Introduction to Statistical Mechanics
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Module No # 01
Lecture No # 03
Method of Steepest Descent

Okay, so now I want to describe to you a method which goes by the name generating function method by which we are going to be able to count how many microstates there are consistent with the constraints that have been provided namely that the total energy is fixed and the total number of particles are fixed. So if you recall in the last several slides, I managed to do the same thing but using a rather wasteful approach namely list all the possible solutions corresponding to the various microstates and simply count them one by one.

So that is wasteful because it requires a lot of computational resources to list all the solutions, so it would be far easier if there were a simpler roundabout way of bypassing the necessity of having to list all the solutions explicitly and instead simply count how many solutions there are without knowing what those solutions are, ok. So that is called the generating function method which I am going to describe to you now.

So before I begin I want to point out that the subject is going to rapidly become quite technical and it is really important for you to be ready with a pen and some paper in hand to and follow along when I do the calculations. So it is not like, physics is not like reading a storybook where you simply you know just listen to you know some video or just read a novel, so you have to actually follow along with pen and paper.

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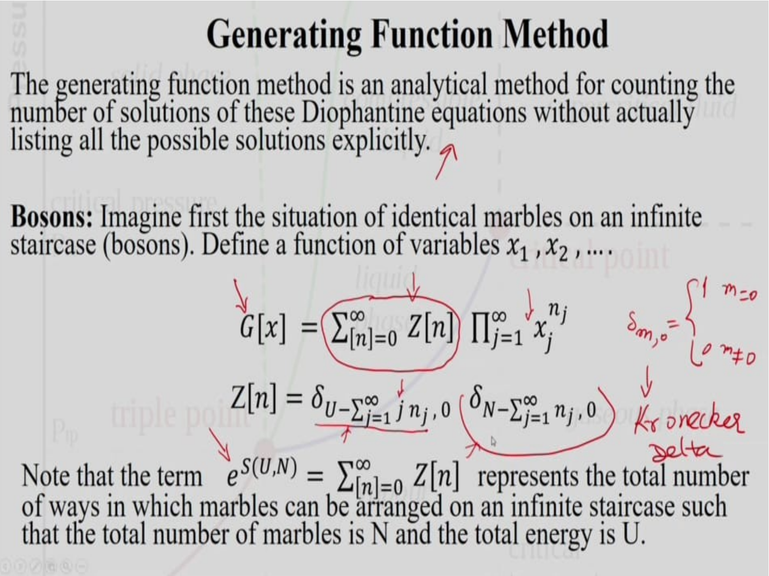

Generating Function Method

The generating function method is an analytical method for counting the number of solutions of these Diophantine equations without actually listing all the possible solutions explicitly.

Bosons: Imagine first the situation of identical marbles on an infinite staircase (bosons). Define a function of variables $x_1, x_2, \dots$.

$$G[x] = \boxed{\sum_{[n]=0}^{\infty} Z[n]} \prod_{j=1}^{\infty} x_j^{n_j}$$

$$Z[n] = \delta_{U-\sum_{j=1}^{\infty} j\, n_j,\, 0} \, \boxed{\delta_{N-\sum_{j=1}^{\infty} n_j,\, 0}}$$

$$\delta_{m,0} = \begin{cases} 1 & m=0 \\ 0 & m\neq 0 \end{cases}$$

Kronecker delta

Note that the term $e^{S(U,N)} = \sum_{[n]=0}^{\infty} Z[n]$ represents the total number of ways in which marbles can be arranged on an infinite staircase such that the total number of marbles is N and the total energy is U.

So let me start with the generating function method, so it is an analytical method which allows me to solve or count the number of solutions of these Diophantine equations that I have been talking about without explicitly listing all the solutions. So in order to do that recall that the number of solutions that I was talking about that I am interested in is really this so it is sum over all the different possibilities where I am constrained by this constraint which says that the total energy is fixed.

So I have assumed that the energies are you know like the steps of a staircase they are all equidistant so that is why there is a j there and this is called a Kronecker delta. So this forces me to assert that the total energy of the system of this microstate rather is U all the time. So and this Kronecker delta forces me to assert that the total number of particles is fixed as N so if you do not remember what Kronecker delta is it is very important for you to know what this is,

So if I write $\delta_{m,0}$ what I meant by this is **1** if m is 0 and it is 0 if m is not 0 so this is called a Kronecker delta ,so after a German mathematician Leopold Kronecker ,ok

$$\delta_{m,0} = 1 \text{ if } m = 0$$
$$0 \text{ if } m \neq 0$$

So I am going to repeatedly use this symbol so it is important for you to know what that is. So now this forces me to conserve energy and forces me to conserve the number of particles. But once that is forced on me then I am free to sum over all the different possibilities and these Kronecker deltas will keep track of whether or not energy and number of particles are conserved.

Now I really want to perform this summation so it turns out that an easier way of doing this is to actually define a more general object called the generating function, so this is called a generating function and I define a whole bunch of variables called x_1 , x_2 , x_3 all the way up to x_∞ and I multiply this number that I am interested in. So before I sum over the n's I multiply with x_1 raised to n_1 , x_2 raised to n_2 and so on and so forth and then I sum over N.

So clearly the answer that I am looking for if I set all the x's to 1 then I get back the thing I have circled in red here. So it is easy to get the answer that I am looking for which is number of microstates consistent with the total energy and total number of particles, all I have to do is first calculate the generating function and set all the x's to 1. Soon as you know already and I have told you several times that the total number of microstates is also the exponential of the entropy.

Because according to Boltzmann the entropy is nothing but the logarithm of the number of microstates so that is exactly what I was talking about that if you set all these x's that are here to 1 and then I get back the answer that I am looking for that means the answers that I have circled here in red.

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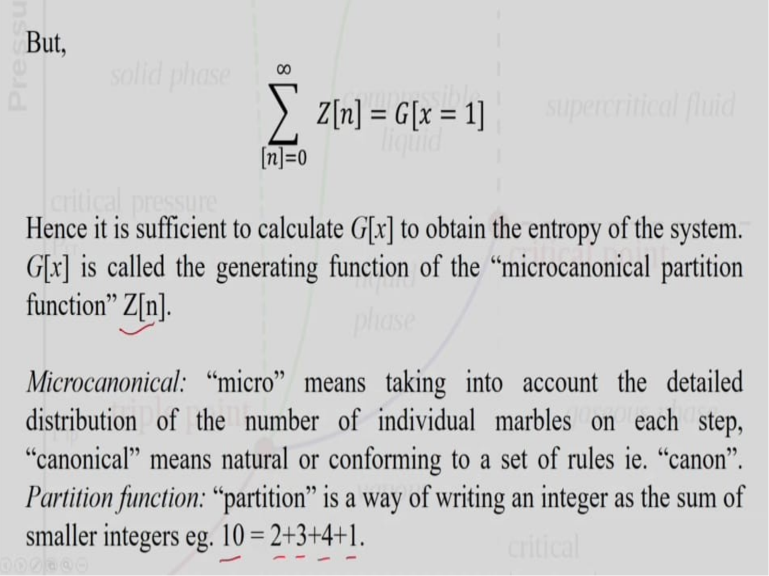

But,

$$\sum_{[n]=0}^{\infty} Z[n] = G[x = 1]$$

Hence it is sufficient to calculate $G[x]$ to obtain the entropy of the system. $G[x]$ is called the generating function of the "microcanonical partition function" Z[n].

Microcanonical: "micro" means taking into account the detailed distribution of the number of individual marbles on each step, "canonical" means natural or conforming to a set of rules ie. "canon". *Partition function:* "partition" is a way of writing an integer as the sum of smaller integers eg. 10 = 2+3+4+1.

So this Z[n] is sometimes called the micro-canonical partition function so what does that mean so micro means taking into account the detailed distribution of the number of individual marbles for example in the example that I gave you. So the individual marbles on each step and that would correspond to the micro adjective there and a canonical actually means conforming to a set of rules canon is just a rule book as it were.

So a partition function the word partition is a way of writing an integer as the sum of other integer so for example you can write 10 as 2+3+4+1. So this is an example of a partition so partition function is just is basically tells you how many ways in which you can partition an integer. So in this case you have constrained also by those requirements that the total energy and number of particles and so on.

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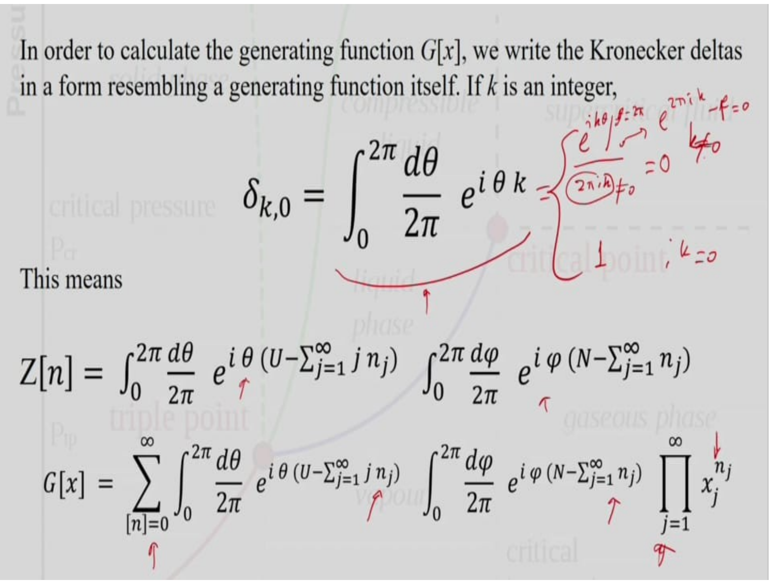

In order to calculate the generating function $G[x]$, we write the Kronecker deltas in a form resembling a generating function itself. If k is an integer,

$$\delta_{k,0} = \underbrace{\int_0^{2\pi} \frac{d\theta}{2\pi}\, e^{i\theta k}}_{\uparrow} = \begin{cases} \dfrac{e^{ik\theta}\big|_{\theta=2\pi}}{\boxed{2\pi i k} \neq 0} = 0 & k \neq 0 \\ 1, & k = 0 \end{cases} \qquad e^{2\pi i k} - 1 = 0$$

This means

$$Z[n] = \int_0^{2\pi} \frac{d\theta}{2\pi}\, e^{i\theta\,(U - \sum_{j=1}^{\infty} j\,n_j)} \int_0^{2\pi} \frac{d\varphi}{2\pi}\, e^{i\varphi\,(N - \sum_{j=1}^{\infty} n_j)}$$

$$G[x] = \sum_{[n]=0}^{\infty} \int_0^{2\pi} \frac{d\theta}{2\pi}\, e^{i\theta\,(U - \sum_{j=1}^{\infty} j\,n_j)} \int_0^{2\pi} \frac{d\varphi}{2\pi}\, e^{i\varphi\,(N - \sum_{j=1}^{\infty} n_j)} \prod_{j=1}^{\infty} x_j^{n_j}$$

So now so how do I calculate this generating function so there is a clever trick to do that and that is to invoke what is called the integral representation of the Kronecker delta. So I want to convince you that this is nothing but the Kronecker delta so if I perform this integration and if k is an integer here then this is equal to precisely the Kronecker delta and why is that ,so suppose k was not 0 and you perform this integration.

What is this going to look like so if k was not 0 so imagine that k was not 0 then what does this look like so this is going to look like $e^{ik\theta/2\pi ik}$ and then I have to make theta go from 0 to 2π. So now because k is an integer and k is not 0 so if k is not 0 this is not 0 and because k is an integer so I am going to get here I am going to get $e^{2\pi ik}$. Then I am going to get $e^0 = 1$.

So because k is an integer this is going to be 0 so the numerator is 0, denominator is not 0 so this whole thing is 0 but what if k is 0 so if k is 0 clearly then this becomes 1. So that when this is 1 I simply integrate over θ and I get 2п and there is already a 2п there so the answer is 1. So I get the result that when k ≠ 0 the answer is 0 and when k = 0 the answer is 1 so this is clearly the Kronecker delta symbol alright.

So now I am going to use this trick to rewrite my constraints, if you recall the constraints involved the Kronecker delta with respect to the energy here and the Kronecker delta with respect to the number of particles so I am going to rewrite that as an integral representation over two angles like θ and φ. So now what is the advantage of doing that? The advantage of doing this is that I bring all these ends that I have to eventually sum over into the exponent here.

So if you see here so I have successfully managed to bring all the n's in the exponent and the reason why that is important and is useful is because the generating function also has n's in the exponent because of this x's. So if all the n's are sitting in the exponent and then you have to sum over all the values of the exponent that should immediately ring a bell and that is called a geometric series. So we are going to use of the fact that we know how to geometric series and what we have done through this device of writing the Kronecker delta in terms of the integral form is that we have successfully converted into a geometric series.

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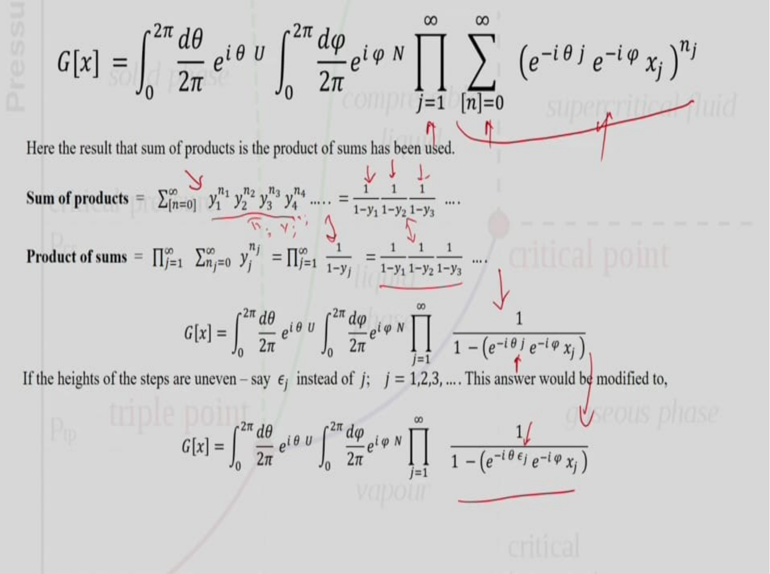

$$G[x] = \int_0^{2\pi} \frac{d\theta}{2\pi} e^{i\,\theta\,U} \int_0^{2\pi} \frac{d\varphi}{2\pi} e^{i\,\varphi\,N} \prod_{j=1}^{\infty} \sum_{[n]=0}^{\infty} \left(e^{-i\,\theta\,j}\, e^{-i\,\varphi}\, x_j\right)^{n_j}$$

Here the result that sum of products is the product of sums has been used.

Sum of products = $\sum_{[n=0]}^{\infty} y_1^{n_1} y_2^{n_2} y_3^{n_3} y_4^{n_4} \ldots\ldots = \frac{1}{1-y_1}\frac{1}{1-y_2}\frac{1}{1-y_3} \ldots.$

Product of sums = $\prod_{j=1}^{\infty} \sum_{n_j=0}^{\infty} y_j^{n_j} = \prod_{j=1}^{\infty} \frac{1}{1-y_j} = \frac{1}{1-y_1}\frac{1}{1-y_2}\frac{1}{1-y_3} \ldots.$

$$G[x] = \int_0^{2\pi} \frac{d\theta}{2\pi} e^{i\,\theta\,U} \int_0^{2\pi} \frac{d\varphi}{2\pi} e^{i\,\varphi\,N} \prod_{j=1}^{\infty} \frac{1}{1-\left(e^{-i\,\theta\,j}\, e^{-i\,\varphi}\, x_j\right)}$$

If the heights of the steps are uneven – say ϵ_j instead of j; $j = 1,2,3,\ldots.$ This answer would be modified to,

$$G[x] = \int_0^{2\pi} \frac{d\theta}{2\pi} e^{i\,\theta\,U} \int_0^{2\pi} \frac{d\varphi}{2\pi} e^{i\,\varphi\,N} \prod_{j=1}^{\infty} \frac{1}{1-\left(e^{-i\,\theta\,\epsilon_j}\, e^{-i\,\varphi}\, x_j\right)}$$

So now you see that this is what going to happen so I am going to rewrite the generating function and it starts to look like this. So all I have to do is sum over all the n's and then I take into account all the different energy levels here. So now of course I have done a clever thing here and that is I have interchanged the summation in the product sequence. So if you recall here there was you know the summation was before and the product was came later.

But here I have done the reverse I have put the summation earlier and the product later so the question obviously is that am I allowed to do that and the answer is yes because of this result here. So if you stare at this sequence of terms here so you have y_1^{n1} , y_2^{n2}, y_3^{n3} and so on. So I have to sum over all the n's so if I sum over all the n's I simply get geometric series etc.,

So now suppose I do the reverse so this is like a product ok so this just nothing but $\Pi_j\, y_j^{nj}$. So instead of doing the product first and summing later suppose I do the reverse I sum each of those y_j^{nj} first and then I take the product so what do I get? I get precisely the same thing because this is going to be y_j and then if I take the product later I get back the same thing.

So there is nothing lost or gained by doing this of course what is gained is basically that I am able to now do the geometric series in a nice way. So now having done this so remember that I am talking about marbles on a staircase where there is no restriction on how many marbles there are per step, so in which case I am allowing myself to sum from $n = 0$ all the way up to $n = \infty$.

So if you remember that I told you earlier that if these marbles represented fermions for example or spinless fermions specifically that I will not be allowed to accommodate more than one marble per step but that we will discuss shortly. But now let us imagine that there is no restriction on how many marbles I can accommodate per step in which case I sum all the way up to infinity and I get this result.

So now all I have to do is I take into account all the steps by multiplying with respect to this index j so for concreteness I had assumed that all the steps are of equal height. But I do not have to, I mean it is very easy thing for you to understand that I simply replace j by εj which represents the height of each step. So I won't, there is no loss of generality in going from here to there. So if the heights of the steps were all uneven clearly this would be the answer and this provided there is no restriction on how many marbles I can have per step ok.

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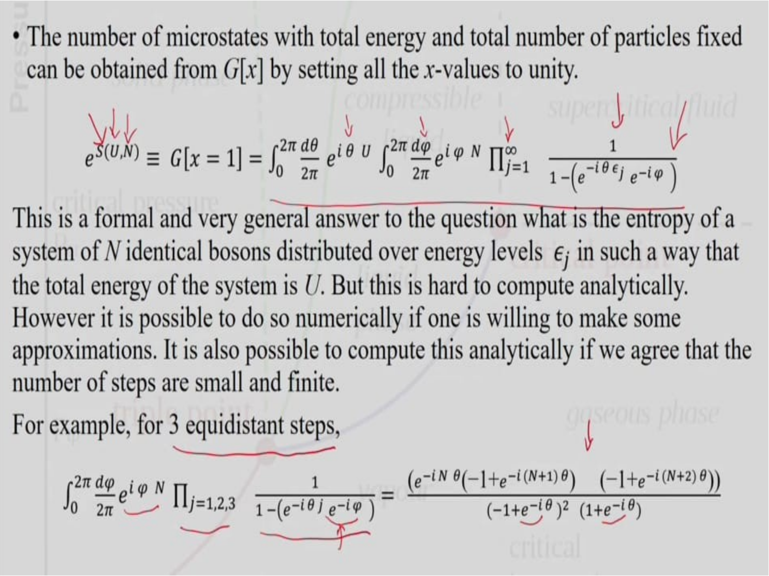

- The number of microstates with total energy and total number of particles fixed can be obtained from $G[x]$ by setting all the x-values to unity.

$$e^{S(U,N)} \equiv G[x=1] = \underline{\int_0^{2\pi}\frac{d\theta}{2\pi}\, e^{i\,\theta\,U} \int_0^{2\pi}\frac{d\varphi}{2\pi}\, e^{i\,\varphi\,N} \prod_{j=1}^{\infty} \frac{1}{1-\left(e^{-i\,\theta\,\epsilon_j}\, e^{-i\,\varphi}\right)}}$$

This is a formal and very general answer to the question what is the entropy of a system of N identical bosons distributed over energy levels ϵ_j in such a way that the total energy of the system is U. But this is hard to compute analytically. However it is possible to do so numerically if one is willing to make some approximations. It is also possible to compute this analytically if we agree that the number of steps are small and finite.

For example, for 3 equidistant steps,

$$\int_0^{2\pi}\frac{d\varphi}{2\pi}\, e^{i\,\varphi\,N} \prod_{j=1,2,3} \frac{1}{1-\left(e^{-i\,\theta\,j}\, e^{-i\,\varphi}\right)} = \frac{\left(e^{-i\,N\,\theta}\left(-1+e^{-i\,(N+1)\,\theta}\right)\quad\left(-1+e^{-i\,(N+2)\,\theta}\right)\right)}{\left(-1+e^{-i\,\theta}\right)^2\ \left(1+e^{-i\,\theta}\right)}$$

So this is the generating function that I have to calculate so my main interest of course is not to get the generating function but to get the entropy of the system and I have told you earlier that the entropy of the system is simply obtained by setting all the x's to 1. So in which case I get back what I was looking for the red circled summation that I started off with. So I set all the x's to 1 and there is only one place where there is an x here that is here so I have set it equal to 1 then what I have to do.

So the entropy is here and the logarithm of this quantity is my entropy. So if I am successful in doing this integration over this θ and over this φ and of course I am able to do this product properly then I am all done. So this is a brilliant way of counting how many microstates there are consistent with the constraints that the total energy is U and the total number of particles is N, without having to explicitly list all the possible solutions of those Diophantine equations.

So this is a very clever way of analytically counting how many solutions there are. Alright so now how do I convince you of the correctness of this it all seems quite abstract and kind of intimidating but it would be less intimidating if I were successful in proving to you or convincing you by taking some simpler examples. So instead of looking at infinitely many steps suppose I look at this specific example of three equidistant steps.

So if you recall that I have told you earlier that if the number of steps are small and the number of particles involved or the marbles involved are small then it really is not much of an effort to list all the solutions explicitly you do not have to it is not it does not take a lot of effort. So you might as well do that so remember that we have already done that once for three marbles and what I want to do is you know use this general formula for three steps and see if it works out to be what I told you earlier by explicitly listing all the solutions.

So now how do I work it out for three equidistant steps so here instead of taking the product over all the different steps. I only take product up to the third step and then all I have to do after doing this is that I have to integrate suppose I first decide to integrate over φ. How does that work?, so I clearly I can do this way that I can pretend that this is some kind of again I revert this back to the binomial type of form and I expand in the powers of this quantity or you can use your computer you can use your favorite software to do this.

Nowadays there is lot of software which does this like Mathematica, MATLAB so there is lot of these symbolic algebra packages which you can use to do it or if you do not want to do that it is very easy that just expand this out in powers of this object just because it is sitting there and then you know how to do it over φ. So I am not going to do this explicitly because it is a little tedious and it is somewhat unpleasant and but you should do it yourself, so if you do it you get this answer.

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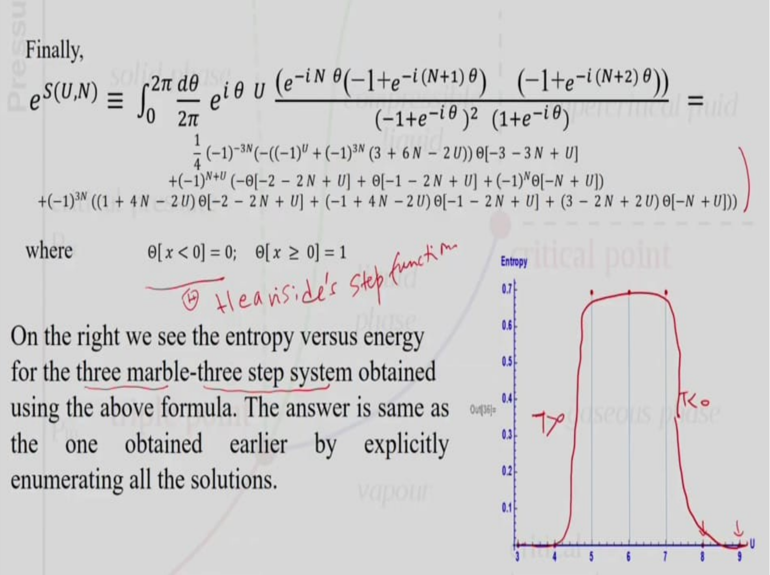

Finally,

$$e^{S(U,N)} \equiv \int_0^{2\pi} \frac{d\theta}{2\pi}\, e^{i\,\theta\, U}\, \frac{\left(e^{-i N\theta}\left(-1+e^{-i(N+1)\theta}\right)\quad \left(-1+e^{-i(N+2)\theta}\right)\right)}{\left(-1+e^{-i\theta}\right)^2\ \left(1+e^{-i\theta}\right)} =$$

$$\left.\begin{array}{c}\frac{1}{4}(-1)^{-3N}(-((-1)^{U}+(-1)^{3N}(3+6N-2U))\,\Theta[-3-3N+U] \\ +(-1)^{N+U}(-\Theta[-2-2N+U]+\Theta[-1-2N+U]+(-1)^{N}\Theta[-N+U]) \\ +(-1)^{3N}((1+4N-2U)\,\Theta[-2-2N+U]+(-1+4N-2U)\,\Theta[-1-2N+U]+(3-2N+2U)\,\Theta[-N+U]))\end{array}\right)$$

where $\Theta[x<0]=0;\quad \Theta[x\geq 0]=1$

Θ Heaviside's step function

On the right we see the entropy versus energy for the three marble-three step system obtained using the above formula. The answer is same as the one obtained earlier by explicitly enumerating all the solutions.

So now of course that is all over this variable this angle called φ but I also have to integrate over θ. So the integral over theta is similar because think of this as some kind of quantity in whose powers you decide to expand and expand this whole thing in powers of $e^{-i\theta}$ for example and then you integrate over θ and when you do that you get this rather nasty looking expression here which involves what is called Heaviside's step function.

So if you do not really follow all this it really does not matter all that much except that I am just using it to convince you of the correctness of this general formula here. So if you are already convinced, this specific example is not that important but nevertheless it is worthwhile it is instructive to go through at least one specific example but as you can see the final answer even for a three step problem is not easy.

Especially because I have not constrained the number of particles N, so N can be as large as it wants so and U can also be as large as it wants only the number of steps are three. So that is the reason why it is little more complicated so this involves what is called Heaviside so it is called Heaviside's step function. So this is the symbol I am going to use this symbol consistently throughout and this is called Heaviside's step function.

So Heaviside was an English mathematician his grandfather apparently was part of a rugby team and that team was called Heaviside's and his grandfather decided to take that as his last name so that is why it is called Heaviside, ok. Now I am going to plot this versus the total energy of the system versus entropy now I am going to now specifically focus on the three marble examples.

So I have already committed myself to studying three steps so in addition I am going to say that the three marbles know three steps three marble systems we have explicitly listed the solutions by hand some time back and at that time we got this plot. So if you rewind and go through the slide that I had described earlier it was precisely this plot, so the entropy was 0 if the energy was three in some units.

So I mean in the units that the energy of the first step is say the energy of the first step when there is one marble sitting on it is one so if you use those units in that case so if the energy was 3 the entropy is 0, if it is 4 is still 0 but if it is 5 it starts to become non 0 and 6 is non 0, 7 is non 0 then 8 again it is 0 because there is crowding at the top if you remember that is I explained this to you. Why entropy starts to fall and beacause the number of available states men are limited because the you have reached the top step already so if the number of steps is fixed then and the the entropy starts to fall so then it becomes 0 again.

So this also has this example that the entropy kind of is non-monotonic that means it kind of goes up and then comes down so that temperature is positive here negative there. So this is an example where the temperature can be both positive as well as negative but then I repeated this three step three marble example to convince you of the correctness of this analytical formula, ok.

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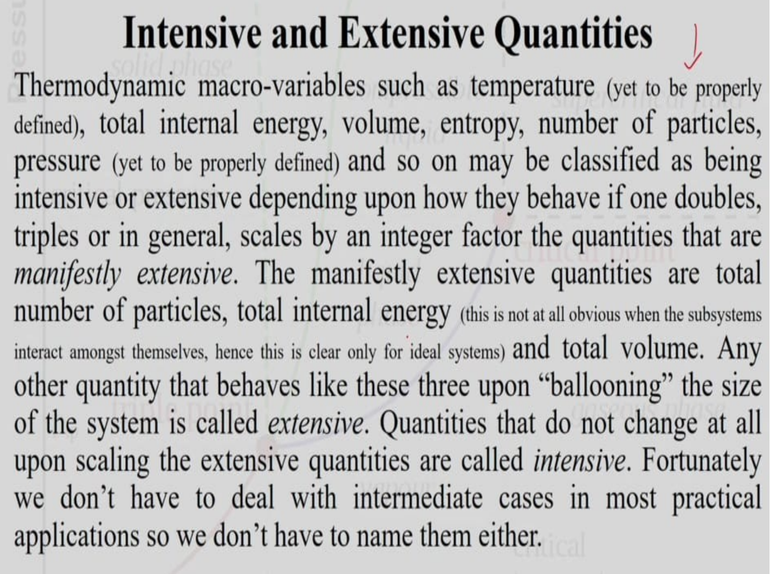

Intensive and Extensive Quantities

Thermodynamic macro-variables such as temperature (yet to be properly defined), total internal energy, volume, entropy, number of particles, pressure (yet to be properly defined) and so on may be classified as being intensive or extensive depending upon how they behave if one doubles, triples or in general, scales by an integer factor the quantities that are *manifestly extensive*. The manifestly extensive quantities are total number of particles, total internal energy (this is not at all obvious when the subsystems interact amongst themselves, hence this is clear only for ideal systems) and total volume. Any other quantity that behaves like these three upon "ballooning" the size of the system is called *extensive*. Quantities that do not change at all upon scaling the extensive quantities are called *intensive*. Fortunately we don't have to deal with intermediate cases in most practical applications so we don't have to name them either.

So now let me ask another question and that is, this is an important concept it is called the concept of extensivity of entropy so if you remember in some of the earlier slides I tried to explain to you why we take the logarithm of the number of ways of arranging the microstates and that is because the number of ways of doing that I told you balloons up exponentially.

But then by implication the logarithm should actually be linear so if I say linear you should ask linear in what? so linear obviously in the size of the system. So if the entropy is linear in the size of the system that is a property known as extensivity, so in this small paragraph I have explained to you that variables such as temperature, I have not properly defined it yet but I am going to do it shortly.

So assuming you know what that is from your earlier knowledge so temperature or you know the total energy volume entropy these are the various quantities that we wish to classify as either being extensive or intensive and the way to classify them is to you know double the size of the system and ask yourself do these quantities also double or do they remain the same. So if they double along with the size of the system for example then you say it is extensive if they do not change at all you call them intensive.

But then I have pointed out here in small print that the total internal energy is extensive only when the subsystems do not interact amongst themselves but if they do interact themselves it is rather hard problem and it is not at all obvious that it is extensive but of course we would not discussing that those issues in this introductory course.

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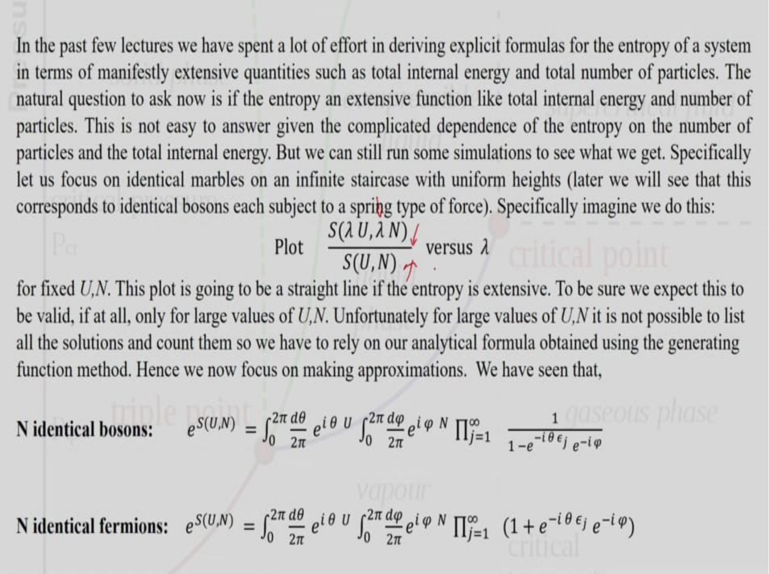

In the past few lectures we have spent a lot of effort in deriving explicit formulas for the entropy of a system in terms of manifestly extensive quantities such as total internal energy and total number of particles. The natural question to ask now is if the entropy an extensive function like total internal energy and number of particles. This is not easy to answer given the complicated dependence of the entropy on the number of particles and the total internal energy. But we can still run some simulations to see what we get. Specifically let us focus on identical marbles on an infinite staircase with uniform heights (later we will see that this corresponds to identical bosons each subject to a spring type of force). Specifically imagine we do this:

$$\text{Plot} \quad \frac{S(\lambda U, \lambda N)}{S(U,N)} \quad \text{versus } \lambda$$

for fixed *U,N*. This plot is going to be a straight line if the entropy is extensive. To be sure we expect this to be valid, if at all, only for large values of *U,N*. Unfortunately for large values of *U,N* it is not possible to list all the solutions and count them so we have to rely on our analytical formula obtained using the generating function method. Hence we now focus on making approximations. We have seen that,

N identical bosons: $$e^{S(U,N)} = \int_0^{2\pi} \frac{d\theta}{2\pi} e^{i\,\theta\,U} \int_0^{2\pi} \frac{d\varphi}{2\pi} e^{i\,\varphi\,N} \prod_{j=1}^{\infty} \frac{1}{1-e^{-i\,\theta\,\epsilon_j}\,e^{-i\,\varphi}}$$

N identical fermions: $$e^{S(U,N)} = \int_0^{2\pi} \frac{d\theta}{2\pi} e^{i\,\theta\,U} \int_0^{2\pi} \frac{d\varphi}{2\pi} e^{i\,\varphi\,N} \prod_{j=1}^{\infty} \left(1+e^{-i\,\theta\,\epsilon_j}\,e^{-i\,\varphi}\right)$$

So what we can do is that we can decide whether the entropy is extensive or not, so that is the question that I am going myself so I have told you that the number of ways of arranging the microsystem balloons up exponentially so by implication the logarithm of that should be linear, so that by implication therefore that the entropy is extensive. So how do I decide whether the entropy is extensive? so recall that I have a general formula for counting how many microstates there are in terms of θ and φ integrations.

So in principle I should be able to plot this ratio for example, so I fix the total energy and total number of particles then I scale up the energy by factor λ, I scale up the number of particles by factor λ and then I divide by the original entropy and if I plot this ratio versus λ and if the entropy is indeed extensive this plot should be linear ,it should be a straight line. So the question is: Is it a straight line?

So obviously the proper answer to this will crucially involve you know how good we are at explicitly evaluating those integrals over θ and φ. So we probably are not going to be able to do this in general and in any event we can suspect that if the number of say particles is small or the number of steps are small etc. The extensivity is not likely because you know there is lot of in some situation the solution exists some situation the solution does not exist.

So there is a lot of abrupt changes that takes place when the number of steps are small or when number of particles are small so linearity is an unlikely possibility. However linearity may actually be quite likely if you work in what is called the thermodynamic limit.

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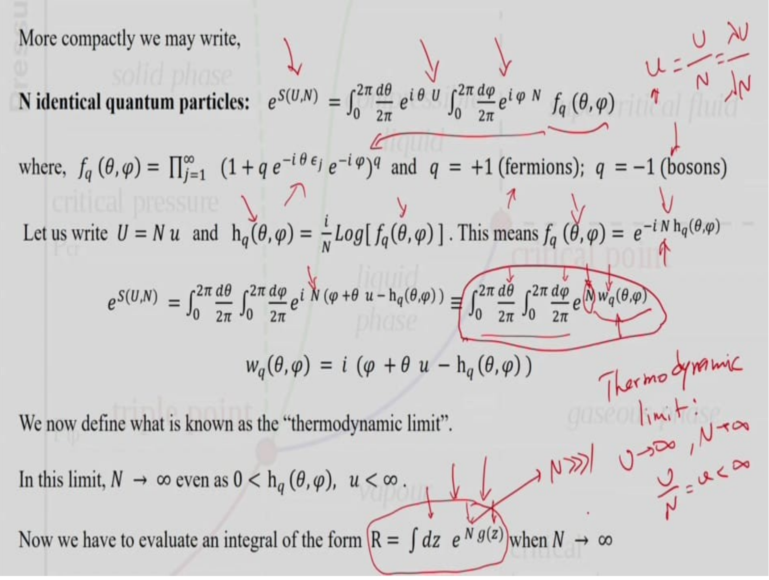

More compactly we may write,

N identical quantum particles: $e^{S(U,N)} = \int_0^{2\pi} \frac{d\theta}{2\pi} e^{i\theta U} \int_0^{2\pi} \frac{d\varphi}{2\pi} e^{i\varphi N} f_q(\theta,\varphi)$

$u = \frac{U}{N} = \frac{\lambda U}{\lambda N}$

where, $f_q(\theta,\varphi) = \prod_{j=1}^{\infty} (1 + q\, e^{-i\theta\epsilon_j} e^{-i\varphi})^q$ and $q = +1$ (fermions); $q = -1$ (bosons)

Let us write $U = N u$ and $h_q(\theta,\varphi) = \frac{i}{N} Log[f_q(\theta,\varphi)]$. This means $f_q(\theta,\varphi) = e^{-iN h_q(\theta,\varphi)}$

$$e^{S(U,N)} = \int_0^{2\pi} \frac{d\theta}{2\pi} \int_0^{2\pi} \frac{d\varphi}{2\pi} e^{iN(\varphi + \theta u - h_q(\theta,\varphi))} \equiv \int_0^{2\pi} \frac{d\theta}{2\pi} \int_0^{2\pi} \frac{d\varphi}{2\pi} e^{N w_q(\theta,\varphi)}$$

$$w_q(\theta,\varphi) = i\,(\varphi + \theta u - h_q(\theta,\varphi))$$

Thermodynamic limit: $U \to \infty$, $N \to \infty$

$\frac{U}{N} = u < \infty$

We now define what is known as the "thermodynamic limit".

In this limit, $N \to \infty$ even as $0 < h_q(\theta,\varphi)$, $u < \infty$.

$N \ggg 1$

Now we have to evaluate an integral of the form $R = \int dz\ e^{N g(z)}$ when $N \to \infty$

So what I mean by that is that I am going to ask myself suppose I you know fix the total energy per particle and then I scale up the number of particles. So extensivity demands that I scale the total energy the same way I scale the total number of particles so if that is the case then all I have to do is fix the ratio of total energy and the number of particles so I denote that by u. Small u is basically the energy total energy per particle so if I fix this then that is going to be the same as this, so even if I scale U and N I get back the original u.

So now I am going to try and see if I can simplify this integration which looks quite formidable actually in general and see if I can evaluate this integration in what is called the thermodynamic limit. So the thermodynamic limit is basically a limit where U tends to infinity N tends to infinity but U/N which is u is fixed ok. So this is called thermodynamic limit so I am going to work in this thermodynamic limit and so recall that this S(U,N) has this form and depending upon whether I am talking about fermions or bosons.

So that means if you have marbles where there is no restriction on how many marbles per step are allowed then that would correspond to bosons and if there is only a maximum of one marble per step that is allowed that is called a fermion. So that is how it works out and I have explained to you why this formula comes out the way it does and now I am going to rewrite this f in this fashion. So I am going to rather define a new quantity called h which is the log(f) multiplied by some prefactor like this. So as a result then I am going to be able to write this f as an exponential with the extensive N sitting right there.

So now I am going to be able to factor out this integration like this so there is an N and something in the bracket which I am going to called w. So eventually I will be forced to reckon with this integration over this two angles of course they were still there earlier and they are still there now. But then the simplification that I have achieved is that I have pulled out this N outside, say so long as I convince myself that this quantity is now intensive.

In other words if I you know scale the total number of particles by λ and I scale the total energy by the same amount then if this does not change at all then it is called intensive. So if I am successful later on in convincing myself that this is intensive then you see that all the extensivity is lumped into this N which is the number of particles in the system. So now I am kind of forced to reckon with this type of an integration where z is some you know so think of θ and φ as some components of a complex variable may be the real part this is the imaginary part.

So in other words this is z so I am going to be forced to think about this as an integral in the complex plane where this is a function of z is described by the real part θ and imaginary part φ so the point is that eventually I am forced to reckon with this type of an integration but crucially where this N is really huge. So now the question is that do mathematics textbooks tell me how to solve this easily, so the answer is yes.

So in complex analysis or complex variables there is a method called the method of steepest descent, I am going to skip that technical details for now because firstly it is not part of this course and I have listed that as a prerequisite, maybe if I get time later I might get back to it. But if you do not know what that is please read your book on complex variables and go to the chapter where they discuss the method of steepest descent.

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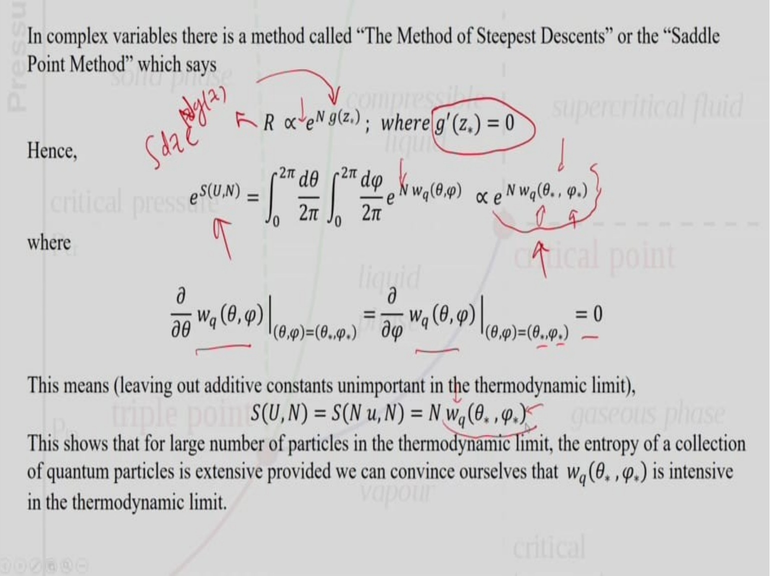

In complex variables there is a method called "The Method of Steepest Descents" or the "Saddle Point Method" which says

$$\int dz\, e^{N g(z)} \quad R \propto e^{N\, g(z_*)} \ ; \ where\ \boxed{g'(z_*) = 0}$$

Hence,

$$e^{S(U,N)} = \int_0^{2\pi} \frac{d\theta}{2\pi} \int_0^{2\pi} \frac{d\varphi}{2\pi} e^{N\, w_q(\theta,\varphi)} \propto e^{N\, w_q(\theta_*\, ,\, \varphi_*)}$$

where

$$\frac{\partial}{\partial \theta} w_q(\theta,\varphi)\Big|_{(\theta,\varphi)=(\theta_*,\varphi_*)} = \frac{\partial}{\partial \varphi} w_q(\theta,\varphi)\Big|_{(\theta,\varphi)=(\theta_*,\varphi_*)} = 0$$

This means (leaving out additive constants unimportant in the thermodynamic limit),

$$S(U,N) = S(N\,u,N) = N\, w_q(\theta_*\, ,\varphi_*)$$

This shows that for large number of particles in the thermodynamic limit, the entropy of a collection of quantum particles is extensive provided we can convince ourselves that $w_q(\theta_*\, ,\varphi_*)$ is intensive in the thermodynamic limit.

But to cut a long story short the steepest descent method says that suppose you want to do this integration and then N is really really large. So if this N is really large then the answer to this integration is simply this, so this I was trying to do this integration and this integration is ,sorry N. So this integration is nothing but it is just this it is proportional to that and where this z^* is basically the 0s of the, it is called the saddle point.

So it is the location of z where the first derivative of g becomes 0 so it is actually a saddle point because it is minimum in one direction and maximum in the other direction so resembling a saddle. So now those details I am going to skip why that is the case and so on and so please look that up from your book on complex variables. So roughly speaking so in the thermodynamic limits this kind of can be approximated using method of steepest descent or the saddle point method to this expression.

So this looks very simple so I have to figure out what does θ^* and φ^* are by simply equating the first derivatives to 0 at the values of θ^* and φ^* so and also if you ignore this proportionality factor here then I can just read off take the logarithm on both sides here and I can read off the expression for the entropy of the system which is basically the total number of particles times this w evaluated at this saddle point.

So obviously if I want to convince myself that entropy is extensive all I have to do is first evaluate this θ^* , φ^* and then insert it into this w and then convince myself that this w is intensive, in other word say that if I scale the system it is not going to change at all.

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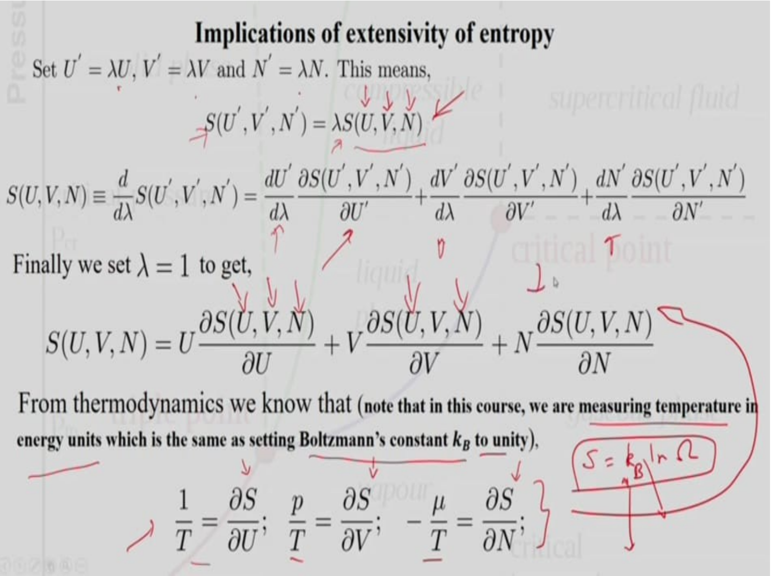

Implications of extensivity of entropy

Set $U' = \lambda U, V' = \lambda V$ and $N' = \lambda N$. This means,

$$S(U',V',N') = \lambda S(U,V,N)$$

$$S(U,V,N) \equiv \frac{d}{d\lambda}S(U',V',N') = \frac{dU'}{d\lambda}\frac{\partial S(U',V',N')}{\partial U'} + \frac{dV'}{d\lambda}\frac{\partial S(U',V',N')}{\partial V'} + \frac{dN'}{d\lambda}\frac{\partial S(U',V',N')}{\partial N'}$$

Finally we set $\lambda = 1$ to get,

$$S(U,V,N) = U\frac{\partial S(U,V,N)}{\partial U} + V\frac{\partial S(U,V,N)}{\partial V} + N\frac{\partial S(U,V,N)}{\partial N}$$

From thermodynamics we know that (**note that in this course, we are measuring temperature i energy units which is the same as setting Boltzmann's constant k_B to unity**),

$$\frac{1}{T} = \frac{\partial S}{\partial U}; \quad \frac{p}{T} = \frac{\partial S}{\partial V}; \quad -\frac{\mu}{T} = \frac{\partial S}{\partial N};$$

$\boxed{S = k_B \ln \Omega}$

So the question is can I do that? but before that let me point out to you that what are the important implications suppose I were able to convince myself that entropy is indeed extensive. So what would be the profound implication why am I so concerned about you know the extensivity of entropy. The reason is because it really leads to some remarkable identities that you should probably know from thermodynamics but I am going to refresh your memory so one of them is called the fundamental relation in thermodynamics.

So suppose so imagine a gas, I will get to the gas later I have been talking about marbles on the staircase but that is not really a classical ideal gas we will get to that later. But suppose you know just for a moment I will appeal to your knowledge from your earlier course work, so if I am talking about an ideal classical ideal gas you know that the entropy really depends on the total internal energy and there is something called the volume of the system which we have not encountered yet.

Because I am talking about marbles on a staircase till now so well eventually I will be encountering volume as well so if I decided to scale the total internal energy of the system the volume of the system and the number of particles in this fashion. Then extensivity simply means that the entropy is just scales the same way, in other words it is also λS.

If this is really the case if entropy is indeed extensive then all you have to do is realize that to get the original entropy its the same as differentiating this with respect to λ so if I differentiate with respect to λ this becomes S and so S becomes the derivative of the scaled entropy with respect to the scale itself. So it is really peculiar but this is an important observation because I can use the chain rule of multivariable calculus and rewrite this as you know there are three independent variables here.

U', V' so each of them depend on this λ so there is an implicit dependence on λ so I can partially differentiate S with respect to U' and then differentiate U' with respect to λ and I do the same with V' and with N' and then finally I set λ to 1, so if I do that I get this nice relation but now I have to appeal to your knowledge of thermodynamics and then you will recall that in thermodynamics the absolute temperature is defined as the reciprocal of derivative of the entropy with respect to internal energy.

Why this is a meaningful definition of temperature is something I will get to a little later so it is not some arbitrary definition there is a deeper physical reason for why temperature is defined like this in thermodynamics. So we will get to that a little later but for now let us assume that you know this from your knowledge of thermodynamics. So similarly a pressure is defined as that this temperature times the rate of change of entropy with volume of course.

When I am differentiating with respect to volume I have to keep the total energy and the total number of particles fixed so if I differentiate it with respect to total energy I have to keep the volume and number of particles fixed and lastly there is something called chemical potential. So the chemical potential is similarly defined as temperature times the rate of change of entropy with the number of particles so there is a sign conversion that you define it with a negative sign.

So these are all from your earlier knowledge of thermodynamics that I am not going to presently derive but I will be deriving them may be in few slides down the role. So if you allow me to do this if you allow me to write this then I am going to be able to insert this into these relations and derive a nice formula but note this in small print I have written here that we are measuring temperature in this course in energy units so which is the same as setting this Boltzmann's constant to unity.

So normally the kind of entropy is defined as k_B times the number of ways of doing this. In fact this formula is you know engraved on the tombstone of Mr. Boltzmann himself and this of course it would be ridiculous if this k_B was set equal to 1 on his tomb stone in which case you would not be paying a tribute to him at all by setting his famous constant to 1 so it is a good thing they did not do that in his tomb stone on his tombstone.

But I am going to do this in this course am going to set k_B to 1 because it is annoying, I would much rather measure temperature in energy units and get rid of this altogether. Alright so now am going to insert all these identities into this relation which is obtained from you know chain rule of multivariable calculus.

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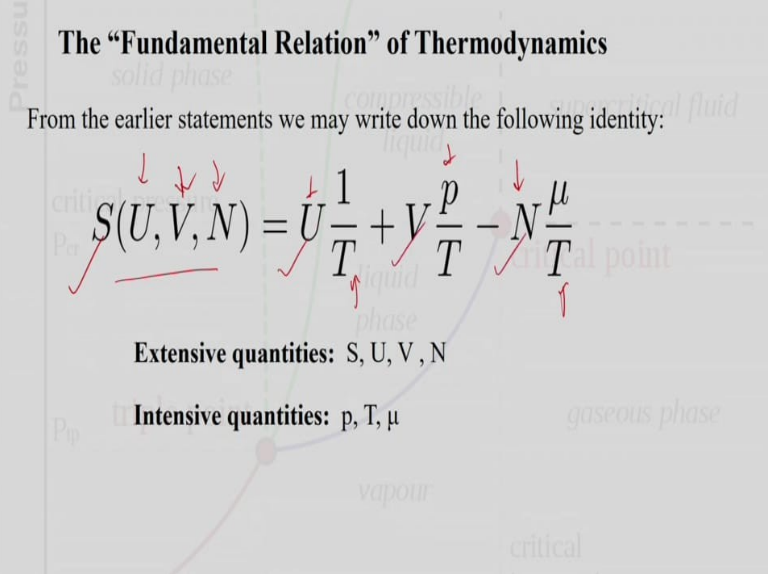

The "Fundamental Relation" of Thermodynamics

From the earlier statements we may write down the following identity:

$$S(U,V,N) = U\frac{1}{T} + V\frac{p}{T} - N\frac{\mu}{T}$$

Extensive quantities: S, U, V, N

Intensive quantities: p, T, μ

And I get this result this beautiful result that says that the entropy of thermodynamics system specifically a gas in this example. So it does not have to be ideal gas by the way I made no commitments about whether the gas is ideal or van der Waals or any other type of gas but it is just a gas. Because there is a volume associated with this and there is number of particles and there is total energy.

So the entropy of this gas is nothing but the total energy divided by absolute temperature plus pressure times volume divided by absolute temperature minus chemical potential times number of particles divided by absolute temperature. So from here it is obvious that the extensive quantities are entropy ,the total internal energy, the total volume and total number of particles and the rest are intensive so the other three pressure, temperature and chemical potential are intensive.

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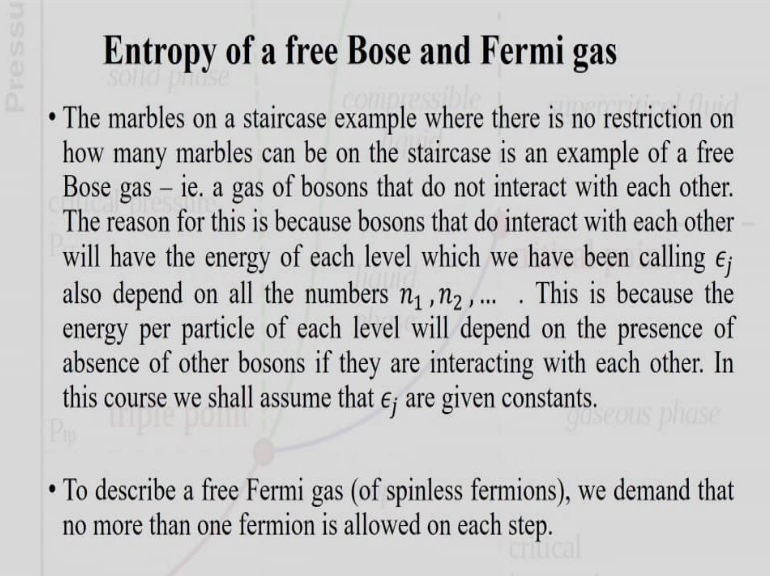

Entropy of a free Bose and Fermi gas

- The marbles on a staircase example where there is no restriction on how many marbles can be on the staircase is an example of a free Bose gas – ie. a gas of bosons that do not interact with each other. The reason for this is because bosons that do interact with each other will have the energy of each level which we have been calling ϵ_j also depend on all the numbers $n_1, n_2, ...$. This is because the energy per particle of each level will depend on the presence of absence of other bosons if they are interacting with each other. In this course we shall assume that ϵ_j are given constants.

- To describe a free Fermi gas (of spinless fermions), we demand that no more than one fermion is allowed on each step.

So I am going to stop here and just to give you a heads up so in the from the next slide onwards am going to discuss the I am going to explicitly derive formulas for the entropy of a Bose gas and a Fermi gas but then in the thermodynamic limit. So I am going to work only in the thermodynamic limit and I am going to use my saddle point or the method of steepest descent approximation to get hold of a nice closed formula for the entropy of a Bose gas and a Fermi gas so hope you will join me for the next hour, thank you.