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**RAFAEL**

Hello. Happy Monday. And welcome to lecture 28. We're going to continue working on statistical

**JARAMILLO:**

thermodynamics, and we'll start with the Boltzmann hypothesis. All right. And what Gibbs is to classical thermal, Boltzmann is to statistically. And so these are really giants, and the reason why their names are all over everything.

My understanding is that Gibbs was a pretty straight shooter, and his biography is a little bit on the boring side. That's my very quick read of it. Boltzmann was a much more turbulent individual. And so it may not have been fun to be Boltzmann, but his biography is a lot more interesting. So if you have a moment, you might read a little bit about his life, anyway, but we're just going to focus on the science.

So here's the preamble. We have this quantity, which we counted microstates,  $\Omega$ . It describes the stability. We haven't put it in these terms, but it follows from everything we've been doing.  $\Omega$  describes the stability of a macrostate because the state with maximum number of microstates will appear. All right.

So this is an observation from what we've done so far. And I hope this is sensible to you. That the state with the maximum number of microstates will appear the most stable. It's the most likely, and if you find yourself in that state, you're very unlikely to get out of that state. So it's going to appear to have this property of stability. And if you remember, towards the beginning of this class, we defined equilibrium as having this property of stability. And so there's some connection there.

And so Boltzmann made that connection with his hypothesis. And his hypothesis is that the entropy is a function of the number of microstates. So the entropy of a macrostate is a function of the number of microstates corresponding to that macrostate. And more than that, he hypothesized that entropy is a monotonically increasing function of  $\Omega$ . So this is a monotonically increasing function. So what that means is that  $\max S$  means  $\max \Omega$ . So we're going to use that. Max entropy means max  $\Omega$ . So that's a hypothesis. All right.

So we're going to consider the form of that function. This is pretty easily done, consider two isolated systems, system A and system B. System A is some stuff. I don't know what it is. And it has number of microstates  $\Omega_a$ , and it has entropy extensive  $S_a$ .

And system B is some other stuff. It's isolated from system A. It's over on a different room, on a different shelf, what have you, and it has microstates  $\Omega_b$  and entropy  $S_b$ . So first of all, entropy is extensive, which means that the total entropy in the system-- like any other extensive quantity, what should the entropy of the whole be? I'll label that total.

**STUDENT:**

Be the entropy of a plus the entropy b.

**RAFAEL** Yeah. Like any other extensive thing, like marbles in a jar or moles of material, you just add them. But the total number of microstates is-- I'll call it combinatoric. I don't know if that's a word. What I mean is, the total number of microstates available if you consider both systems is what? You can have microstate 1 and all of these, and you can have microstate 2 and all of these, and microstate 3 and all of these, and so forth. So what's the expression for the total number of microstates considering both systems at the same time?

**STUDENT:** Is it the product of a and b?

**RAFAEL** It's the product, yeah. All right. So entropy is additive, but omega is multiplicative. So that means f of omega total, which is f of omega a times omega b, is f omega a plus f omega b. We're using both of these properties now. So who knows a function that has this property, the function of the product is the sum of the Function

**STUDENT:** Log?

**STUDENT:** Logs?

**RAFAEL** Yeah. So we come up with this conclusion, which is that this function we're looking for, which is entropy, is proportional to log of omega. And we're going to right now just have a-- we have a pre factor out there. It doesn't change. And so we're going to call that pre factor k, and we'll put a b under it because it be Boltzmann constant. We don't know what it is yet, Boltzmann's constant. And this is known as Boltzmann's entropy formula.

So just like that, we have a pretty simple-looking equation that gives us the entropy for a system as a function of the number of microstates. That's pretty cool. All right. So we still don't know what Boltzmann's constant is, but that's OK. So let's see what some implications of that are. We'll start with the same configurational entropy, which we have talked about throughout the term.

Configurational entropy, so what is? It's a number of ways to configure a system and space. So I'm going to draw a grid. This is going to be simply suggestive. We're not going to analyze my drawing because I'm just going to be rough about it. Let's just put a particle here and a particle here and a particle here and a particle here. What we're going to do is we're going to count the number of ways to distribute n molecules into r boxes. And we're going to have those boxes sufficiently small such that no box has more than one molecule.

So we're dividing space up into tiny, tiny, tiny little voxels Well, we know how to do this already. We talked about this the other time. This is just r choose n, and that's r factorial-- wait, sorry-- over n factorial-- there's an error in the notes there-- r minus n factorial, r choose n. Good. So now what we're going to do is we're going to let the total number of boxes be the total volume divided by some little volume b.

And so this is total volume and this is a little voxel. And we can say corresponds to volume-- we can say this corresponds to the volume of a molecule. It's a tiny, tiny little amount of space, but it enforces our condition here that the boxes cannot have more than one molecule.

So now it can be shown-- you will apiece that-- can be shown that the log of r choose n-- you're going to take the log of omega, that's the Boltzmann hypothesis, Boltzmann entropy formula thing, so you're going to take the log of this binomial coefficient, the log of r choose n is approximately n log r for r very, very much larger than n.

So  $r$  very, very much larger than  $n$  corresponds to-- let's say a gas. Most of space is empty. There's a much larger number of voxels of space than there are molecules that fill them. So that's like a gas. And this is a-- that's a problem on a current PSET. So far so good.

Now what we're going to do, now let system expand from volume  $V$  to  $2V$ . So we're going to do an expansion of this gas, and we're going to calculate  $\Delta S$ . We're going to do this using statistical thermodynamics now. We're not going to do it the way we did a month and a 1/2 ago. You have Boltzmann's constant times  $n$ , and let's see.  $\log 2V$  over  $b$  minus  $\log V$  over  $b$ . And we can collect terms and simplify. This is  $k_B n \log 2V$  over  $V$  equals  $k_B n \log 2$ .

So this here,  $k_B n$ , this is  $R$   $n$  equals Avogadro's number. We recall this from the classical derivation, isothermal expansion of an ideal gas. This is the same result for isothermal expansion of ideal gas.  $\Delta S$  equals  $R \log V_{\text{final}} / V_{\text{initial}}$ . So this is one way to start identifying what that Boltzmann constant is. Boltzmann's constant is  $R$  divided by Avogadro's number. That's cool. That's neat.

We've done this weird statistical thing, and good, old Ludwig came up with this. And we find that when we calculate a simple case, we get functionally the same thing as when we calculated this case, when we didn't know anything about molecules. And we were just dealing with classical thermodynamics. We can make the connection via the coefficients. That's cool. Great. Questions about this? Because I'm going to move on to the next thing that Boltzmann did.

The next thing we're going to do, and what we're really building up to here, is the maximum entropy condition, maximum entropy condition and the Boltzmann distribution. So we get Boltzmann hypothesis, Boltzmann entropy formula. And this is going to be Boltzmann distribution, this Boltzmann's constant Boltzmann's name is everywhere. We're going to set this up and do most of it, but this will carry over into lecture 29. It's that essential that it's worth taking the time. All right.

So what we're going to do? We're going to consider  $n$  total particles distributed over  $r$  states according to the occupation numbers. We have these occupation numbers from last time. All right. That's a set of numbers,  $n_1$  of 1,  $n_2$  of 2, and all over-- all the way up to  $n_r$  of  $r$ . So how many states are-- how many particles in each state? And we're going to calculate the entropy of this thing.

So again, taking from last time, from our last lecture, is going to be  $k_B$  time to  $\log n_{\text{total}}$  over product  $n_i$  of  $i$ , everything factorial. Now, I'm going to use Sterling's approximation to get to the next line, which is going to be  $k_B [n_{\text{total}} \log n_{\text{total}} - n_{\text{total}} + \sum n_i \log n_i + \sum n_i]$ . So I use this Sterling approximation, and then I'm going to use the fact, the sum over  $i$ ,  $n_i$  equals  $n_{\text{total}}$ , so the sum of where all the particles are equals all the particles.

So I can simplify a little bit. This equals  $k_B [n_{\text{total}} \log n_{\text{total}} - \sum n_i \log n_i]$ . And now I can condense this a little bit. I'm going to split the numerator and denominator, figure the minus sign, and I get a  $\log n_i / n_{\text{total}}$ . So so far, just playing with numbers. So I have the entropy is a sum for  $n_i \log n_i / n_{\text{total}}$ . By the way, this kind of looks like  $x \log x$ , doesn't it? It kind of looks like our ideal entropy formula. Anyway, just a passing observation.

All right. So that's fine. Here's the science inside. The distribution of occupation numbers, the distribution of occupation numbers is an unconstrained internal variable. That means that those particles are going to fluctuate. They're going to fluctuate in and out of different states, and that's an unconstrained process.

So in our previous example, you had particles in a box. And I you could imagine these particles in general move. They could jump in between boxes. That's an example of jumping in between states, we're going to make this a little more general and not limited to states being positions in space. We're going to have a more general expression. We're going to say, let's say, state  $i$  minus 1. We have state  $i$  and state  $i$  plus 1, so forth. And we're going to allow that--

At any given moment, let's say there's four particles in this state. Let's say there's two particles in this state. And there was a third, but that particle jumped. It fluctuated and went over here. This is simply visually acknowledging that the states are fluctuating. The particles are fluctuating between them. These fluctuations can and will happen.

So if that's happening, the maximum entropy condition,  $S$  equals  $S$  max, requires that  $S$  is what? Stationary. As we have done now so many times in this class, it has to be stationary with respect to all unconstrained internal processes. So this conceptually, where we're going is the following. We did something like this before. We've done it multiple times.

When we had two systems that can exchange volume, we require the entropy to stationary with respect to that. And we got the mechanical equilibrium condition. Pressures are equal. And we had two systems that can exchange energy. We wrote out the max entropy condition, and we require that the entropy is stationary with respect to the energy exchange. And we got the thermal equilibrium condition. We got the temperatures are equal.

And likewise with systems that could exchange particle number, we got chemical potential being equal. Adding that whole thing up, we call that thermodynamic equilibrium. So now we're doing something slightly different. We're requiring this entropy stationary with respect to exchange between different states. And it's pretty general right now. So a little bit vague, but there are clear similarities to what we've done earlier in the class. At least there are mathematical similarities.

So  $ds$  prime-- that's write that out-- equals minus Boltzmann's constant. And what I'm doing is I'm just taking the total derivative, so  $L \log n$  of  $i$ ,  $dn$  of  $i$ -- see-- plus  $n$  of  $i$  over  $n$  of  $i$   $dn$  of  $i$  minus  $\log$  of  $n$  total  $dn$  of  $i$  minus  $n$  of  $i$  over  $n$  total-- just taking the total derivative of the expression on the previous slide. And this simplifies pretty readily. And I get minus Boltzmann constant and the sum over  $\log n$  of  $i$  over  $n$  total  $dn$  of  $i$ .

All right. Just, again, making this explicit. I just took the total derivative of this using the chain rule. All right. So that's the  $S$ , and I have all my little unconstrained internal processes here, little fluctuations between the occupation numbers. All right. Now let's apply my constraints. That's what we did before, and that's what we'll do again. And in this case, I'm going to apply isolation constraints.

Isolation constraints, so I want my system to be isolated. Max entropy is the equilibrium condition for an isolated system. We remember that. So here's my little fluffy-- pink insulation here surrounding my system, and I've got system surroundings and what? The boundary is rigid. It is impermeable, and it is insulating. All right.

Now we're going to allow that the states  $I$  have different energies. That  $e_{sub\ i}$  be the energy per particle state  $I$ . And I don't want to just slip this in there. This is kind of new. This is kind of new for us because previously in the baby book, and even just 15 minutes ago in this example of configuration entropy, we had this idea that space was somehow flat and uniform. And the energy of each particle would not be dependent on its position. All right.

So if the states are positions, maybe you have a gravitational potential, or maybe you have an electric field. Maybe this a battery, and there's an electric potential. And maybe the particles are charged, and then you can imagine energy and space becoming conflated. But more generally, there's no reason why these states have to be positions in space. They could be spin states or vibrational states. They could be rotational states. They can be anything that is distinct. Different states have a particle in general. These different states can have different energies per particle.

So  $e_{sub\ i}$  equals the energy per particle and state  $I$ . And so we're going to then say the total internal energy is pretty simple. It's just adding up all the energies,  $e_{sub\ i}$  times  $n_{sub\ i}$ . And that means that  $du$  equals  $e_{sub\ i} dn_{sub\ i}$ . Its conservation of energy. So you're going to study a system of elastic collisions in the lab. And the individual particle energy isn't going to be changing, but I think you can trust that the total system energy for elastic collisions or rigid billiard balls, that doesn't change. So one gains and other loses and so forth.

And likewise, we have the total number of particles. And this is a pretty simple expression. This is the sum  $n_{sub\ i}$ . And that means  $dn_{total}$  equals the sum  $dn_{sub\ i}$ . I'm sorry I forgot. This is going to be 0, and this is going to be 0, conservational of mass, conservation of mass. So now I have some mathematical ways to apply these conditions.

And I'll just make a note in passing, this really is beyond the scope of this class, but those who are interested, conservation of volume, you might say, what about volume? Before, two months ago, you were considering volume, energy particle number and volume. We're not touching conservational volume right now, but it's connected to the  $E_{sub\ i}$  being constant.

When I took  $du$ , I didn't apply the chain rule and allow the  $E_{sub\ i}$  to change. I assumed they were constants. And that comes from the conservational volume. So when you take quantum mechanics next semester, this comes out right away, so. All right. But we're not going to touch it here.

So this is a case of constrained optimization, constrained optimization. Constraint optimization is the most important application of calculus in engineering, in business. It's in general what you do in Sloan and what you do in course 16 and course 2. A little bit less in course 3, but you should remember this from calculus.

So we want to optimize that function, subject to constraints, that the energy and the total particle number are fixed. So we're going to use the method-- anyone remember? What method are we going to use? Is it from multi? French name.

**STUDENT:** The Lagrange multiplier?

**RAFAEL JARAMILLO:** Yeah. Thank you. We're going to use [INAUDIBLE] of the Lagrange multipliers. So in your calculus textbook, you would have used the del operator. I'll just write that here just for familiarity, but then we'll switch back to our operator. And so what do we have? Del, the thing we want to optimize, plus del, the things which are conserved. And we have Lagrange multipliers.

So we have  $\sum_i n_i$  total and  $\sum_i u_i$ , and this whole thing is going to be 0. This is written as in your calc textbook with the  $\delta$  operator, but we're going to write this way,  $\sum_i ds + \alpha \sum_i dn_{\text{total}} + \beta \sum_i du = 0$ . And  $\alpha$  and  $\beta$  are Lagrange multipliers.

I was talking to my wife about this actually. She teaches college math. And it does seem this is the most important application of calculus outside of some specialty areas, at least the most widespread. Anyway. So we're going to substitute our expressions. We have expressions for  $ds$  and  $du$  and  $\sum_i n_i$  total and collect terms. That's what we're going to do. So we substitute our expressions, and we collect terms, and we get the following,  $\sum_i \left( -k_B \beta \log \frac{n_i}{N} + \alpha + \beta \epsilon_i \right) dn_i = 0$ .

So what is this functional form? What is this form? This is just like we did two months ago, starting about two months ago, for the case of unary systems. We have here a set of unconstrained independent variables. And so we want this whole thing to be zero. How do we ensure that this whole thing is zero? Remember these differential forms? What did we call the pre factor in front of the differential of the independent variables?

**STUDENT:** You just said the coefficients equal zero.

**RAFAEL JARAMILLO:** Coefficient, right? Exactly. We're going to set each coefficient to zero. So let's do that,  $-k_B \beta \log \frac{n_i}{N} + \alpha + \beta \epsilon_i = 0$ . I'm going to rearrange  $\log \frac{n_i}{N} = \frac{\alpha + \beta \epsilon_i}{k_B}$ ,  $\frac{n_i}{N} = e^{\frac{\alpha + \beta \epsilon_i}{k_B}}$ . And this is true for each state  $i = 1, 2, \dots, r$ .

So we're not there yet, but we just had something really important to happen. This is a distribution function. All right. This is describing the occupancy of state  $i$ . And it's a fractional occupancy. It's  $\frac{n_i}{N}$ , so the fraction of particles that are in state  $i$ . And it's exponentially dependent on the energy of state  $i$ . All right.

So I want you to notice two things here. I'll just repeat what I said. That this is a distribution function. That's a very useful thing. That's a distribution function, and it's exponential in  $\epsilon_i$ . But we haven't finished yet because we have these Lagrange multipliers. So we don't know what those are yet.

So we're going to determine one of them now, and we'll determine the other one on Wednesday. So we're going to determine  $\alpha$  by normalization. What do I mean by that? What I mean by that is the sum over all of  $i$ ,  $\sum_i \frac{n_i}{N} = 1$  -- what is this sum, sum over all of  $i$ ,  $\sum_i \frac{n_i}{N}$ ?

**STUDENT:** Just one.

**RAFAEL JARAMILLO:** Yeah, it's one. It's one. So if we set that equal to 1, we get the following,  $1 = \sum_i \frac{n_i}{N} = \sum_i e^{\frac{\alpha + \beta \epsilon_i}{k_B}}$ . And we're going to give this thing a name. We're going to call it the partition function. The partition function  $Q$  is the sum over all possible states  $e^{\frac{\alpha + \beta \epsilon_i}{k_B}}$ . Boltzmann. So for now, it's just a name. What does that mean? It normalizes the distribution.

Why is it called partition function? It describes all the different ways that the energy can be partitioned in the system. So it's a sum over all the states, somehow characterizing the system and all the ways energy can be partitioned in them. Partition function normalizes the distribution function.

So this distribution function,  $n_i$  over  $n_{\text{total}}$  is equal to  $e^{-\beta \epsilon_i}$  over  $k_B T$  divided by  $Q$ . So it looks like I end it about five minutes early, but better that than rush through the derivation of a determination of  $\beta$ . So I'm going to stop now and take questions.

**STUDENT:** Could you explain the Lagrange multipliers a little bit? I can't find it.

**RAFAEL JARAMILLO:** Yeah. So you want to subject-- you want this to be 0 subject to the constraint that this is 0 and also this is 0. And you know these are 0 because you're applying those constraints. And so you can add these to the equation of  $\delta S = 0$  without fundamentally changing the equation. And then  $\alpha$  and  $\beta$  are not necessary mathematically, but they generalize the situation.

And so then you can effectively relax-- you can relax your constraints here, and the overall constraint is maintained by  $\alpha$  and  $\beta$ . So your method of Lagrange multipliers is only valid with-- the equations that result from this appear as if they might be valid even when the constraints on total number of particles and energy relax, but they're not. You have to remember that. The equations that we get from this method are only applicable when  $U$  and  $N$  are fixed.

So that's the concept point here. And so when we derive a distribution function, we have this distribution function, or we have this form here. And this, of course, also relates to the Arrhenius rate law. So we're getting there. And people will see this distribution function so often in natural sciences that it's important to remember it's not always true. It is very specifically true that it is the distribution function that maximizes entropy under this condition. So I think that's the concept here. So don't apply it willy-nilly.

**STUDENT:** Thank you.

**RAFAEL JARAMILLO:** But you don't have to worry. This isn't a calculus class in the sense that I'm going to ask you to derive this or even repeat this derivation, but I do want you to know where this comes from, because this is going to start becoming second nature, not necessarily in the next week and a 1/2. But this distribution function is going to be so familiar to you by the time you're a fourth year student in material science. It's good to remember that it comes from somewhere, and it's subject to assumptions.