Statistical Thermodynamics for Engineers
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Lecture 13
The Molecular Partition Function and Its Relationship with Classical Thermodynamics

So, welcome to lecture 10 of the course Statistical Thermodynamics for Engineers. So, this time we are going to an example problem first. So, it is an example problem.

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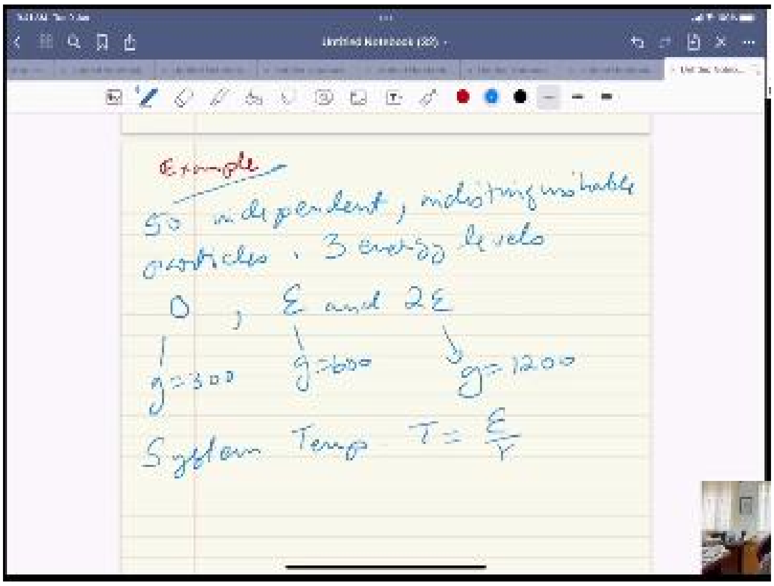

Example

50 independent, indistinguishable particles, 3 energy levels

0, ε and 2ε

$g=300$ $g=600$ $g=1200$

System Temp $T = \frac{\varepsilon}{k}$

So, let us assume that there are 50 independent indistinguishable particles. There are three energy levels let us assume the energy level is 0 at about unit of energy of 0 E and say 2E. So, the degeneracy of the first level is 300, degeneracy of the second level is 600 and degeneracy of the third energy level is 1200. So, the system temperature which is written as T is E by K.

So, first step is that if somebody asks you calculate the partitional function calculate the partition function. So, the partition function is written as Z which is summation over j g j exponential minus j by kT.

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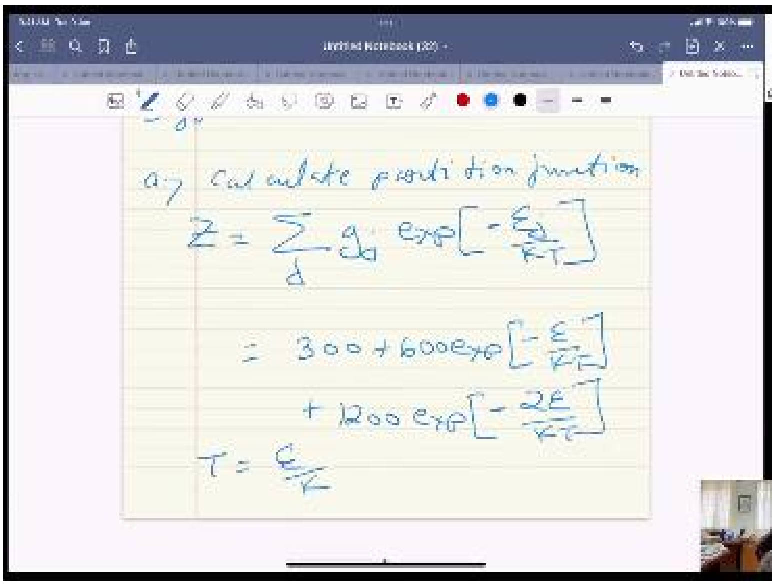

a) Calculate partition function

$$Z = \sum_j g_j \exp\left[-\frac{E_j}{kT}\right]$$

$$= 300 + 600\exp\left[-\frac{E}{kT}\right] + 1200\exp\left[-\frac{2E}{kT}\right]$$

$$T = \frac{E}{k}$$

So, now this can be this can be written there are 3 energy levels as we know so, first one is 300 because the energy is 0, the second one is 600 into exponential minus E by kT and the third one is 1200 exponential minus 2E by kT and recall the temperature is E by K.

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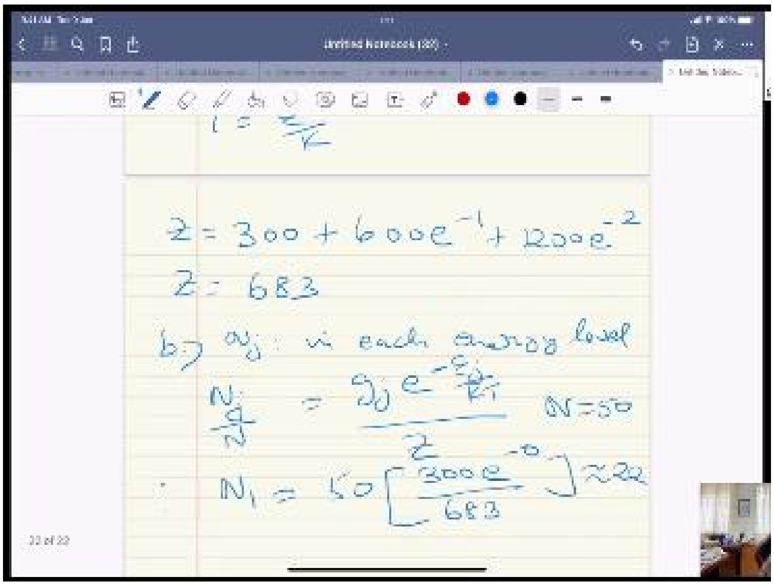

$$Z = 300 + 600e^{-1} + 1200e^{-2}$$

$$Z = 683$$

b) N_j in each energy level

$$\frac{N_j}{N} = \frac{g_j e^{-\frac{E_j}{kT}}}{Z} \qquad N = 50$$

$$N_1 = 50\left[\frac{300e^{-0}}{683}\right] \approx 22$$

So, the partition function therefore becomes 300 plus 600 E to the power of 1 plus 1200 E to the power of minus 2. This is if you do it properly this will be 683. So, now the next question is that find the number of particles N sub j particles in each energy level compute that.

So, N sub j by N is equal to as we already know g sub j e to the power minus e sub j by kT divided by the total partition function. So, therefore N sub 1, N is equal to as we know is 50 this is given so this is 50 into 300 into e to the power of minus 0 divided by 683 so, this gives you rough to 22. So, second one is roughly 22. So, similarly you can do the other calculations as well.

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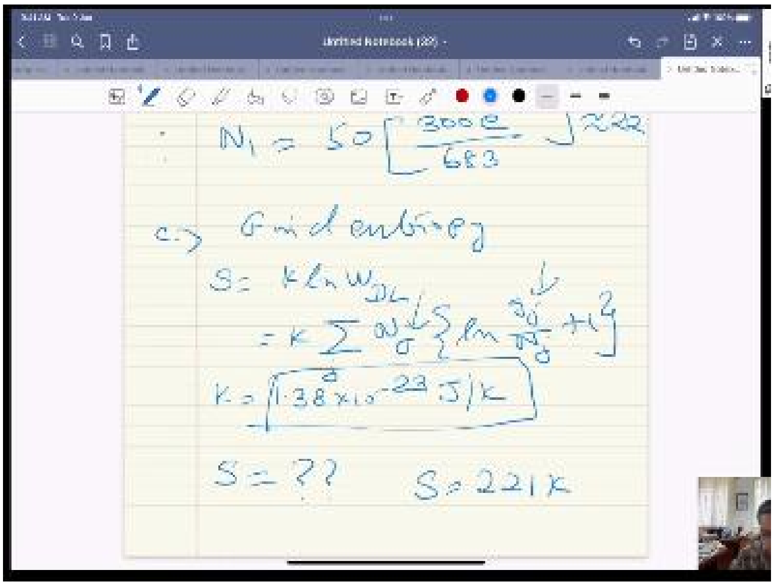

$N_1 = 50\left[\frac{300e}{683}\right] \approx 22$

c.> Find entropy

$S = k \ln W_{DL}$

$= k \sum_j N_j \left\{\ln \frac{g_j}{N_j} + 1\right\}$

$k = \boxed{1.38 \times 10^{-23}\ J/K}$

$S = ??$ $S = 221\,k$

So, the last one is to say say find entropy of such a system so the entropy as we know is S, k ln this is the dilute- limit so this means k summation over j, N sub j, ln g sub j by n sub j plus 1. So, here we came as we know is 1.38 into 10 to the power of minus 23 joules per Kelvin.

So, S we can calculate from here, so, because you know that different N sub j's now from the previous example g sub j's are known. So, this should be a fairly straightforward piece of calculation which will give you the total value of entropy. So, if you do it properly this will be S is equal to 221 k where k value is this. So, you can find out what will be the total value. So, this is one example by which you can work out a problem given the tools that you have learned.

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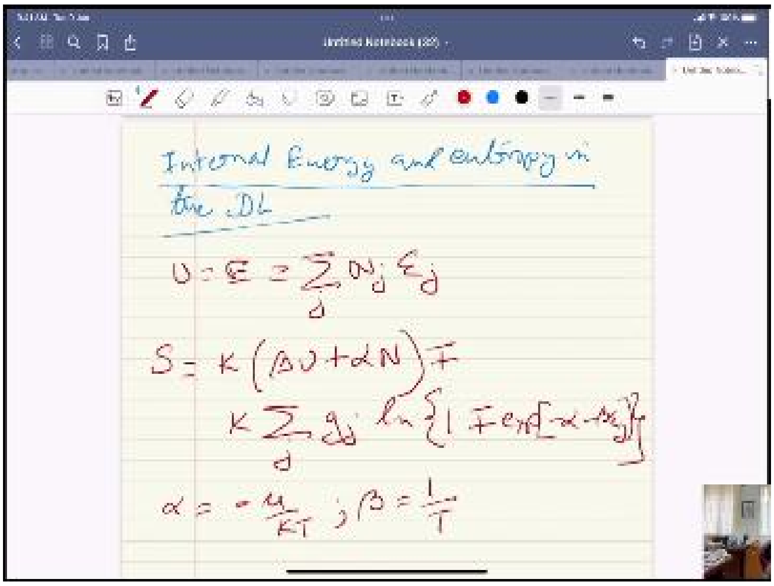

Internal Energy and entropy in the DL

$$U = E = \sum_j n_j \epsilon_j$$

$$S = k(\beta U + \alpha N) \mp k \sum_j g_j \ln\{1 \mp \exp[-\alpha - \beta\epsilon_j]\}$$

$$\alpha = -\frac{\mu}{kT}; \beta = \frac{1}{T}$$

So, now let us find out a few other things that internal energy and entropy and entropy in the dilute limit. So, as we know U is equal to E is equal to summation over j, N sub j, e sub j. So, S will be equal to k beta U plus alpha N minus plus k summation over j, g sub j, ln 1 minus plus exponential minus alpha minus beta e sub j. Where alpha as we know is minus Mu by kT whereas beta is equal to 1 over T. This is already known so this is the total expression that we have.

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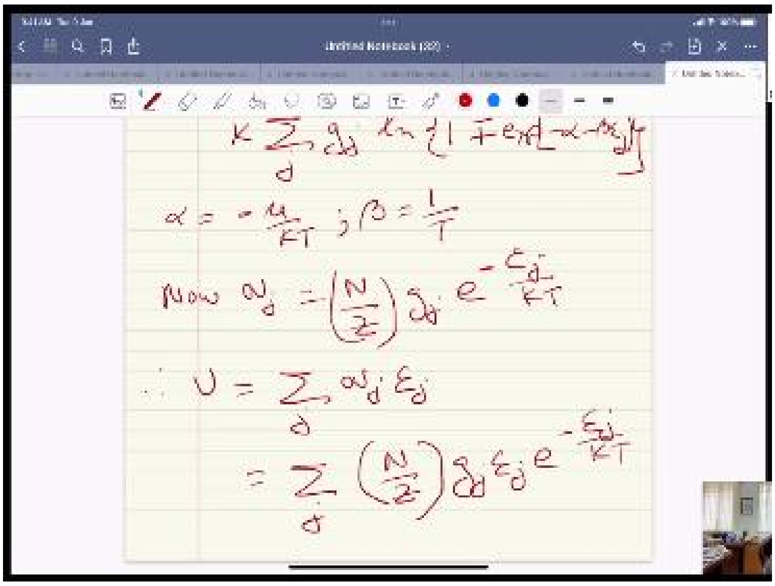

$$k \sum_j g_j \ln\{1 \mp \exp[-\alpha - \beta\epsilon_j]\}$$

$$\alpha = -\frac{\mu}{kT}; \beta = \frac{1}{T}$$

Now $n_j = \left(\frac{N}{Z}\right) g_j e^{-\frac{\epsilon_j}{kT}}$

$$\therefore U = \sum_j n_j \epsilon_j$$

$$= \sum_j \left(\frac{N}{Z}\right) g_j \epsilon_j e^{-\frac{\epsilon_j}{kT}}$$

So, now NJ is equal to N by Z, g sub j exponential minus e sub j by kT. So, therefore U will be equal to summation of J as we know NJ, e sub j. So, this will be then equal to J, N by Z that is a partition function g sub j, e sub j exponential e sub j by kT.

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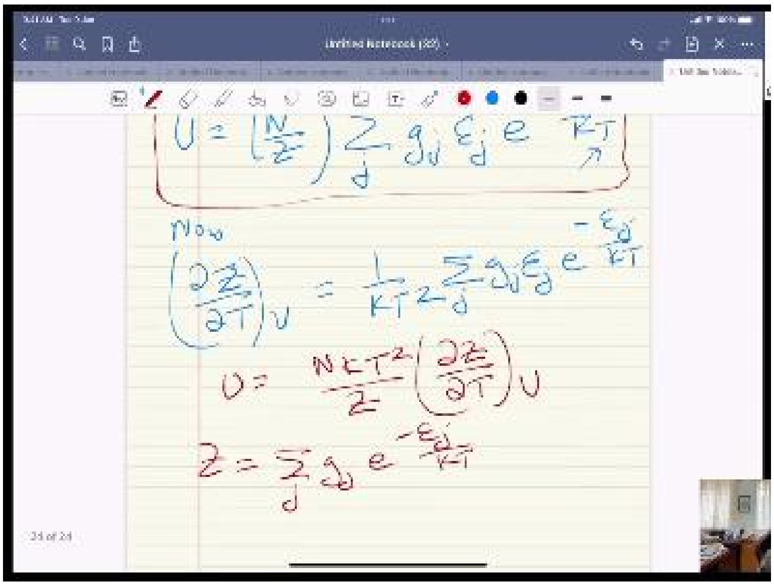

$$U = \left(\frac{N}{Z}\right)\sum_j g_j \epsilon_j e^{\frac{\;}{kT}}$$

Now

$$\left(\frac{\partial Z}{\partial T}\right)_V = \frac{1}{kT^2}\sum_j g_j \epsilon_j e^{-\frac{\epsilon_j}{kT}}$$

$$U = \frac{NkT^2}{Z}\left(\frac{\partial Z}{\partial T}\right)_V$$

$$Z = \sum_j g_j e^{-\frac{\epsilon_j}{kT}}$$

So, in other words in other words U, U is given as N over Z summation over J, g sub j, e sub j exponential minus e sub j by kT. So, this is U in terms of the partition function the total number of particles, the degeneracies, the energy level values and the temperature.

So, this is the form of U now as we know DZ by partialT at constant volume can be written as 1 over kT square summation over J, g sub j, e sub j exponential minus e sub j by kT. So, now U therefore because if you look at the terms U can therefore be written as NkT square by Z into DZ by partialT at constant V. Z we already know, Z was given as summation over j, g sub j exponential minus e sub j by kT.

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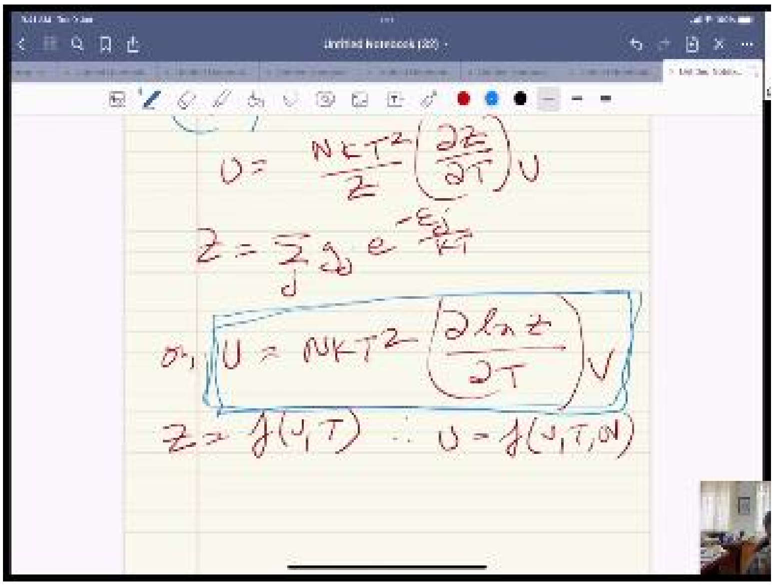

$$U = \frac{NkT^2}{Z}\left(\frac{\partial Z}{\partial T}\right)_V$$

$$Z = \sum_j g_j e^{-\varepsilon_j/kT}$$

$$\text{or, } \boxed{U = NkT^2\left(\frac{\partial \ln Z}{\partial T}\right)_V}$$

$$Z = f(V,T) \quad \therefore \quad U = f(V,T,N)$$

So, it can also be written as say U can further be written as NkT square Z by partialT at constant V. So, this provides the first explanation of U so Z is a function of V comma T so therefore U is a function of V, T, N.

So, we know this so this is how you calculate if you are given the partition function this is how you calculate the value of U. So, this is how you calculate the value of the internal energy.

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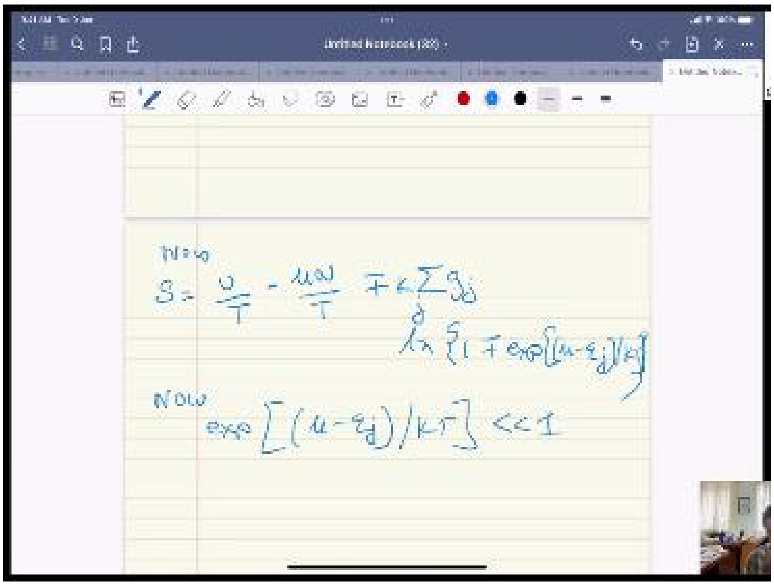

Now

$$S = \frac{U}{T} - \frac{\mu N}{T} \mp k\sum_j g_j \ln\left\{1 \mp \exp\left[(\mu-\varepsilon_j)/kT\right]\right\}$$

Now

$$\exp\left[(\mu-\varepsilon_j)/kT\right] << 1$$

Now, now let us put as S is equal to U by T minus Mu N by T minus plus this is also known we have done it before so j, g sub j, g sub j ln, 1 minus plus exponential Mu minus e sub j by kT. Now, exponential Mu minus e sub j by kT is much much less than 1.

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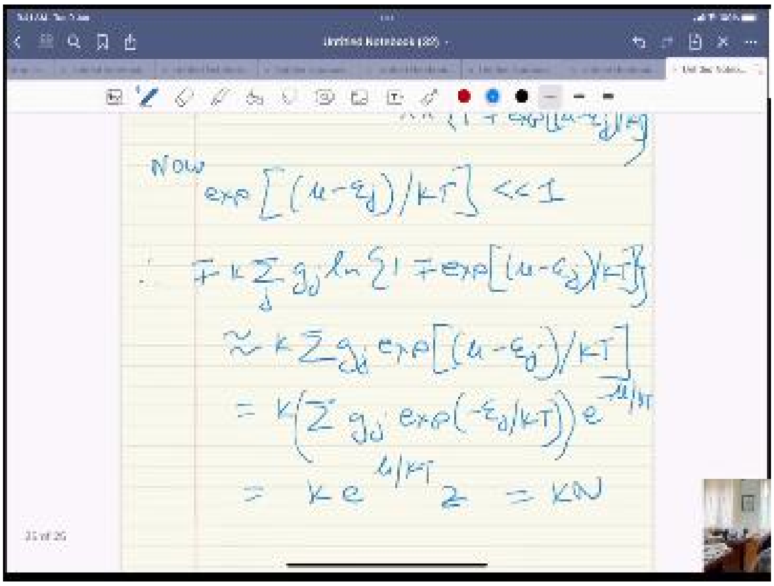

Now

$$\exp[(\mu-\epsilon_j)/kT] << 1$$

$$\mp k\sum_j g_j \ln\{1 \mp \exp[(\mu-\epsilon_j)/kT]\}$$

$$\approx k\sum g_j \exp[(\mu-\epsilon_j)/kT]$$

$$= k\left(\sum g_j \exp(-\epsilon_j/kT)\right) e^{-\mu/kT}$$

$$= k e^{\mu/kT} Z = kN$$

So, therefore if that is the case minus plus k summation j, g sub j ln 1 minus plus exponential Mu minus e sub j by kT. It is almost equal to k summation g sub j exponential Mu minus e sub j by kT. This is further equal to k, g sub j exponential minus e sub j by kT, e to the power of minus Mu by kT this is equal to k e to the power Mu by kT into Z which is equal to kN.

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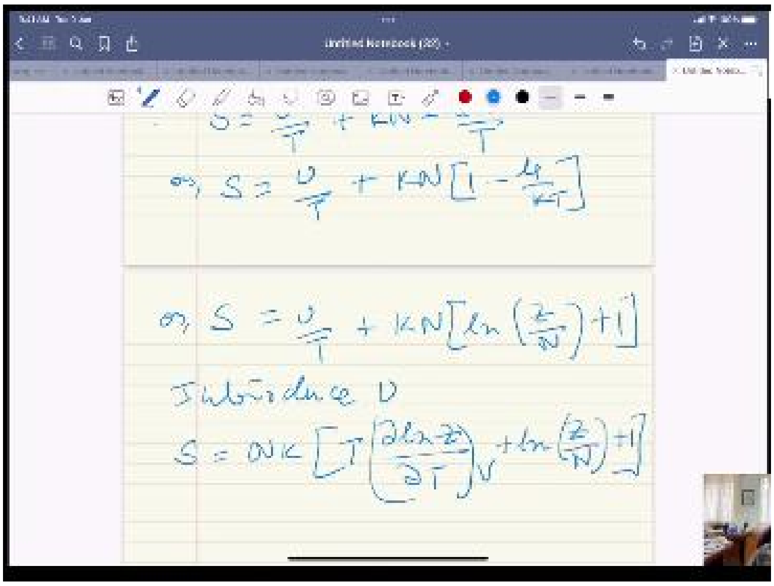

or, $S = \frac{U}{T} + kN\left[1 - \frac{\mu}{kT}\right]$

or, $S = \frac{U}{T} + kN\left[\ln\left(\frac{Z}{N}\right) + 1\right]$

Introduce U

$$S = Nk\left[T\left(\frac{\partial \ln Z}{\partial T}\right)_V + \ln\left(\frac{Z}{N}\right) + 1\right]$$

So, therefore S is equal to U by T plus kN one minus Mu by kT or S is equal to U by T plus kN 1 minus Mu by kT. Or further or (())(11:50) U by T Plus kN into ln Z over N Plus 1. So, if you introduce U now U therefore S becomes equal to NK, T, D ln Z by partialT, V plus ln, Z over N plus 1.

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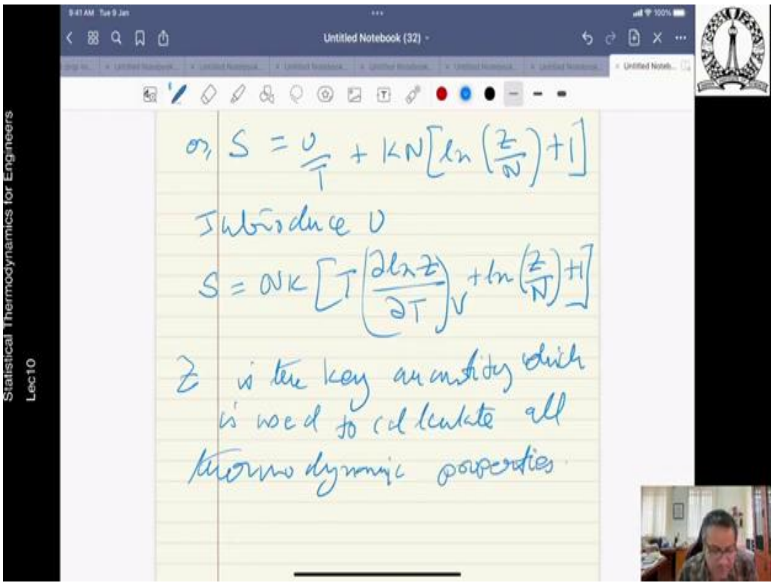
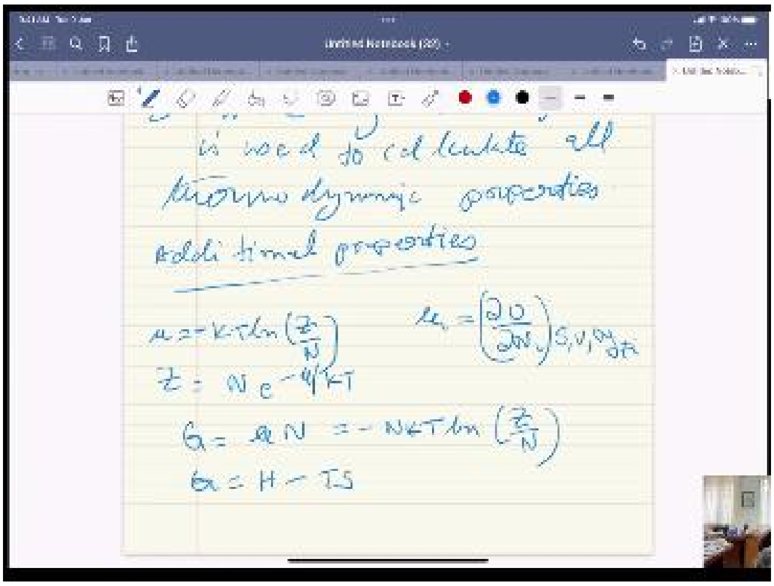


or, $S = \frac{U}{T} + kN\left[\ln\left(\frac{Z}{N}\right)+1\right]$

Introduce U

$S = Nk\left[T\left(\frac{\partial \ln Z}{\partial T}\right)_V + \ln\left(\frac{Z}{N}\right)+1\right]$

Z is the key quantity which is used to calculate all thermodynamic properties



is used to calculate all thermodynamic properties

additional properties

$\mu = -kT\ln\left(\frac{Z}{N}\right)$ $\mu_i = \left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_{j\neq i}}$

$Z = N e^{-\mu/kT}$

$G = \mu N = -NkT\ln\left(\frac{Z}{N}\right)$

$G = H - TS$

So, as we can see Z is the key quantity quantity which is used which is used to calculate calculate all thermodynamic properties all thermodynamic properties. So, Z is a very key advantage so, if that we calculated U, we calculated S, now we can do some additional properties too.

So, as you can see that all the properties so Z was a function of what it was a function of the micro states it was dependent on the degeneracy it was dependent on the on the energy values it was dependent also on temperature.

So, now what we have done is that all these macroscopic properties like U, S and we will see some more. They are all can be cast in terms of this partition function, molecular partition function and the molecular partition function was once again dependent on the most probable distribution.

So, all these factors you can see the interlinking so Z is a stat thermal concept and how we have used it to calculate different macroscopic properties, different macroscopic thermodynamic properties.

So, for example Mu can be written as minus kT, ln Z over N. Z is equal to NE minus U by kT. So, this is 1 so Mu I is equal to del U by del N I. For example, where you have S V NJ not equal to I. Similarly, we can also have G the Gibbs is equal to minus NkT, ln, Z over N, G is further given as H minus TS.

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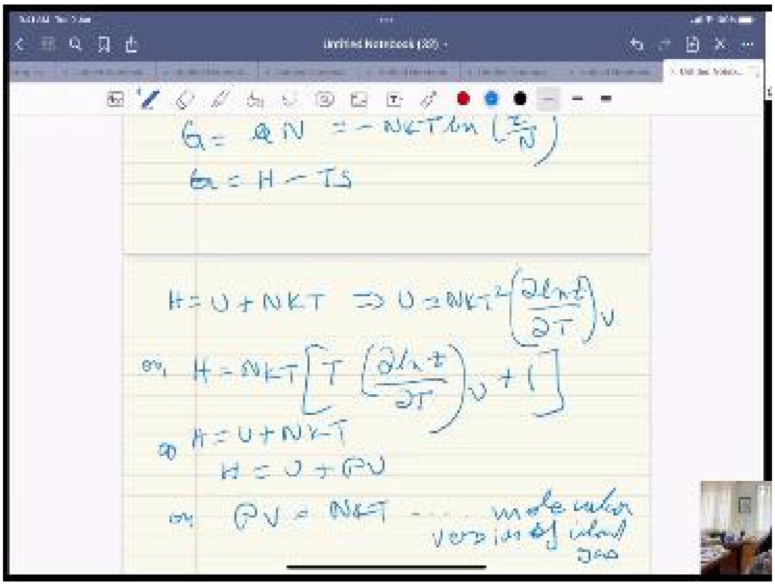

$G = \mu N = -NkT \ln\left(\frac{Z}{N}\right)$

$G = H - TS$

$H = U + NkT \Rightarrow U = NkT^2\left(\frac{\partial \ln Z}{\partial T}\right)_V$

or $H = NkT\left[T\left(\frac{\partial \ln Z}{\partial T}\right)_V + 1\right]$

or $H = U + NkT$

$H = U + PV$

or $PV = NkT$ …… molecular version of ideal gas

So, H is further written as U plus NkT. Now, U we already found out it is NkT square partial ln Z by partialT at constant V or in other words H is equal to NkT T D ln Z by partialT at V plus 1. So, as you can see now from this you can cast it in other, so this is this is the value of H.

So, H is also written as U plus PV or PV is equal to NkT. Because H here can be written as U plus NkT. So, this is like the molecular version of the ideal gas, version of ideal gas, ideal gas.

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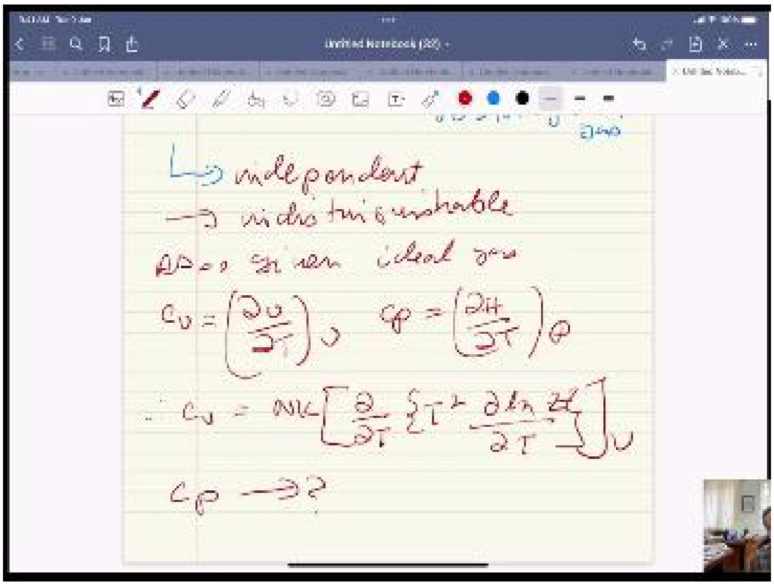

↳ independent

→ indistinguishable

Also given ideal gas

$C_V = \left(\frac{\partial U}{\partial T}\right)_V \quad C_P = \left(\frac{\partial H}{\partial T}\right)_P$

$\therefore C_V = NK\left[\frac{\partial}{\partial T}\left\{T^2 \frac{\partial \ln Z}{\partial T}\right\}\right]_V$

$C_P \rightarrow ?$

So, this is assumes once again if you recall that these are independent independent and they are indistinguishable remember the mistake that Boltzmann made for the Boltzons. Also, also given ideal gas if you consider it as ideal gas then of course what we can write is CV is equal to DU by partialT that is constant V and CP is equal to DH by partialT, P.

So, therefore CV can be written as NK is the differential T square D ln Z divided by partialT. And all these are computed at constant V so you can find out CP in the same way. So, as we can see so that is left as a kind of like a homework problem that you can find out CP in the same way.

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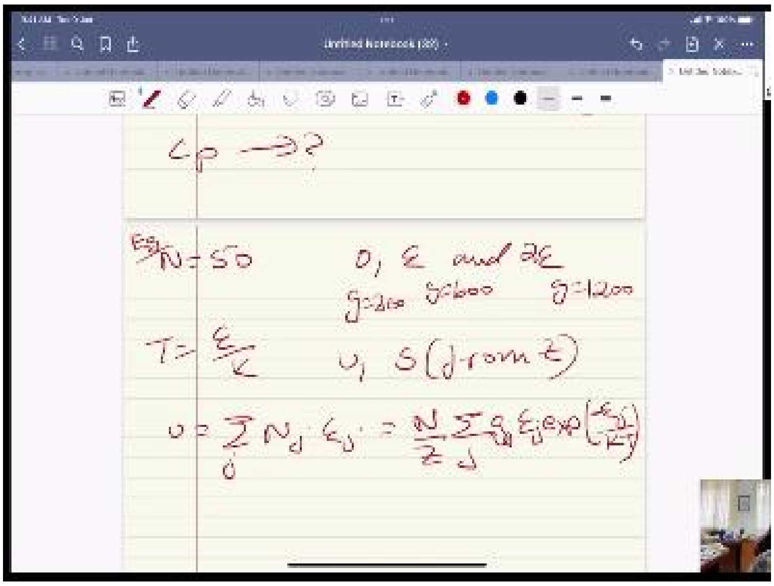

$C_p \longrightarrow ?$

Eg $N = 50$ $\quad 0,\ \varepsilon$ and 2ε

$g = 300 \quad g = 600 \quad g = 1200$

$T = \frac{\varepsilon}{k}$ $\quad U,\ S$ (from Z)

$$U = \sum_j N_j \varepsilon_j = \frac{N}{Z} \sum_j g_j \varepsilon_j \exp\left(\frac{-\varepsilon_j}{kT}\right)$$

Now let us do a small practice problem, so, again we assume that N is equal to 50. This this is a this is an example, now N is equal to 50. There are three energy levels once again that is 0, E and 2E and this is once again G300 we are taking the same example G is equal to 600 and G is equal to 1200, temperature is given by E by K well our task is to find out U and S. S, this would be from Z. So, solution is U is summation of NJ, e sub j. So, this is given as N over Z summation over J, g sub j, e sub j exponential minus e sub j by kT.

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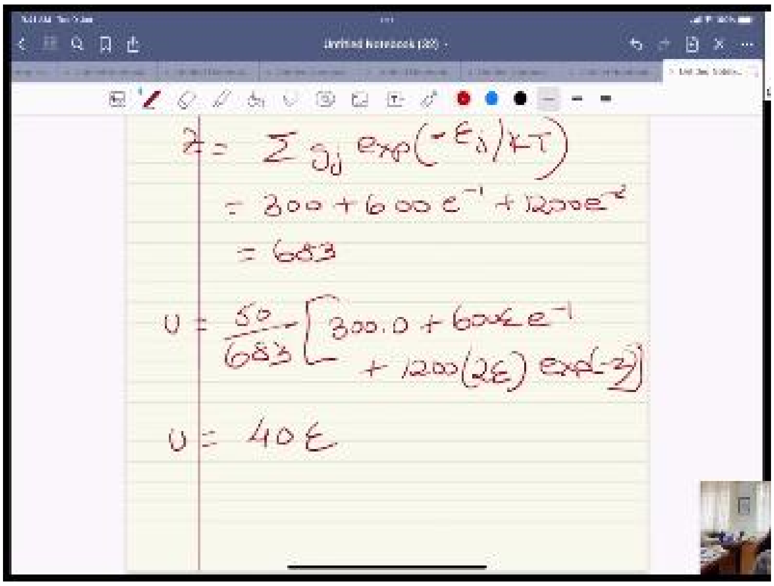

$$Z = \sum g_j \exp(-\varepsilon_j/kT)$$

$$= 300 + 600\, e^{-1} + 1200\, e^{-2}$$

$$= 683$$

$$U = \frac{50}{683}\left[300.0 + 600\varepsilon\, e^{-1} + 1200(2\varepsilon)\exp(-2)\right]$$

$$U = 40\varepsilon$$

So, Z is equal to summation g sub j exponential minus e sub j by kT which is equal to 300 plus 600 E to the power minus 1 plus 1200 E to the power of minus 2 is equal to 683. So, U is equal to then 50 by 683 N is N is 50.

Now, you plug in the values so 300 into 0 plus 600 into E into exponential minus 1 plus 1200 into 2E exponential minus 2. So, that is the whole thing so U becomes equal to if you plug in all the numbers is 40E.

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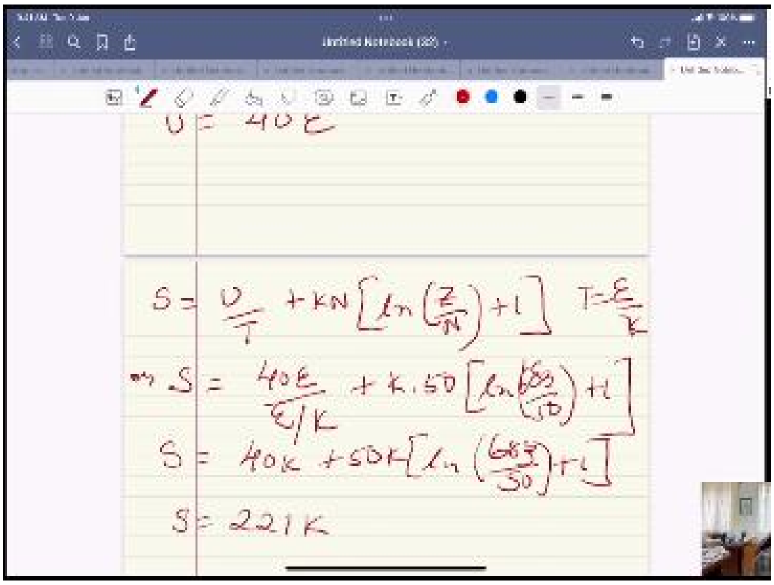

$U = 40E$

$S = \frac{U}{T} + kN\left[\ln\left(\frac{Z}{N}\right)+1\right] \quad T = \frac{E}{k}$

$\Rightarrow S = \frac{40E}{E/k} + k.50\left[\ln\left(\frac{683}{50}\right)+1\right]$

$S = 40k + 50k\left[\ln\left(\frac{683}{50}\right)+1\right]$

$S = 221k$

Similarly, if we go to the next one you will find that S is equal to U over T plus kN, ln, Z over N plus 1 T is equal to epsilon by K, or S is equal to 40 E by E by K plus K into 50 ln, this is 683 divided by 50 plus 1. So, S is equal to 40 K plus 50 K into ln 683 by 50 plus 1. So, S becomes 221 K. So, this is this was found out in terms of the partition function.

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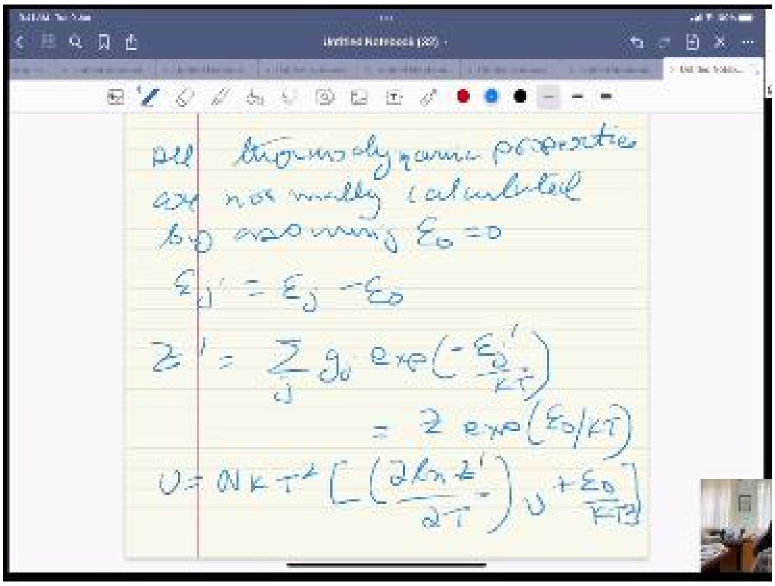

all thermodynamic properties
are normally calculated
by assuming $\varepsilon_0 = 0$

$$\varepsilon_j' = \varepsilon_j - \varepsilon_0$$

$$Z' = \sum_j g_j \exp\left(-\frac{\varepsilon_j'}{kT}\right)$$

$$= Z \exp(\varepsilon_0/kT)$$

$$U = NkT^2\left[\left(\frac{\partial \ln Z'}{\partial T}\right)_V + \frac{\varepsilon_0}{kT^2}\right]$$

So, thermodynamics so, all thermodynamic properties are normally calculated by assume all thermodynamic properties, dynamic properties properties are calculated normally calculated calculated by assuming E naught is equal to 0.

So, any properties is dependent on the choice of E naught so e sub j for example is e sub j minus E naught. So, therefore Z prime we define it like that is J just hold on what this means exponential minus e sub j prime by kT is equal to equal to Z Exponential E naught by kT. So, this is how we define Z prime. Similarly, U can be written as NkT square as we know already so, this is ln Z prime by delta T V plus E naught divided by kT square.

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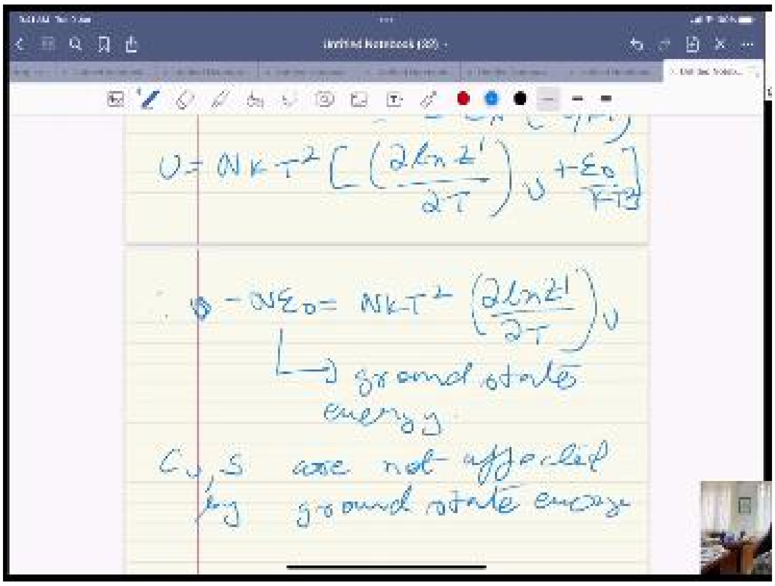

$$U = NkT^2\left[\left(\frac{\partial \ln Z'}{\partial T}\right)_V + \frac{\varepsilon_0}{kT^2}\right]$$

$$\therefore U - \underbrace{N\varepsilon_0}_{\text{ground state energy}} = NkT^2\left(\frac{\partial \ln Z'}{\partial T}\right)_V$$

C_V, S are not affected by ground state energy

So, therefore, U minus U minus NE naught is equal to NkT square D ln Z prime divided by partialT at constant V. So, this is this is like what we called a ground state ground state energy. So, CV S are not affected are not affected affected by ground state energy, by ground state energy.

As you can see they are not affected by ground state energy but, U is U is affected.

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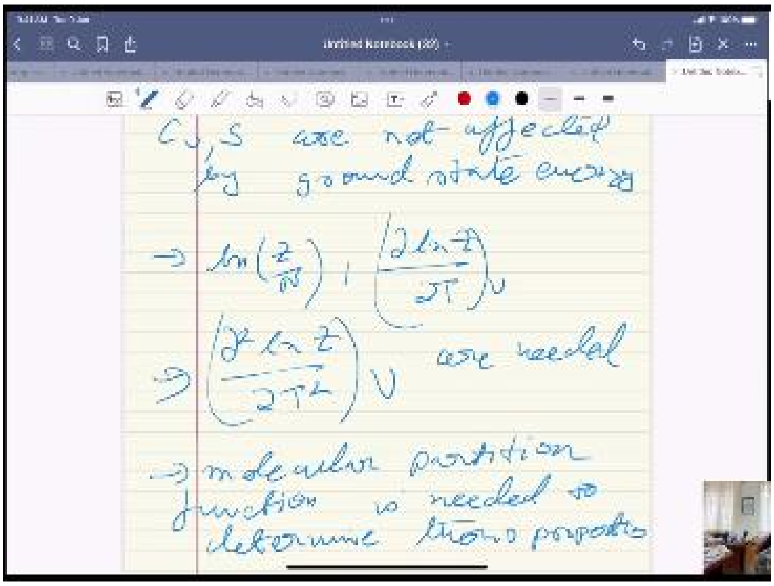

C_V, S are not affected by ground state energy

$\rightarrow \ln\left(\frac{Z}{N}\right), \left(\frac{\partial \ln Z}{\partial T}\right)_V$

$\rightarrow \left(\frac{\partial^2 \ln Z}{\partial T^2}\right)_V$ are needed

→ molecular partition function is needed to determine thermo properties

So, what we need for calculating any of these quantities is ln Z over N this is one term, then lnZ, partialT constant V, D square ln Z by partialT square and constant V, these are the properties which are basically needed.

If you want to calculate all the numbers, all the thermodynamic properties that are concerned over here. So, the idea is now, now that we know a lot about what these quantities are all about so, the molecular we can see common thing is that molecular partition function partition function function is needed is needed to determine to determine thermodynamic properties, thermal properties. It is needed for determining the thermodynamic properties.

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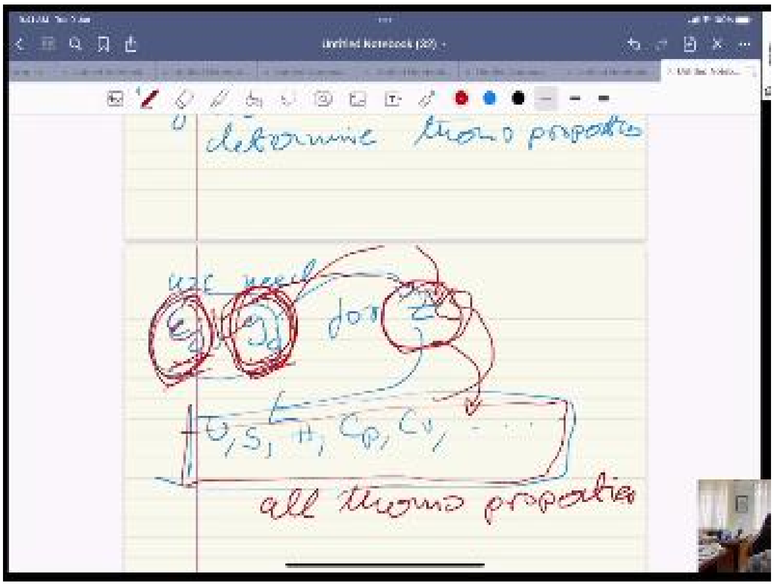

So, we need for example we need e sub j and g sub j for calculating Z which further once you know these two you can calculate this and this further allows you to calculate U, S, H, C sub p, C sub v etc etc. So, all macroscopic properties as we saw can be calculated from the partition function, partition function is further determined by the degeneracy and the energy of each energy level.

So, how do you calculate these two is the fundamental question. Because once these two are calculated you can calculate the molecular partition function, once you know the molecular partition function all the thermodynamic all the thermodynamic properties can be calculated at the macro scale but the question is, how to determine Z? Because Z is determined, is dependent on g sub j and e sub j. So, who gives you the value of degeneracy? And who gives you the value of your energy?

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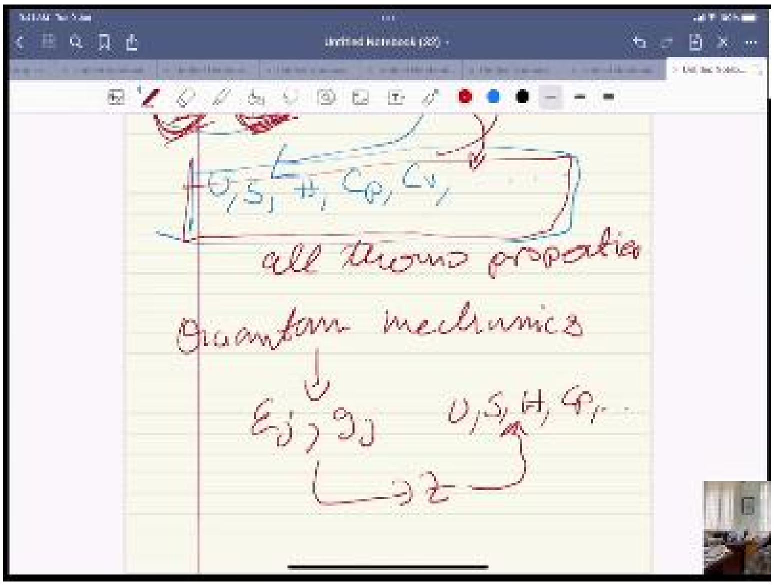

So, this will require an understanding of quantum mechanics. So, this is what we are going to do next that quantum mechanics is needed to calculate your e sub j and g sub j and this will be further needed to calculate Z. Z will be further needed to calculate U, S etc etc H, and you know C sub p all the other thermodynamic properties that you require for any calculations as such.

So, the requirement is now we need to shift gears and go and delve that we know the statistical thermodynamics framework now. We now know how to use statistical thermodynamics to calculate macroscopic properties. We also know how the distributions of particles actually determine the final outcome of the properties.

And we know that if you average it over an assembly of particles you would essentially get all the all the properties that you can hope for. Only thing is that so far we have started that we know e sub j we know g sub j. So, somebody is providing with those values. So, who that somebody is that comes from your quantum mechanical calculations per se.

So, that is what we are going to do in the next lecture. So, in this particular lecture we have covered a lot. We have covered a couple of sample problems for example, we have also determined how specific quantities can be extracted from the partition function like internal energy and entropy especially in the dilute limit.

How they can be extracted easily from the partition function and partition function provided that you give the values of these and the degeneracy values. So, like that but we have developed a framework by which we can evaluate all these terms, all this macroscopic property with ease.

Now, the point remains that how to calculate? How to go the next step and find out that how this microscopic properties can evolve from a quantum mechanical perspective? So, you saw how the molecular partition function is cornerstone in these particular calculations in these particular calculations.

So, in the next, from the next class onwards we are going to start looking at quantum mechanics and we are going to see that how so far we have done a lot of statistics a lot of analysis.

Now, we are going to do something on the quantum mechanics and see that what can be the how we can calculate these energy levels and the degeneracies that comes out of it? So, (())(27:14) schrodinger wave equation etc will come in very handy. So, we end this lecture 10 and we will see you in lecture 11. Thank you.