Introduction To Statistical Mechanics

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Lecture - 21
Tutorial - III

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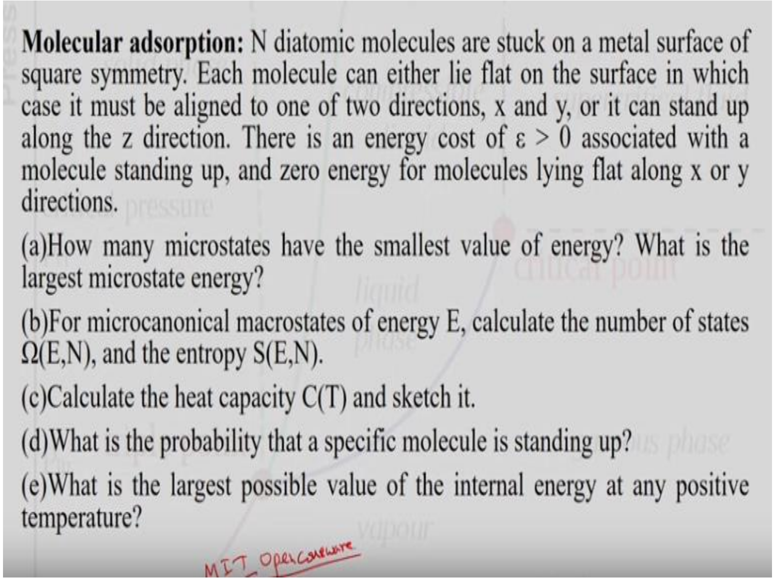

Molecular adsorption: N diatomic molecules are stuck on a metal surface of square symmetry. Each molecule can either lie flat on the surface in which case it must be aligned to one of two directions, x and y, or it can stand up along the z direction. There is an energy cost of $\varepsilon > 0$ associated with a molecule standing up, and zero energy for molecules lying flat along x or y directions.

(a)How many microstates have the smallest value of energy? What is the largest microstate energy?

(b)For microcanonical macrostates of energy E, calculate the number of states $\Omega(E,N)$, and the entropy $S(E,N)$.

(c)Calculate the heat capacity $C(T)$ and sketch it.

(d)What is the probability that a specific molecule is standing up?

(e)What is the largest possible value of the internal energy at any positive temperature?

MIT_OpenCourseware

So I am going to introduce one more question so I have to point out that these questions have been borrowed from a source which is very well known and that is the MIT open course ware because they have some standard questions which are worth solving the solutions are mine but the questions are theirs. So but I hope you will enjoy them because I found them very exciting okay.

So in this problem the phenomenon of molecular adsorption is being considered. So molecular adsorption is basically the situation where molecules stick to a metal surface and so as a result see when they stick to the metal surface and molecules have a finite size. So for example in this case the, we think of a diatomic molecule which has 2 atoms and a bond length in between. So when they are stuck to the you can stick a molecule to the metal surface in one of three ways.

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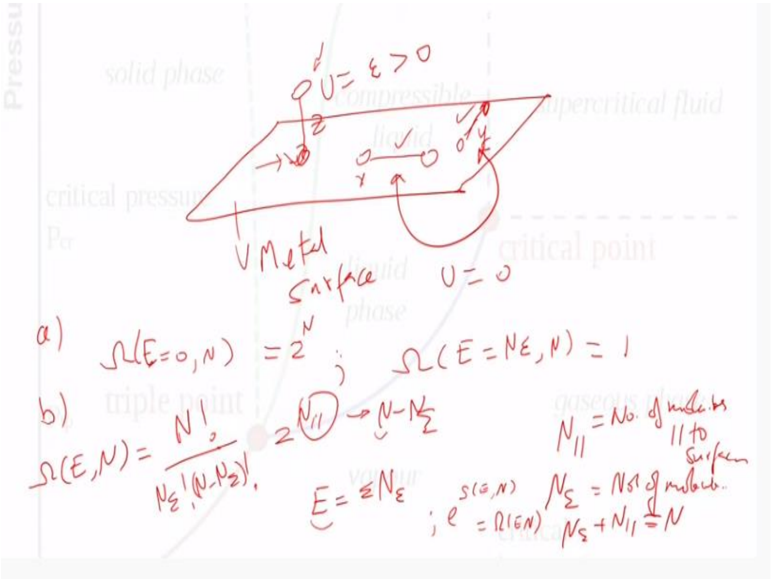

a) $\Omega(E=0,N) = 2^N$; $\Omega(E=N\varepsilon,N) = 1$

b) $\Omega(E,N) = \frac{N!}{N_\varepsilon!(N-N_\varepsilon)!} 2^{\boxed{N_{\parallel}}} \rightarrow N-N_\varepsilon$

$E = \varepsilon N_\varepsilon$; $e^{S(E,N)} = \Omega(E,N)$

$N_{\parallel}$ = No. of molecules $\parallel$ to surface

N_ε = No. of molecules

$N_\varepsilon + N_{\parallel} = N$

So either you can so let me draw a picture of that so imagine that this is the metal surface so you can have a molecule that is stuck like this or you can have a molecule so this is a diatomic molecule so you have 2 atoms here and here and this is the bond length and this is the metal surface okay. So this is the metal surface and this is the diatomic molecule.

So now you can the diatomic molecule can stand upright or it can lie down flat on the surface but then this is a kind of a metal surface which prevents the orientation of this molecule to be anything other than these two possibilities so then the metal does not allow this molecule to just randomly orient itself when it is lying flat so it has to be either this or this. So there are 3 possibilities but then there the energy cost associated so then if the molecule is lying flat the energy for lying flat is 0 but then the energy for standing upright is positive. So it costs energy to stand upright but costs no energy to lie down except that you are only allowed to lie down along say 2 of the axes which we think of as x and y axis okay and this is the z axis. So let us get back to the questions so the question asks is how many microstates have the smallest value of energy.

So imagine that there are N such diatomic molecules and they are asking what is the how many microstates have the smallest value of energy. So clearly the energy is smallest when all the molecules are lying flat on the surface. So when all the molecules are lying flat on the surface so you have to ask yourself how many ways are there to ensure that all the N molecules are lying flat on the surface.

So keep in mind that each molecule can either lie along the x axis or y axis when they are lying flat on the surface. So for each molecule there are two possibilities for lying flat on the surface. So for N molecules the number of possibilities is 2^N and the energy is 0. So if the energy is 0 so this is ε so I should not confuse my handwriting this is ε and this is capital E so this is Latin that is Greek.

So you see the number of ways in which you can the number of microstates when the molecules are lying flat on the surface is 2^N. So the other question they are asking is what is the largest microstate energy. So the largest energy is achieved when all the molecules stand upright so when all the molecules stand upright then clearly that is when the energy is largest and the largest energy is Nε and the number of ways in which you can achieve that is clearly there is only one way.

That is all of the molecules just stand upright and that is all there is to it is so you have this situation where this is 1 and that is the end of story. So the largest energy is Nε and there is only one way of achieving that. So that is the answer to part A so what is part B,part B says so instead of largest or smallest energies. So imagine there is some something between says some energy E which is in between the largest and smallest energies.

Then you are asked to calculate the number of microstates. So the number of microstates are now going to be 2^ $N_{||}$. So this is the number of molecules that are lying parallel to the surface. So I am going to define $N_{||}$ as the number of number of molecules parallel to a surface where Nε is the number of molecules perpendicular to surface. So Nε + $N_{||}$ is N which is fixed.

So capital N is fixed so the general case will involve two raise to a so if there are $N_{||}$ number of molecules lying flat so it is 2^N for the number of ways in which you can rearrange those molecules. So remember that each molecule is distinct so they are all labelled so every molecule is different and you know which molecule is which so if you decide that there are $N_{||}$ molecules lying flat then you can choose one of them to be along the x or y.

So there are two possibilities for each molecule and remember that $N_{||}$ number of molecules so the total number of ways in which you can ensure that the $N_{||}$ number of molecules are lying flat is 2^ $N_{||}$. But then remember that all you are given is that you are given a capital N number of molecules but then nobody is forcing you to select a particular set of $N_{||}$ molecules to lie flat.

So you have to count the number of ways in which you can select which molecules you have decided to make upright and which of them you have decided to allow them to lie flat. So now imagine that so if you, if you decide that Nε is the number of molecules that are up right then the number of ways in which you can select Nε number of molecules to remain upright from a collection of N molecules is clearly

$$\Omega(E,N) = \frac{N!}{N_{\varepsilon}!\,(N-N_{\varepsilon})!}$$

Which is $N_{||}$! basically so now so this is the full story of the entropy or rather the number of microstates so remember that the energy of the system is ε times the number of upright molecules because the number of, the energy of the molecules that are lying flat is 0. So you just have to count the energy so you just have to count how many upright molecules there are and each upright molecule contributes an energy ε.

So it is ε times Nε is the total energy of the system so this also can be written as N-N ε. So you see the total number of microstates is now expressed completely in terms of the energy of the system and the total number of molecules. So that is what it is okay so that is the answer to part B well sort of because I am also asked to find the entropy and you know what it is it is $e^{S(E,N)} = \Omega(E,N)$. So log of omega is just the entropy alright.

So next part says calculate the heat capacity but before I think this is jumping the gun so I am going to first calculate the canonical partition function. So remember what canonical partition function is. So here we have assumed that the total energy is fixed so but in the canonical formalism these molecules. So this metal surface and the molecules are in contact with some environment heat to the heat reservoir.

So the energy can flow in and out of the system and then they come to an equilibrium and when they come to an equilibrium the temperatures equalize. So it is the temperature which equalizes so I am going to have to study the canonical formalism.

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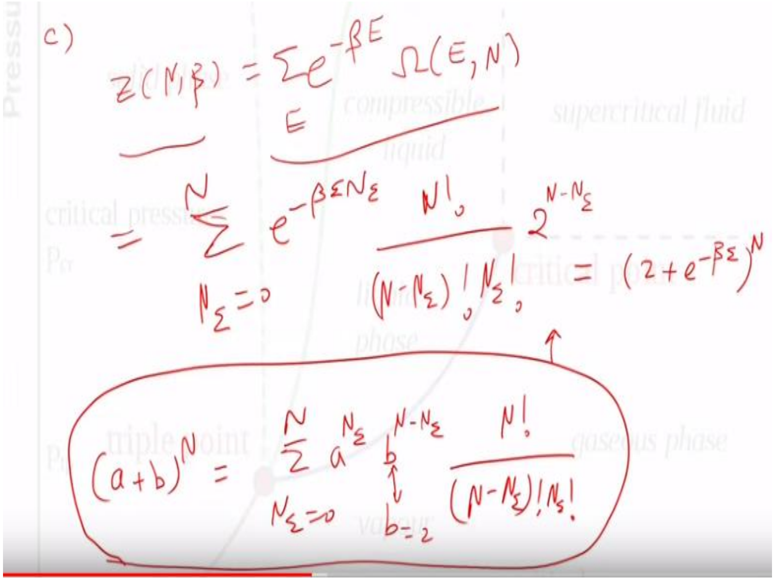

c)

$$Z(N,\beta) = \sum_{E} e^{-\beta E}\,\Omega(E,N)$$

$$= \sum_{N_\varepsilon=0}^{N} e^{-\beta\varepsilon N_\varepsilon} \frac{N!}{(N-N_\varepsilon)!\,N_\varepsilon!}\,2^{N-N_\varepsilon} = (2+e^{-\beta\varepsilon})^N$$

$$(a+b)^N = \sum_{N_\varepsilon=0}^{N} a^{N_\varepsilon}\, \underset{b=2}{b}^{N-N_\varepsilon} \frac{N!}{(N-N_\varepsilon)!\,N_\varepsilon!}$$

So the canonical formalism is basically described in this fashion. So you take the energy which is so-so the canonical partition function is basically sum over all the energies okay. So what I have to do now is to calculate the canonical partition function. So the canonical partition function is basically given by this formula. So it relates the so I am trading the energy for temperature and this is how you do it.

So you write the canonical partition function in this fashion and so now remember that I have already told you what this is. So this is basically instead of so remember that the energy is just proportional to the number of upright molecules. So instead of summing over energies I might as well sum over the number of upright molecules. So you can have a situation where there are no molecules all of them are lying flat.

Or you can have the other extreme where all the molecules are upright so I have to sum over all the intermediate stages as well so starting from one extreme to the other. So this is what it is and I have to substitute the number of microstates here. So now so this is what this is now remember that so you might be wondering how do I do this summation so remember that so finally this is going to be after summation this is going to just be a function of the β which is inverse temperature and the total number of particles.

So this summation looks complicated except that when you realize that there is something called the binomial expansion. So if you remember that this is nothing but

$$(a+b)^N = \sum_{N_\varepsilon=0}^{N} a^{N_\varepsilon} b^{N-N_\varepsilon} \frac{N!}{(N-N_\varepsilon)!\,N_\varepsilon!}$$

So this is the binomial expansion that you are all aware of. So all I have to do is you know compare this with this and you will see that this is easily written as.

So this is 2 so I can identify b with 2 okay and a with this one. So if I identify b with 2 and a with $e^{-\beta\varepsilon}$ and this is what that is. So just from binomial expansion you know that this is my partition function.

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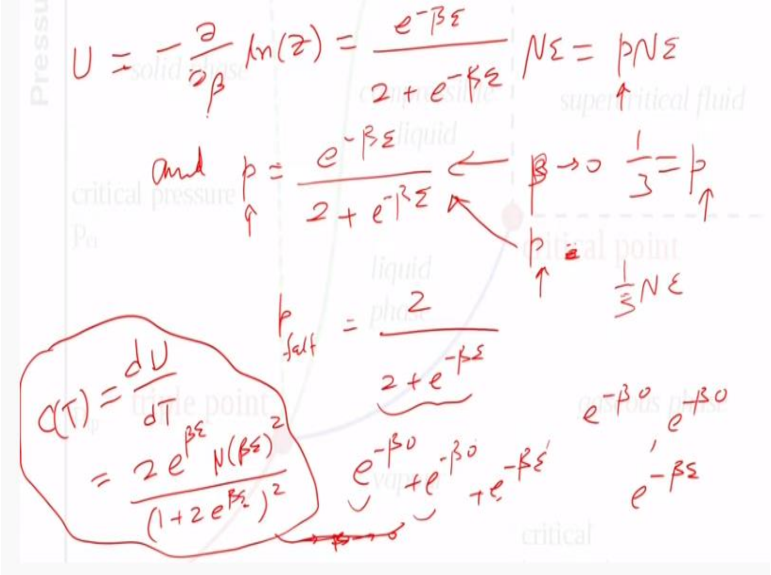

So now that I have got the canonical partition function I can go ahead and calculate the average energy which is nothing but

$$U = -\frac{\partial}{\partial\beta}\ln(Z) = \frac{e^{-\beta\varepsilon}}{2+e^{-\beta\varepsilon}} N\varepsilon = pN\varepsilon$$

And $p = \frac{e^{-\beta\varepsilon}}{2+e^{-\beta\varepsilon}}$. So this is the probability for a molecule to remain upright.

So P is the probability that the molecule is upright so you see that there are 3 possibilities so this is so the molecule is upright is this. So this is identical to you know well I can put a P up right there so this is P upright but then there is also the P flat. So the P flat the probability that is flat is $\frac{2}{2+e^{-\beta\varepsilon}}$ so the 2 is because you know it is 1 + 1 so it is either in the x direction or the y direction.

So this is also you know the probability that it is xy and the energy is 0 e raised to -0 e raised to -0 then e ^ - β ε. So these are the 3 I mean if this energies were there it would be so actually this is nothing but $e^{-\beta 0} + e^{-\beta 0} + e^{-\beta\varepsilon}$ so x direction y direction no energy no energy ε energy when it is up right so that is what it is.

So the heat capacity is defined as the rate of so one can work this out and this comes out as

$$C(T) = \frac{dU}{dT} = \frac{2\,e^{\beta\varepsilon}N(\beta\varepsilon)^2}{(1+2e^{\beta\varepsilon})^2}$$

So that is going to be my specific heat at finite temperature and now you can ask yourself various interesting questions what is the low temperatures specific heat. So when temperature is very low you can expect β to be very large.

So when β is very large you will see that it is going to be exponentially suppressed. So this is going to be large and so it is going to the specific heat is going to turn to 0 quickly okay. So that is because you see at very low temperatures what is going to happen is that if the system is going to be in the ground state and then you see you will need an enormous amount of energy to even you know kick out a molecule and make it up right.

So it is kind of the specific heat is going to be 0 so it is we cannot you would not be able to change the energy by changing temperature when you are at very low temperatures because so it is kind of energetically unfavourable for that. So that is the reason why the specific heat tends to 0 so now at very large temperatures β is 0. So when β is 0 at very large temperatures what happens is that you get a situation which is called the equipartition of energy.

So that means all the degrees of freedom share the energy equally so you see that in this problem there are 3 degrees of freedom. So the one is the x direction the other is y direction and thus the third of the upright which is the s_z direction. So at very high temperature so it kind of becomes democratic in the sense that temperature overwhelms the energy source scales like ε in the problem.

So this system kind of ignores the presence of this energy scale ε and kind of evenly distributes its energy into all the different degrees of freedom. So even though energetically the upright is less favoured but the temperature is so high that that it kind of overwhelms that bias and becomes kind of uniform over all the degrees of freedom. So as a result so even the formula itself tells you that when β tends to 0 which is high temperature so you see this is going to basically okay so I mean this is not the specific heat I am interested in the total energy here. So when β tends to 0 you know I am talking about this so when β tends to 0 this becomes 1/3 so this becomes the probability of it being upright is 1/3 the probability of it being on the x-axis is 1/3.,the probability of it being along the y-axis is 1/3 so they are all equal so as a result the maximum energy that the system can have is well at very high temperature is at when the system is at very high temperatures and the maximum energy is 1/3 times N ε because there is when it is on the it is lying flat the energy is 0. So it is going to be one-third times and this is the maximum energy the system can have at positive temperatures okay.

So that is the so that is the question they had asked yeah so that is more or less the end of this problem. So it is an interesting problem because it teaches you know what specific heat is and how to you know take a problem description and how to you know relate it to the concepts that we have learnt in this course. So the next problem is related to oxygen molecule.

So an oxygen molecule is by and large ininteresting is just a molecule which has some kinetic energy and it is just runs around in a box if you just trap oxygen molecules in a you know a box it is just you know just moves around and bounces of the walls. But the only interesting thing about the oxygen molecule is that it has an intrinsic magnetic moment which behaves like a spin one object.

So that means the magnetic moment is quantized and it has so it is projection can be either $-\hbar$, 0 or + $\hbar$. So these are the 3 possible values of the spin and the Hamiltonian for such an ideal gas of N molecules can be written like this.

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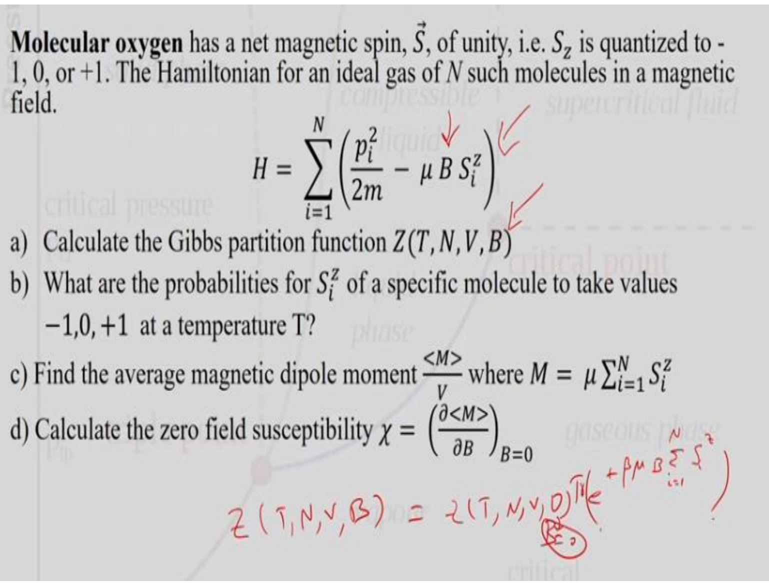

Molecular oxygen has a net magnetic spin, $\vec{S}$, of unity, i.e. S_z is quantized to -1, 0, or +1. The Hamiltonian for an ideal gas of N such molecules in a magnetic field.

$$H = \sum_{i=1}^{N}\left(\frac{p_i^2}{2m} - \mu B S_i^z\right)$$

a) Calculate the Gibbs partition function $Z(T,N,V,B)$

b) What are the probabilities for S_i^z of a specific molecule to take values $-1,0,+1$ at a temperature T?

c) Find the average magnetic dipole moment $\frac{<M>}{V}$ where $M = \mu\sum_{i=1}^{N} S_i^z$

d) Calculate the zero field susceptibility $\chi = \left(\frac{\partial <M>}{\partial B}\right)_{B=0}$

$$Z(T,N,V,B) = Z(T,N,\underset{\boxed{B=0}}{V,0})\,Tr\left(e^{+\beta\mu B\sum_{i=1}^{N} S_i^z}\right)$$

So the question here is to calculate the partition function for this gas. So you can see that because there is no there is no inter relation between the spin degrees of freedom and the kinetic energy. So you can study this problem separately so there is a magnetic field which is coupling this is an applied magnetic field which couples to the intrinsic spin there. So there is going to be diamagnetism.

So if you remember that is what we said but we are going to ignore all those aspects because so that is the uninteresting part of it so as well understood so the problem is that we want to focus on this in any case is the homework problem. So it says treat the kinetic part using classical physics and this is quantum clearly because either -1,0 or + 1 and so the rest of the questions are this what is the probability for the z- component of the spin to take one or the other values at some temperature.

So you want to the canonical partition function and answer this question. So then find the average magnetic moment of the gas and then find the zero field susceptibility so let us see if we can answer this so I am going to ignore the kinetic part of it because that is the classical ideal gas partition function. So it just decomposes into two pieces so I am going to write this as Z(T,N,V,B) = Z(T,N,V,0) that means B=0 okay, times $Tr(e^{\beta\mu B\sum_{i=1}^{N} S_i^z})$

So B=0 so the only thing interesting is this so I will have to trace out this answer the question. So let us start answering.

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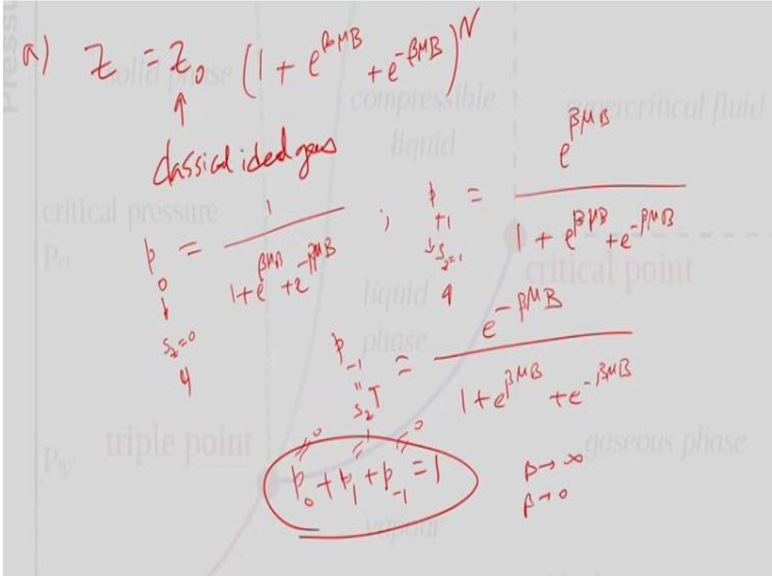

So what is the answer to that is $Z = Z_0(1+e^{\beta\mu B} + e^{-\beta\mu B})^N$ trace means you sum over all the possible values so it gave me 3 values 0 -1 or +1. So when it is 0 it is 1 so it is + 1 its this -1 is that so this is going to be my answer and so that is my partition function.

So what is the probability that you know the value of Z is same one or the other value. So the probability that it is 0 is $\frac{1}{1+e^{\beta\mu B}+e^{-\beta\mu B}}$. So this is the probability that it is the spin projection is 1 s_z is 0 this is the probability the probability that the Sz is 1 yes so remember when Sz is 1 it is + e raised to β μ.

So it is $\frac{e^{\beta\mu B}}{1+e^{\beta\mu B}+e^{-\beta\mu B}}$. So lastly the probability that it is - 1 is $\frac{e^{-\beta\mu B}}{1+e^{\beta\mu B}+e^{-\beta\mu B}}$. So you see if you put them all together you get you know our probability is conserved okay. So this is the probability that the spin projection is at a given temperature.

So the probability that the spin projection is 0 probability spin projection is 1 probability is -1 put them all together it is 1. So this is the probability that a given particle has that kind of spin. So you work out that what happens at where yes at very low temperatures what do you expect and what do the formulas say and so I mean you learn let us we cannot even think about it right now so at very low temperatures what is β? B is very large so when β is very large so this dominates so you see the probability that Sz is 0 is negligible.

So here because very large the probability that is -1 is even more negligible but then the probability that Sz is 1 is close to 1. So in other words when β tends to infinity which is low temperatures at very low temperatures this is more or less 0 this is more or less 0 this is more or less 1 okay so that means all the spins are parallel to the applied magnetic field which is what you expect at very low temperatures.

At very high temperatures when β is tends to 0 you expect them, you expect equipartition that means you will find that all the probabilities are equal so one-third, one-third, one-third so that is what you get okay so when β tends to 0 you get one-third, one-third, one-third all right. So that is fairly obvious and part C find the average magnetic moment. So average magnetic moment is basically the derivative of the partition function with respect to β times B.

So because if you take β times B as parameter and differentiate with respect to that you exactly bring down this M and then so you just have to deal with that okay. So yeah so I am just going to differentiate with respect to β B.

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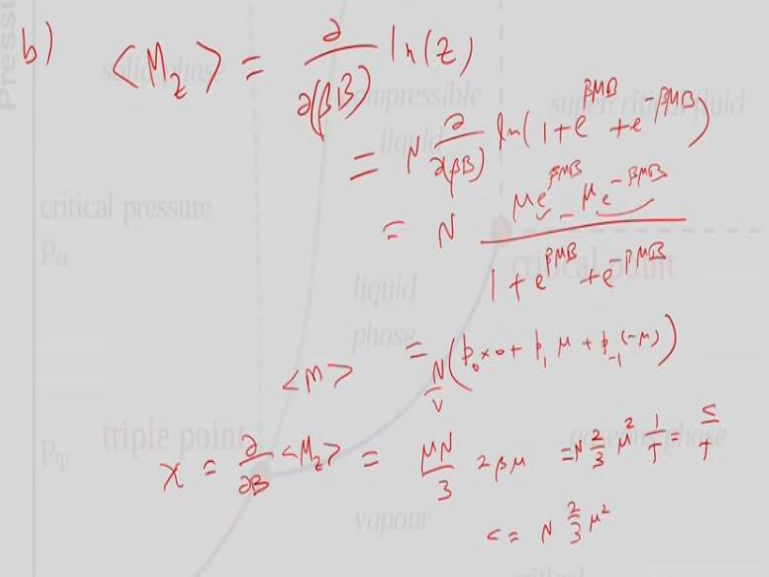

b) $\langle M_z \rangle = \frac{\partial}{\partial(\beta B)} \ln(Z)$

$= N \frac{\partial}{\partial(\beta B)} \ln(1 + e^{\beta \mu B} + e^{-\beta \mu B})$

$= N \frac{\mu e^{\beta \mu B} - \mu e^{-\beta \mu B}}{1 + e^{\beta \mu B} + e^{-\beta \mu B}}$

$\langle m \rangle = \frac{N}{V}(p_0 \times 0 + p_1 \mu + p_{-1}(-\mu))$

$\chi = \frac{\partial}{\partial B}\langle M_z \rangle = \frac{\mu N}{3} 2\beta\mu = N\frac{2}{3}\mu^2\frac{1}{T} = \frac{C}{T}$

$C = N\frac{2}{3}\mu^2$

So the answer to part B is average MZ is basically differentiate by β B with respect to lnZ and so and what is lnZ. lnZ is basically N($1 + e^{\beta\mu B} + e^{-\beta\mu B}$) okay. So if I differentiate this I get e raised to the power β µ B if I differentiate this I get okay so that is my answer. So that is the average magnetic moment so that is fairly obvious because see so look the spin can be either 0 or -1 or +1. So if it is 0 then it does not contribute to the magnetic moment if it is +1 it contributes in this way this is the probability that it is +1 this divided by Z and when it is -1 it is -µ.

So the moment is + μ if it is 1 is -μ if it is - 1 and - 1 the probability is that so it is just what the moment is time is the probability. So this is basically p0 times 0 +p1 times μ + p-1 times – μ. So that is what that is times N alright so that is the average magnetic moment okay per unit volume if you want divide by the density so that is going to be the density of oxygen molecules.

So find the susceptibility at zero field so susceptibility basically means that you apply a small field apply a small magnetic field and you magnetize the molecules slightly. So the magnetization is proportional to the applied magnetic field. So the question is what does that become so χ becomes d/dB so you see most of that look when B 0 magnetic moment is also 0 because there will be μ -μ.

So that means if you do a Taylor series clearly the leading term comes from here so actually so you might as well think of this as 0 so it is mu N/3 times twice β mu B is the leading term right. So and if I differentiate with respect to B this goes away so that is the answer. So it is

$$\chi = N\frac{2}{3}\mu^2\frac{1}{T}$$

So it is basically Curie law so it is C/T so the Curie constant is $N\frac{2}{3}\mu^2$

So the 0 field susceptibility is inversely related to temperature okay I am going to stop here and we will discuss the other problems next time.