Advanced Thermodynamics and Molecular Simulations
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Lecture - 16
Canonical Ensemble: Helmholtz Free Energy, Averages and Fluctuations, Specific Heat, Deriving Ideal Gas Law

Hello, all of you. So in the last lecture we have been discussing the canonical ensemble and basically the meaning of the temperature or the variable β that we defined in the last class.

So in today's lecture, we will take the canonical ensemble a bit further and talk about how can we write Helmholtz free energy for the canonical ensemble as a function of the partition function and then I will discuss briefly how to compute the averages and fluctuations using the canonical ensemble.

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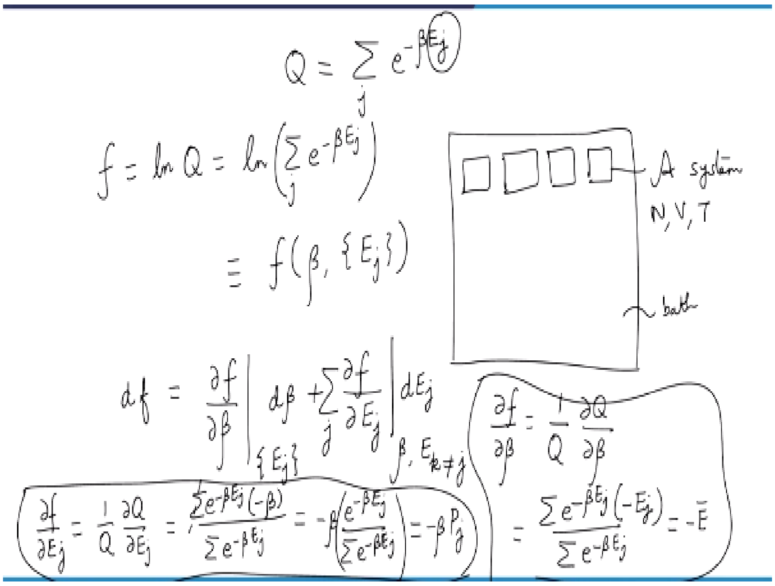

$$Q = \sum_j e^{-\beta E_j}$$

$$f = \ln Q = \ln\left(\sum_j e^{-\beta E_j}\right)$$

$$\equiv f(\beta, \{E_j\})$$

$$df = \left.\frac{\partial f}{\partial \beta}\right|_{\{E_j\}} d\beta + \sum_j \left.\frac{\partial f}{\partial E_j}\right|_{\beta, E_{k \neq j}} dE_j$$

$$\frac{\partial f}{\partial E_j} = \frac{1}{Q}\frac{\partial Q}{\partial E_j} = \frac{e^{-\beta E_j}(-\beta)}{\sum e^{-\beta E_j}} = -\beta\left(\frac{e^{-\beta E_j}}{\sum e^{-\beta E_j}}\right) = -\beta P_j$$

$$\frac{\partial f}{\partial \beta} = \frac{1}{Q}\frac{\partial Q}{\partial \beta} = \frac{\sum e^{-\beta E_j}(-E_j)}{\sum e^{-\beta E_j}} = -\bar{E}$$

So essentially, where we were so far is that we have defined a partition function for the ensemble and now I am talking about the systems that are same in the ensemble, not really the close contact that we assumed earlier in the last class. In this case, let us say again, going back to our earlier treatment, we have some 'A' systems each having some number some volume and temperature and they are forming an ensemble. So of course, they are not in any close contact except with the bath and the bath is infinite and that maintains the temperature of the system but the energy of the systems can be different, which are characterized by E_j that refers to different energy levels that are possible in the system.

$$Q = \sum_j e^{-\beta E_j}$$

So now I can define a variable-

$$f = \ln Q = \ln(\sum_j e^{-\beta E_j}$$

So now I can define a variable ln of Q or ln of summation over j $e^{-\beta Ej}$ and it turns out this particular function has very interesting significance, and it relates to the idea of Helmholtz free energy. So if I start with this function, what we can notice is this function is a function of the β variables and the E_j variables and therefore, I can represent the total change in this function df as the change in the β variable represented by a partial derivative which change because of a change in β variable. So it is-

$$df = \left.\frac{\partial f}{\partial \beta}\right]_{\{E_j\}} + \sum_j \left.\frac{\partial f}{\partial E_j}\right]_{\beta, E_k \neq j} dE_j$$

So now if I find-

$$\frac{\partial f}{\partial \beta} = \frac{1}{Q}\frac{\partial Q}{\partial \beta} = \frac{\sum e^{-\beta E_j}(-E_j)}{\sum e^{-\beta E_j}} = -\bar{E}$$

So just like we can do that, we can also find-

$$\frac{\partial f}{\partial E_j} = \frac{1}{Q}\frac{\partial Q}{\partial E_j} = \frac{\sum e^{-\beta E_j}(-\beta)}{\sum e^{-\beta E_j}}$$

Let us say if we are doing for e_0 e_1, e_2 and so on, if I do with respect to e_0 only the term containing e_0 will give me a derivative, everything else will give me zero. So this thing is then equal to-

$$\frac{\partial f}{\partial \beta} = -\beta\left(\frac{e^{-\beta E_j}}{\sum e^{-\beta E_j}}\right) = -\beta P_j$$

And this quantity we already have obtained and that is the probability of the states of energy E_j.

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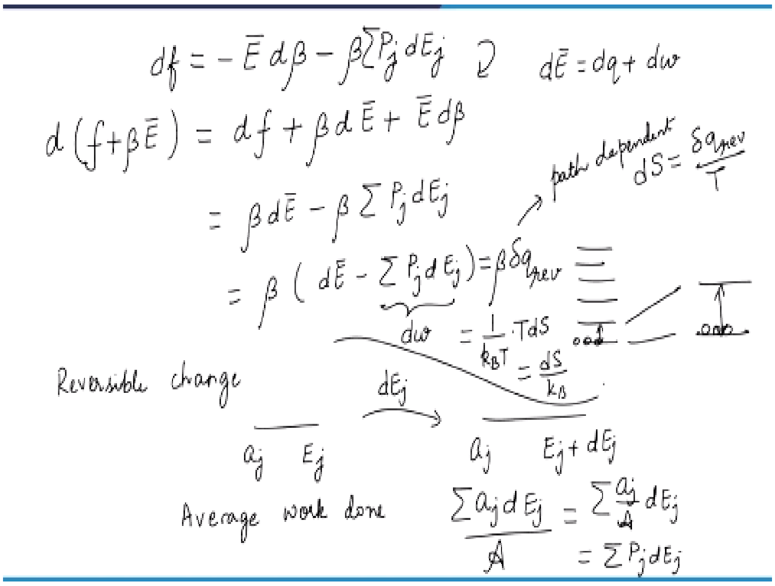

$$df = -\bar{E}\,d\beta - \beta\sum P_j\,dE_j \qquad d\bar{E} = dq + dw$$

$$d(f+\beta\bar{E}) = df + \beta\,d\bar{E} + \bar{E}\,d\beta$$

$$= \beta\,d\bar{E} - \beta\sum P_j\,dE_j$$

$$= \beta(\underbrace{d\bar{E} - \sum P_j\,dE_j}_{dw}) = \beta\,\delta q_{rev} = \frac{1}{k_BT}\cdot T\,dS = \frac{dS}{k_B}$$

path dependent $dS = \frac{\delta q_{rev}}{T}$

Reversible change

$$a_j \quad E_j \xrightarrow{dE_j} a_j \quad E_j + dE_j$$

Average work done $\frac{\sum a_j\,dE_j}{A} = \sum \frac{a_j}{A}\,dE_j = \sum P_j\,dE_j$

So therefore, if I now put whatever we have got here and earlier in the previous expression what we find is-

$$df = -\bar{E}d\beta - \beta\sum P_j dE_j$$

$$d(f + \beta\bar{E}) = df + \beta d\bar{E} + \bar{E}d\beta$$

$$= \beta d\bar{E} - \beta\sum P_j dE_j$$

$$= \beta(d\bar{E} - \sum P_j dE_j$$

Now let us look at the second term in the expression and think that we are doing a reversible process in this canonical system. We start with some NVT and now we are changing the volume by a small amount and due to the change in volume the energy changes by dE_j right. So then for a reversible change you may recall that when we discussed like what the heat and work is doing to the system, I told you that when I am adding heat, you get an extra quanta of energy and that quanta can be distributed in all the states but when I do work, I am essentially changing the energy level spacing.

So what will happen then is if you had some systems a_j, which had energy E_j, after doing this kind of a work, the energy of those particular states will change from Ej to $E_j + dE_j$. The key point is that the occupation level of states are not changing, only the energy level of a particular state is changing when I am doing the work. When I am adding heat, then of course you will have more distribution of quanta of energy because we thought that it will addition of an extra quanta of energy. In some sense work is also an addition of quanta, but what the work is doing it is changing the energy levels to different values. So then let us say if you have certain number of states here, certain number of states are still going to be there but those states are going to have higher energy than the previous configuration before the work was done.

So if we go with this particular idea, then the average work done can be thought of as a j multiplied with dE_j. So all the a_j systems we are doing a_j multiplied with dE_j work. And this has to be averaged over all the systems in the ensemble and of course, this has to be summed over all the possible energy levels. So this essentially gives me-

$$Average\ work\ done = \frac{\sum a_j dE_j}{A} = \sum \frac{a_j}{A}\ dE_j = \sum P_j dE_j$$

So now if I invoke the first law of thermodynamics, then you have-

$$d\bar{E} = dq + dw$$

The energy the change in internal energy is equal to the heat added plus the work done. So for a reversible process, what we have here is this is equal to β and change in the heat, because we are doing energy minus work and that must be equal to the heat added and we already have assumed that the process is reversible. So that is-

$$d(f + \beta\bar{E}) = \beta\delta q_{rev}$$

And I put a δ here just to indicate that this is a path dependent thing unlike energy that is a state function in fact, Q is also path dependent.

So now if I use that argument of Clausius, what Clausius has said is that my change in the entropy dS is equal to my heat added for a reversible process divided by temperature i.e.-

$$dS = \frac{\delta q_{rev}}{T}$$

So using the definition of β I found in the last class, we have β is equal to 1 by $k_B T$ and I can replace δQ reversible by TdS.

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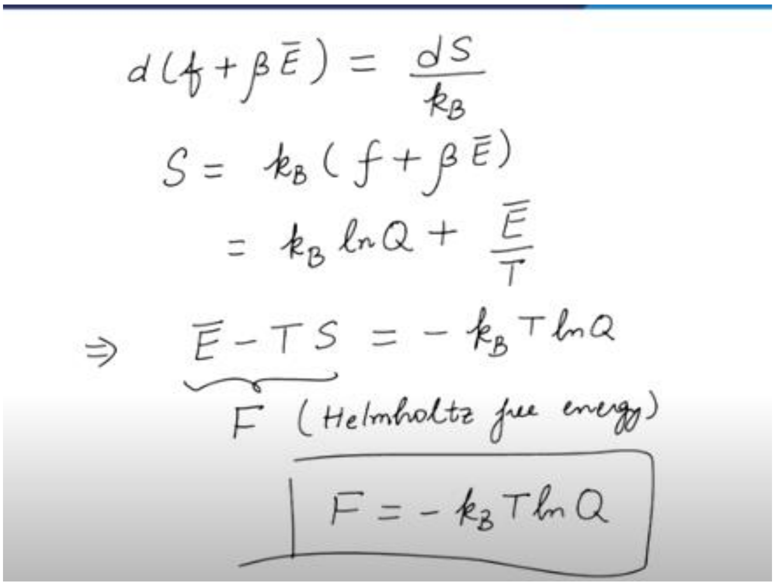

$$d(f+\beta\bar{E}) = \frac{dS}{k_B}$$

$$S = k_B(f+\beta\bar{E})$$

$$= k_B \ln Q + \frac{\bar{E}}{T}$$

$$\Rightarrow \underbrace{\bar{E} - TS}_{F} = -k_B T \ln Q$$

F (Helmholtz free energy)

$$\boxed{F = -k_B T \ln Q}$$

So-

$$d(f+\beta\bar{E}) = \frac{1}{k_B T}.TdS = \frac{dS}{k_B}$$

Or in other words, I can write S as-

$$S = k_B(f+\beta\bar{E}) = k_B \ln Q + \frac{\bar{E}}{T}$$

So this we can also rearrange and we can see we can write as-

$$\bar{E} - TS = -k_B T \ln Q$$

And $\bar{E} - TS$ is the definition of my Helmholtz free energy. And therefore, you have Helmholtz free energy as a function of the partition function in the canonical ensemble i.e.-

$$F = -k_B T \ln Q$$

That should not be unusual, because we have earlier established that whenever the control variables are the number of molecules, the volume and temperature, we should be using the Helmholtz free energy. If in this case the control variables were the number of molecules, pressure and temperature we would have gotten the Gibbs free energy. But the fact that it is coming as a simple function of the partition function tells me that if I know Q that is equivalent to of knowing the Helmholtz free energy and if I know the Helmholtz free energy, I can do thermodynamics and get all the properties and that is indeed true that as I said in the last class as well, that Q works as both a normalizing function and a generating function. So knowledge of partition function is like giving you the knowledge of the entire thermodynamic behavior for the particular system.

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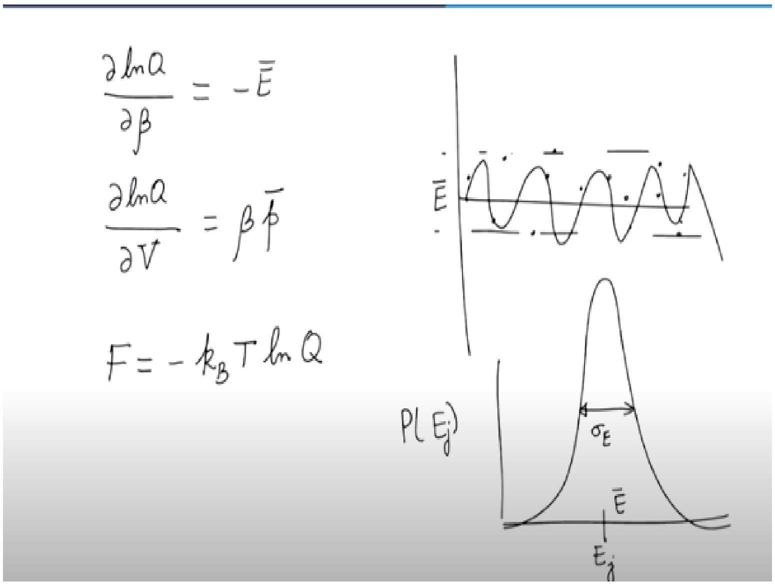

So we already have seen how it works. But just to recap-

$$\frac{\partial \ln Q}{\partial \beta} = -\bar{E}$$

$$\frac{\partial \ln Q}{\partial V} = \beta \bar{p}$$

And,

$$F = -k_B T \ln Q$$

What is interesting is that not only this idea of partition function is useful to get the average value of quantities, in this case the energy and the pressure but it is also important to get the fluctuations of those quantities from the average. And what do I mean by fluctuations is the following. So when I said that the energy has an average value of E bar, all I mean is that my energy of different states will average to this particular value, but I do not mean that every state has the same energy. So if you have for example so many states in the ensemble, they may happen to have energies higher than or lower than this particular E bar value only if I do an average over that we should get the E bar value. But the point on the central limit theorem that tells me is that as I increase the number of systems, what we will notice is that this fluctuations in this E value will start to decrease.

Now let us see how exactly it works out and how the idea of partition function can give me the value of the fluctuations. So let us say for example, you have some standard deviation of whatever distribution of energy you have the other way to think about it is we can plot the probability of having an energy E_j versus E_j and this is going to peak around some E bar value. So we are interested in what is the width of this distribution or the standard deviation of this particular distribution.

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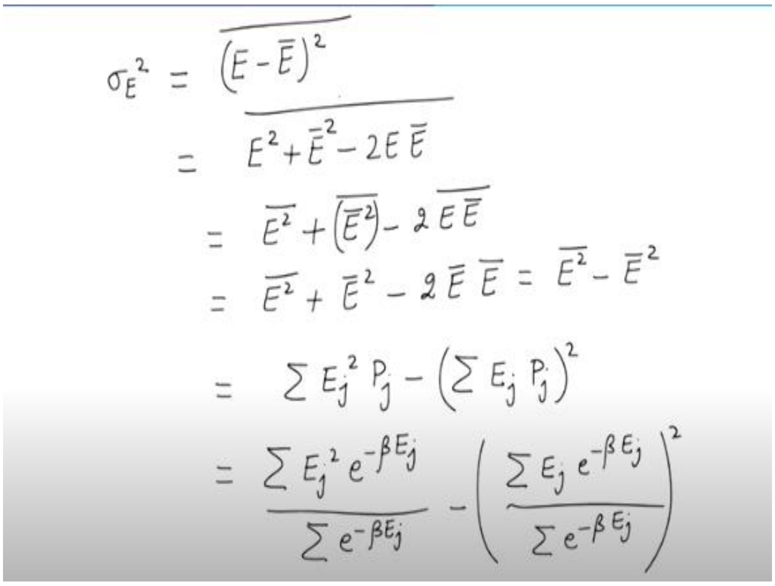

$$\sigma_E^2 = \overline{(E-\bar{E})^2}$$

$$= \overline{E^2+\bar{E}^2-2E\bar{E}}$$

$$= \overline{E^2} + \overline{(\bar{E}^2)} - 2\overline{E\bar{E}}$$

$$= \overline{E^2} + \bar{E}^2 - 2\bar{E}\bar{E} = \overline{E^2} - \bar{E}^2$$

$$= \sum E_j^2 P_j - \left(\sum E_j P_j\right)^2$$

$$= \frac{\sum E_j^2 e^{-\beta E_j}}{\sum e^{-\beta E_j}} - \left(\frac{\sum E_j e^{-\beta E_j}}{\sum e^{-\beta E_j}}\right)^2$$

So the standard deviation can be defined in the following way the variance or the square of standard deviation for the energy is essentially-

$$\sigma_E^2 = \overline{(E-\bar{E})^2}$$

so bar I am using to represent the average. So I compute deviation for all the energy values with respect to the mean value square it and then averaged it. So clearly if I do not square, then you can have both positive deviations and negative deviations and they will, they may as well cancel out and it does not represent the fluctuations from the average value. When we square it, both positive and negative deviations add up. So it is a better measure of fluctuations in this particular quantity.

So I can write this thing by taking a expanding this square term you have-

$$\sigma_E^2 = \overline{(E^2+\bar{E}^2-2E\bar{E})}$$

$$= \overline{E^2} + \overline{\bar{E}^2} - \overline{2E\bar{E}}$$

Now clearly, for the first term, we have to compute E squares and average it and they will be different for every state but in the second term, it has already been averaged. So you have E bar square. So if I take average of this again I should get the same quantity again. So this will be-

$$\sigma_E^2 = \overline{E^2} + \overline{E^2} - 2\bar{E}\bar{E} = \overline{E^2} - \overline{E^2}$$

So now using the definition of the averages, we can write this as-

$$\sigma_E^2 = \sum E_j^2 P_j - \left(\sum E_j P_j\right)^2$$

$$= \frac{\sum E_j^2 e^{-\beta E_j}}{\sum e^{-\beta E_j}} - \left(\frac{\sum E_j e^{-\beta E_j}}{\sum e^{-\beta E_j}}\right)^2$$

And now let us see how we can get the same quantity, if I simply take the second derivative of my Q.

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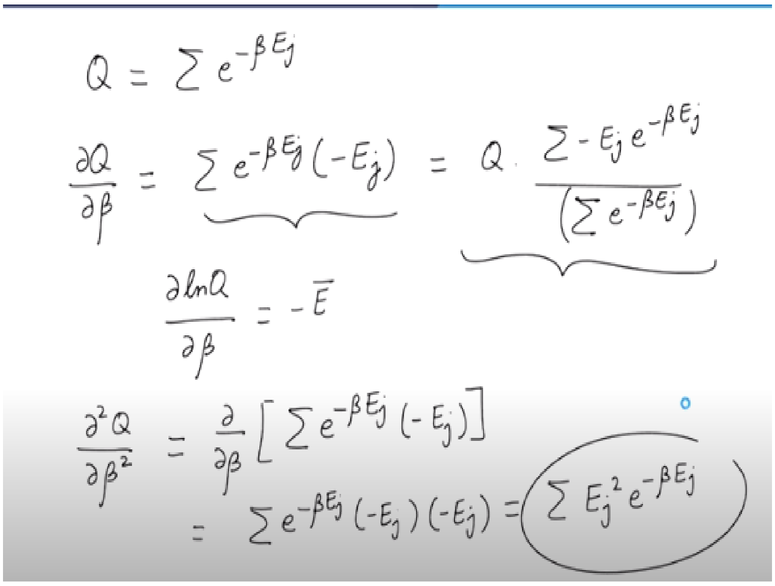

$$Q = \sum e^{-\beta E_j}$$

$$\frac{\partial Q}{\partial \beta} = \underbrace{\sum e^{-\beta E_j}(-E_j)} = Q \cdot \underbrace{\frac{\sum -E_j e^{-\beta E_j}}{\left(\sum e^{-\beta E_j}\right)}}$$

$$\frac{\partial \ln Q}{\partial \beta} = -\bar{E}$$

$$\frac{\partial^2 Q}{\partial \beta^2} = \frac{\partial}{\partial \beta}\left[\sum e^{-\beta E_j}(-E_j)\right]$$

$$= \sum e^{-\beta E_j}(-E_j)(-E_j) = \boxed{\sum E_j^2 e^{-\beta E_j}}$$

So let us say I start with my Q as-

$$Q = \sum e^{-\beta E_j}$$

And,

$$\frac{\partial Q}{\partial \beta} = \sum e^{-\beta E_j}(-E_j) = Q.\frac{\sum -E_j e^{-\beta E_j}}{(\sum e^\wedge(-\beta E_j)}$$

$$\frac{\partial \ln Q}{\partial \beta} = -\bar{E}$$

Now let us take a derivative of this quantity one more time, and let us see what do we get. So if I find-

$$\frac{\partial^2 Q}{\partial \beta^2} = \frac{\partial}{\partial \beta}\left[\sum e^{-\beta E_j}\left(-E_j\right)\right] = \sum e^{-\beta E_j}\left(-E_j\right)\left(-E_j\right) = \sum E_j^2 e^{-\beta E_j}$$

So if I start with this, if I put that in the expression right here, what we notice is that I can write my σ_E^2 as-

$$\sigma_E^2 = \frac{\sum E_j^2 e^{-\beta E_j}}{\sum e^{-\beta E_j}} - \left(\frac{\sum E_j e^{-\beta E_j}}{\sum e^{-\beta E_j}}\right)^2$$

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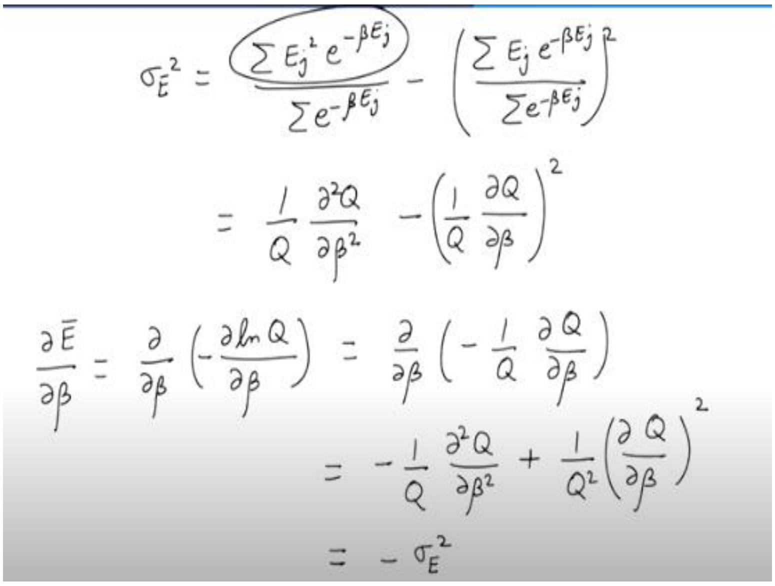

$$\sigma_E^2 = \frac{\boxed{\sum E_j^2 e^{-\beta E_j}}}{\sum e^{-\beta E_j}} - \left(\frac{\sum E_j e^{-\beta E_j}}{\sum e^{-\beta E_j}}\right)^2$$

$$= \frac{1}{Q}\frac{\partial^2 Q}{\partial \beta^2} - \left(\frac{1}{Q}\frac{\partial Q}{\partial \beta}\right)^2$$

$$\frac{\partial \bar{E}}{\partial \beta} = \frac{\partial}{\partial \beta}\left(-\frac{\partial \ln Q}{\partial \beta}\right) = \frac{\partial}{\partial \beta}\left(-\frac{1}{Q}\frac{\partial Q}{\partial \beta}\right)$$

$$= -\frac{1}{Q}\frac{\partial^2 Q}{\partial \beta^2} + \frac{1}{Q^2}\left(\frac{\partial Q}{\partial \beta}\right)^2$$

$$= -\sigma_E^2$$

So the first term now becomes the second derivative of Q with respect to β. So it is-

$$\sigma_E^2 = \frac{1}{Q}\frac{\partial^2 Q}{\partial \beta^2} - \left(\frac{1}{Q}\frac{\partial Q}{\partial \beta}\right)^2$$

$$\frac{\partial \bar{E}}{\partial \beta} = \frac{\partial}{\partial \beta}\left(-\frac{\partial \ln Q}{\partial \beta}\right) = \frac{\partial}{\partial \beta}\left(-\frac{1}{Q}\frac{\partial Q}{\partial \beta}\right) = -\frac{1}{Q}\frac{\partial^2 Q}{\partial \beta^2} + \frac{1}{Q^2}\left(\frac{\partial Q}{\partial \beta}\right)^2 = -\sigma_E^2$$

So therefore, what we have been able to establish is that I can not only write E bar as a function of Q, we can also represent the fluctuation in the energy σ_E also as a function of Q. In other words, once I know E bar I can also find σ_E^2. But E bar I have found using Q. So I can find both the mean and the fluctuation using the idea of E bar. So now I can write this particular quantity as-

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

$$\frac{\partial \bar{E}}{\partial \beta} = \frac{\frac{\partial \bar{E}}{\partial T}}{\frac{\partial \beta}{\partial T}} = \frac{\partial \bar{E}}{\partial T} / (\frac{\partial}{\partial T}\left(\frac{1}{k_B T}\right) = -k_B T^2 \left(\frac{\partial \bar{E}}{\partial T}\right)$$

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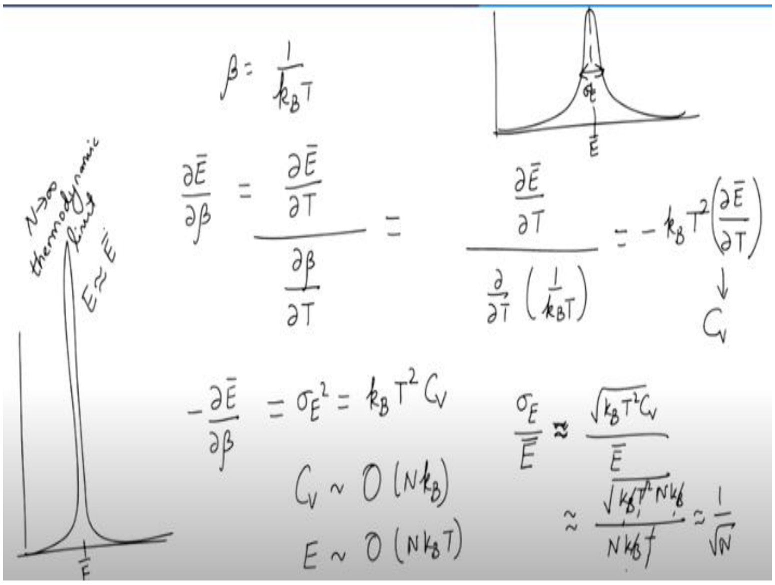

Now what we can notice here is that the derivative of energy with respect to temperature has a physical meaning it is the definition of my specific heat. In this case, we are working in canonical ensemble so the volume is constant. So this essentially is the specific heat at constant volume. So not only the fluctuations are always present, but fluctuations also have a physical meaning in this case fluctuation refers to the specific heat.

So essentially my-

$$-\frac{\partial \bar{E}}{\partial \beta} = \sigma_E^2 = k_B T^2 C_v$$

Now let us take an example of an ideal gas. So for an ideal gas the C_V is of the order of N multiplied with k_B. And the energy is of the order of N multiplied with $k_B T$. When I say order of, there can be some multiple there that is not very important here. So if I find my σE by E bar, that is if I take the ratio of the standard deviation to the mean value, this will be going like-

$$C_v \sim O(N k_B)$$

$$E \sim O(N k_B T)$$

$$\frac{\sigma_E}{\bar{E}} \approx \frac{\sqrt{k_B T^2 C_V}}{\bar{E}} \approx \frac{\sqrt{k_B T^2 N k_B}}{N k_B T} \approx \frac{1}{\sqrt{N}}$$

So what this means is as N increases, as the number of molecule increases your ratio of the standard deviation to the mean that characterizes the magnitude of fluctuation is actually decreasing. And actually, if the N is very large, we may pretty much assume that the distribution is extremely narrow around the point E bar for large N pretty much going to infinity and therefore, for N going to infinity what we refer as thermodynamic limit we can pretty much say that the energy of system is roughly equal to E bar.

So keep in mind although we are saying that the energy of a system is always equal to E bar or roughly equal to E bar because the fluctuations are less that does not mean that I am discarding the effect of fluctuations because fluctuations are really having a physical meaning here the specific heat refers to the magnitude of fluctuations. So if I say fluctuations are zero that will mean that the specific heat is zero. That is not true here all I mean to say when I say that my energy is close to E bar is that the deviation from the E bar of energy is very small as the N increases, right. So the error that we make by this assumption of energy being equal to the average energy that error will be small that is not to say that the fluctuation itself are negligible, fluctuations are always present and they have a strong physical significance. In fact, for systems for which N is not so large, then the fluctuations have magnified effect simply as a result of the central limit theorem.

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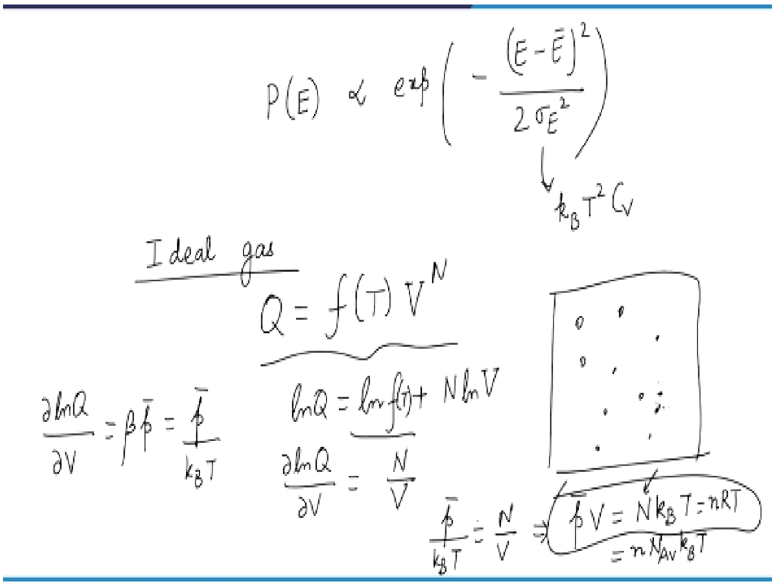

$$P(E) \propto \exp\left(-\frac{(E-\bar{E})^2}{2\sigma_E^{\,2}}\right) \qquad \sigma_E^{\,2} \rightarrow k_B T^2 C_v$$

Ideal gas

$$\underbrace{Q = f(T)\,V^N}$$

$$\ln Q = \underline{\ln f(T)} + N \ln V$$

$$\frac{\partial \ln Q}{\partial V} = \beta \bar{p} = \frac{\bar{p}}{k_B T}$$

$$\frac{\partial \ln Q}{\partial V} = \frac{N}{V}$$

$$\frac{\bar{p}}{k_B T} = \frac{N}{V} \Rightarrow \boxed{\bar{p}V = N k_B T = nRT} = n N_{Av} k_B T$$

Now going further just like what we did for the coin toss example We can also write the distribution of energy as something like proportional to exponential of-

$$P(E) \propto \exp\left(-\frac{(E-\bar{E})^2}{2\sigma_E^2}\right)$$

And,

$$\sigma_E^2 = k_B T^2 C_v$$

And that itself means that the specific heat does affect the distribution, but the magnitude of that in comparison to the average energy decreases as the number of molecules increases in the particular system. So this was all about the canonical ensemble.

In the next lecture, we will take one step further and talk about what is known as a grand canonical ensemble. So in the grand canonical ensemble, unlike the canonical ensemble, the number of molecules can also change that would correspond to a case when the systems can exchange both mass and energy and as you may expect, when I do the grand canonical ensemble, I will still have a partition function, but that partition function will not be the same as the canonical partition function. Nonetheless, using the idea of a partition function, we can still evaluate properties in the grand canonical ensemble.

So I hope to have convinced you that as we determine like what is the appropriate ensemble for the system to work in the next step is always to determine the partition function and once we have the partition function, we can go ahead and find all the properties. So before I close in here, let us take one simple example and see how exactly it works out.

So it turns out for the case of an ideal gas and I am not going to derive the expression, but the partition function is something like a function of temperature multiplied with volume to the power N when you have N molecules in the system.

$$Ideal\ gas\ (Q) = f(T)V^N$$

Now it is not so difficult to see why it is true, because in the ideal gas case, we are assigning no volume to each of the molecules. So they can pretty much be anywhere in the entire volume and they can also sit on top of each other. So there is no exclusion, because we are assuming that particles are of 0 size. So roughly speaking, the number of ways in which I can place one particle is going like volume V. So number of ways we can place two particle is like V multiplied by V, V^2. So the number of ways we can place N particles must be V^N that is the simplest equation of state that one can imagine.

So for this particular case, let us see how it works in right here. So let us say if I am interested in the pressure, so I know that-

$$\frac{\partial \ln Q}{\partial V} = \beta \bar{p} = \frac{\bar{p}}{k_B T}$$

If I compute ln Q in this case, it is ln of f by the way, this f has nothing to do with the previous f I discussed, some function arbitrary function plus N ln V. But this function is of temperature. So if I do-

$$\ln Q = \ln f(t) + N \ln V$$

$$\frac{\partial \ln Q}{\partial V} = \frac{N}{V} = \frac{\bar{p}}{k_B T} = \bar{p}V = N k_B T = nRT$$

If I work in terms of the moles of molecule, this is small n moles multiplied with Avogadro number k B T. And Avogadro number multiplied with the Boltzmann constant is my gas constant R. So that gives me p bar V is equal to nRT. That is the form we are quite used to, right. So once we know the partition function we can find all the properties.

The question however is how do we get the partition function and that is something that is not very trivial thing to do. And clearly we have not discussed how to get the partition function so far. We know once we have partition function, what to do with it.

But how exactly we know for a substance what should be the partition function that really becomes slightly different topic and we will do few examples in the later part of this course. So with this I stop here. Thank you.