Statistical Thermodynamics for Engineers
Professor Saptarshi Basu
Indian Institute of Science, Bengaluru
Lecture 35
Supplementary Video 11 Problem Solving 3

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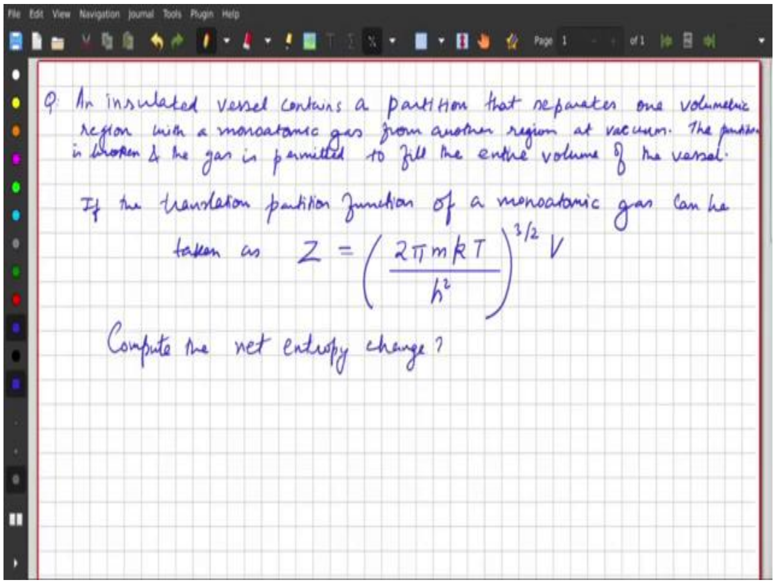
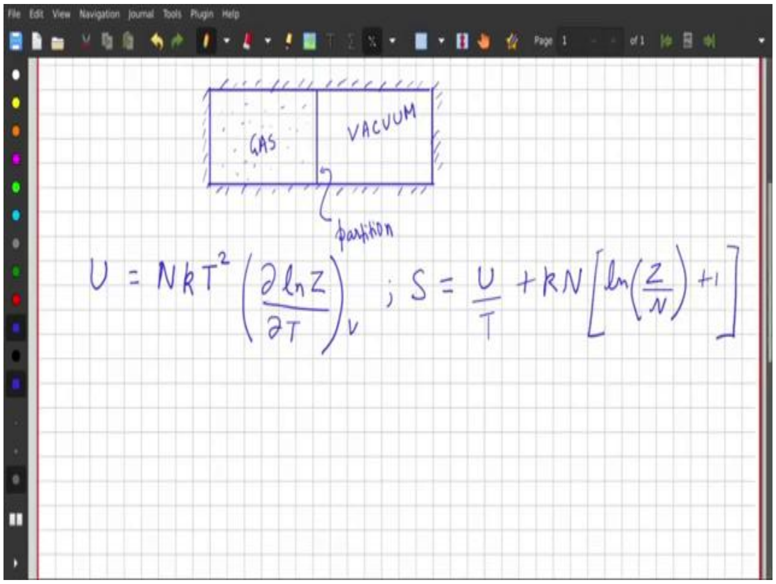


Q. An insulated vessel contains a partition that separates one volumetric region with a monoatomic gas from another region at vacuum. The partition is broken & the gas is permitted to fill the entire volume of the vessel.

If the translation partition function of a monoatomic gas can be taken as $Z = \left(\frac{2\pi m k T}{h^2}\right)^{3/2} V$

Compute the net entropy change?



$$U = NkT^2\left(\frac{\partial \ln Z}{\partial T}\right)_V \; ; \; S = \frac{U}{T} + kN\left[\ln\left(\frac{Z}{N}\right) + 1\right]$$

Hello, everyone, welcome to another session of supplementary videos for the course statistical thermodynamics for engineers and we will be continuing our problem-solving sessions. So, let us start with the problem that we want to tackle and the problem that we will be solving is let me write (())(00:32) state problem statement first. So, the question is an insulated vessel contains a partition that separates one volumetric region with a mono atomic gas from another region at vacuum partition is broken and the gas is permitted to fill the entire volume the vessel and there is something which is given.

So, the given is if the translational partition function of monatomic gas can be taken as Z equals 2 pi m multiples constant density (())(03:05) divided Planck's constant square power 3 half's V. So, that is the translation partition function for the monatomic gas and given that the question is compute the net entropy change during the process.

So, let us draw the schematic of the situation we are dealing with so, let us say this is the container that we have vessel that (())(03:51). So, this is an insulated vessel and this is insulated that means the vessel cannot exchange either matter nor energy from anywhere outside this vessel so it is a isolated system its given. And part and there is a partition in between and one side contains a gas monoatomic gas this is filled with monoatomic gas, this is vacuum.

And what we do is? We removed the partition. So, this is the partition if we remove the partition and the gas fills up the entire vessel. And you see this is a non-equilibrium process and moment you remove the partition the gas will distribute uniformly throughout the entire volume and the question is during this entire process when the partition is removed, calculate the total entropy change. So, that is a classic problem in thermodynamics and we will be tackling and solving this problem in 2 ways.

So, let us do it first using the partition function using statistical thermodynamics. So, if you recall, the internal energy let us say U is given by in terms of the partition function is given by N Boltzmann constant T square times the partial of the logarithm of the partition function with respect temperature at constant volume.

That you recall from our lectures the main lectures from where we saw how partition how important partition function is and partition function helps us to compute all other thermodynamic quantities. So, this is the internal energy and similarly, the entropy is given by the relation U over T plus kN (())(06:15) of the partition function than over particles plus 1. So, those are the internal energy and the entropy in terms of the partition function and its given. So, what is given?

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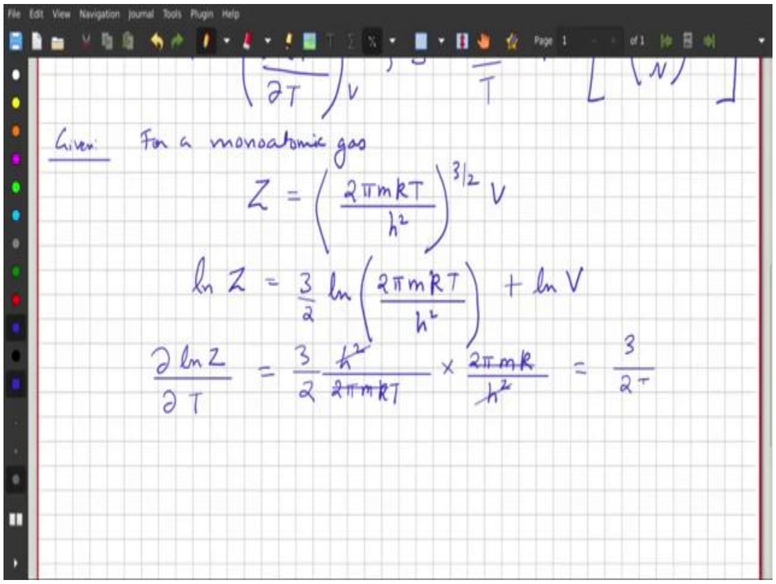
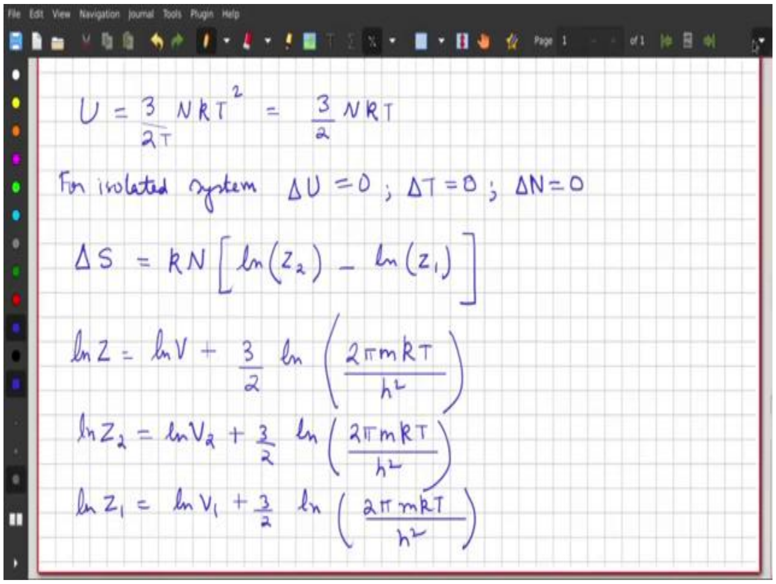


Given: For a monoatomic gas

$$Z = \left(\frac{2\pi m k T}{h^2}\right)^{3/2} V$$

$$\ln Z = \frac{3}{2} \ln\left(\frac{2\pi m k T}{h^2}\right) + \ln V$$

$$\frac{\partial \ln Z}{\partial T} = \frac{3}{2} \frac{\cancel{h^2}}{\cancel{2\pi m k} T} \times \frac{\cancel{2\pi m k}}{\cancel{h^2}} = \frac{3}{2T}$$



$$U = \frac{3}{2T} N k T^2 = \frac{3}{2} N k T$$

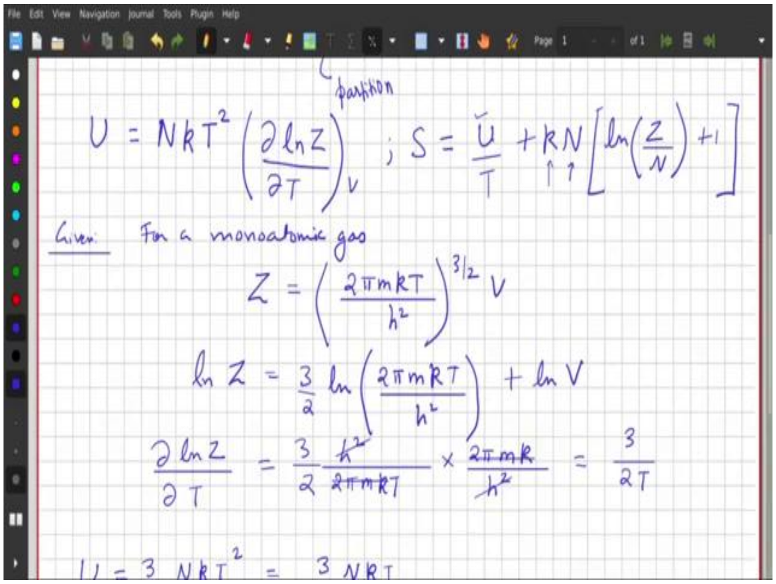
For isolated system $\Delta U = 0$; $\Delta T = 0$; $\Delta N = 0$

$$\Delta S = kN \left[\ln(Z_2) - \ln(Z_1)\right]$$

$$\ln Z = \ln V + \frac{3}{2} \ln\left(\frac{2\pi m k T}{h^2}\right)$$

$$\ln Z_2 = \ln V_2 + \frac{3}{2} \ln\left(\frac{2\pi m k T}{h^2}\right)$$

$$\ln Z_1 = \ln V_1 + \frac{3}{2} \ln\left(\frac{2\pi m k T}{h^2}\right)$$



partition

$$U = NkT^2\left(\frac{\partial \ln Z}{\partial T}\right)_V \; ; \; S = \frac{\breve{U}}{T} + \overset{\uparrow}{k}\overset{\uparrow}{N}\left[\ln\left(\frac{Z}{N}\right) + 1\right]$$

Given: For a monoatomic gas

$$Z = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V$$

$$\ln Z = \frac{3}{2}\ln\left(\frac{2\pi mkT}{h^2}\right) + \ln V$$

$$\frac{\partial \ln Z}{\partial T} = \frac{3}{2}\frac{\cancel{h^2}}{\cancel{2\pi mk}T} \times \frac{\cancel{2\pi mk}}{\cancel{h^2}} = \frac{3}{2T}$$

$$U = 3\ NkT^2 = 3\ NkT$$

Given the for a monoatomic gas we have the partition function as 2 pi m kT whole divided by x square power 3 half's V. Let us take, so, in order to take the derivative (())(06:57) the log logarithm of both sides the natural logarithm logs Z is 3 half log 2 pi m kT by h square plus log V and you see if we differentiate this with respect to temperature. So, derivative of logs Z partial derivative with respect to temperature is given by 3 half derivative of log is 1 over that thing.

So, this becomes h square divided by 2 pi m kT times the derivative of the argument of the logarithm. So, that becomes 2 pi m k by h square and the derivative of T with respect to T is 1. So basically, square square gets cancel and we are left with 2 pi mk gets cancel 2 pi mk gets cancel left with 3 over 2T.

So, the internal energy becomes 3 over 2T that is the partial derivative of log Z with respect to T multiplied by N Boltzmann's constant T square. So, this simplifies to 3 over 2 N Boltzmann's constant T the internal energy given (())(08:58) T or the particles now. Since this is an isolated system hence for isolated system there is no energy exchange either in form of matter or in terms of work done or heat.

So, therefore, the internal energy change as you can see is 0 which tells us that the temperature change is 0 and says no matter exchange is occurring there is no change in the number of particles. So therefore, the entropy change if you see using the situation so if U does not change these T does not change, k Boltzmann's constant N does not change the only when entropy can change is when the partition function itself changes.

So therefore, delta S the change in entropy becomes kN log of Z2 minus log of Z1 that is the change in entropy in terms of the partition function and the logarithm (())(10:15) log Z is log V plus 3 half log 2 pi m kT by h square and if we do it for the 2 states N state comes V2 plus 3 half log 2 pi m kt by h square Z1 (())(10:53) log 2 pi m k T by h square.

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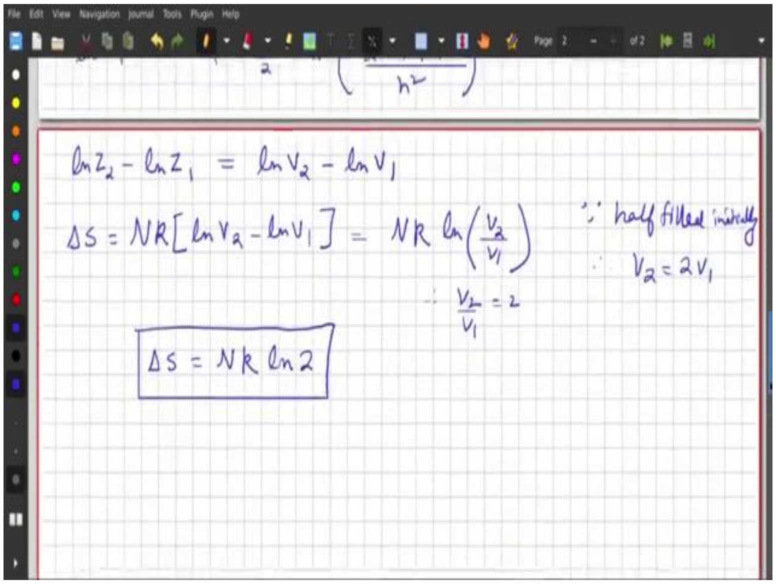

$$\ln Z_2 - \ln Z_1 = \ln V_2 - \ln V_1$$

$$\Delta S = Nk[\ln V_2 - \ln V_1] = Nk \ln\left(\frac{V_2}{V_1}\right)$$

$\because$ half filled initially

$\therefore V_2 = 2V_1$

$\therefore \frac{V_2}{V_1} = 2$

$$\boxed{\Delta S = Nk \ln 2}$$

And therefore, we have log Z2 minus log Z1 is nothing but log V2 minus log V1 therefore entropy changes it written as N Boltzmann's constant log V2 minus log V1 or it written as Nk log V2 over V1 and since it was initially half filled initially therefore, we have the V2 is twice of V1 therefore V2 by V1 is 2 so this becomes. Therefore the entropy (())(12:02) Nk log 2. So, that is the entropy change in terms of the number of particles Boltzmann's constant for the process that we were initially there was gas in half of the container and partition was separating it we break the partition the gas fills the entire vessel and entropy change is given by this.

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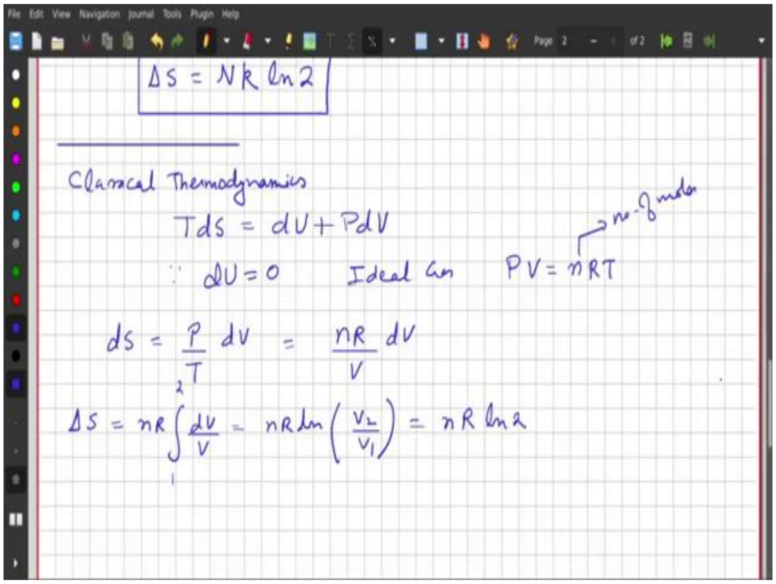


$$\boxed{\Delta S = Nk \ln 2}$$

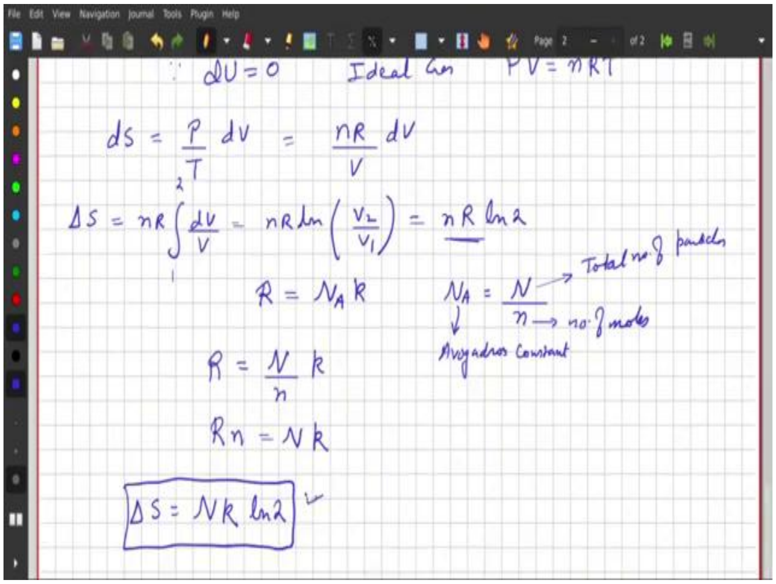
Classical Thermodynamics

$$TdS = dU + PdV$$

$\because dU = 0$ Ideal Gas $PV = nRT$ → no. of moles

$$dS = \frac{P}{T} dV = \frac{nR}{V} dV$$

$$\Delta S = nR \int_1^2 \frac{dV}{V} = nR \ln\left(\frac{V_2}{V_1}\right) = nR \ln 2$$



$\therefore dU = 0$ Ideal Gas $PV = nRT$

$$dS = \frac{P}{T} dV = \frac{nR}{V} dV$$

$$\Delta S = nR \int_1^2 \frac{dV}{V} = nR \ln\left(\frac{V_2}{V_1}\right) = \underline{nR \ln 2}$$

$R = N_A k$

$N_A = \frac{N}{n}$, N → Total no. of particles, n → no. of moles

N_A ↓ Avogadros Constant

$$R = \frac{N}{n} k$$

$$Rn = Nk$$

$$\boxed{\Delta S = Nk \ln 2} \checkmark$$

Let us, see whether we can come to a similar expression from classical thermodynamics point of view. Let us say from classical thermodynamics let us use the tedious equation is given by dU plus PdV and since dU is 0, some isolated system and (())(12:58) ideal gas, PV is equal to nRT and this is the number of moles and the ideal gas law.

So, using this we can write dS becomes P over T dV and P over T invert nR by V dV therefore delta is equal to nr dV by V from 1 to 2 (())(13:42) nr log 2 by V1 and just now we saw V2 by V1 is 2, this is nr log 2. Realizing the fact that the universal gas constant can be written in terms of the Avogadro's number NA times the Boltzmann constant k and Avogadro's number as N divided by the number of moles, this is the number of moles. This as the total number of particles and this is Avogadro's number draws constant.

As using this what we have is NA R can be written capital N by small n times k R times small n times k (())(15:03) see it here we had nR but nR we saw same as Nk that means delta S Nk 2. You recall from statistical thermodynamics we come up this similar with this. So, that gives us the expression for the total entropy change during the expansion process. When the gas occupied initially half volume and then expanded after the removal of the partition between.

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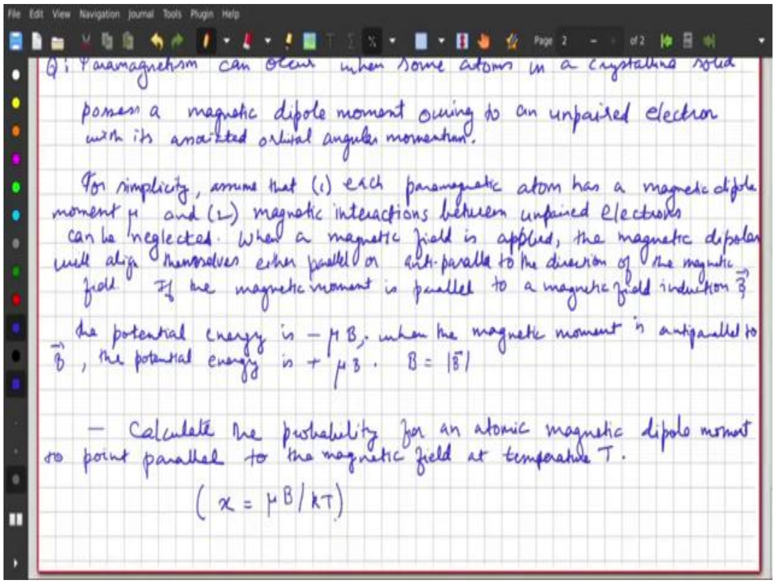
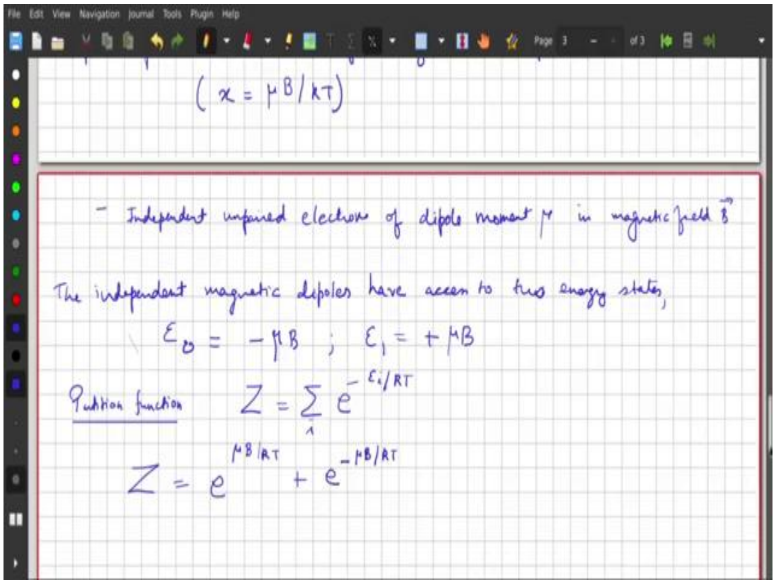


Q: Paramagnetism can occur when some atoms in a crystalline solid possess a magnetic dipole moment owing to an unpaired electron with its associated orbital angular momentum.

For simplicity, assume that (1) each paramagnetic atom has a magnetic dipole moment μ and (2) magnetic interactions between unpaired electrons can be neglected. When a magnetic field is applied, the magnetic dipoles will align themselves either parallel or anti-parallel to the direction of the magnetic field. If the magnetic moment is parallel to a magnetic field induction $\vec{B}$ the potential energy is $-\mu B$, when the magnetic moment is antiparallel to $\vec{B}$, the potential energy is $+\mu B$. $B = |\vec{B}|$

– Calculate the probability for an atomic magnetic dipole moment to point parallel to the magnetic field at temperature T.

$$(x = \mu B / kT)$$



$$(x = \mu B / kT)$$

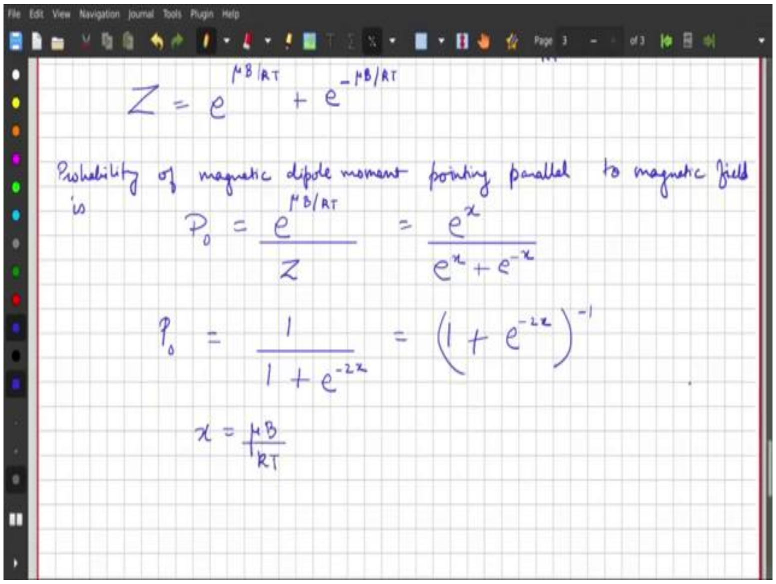
– Independent unpaired electron of dipole moment μ in magnetic field $\vec{B}$

The independent magnetic dipoles have access to two energy states,

$$\varepsilon_0 = -\mu B \; ; \; \varepsilon_1 = +\mu B$$

Partition function $\quad Z = \sum_i e^{-\varepsilon_i/RT}$

$$Z = e^{\mu B/RT} + e^{-\mu B/RT}$$



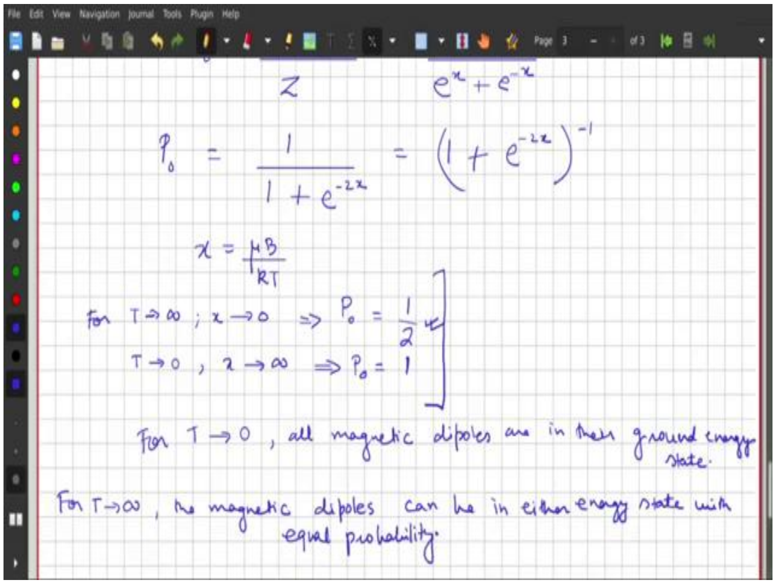
$$Z = e^{\mu B/RT} + e^{-\mu B/RT}$$

Probability of magnetic dipole moment pointing parallel to magnetic field is

$$P_0 = \frac{e^{\mu B/RT}}{Z} = \frac{e^{x}}{e^{x}+e^{-x}}$$

$$P_0 = \frac{1}{1+e^{-2x}} = \left(1+e^{-2x}\right)^{-1}$$

$$x = \frac{\mu B}{RT}$$



$$Z \qquad e^{x}+e^{-x}$$

$$P_0 = \frac{1}{1+e^{-2x}} = \left(1+e^{-2x}\right)^{-1}$$

$$x = \frac{\mu B}{RT}$$

For $T \to \infty$; $x \to 0$ $\Rightarrow P_0 = \frac{1}{2}$

$T \to 0$, $x \to \infty$ $\Rightarrow P_0 = 1$

For $T \to 0$, all magnetic dipoles are in their ground energy state.

For $T \to \infty$, the magnetic dipoles can be in either energy state with equal probability.

So, now we will be in the next problem. So, let us continue with another problem. So, the next problem is let me write down the question statement so this is related to paramagnetism can occur when some atoms in a crystalline possesses a magnetic dipole moment owing to go an unpaired electron with its associated orbital angular momentum. So, that is what paramagnetism is this is a concept in (())(17:56) matter physics and let me complete the problem statement.

So, for simplicity assume the number one each paramagnetic atom has a magnetic dipole moment mu and 2 magnetic interactions between unpaired electrons can be neglected therefore, when a magnetic field is applied the magnetic dipole will align themselves either parallel or anti parallel to the direction of the magnetic field.

So, let us say if the magnetic moment is parallel to a magnetic field induction B the potential energy is minus mu B and when the magnetic moment this anti-parallel to be the potential energy is plus mu B where B is magnetic field. The question is calculate the probability for an atomic magnetic dipole moment on to point parallel to the magnetic field at temperature T, is also given that we use this grouping x is mu B by kT.

So, let us see how we tackle this so, it is given in the problem that using the simplified assumptions that independent unpaired electrons of dipole moment mu in magnetic field B. The independent magnetic dipoles have access to 2 energy states there are 2 energy states. So, the independent magnetic dipoles have access to 2 energy states epsilon 0 that is minus mu times B and epsilon 1 that is plus mu times B.

So, let us go to the partition function Z is given sum over i e to the power minus epsilon i by k times T. So, therefore, the partition function Z becomes e to the power mu B by kT plus e power minus mu B by kT (())(25:52) therefore probability of magnetic dipole moment pointing parallel to magnetic field is given by P let us call that state 0 to its parallel.

Because when it is parallel as energy state of minus mu B (())(26:48) plus that corresponds to the 0th energy state which is this, this becomes e to the power mu B by kT, divided by the partition function and therefore, let use the grouping mu b kT call that x so, this becomes e to the x and the partition function therefore becomes e to the x plus e to the minus x.

And therefore, let us divide the numerator and denominator by e to the x this becomes 1 over 1 plus e to the minus 2x and therefore this can be written as 1 plus e to the minus 2x whole to the power minus 1, keep in mind x is the group mu B by kT. So, let us see, for let us say for T tends to infinity this means x tends to 0 and if x tends to 0 P0 this becomes 1 and P0 becomes half and let us say for t tends to 0 x tends to infinity and that implies P0 (())(28:29) this extends to infinity to the minus into this becomes 0. So, this becomes 1.

So, what the (())(28:36) limits of temperature is telling us is that for low very very low temperature that is for t tends to 0, all magnetic dipoles are in there lowest energy state that is in their ground energy state and for very high temperature limit that is t tends to infinity the magnetic dipoles can be in either energy state with equal probability, the probability that we computed was half with equal probability. And since there were 2 states the probability was half.

So, that is the end of this problem. So, you see very used to very important ideas the main idea was the computing the partition function. In most problems in statistical thermodynamics is related to computing the partition functions once you know the partition function, rest, everything follows basically from there. So, that is what we will be that is for the segment and we will be seeing you in next segment. Thank you.