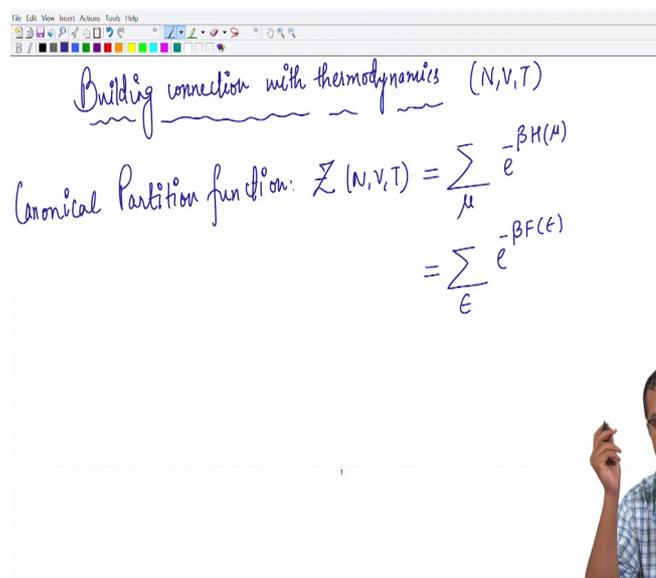


Statistical Mechanics
Prof. Ashwin Joy
Department of Physics
Indian Institute of Technology, Madras

Lecture – 16
Two Level Systems (Canonical Ensemble)

Good afternoon students. In the last class, we looked at the partition function of a system in canonical ensemble; system was in contact with the heat bar which maintained its temperature to t , and this was done at the expense of exchange of energy. So, in this class, we will start off from where we left and build a connection with thermodynamics for such systems.

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Building connection with thermodynamics (N, V, T)

Canonical Partition function: $Z(N, V, T) = \sum_{\mu} e^{-\beta H(\mu)}$
 $= \sum_{\epsilon} e^{-\beta F(\epsilon)}$

So, the motivation or the agenda of the lecture would be to build connection with the thermodynamics. Now, by this I mean that we live in a world of large number of particles where n tends to infinity, volume tends to infinity such that the number density it is a finite number. So, if you want to do an experiment on an ideal gas or magnetic solid, you are typically looking at degrees of freedom that are large in number. And what you really measure by a probe or by observing systems for a long duration is a thermodynamic quantity which is an average of many small degrees of freedom in the system.

So, since we are measuring averages, we have basically interested in thermodynamics of any system. So, using what we developed in statistical mechanics so far we can derive

thermodynamics. So, I will start off with the recollection that we arrived at partition function in the canonical ensemble. So, I am going to write down the canonical partition function as the macro status N, V, T thermodynamic macro state. And we got the expression for the partition function as summation overall the microstates e to the power minus beta H which the Hamiltonian of the microstate.

But we said that we are interested in a representation in terms of energy not microstates, because there are many micro states which may have the same energy so called degenerate microstates. So, we reduced it to the representation in terms of energy and when you do that we observe that the Boltzmann factor is now in terms of the free energy the function of energy e ok, free energy for the internal energy e .

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The whiteboard content includes the following text and equations:

$$Z = \sum_e e^{-\beta F(e)}$$

$$\approx e^{-\beta F(e^*)}$$

"Saddle point approximation"

e^* maximizes the $e^{-\beta F(e)}$

e^* minimizes $F(e)$

And we said that this the summation involves the large number of energy states, so it can be approximated by the largest value in the same and which is e to the power minus beta F the energy which minimizes F ok. So, by saddle point which was discussed stated without proof, so here I would like to remark that this E star maximizes the (Refer Time: 04:23) which is e to the power minus beta F , and minimizes the free energy ok. So, E star is a maximum of e to the power minus beta F , but it is the minimum of the free energy.

So, conceptualize means that if you leave a system connected to heat bath allow to equilibrate. The state of equilibrium would be the state of minimum free energy. The naturally evolution of a system is to continue evolving and exchange energy with the

thermostat, so that the thermodynamic value of e which is E star actually minimizes the free energy of the system. So, the natural evolution of a system is towards the direction of minimizing free energy, and this is also what we have mathematically done here. I have said that the entire summation is contributed from the value of the summation it comes with the minimum of free energy.

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Average energy: $E = \langle H \rangle = \sum_{\mu} H(\mu) p(\mu) = \sum_{\mu} H(\mu) \frac{e^{-\beta H(\mu)}}{Z(N,V,T)}$

$$= \frac{-\partial}{\partial \beta} \sum_{\mu} e^{-\beta H(\mu)}$$

$$= -\frac{1}{Z} \frac{\partial Z}{\partial \beta}$$

$$= -\frac{\partial}{\partial \beta} \ln Z$$

Now, I am going to construct the first meaningful quantity the simplest quantity in thermodynamics is the average energy. So, why not compute something that is the easiest. So, the average energy I will say it is E is nothing but the expectation value of the Hamiltonian and that can be computed by simply the average of my Hamiltonian weight with the probability p of μ ok. And if I recall this p of μ from the previous lecture is nothing but simply the Boltzmann factor e to the power minus beta H μ over the canonical partition function.

And I can write this as simply minus of d over d beta into summation over μ e raised to minus beta H μ over the partition function. And finally, this can be seen to be just 1 upon Z just minus 1 upon Z d over d beta Z , which is nothing but minus ∂ over β of $\ln Z$. And this is nothing but the average energy in the system.

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The whiteboard contains the following content:

- At the top, the equation $= -\frac{1}{Z} \frac{\partial Z}{\partial \beta}$ is written.
- Below it, a red box encloses the equation $E = \langle H \rangle = -\frac{\partial}{\partial \beta} \ln Z$. A circled '1' is written to the right of the box.
- Two red arrows point downwards from the box. The left arrow points to the word "Macroscopic" and the right arrow points to the word "Microscopic".
- Below the box, the text "From thermodynamics, $E = F + TS \quad \therefore F = E - TS$ " is written.

A man in a blue and white checkered shirt is sitting in front of the whiteboard, looking down at a notebook.

So, what I am going to do is just underline this important result. So, we can already see some kind of a building we know some kind of a bridge that has been built between statistical mechanics which is basically here the microscopic information and the thermodynamic which is macroscopic where you require large degrees of freedom and averages over these degrees of freedom on the left hand side.

And now we can actually find out relationships between free energy and the partition function, so that can be done by saying that let us say we call this expression as 1. From thermodynamics, I already know that internal energy is equal to free energy minus T S (Refer Time: 09:38) energy minus T S. So, I can write down so I think its F plus T S ok, because in the free energy is written as E minus T S.

(Refer Slide Time: 10:13)

The whiteboard contains the following handwritten text:

From thermodynamics, $E = F + TS$ $\therefore F = E - TS$

$dE = dF + Tds + sdT$

~~$dE = dF + PdV - \mu dN + dE + sdT$~~

$dF = -PdV + \mu dN - sdT$

$S = -\left. \frac{\partial F}{\partial T} \right|_{N,V}$

The word "Macroscopic" is written in red at the top. A blue circle highlights the equation for entropy, and a blue arrow points from it to the sdT term in the dE equation above.

So, just recall that if I take derivative and both side, differential and both sides. So, small change if I considered a small change in internal energy then this is equal to a small change in free energy plus $T ds$ plus $S dT$. But I know that from first law of thermodynamics, I can write down this $T ds$ as the pressure volume work, the pressure volume work minus μdN plus some internal energy change, and this is the $S dT$ ok.

So, you can knock off the internal energy change from both sides and simply see that dF is nothing but minus $p dv$ plus μdN minus $S dT$ which allows me to write down for entropy as minus of D by dT at constant N, V conditions. What do I with this, well I am going to substitute what I have just obtained for this entropy.

(Refer Slide Time: 12:15)

The image shows a whiteboard with handwritten mathematical derivations. At the top, the partial derivative of energy with respect to temperature at constant number of particles and volume is circled: $\left. \frac{\partial E}{\partial T} \right|_{N,V}$. Below this, the energy is expressed as $E = F - T \left. \frac{\partial F}{\partial T} \right|_{N,V}$. This is then simplified to $E = -T^2 \frac{\partial}{\partial T} \left(\frac{F}{T} \right) = -T^2 \left[\frac{-F}{T^2} + \frac{1}{T} \frac{\partial F}{\partial T} \right]$. A horizontal line separates this from the final equation: $E = -k_B T^2 \frac{\partial}{\partial T} \left(\frac{F}{k_B T} \right)$. In the bottom right corner, a man in a blue checkered shirt is visible, looking at the whiteboard.

And write down my equation as E equal to F minus dF by dT at constant N, V into temperature T fine. So, I can write this also by taking a temperature derivative, let me if I take a temperature derivative of F over T. So, I get the first term as minus 1 by T square into F, but I want an F. So, what do I do is basically I multiply this entire thing with minus T square. So, you can see the first term would be minus T square into minus F by T square plus 1 by T into dF by dT ok. So, this will give me your right hand side ok, so that is why I have written it like this. And so you can now write down your energy E as minus k B T square d by dT of F by k B T just multiplying and dividing by k B ok.

(Refer Slide Time: 14:31)

The image shows a whiteboard with handwritten mathematical derivations. At the top, the energy equation is repeated: $E = -k_B T^2 \frac{\partial}{\partial T} \left(\frac{F}{k_B T} \right)$. Below this, a note says "Noting $\frac{\partial}{\partial \beta} \equiv \frac{\partial}{\partial (1/k_B T)} \equiv -k_B T^2 \frac{\partial}{\partial T} \dots \beta = \frac{1}{k_B T}$ ". A blue arrow points from this note to a red-bordered box containing the final equation: $E = \frac{\partial}{\partial \beta} (\beta F)$. In the bottom right corner, a man in a blue checkered shirt is visible, looking at the whiteboard.

And noticing that I can compute a derivative with respect to beta and convert into derivative respect to T by simply saying that this is nothing d over 1 upon k B T which is nothing but I can take k B up stakes, but minus sign will incur and this will become a second derivative sorry this will become minus k B T into d by minus k B T square into d by dT.

So, I can write down this noticing what I have just written E as nothing but d over d beta of beta F ok, because 1 upon beta is nothing but 1 upon k B T ok. So, the operator minus k T square into d by dT is nothing d by d beta. Now, you can compare this where through what I have written here equation 1. So, this is also an expression between relationship between energy and ln z. So, if I compare the right hand side here minus d by d beta ln z the right hand side here d by beta F.

(Refer Slide Time: 16:33)

The image shows a digital whiteboard interface with a toolbar at the top. The main content is handwritten in blue ink. A red box highlights the equation $E = \frac{\partial (\beta F)}{\partial \beta}$, with a red line pointing to a circled '2' to its right. Below this, the text 'Comparing (2) with (1)' is written. In the bottom right corner, a man with glasses and a checkered shirt is visible, looking towards the whiteboard.

So, I am calling this as equation 2. And just comparing 2 with 1, you can write down you can get one more bridge between statistical mechanics and thermodynamics.

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The whiteboard contains the following handwritten text:

- At the top, the word "Composing" is written in a cursive style.
- In the center, the equation $F = -\frac{1}{\beta} \ln Z$ is enclosed in a hand-drawn rectangular box.
- To the right of the box, there is a circled number "3" with a line pointing towards the box.
- Below the box, the question "What is the relationship between E^* & $E = \langle H \rangle$?" is written.

A man with glasses and a blue checkered shirt is seated in front of the whiteboard, looking towards the camera.

You can write down you can write down free energy F is equal to minus 1 upon beta $\ln z$ ok. So, this is one more bridge that connects the microscopic world with the macroscopic observations and all connections with thermodynamic start from this bridge. Now, you would be wondering, what is the relationship between the energy that minimizes free energy, and the average energy that I have just derived which is nothing but the expectation value of the Hamiltonian. Well, I have already indicated that this E^* is same as E . But if you want to study this in more detail, so this is a thermodynamic energy or the average value of the energy.

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The whiteboard contains the following handwritten text:

- At the top, the question "Q: What is the relationship between E^* & E ?" is written.
- Below the question, an arrow points from E^* to the phrase "most probable".
- Another arrow points from E to the phrase "Thermodynamic".
- Below these, the text "Ensemble equivalence: As $N \rightarrow \infty$ (thermodynamic limit)" is written, with "Ensemble equivalence" underlined.

A man with glasses and a blue checkered shirt is seated in front of the whiteboard, looking towards the camera.

And this is the most probable energy. So, these are interchangeable because actually if I leave a system with large degrees of freedom and wait for it to become equilibrated with a reservoir. And I ask myself a question that what is the average energy of the system, well I can very easily say that it will be nothing but the most probable energy, because the system would be pending most of its time near the thermodynamic energy.

It will go above and below it, so the most probable energy and thermodynamic energy are interchangeable. And this correspondence becomes even better as a system size becomes infinity. So, you can easily see that connection by some sort of an ensemble equivalents. So, the answer lies in the ensemble equivalents which simply say that as N goes to infinity when you are reach thermodynamic limit, the canonical ensemble and micro canonical ensemble become the same or indistinguishable.

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Canonical Ensemble (N, V, T) \longrightarrow Micro-canonical Ensemble (N, V, E)

$$E = \langle H \rangle = -\frac{\partial}{\partial \beta} (\ln Z)$$

So, the canonical ensemble that is the ensemble that is of N, V, T converges to micro canonical ensemble, they become the same. And this is easy to understand. It means that if you take a system and increase the number of particles to a large value in thermo started, as the number of particles goes infinity, the energy of the system also becomes as good as constant. Of course, this is the small spread what I mean to say that the spread over mean becomes a diminishing number. And this can be proved by simply looking at the fluctuation in the total energy. So, I have already computed E which is the average of

the Hamiltonian and that was shown to be minus d over b beta of ln z. And we have also and we can also compute what is the variance or width of energy.

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The whiteboard shows the following derivation:

$$E = \langle H \rangle = -\frac{\partial}{\partial \beta} (\ln Z)$$

$$\text{Variance of } E: \langle H^2 \rangle_c = \langle H^2 \rangle - \langle H \rangle^2$$

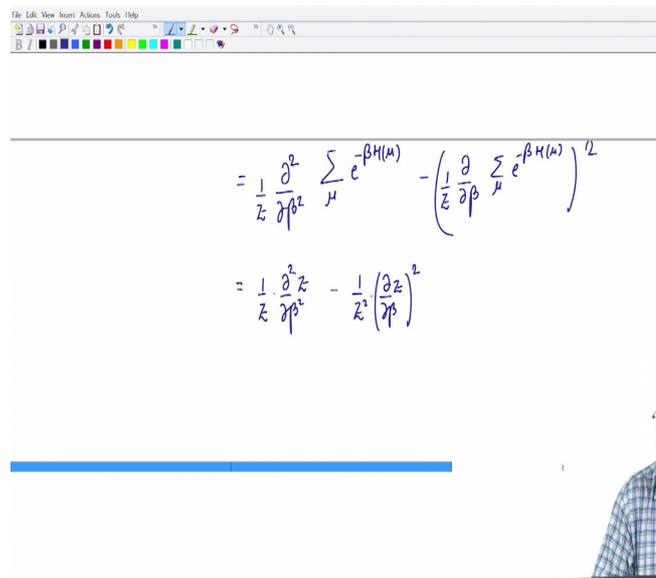
$$= \sum_{\mu} H^2(\mu) \frac{e^{-\beta H(\mu)}}{Z} - \left(\sum_{\mu} H(\mu) \frac{e^{-\beta H(\mu)}}{Z} \right)^2$$

$$= \frac{\partial^2}{\partial \beta^2} (\ln Z)$$



The variance would be the second cumulant of the Hamiltonian ok. Now, this is defined as the second moment minus square of the first moment. So, the technique remains same, very similar to calculate it. Here I would simply take to compute the second moment, I will simply measure the average of the you know Hamiltonian square. And to compute the square of the first moment I will simply take the first moment here and square the entire thing ok. And this can be very simply written as d square by d beta square ok. I need a new page. So, I will running out of space here. So, I will write down this in the new page.

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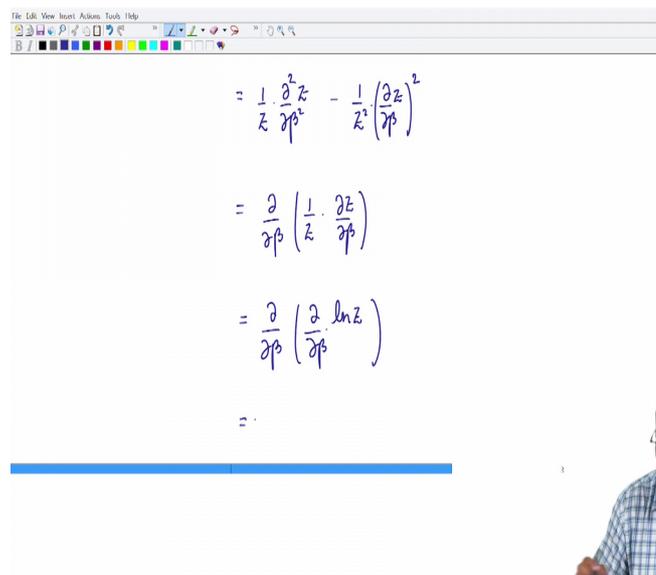


$$= \frac{1}{z} \frac{\partial^2}{\partial \beta^2} \sum_{\mu} e^{-\beta H(\mu)} - \left(\frac{1}{z} \frac{\partial}{\partial \beta} \sum_{\mu} e^{-\beta H(\mu)} \right)^2$$

$$= \frac{1}{z} \frac{\partial^2 z}{\partial \beta^2} - \frac{1}{z^2} \left(\frac{\partial z}{\partial \beta} \right)^2$$

So, I can write this as so each derivative beta will pull out minus H, I need h square. So, I will take two successive derivatives and polar 2 minus Hs. So, this would be just divided by z. And here I will take just one derivative is enough to pull out a single H and entire thing is squared. Notice that if I do it over dp title pull out minus h this is nothing but 1 upon z d square d beta square of z minus 1 upon z square d by d beta of z the whole square ok.

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$$= \frac{1}{z} \frac{\partial^2 z}{\partial \beta^2} - \frac{1}{z^2} \left(\frac{\partial z}{\partial \beta} \right)^2$$

$$= \frac{\partial}{\partial \beta} \left(\frac{1}{z} \frac{\partial z}{\partial \beta} \right)$$

$$= \frac{\partial}{\partial \beta} \left(\frac{\partial \ln z}{\partial \beta} \right)$$

So, now you can write this as $\frac{d}{d\beta} \left(\frac{1}{z} \frac{dz}{d\beta} \right)$. So, the by chain rule, it will give you the first term $\frac{1}{z} \frac{d^2 z}{d\beta^2}$ minus $\left(\frac{1}{z} \frac{dz}{d\beta} \right)^2$. And I already know what is the quantity inside the bracket which is nothing but $\left(\frac{d}{d\beta} \ln z \right)^2$.

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$$\langle H^2 \rangle_c = \frac{\partial^2}{\partial \beta^2} \ln Z = -\frac{\partial E}{\partial \beta} = k_B T^2 \frac{\partial E}{\partial T} = k_B T^2 C_v$$

$$\langle H^2 \rangle_c = k_B T^2 C_v$$

"Fluctuations in energy is related to heat capacity"

So, this is nothing but second derivative of $\ln z$. Remember I was computing the second cumulant of the energy. Now, where actually see that this quantity here itself is a unknown quantity ok. So, this is like the negative of the energy. So, I can write this as negative $\frac{d}{d\beta}$ energy or mean energy. And I know $\frac{d}{d\beta}$ is negative $k_B T^2 \frac{d}{dT}$. Since if you recall $\frac{d}{d\beta}$ is negative $k_B T^2 \frac{d}{dT}$ ok. And finally, you can see that $\frac{d}{dT}$ is nothing but heat capacity at constant volume. So, all these derivatives are at constant volume because we are doing in canonical ensemble problem.

So, the heat capacity of the system at constant volume is nothing but it is related directly to the second cumulant of energy. So, fluctuations in heat energy in a canonical ensemble are directly related to heat capacity. So, fluctuations are important they tell you something about the material property of the system fluctuations in energy or important quantities, and they are related to property of the system.

We are not the very meaning full. So, how was system undergoes energy exchange with the reservoir. And the nature these fluctuations decide what will be the heat capacity. So,

near phase transition for example, if these fluctuations become very large or diverging, the heat capacity of the system near such phase transitions would diverge ok. So, they are related to properties in a system in a very very in a very connections are very deep is what I would like to say.

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$\langle H^2 \rangle_c \sim N$ "Scales with system size"
 Width or Standard deviation: $\langle H^2 \rangle_c^{1/2} \sim N^{1/2}$
 Compute width/mean = $\frac{N^{1/2}}{N} \sim \frac{1}{N^{1/2}} \xrightarrow{N \rightarrow \infty} 0$

Now, you can also say that the this variance is scaling with system size because heat capacity is scales with system size ok. You can also see it here. So, I am going to write on this first. So, heat capacity is property which is extensive it scales with system size. Specific heat is intensive because heat capacity by N specific heat which is an intensive quantity, but heat capacity is extensive. We can also see here. I know that this guy E is extensive the total energy $3/2 n k T$ scales with N. And beta is intensive the entire quantity here is extensive and. So, it is not surprising that we find our variance of energy or second cumulant of Hamilton scale with system size.

So, I would compute the width or the standard deviation, you see let us let us compute the width or the standard deviation it is nothing but the square root of the variance this will scale as square root of N. And now you can compute the like I was saying compute the ratio of width over mean of the energy distribution. So, width over mean would width has already been, so width is basically the width has already been computed here which is square root of N ok. And the mean is the energy itself; I know energy scales as n

because energy goes as $3/2 N k T$. So, the width over mean will scale as $1/\sqrt{N}$ upon N to the power half and as N goes to infinity in the thermodynamic limit this will go to 0.

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The whiteboard contains the following handwritten text:

Compute width/mean = $N^{1/2}/N \sim 1/N^{1/2} \xrightarrow{N \rightarrow \infty} 0$

$p(\epsilon) = \frac{e^{-\beta F(\epsilon)}}{Z(N, V, T)} \longrightarrow \frac{e^{-\frac{\epsilon - \langle H \rangle}{2 \langle H^2 \rangle_c}}}{(2 \pi \langle H^2 \rangle_c)^{1/2}}$

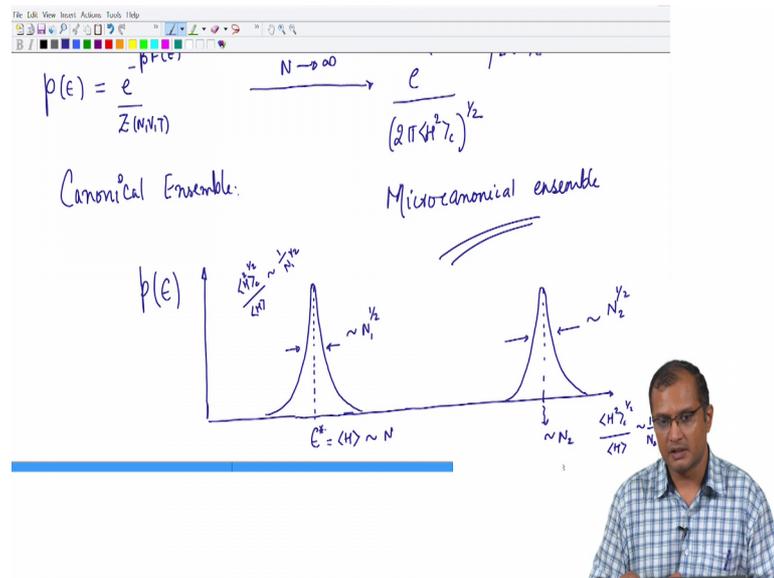
Canonical Ensemble: Microcanonical ensemble

In the bottom right corner, a man with glasses and a blue checkered shirt is visible, looking at the whiteboard.

So, which means that my energy distribution energy of a canonical system in thermal equilibrium with a heat bath which was shown to be e to the power minus beta F E over the canonical partition function. So, this is what I know from canonical ensemble in the large N limit becomes a Gaussian distribution. It becomes a Gaussian distribution because energy is a random variable. And it is a sum of energies of each particle which itself is a random number. So, you sum of random numbers large number of them gives you one value of energy and energy itself is a random variable.

So, you know by central limit theorem, these random variables which are themselves sum of large number of random variables should be normally distributed. So, I am go to write it as e to the power minus $(E - \langle H \rangle)$ or I can write it as instead of this, I can also write it as you know I can write it as $E - \langle H \rangle$ as you shall see that this is also $(E - \langle H \rangle)$ divided by twice sigma square, now square is basically our second cumulant. And I need to normalize this distribution. So, this is $2 \pi \sigma^2$ square root. And there is a; this is a Gaussian distribution ok. So, this is the canonical ensemble. Now, why does this become a canonical ensemble it will be very clear.

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You see this distribution if I plot as n goes to infinity, because I know I need to invoke central limit theorem, I need to have large number of random variables which adapt to a random variable which is normally distributed. So, I know from centre limit theorem mine has to be infinity only then I can invoke central limit theorem. So, I can compute I can actually draw the distribution and understand what is going on as you know it is a well known fact that a picture is worth a thousand words. So, let us sketch a picture here.

So, this is our energy distribution and this is a Gaussian that is centered at the most probable value of the Gaussian. So, I am going to call it as E^* . But if I look at my distribution here, well this distribution has a peak which is also at \bar{H} . So, this is also equal to the mean value of energy. And whatever is the width here which is proportional to I would say it scales as square root N as N goes to infinity my distribution actually moves on the right hand side ok, it becomes wider.

So, as a bigger N , if I take the distribution would be sitting at value which is value of energy which is on the higher side. So, if I go if I increase N , what would happen is the distribution gets wider, but the ratio of width to mean syllabus suppose I say this is N_1 and this is N_2 I know this will scale as N . So, here the location of this would also scale as N , so N_2 .

So, the ratio of width over mean here it was 1 upon so the ratio of E^* over E^* over edge in of the ratio of width over mean which was going as 1 upon square root of N is

much smaller here ok. So, this means that the distribution gets wider, but what is happening is in the ratio of width over mean is now much smaller though it has also worked very far away on the right.

The (Refer Time: 37:28) does become wider I have shown the peak becoming smaller, because I want to conserve the area under the curve, so it gets smaller and smaller and gets wider and wider. But not only that its location of the mean also gets far away into the right such that the value of the width over mean becomes diminishing in the thermodynamic limit.

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The screenshot shows a whiteboard with the following content:

- At the top, there is a toolbar and some faint text: $E = \langle H \rangle \sim N$, $\sim N^2$, $\langle H \rangle \sim N^2$.
- In the center, handwritten text reads: "As $N \rightarrow \infty$, the distribution has negligible width/mean $\sim 1/N^{1/2} \rightarrow 0$ ".
- At the bottom right, there is a small inset image of a man with glasses, wearing a blue checkered shirt, looking down at something in his hands.

And eventually as N goes to infinity, this would be a sharp distribution further down the line ok. So, it would be like a spike almost a spike whose width is definitely larger than the previous two, but it is so far away on the right that the ratio of width over mean would be diminishing number. So, eventually the distribution has negligible. So, this would be eventually what you would get as you continue in this thing down the line the ratio of width over mean which is basically 1 upon square root N which goes to 0 . So, now, you as essential recovered micro canonical ensemble and the limit N tending to infinity is basically the take home message ok.

It is not the width alone that decides your while property of the distribution, it is also the mean of the distribution ok. Suppose, you have 100 rupees in your pocket, and the amount of your let us say your expenses are related to the uncertainty or whatever the

fluctuation of money in your pocket. In case of suppose it is uncertain that you would be you would have you would have 10 rupees here and there over 100. Now, 100 is you know 10 is the square root of 100. But so 10 is what your expense would be, if your income is 100.

Now, suppose you go to if you raise your income to 100 now your expenses are let us square root N which is you know square root of 1000, which is now if you compute your ratio of expense to your income and definitely in the limit of very large income this ratio would be a very very small number, because let us say your income becomes 10 to the power 4. So, your expense would be 100 which is the square of 10 to the power 4.

So, the ratio of 100 over 10000 is definitely 1 by 100, whereas the ratio of 10 over 100 is 1 by 10. So, 1 by 100 is much smaller than 1 by 10. Similarly, if your income becomes 10 to the power 5 or 10 to the power 6, so your expenses would be 1000. So, ratio of your expense or income would be 1 upon 1000, so it became 1 by 10, 1 by 100, 1 by 1000.

So, eventually it is not your expenses are growing, you would argue that my expenses are also growing I was expecting 10 when I was earning 100. Now, I am you know spending 100, but my income is also 1000. So, definitely your expenses are increasing, I will not say that your expense which is the width the analogy width is not going to 0, it is increasing, but the ratio of your expenses over your income is a diminishing quantity.

So, I would say that you have no expense as your salary becomes 10 to the power 6 if you earn a million bucks in a month, I would say that you have essentially your expenses are 0, so that is the analogy I have given here that the width alone does not signify anything it has the ratio of width over mean that signifies the nature of the distribution. And I argue that the distribution becomes delta function in the limit n tending to infinity essentially. So, here at this point, I would like to break and take an example.

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The image shows a whiteboard with handwritten text and a diagram. At the top, there is a menu bar with options like 'File', 'Edit', 'View', 'Insert', 'Actions', 'Tools', and 'Help'. Below the menu bar, the text 'Example: Two-level system (N, V, T)' is written. Underneath, two energy levels are depicted: a higher level labeled 'E' and a lower level labeled '0'. A bracket on the right side of these levels is labeled 'Two levels'. Below the energy levels, the text 'n_i represents excitation' is written. In the bottom right corner of the whiteboard area, a man with glasses and a blue checkered shirt is visible, looking towards the whiteboard.

In fact, I am going to do this problem with all of you. Hence example is the familiar two-level system in canonical conditions. So, our two-level system comes back, but this time it is in contact with the heat reservoir. It is not a constant energy two-level system, it is two-level system where its energy can fluctuate which means a number of particles in the excited state is a function that depends on temperature.

So, our two-level system is back and let us draw remember the two-level system. You had two energy levels 0 and epsilon for simplicity. So, you had two levels. And let us say you have some particles here and some particles in the ground state. And suppose I pickup any particle i , then n_i represents excitation meaning that our n_i can have values either 0 or 1 ok.

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$L, 0$ (ground)
 1 (Excited)

$$H(\mu) = E = \sum_{i=1}^N n_i \epsilon_i$$

Canonical Partition Function:

$$Z(N, V, T) = \sum_{\mu} e^{-\beta H(\mu)}$$

$\mu: \{n_1=1, n_2=1, n_3=0\}$

So, 0 being it is in the ground state and this being it is in the excited state fine. So, I know that my energy of the total system can be written as nothing but summation over $n_i \epsilon_i$, and i will run from 1 to the total number of particles in the system eventually this will be nothing but $N \epsilon$ total number of particles that are excited in some sense fine.

So, what I am going to do here is instead of looking at this system from the point view of energy, I will say I do not want to adopt this procedure. I did in the case of canonical ensemble I want to deal the system canonically. So, I will write down the canonical partition function. Why is this approach pursued, because I have a systematic constant temperature its energy can change.

So, our variable $N \epsilon$ is no longer meaningful variable because in $N \epsilon$ keeps on changing ok, so that is why I do not want to do to the problem starting with constant energy because energy is no longer going to be constant ok. So, our canonical partition function which is $Z(N, V, T)$, if you recall this is nothing but summation over all microstates, $e^{-\beta H(\mu)}$ ok.

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$$Z(N, V, T) = \sum_{\mu} e^{-\beta H(\mu)}$$

$$= \sum_{\{n_i\}} e^{-\beta H(\{n_i\})}$$

$$= \sum_{\{n_1, n_2, \dots, n_N\}} e^{-\beta \sum_{i=1}^N n_i \epsilon_i}$$

$\mu_1: \{n_1=1, n_2=1, n_3=0, \dots, n_N=1\}$
 $\mu_2: \{n_1=0, n_2=0, n_3=1, \dots, n_N=1\}$
 \vdots
 $\mu_N: \{n_1=1, n_2=1, \dots, n_N=0\}$

Now, our microstate for a given value of temperature is nothing but the specified values of excitation. So, means what is it simply means that a given microstate is like suppose I say that this is one microstate this basically means that you can have your n_1 that is the excitation of first particle as 1, n_2 as 1, n_3 as 0 and so on some specified values of this n_i 's, all the way to the last value which is n_N . Now, this will give you a total value of energy which is my H of n_i .

Now, this excitation will change between microstates. So, μ_2 may have different values of these excitations. So, n_1 may be 0, and n_2 may be 0 n_3 may be 1, and n_N may be again 1. So, each microstate is set of specified values of n_i 's in such a way that the temperature is t in the thermodynamic limit energy is not fixed anymore. So, you can actually make all n_i 's to be 1. This would be like all particles are in the top floor or the excited state which we know is a very difficult thing to obtain, but in principle that realization is also allowed, there are no problems with that realization being allowed is because the probability of that realization will be essentially 0 from statistical mechanics.

So, the probability it is take care themselves we do not have worried about it. Statistically a probability is still there; however, small it is. So, microstates like these are basically nothing but a collection of these you know all these values of a excitations. So, I can write down this summation as summation over all possible values of n_1, n_2 , up to n_N e raised to minus beta. Now, Hamiltonian is nothing but summation for a specified

value of excitation the Hamiltonian is nothing but summation i going from 1 to n , $n_i \epsilon_i$ is the Hamiltonian right. If you are, if you have forgotten you can write down the Hamiltonian of a microstate as nothing but the energy which is summation i $n_i \epsilon_i$ ok, that is what I have written here for the Hamiltonian.

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$$\begin{aligned}
 & \{n_1, n_2, \dots, n_N\} \\
 & = \sum_{\{n_1, n_2, \dots, n_N\}} e^{-\beta \epsilon n_1} \cdot e^{-\beta \epsilon n_2} \dots e^{-\beta \epsilon n_N} \\
 & = \sum_{n_1=0,1} e^{-\beta \epsilon n_1} \sum_{n_2=0,1} e^{-\beta \epsilon n_2} \dots \sum_{n_N=0,1} e^{-\beta \epsilon n_N} \\
 & = \left(\sum_{n_1=0,1} e^{-\beta \epsilon n_1} \right)^N = \left(1 + e^{-\beta \epsilon} \right)^N
 \end{aligned}$$

So, I can write this as summation all possible values. This will be nothing but e raised to minus beta epsilon n_1 into e raised to beta epsilon n_2 fine, because you have powers added up in the exponent. So, you have the n_i 's added up in the exponent it splits up into products. So, I can now add it as summation n_1 going from 0 to 1, n_1 can only take 0 or 1 e raised to minus beta epsilon 1 into these are all independent variables.

So, they the summation are independently applied all the way to summation on n which is 0, 1 e raised to minus beta epsilon n . Now, please look at this summation they are all independent which means I can simply take one of them and raise it to power N ok, and which is nothing but if I take the values of n_1 0 and 1, this becomes 1 plus e raised to minus beta ϵ to the power N that is my partition function that simple.

Now, partition function is ready you can connect thermodynamics the stat mec. So, with the partition function just recently computed the first thing I am going to do a set up the bridge which is minus 1 over beta $\ln z$ this open up the connection with thermodynamics ok.

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The image shows a digital whiteboard interface with a toolbar at the top. The main content is handwritten text and equations in blue ink. The text reads "Building connection with thermodynamics". Below it, the free energy equation is written as $F = -\frac{1}{\beta} \ln Z = -\frac{1}{\beta} N \ln(1 + e^{-\beta \epsilon})$. Below that, the internal energy equation is written as $E = -\frac{\partial}{\partial \beta} (\ln Z) = -N \ln(1 + e^{-\beta \epsilon})$. In the bottom right corner, there is a small video inset showing a man in a blue and white checkered shirt looking down at a device.

So, this is nothing but minus one upon beta logarithm of partition function that I have just obtained as while look at definition it is just n times logarithm of 1 plus e raised to minus beta e ok. As you can see the free energy is extensive its scales has N, because beta is intensive and ln 1 plus e beta is also an intensive quantity the argument of ln is also intensive. There is only one quantity in the definition of free energy which makes it extensive and it must be extensive all energy scales are extensive scales as N because of this N ok.

So, now I can compute the total energy of the system total energy is very straight forwardly computed its minus of d by d beta of ln z ok. So, so you can write down this as minus N ln 1 plus e raised to minus beta E fine that is your internal energy and ok.

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The image shows a whiteboard with handwritten mathematical equations. At the top, there is a toolbar with various drawing tools. The equations are:

$$E = -\frac{\partial}{\partial \beta} (\ln Z) = -N \ln(1 + e^{-\beta \epsilon})$$

Recall, $F = E - TS$

$$\text{then, } S = (E - F)/T = -\frac{N}{T} \ln(1 + e^{-\beta \epsilon}) + k_B N \ln(1 + e^{-\beta \epsilon})$$

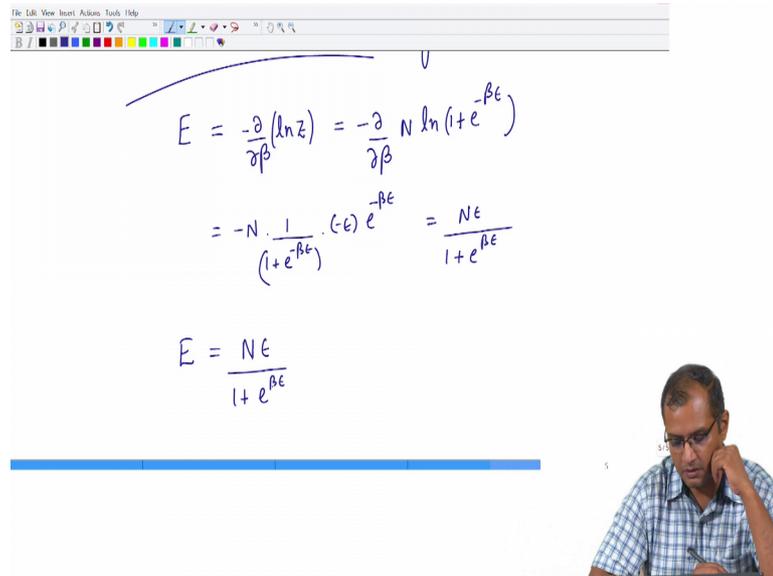
In the bottom right corner, there is a small video inset of a man with glasses, wearing a blue and white checkered shirt, looking towards the camera.

So, now you can recall that our free energy is connected to internal energy from this expression. So, I can compute what is my entropy. Simply, we can write it as E minus F over T ok, E and F are both computed here. So, I am going to write down E and F as minus N by T into $\ln(1 + e^{-\beta \epsilon})$ ok. And minus F by T would simply be plus $k_B N \ln(1 + e^{-\beta \epsilon})$ ok.

So, F is already minus 1 upon beta ok, it is like yeah if I multiply it by minus 1 by T, so I just have a k_B there, so that is the expression for entropy. So, this ends the discussion on two-level system. So, when we meet in the next class, we will talk about the ideal gas as example of canonical ensemble. These two examples will together constitute a case for each degree of freedom being discrete and degrees of freedom being continuous. So, the two-level system is the discrete example for canonical ensemble.

And in the next class when we will look at the ideal gas, we will take it as case of continuous degrees of freedom. So, I will show you how you compute partition function in the case of a system, which where the degree of freedom are continuous. So, we break here, and we meet again next class and will take it from here.

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$$E = -\frac{\partial}{\partial \beta} (\ln Z) = -\frac{\partial}{\partial \beta} N \ln(1 + e^{-\beta \epsilon})$$
$$= -N \cdot \frac{1}{(1 + e^{-\beta \epsilon})} \cdot (-\epsilon) e^{-\beta \epsilon} = \frac{N \epsilon}{1 + e^{-\beta \epsilon}}$$
$$E = \frac{N \epsilon}{1 + e^{-\beta \epsilon}}$$

So, basically what I mean by the by this connection is that I want to derive some thermodynamic quantities from partition function. The first quantity that comes to my mind as always is energy. And I know the average energy of the system from statistical mechanics is nothing but negative derivative of logarithm of the partition function like, which is derived in the last discussion. So, this is nothing but negative derivative $\ln Z$ is nothing but $N \ln(1 + e^{-\beta \epsilon})$.

And when you take the derivative, what you get is $N \epsilon / (1 + e^{-\beta \epsilon})$. So, this is nothing but $N \epsilon / (1 + e^{-\beta \epsilon})$. So, this should you should ring bells with your previous encounter with the energy of the two-level system in the micro canonical ensemble that is you can see here as usual the two basically to make the energy greater than $N \epsilon / 2$ ok.

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$1 + e^{\beta \epsilon}$

To reach $E = N/2 \epsilon \Rightarrow e^{\beta \epsilon} \rightarrow 1$

$\beta \rightarrow 0 \quad T \rightarrow \infty$

"Maximum energy corresponds to half filled excited state."

Free energy: $F = -\frac{1}{\beta} \ln Z$

So, if I want to reach E equals to N by 2 epsilon, you have to make e raised to beta epsilon as 1. So, 1 by 1 in the denominator will give you 1 plus 1 will give you 2 in the denominator. And that will make the energy N by 2 epsilon and the only condition in which e raised to beta epsilon becomes 1 is when beta tends to 0. And beta tends to 0 means your temperatures have become infinite. Now, this is not disagree at all with what I have discovered in the micro canonical case.

Let us also you know so the conclusion here is that in two-level systems maximum energy. So, if you connect it with thermo state only at infinite temperature, you can push more than half the number of particles excited state. So, maximum energy corresponds to half filled excited state, you cannot exceed more than that ok. So, push it beyond half-filled required temperature is more than infinity, so that is in clearly not possible.

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Free energy: $F = -\frac{1}{\beta} \ln Z$
 $= -\frac{1}{\beta} N \ln(1 + e^{-\beta \epsilon}) \sim N$

Entropy: $S = (E - F)/T$ $E - TS = F$
 $= \frac{N \epsilon}{1 + e^{\beta \epsilon}}$

Now, free energy here another very important thermodynamic quantity is nothing but negative 1 over beta logarithm of Z. So, this is nothing but logarithm of Z is nothing but N logarithm 1 plus e raised to minus beta E ok, which again as usual scales with N, because beta is intensive.

I can also write down entropy, which is nothing but from the first law of from thermodynamics, I can write down entropy as E minus F over T since you can write down E as E minus T S as your free energy (Refer Time: 62:25) free energy ok. So, substituting the value of E and F here what we get basically if I write down energy, which is N epsilon 1 plus beta epsilon E raise to beta epsilon, this is my energy minus free energy which is already minus 1 upon beta.

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Entropy: $S = (E - F) / T$

$$= \left[\frac{NE}{1 + e^{-\beta E}} + Nk_B T \ln(1 + e^{-\beta E}) \right] / T$$

$$= \frac{Nk_B \beta E}{1 + e^{-\beta E}} + Nk_B \ln(1 + e^{-\beta E})$$

$$S = Nk_B \left[\frac{\beta E}{1 + e^{-\beta E}} + \ln(1 + e^{-\beta E}) \right]$$

So, I am going to write it as plus $k_B T$ $N k_B T$ into $\ln(1 + e^{\beta \epsilon})$ the entire thing divided by T fine. If free energy is already minus $N k_B T \ln(1 + e^{-\beta \epsilon})$ and so I can write this as $N \epsilon / T$ into over $1 + e^{-\beta \epsilon}$ plus $\ln(1 + e^{-\beta \epsilon})$ that is the final answer.

So, you can write your answer in terms of β $N k_B$ into $\beta \epsilon$ ok. So, $1/T$ is nothing but $k_B \beta$. And I am going to take and remaining is just $n k_B$ into $\ln(1 + e^{-\beta \epsilon})$ and you can simply take $N k_B$ outside what you get is nothing but $\beta \epsilon / (1 + e^{-\beta \epsilon})$ plus $\ln(1 + e^{-\beta \epsilon})$ fine.

So, this is the expression for entropy of the two-level system, and this is where we end today's discussion on the two-level system as a discrete degree of freedom example. In the next class, we will look at the classical ideal gas as another working example of canonical ensemble ok. So, we break here, and we meet in the next class.