

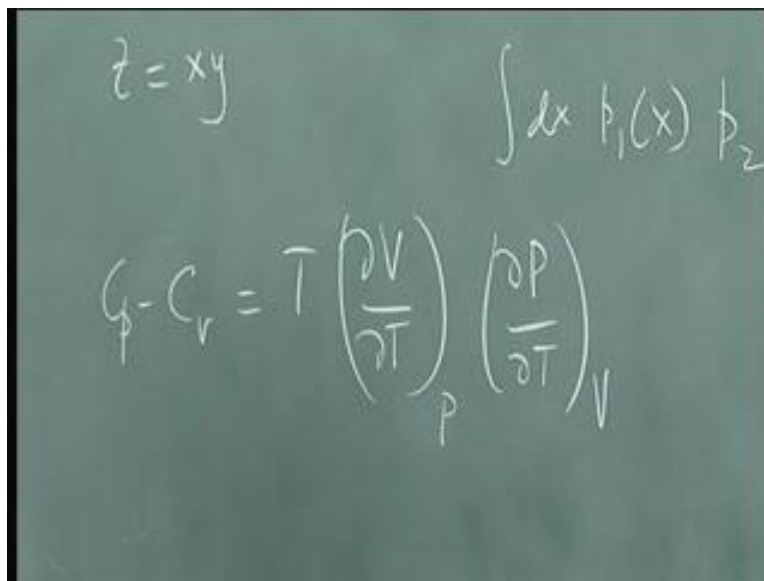
Classical Physics
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Lecture No. # 31

Let us go through the statements and you will chorus true or false. As I read them out the chemical potential of thermodynamics system is an extensive quantity. This is true or false, it is an intensive quantity. We also know that it is the Gibbs energy per particle so, right away that tells you. That it is an intensive quantity any definition of it will tell you that, it is an intensive quantity. The slope of liquid gas coexist in it is curve in the tp plane is always positive and this is a true statement, because the entropy of the gas is greater than that of the liquid and the specific volume is also greater. So, according to Maxwell's relation, the slope is positive always the square of mean of random variable can never exceed the mean of it is square, this is a true statement.

It could be equal to it is square in which case, what would you conclude? There is just a delta function distribution, it is a sure variable. It is no longer a random variable single value, if it takes on sample space as one particular value, that is it, this is equal otherwise it is always less.

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The image shows a chalkboard with several mathematical expressions written in white chalk. In the top left, the equation $z = xy$ is written. In the top right, the integral $\int dx p_1(x) p_2$ is written. In the center, the equation $C_p - C_v = T \left(\frac{\partial V}{\partial T} \right)_P \left(\frac{\partial P}{\partial T} \right)_V$ is written, with the subscripts P and V positioned below the respective partial derivative terms.

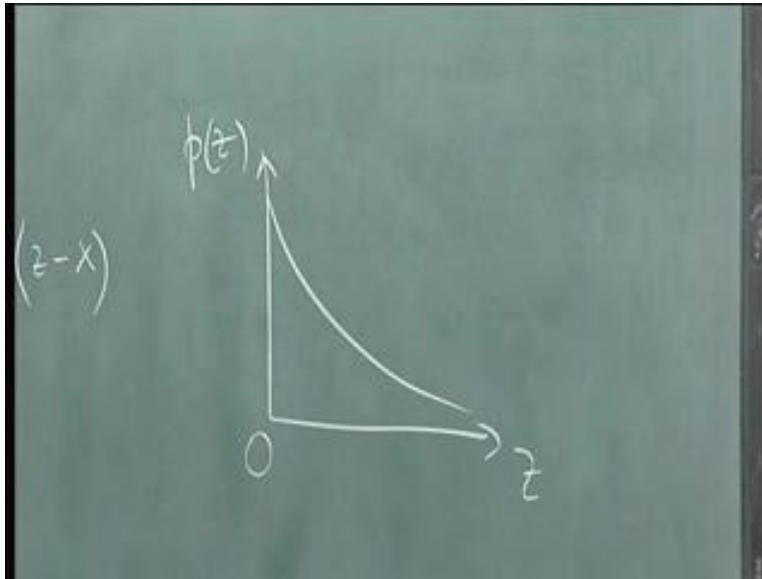
Now, the next one many people had made small errors in it I said that if you had a variable z equal to x and y who are independent random variables with prescribed probability distributions. Then I said the distribution of z is given by $dx p_1$ of $x p_2$, this is the distribution of density of y z minus x . That is of course not true, this is the distribution of the random variable z equal to x plus y , that is it so, not $x y$ certainly $x y$ is little more complicated. Because you have to write the delta functions z equal to $x y$ and then it will integrate over x .

For example and when you take the y out and you get a one over mod y so, it is quite a complicated thing for Maxwell in distribution of velocities. In a classical ideal gas the mean speed of the molecule is equal to the root mean square speed of a molecule. This you know from high school is not true. They work different they too work quite different the mean speeds the median speed the most probable speed and the rms speed are all different from each other. They are all dimensionally, they are all proportional to kt over n square root of kt over n multiplied by various factors, like 8π or 3 or some such thing, which you can compute? The relation c_p minus c_v equal to $t \Delta v$ over Δt at $p \Delta p$ over Δt at v , it is of course valid for a classical ideal gas.

Because this difference is equal to this the gas constant on the right hand side for a single mole, but this relation is valid for thermodynamic relation and it is valid for all gas certainly not necessarily restricted to the classical ideal gas. That too most people got the right answer in a system at thermal equilibrium at temperature t , the mean value of any absorbable is equal to it is most probable value not true. They need not be even a unique most probable value at all; you could have a flat distribution. For example, then there is no single most probable value everything is equally probable. So, the mean is not the same as the most probable value and I do not know why many people tick this by the way the probability density of the atmosphere. If you assume that this is just due to gravity and everything is at a constant temperature.

As you go up the probability of finding the molecule at greater height, it is exponentially decaying as a function of height decays exponentially. So, what is the most probable value the floor that is the everything it is got.

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So, that is the most probable value, because once you have a distribution as a function of the height. Once you have a density function that tapers off exponentially, this is in fact the most probable value. If this were true that the mean value is equal to the most probable value and you know the scatter about the mean is very low. We should all have died of suffocation long ago, since we have not clear if it is mixed blessing or not?

Since we have not it is clear? That the mean value is not equal to the most probable value, in fact it is enormous scatter always. Let f denote the Helmholtz free energy of a substance then $\frac{\partial^2 f}{\partial t^2}$ at constant v and n must be negative definite true this statement is true, because this is related to the specific heat minus. This quantity is related to the specific heat at constant volume and that we know is got to be positive definitely. When a biased coin is tossed repeatedly till a head is obtained for the first time and then of course you stop. You say the probability p^n that head is obtained for the first time in the n th toss and n is a random variable, here is n minus $1 - q$ plus p false. What is the right answer? It is clear?

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The image shows a chalkboard with handwritten mathematical equations. The first equation is $P_n = q^{n-1} p$. Below it, the sum of probabilities from $n=1$ to infinity is shown: $\sum_{n=1}^{\infty} P_n = p \sum_{n=1}^{\infty} q^{n-1} = \frac{p}{1-q} = 1$.

That P_n in this case must be equal to q to the power n minus 1 and then a p . Because the first n tosses you must have failure the probability, for that is q and then in the last toss the n th toss you have this. By the way what is the mean number of tosses that we have to you had to normalize this probability to make sure, this is normalized to one. So, certainly if it is not normalized to one then there is no guarantee, which the event will occur at all. What is the normalization? I would suggest, I mean you must have n equal to 1 to infinity, this must be equal to unity. Because you must get if this event is a sure event, you are going to get a head sooner or later then either you get it in the first or the second or the third, somewhere along the line, you have to get it.

Therefore, this must be normalized to unity so, sum all the way up to infinity should be normalized to infinity. Otherwise it is not a proper random variable, this event is not even a certain event, but if it is normalized to unity it is certainly is so, what is this? Equal to that is certainly true. So, it is a definite event, it is going to happen the note the very important point here. The reason I am able to add this p_n and then say that is normalized to unity is, because the different events are exclusive of each other. If for the first time you get a head in the fifteenth toss, you are guaranteed that you did not get it in the first fourteen. They are not inclusive then of course you cannot normalize in this fashion so, probability is fairly subtle and because the probability of getting a head. For the first time in the n th toss is for each n a different event and excludes all other events. Therefore you can normalize it to this.

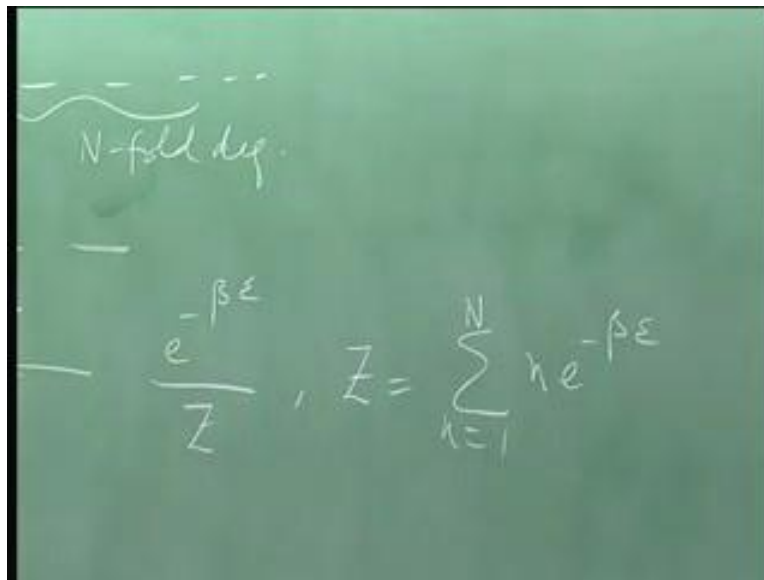
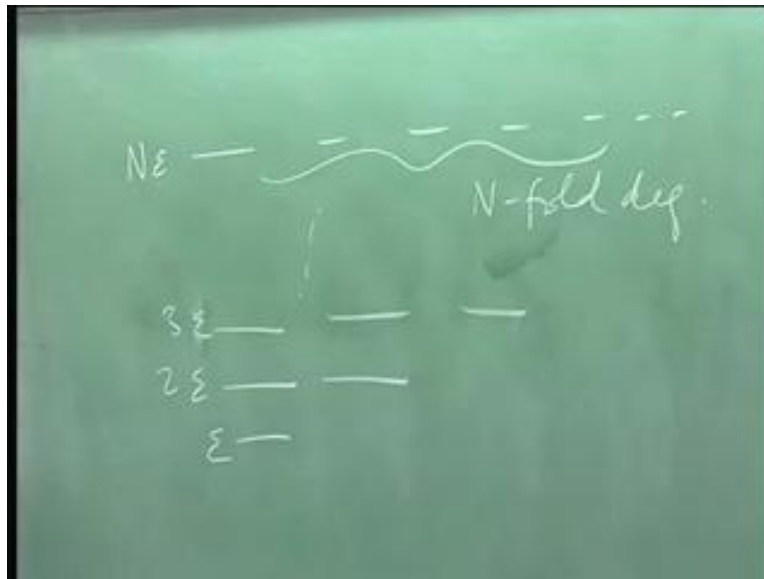
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The image shows a chalkboard with handwritten mathematical equations. The top equation is $\langle n \rangle = \sum_{n=1}^{\infty} n P_n$. Below it, a fraction is written: $\frac{\langle n \rangle}{\sum_{n=1}^{\infty} P_n} = \frac{1}{p}$. The denominator of the fraction is the sum of probabilities, which is equal to 1. The result is $\frac{1}{p}$.

By the way how many coins should I toss on the average? How many tosses should I make in order to get a head for the first time? You know what is the average number in order to get a head? What is the average of this P_n pardon me it is 1 over p is that reasonable and this is equal to 1 over p is that can of course work this out, but is this a reasonable answer. That it is 1 over p , because p is a half expecting two tosses on the average I would get a head for the first time in one of the two tosses, but as p goes to zero what happens to this? Of course you got a toss in large number of times and if p is one the first shot you got it.

So, if I say p equal to 0 , 1.5 or like you three check points, it works for all three not a proof, but of course that is certainly reasonable answer. This is certainly true I urge you to find the variance of this it is a geometric distribution; this guy is a geometric distribution so, find the variance of this and so on. This is also the distribution same geometric distribution, the similar thing is also going to give you in black body radiation. The probability that you have n photons of a given frequency in black body radiation is also geometrically distributed. We will see that in quantum physics course so, the geometric distribution occurs in many physical applications.

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That is what we are looking at? So, let us go in to the next problem, which was the fill in the blanks, you have the system with n possible energy levels and the first one is the ground state ϵ is non degenerate and then this two ϵ it is twice degenerate.

This is three ϵ and it is three fold degenerate and it goes up to n ϵ , which has got n fold degenerate. Then you are asked to find the total number of distinct states of system and all, you have to do is to add up all these fellows here. The total number of states is 1 plus 2 plus 3 up

to n , which is n times n plus 1 over 2 . So, that of course immediate the probability that the system is in it is ground in it is ground state. You have to actually take the relative probability for it to be in the ground state, which is proportional to e to the minus beta times the corresponding energy. Which is ϵ , but you must divide by the partition that probability, that it is in it is ground state, this probability is e to the minus beta ϵ , but it is divided by the partition function.

This partition function is the sum over all states, so it is from n equal to one to capital n , $n e$ to the minus beta ϵ . Now that is arithmetic or geometric series and you can sum this it is a finite series and you can sum it. What is 1 plus x plus x square up to x to the power capital n 1 minus x to the power n plus over 1 over 1 minus x is there a restriction on x . It is a finite series do not need a restriction. What if you go up to infinity $\text{mod } z$ should be less than unity, what happens? If $\text{mod } z$ is equal to unity, this series diverges $\text{mod } z$ equal to infinity, what about this series? Since you are doing all sorts of things, let us always ask peripheral questions.

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$$f(z) = 1 + z + z^2 + \dots + \dots$$

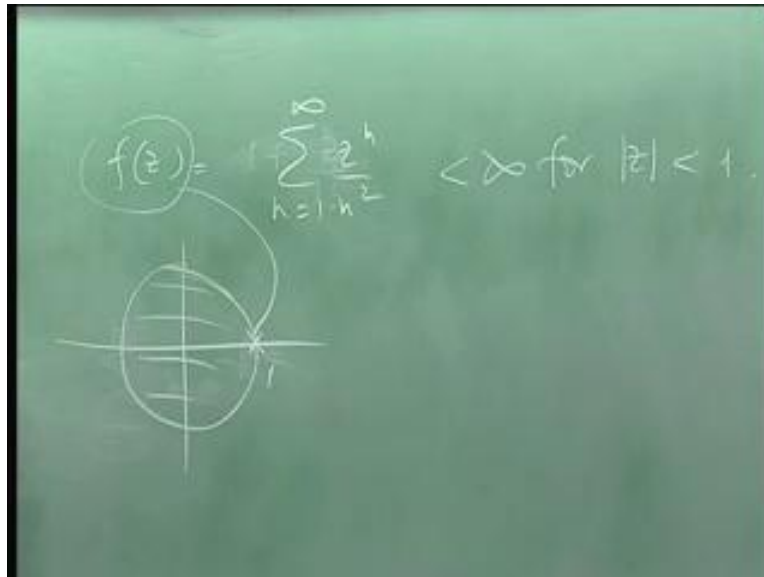
$$= \frac{1}{1-z}, \quad |z| < 1$$

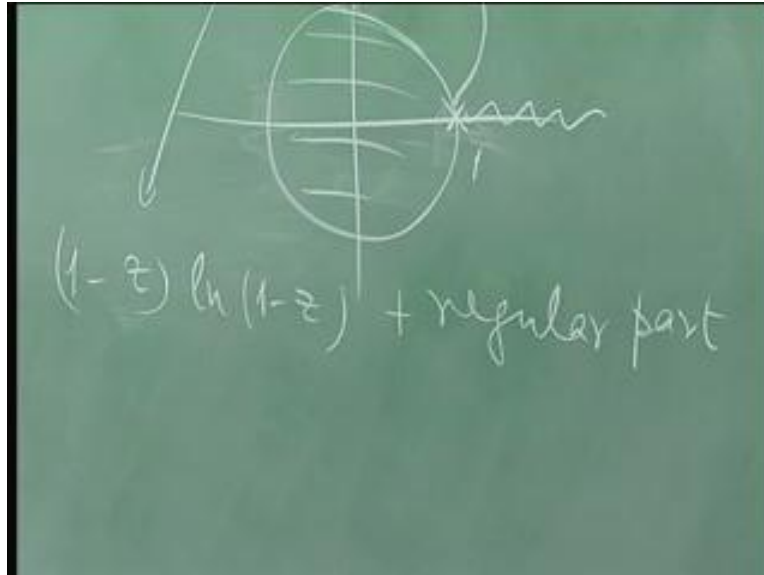
What about this series 1 plus z plus z square plus up to infinity, what is the value of their sum so, let me call this f of z equal to 1 over 1 minus z under, what conditions $\text{mod } z$ less than one?

What happens? If $\text{mod } z$ is equal to 1 by diverges only, if you put z equal to 1. Suppose I put z equal to minus 1, what do I get still diverges why do you say that? So, it does not diverge I mean it is $1 - z + z - 1 + z - 1 + z - 1$, it oscillates it oscillates. It does not converge absolutely and then take modulus, it does not converge and all that, but it oscillates. What happens? If I put z equal to i , it still oscillates, but over several values four values and so on. What is the only value for, which it actually blows up z equal to 1 and indeed the sum itself has, is an analytic function of z , which has got a simple polar z equal to 1. But at other places it actually does not diverge outside for $\text{mod } z$ greater than 1, what happens series is infinite it formally diverges?

On a circle of convergence a power series can do strange things it may actually converge, in some point it may oscillate. It may even absolutely converge at all points and yet the function that it represents will have a singularity, at least one singularity on the circle of convergence, but the series itself may actually converge.

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In fact look at this series let me give an extreme example, let me take this example z to the power n over n square n equal to 1 to infinity. Look at the series what is the radius of convergence, when does it converge. $|z| < 1$, you see as long as in the denominator, you have some power of n , you are going to do the ratio test.

There is some term n to some power over n plus one to some power and limit n goes to infinity and that part will go to 1. And you are going to just get z mod z so; this converges from mod z less than infinity for mod z less than 1. So, I know that in the complex z plane, here is 1 and this series converges absolutely inside here. I also know if I put z equal to mod z greater than 1, wherever I put it is just an infinity diverges, but on this circle of convergence. You agree that it is going to have it is largest value, since all the coefficients are positive and real and positive. This series will numerically have it is largest value at z equal to 1.

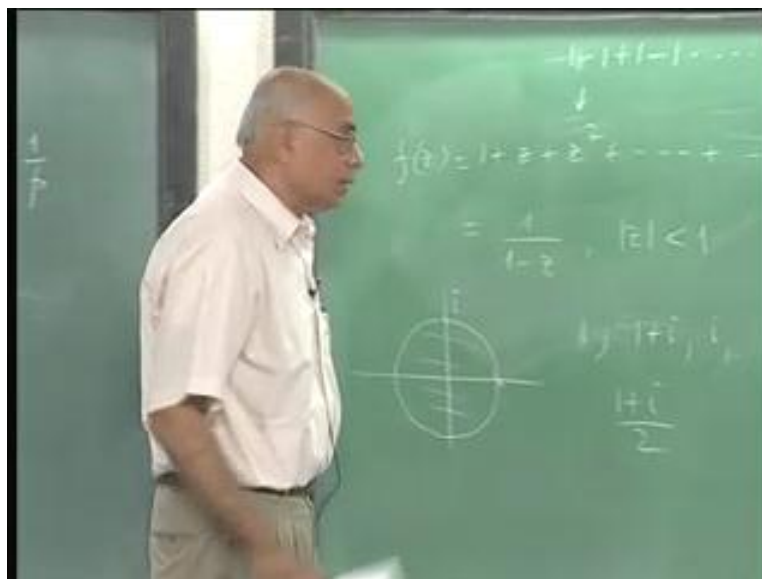
Because if I put minus 1 some terms would become negative and there would be cancellation, while I put z equal to i . There would be oscillations it is going to have it is largest value at z equal to one, but you put z equal to 1. What happens? Size magnitude takes modulus of this complex number. So, if I take mod f of z that gives me the magnitude of this number then of course it is largest for z equal to 1, but I put z equal to 1. What happens? It is $\pi^2/6$ of two and therefore, for all z on the unit circle for z not equal to 1. It is got to be smaller in numerical magnitude and finite and yet it diverges for all mod z greater than 1.

So, here is a series which is absolutely convergent in it is circle of convergence inside, as all series are diverges outside, but on the circle of convergence. It actually converges and that too absolutely at all points on circle of convergence and yet the function that it represents. Must have at least one singularity on the circle of convergence and it does the singularity will in this case always happen at z equal to 1. Because that is, where it becomes largest so, there is this function this function f of z has a singularity at this point.

In fact it has a logarithmic singularity there is a branch cut learning out in that fashion, but you see that singular part. In this function, in this case that goes like $1 - z \log 1 - z$ plus a regular part. So, there is very much a singularity a branch cut, but if you put z going to 1. What happens to that singular part? What is the limit of $1 - z \log 1 - z$ as z goes to 1, 0.

The power is stronger than the $\log x$, $\log x$ as x goes to zero. So, this actually vanishes, but it does not stop the function from having a singularity. The singular part vanishes like square root of z , it is singular at z equal to zero, but it vanishes at that point all the values of different branches coincide at that point. Just like 1 over square root of z blows up at z equal to 0, it is got a branch point, but the values coincide at the point at infinity. So, in the same sense you can have strange behaviors for power series take this series come back here take this series.

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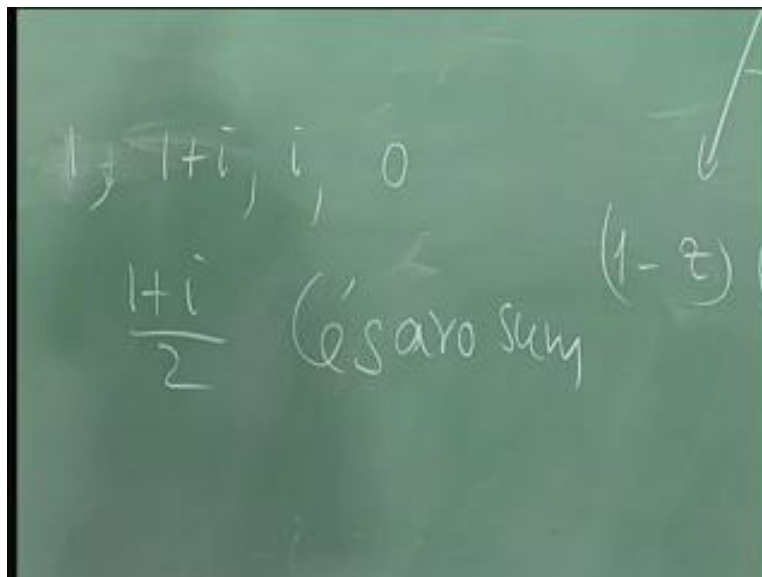


Now, I know that it has a pole at this point and it diverges outside converges absolutely inside, but on this circle it oscillates. And it is not that this function is useless, because let us put z equal to minus 1.

What do you get this side gives me minus of 1 minus 1 plus 1 minus 1 dot dot dot. So, what are the partial sums? If I keep the first term it is 1, if I keep the second term it is zero, if I keep up to three terms it is one again. So, how many different sums do you get? Two and what is the arithmetic average half? What happens you take the mask the function and put z equal to minus 1? You get a half. Look at z equal to i just put z equal to i what are the partial sums? You end up with the first term is one the second so, you have 1 plus i and you keep three terms 1 plus i minus 1. So, 1 and you keep four terms zero and that is it and since z to the power four. Now, is once again one we are going to start all over again, what is the arithmetic average?

1 plus i because two plus two, i divided by four so, it is 1 plus i divided by 2. That is the arithmetic average, you put z equal to i what do you get here? 1 plus i over 2. So, it gives you the arithmetic average of all the possible partial sums and this is called the Cesaro sum.

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So, it is not totally useless the series representation is not totally useless it actually giving you some information about the series. So, power series can do strange things and that is a subject by itself. The probability that it is in the ground state, we found the probability that it is.

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Yes, just a system I do not care about particle just a system. I never said it is a system of particles it is just a system, which has this one. Know why should everything be a system of particle it could be a one particle with these possible energy levels it could be a single particle.

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No, I am not even talking about the system of particles here, and then I have start specifying for you. What is the energy of each particle in order to tell you the microstate of the system? I am not even saying that I am just saying a system has these possible energy levels. So, the system could be one particle or it could be one object, which has these possible levels. So, that is the reason I worded carefully say. No, particle involved later when we do quantum statistics and so on. We are going to start putting particles into these energy levels and am going to say it is possible, one particle energy levels are the following. And I put so, many particles in well the system.

Let us take this class that is a system, I do not tell you what this class? Is right? The ground state is when everybody is sleeping the first excited state is when one person is awake and the second excited state, when two people are awake and so on. So, I can define a state so, what do you mean by a ground state of a system? It is a lowest possible energy level of the system that is it. So, whenever I say ground state of a system, it means the lowest possible energy level.

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What you said?

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I am not even talking about, which system it is? I am giving you information saying that this system is found to have these possible energy levels. Now the question you should ask is why I

should have discrete energy levels. All my experience with classical physics tells me that the energy levels of the possible system, like a particle would be continuous, like kinetic energy. For example, the answer is in quantum mechanics because our experience with quantum mechanics tells us, that there are situations where a given system could be an atom or electron or single particle or oscillator or whatever. Has discrete energy levels the only possible values of the energy of the system are discrete a set of discrete, which may be finite in number, which may be infinite in number, it may be equally spaced non equally spaced.

This particular thing is a toy model caricature, if you like where I have told you? That the ground state is the single state of the system first excited state, there are two possible states, but with same numerical value of the energy and so on and that is called degeneracy. Now, when we do quantum mechanics we will talk about where this degeneracy comes from and in general, it comes from some symmetry in the problem. Now, we are asking how we measure these energy levels and so on. That is how do you distinguish between different degenerate levels? Very good point the way you distinguish it is there is some other quantities physical quantity, whose values are different in the two states, but the energy is common just like in the hydrogen atom. When you say that the second state two s and two p the energy is exactly the same?

It is one fourth of 13.6 electron volts minus whatever, but the angular momentum state of the electron is different one corresponds to zero angular momentum state the other corresponds to quantum number one. So, you have to make a measurement of the n angular momentum, which will help you to distinguish between these two states. So, degeneracy is always with regard to some other variable, which can also be measured simultaneously along with the Hamiltonian, but which will have different level different values for the different states. There could be further sub degeneracy within the degeneracy and so on. But always with another quantity another physical quantity, but when we do quantum mechanics this will become completely clear. The probability that it has it is highest energy state and this is a slightly tricky question.

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A chalkboard with handwritten mathematical expressions. At the top, there are two equations: $k=1$ and $l=g$. Below them, the expression $\frac{N e^{-\beta N \epsilon}}{Z}$ is written. The N in the numerator is written as a capital letter. The Z in the denominator is written as a capital letter. There are some faint, illegible markings on the board.

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A chalkboard with handwritten mathematical expressions. The main expression is $\frac{2 e^{-2\beta \epsilon}}{Z}$ followed by a greater-than sign and $\frac{e^{-\beta \epsilon}}{Z}$. The Z in the denominator of the second fraction is crossed out with a large 'X'. There are some faint, illegible markings on the board.

It is actually $n e^{-\beta n \epsilon}$ over Z that is the probability, that it has it is highest possible energy. That energy is $n \epsilon$ so, the probability is proportional to $e^{-\beta n \epsilon}$ divided by the partition function, but there are capital n ways in which this could have happened? It could have been any one of those states and then the next one was like this and the next one like this.

It could have been in any one of these states and I am not worried about, which states it is in. Therefore, it could be here or here or here and as you know in probability addition is the operation. When you have this or option or means add and means multiply in probability theory. Then if the temperature exceeds the certain value t till the probability that the system has an energy $2n\epsilon$, actually exceeds the probability, that it has a lower energy. By this e to the minus $\beta\epsilon$ you are always saying that the lower energy levels are more probable than the higher energy levels. You see you have two of these guys and you have only one of this people. So, now this is going to happen if $2e^{-\beta\epsilon}$ at some temperature $\tilde{\beta}$ is greater than $e^{-\beta\epsilon}$.

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The image shows a chalkboard with the following equation written on it:

$$\bar{E} = \frac{E_1 + 2E_2 e^{-\beta\epsilon}}{1 + 2e^{-\beta\epsilon}}$$

Since, this is a positive number. You can score it off on to this side and then you solve for $\tilde{\beta}$ condition that these two are equal and beyond it is greater and then of course you discover that $\tilde{\beta} = \epsilon / (k_B \ln 2)$.

Above this temperature you are more probable that the higher states will be occupied, because the temperature is higher. Now, β is getting smaller and then the factor two here dominates and takes over and then you are going to have higher level is in fact more probable. By the way this is the reason why as you go to higher temperatures, it is clear? That more and more states are going to get occupied you can be kicked upstairs by this thermal energy kt of the heat bath and if

there is sufficient degeneracy up there. You actually find it more probable that the system is in higher level than in a lower level. That is the effect of temperature and it is dramatically manifested in astrophysics, because we will do this. When you look at the energy levels of hydrogen atom, it will turn out that there is under suitable conditions.

A finite probability that in a cloud of hydrogen atoms some of them will be ionized, they will in fact be such a high energy level that they are not even in the bound state. They are completely ionized and then they emit characteristic spectral lines and this is the reason. Why all of astrophysics is possible? It is possible, because of ionization formula, which tells you in an interstitial cloud gas, cloud of there is called as astrophysics. What is the probability that you have spontaneous ionization and then of course the radiation that comes from it is? What is measured and it is called Saha's ionization formula, it is a very famous formula, which Meghnad Saha discovered. And wrote in a very earlier paper very well known formula, which we will talk about and is in fact the basis of astrophysics in some sense.

So, it is based on this very simple consideration here that as you increase the temperature and you have sufficient degeneracy it is possible to have higher excited levels in the limit t goes to 0. The probability that the system has energy two epsilon s , you see when you go to t equal to zero t tending to zero the probability is relative probabilities of all the excited states relative to the ground state will go to zero.

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The image shows a chalkboard with handwritten mathematical expressions. At the top left, it says $\beta \rightarrow \infty$. To the right, there is a fraction $\frac{e^{-\beta \epsilon}}{2e^{-2\beta \epsilon}}$. Below this, a large parenthesis contains a series: $(e^{-\beta \epsilon} + 2e^{-2\beta \epsilon} + \dots)$. The fraction above is positioned as if it were the denominator of a larger expression, with a horizontal line underneath it.

Of course even the ground state, because now the ground state is $e^{-\beta \epsilon}$ over z and this z is $e^{-\beta \epsilon} + 2e^{-2\beta \epsilon} + \dots$ up to n . Now you have to find out what happens as β tends to plus infinity, which is t going to zero then this term is much smaller than this term and so on. And all these terms die out and this ratio is one so, as t goes to zero. The probability of any higher excited state will actually go to zero, because for example, the first excited state that it is an energy two epsilon would be twice and a two here. Now, let β go to zero this term dominates over that term and these are negligible compared to this term.

The whole answer goes like $e^{-\beta \epsilon}$, which goes to zero as β tends to infinity. So, all the higher states have zero probability and you will be in the ground state whether the ground state itself can be degenerate or not is a deep and delicate question. This we will talk about in the quantum course, because there is the t going to zero it is really completely quantum mechanical, there is a phenomenon called spontaneous break down of symmetry. Then we talked about base transition in the context of quantum physics, we will talk about that in great detail in the limit t goes to infinity. Then of course every states seems to become equally probable, because β goes to zero and all this $e^{-\beta \epsilon}$ factors are all unity.

Then the probability that the system is in a particular one of the states corresponding to energy $n \epsilon$ so, it could be this or this, but one particular state. This one particular one so, you have to choose this state of all the other states, but everything is equally probable. And there are $n + 1$ states and therefore the answer is just the reciprocal of the total number of states everything is equally probable. So, at t going to infinity you really do not have need for statistical physics. Once you have just the density of a state everything is equally probable and that is the end of matter. So, that is the answer to the last one of the portion here. Then the thermodynamics question many people got this, but several of you have not pointed out. Of course once I give answer, I realize this enormous talent had obtained the correct answer by various techniques.

If these techniques were all legitimate there would be unsolved problems at all. Theorem the four color theorem Poincaré conjecture Riemann hypothesis everything would have been proved, because the proof is very well known technique amongst student. I do not have to tell you, but I do have to tell you that ever. Since, they have solidified that there have been students and therefore many of these techniques are not as original as you perhaps might imagine fondly the standard. Of course technique in my days was to you having to prove something or the other you start here and keep writing. You start here and write backwards the proof is actually to be found in the edge, because there is a finite discontinuity between this and this crucial point missing point is right there.

So, in this case I penalize those of you who have not pointed out that at constant temperature.

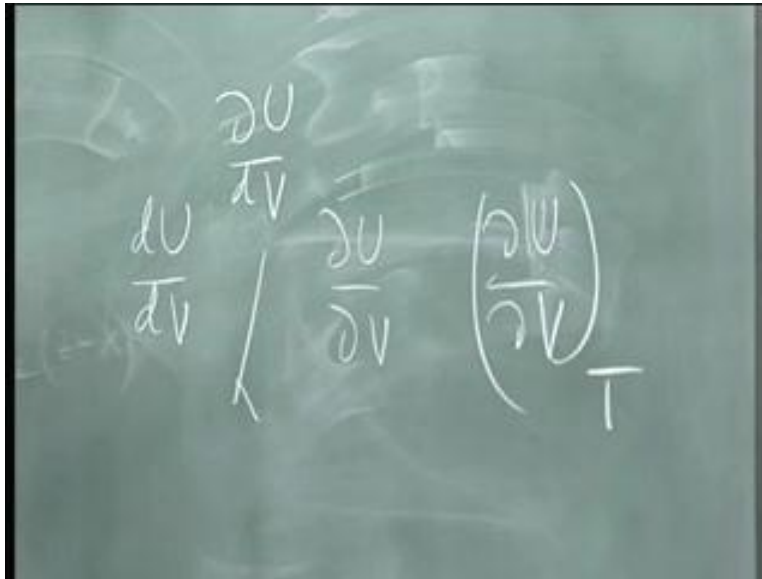
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$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$
$$dS = \left(\frac{\partial S}{\partial V}\right)_T dV + \left(\frac{\partial S}{\partial T}\right)_V dT$$

Write du if it is a function of u and v you could write this as $\Delta v \frac{du}{dv} + \Delta u \frac{du}{dt}$ at constant v or similarly for s ds it is equivalent ds over Δv at constant t dv plus ds over Δt at constant v dt .

Of course at constant temperature these guys go away and therefore you write allowed to write this or this, but you are not allowed to do it otherwise. So, you have to specifically say since it is isothermal otherwise it is not true. I agree that once you know the answer it is just the integral of 1 over a over v square and therefore you know what it is? And that is very convenient it comes out and so on.

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But this is not correct even less correct are statements like du over dv . I do not know what that means? Because it is a function of at least two variables at constant n . So, this does not even have meaning this statement here well one starts with that, then in the next step you tentatively write this and then in the third step it becomes this fully fledged with t . Now, you boldly assert this there are those among you who perhaps, because you have been too close to computers for too often have not gone quite the distance. I did see a couple of δu over dv and I did see a couple of that it is all being recorded by the way. So, those future generations of students will know that, we are aware of these techniques and they will not use these they may use others, but they have to exercise their minds little bit.

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The image shows a chalkboard with the following handwritten equations and annotations:

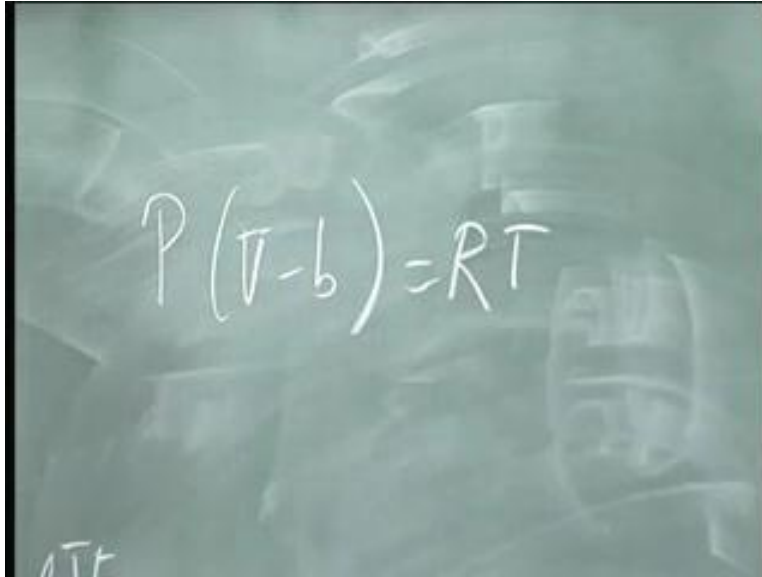
- At the top left, the expression $T ds - p dv$ is written.
- Below it, the equation $T \left(\frac{\partial s}{\partial T} \right)_v dT + \left\{ T \left(\frac{\partial s}{\partial v} \right)_T - p \right\} dv$ is written.
- Under the first term, $C_v dT$ is written with a wavy line underneath.
- Under the second term, $T \left(\frac{\partial p}{\partial T} \right)_v - p$ is written.
- An arrow points from the second term to the right, where the expression $\frac{a}{v^2} dv$ is written.

So, that is so, the solution is straight forward solution is value I write in many ways du is $t ds$ minus $p dv$. So, we do not need any of this and that is it this is all you have to use. By the way many of you have said that this is true for an isothermal process not necessarily too this is true. In general several others have said that by the first law of thermodynamics you get this, but I put it to you that you have also put in the second law of thermodynamics. Because otherwise there is no way of writing this the second law says that for a reversible process dq over t is the perfect differential ds , otherwise dq is greater than equal to $t ds$ or whatever and therefore that inequality becomes an equality for reversible process and then it is this. So, this is already incorporated the conservation of energy as well as the second law of thermodynamics statistics comes in here.

This is statistics entropy now if I regard this as function of s of t and v . For example, this is Δs over Δt at constant v dt plus $t \Delta s$ over Δv at constant v dv minus p and you combine it to this guy. And at constant temperature this goes away otherwise what is this equal to otherwise it is equal to cv , this is $cv dt$ by definition, this is $cv dt$. It sits there, but once you are at constant temperature it goes away so, if this goes away. Then the matter is very straight forward, you just have this and of course I use this as Δp over Δt at constant v minus p dv and this goes for vandovers gas this goes to a over v square dv .

This is very reasonable, because the b term in the van der Waals equation is in an exclusion term excluded volume the repulsive part, but the a is the attractive part long range attractive part. That is what causes a change in the potential energy of the system change in the internal energy of the system. The other is just a geometrical constraint what would happen?

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$$P(V-b) = RT$$

If I had p times v minus b equal to $r t$, suppose I change the equation of state of an ideal gas to include the excluded volume to take into account. The fact that you have hardcore repulsion for very small distances I put this v minus b .

This is also a possible equation of state, but it does not take the attraction into account. What would happen to this change in internal energy? And an isothermal expansion it would be zero, because you said a equal to zero, it goes away it goes to zero. So, it is entirely a consequence of the attractive part of the potential. So, once you have this then the change in the internal energies is of course a time 1 over v 1 minus 1 over v . You do not need to really remember formulas for the work done in an isothermal expansion and \log this and \log that and so on. Those statements are all specific to the ideal the classical ideal gas or to other equal gases, whose equations of states. You know, but that term cancels out in between this point and that point the term cancel and it is only this interaction part that plays a role.

This is how you compute it? What is c_p minus c_v for a van der Waals gas is it r it is not r . You got to go back to that thermodynamic identity and you have to compute it and of course a and b will play a role in this fashion. In general you do not know what c_p and c_v are as it is, but when you have statistical mechanics. You tell me something about the energy levels of the system, and then you can compute what c_p is, is you can compute? What c_v is, because you can actually calculate c_p and c_v as second derivatives of some free energies. Since you can calculate the free energy from the partition function the job is done.

What is the physical significance of the variance of the energy of a system in the canonical ensemble is it a measurable.

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$$\langle E \rangle = \frac{\sum_i E_i e^{-\beta E_i}}{Z} = -\frac{\partial}{\partial \beta} \ln Z$$

$$Z = \sum_i e^{-\beta E_i}$$

So, let us write this down remember that the internal energy u was equal to just the expectation value of the Hamiltonian average energy. This is equal to summation over the states of the system $e^{-\beta E_i}$ over summation i states i $e^{-\beta E_i}$ and this is minus delta over delta beta log z . This quantity is the partition function z that is the internal energy or if you like better still I write it as the average energy where use the usual symbol. This is the expectation value average value of the energy of the system, the Hamiltonian of the system.

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A chalkboard with the equation $\langle H^2 \rangle - \langle H \rangle^2$ written in white chalk. The chalkboard is slightly out of focus, and there are some faint markings and a bracket visible in the background.

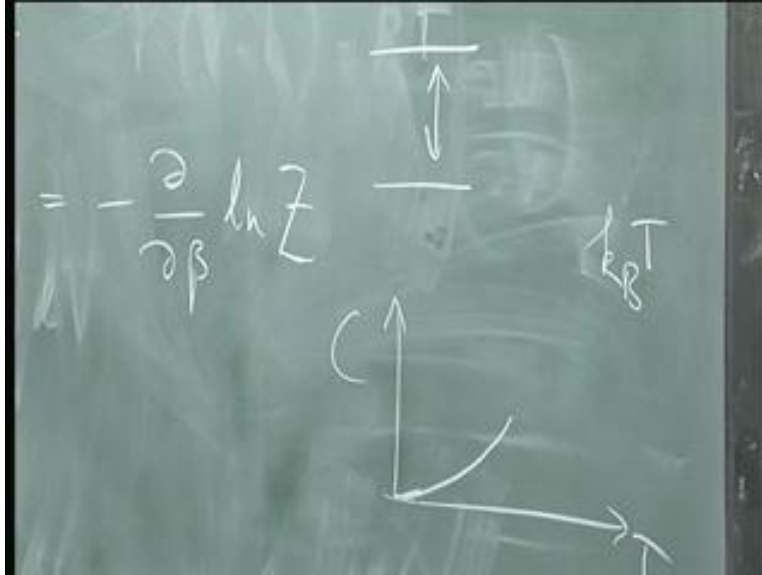
A chalkboard with the equation $\langle H^2 \rangle - \langle H \rangle^2 \sim T^2 \frac{\partial^2 U}{\partial T^2}$ written in white chalk. The chalkboard is slightly out of focus, and there are some faint markings and a bracket visible in the background.

The variance is actually $\langle H^2 \rangle - \langle H \rangle^2$ that is the variance, in the energy and this can be computed, because to calculate. This all I have to do is put square here E_i square do the summation. Then this quantity here is related finally to $\frac{d^2 U}{dT^2}$ over T^2 times various things so, there is a T^2 and things like that. Now, what is this quantity? So, it is related to $\frac{dU}{dT}$ finally. Now, what is this quantity specific heat at constant volume? So, it is a simple identity proved.

You can actually compute this number and it turns out that physically, when you put a system in contact with a heat bath thermal equilibrium with a heat bath at temperature t . The energy of the system is of course fluctuating. You can write the average energy down that is given by this simple formula, but the variance of the energy the scatter about the average. Also has physical significance and it is in fact directly relate to the specific heat of the system. What does the specific heat of the system actually tell you it tells you the capacity of this system to absorb energy and then of course as the consequence change it is temperature, if the conditions are right? So, if it turns out and this we will see very often, if it turns out that at very low temperatures a systems energy levels are quantized this will follow from quantum mechanics, it will turn out that there is a ground state of a system the lowest energy level.

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Then if it turns out that, there is a gap and then there are excited states of this kind and as the quantum numbers increase, it is possible? That there is continuum of energy, but at very low temperature it would be only this state that dominates as it goes to absolute zero. Now, you can ask what the specific heat of the system goes to do well, the specific heat measures the capacity of system to absorb energy. What you are doing is to put in contact with heat bath, which supplies a certain amount of energy, which is typically of the order $k_B T$ per degree of freedom of the heat bath's degree of freedom.

If this energy is much smaller than this gap here and the energy levels are quantized. This system has to be either here or here and so on. It cannot be anywhere in between then it simply cannot absorb this energy, which means that when you have a system with a gap in the spectrum of it is energy very low temperature. You expect the specific heat to go to zero as T tends to zero, you expect it to go to absolute zero to zero at absolute zero. And the question is how does it do it like? What power? So, you could say the specific heat c as T goes to zero, but the question is how this is exponentially fast is it? Like $e^{-1/T}$ or is it like T or T^2 , whatever that is a very crucial and sensitive question.

It tells you a great deal about the system itself and we will see when we do quantum statistics, that if you have a finite gap here. Typically this thing will go like $e^{-1/T}$ extremely flat, but if there is no finite gap, if there are excitations possible. Even at very small energies, which are not separated from the ground state by significant amounts then the specific

heat will go to zero. Like some power of T and this is at the root of Debye T^3 specific heat law. So, the specific heat of crystals at very low temperature it is also the specific heat of black body radiation, whereas you know by the Stephen Boltzmann law the energy the internal energy is proportional to T to the power 4.

u is proportional to T to the power 4 for a black body radiation, therefore the specific heat is proportional to T^3 . Now, tell me physically although we have not talked about this at all, why should that happen for black body radiation it looks like the energy spectrum is almost continuous. You already know the answer why is that for radiation, there is specific heat goes like T^3 , which means that there is no gap. That means that the energies can be continuously why is that physically? Why should that be the case? Why should it be that? If I take collection of photons, which is what black body radiation is? Why it should be that the energy levels are practically continuous.

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Yes and what is the quantum of energy? It is $h\nu$ for a photon of frequency ν and what is the range of ν ? How small can ν be black body radiation, which means all frequencies are present from zero to infinity? So, it is possible to add photons of arbitrarily small energy as ν goes to zero and from the ground state upwards these fellows will add. And then you do not have significant changes in energy and therefore no matter, how small the energy gap is you can always any kT can be apportioned into any number of photons or arbitrarily small energy. So, for such a system I would expect this how come it is happening for crystals. Now I am jumping they done a lot how come, it is happening to crystals, where would this come from.

I have atoms in rigid lattice and they are vibrating, how come energy can know that? I am saying the specific heat goes like T^3 at small temperature low temperatures. How come that is happening the frequency with, which they vibrate is not a single frequency. There is a whole spectrum of frequencies and there are collective excitations of the whole crystal, whereas you make the wavelength go to infinity or the wave number goes to zero. The amount of energy required will also goes to zero, there are deep reasons of symmetry breaking for this and we will discuss this thing, this in some greater detail. So, once again you can see that there is lot of

physics, which you can read out from these formulas, which we write down here. What happens at extremely low temperature is, what happens at very high temperature and so on.

We will discuss this when we do quantum physics in much greater detail so, much for this and I think with this. We close this chapter about statistical mechanics and then we take up next topic, which according to the syllabus. We have to discuss two other things one is relativity special relativity and symmetries that symmetries. Now, what I should like to do is discuss symmetries first, because we are almost there, if we have been talking about rotations. We have been talking about transformations, we have been talking about some little bit of quantum mechanics. We have certainly been talking about phase transitions many of which break symmetry then natural thing to do is to discuss symmetries first. And then we go on and finally discuss relativity and in relativity I will discuss this from the point of view of a symmetry group.

So, that there is a unification here and from the point of view of kinematics namely, you start with Lorentz transformation formulas or anything like that. I will assume you are already familiar with the Lorentz transformation laws, but we will motivate it. I will motivate this and say where it comes from and we will focus on the group aspects of it. The Lorentz group and how it relates to rotation group and so, on and so, forth. So, this is the way we would like to do this several ways, in which we could start and get into this is necessarily going to be a little discontinuity in the topic. So, it depends on what you would like to do? Should I do this by introducing a little bit of group theories so, that it can have a common language convenient language to do this?

Should we do this from? The point of view of phase transitions, which means I use words which you might. You may not have been used technical meaning may not have been discussed so, perhaps I will do this in terms of defining what a group is transformations are and so on and so forth. I will take it from there soon.