Introduction to Statistical Mechanics

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Tutorial - V

Okay so in this example, I am considering what is called a Langmuir isotherm. So, in this problem, we imagine an ideal classical gas of atoms or molecules that is in contact with the surface of a catalyst. So, the idea is that the catalyst, it is a chemical compound which accelerates the chemical reactions but in this particular context what the catalyst does for this limited application, the catalyst merely acts as a surface on which the molecules of the ideal gas come and stick to it.

So, the idea is that there is an energy. So, in other words, in order for the catalyst to stick to the surface, it has to have a certain energy. So, that means once it sticks to the surface that the energy is basically epsilon relative to a particle that is at rest. So, the energy of the molecule that stuck to the surface is epsilon whereas the energy of a molecule that is at rest is 0.

So, the idea is that, so given these situations, firstly regardless of whether or not there is a catalyst part a says show that the chemical potential of the ideal gas is related to temperature and pressure in the following way.

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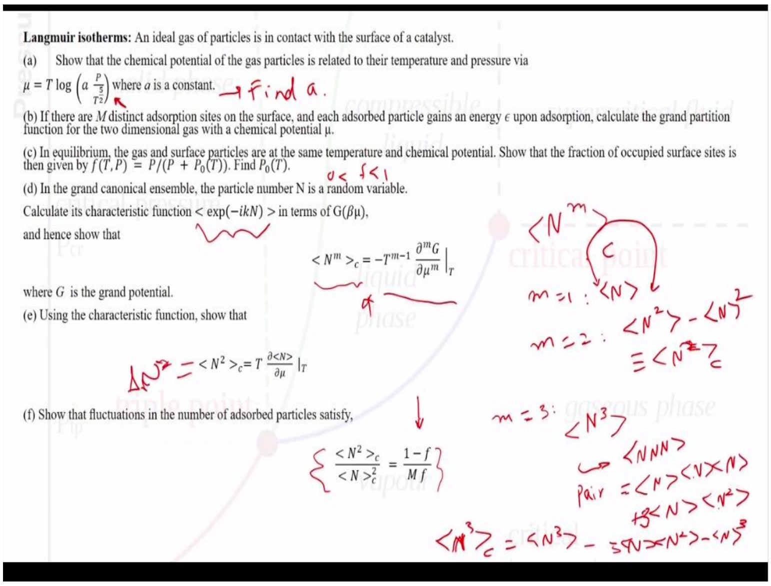

Langmuir isotherms: An ideal gas of particles is in contact with the surface of a catalyst.

(a) Show that the chemical potential of the gas particles is related to their temperature and pressure via

$\mu = T \log\left(a \frac{P}{T^{\frac{5}{2}}}\right)$ where a is a constant. → find a.

(b) If there are M distinct adsorption sites on the surface, and each adsorbed particle gains an energy ϵ upon adsorption, calculate the grand partition function for the two dimensional gas with a chemical potential μ.

(c) In equilibrium, the gas and surface particles are at the same temperature and chemical potential. Show that the fraction of occupied surface sites is then given by $f(T,P) = P/(P + P_0(T))$. Find $P_0(T)$.

$0 < f < 1$

(d) In the grand canonical ensemble, the particle number N is a random variable.

Calculate its characteristic function $< \exp(-ikN) >$ in terms of $G(\beta\mu)$,

and hence show that

$$< N^m >_c = -T^{m-1} \frac{\partial^m G}{\partial \mu^m}\Big|_T$$

where G is the grand potential.

(e) Using the characteristic function, show that

$$\Delta N^2 = < N^2 >_c = T \frac{\partial <N>}{\partial \mu}\Big|_T$$

(f) Show that fluctuations in the number of adsorbed particles satisfy,

$$\left\{ \frac{< N^2 >_c}{< N >_c^2} = \frac{1-f}{M f} \right\}$$

$\langle N^m \rangle \quad c$

$m = 1 : \langle N \rangle$

$m = 2 : \langle N^2 \rangle - \langle N \rangle^2$

$\equiv \langle N^2 \rangle_c$

$m = 3 : \langle N^3 \rangle$

$\hookrightarrow \langle NNN \rangle$

pair $= \langle N \rangle \langle N \rangle \langle N \rangle$

$+3 \langle N \rangle \langle N^2 \rangle$

$\langle N^3 \rangle_c = \langle N^3 \rangle - 3\langle N \rangle\langle N^2 \rangle - \langle N \rangle^3$

And that is the chemical potential is temperature times log of a constant times pressure divided by temperature raise to 5 halves and also we are supposed to find a. So, find the explicit form of this constant a, because we know that this is an ideal classical gas, so we expect to be able to know everything about it. So, this problem that means the part a only relates to classical ideal gas independent of whatever else is there.

So, now coming back to the situation when there is a catalyst, so imagine that there are M distinct adsorption sites, so adsorption means basically the act of the molecule sticking to the surface. So, there will be many sites at which the molecules can sit. So, they have to sit in one or the other sites. So, imagine that the M such sites. So, when a molecule sits on one of those sites on the surface of the catalyst, the particle gains an energy epsilon.

So, given this fact, we are asked to find the grand partition function for this situation when it is given that the chemical potential is mu. So, in part c, we are told that the gas that is surrounding that catalyst which is the ideal classical gas and molecules of the gas that are stuck to the surface of the catalyst, they are in thermodynamic equilibrium. So, as a result their chemical potentials are the same and that temperatures are also equal.

So, given these observations, we are asked to, making use of these observations, we are asked to show that the fraction of sites that are occupied is actually given by a certain formula. So, this is interesting because you will be able to using the ideas of statistical mechanics that we have invented till now. We will be able to calculate a very tangible, useful quantity namely the fraction of sites on the surface of the catalyst that are occupied by the molecules of the ideal gas.

So, in particular, we are able to show that the fraction is given by this formula P divided by where P is the pressure, pressure of the ideal gas that is. So, pressure divided by pressure plus something will depend on temperature but not on pressure. So, that means that there is some function of temperature. So, you can see that this is basically this f is less than 1, greater than 0. So, f will always be less than 1, greater than 0.

So, and we are also asked to find an explicit form for P0 okay. So, in part d, we are asked to calculate the average of, so keep in mind that in a grand N symbol, the number of particles in the ideal gas is not fixed. So, given that idea, that we are asked to find the expectation value of, so this is in some sense called generating function of the moments of the number fluctuation. So, I will tell you what I mean by that subsequently.

So, this is called the characteristic function or the generating function of the moments of the number fluctuations. So, we are asked to find the average of this quantity e raise to - ikN in terms of that there is a grand partition function or in fact in terms of the Gibbs free energy if you like. Basically, you are expressing in terms of chemical potential rather than number of particles, so the number of particles fluctuates but then the chemical potential is fixed.

So, as a result, the e raise to - ikN does not have a specific value. So, it also fluctuates but its average will have a specific value which you can express in terms of the Gibbs free energy, so it so happens that you will be able to write this. So, I will have to explain to you what this notation means. See, this is called the connected, so if I write Nm c, so this is called the connected part of the Mth power of the number of particles.

So, let us imagine that if M is 1, clearly this is the same as average of N though there is nothing special when M is 1, but when M is 2 what this really means is it is not really N squared but it is actually N squared - N whole squared. So, this is what it means. So, this is what connected part. So, this is N squared connected average okay. So, the average of the connected part of N squared means the standard deviation.

So, you might be wondering what it would correspond to N is 3, so if N is 3, so you see if I decide to, so the whole idea is that you take a whole bunch of N’s and then you try to pair it up in as many ways as you can okay and then you will see that the average of N cubed is not going to be those pairings because there will be something left over and that left over is basically called a connected part.

So, if I try to pair it, suppose I try to pair up things, so this is going to look like NNN. So, this is, so I can pair it up in various ways. So, I can either pair up like this, like this, like this okay or I can leave out one of the N’s and pair up the other ones and there are 3 ways of doing that because the 3 ways I can select one of the N’s. So, I can choose to pair up like this, is not it, or I can choose to not pair up at all okay.

So, now the connected part of N cubed is basically defined as N cubed – 3N N squared okay times – N cubed. So, that is called a connected part of N cubed, average of N cubed. So, that is what the subscript c refers to. So, the subscript c refers to the idea that if you wish to calculate the average of N cubed only the connected parts, what you are required to do is that you are required to subtract out all the pairings that are possible okay.

And then you will end up with an expression of this sort. So, now we are asked to show that the average of the Mth power of N, the connected part, the connected average is related to the Mth derivative of the Gibbs free energy with respect to chemical potential alright. So, that is the part d. So, in part e, we are asked to use this derivation thus whatever we just derived and show that the connected part of the square.

But this is basically is the RMS value of N, square of the RMS value is basically the fluctuation in the number of particles and that is related to the rate of change of average number of particles with the chemical potential and then from here we are asked to show that the fluctuations are relative strengths of the fluctuations of the number of particles divided by the square of the number of particles is given by this ratio which is related to the number of, that the fraction of adsorbed particles on the surface of the catalyst.

So, in other words, that is obvious that I write so because the number of particles on the surface when the particles are adsorbed on the surface of the catalyst, those particles necessarily have to come from the surrounding ideal gas. So, the fluctuations in the number of particles in the ideal gas is related to how many particles are stuck to the surface of the catalyst. So, the only point is that it is not a simple additive relation.

Because there is a temperature involved and there is a chemical potential involved. So, there is the whole system can you know take in particles and take out particles as well. So, there is a chemical potential involved. So, it is the chemical potential that is equal to I mean is the chemical potential of the molecules that are stuck on the surface of the catalyst are equal to the chemical potential of the molecules of the ideal gas rather then it is not the number of particle that is constant, is the chemical potential that is constant okay.

So, that is why we get this relation. So, this is the problem of the Langmuir isotherms and we have been asked to you know verify these assertions. So, the question is how do you do this?

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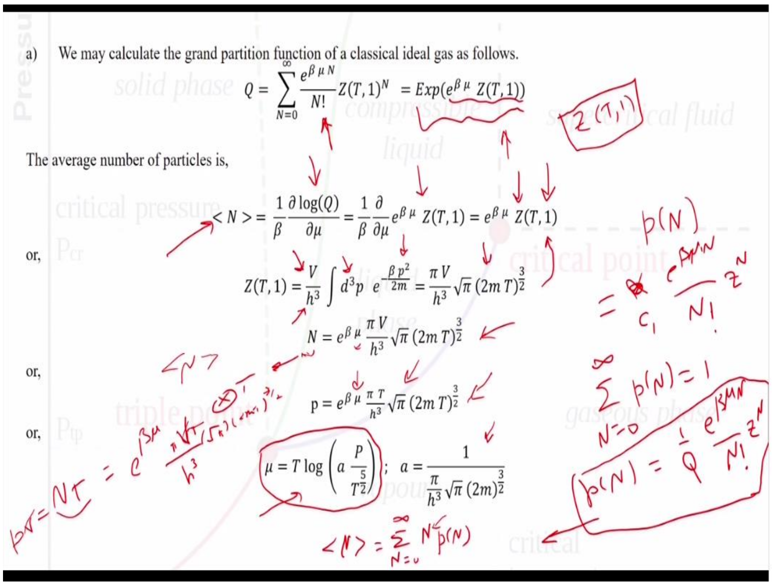

a) We may calculate the grand partition function of a classical ideal gas as follows.

$$Q = \sum_{N=0}^{\infty} \frac{e^{\beta\,\mu\,N}}{N!} Z(T,1)^N \;= Exp(e^{\beta\,\mu}\, Z(T,1))$$

The average number of particles is,

$$< N > = \frac{1}{\beta}\frac{\partial \log(Q)}{\partial \mu} = \frac{1}{\beta}\frac{\partial}{\partial \mu} e^{\beta\,\mu}\, Z(T,1) = e^{\beta\,\mu}\, Z(T,1)$$

or,

$$Z(T,1) = \frac{V}{h^3}\int d^3p\; e^{-\frac{\beta\,p^2}{2m}} = \frac{\pi\,V}{h^3}\sqrt{\pi}\,(2m\,T)^{\frac{3}{2}}$$

$$N = e^{\beta\,\mu}\,\frac{\pi\,V}{h^3}\sqrt{\pi}\,(2m\,T)^{\frac{3}{2}}$$

or,

$$\text{p} = e^{\beta\,\mu}\,\frac{\pi\,T}{h^3}\sqrt{\pi}\,(2m\,T)^{\frac{3}{2}}$$

or,

$$\mu = T\log\left(a\,\frac{P}{T^{\frac{5}{2}}}\right);\quad a = \frac{1}{\frac{\pi}{h^3}\sqrt{\pi}\,(2m)^{\frac{3}{2}}}$$

$Z(T,1)$

$p(N)$

$= c_1 \frac{e^{\beta\mu N}}{N!} Z^N$

$\sum_{N=0}^{\infty} p(N) = 1$

$p(N) = \frac{1}{Q}\frac{e^{\beta\mu N}}{N!} Z^N$

$<N> = \sum_{N=0}^{\infty} N\, p(N)$

$<N>$

$pV = NT = e^{\beta\mu}\, \frac{\pi V T}{h^3} (\sqrt{\pi})(2mT)^{3/2}$

Okay, so I have written down the solution already because I just want to avoid you know very lengthy handwritten calculations, which might not be very legible to you. So, I tried that once, I am going to mix it up, you know I tried writing it once, so now I am going to type it out okay. Part a, what does part a ask us to do? It says show that the chemical potential is given by that relation.

So, in order to find chemical potential and notice that it is related to the pressure and then notice that the pressure itself from ideal gas relation PV equals NT, it is relatable to the number of particles or number of particles per unit volume. So, we are going to be using this idea, so we have to calculate the grand partition function and you see notice that the grand partition function is given by so if there is exactly one particle in the system, I define the canonical partition function of the system to be Z T, 1 okay.

So, Z T, 1 is the canonical partition function of the system with exactly one particle. So, we will subsequently learn how to calculate that as well, but just let us denote it by say T, 1. So, now given if that is the case, then for N particles, we know that because they are all independent, it is going to be Z raise to N, Z T, 1 raise to N divided by N factorial.

So, that means you see that this is the Gibbs factor that you have to introduce to ensure that you know your free energies are extensive. So, we have discussed that quite thoroughly earlier and we know that. So, basically you have to actually make sure that you do not distinguish between different permutations of the same configuration of particles. So, you have to divide between all the configurations.

So, there is no really derivation, there is no proper derivation for this except that it is mandated by our requirement that the free energies be extensive. Now, this times e raise to beta mu N is something that we have to do if the number of particles are not fixed. Then, what we have to do is basically multiply this by e raise to beta mu N and sum over all the N's. So, this is in some sense some kind of a discrete Laplace transform if you like.

So, that is what we are doing here. So, now what we are doing? When we do this is we trade the number of particles in the system which is now not fixed, so it can fluctuate and we are trading that with the chemical potential which is fixed. So, now the system is exchanging particles with the surroundings and it is able to fix its chemical potential rather than its number of particles.

So, the final answer comes out to be this. We are going to use this later on. Right now, let us keep it here okay. So, now the average number of particles is by definition, the derivative of the log of Q with respect to chemical potential. So, if you are wondering why that is the case, see it is look this is basically the probability of finding the particle with you know if rather finding the system with N particles right.

Well, it is kind of its proportional to that. So, this is proportional to e raise to beta mu N over N factorial and Z raise to N. So, this is the probability of finding the system with N particles. So, N particle is this. So, as a result, the actual, so though if you want to calculate the proportionality constant, so if you write that as C1, then clearly this is 1. So, this is 1. So, that means your pN is going to be this basically 1 by Q where Q is defined as that summation times e raise to beta mu N over N factorial.

So, this is the probability of finding the system with N particles in it okay. So, if this is the case, then average number of particles is going to be just a summation over N = 0 to infinity N times pN clearly. So, the question is how do you calculate this? So, if I multiply this by N, so that is the same as differentiating this whole you know taking Q differentiating with respect to mu.

So, if you differentiate with respect to chemical potential, you have noticed that there is only the mu dependence is only here in the exponential. So, if you differentiate with respect to chemical potential, you bring down a beta N. So, then the beta is a constant as far as this analysis is concerned, so it goes out and then the N comes downstairs and so that is exactly what this is. We want it downstairs because of this.

So, then you divide out by Q, so first you differentiate Q and divide by Q. So, that is the same as differentiating the log of Q. So, differentiating the log of Q is basically differentiating Q and dividing by Q. So, as a result, this is the formula. I mean I am sure you understand what I am saying. So, log of Q is because this is the answer log of Q is nothing but what is sitting inside these brackets namely this.

So, I will just go ahead and differentiate with respect to mu and I get this result. So, this is the average. This is how the average number of particles of a classical ideal gas is related to its chemical potential mu okay. So, the only thing that remains now is to be able to calculate the canonical partition function of a classical ideal gas with precisely 1 particle in it, namely this Z T, 1. So, the question is how do you do this?

So, we all know how to do that and that is just you know the phase space integral. So, phase space of 1 particle is basically 6-dimensional because there are 3 dimensions for a momentum and 3 dimensions for position. So, when you integrate over position, you get volume because that is unaffected by temperature. So, the integration over because there is no potential energy in the system, the integration over the volume is unaffected by the temperature.

And so it factors out into a volume divided by of course there is the Planck's constant even though we are studying classical statistical mechanics, we are forced to remember, we were forced to introduce pixels and you know when we made contact with when we insisted that the classical statistical or the classical ideal gas should emerge as a limiting case of the quantum gas, we were forced to conclude that those pixel sizes are basically proportional to the Planck's constant.

So, it is, so the quantum nature of the system refuses to go away. So, it kind of survives as a pre-factor. So, even though for the most part, it really disappears but it still survives as a pre-factor namely it makes the whole thing dimensionally consistent. So, that is the limited role

Planck's constant plays in classical statistical mechanics. It makes things dimensionally correct. So, the partition function of a classical ideal gas is evaluated in this way.

First, you integrate over all the positions, it gives you volume here and then because of this pixels, you have to divide by h cubed and then you will have to integrate over the p is the momentum components, but then keep in mind that now there is a temperature dependence because we are talking about canonical partition function. So, there is an energy associated with the molecules which is p squared by 2m.

But then the system is free to exchange energy with its surroundings. So, as a result, the probability of this weight associated with the molecule possessing an energy of p squared by 2m and that weight is I think but e raise to – beta e where e is p squared by 2m as the Boltzmann weight. So, that is what this is. So, e raise to minus beta e. So, now we will have to integrate over all the moment keeping in mind that there is a Boltzmann weight in the problem.

So, having done this, we obtain this formula for the partition function of a single molecule okay. So, now that depends on volume and temperature. So, once you do this, you can complete this story which relates the average number of particles in a grand canonical ensemble to its chemical potential. So, the reason why the story was not complete is because we had not calculated the canonical partition function as a function of temperature.

So, now that we have done it, we go ahead and use it or substitute this answer here and we get the average. Notice that henceforth I shall omit this average symbol as it is very annoying. We all know what we are talking about. So, I mean it is really contradiction to speak of number of particles and chemical potential in the same breath, but then it is so my implication what we really mean even if we write it like this, we really mean it is the average number of particles that we are talking about okay.

So, the average number of particles is related to the chemical potential and temperature in this way, but now also note that this will enable us to write down the pressure directly because we are going to use the familiar relation that PV is NT. So, you multiply both sides by temperature and then NT on the left side becomes if you multiply both sides of this by temperature, so this becomes NT equals you know the rest of it, e raise to beta mu pi VT over h cubed times square root of pi times 2m T raise to 3 halves okay.

So, this is V times T. So, this NT is nothing but PV. Now, that V, V cancels and then you get a pressure which is related to temperature. So, you can see that the pressure is a chemical potential and temperature. So, that basically enables us to invert this relation and express the chemical potential in terms of the pressure and temperature and then when you invert this, it becomes this and then this constant of proportionality can be read off from this formula.

And it is precisely this. So, you see that it depends only on some fundamental constants like Planck's constant and so on and of course the mass of the molecules alright. So, that is the answer to part a, so which are stressed to verify this relation namely verify that the chemical potential is related to you know the log of the pressure divided by temperature raise to 5 halves. So, this is for a classical ideal gas, alright.

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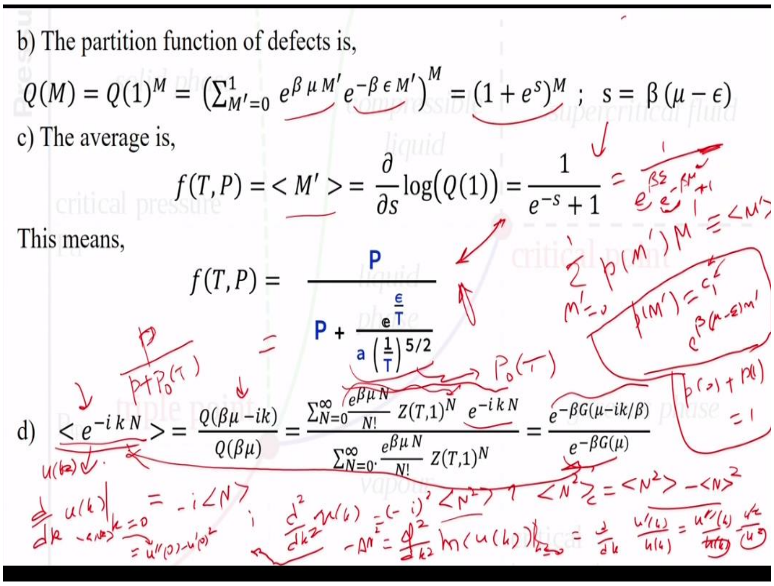

b) The partition function of defects is,

$$Q(M) = Q(1)^M = \left(\sum_{M'=0}^{1} e^{\beta\mu M'} e^{-\beta\epsilon M'}\right)^M = (1+e^s)^M \; ; \; s = \beta(\mu-\epsilon)$$

c) The average is,

$$f(T,P) = < M' > = \frac{\partial}{\partial s}\log(Q(1)) = \frac{1}{e^{-s}+1} = \frac{1}{e^{\beta\varepsilon}e^{-\beta\mu}+1}$$

$$\sum_{M'=0}^{1} p(M')M' \equiv <M'>$$

$$p(M') = c_1 e^{\beta(\mu-\varepsilon)M'}$$

$$p(0)+p(1) = 1$$

This means,

$$f(T,P) = \frac{P}{P + \frac{e^{\frac{\epsilon}{T}}}{a\left(\frac{1}{T}\right)^{5/2}}} = \frac{P}{P+P_0(T)}$$

d) $$< e^{-ikN} > = \frac{Q(\beta\mu - ik)}{Q(\beta\mu)} = \frac{\sum_{N=0}^{\infty} \frac{e^{\beta\mu N}}{N!} Z(T,1)^N \; e^{-ikN}}{\sum_{N=0}^{\infty} \frac{e^{\beta\mu N}}{N!} Z(T,1)^N} = \frac{e^{-\beta G(\mu - ik/\beta)}}{e^{-\beta G(\mu)}}$$

$u(k)$

$$\frac{d}{dk}u(k)\Big|_{k=0} = -i<N> \; ; \; \frac{d^2}{dk^2}u(k) = (-i)^2<N^2>$$

$$-<N^2> = u''(0) - u'(0)^2$$

$$<N^2>_c = <N^2> - <N>^2$$

$$-\Delta N^2 = \frac{d^2}{dk^2}\ln(u(k))\Big|_{k=0} = \frac{d}{dk}\frac{u'(k)}{u(k)} = \frac{u''(k)}{u(k)} - \frac{u'^2}{u^2}$$

So, what is part b? So, part b says so if there are M distinct adsorption sites on the surface and each adsorbed particle gains an energy epsilon upon adsorption, calculate the grand partition function for these you know adsorbed particles when they have a chemical potential mu. So, how do you do this? Notice that the adsorption process is independent, so that each molecule adsorbs independent of the others.

So, in order to find the partition function for M sites, it is sufficient to find the partition function for 1 site and you know just make M copies of it. So, in other words, it is Q of 1 raise to M. So, that is the partition function for M sites okay. So, how do you find the partition function for 1 site? So, that is clearly easy because first of all there is the Boltzmann weight. So, remember that each molecule that is adsorbed has an energy of epsilon in excess of the energy it had at rest, which we take to be 0.

So, there is a Boltzmann weight, which basically tells you that it is e raise to - beta epsilon times M dash where M dash is basically the occupation number of that side. So, M dash is either 0 or 1. Well, a given site can either be occupied by an atom or be empty okay. So, that is the Boltzmann weight and then so if it is empty, there is no Boltzmann weight. So, there is no energy of the particle is there only if there is a particle okay.

So and a site cannot occupy, I mean cannot accommodate more than one particle. So, the other thing we have to do is basically because the number of particles is not really fixed, so we have to also take into account the idea that there is a chemical potential in the problem. So that adjusting the chemical potential allows you to adjust how many particles are you know deciding to stick to the surface.

So, we do not, we only have a handle over the average number of so we can control the average number of particles and the problem by adjusting the chemical potential. We cannot really control how many particle there actually are. So, that fluctuates. So, to take that into account, we have to introduce this you know this device which is basically what we do in the grand canonical ensemble where we introduce the chemical potential in this fashion.

So, there is e raise to beta mu times the occupation number and now you sum over the occupation number so whether the site is occupied or empty. So, when you sum it over, you get this result okay. So, now what we are being asked to do is find the average occupancy of a given site on the catalyst. So, the answer is basically clearly it is I have told you several times before, so you have to bring in an M dash here.

So, the average, so as usual it is like you know pressure probability times M where M is 0, 1 and then this probability M dash is proportional to e raise to beta mu - epsilon M dash. So, how do you find this C1, you just say well the sum over well in this case, it is kind of extravagant to do a summation because it is clearly okay. So, this is average of M dash. So, this is C1 which is a normalization constant because this +p1 is 1 okay.

So, that is the normalization that fixes your C1 and so that is effectively same as taking log and differentiating with respect to s where s is everything in the exponent except M dash okay. So, when you differentiate with respect to x, you could bring in an M dash and then you are effectively finding its average. So, when you do all this, you get this result okay. So, that is your, that is the fraction of adsorbed sites that are occupied by the gas molecule, the ideal gas molecules.

So, now keep in mind that this going from here to here seems rather quick. So, let me explain to you how I did that. Well, remember this s is this, so this is nothing but e raise to beta epsilon times e raise to - beta mu + 1 okay. So, now question is you see this part is fine it is given, temperature is given, epsilon is given but nu is not given, but then remember that we just calculated what mu is.

We spent a lot of time calculating mu and we know that the chemical potential is this. So, what we are going to do is take that chemical potential and substitute it here okay. So, when you do that and simplify, you get this expression okay where that a is this a okay. So, this basically verifies the answer to part c which I remember that the part c had asked us to show that the fraction of occupied sites is pressure divided by pressure + P0 T.

So, we are asked to find this form of this P0 T and this is your P0 T as it were okay alright. So, that is part c. So, now we come to part d which has asked us to find the generating function of the number fluctuations. So, now let me explain to you a little bit why this is the generating function of number fluctuations. So, now if I take, you see if I take this and differentiate with respect to k.

Suppose, I call this U of k okay. So, now suppose I differentiate U of k with respect to k and then I put k = 0, what do I get? If I differentiate with respect to k, I get – iN, but then I put k = 0 later. So, in other words, this becomes minus sorry differentiate with respect to k, I bring down a - iN and the rest of it remains as e raise to – ikN, but then finally I put k = 0. So, as a result, it becomes the average of – iN.

So, it is – i times the average of N. So, you see differentiating U with respect to k and putting k = 0 gives me average of k's. Now, suppose I do it twice, so if I differentiate with respect to

U twice and then put k = 0, what do I get? So, if I differentiate it twice, I get - i squared times the average of N squared. So, now this is nice except that this is not what I want. I want only the connected part.

So, the connected part of N squared is the N squared average - N average squared. So, how do I get that is there a way to directly get that from here? The answer is yes. So, instead of differentiating U of k, what you should do really differentiate ln of U of k with respect to k twice and then you put k = 0, so what will happen if you differentiate with respect to ln of U of k okay.

So, you will get this relation and why is that okay. So, let me do that here. So, if I differentiate with respect to k once before I put k = 0. So, if I differentiate with respect to k once, it becomes U dash k by Uk. Now, if I differentiate with respect to k again okay, so this becomes Q dash dash k by Uk - U dash squared by U squared okay. So, now I put k = 0, so then this U of k and u of squared becomes 1 and then it becomes U dash dash k at k = 0, U dash dash 0 – U dash 0 squared.

So, then that is therefore, so this becomes U dash dash 0 – U dash 0 squared. What is U dash dash 0? This is U of k. So, U dash dash 0 is basically minus, it is basically – N squared average. So, that is what this is. Then, U dash 0 is nothing but - i times average of N and square of that is – of N average square. So, this formula is going to be - delta N squared, so where a delta N is the RMS value okay.

So, basically that is the reason why we take the log of this and differentiate as many times as you want and you get the fluctuations of the Nth order. so if I differentiate take log of average of e raise to – ikN that is this quantity, I take the log of this and differentiate M times with respect to k, so what I get is basically the Mth order, there is a Mth order fluctuation of the number of particles okay.

So, the question is how do I do that? So, in order for us to calculate this generating function, so now you know why this is called the generating function of the fluctuations of the number of particles because if you take the logarithm of this quantity and differentiate M times, you are actually calculating the Mth order fluctuation of the number of particles. So, now look in order to do this, see doing this is same as doing this.

Why is that, because you see, you stare at this and you replace beta mu by beta mu – ik. So, what you are trying to do is basically is well okay. I am going to do this as well, but it so happens that these 2 are related because remember that it is the, we are going to actually make use of the idea that the partition function of the adsorbed particles and the actual, I mean the classical particles are basically the same but they have different expressions.

You will look at the classical expression, so and that is for classical ideal gas is this and then you replace beta mu by beta mu – ik. So, what is going to happen is that there is an e raise to ikN that comes out. Now, remember that this is nothing but the probability that the particle has N or rather the system has N particles in it. So, this is, this quantity is proportional to that. So, now you are going to multiply that probability by e raise to – ikN, then sum over all the particles.

So, as a result, you are of course going to be calculating the average of e raise to – ikN. So, calculating e raise to – ikN is same as taking a beta mu and replacing by beta mu – ik and dividing by Q beta mu okay. So, that is the reason why I have written it like this, but then notice that Q is nothing but it is related to the Gibbs free energy or basically the free energy of the system.

So, Q is e raise to - beta times the free energy. So, it is going to be related to the free energy in this fashion. Well, let us see what part d was actually was. Part d was to show that the Nth order fluctuation of the number of particles is related to the Mth derivative of the free energy with respect to chemical potential okay. So, let us do that. So, in order to do that, the first step is to write the generating function of the fluctuations of the number of particles in terms of the free energy and that is what we have done here.

So, now that we have done this. So, we are going to take log of on both sides, so this is related to this. So, we are taking log on both sides and then differentiating M times, so their own left side becomes the Mth order fluctuations, fluctuation in the number of particles and then let us see what the right side becomes.

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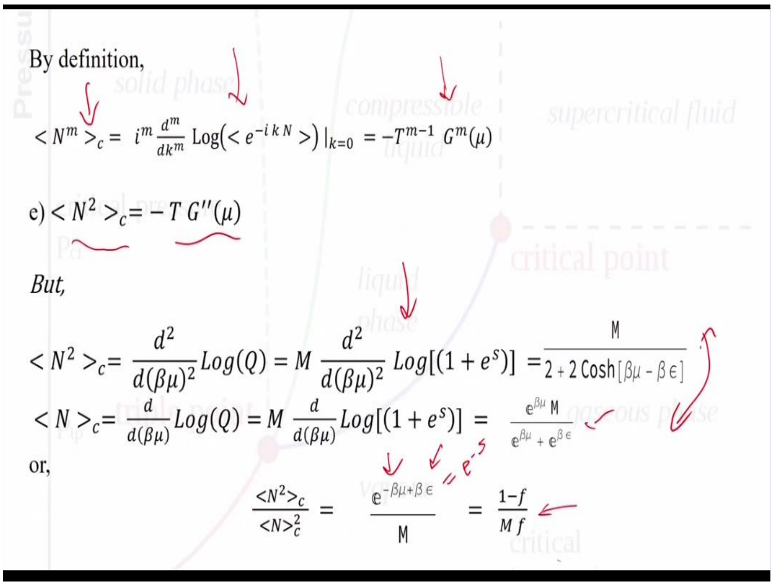

By definition,

$$< N^m >_c = i^m \frac{d^m}{dk^m} \text{Log}(< e^{-i\,k\,N} >)\,|_{k=0} = -T^{m-1}\, G^m(\mu)$$

e) $< N^2 >_c = -T\, G''(\mu)$

But,

$$< N^2 >_c = \frac{d^2}{d(\beta\mu)^2} Log(Q) = M\, \frac{d^2}{d(\beta\mu)^2}\, Log[(1+e^s)] = \frac{M}{2 + 2\,\text{Cosh}[\beta\mu - \beta\epsilon]}$$

$$< N >_c = \frac{d}{d(\beta\mu)} Log(Q) = M\, \frac{d}{d(\beta\mu)} Log[(1+e^s)] = \frac{e^{\beta\mu}\, M}{e^{\beta\mu} + e^{\beta\epsilon}}$$

or,

$= e^{-s}$

$$\frac{<N^2>_c}{<N>_c^2} = \frac{e^{-\beta\mu+\beta\epsilon}}{M} = \frac{1-f}{M\,f}$$

So, the right side actually, so this is the left side, this is what it becomes the Mth order, so it becomes this, but then the right side clearly becomes the Mth derivative of because there is only k is only in the exponent, I mean the numerator rather, so when you take log, it becomes the difference between the numerator and denominator logs and then if you differentiate M times with respect to k, the denominator does not contribute at all.

And the log of the numerator only contributes and then you get the Mth derivative of the free energy with respect to chemical potential okay. So, this is fairly obvious and so now specializing to the case of M = 2, so we have been asked to find the variance or the RMS standard deviation of the number of particles. So, that is going to be proportional to the second derivative of the free energy with respect to chemical potential okay.

So, we can go ahead and now notice that we are going to make explicit use of the fact that these grand partitions for the gas and the adsorbed particles are the same, so because of that I do not necessarily have to use this, I could use this also. So, if I decide to use this for Q, so if I decide to use this for Q, I get these types of results for the fluctuations to I take log Q and differentiate twice with respect to beta mu.

And I get this result and then the average is when I differentiate once I get this okay. So, now if I take the ratio of these 2 quantities, I will be able to show that it is basically the fluctuation, the numerator is the RMS square of the number of the fluctuation of the RMS square of the number of particles that denominator is the square of the average number of particles.

So, the ratio of the 2 is immediately comes out of this quantity which is e raise to - beta mu + beta epsilon divided by M where M is the number of absorbable sites that are there on the catalyst. So, M is the number of sites available on the catalyst. So, now remember that we just we have calculated this F in terms of this s. So, we know what F is in terms of s. So, if you go ahead and use that, so this is nothing but e raise to.

So, notice that s is nothing but e raise to beta mu – epsilon. So, this is nothing but e raise to – s. So, we know F in terms of e raise to – s. So, if you substitute that, you get this result. So, this is what you have been asked to do in part e okay. So, that is the story of this Langmuir isotherms okay. So, you see that is a rather detailed question and it is not something that and it is a moderately difficult question but it also it is very instructive because it teaches you a lot of new things.

And then it makes explicit use of many concepts that we have developed in statistical mechanics till now, which is temperature, chemical potential, grand partition function, Gibbs free energy and you know a host of other things like ideal gas equation of state, canonical partition function also alright. So, now let me go to the next problem. So, what is the next problem?

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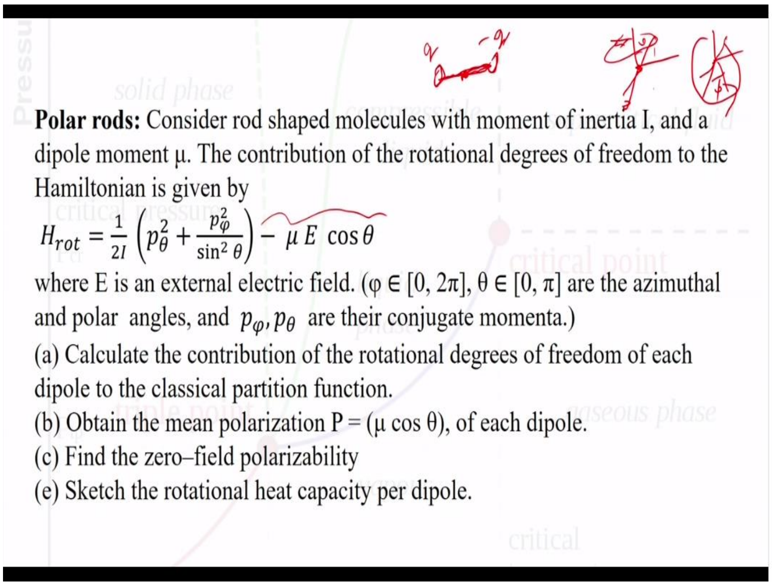

Polar rods: Consider rod shaped molecules with moment of inertia I, and a dipole moment μ. The contribution of the rotational degrees of freedom to the Hamiltonian is given by

$$H_{rot} = \frac{1}{2I}\left(p_\theta^2 + \frac{p_\varphi^2}{\sin^2\theta}\right) - \mu E \cos\theta$$

where E is an external electric field. ($\varphi \in [0, 2\pi]$, $\theta \in [0, \pi]$ are the azimuthal and polar angles, and p_φ, p_θ are their conjugate momenta.)

(a) Calculate the contribution of the rotational degrees of freedom of each dipole to the classical partition function.

(b) Obtain the mean polarization P = ⟨μ cos θ⟩, of each dipole.

(c) Find the zero–field polarizability

(e) Sketch the rotational heat capacity per dipole.

So, in the next problem, I consider at this problem of polar rod. So, imagine a molecule that is shaped in the form of a rod, which has a moment of inertia I about its you know center and then it has a dipole moment mu. So, imagine that it is an electric dipole, so the rod is kind of, you can think of you know charge Q and a charge - Q connected by you know insulating just like an insulating stick, as an insulating stick which connect.

So, this is my molecule, one is charge Q, the other is charge – Q. This is basically the chemical bond; I mean the stick is the chemical bond. So, this is a rod-shaped molecule and it has moment of inertia about this point which is called I whichever it is kind of symmetrical. So, yeah okay, so now in the absence of any external fields, the kinetic energy is clearly related to the, so you can do your normal Hamiltonian mechanics.

So, I am not going to tell you how to do this. So, it comes about, so you have to identify your, you know generalized coordinates. So, you see how many generalized coordinates does this molecule have? So, suppose you keep the center fixed, so if you have center fixed, then you have 2 generalized coordinates, which are the 2 angles. So, you have 2 angles okay. So, you can you know spin about this, you can keep phi fixed and spin this way okay.

So, that is theta or you can alternatively do the reverse which is keep theta fixed okay. So, here you keep theta fixed and change phi, so you spin around like that or you keep phi fixed and you go round and round like that. So, I mean you can go round and round like this keeping this angle fixed. So, these are 2 mutually perpendicular motions. So, you can either keep theta fixed and go round and round like this parallel to the XY plane or you can you know go like that, so perpendicular to the XY plane.

So, you can either go parallel to the XY plane near orbit and go parallel to the XY plane or perpendicular. So, these are mutually perpendicular things you can do and then associated with each angle, there is a generalized momentum. So, then P theta has it, so its, so P theta remembered as dimensionally p theta and p phi are angular momentum because it is conjugate to the angle.

So, theta is an angle, the momentum conjugate to the angle is an angular momentum. So, phi is also an angle. So, the conjugate to the angle phi is the angular momentum p phi. So, the energy is going to be p theta squared by 2I which is the angular momentum squared by twice the moment of inertia and angular momentum in the phi direction squared divided by 2I times sin squared theta.

So, that sin squared theta comes because you have to have the projection on the XY plane, the projection is sin theta. So, you are going to take that into account okay. So, that is the kinetic energy of the rod. Now, when there is an electric field, so now these 2 charges that are sitting at the ends, they are going to experience electrostatic force and that electrostatic force manifests itself as a potential energy and that is going to look like this.

So, the total energy is actually the kinetic energy of rotation - mu times e cos theta okay. So, you might be wondering why am I considering only the rotational degrees of freedom, what about the center of mass degree of freedom? That is uninteresting because I am only, in this problem I am only concerned about the properties of the molecule, the rotational aspects of the molecule.

Of course, the molecule is not going to stay still in the center of mass. I mean there are many molecules in your gas and then each molecule roams around on its own but that is not going to affect the rotational degrees of freedom and I can independently study them without taking into account the translational degrees of freedom. So, in other words, calculate the partition function ignoring the translational degree of freedom of the center of mass.

So, of course also taking into account the existence of the potential energy, so that is part a. Part b is find the average polarization of the each molecule. So, remember that the polarization of each molecule is mu times cos theta. So, we are supposed to find the average of this in the canonical ensemble that is keep in mind that now the implication is that the molecules of the ideal gas are in contact with a thermal reservoir.

And they exchange energy with the reservoir and as a result they come to a thermal equilibrium which is at some temperature T which is common to the reservoir in the system. So, in this situation, we are asked to find the average polarization of each dipole as a function of temperature. So, clearly in this problem, the electric field tries to align all the dipoles along the electric field but then the temperature tries to spoil that by randomizing all that direction.

So, there is a competition between temperature on the one hand which is trying to make everything isotropic and the electric field which is trying to make everything aligned to the electric field. So, the end result is some kind of a compromise where there is an average dipole moment which is proportional to the applied electric field and also depends on temperature.

So, that is what we have been asked to calculate and part c says find the polarizability. So, that means the idea is, so the polarizability is basically the degree to which the average. So, in other words, for small electric field, the average polarization is going to be proportional to the applied electric fields. So, the proportionality constant there is going to depend on temperature and it is called the polarizability.

And lastly we are asked to find the heat capacity of the gas per dipole. So, heat capacity of the dipole. So, in other words, the first supposed to calculate the net energy of the system and there is the average energy of the system and then find the derivative with respect to temperature which gives you heat capacity okay.

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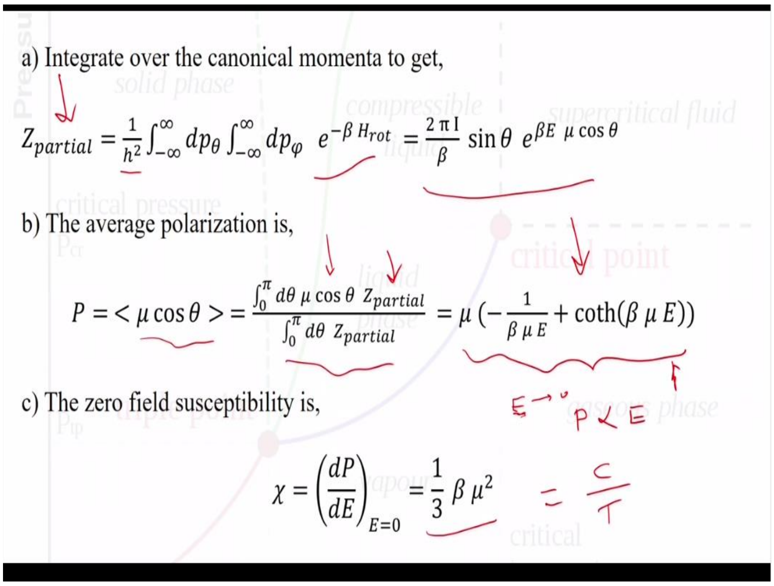

a) Integrate over the canonical momenta to get,

$$Z_{partial} = \frac{1}{h^2}\int_{-\infty}^{\infty} dp_\theta \int_{-\infty}^{\infty} dp_\varphi \; e^{-\beta H_{rot}} = \frac{2\,\pi\,I}{\beta} \sin\theta \; e^{\beta E\;\mu\cos\theta}$$

b) The average polarization is,

$$P = <\mu\cos\theta> = \frac{\int_0^\pi d\theta\;\mu\cos\theta\;Z_{partial}}{\int_0^\pi d\theta\;Z_{partial}} = \mu\left(-\frac{1}{\beta\,\mu\,E} + \coth(\beta\,\mu\,E)\right)$$

$E \to 0$

$P \propto E$

c) The zero field susceptibility is,

$$\chi = \left(\frac{dP}{dE}\right)_{E=0} = \frac{1}{3}\,\beta\,\mu^2 = \frac{C}{T}$$

So, now let us get on with it. Let us do part a. So, part a is clearly you know p theta and p phi have dimensions of angular momentum. So, to make things dimensionless, we have to divide by h square, h is a dimension of angular momentum and so now we multiply by e raise to - beta h rotational degree of freedom and then after integrating over the momenta, we end up with this result okay.

So, that is part a. So, in other words, after integrating over the rotation, so p theta and p phi are the angular momenta of rotation in the theta and phi directions. So, after you take into account the rotations, integrate over all the rotations, you end up with a result which depends only on theta. So, that is the partial partition function. If you integrate over theta also, you get the complete partition function.

So, before integrating over theta, you get the partial Z which is the canonical partition function before integrating over theta. Well, the reason why I did not integrate over theta is because I do not really necessarily want only the complete partition function, but I also want to calculate the average of the dipole moment. So, the average of the dipole moment is given by the, so the moment, dipole moment of the molecule times the canonical partition function.

The partial partition function integrated over the angles divided by that complete partition function. So, when you do this integration, you get this result okay. So, it is a reasonably straightforward thing to do, but then nobody ever does it these days and nobody even looks at any tables in the olden days, people used to rush to the library and pick up some dusty table of integrals and flip through that bulky book and find some integration like that.

But nowadays you know the software which does it for you, we just you know pick up your favorite computer, algebra package and just integrate, do the integration and my favorite is Mathematica and I have used that, I have used Mathematica to arrive at this result okay. So, now the zero field susceptibility is basically the, so as a result remember that if you take, if electric field is very small, so this P is proportional to E.

So, P is going to if you Taylor expand this result, so notice that in general it is some complicated function of E but then if E is very small, you can convince yourself that a Taylor expansion of this quantity is this function of E is going to lead to a term or lead to a function which is proportional to E. So, the proportionality constant is depends on temperature and that is how it is.

So, it comes out as 1/3 mu squared, mu is the intrinsic dipole moment of that rod divided by temperature. So, this is reminiscent of, it is not reminiscent, it is the Curie law. So, remember that this is Curie’s law, which tells you the susceptibility. So, but then this is not magnetism, this is really electrostatics. So, that is the only thing you have to keep in mind. So, it is 1 by temperature.

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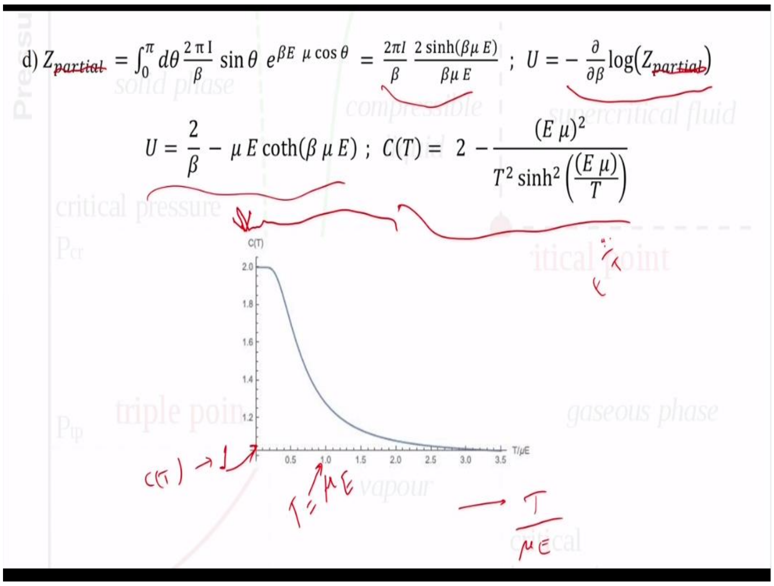

d) $Z_{\cancel{partial}} = \int_0^{\pi} d\theta \frac{2\pi I}{\beta} \sin\theta \, e^{\beta E \mu \cos\theta} = \frac{2\pi I}{\beta} \frac{2\sinh(\beta\mu E)}{\beta\mu E}$; $U = -\frac{\partial}{\partial\beta} \log(Z_{\cancel{partial}})$

$U = \frac{2}{\beta} - \mu E \coth(\beta \mu E)$; $C(T) = 2 - \frac{(E\mu)^2}{T^2 \sinh^2\left(\frac{(E\mu)}{T}\right)}$

So, now well in part d, what was the question in part d where I skipped this is supposed to be d okay. Find polarizability, well this is actually not susceptibility, it is polarizability. So, a part d is basically the rotational heat capacity. So, in other words we are supposed to find the average energy of the system. So, the average energy of the system is basically the, well this is not the partial thing, it is the full thing.

So, this is wrongly written here. It is the full, after integrating over the angles. So, it is the full Z. So, you take the log of the full Z and differentiate with respect to beta and put a minus sign, that is going to be the average total energy of the system and then the answer is going to that full Z is going to depend on temperature and electric field in this fashion, when you differentiate with respect to beta which is the inverse temperature.

I get this result for the net energy of the system. So, now if I differentiate with so keeping in mind that beta is inverse temperature, I differentiate this with respect to temperature I get this result. So, which tells you that the specific heat of the system depends on temperature and this is rather interesting way. So, now I am going to plot this, the specific heat, this function here versus temperature in units of mu E.

So, temperature in units of mu E is the x-axis and the y-axis is the specific heat which I have just derived okay. So, now how does this look like? So, it looks like this. This is very interesting because it tells you that at very low temperatures, so that means for temperatures very small compared to mu E, the specific heat is nearly constant. So, that is the reason because the reason for that is at very low temperature the sin hyperbolic is basically an exponentially increasing function, so it is e raise to 1 by T, something by T.

So, when T tends to 0, it is exponentially blows up, but then remember that sin hyperbolic is sitting in that denominator. So, this whole thing becomes exponentially suppressed. The specific heat is going to be imperceptibly different from 2 unless the temperature becomes sufficiently close to mu E. So, long as temperature is substantially smaller than mu E, the specific heat is imperceptibly different from 2.

So, which is why the specific heat appears to be flat at 2, so that means it was at absolute zero it is certainly 2 but then it continues to be more or less 2 for long time until T becomes an appreciable fraction of mu E. So, it is only then, then it is going to start to show signs of change, then it is going to change in a smooth way in this fashion and it is going to drop off and then when temperature is very large, so now this is actually 1 is temperature equals mu E.

So, this is the scale of temperature equals mu E. So, when temperature is very less than mu E, it is going to look more or less flat and equal to mu, equal to 2 but then my temperature is much larger than mu E that is this region. So, you can see that it actually saturates to C of T becomes 1, so that is here. So, it kind of hovers between 1 and 0, so the specific heat's maximum value is 2, minimum value is 1 and it kind of tapers off and stops at 1.

So, that means for temperatures large compared to mu E, the specific heat becomes 1 and remains there forever. So, that is the story of the specific heat of the polar rod. So, this is how, so in this problem also, you have noticed that you have been using a whole bunch of concepts certainly using statistical mechanics namely canonical partition function and how to find averages and so on.

But you are also explicitly making use of rotational mechanics of classical systems and something you should brush up in case you had forgotten okay alright.

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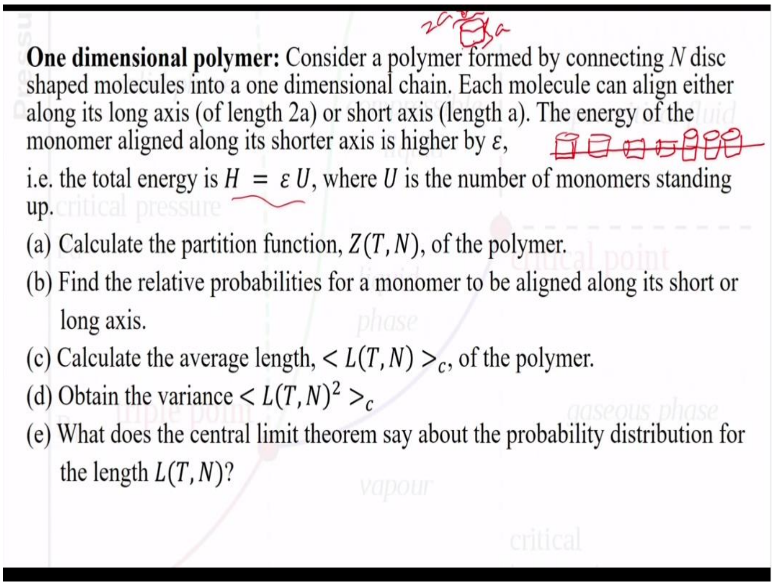

One dimensional polymer: Consider a polymer formed by connecting N disc shaped molecules into a one dimensional chain. Each molecule can align either along its long axis (of length 2a) or short axis (length a). The energy of the monomer aligned along its shorter axis is higher by ε, i.e. the total energy is $H = \varepsilon U$, where U is the number of monomers standing up.

(a) Calculate the partition function, $Z(T, N)$, of the polymer.

(b) Find the relative probabilities for a monomer to be aligned along its short or long axis.

(c) Calculate the average length, $< L(T, N) >_c$, of the polymer.

(d) Obtain the variance $< L(T, N)^2 >_c$

(e) What does the central limit theorem say about the probability distribution for the length $L(T, N)$?

So, let us get to, let us move to a new problem and that new problem is called the one-dimensional polymer. So, this is also a very interesting problem. So, the problem here is that, so it is a polymer is basically a long, it is a kind of a chain molecule. So, it is actually a molecule made of smaller molecules which are kind of weakly linked to you know kind of you know one-dimensional manner.

So, it is a long, it is a huge molecule but the smallest units are also molecules as you can imagine the smallest unit to be something like a disk. So, in other words, a disk is something which has or I think it is better to think of it as a drum, just think of it as a drum. So, each molecule has a shape of a drum. So, this side is a, this side is 2a. So, the thickness of the drum is a, the diameter of the drum is 2a.

So, each molecule looks like a drum and then the idea is that you can connect a whole bunch of these drums like this okay. So, you can either, so that drum can be upright or it can be like this also. So, they are all closely linked. So, this is your polymer. So, they can be like this. So, you can have a huge polymer of this sort.

So, the smaller molecules can be upright or lying down. So, when they are upright, so like this, there is an energy which is epsilon which is associated with each upright molecule surface lying down the energy 0, if it is upright, the energy is epsilon and clearly for the polymer, the total energy is equal to epsilon times the total number of upright molecules, upright these fundamental units, these disk-shaped or drum-shaped molecules.

So, now given this background, we are asked to find various things. So, part a, we are asked to find the partition function of the polymer, the canonical partition function. So, in part b, we are asked to find the relative probabilities for the, so these are called monomers okay. So, the full molecule is called a polymer, the smallest pieces are called monomers. So, the question is what is the probability for a given monomer to be aligned flat or for it to be upright?

So, that there are going to be different probabilities and put together they are going to be, it is going to be 1. So, the sum of these 2 probabilities is 1. So, there is some probability for it to be upright of some probability for it to be lying down. So, the question is we are asked to find both these probabilities okay. So, the third question that we are asked to do is find the average length of the polymer okay.

And then we are asked to find the variance which is the standard deviation, the RMS value of the length. See notice that of course you might be wondering why is there such a RMS deviation that is because the implication is that this polymer does not have a fixed energy. It actually interacts with its surroundings and its energy flows in and out of the polymer. In other words, it kind of gets the monomers get excited or deexcited.

As a result, an upright monomer can suddenly decide to lie flat or a monomer that is lying flat can kind of decide to become upright and then when it decides to become upright, there is an energy cost associated with that and then that comes from that is supplied by the surroundings. So, there is going to be some kind of an interplay between temperature and the number of upright monomers.

So, I noticed that the length of the polymer depends on, so it is going to be different. Well, if all the monomers are upright, then the length of the polymer is just a times the number of monomers but if all of them are flat, its 2a times the number of because when each monomer is flat, it kind of occupies a length 2a along the straight line, along the straight axis of that polymer. So, if it is upright, it only occupies a distance of or a size of a on that axis.

So, if all of them are upright and the length of the polymer is a times the number of monomers but if all of them are flat, its 2a times the number of monomers. So, the length actually fluctuates between being on the one extreme a times the number of monomers all the way to being 2a times the number of monomers. So, the actual length will be somewhere in between because that will depend upon the temperature.

So, we are asked to find such an average length which will be somewhere in between you know N times a and N times 2a where N is the number of monomers and now the average is not the whole story because that is going to you have to determine the fluctuations of the length in order to convince yourself or decide whether the fluctuations are going to be important or not.

For that, we are asked to find the RMS value of the fluctuations of the length of the polymer and then finally if the number of monomers in that polymer is very large, then there is a very well-known theorem in probability theory that says that you know any distribution that which is the sum of a large number of random variables approaches a Gaussian distribution or a normal distribution.

So, that is called central limit theorem and in this last part, we are asked to verify this central limit theorem in this particular example by working out the large N limit of the probability of you know for the length to be a certain value. So, you first find, so part e implicitly asks you to find the probability that a polymer has a certain length and show that the probability distribution actually peaks at a certain value.

So, that probability is you know overwhelmingly significant only nearly. So, if the number of such monomers is huge, then it is overwhelmingly likely for it to be near the average. So, in other words only the probability distribution close to the average matters and close to the average is basically a, it is like a Gaussian distribution. So, that is basically the central limit theorem which you are asked to verify okay.

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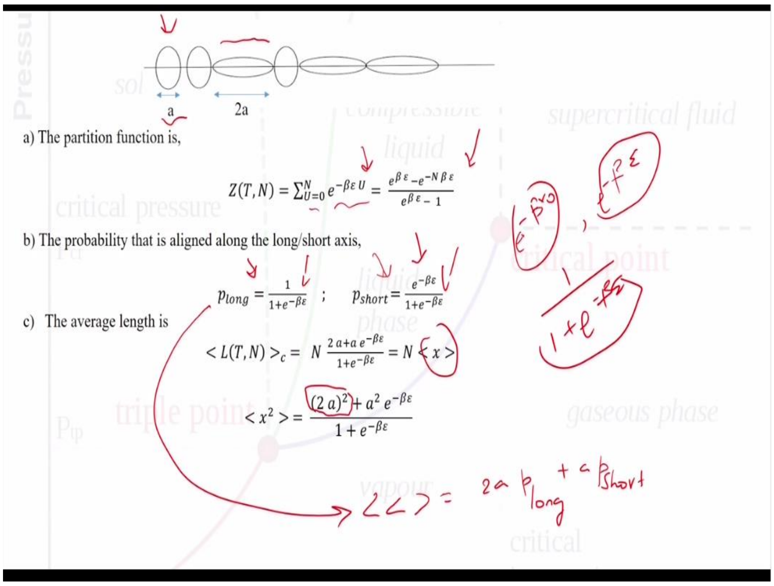

a) The partition function is,

$$Z(T,N) = \sum_{U=0}^{N} e^{-\beta\varepsilon\, U} = \frac{e^{\beta\varepsilon} - e^{-N\beta\varepsilon}}{e^{\beta\varepsilon} - 1}$$

b) The probability that is aligned along the long/short axis,

$$p_{long} = \frac{1}{1+e^{-\beta\varepsilon}} \;;\quad p_{short} = \frac{e^{-\beta\varepsilon}}{1+e^{-\beta\varepsilon}}$$

c) The average length is

$$< L(T,N) >_c = N\,\frac{2a + a\,e^{-\beta\varepsilon}}{1+e^{-\beta\varepsilon}} = N < x >$$

$$< x^2 > = \frac{(2a)^2 + a^2\,e^{-\beta\varepsilon}}{1+e^{-\beta\varepsilon}}$$

$e^{-\beta \cdot 0}$, $e^{-\beta\varepsilon}$

$\frac{1}{1+e^{-\beta\varepsilon}}$

$\langle L \rangle = 2a\, p_{long} + a\, p_{short}$

Let us get on with it and so how do you do that, so this is a picture that I have written, so which is similar to what I had written there. So, this is a molecule that is kind of upright. So, it occupies a distance a and this is a molecule that is lying down, so it occupies a distance 2a. So, this is your polymer and these are your monomers. So, now the question is how do you find the canonical partition function.

You first find the number of upright molecules and then you add up all the upright molecules from 0 to capital N and you get this result okay. So, it is also clear that for a given molecule, the Boltzmann weights, so if it is, you see remember that if it is lying down, the energy is 0. So, the Boltzmann weight associated with that is e raise to - beta times 0. So, this is if it is lying down but if it is upright, the Boltzmann weight is e raise to - beta epsilon.

So, you see, it is so in other words, the total weight is 1 + e raise to - beta epsilon. So, probability for given molecule to be lying down is basically 1 this thing divided by the total weight which is this. So, this is the probability for it to be lying down and the probability for it to be upright is this weight and the weight that is the probability is upright divided by the total weight.

So, this is the probability that the molecule is either upright in this case or it is lying down in that case. So, the average length of the molecule is given by the length when it is, so it is basically the average length is going to be 2a right times P long + a times P short. So, that is the average length of the polymer and then remember that is on an average length of a given molecule.

So, it is kind of what I mean by that is that you know you just imagine an ensemble of large number of molecules and you decide which one is lying down, which one is upright and then you find the average length that is contributed by that one molecule and then that average is going to be average x and then you multiply by the number of molecules present or the number of monomers that are present in that polymer molecule.

So, that is going to give you the length of the polymer. So, now similarly the square of the length contributed by each monomer is also writable like this. So, if it is lying down, the square that is contributed is 2a squared because if it is lying down, the length that is contributed is 2a and the square of that length is 2a squared but if it is upright, the length that is contributed is a and it is a squared.

But then the associated probabilities are this when it is upright and this when it is lying down. So, that is the reason why you get this result which is the average of the square of x. So, it is going to be the square of this length contributed by each molecule okay.

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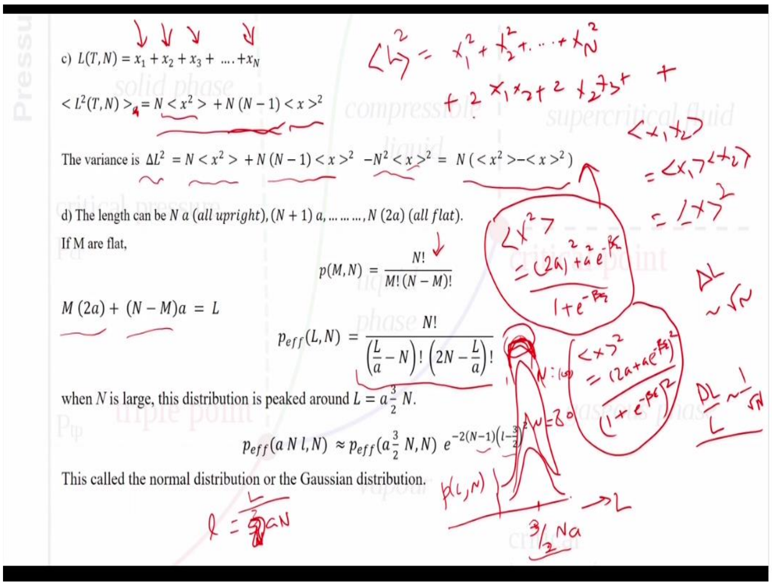

c) $L(T,N) = x_1 + x_2 + x_3 + \ldots. + x_N$

$< L^2(T,N) >_a = N < x^2 > + N(N-1) < x >^2$

The variance is $\Delta L^2 = N < x^2 > + N(N-1) < x >^2 - N^2 < x >^2 = N(< x^2 > - < x >^2)$

d) The length can be $N\,a$ (*all upright*), $(N+1)\,a, \ldots\ldots\ldots, N\,(2a)$ (*all flat*).

If M are flat,

$$p(M,N) = \frac{N!}{M!\,(N-M)!}$$

$M\,(2a) + (N-M)a = L$

$$p_{eff}(L,N) = \frac{N!}{\left(\frac{L}{a} - N\right)!\,\left(2N - \frac{L}{a}\right)!}$$

when N is large, this distribution is peaked around $L = a\frac{3}{2}N$.

$$p_{eff}(a\,N\,l, N) \approx p_{eff}(a\frac{3}{2}N, N)\, e^{-2(N-1)(l-\frac{3}{2})^2}$$

This called the normal distribution or the Gaussian distribution.

So, that other question is that what they are asking is what is the average of the square of the length of each molecule okay? So, this is not connected, this is just L square. So, remember that the length of each molecule is the length contributed by the first molecule which is x1, length contributed by the first monomer which is x1, length contributed by the second monomer which is x2 and third monomer which is x3 and finally the last monomer which is xN. So, it is put together, all of them put together is the length of the polymer molecule.

And now, if you square this, so if you take the square of this, this is going to be x1 squared + x2 squared + dot dot dot + xN squared but then there is also going to be 2x1 x2 + 2x2 x3 +, so all the, you know N variables taken 2 at a time. So, that is going to be, so if you take the average of this, it is going to be average of x1 squared + average of x2 squared + etcetera but then notice that average of x1 squared is the same as average of x2 squared is the same as average of x3 squared.

So, the N of them there, so it is each of them is equal to average of x squared but then see here if I take the average of x1, x2 it is basically the average of x1 times the average of x2 because x1 and x2 are independent as far as I mean they independently decide whether they want to remain upright or they want to lie down flat. So, they independently decide. So, the average of x1 times x2 is the average of x1 times average of x2.

So, as a result this is going to be average of x squared okay and so the rest of it is basically you just have to count how many ways there are of selecting 2 such variables to sit next to each other from a collection of N variables. So, that is going to be 1/2 into N into N – 1, that is the how many ways there are of selecting 2 variables to sit next to each other from a collection of N variables.

So, that multiplied by this 2 will cancel out and you get N into N – 1 times average of x squared. So, this is the average of the square of the length of the polymer. So, now the variance is basically this quantity which is the average of the square of the length of the polymer minus the average of the length square. So, it is average of the square of the length minus the average of the length square.

So, that is the variance squared. So, the variance squared is basically the variance, some people call this variance. So, the variance is the difference between these 2 and when you find the difference, it comes out to be nicely this. So, it is basically delta x squared in other words times N okay and then so that is the end of story because we have told you what delta x, what x squared is and what is average of x is.

So, you just have to find the square of I mean you just have to calculate this. So, average of x squared is 2a squared + a squared – e raise to – beta epsilon + 1 - e raise to – beta epsilon. So, this is average of x squared and average of x squared is nothing but is the squared okay. So, it is going to be 2a + a times e raise to - beta epsilon squared over 1 + e raise to – beta epsilon squared. So, that is what average of x squared is and the difference is what we are asked to calculate here.

So, it is going to be, it is not 0 in other words okay. So and of course it is, you see the delta L is proportional to square root of N. So, delta L by L is 1 over square root of N. So, that is clearly what we are talking about in throughout this course that for thermodynamically large system. So, if N is very large, if the number of monomers is very large, then you can ignore the fluctuations of, so this is the thermodynamic fluctuation delta L can be ignored.

Because it is suppressed relative to the average length, so the average is more or less the whole story if the number of monomers is enormous compared to 1 and that is typically the case okay. So, continuing in that vein, so suppose I want to calculate the probability that from a collection of N monomers, what is the probability that M of them are lying flat? So, the answer is clearly this.

Because it is proportional to the number of ways in which you can, you know select M you know from a collection of N and you decide that they are going to lie flat okay. So, that is going to be the number of ways in which you can select M monomers from a collection of N monomers and you decide that they are going to lie flat. So, now you can express this M in terms of the length of the monomer.

Because if M are lying flat, it is the length contributor is 2a per monomer that is lying flat and the remaining number of monomers are N – M and they are going to be upright. So, the total length is L and M is related to N in this fashion. So, M is related to L in this fashion. So, now you can see that if you plot this, if you fix N and you plot it, you will see that, it is kind of, so this function kind of peaks at P of L, N.

So, it peaks at 3 by 2 Na, so if you plot this function of L, it is going to peak like this. Now, as N increases, it becomes sharper and sharper. So, it kind of so for N equals 100, N equals 80 like that. So, as you increase N, it becomes very sharp and so for very large N, most of the probability, so it is going to be concentrated in a window around L equals 3 by 2 N. So, in other words is consistent with this idea that when N is very large, the fluctuations are suppressed.

So, it is sufficient for you to consider this function close to L equals 3 by 2 Na. So, all you have to do is expand this, Taylor series expand this in close to L equals 3 by 2 Na. So, I am now going to actually do this but I will leave it probably as an exercise but it is easy to see that it is kind of it is going to look like this. So, anything that looks like this is a kind of a Gaussian.

So, you can think of it as a Gaussian, which so it kind of peaks. So, it reaches a maximum at L equals L means 3 by 2 Na L over that sorry without this L by Na. So, when L, small l is 3 by 2 that is when it peaks. So, small l is length in units of Na. So, it is going to do this. So, it is going to peak at L equal to 3 by 2 and then it is going to taper off quickly and then how quickly it tapers off depends on how large the N is.

So, if N is very large compared to 1, which is what we expect here, so it is going to taper off very rapidly. So, implying that therefore the distribution is more or less, most of the weight of the distribution is close to the peak and close to the peak it is a normal distribution or a Gaussian distribution. So, that verifies the central limit theorem of statistics which is well known to mathematics people okay.

So, that is the story of these polar rods. So, maybe in the next set of problems, I might discuss others similar interesting problems. So, I hope you will join me for that. Thank you.