Thermodynamics: Classical to Statistical

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Lecture-15

Calculation of different thermodynamical quantities using canonical partition function

We have obtained canonical partition function

$$Q(N,V,\beta) = \sum_j e^{-\beta E_j(N,V)}$$

E_j is function of number particles and volume where j is number of states. We have also obtained probability of j-th state,

$$p_j(N,V,\beta) = \frac{e^{-\beta E_j(N,V)}}{Q(N,V,\beta)}$$

Since we have obtained partition function as well as the probability, now we can calculate all the thermodynamic quantities like average energy (<E>). .

Average Energy $\langle E \rangle = \sum_j p_j(N,V,\beta) E_j(N,V)$

If you remember that probability of any variable $x = \sum_j x_j p_j$, we already discussed this which is very similar to this.

Now if we substitute the value of probability p_j, we will obtain,

$$\langle E \rangle = \frac{\sum_j e^{-\beta E_j(N,V)} E_j(N,V)}{Q(N,V,\beta)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

This is the expression we obtain for average energy. Now, if we closely look at the expression for partition function as well as the expression 1, we see that in the denominator we have Q and in the numerator we have $\sum_j e^{-\beta E_j(N,V)} E_j(N,V)$, it says that we need to take log of Q first and then we need to differentiate Q with respect to beta then what we get is like very similar to expression 1 let us see

So we have Q, now we will take lnQ and differentiate lnQ with respect to β keeping number of particles and volume constant,

$$\left(\frac{\partial \ln Q(N,V,\beta)}{\partial \beta}\right)_{N,V} = \frac{\sum_j e^{-\beta E_j(d,v)} \times (-Ej\ (N,V))}{\sum j e^{-\beta E_j(N,V)}} \quad \ldots\ldots\ldots\ldots\ldots(2)$$

Now, if we compare expression 1 and expression 2, we get

$$<E> = - \left(\frac{\partial \ln Q(N,V,\beta)}{\partial \beta}\right)_{N,V}$$

So this is the expression for average energy, if you know the partition function you can easily calculate average energy and this average energy is nothing but the internal energy that we have used in classical thermodynamics.

Now, we will prove also that β is $1/K_BT$, where K_B is Boltzman constantant and T is the absolute temperature. So in terms of temperature we can write

$$<E> = k_B T^2 \left(\frac{\partial \ln Q(N,V,\beta)}{\partial T}\right)_{N,V}$$

Now we will calculate average pressure. Since, we are dealing with canonical partition function, in canonical partition function number of particles, volume and temperature fixed, so pressure can fluctuate, so we will calculate average pressure. To do this, we will start with the expression for average energy. Now,

$$<E> = U = \sum_j p_j (N,V,\beta)\ E_j\ (N,V)$$

So we can further proceed like this

$$dU, = \sum_j p_j dE_j\ (N,V,) + \sum_j E_j\ (N,V)\ dp_j$$

then this above expression can be reduced further to

$$dU = \sum j\ p_j \left(\frac{\partial E_j}{\partial v}\right)_N dv + \sum_j E_j\ (N,V)\ dp_j \quad \ldots\ldots\ldots\ldots\ldots(3)$$

From thermodynamics, we know,

$$dU = \partial w + \partial q$$

and if the process is a reversible, one can write

$$dU = \delta w_{rev} + \delta q_{rev}$$

we can further proceed and write

$$dU = -PdV + \delta q_{rev} \text{ ………………………..(4)}$$

Now if you compare the coefficients of dV of equation 3 and 4, what we obtained

$$p_j = \left(\frac{\partial E_j}{\partial V}\right)_N \text{ ……………….(5)}$$

This is because average pressure we can also write like <P> = = $\sum_j p_j (N,V,\beta)\, P_j (N,V)$

Now we know the expression for probability. If we substitute the expression for probability here we get $$<P> = = \frac{\sum e^{-\beta E_j}\left(-\left(\frac{\partial E_j}{\partial v}\right)_N\right)}{Q}$$

We know

$$Q(N,V,\beta) = \sum_j e^{-\beta Ej(N,V)}$$

we will take log of Q and we will differentiate ln Q with respect to V keeping N and β consant.

$$\ln Q(N,V,\beta) = \ln\left(\sum_j e^{-\beta Ej(N,V)}\right)$$

.

$$<P> = k_B T\left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta}$$

So, this is the expression for average pressure.

So far we have assumed that $\beta = 1/k_BT$, we will prove it now.

We will start with average pressure. We just discussed

$$<E> = \sum_j p_j\ E_j = \frac{\sum j\ Ej\ (N,V)\ e^{-\beta E_j(N,V)}}{\sum j\ e^{-\beta E_j(N,V)}}$$

Now, we will differentiate average energy with respect to volume keeping N and beta constant

We will get,

$$\left(\frac{\partial \langle E \rangle_j}{\partial V}\right)_{N,\beta} = \frac{\sum j \left(\frac{\partial E_j}{\partial v}\right)_N e^{-\beta E_j(N,V)}}{\sum j\ e^{-\beta E_j(N,V)}} + \frac{\sum j\ Ej\ (N,V) e^{-\beta E_j(N,V)} \times (-\beta) \times \left(\frac{\partial E_j}{\partial v}\right)_N}{\sum j\ e^{-\beta E_j(N,V)}}$$

$$- \frac{\sum j\ Ej\ (N,V) e^{-\beta E_j(N,V)} \times \sum j\ e^{-\beta E_j(N,V)} \times (-\beta) \times \left(\frac{\partial E_j}{\partial v}\right)_N}{(\sum j\ e^{-\beta E_j(N,V)})^2} \ldots\ldots\ldots(6)$$

We can further simplify this one.

Now, if we look at the first term what do we get? The first term gives you minus of average pressure. So the first term, gives us average pressure. Now, if we see the second term, we have plus beta. We can take beta out and then if we take the minus sign in minus $\left(\frac{\partial E_j}{\partial V}\right)$, we get Pj that is pressure. So we get average of pressure times energy from second term.

Now, if we look at the third term, the first term gives us the average energy. Now, if we split the denominator into two different $\sum j\ e^{-\beta E_j}$ term, the first term gives us the average energy minus E average and the second term gives us pressure. Then we have one beta term also.

$$\left(\frac{\partial \langle E \rangle_j}{\partial V}\right)_{N,\beta} = -\langle P \rangle + \beta \langle PE \rangle - \beta \langle E \rangle \langle P \rangle \ldots\ldots\ldots\ldots..(7)$$

So this is the expression we have got, if we differentiate average energy with respect to volume.

Now for those who did not understand how we arrived at this expression, I will just show those things there. Now we will go back and check the expression of this.

So in equation 6, the first term in the right hand side we have $\frac{\sum j \left(\frac{\partial E_j}{\partial v}\right)_N e^{-\beta E_j(N,V)}}{\sum j\ e^{-\beta E_j(N,V)}}$.

$\frac{e^{-\beta E_j(N,V)}}{\sum j\ e^{-\beta E_j(N,V)}}$ this term gives usp_j, probability. So the first term reduces to $\sum j \left(\frac{\partial E_j}{\partial v}\right) p_j(N,V,\beta)$ and this is nothing but minus of average pressure. So this is the first term in the right hand side of equation 1.

$$\frac{\sum j \left(\frac{\partial E_j}{\partial v}\right)_N e^{-\beta E_j(N,V)}}{\sum j\ e^{-\beta E_j(N,V)}} = \sum j \left(\frac{\partial E_j}{\partial v}\right) p_j(N,V,\beta) = -\langle P \rangle$$

In the second the term of expression 6, we have $\frac{\sum j\ Ej\ (N,V)e^{-\beta E_j(N,V)} \times (-\beta) \times \left(\frac{\partial E_j}{\partial v}\right)_N}{\sum j\ e^{-\beta E_j(N,V)}}$.

Now, if we further reduce this one and write this as $\frac{\beta \sum j\ Ej \times (-\left(\frac{\partial E_j}{\partial v}\right)_N) e^{-\beta E_j}}{\sum j\ e^{-\beta E_j(N,V)}}$. So $\frac{e^{-\beta E_j}}{\sum j\ e^{-\beta E_j(N,V)}}$ is nothing but probability. So we can write it like $\beta \sum_j E_j P_j p_j$. E_j P_j is nothing but variabl now.

We can write β<PE>. This is the second term of equation 6 that is present in the right hand side.

Now, what about the last term or third term? The third term in the expression 6 present in the right hand side is $\frac{\sum j\ Ej\ (N,V)e^{-\beta E_j(N,V)} \times \sum j\ e^{-\beta E_j(N,V)} \times (-\beta) \times \left(\frac{\partial E_j}{\partial v}\right)_N}{(\sum j\ e^{-\beta E_j(N,V)})^2}$

Now we can simplify this one like $\frac{\sum j\ Ej\ (N,V)e^{-\beta E_j}}{(\sum j\ e^{-\beta E_j})^2} \times \sum j\ e^{-\beta E_j} \times (-\beta) \times \left(\frac{\partial E_j}{\partial v}\right)_N$.

$$\Rightarrow \frac{\sum j\ Ej\ (N,V)e^{-\beta E_j}}{\sum j\ e^{-\beta E_j}} \times \frac{\beta \sum j\ e^{-\beta E_j} \{-\left(\frac{\partial E_j}{\partial v}\right)_N\}}{\sum j\ e^{-\beta E_j}}$$

So the first term here gives $E_j p_j$ and the second term gives us P_j. This gives us β <E> <P>. That is how we arrived at equation 7, we name this one as equation 7.

Now, we consider average pressure and will differentiate pressure with respect to β. We know average pressure is nothing but $<P> = \sum_j p_j (N,V,\beta) P_j (N,V)$ Now, we substitute the value of p_j here and we get the value of average pressure.

$$<P> = \frac{\sum j \left(\frac{\partial E_j}{\partial v}\right)_N e^{-\beta E_j(N,V)}}{\sum j\ e^{-\beta E_j(N,V)}}$$

Now we will differentiate average pressure with respect to β keeping N and V constant.

$$\left(\frac{\partial <P>}{\partial \beta}\right)_{N,V} = - \frac{\sum j \left(\frac{\partial E_j}{\partial v}\right)_N e^{-\beta E_j} \times (-E_j)}{\sum j\ e^{-\beta E_j}} + \frac{\sum j \left(\frac{\partial E_j}{\partial v}\right)_N e^{-\beta E_j}}{(\sum j\ e^{-\beta E_j})^2} \times \sum j\ e^{-\beta E_j} \times (-E_j)$$

If we further simplify this expression we get

$$\left(\frac{\partial <P>}{\partial \beta}\right)_{N,V} = -<EP> + <P> <E> \ldots\ldots\ldots\ldots\ldots(8)$$

From equations 7 and 8 we get

$$\left(\frac{\partial <E>}{\partial V}\right)_{N,\beta} + \beta\left(\frac{\partial <P>}{\partial \beta}\right)_{N,V} = -<P> \quad \ldots\ldots\ldots\ldots(9)$$

Again from first law of thermodynamics we know

$$dU = TdS - PdV$$

Now we differentiate this with respect to V keeping temperature constant and get

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$$

$$\Rightarrow \left(\frac{\partial U}{\partial V}\right)_T - T\left(\frac{\partial S}{\partial V}\right)_T = -P \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(10)$$

.Again $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

So this is one of the Maxwell relation. So our equation 10 becomes

$$\left(\frac{\partial U}{\partial V}\right)_T - T\left(\frac{\partial P}{\partial T}\right)_V = -P \ldots\ldots\ldots\ldots\ldots\ldots (11)$$

Now if we compare equation 11 and equation 9, we get β is proportional to 1/T and it has been found that the proportionality constant is nothing but Boltzmann constant. The proportionality constant turns out to be $1/K_B$ by comparison with expressions for the average energy or average pressure with known thermodynamic equations. So we proved that

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

Next we consider the calculation of entropy. Suppose, we are considering a function where

$$f = \ln Q$$

So $f(\beta, E_1, E_2,...) = \ln \sum j\, e^{-\beta E_j} \quad \ldots\ldots\ldots\ldots(1)$

.

So we can write, $df = \left(\frac{\partial f}{\partial \beta}\right)_{E1,E2,...} d\beta + \sum_k \left(\frac{\partial f}{\partial E_k}\right)_{\beta,E1,E2,...} dE_k \quad \ldots\ldots\ldots\ldots(2)$

$$\Rightarrow\ df = -\langle E\rangle\, d\beta - \beta \sum_j p_j\, dE_j$$

$$\Rightarrow\ d(f + \beta \langle E\rangle) = \beta\, (d\langle E\rangle - \sum_j p_j\, dE_j)$$

$$\Rightarrow\ d(f + \beta \langle E\rangle) = \beta\, (dU - \delta w_{rev})$$

$$\Rightarrow\ d(f + \beta \langle E\rangle) = \beta\, \delta q_{rev} = \frac{\partial q_{rev}}{k_B T}$$

$$\Rightarrow\ k_B\, d(f + \beta \langle E\rangle) = dS$$

$$\Rightarrow\ S = k_B f + \frac{\langle E\rangle}{T} + \text{constant}$$

Now, we are more interested into difference in entropy rather than absolute entropy. So we can safely ignore the constant term. So, if we ignore the constant term we get

$$S = k_B f + \frac{\langle E\rangle}{T}$$

Now we have obtained so far average energy, average pressure and entropy value.

Now, we can calculate basically all thermodynamic quantities like enthalpy. We know enthalpy

$$H = U - \langle P\rangle V$$

If we differentiate with respect to T then we have

$$H = k_B T^2 \left(\frac{\partial \ln a}{\partial T}\right)_{N,V} - k_B T \left(\frac{\partial \ln a}{\partial \ln V}\right)_{N,\beta}$$

As the value of average pressure is $k_B T \left(\frac{\partial \ln a}{\partial \ln V}\right)_{N,\beta}$. If we take the V in the denominator we get this, these are the constant N and β.

We can calculate Helmholtz free energy because

$$A = U - TS$$

and we substitute all the values here we get

$$A = U - T\, k_B \ln Q - U$$

$$\Rightarrow\ A = k_B T \ln Q$$

Similarly, we can also calculate Gibbs free energy G like,

$$G = H - TS$$

by substituting the values of H and S. So basically we can calculate all thermodynamic quantities if we know the partition function.