \frac{1}{T}$$

$$= \frac{1}{2} k_B T$$

-4-

I have plus here, then I have plus here, I have a plus here. I have plus here. I have a plus here and that is giving us $k_B T^2$ square by half into $1/T$ is half $k_B T$. And that is the average energy of particle in a box in 1-dimensional box. So if I now take it to the 3-dimensional box, you can see that there is all the dimensions are independent.

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$$\begin{aligned}
 &= \frac{(+k_B T^2)}{2} \times \frac{1}{(2\pi m k_B T)^{1/2}} \times \frac{1}{4} \times \frac{1}{(h^2)^{1/2}} k_B T \\
 &= \frac{+k_B T^2}{2} \times \frac{1}{T^{1/2}} \times \frac{1}{T^{1/2}} \\
 &= \frac{k_B T^2}{2} \times \frac{1}{T} \\
 &= \frac{1}{2} k_B T
 \end{aligned}$$

$$\begin{aligned}
 \langle E \rangle_{3D} &= \frac{1}{2} k_B T + \frac{1}{2} k_B T + \frac{1}{2} k_B T \\
 &= \frac{3}{2} k_B T
 \end{aligned}$$

Therefore the average energy for a 3-D box will become half k B T plus half k B T plus half k B T, is equal to 3 by 2 k B T. Now you know that from the equipartition theorem that for every dimension there is half k B T energy is there for translation and therefore for 3-dimensional system the average energy classically is also 3 by 2 k B T. So we can see that for non-interacting systems like particle in a box which does not interact with anything, and does not have any, so it has only the translational energy, the average energy is also giving us the same value.

If we use the classical description, classical kinetic energy, like P square by 2 m and that also average you are going to as 3 by 2 k B T. So that is one of the example that how the average energy is coming to be 3 by 2 k B T using the formula of molecular thermodynamics. So all that we have done is that we have taken all possible energy values like n square h square by 8 m L square and weighted them by their corresponding Boltzmann probability which is e to the power minus E i by k B T. And then we took the average of that. And once we do that, we are getting to see that it is nothing but 3 by 2 k B T.

So like that you can apply this for many different possible systems and then you are going to get the desired observable values from what we see in the classical thermodynamics. So that is where the connection between molecular thermodynamics and classical thermodynamics takes place. So for example, when you do simulations, computer simulations of particles, there also we actually move atoms and molecules every time, every timestamp. So we have their positions and coordinates and then velocities and after that, after doing the simulations,

after generating so many different microstates from the simulation, we calculate the average property.

Like energy is free energies and all that and that reproduce the experimentally observable quantities. For example, binding energy of two proteins, we can do that from simulations just because we know that by following the formula of statistical thermodynamics once you calculate average property, is going to correspond to the macroscopically experimentally observable quantity, without that molecular thermodynamics would not have worked. So that is where the connection lies.

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Using Particle in a box

So, partition function $Q = \sum_n e^{-\beta E_n} = \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} e^{-\frac{n^2 h^2}{8mL^2}} = \left(\frac{2\pi mk_B T}{h^2}\right)^{3/2} V$

For 3D box, $E_i = \frac{h^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2)$. Since all x, y, z are independent,

$$Q = \left(\frac{2\pi mk_B T}{h^2}\right)^{3/2} V$$

$$\langle E \rangle = \sum_i E_i p_i$$

$$= \sum_i \left(\frac{E_i e^{-\frac{E_i}{k_B T}}}{e^{-\frac{E_i}{k_B T}}} \right) = k_B T^2 \frac{\partial \ln Q}{\partial T} = k_B T^2 \frac{\partial}{\partial T} \left[\ln \left\{ \left(\frac{2\pi mk_B T}{h^2}\right)^{3/2} V \right\} \right]$$

$$= k_B T^2 \left[\frac{\partial}{\partial T} \left(\ln T^{3/2} \right) + \frac{\partial}{\partial T} (\text{terms independent of } T) \right] = k_B T^2 \times T^{-3/2} \times \frac{3}{2} T^{1/2} = \frac{3}{2} k_B T$$

So, average energy of a particle in 3D box is $3/2 k_B T$. For n particles it is thus $3/2 nk_B T$.

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So you can see the derivation here also. And you can see that yes, here also you can see that this is plus $k_B T$ square and I have done directly for the 3-dimensional box in this particular case.

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Entropy in a nutshell

For a spontaneous process, the system increases towards a more probable state.

W of the most probable state is the highest

Energy is conserved; distribution of energy is not !

Entropy is nothing but the distribution of energy



So now just brief review, entropy in a nutshell, is that for a spontaneous process system increases towards a more probable state. That is what the second law of thermodynamics from the statistical point of view. W of the most probable state is the highest. So when you calculate W from many different distributions, but the W corresponding to the most probable distribution will have the highest value and that is enough, that is the only one that you have to take. We have seen that energy is not conserved, energy is conserved but the distribution of energy is not conserved because we can either accumulate all the energy in one place or we can that is called a pick distribution or we can make it flatter and that is flat distribution.

And because the distribution is not constant, we know that entropy also will not be constant because entropy will go by the probabilities of distributing these energies. Okay, as I said, entropy is nothing but the distribution of energy.