Fundamentals of Statistical Thermodynamics

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Lecture – 18

Further discussion on q (Partition function), U(Internal energy) and S (Entropy) ∞

In this lecture, we will further discuss about the meaning of negative temperature and how negative temperature can affect the various quantities that we have discussed so far, that is, partition function, internal energy and entropy. We have already discussed that under what conditions this temperature can be negative. And if you recall the previous lecture, we considered two-level system and, in this lecture, also our discussion is also going to be on two-level system.

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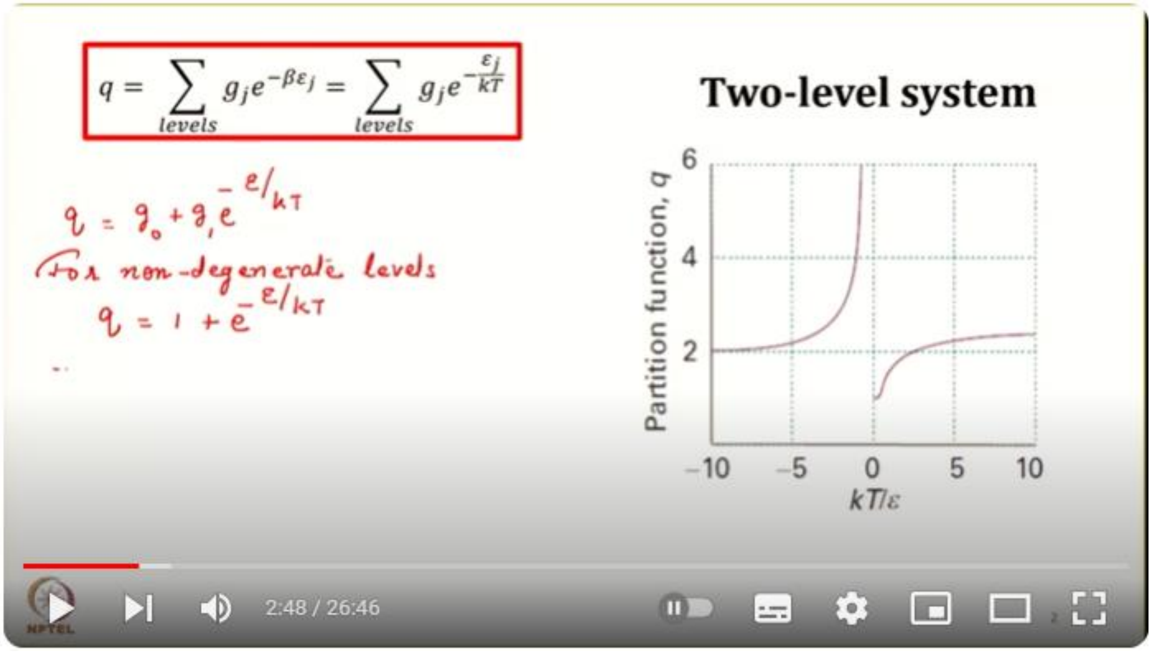

$$\boxed{q = \sum_{levels} g_j e^{-\beta\varepsilon_j} = \sum_{levels} g_j e^{-\frac{\varepsilon_j}{kT}}}$$

$q = g_o + g_1 e^{-\varepsilon/kT}$

For non-degenerate levels

$q = 1 + e^{-\varepsilon/kT}$

Two-level system

In two-level system, we discussed that if the population of upper level exceeds that of the lower level, then the temperature will be negative. Now let us see how it affects the partition function. D partition function q will be equal to $g_o + g_1 + e^{-E/kT}$ for a two-level system.

If there is degeneracy or if the system is non-degenerate, let us say for non-degenerate systems, non-degenerate energy levels, then q can be written as 1 + $e^{-E/kT}$. Our now goal is to discuss T varying from + 0 to ∞ and T varying from - 0 to ∞. Remember that the formula does not restrict temperature less than 0. First let us talk about T greater than 0.

We talk in general about extremes, but the variation over entire temperature range is shown in this figure. Let us first talk about T approaching a value of + 0. If T is + 0, then q will be equal to 1 + exponential - ∞. That means q will approach a value of 1 and that is what you see over here. Now let us take the other extreme.

When T approaches + ∞, then q will be equal to 1 + exponential - E over k into ∞ is ∞. This becomes, that means q approaches a value of 2. Either it will approach a value of 2 or it will be approaching a value of $g_o + g_1$. So that is why here the variation is not ended at 2, but you know it can depend upon degeneracies. If both are non-degenerate, then it will be approaching a value of 2.

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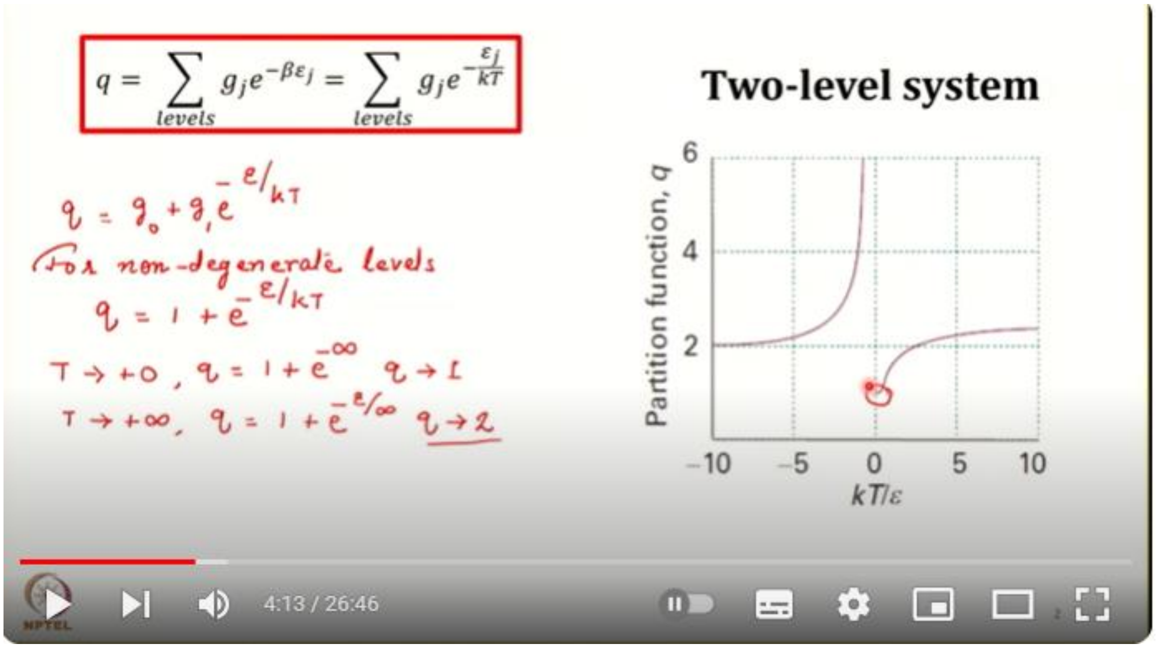

$$\boxed{q = \sum_{levels} g_j e^{-\beta\varepsilon_j} = \sum_{levels} g_j e^{-\frac{\varepsilon_j}{kT}}}$$

$q = g_0 + g_1 e^{-\varepsilon/kT}$

For non-degenerate levels

$q = 1 + e^{-\varepsilon/kT}$

$T \to +0$, $q = 1 + e^{-\infty}$ $q \to 1$

$T \to +\infty$, $q = 1 + e^{-\varepsilon/\infty}$ $\underline{q \to 2}$

Two-level system

So we have explained this variation and this is T is equal to 0 and positive onwards. This discussion we have had in other numerical problems earlier. Now let us talk about T approaching a value of - 0 from negative side. Then q is equal to 1 + exponential - 0 negative negative becomes positive. I am talking about here, substituting here, - 0 minus minus becomes positive and what I have is - E upon kT is 0.

This is exponential since minus minus becomes positive, this will be. So that means q becomes very high. In fact, moving towards ∞ and that is what you see over here. It's rising very sharply when temperature is approaching - 0, then q is increasing very sharply. Let us now discuss the next one.

When T approaches - ∞, then q will be approaching what? $1 + e^{-E/\infty}$ which is $1 + e^{0}$. That means q will approach a value of 2 and that is what you see over here. So, for a two-level system, see how the partition functions varies with temperature when you consider positive side of the temperature or negative side of the temperature. But the point that is to be noted over here that there is a discontinuity, it is not continuous. At T is equal to 0, there is a discontinuity. Let us talk about the internal energy also. For a two-level system, the partition function is like this and internal energy is also showing a discontinuity. The way we have shown it for partition function, same way we can show for the internal energy. Let us do that. Since we are talking about two-level system and let me take the simplest one 0 and E.

So what I have is q is equal to $1 + e^{-\beta E}$. This is Q for this system. U - U(0) will be equal to - N by q del q by del β at constant volume. That we know. So, what I have now is U - U(0) is equal to - N divided by $1 + e^{-\beta E}$ into derivative of this $e^{-\beta E}$ into - E.

So I have U - U(0) is equal to N times E into $e^{-\beta E}$, negative negatives are consumed to become positive sign, $1 + e^{-\beta E}$. I can rewrite this U - U(0). If I multiply and divide by exponential β E, then I get this over exponential β E + 1. This is how the internal energy will vary with temperature. We will discuss it little bit more.

So, we have derived now this expression that internal energy is given by N E divided by exponential β E + 1. Let us discuss the conditions. When β approaches a value of ∞, when β approaches ∞, β is equal to 1/kT. Remember β is 1 over k T. When β approaches ∞ means temperature approaches 0.

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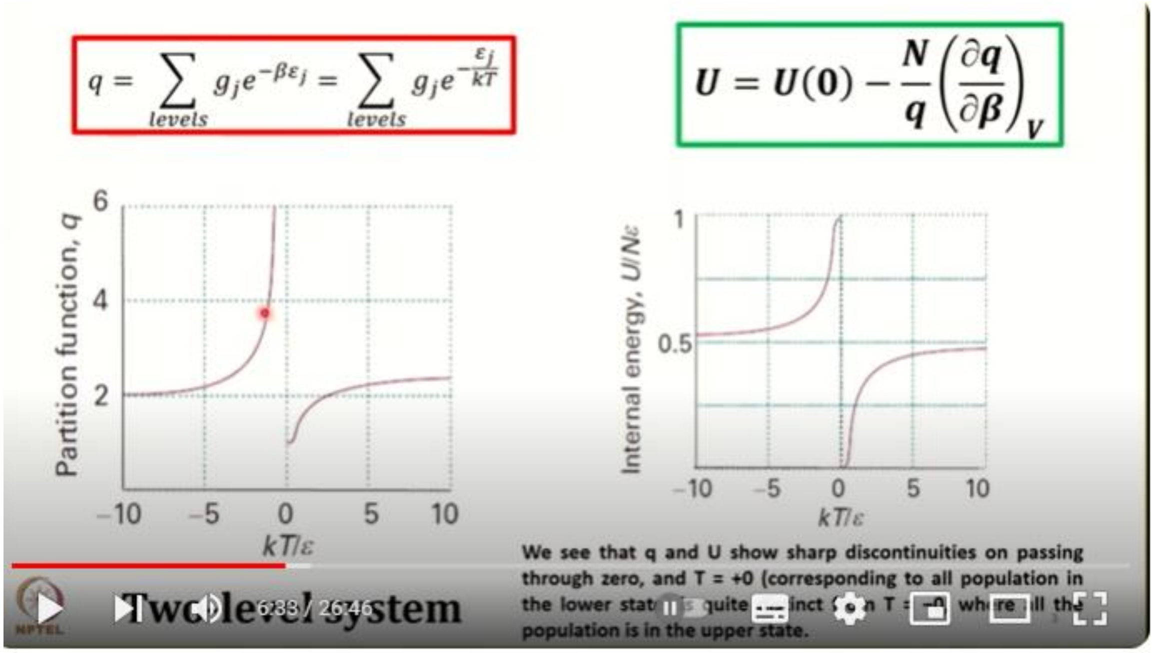

$$q = \sum_{levels} g_j e^{-\beta\varepsilon_j} = \sum_{levels} g_j e^{-\frac{\varepsilon_j}{kT}}$$

$$U = U(0) - \frac{N}{q}\left(\frac{\partial q}{\partial \beta}\right)_V$$

We see that q and U show sharp discontinuities on passing through zero, and T = +0 (corresponding to all population in the lower state) is quite distinct from T = −0 where all the population is in the upper state.

Temperature approaches 0. So then, U will approach a value of 0. Because when β approaches ∞, temperature approaches 0, U approaches 0. And when do we have the total energy equal to 0? When all the molecules are in the ground state. That means this situation, U approaches 0 as β approaches ∞, that is as T approaches 0 when only the lower state is occupied.

And you can notice over here also, when T approaches 0, then internal energy approaches a value of 0. Okay, now let us consider the next extreme when β approaches a value of 0. Let us say, when β approaches a value of 0, that means T is approaching a value of ∞. In that case, what will be U - U(0)? U - U(0) will be N e divided by exponential β is 0 tending to 0. 0 + 1 which is 0.5 times N e. And that is what you are seeing over here. When temperature becomes very very high, the value of U by N e is approaching 0.5. Let us now consider the other case.

When β approaches - ∞, that means T will approach a value of - 0. Then what happens? Then U will be what? U - U(0) will be equal to T is - 0. That means you have N e divided by, when β is - ∞, that means 1 over ∞ which becomes 0. I can write here β is $e^{-\infty+1}$. This is equal to N times e.

That means U divided by N e will approach a value of 1. That is what you see here. The next one, when β approaches - 0, that means T approaches - ∞, then what we have? Then U - U(0) is equal to N e over e^{0}, in fact - 0 + 1. So 0 over e^{-0} is 1, which is 0.

5 N e. That is what you see over here. So the variation is from 1 to 0.5 and here is from 0 to 0.5. It's another way of looking at that when the temperature becomes very high, then both the states are equally likely to be populated. So therefore, the value will start from 0 to half. U by N e will become half. Let us read the comments. Note that U approaches 0 as β approaches ∞, that is as T approaches 0 when only the lower state is occupied and U approaches N e as β approaches $-\infty$, that is T approaches - 0, we see that a state with T is equal to - 0, here you see, is hotter than the one T is equal to + 0. So, you see the meaning of T negative - 0 is hotter than the one with T + 0. And also note down that in this figure as you see, what we see is that Q and U show sharp discontinuities. We see sharp discontinuities on passing through 0 and T is equal to + 0 corresponding to all populations in the lower state is distinct from T is equal to - 0 where all the population is in the upper state. This is consistent with when we introduced that when the temperature can be negative for a two-level system. This is how the internal energy will change with temperature on both sides of T equal to 0. Let's further discuss now, what does it mean? When T is equal to 0 or T greater than 0 or T less than 0, we notice there is a sharp discontinuity. We also notice that when T is positive, that means we are talking about when T, when you are approaching T is equal to + 0, you are talking about cooling, cold. But when we are talking about T negative and when T is approaching - 0, you can see here the system here is much hotter than the one which is equal to T + 0. Are these discontinuities carried to when we talk about entropy? We will see about entropy here and we can use the same expression that we derived for U - U(0). What we have S is equal to U - U(0), we had N E over, I will retain T here and you have exponential β E + 1, this is U - U(0) by T + N k log q is 1 + $e^{-\beta E}$.

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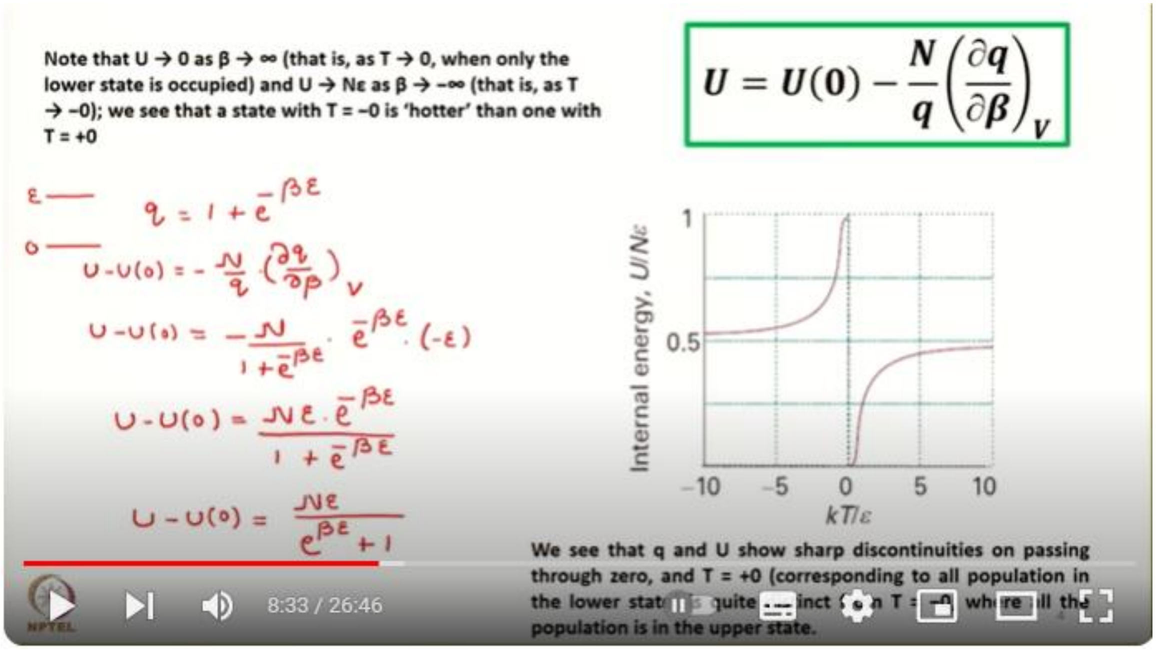

Note that U → 0 as β → ∞ (that is, as T → 0, when only the lower state is occupied) and U → Nε as β → −∞ (that is, as T → −0); we see that a state with T = −0 is 'hotter' than one with T = +0

$$U = U(0) - \frac{N}{q}\left(\frac{\partial q}{\partial \beta}\right)_V$$

$$q = 1 + e^{-\beta\varepsilon}$$

$$U - U(0) = -\frac{N}{q}\left(\frac{\partial q}{\partial \beta}\right)_V$$

$$U - U(0) = -\frac{N}{1 + e^{-\beta\varepsilon}} \cdot e^{-\beta\varepsilon} \cdot (-\varepsilon)$$

$$U - U(0) = \frac{N\varepsilon \cdot e^{-\beta\varepsilon}}{1 + e^{-\beta\varepsilon}}$$

$$U - U(0) = \frac{N\varepsilon}{e^{\beta\varepsilon} + 1}$$

We see that q and U show sharp discontinuities on passing through zero, and T = +0 (corresponding to all population in the lower state) is quite distinct from T = −0 where all the population is in the upper state.

This is for a two-level system; we are talking about two-level system. Here we see some continuity. Let's say when I talk about T approaching 0, then β is approaching ∞, β is 1 over k T and then what is the value of S approaching? If β is ∞, then since ∞ is appearing in denominator, this term, first term, this disappears and if I put β as ∞, exponential - ∞ is 0 and N k log 1 in that case is 0. I repeat, when β approaching ∞, there is ∞ in the denominator, so this disappears and β is ∞, exponential - ∞ is 0, so I have N k log 1, log 1 is 0, that means in this case S approaches 0 and you can notice over here. And when T approaches ∞, then β approaches 0, then what do we have? When β approaches 0, T approaches ∞, then we have

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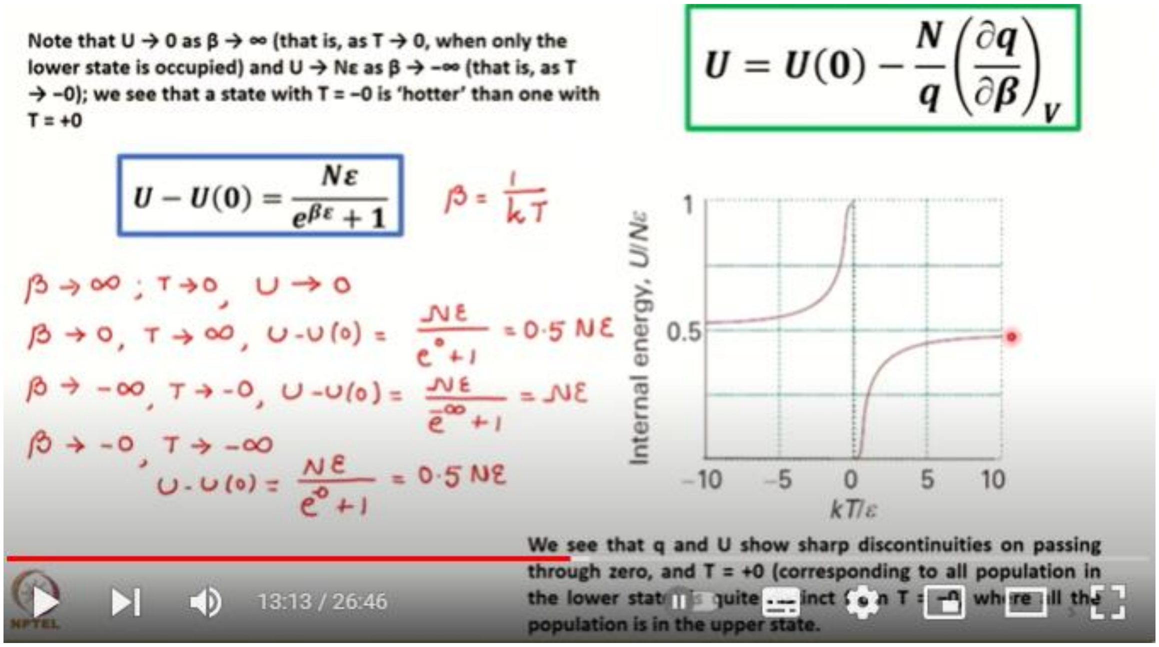

Note that U → 0 as β → ∞ (that is, as T → 0, when only the lower state is occupied) and U → Nε as β → −∞ (that is, as T → −0); we see that a state with T = −0 is 'hotter' than one with T = +0

$$\boxed{U = U(0) - \frac{N}{q}\left(\frac{\partial q}{\partial \beta}\right)_V}$$

$$\boxed{U - U(0) = \frac{N\varepsilon}{e^{\beta\varepsilon} + 1}} \qquad \beta = \frac{1}{kT}$$

$\beta \to \infty$; $T \to 0$, $U \to 0$

$\beta \to 0$, $T \to \infty$, $U - U(0) = \frac{N\varepsilon}{e^{0}+1} = 0.5\,N\varepsilon$

$\beta \to -\infty$, $T \to -0$, $U - U(0) = \frac{N\varepsilon}{e^{-\infty}+1} = N\varepsilon$

$\beta \to -0$, $T \to -\infty$

$U - U(0) = \frac{N\varepsilon}{e^{-0}+1} = 0.5\,N\varepsilon$

We see that q and U show sharp discontinuities on passing through zero, and T = +0 (corresponding to all population in the lower state) is quite distinct from T = −0 where all the population is in the upper state.

There in the denominator, so this term disappears and β approaches 0, then this term becomes 1, e $^{- \beta E}$ becomes 1, that means in that case your S will approach a value of N k log 2 and log 2 is 0.693 and that is what you observe the value over here, it approaches a value of 0.693. Similarly, you can talk about when T approaches - ∞, - ∞, anyway when ∞ comes in the denominator, the first term will become 0 and T is - ∞, that means β is approaching - 0. So therefore, when you put β is - 0, exponential 0 and here what you have S will approach N k log 2 and that is what you observe over here. Therefore, the entropy of the system is 0 on either side of T equal to 0 and rises to Nk log 2 as T approaches + - ∞. At T + 0, only one state is accessible and that is the lower state. Now note down that the functions that we just plotted, for example, if I start from partition function, the partition function here was plotted against k T by epsilon and in the next one, internal energy was plotted against k T by epsilon and even entropy when we talked about was plotted against k T by epsilon and if instead of k T by epsilon, I choose to plot against epsilon upon k T, then the variation is going to be as shown in these figures.

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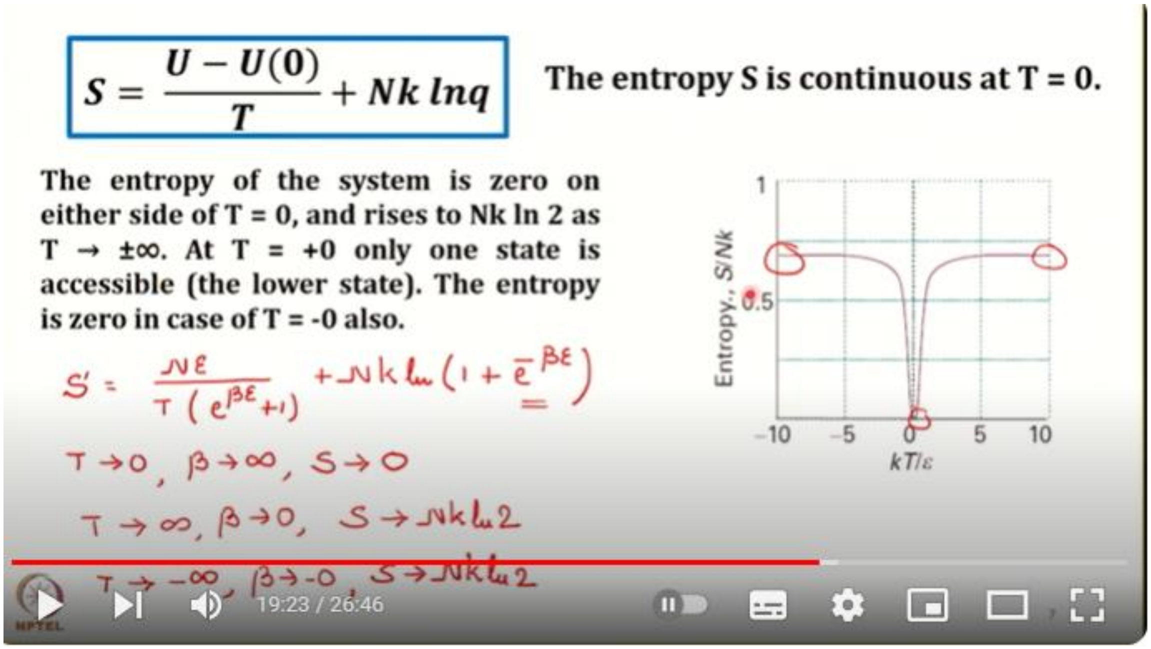

$$\boxed{S = \frac{U - U(0)}{T} + Nk\,lnq}$$

The entropy S is continuous at T = 0.

The entropy of the system is zero on either side of T = 0, and rises to Nk ln 2 as T → ±∞. At T = +0 only one state is accessible (the lower state). The entropy is zero in case of T = -0 also.

$$S' = \frac{N\varepsilon}{T(e^{\beta\varepsilon}+1)} + Nk\ln(1+\underset{=}{e^{-\beta\varepsilon}})$$

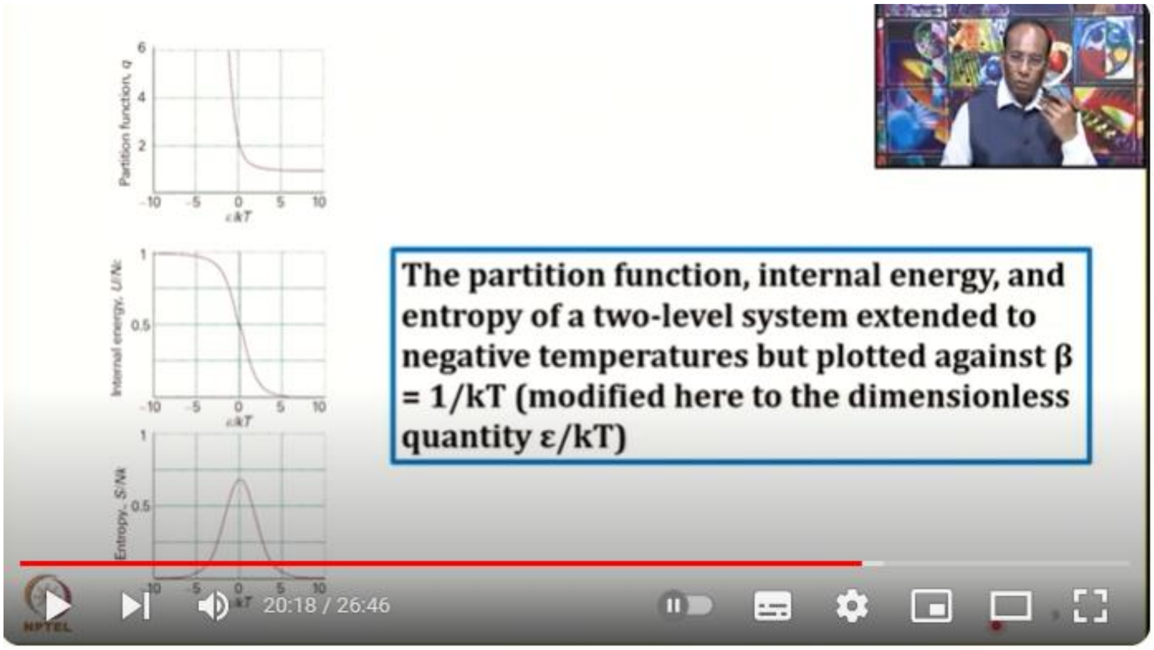
$T \rightarrow 0,\ \beta \rightarrow \infty,\ S \rightarrow 0$

$T \rightarrow \infty,\ \beta \rightarrow 0,\ S \rightarrow Nk\ln 2$

$T \rightarrow -\infty,\ \beta \rightarrow -0,\ S \rightarrow Nk\ln 2$

So the behavior of the plot obviously will depend upon how we represent it. Now we can get a little bit more insights into the dependence of thermodynamic properties on temperature that can be obtained by noting the thermodynamic result. The thermodynamic result that I am talking about here is T is equal to del U by del S at constant volume. From where this comes, first law of thermodynamics, dU is equal to dq + dW and you remember that the fundamental equation, what was that? dq is equal to T dS that means I will write dU is equal to T dS - P dV, dW is - P dV. So therefore, I can connect del U del S with temperature, I can have a pure thermodynamic definition of temperature.

See Slide time:20:18



The partition function, internal energy, and entropy of a two-level system extended to negative temperatures but plotted against β = 1/kT (modified here to the dimensionless quantity ε/kT)

That means the pure thermodynamic definition of temperature thus becomes T is equal to del U by del S at constant volume. It comes from this. You fix the volume, constant and T becomes del U by del S at constant volume. If you plot entropy in the units of S by nK against internal energy, it will show this kind of behavior and that you can obtain by using the appropriate expressions. But what is more important here is to recognize that when S is plotted against U for a two-level system, we see that entropy rises as the energy is supplied to the system, provided T is greater than zero.

However, the entropy decreases as the energy is supplied at T less than zero. So what does it mean? That if you supply energy, del U is positive and the entropy decreases, del S is negative. That means we are talking about negative temperature. Physically, the increase in entropy for T greater than zero corresponds to increasing accessibility of the upper state, we have discussed it earlier, and the decrease for T less than zero corresponds to shift towards population of the upper state alone as more energy is packed into the system. Same thing we have discussed in the earlier slides.

Recall the second law of thermodynamics. The efficiency of heat engines, which of course is a direct consequence of second law, is given by one - T cold by T hot. Fine.

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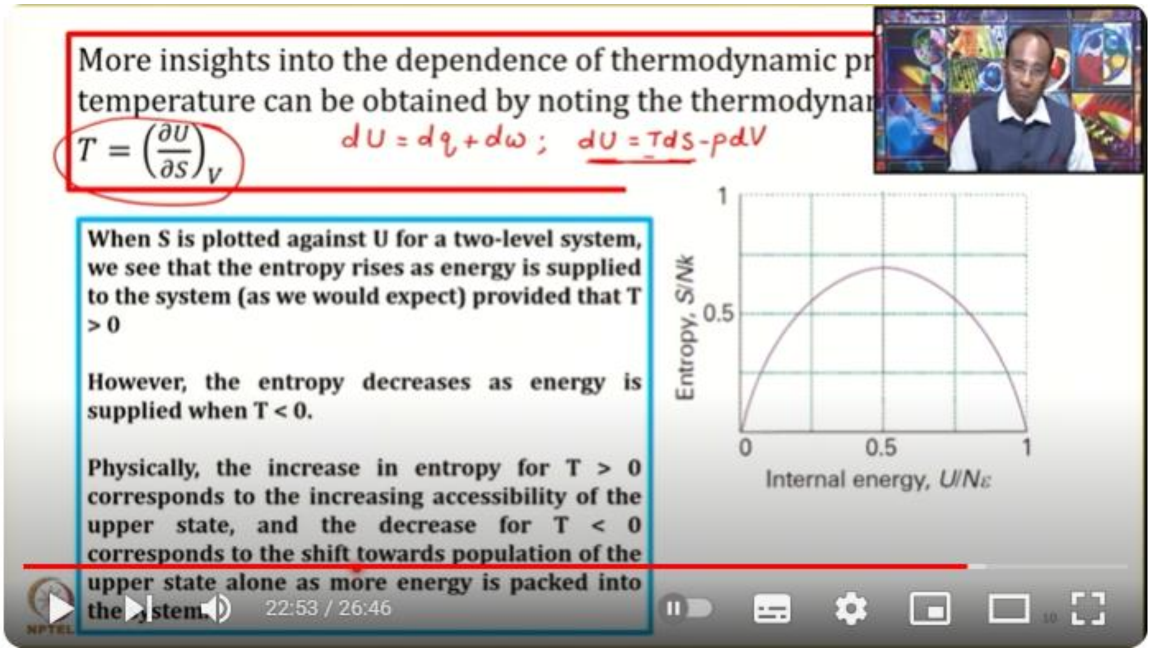


More insights into the dependence of thermodynamic pr
temperature can be obtained by noting the thermodynar

$T = \left(\frac{\partial U}{\partial S}\right)_V$

$dU = dq + d\omega$; $dU = Tds - pdV$

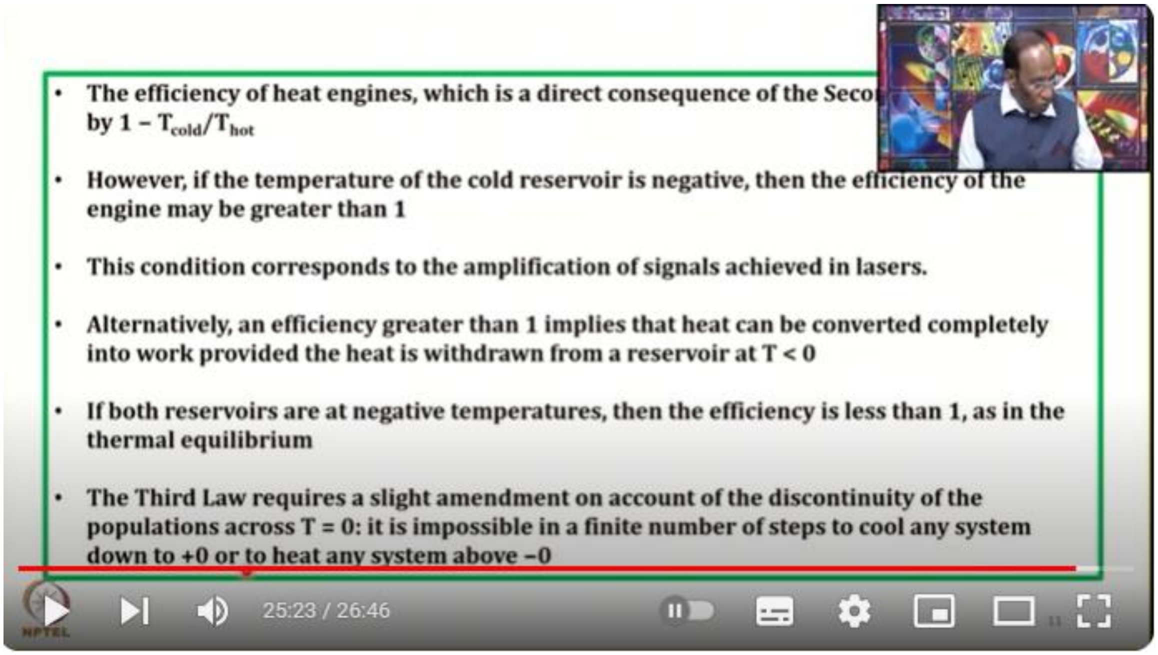
When S is plotted against U for a two-level system, we see that the entropy rises as energy is supplied to the system (as we would expect) provided that T > 0

However, the entropy decreases as energy is supplied when T < 0.

Physically, the increase in entropy for T > 0 corresponds to the increasing accessibility of the upper state, and the decrease for T < 0 corresponds to the shift towards population of the upper state alone as more energy is packed into the system.

That means if the temperature of the cold reservoir is negative, if T is negative, then this negative becomes +. Then the efficiency of engine may be greater than one, if we talk about the negative temperature. This condition corresponds to amplification of signals achieved in lasers.

See Slide time:25:23



- The efficiency of heat engines, which is a direct consequence of the Seco by 1 – T_{cold}/T_{hot}
- However, if the temperature of the cold reservoir is negative, then the efficiency of the engine may be greater than 1
- This condition corresponds to the amplification of signals achieved in lasers.
- Alternatively, an efficiency greater than 1 implies that heat can be converted completely into work provided the heat is withdrawn from a reservoir at T < 0
- If both reservoirs are at negative temperatures, then the efficiency is less than 1, as in the thermal equilibrium
- The Third Law requires a slight amendment on account of the discontinuity of the populations across T = 0: it is impossible in a finite number of steps to cool any system down to +0 or to heat any system above –0

As I said that this advanced level you will study later on. Alternatively, what is the meaning of efficiency greater than one? It means that heat can be converted completely into work, provided the heat is withdrawn from a reservoir which is at a negative temperature. Now, if both the reservoirs are at negative temperatures, then efficiency is less than one as in the thermal equilibrium. Because if both are negative, negative negative become positive, and overall negative sign remains over there. Now, this all discussion may lead us to conclusion, which is accepted and as mentioned in several textbooks, that the third law may require a slight amendment on account of discontinuity of populations across T equal to zero.

Based upon our discussion that how these various thermodynamic quantities vary when T is on the positive side of zero or on the negative side of zero. And what the amendment is suggested is that it is impossible in a finite number of steps to cool any system down to + zero or to heat any system above - zero. So, what we have discussed in this lecture is that when negative temperature is possible, what is the meaning of negative temperature and how the negative temperature can affect the variation of thermodynamic properties as a function of temperature. How to achieve this negative temperature or under what conditions, what techniques can be used to describe this negative temperature are beyond the scope of current discussion. You will study at a later level, but I am sure that the meaning of negative temperature is clear. Thank you very much. Thank you.