Thermodynamics for Biological Systems: Classical and Statistical Aspects

Prof. Sanjib Senapati
Department of Biotechnology
Indian institute of Technology - Madras

Lecture – 62
Gibbs Paradox

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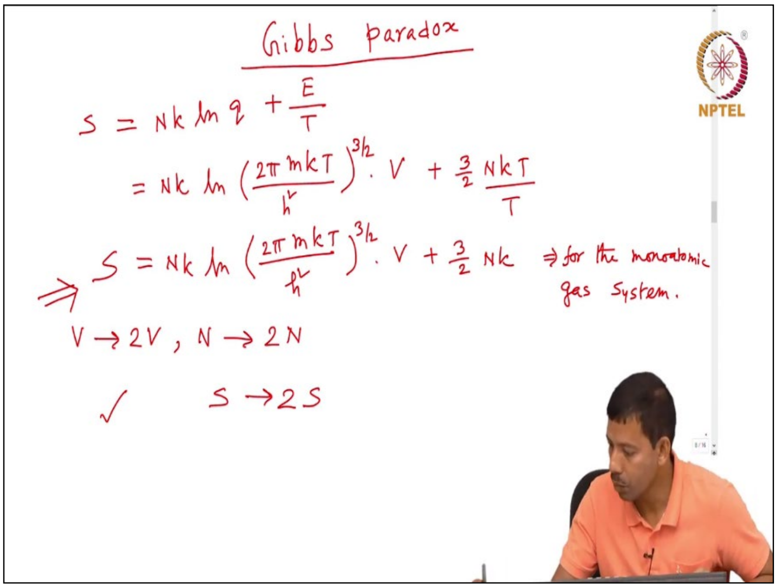

Which I will be talking is called the Gibbs paradox this is very important in statistical thermodynamics so we got entropy is equal to

$$S = Nk \ln q + \frac{E}{T}$$

$$S = NK \ln \left(\frac{2\pi mkT}{h^2}\right)^{3/2} .V + \frac{3}{2} NK$$

this is the entropy for the monoatomic gas system.

Now as all of you know that entropy is an extensive quantity. So, what is the definition of extensive quantity is that if you increase the volume or number of moles of the system the extensive property also doubles up or as intensive quantity like density it does not change even though you increase the volume to double the density of the system will remain the same. And as you know entropy S is an extensive quantity.

So, if I increase if I increase the volume of the system to 2V if I increase the number of particles of the system from N to 2N my entropy S should lead to 2S right. So, since entropy is an extensive quantity let us see whether this expression of entropy what we get for the mono atomic gas system is holding this or it is breaking.

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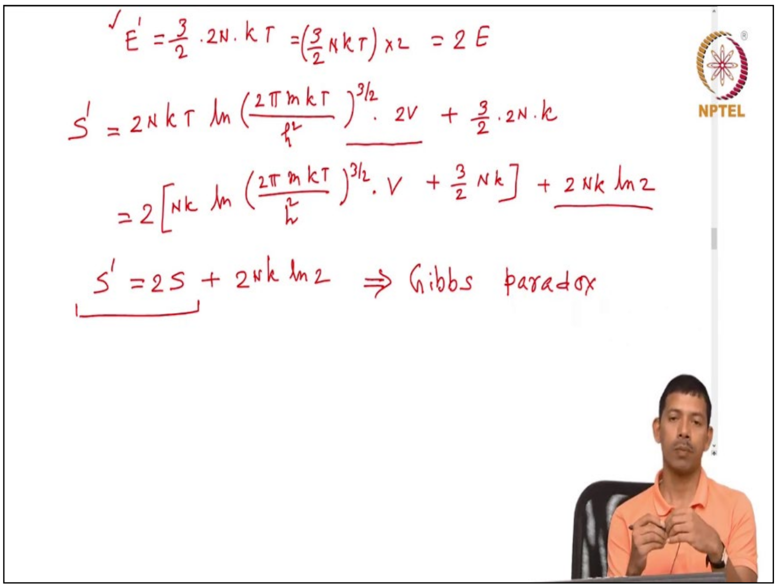

So, let us let us first see what happens to the energy? So the energy of the system let us say E prime is the new energy after we increase the number of moles number of particles and the volume to double. So, a new energy E prime would be

$$E' = \frac{3}{2}\, 2NkT = \left(\frac{3}{2}\, NkT\right) \times\, 2 = 2E$$

so 2E, so E was my total energy before and E prime is my next new energy after I made the system double.

So this is valid that energy is also an extensive quantity so this quantity has doubled up when I increase the volume and the model what happens to the entropy? So, let us say S prime is my new entropy after I increase the volume and the particle number.

$$S' = 2NK \ln \left(\frac{2\pi mkT}{h^2}\right)^{3/2} .2V + \frac{3}{2}\, 2NK$$

$$S' = 2S + 2Nk \ln 2$$

So my S prime instead of becoming just 2S it also has an extra term and this is called the Gibbs paradox. So, before whats the meaning of of Gibbs paradox is that before Gibbs pointed this out whatever expressions we had used for q and mainly q the partition function was based on that definition of q and when Gibbs pointed this out that entropy which is an extensive quantity is not fulfilling this even for a simple monoatomic gas.

So, then scientists had to think that the definition of q has some problem. And what could be the origin? The origin if you remember we basically started from the definition of thermodynamic probability W, we started from thermodynamic probability definition W is equal to n factorial divided by n1 factorial n2 factorial n 3 factorial. So, Gibbs said that there is a problem in that definition of thermodynamic property.

And we and the problem is as you remember thermodynamic probability basically keeps a number of microstates. So, Gibbs said that there is a problem in counting the number of microstates. We are basically over counting and how we are over counting we are over counting by assuming the particles are distinguishable. If you recall that that definition of thermodynamic probability W n factorial divided by n1 factorial n2 factorial n3 factorial and so on and so forth.

It was fulfilling the particular macrostate and it was giving the right number of microstate for each macrostate. And to get that we assume that particles are distinguishable but in practice particles in a quantum system or in a classical system they are completely indistinguishable. And there is the problem Gibbss pointed out that since particles are not distinguishable we over counted them and because of that were counting there was a problem in the definition of q and that is where we get this paradox that entropy is not showing as an extensive property.

So, we have to now find out the actual the correct definition of thermodynamic probability W which we will see next.