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**RAFAEL
JARAMILLO:**

We're going to move on now from CALPHAD. There's a couple, but we're going to move on. And we're going to do statistical thermodynamics for three or four lectures.

All right. So a note on the reading here, almost everything that we're going to cover is going to be in chapter 6. In the syllabus, I also have a signed chapter 3 of a different book by Chandler, and that PDF is on the website. That is a more advanced book.

You don't really need the formalism in that book to do the problem sets, for instance, or to succeed on exam 3. So I would say that reading is quasi-optional. I hesitate to say that because I wonder whether anyone would read it at all. But it helps to know that because it is a more advanced book.

I find that presentation in Chandler to be just masterful. I really like that book. I like how it's written. I like how the material's presented. I like how it's presented better than the way DeHoff half presents this topic. But that said, it is a little bit more advanced than we need. So it's good that you know that.

So let's talk about microstates-- macrostates, and microstates. Macrostates and microstates. So let's start with microstates.

A microstate-- this is key, foundational definitions. This is a description of the state of every atom in a system, every atom in a system.

So that's kind of, crazy, right? That's a crazy thing to think about. It's describing every atom in a system. In practice, we almost never do it. But in theory, it's the foundation of this topic.

So, for example, if you have a mole of atoms-- let's say, an ideal gas, a mole of argon atoms, you have on the order of 10^{23} velocity, position pairs. So you have velocity, and you have position. These are vectors, and they're indexed by atom. And you have 10^{23} of these pairs, so just an ungodly amount of data.

And for those of you who don't know, this script is often used to indicate on the order of, so of in the order of 10^{23} velocity and position pairs. OK.

A macrostate is a description of a system on macroscopic length scale averaging over microscopic. And by microscopic, I mean that is atomic or molecular processes.

So macrostates are what we have been dealing with to date in class. And so we know that even if we might have 10^{23} atoms, we can describe the state of the system with a very small number of parameters, like pressure, temperature, and mole number.

So at times, we can imagine the atoms zooming around. At times, we can imagine that, right? And you could draw pictures, right? So this is going back to the baby book. This baby book is called *Statistical Physics for Babies*. So we're back to the baby book.

And so we imagine that we can draw pictures of where the atoms are and how they're moving. This is velocity-position pairs. But we never actually do it, right? We never really do it. We characterize a system by the pressure and the density and the temperature, a small number of variables.

So we're going to spend some time counting microstates. Because it's really through counting microstates that the profound nature of this emerges. Here's a simple example. This is right from DeHoff.

So this is combinatorics. Let's say four particles, A, B, C, and D, and two possible states for each particle, 1 and 2.

So you can imagine these states are two boxes. You can imagine a carton that's separated into two boxes. We'll call this 1. We'll call this 2. And you can put some particles in here, and you can put some particles in here. And we're going to figure out how to distribute the particles.

So let's do some counting, so state 1, state 2 OK. So we can have all the particles in state 1. We can have three particles in state 1,

We can have two particles to state 1. And I'm going to imagine-- you could continue filling this in if you wanted to. So these are a list of all possible micro-- I need to be careful with my writing.

This is a list of all possible microstates. You can imagine listing these out. So now I'm going to tell you what the macrostates are. Macrostate 1, macrostate 1 is going to be something described as follows-- all particles in state 1.

Macrostate 2, macrostate 2 is going to be three particles in state 1. Macrostate 3, macrostate 3 is going to be two particles in state 1.

And you can continue to delineate these. And now we're going to count. So macrostate 1, macrostate 1, that's macrostate 1. So how many different microstates are there within macrostate 1?

AUDIENCE: Just one.

RAFAEL JARAMILLO: Just one, that's right. OK. Macrostate 2 has these microstates. So how many microstates are there that are consistent with this macrostate definition?

AUDIENCE: Four.

RAFAEL JARAMILLO: Four. There are four states that are consistent with this macrostate. So what we're doing here is we're defining microstates and then we're counting macrostates. Define microstates, count microstates. That's what we're doing.

So let's do this a little bit more general. Well, before I do the general case, let me again-- the baby book is fantastic here, right? The baby book does exactly this. DeHoff and baby book are very similar books.

So here is a case of six particles and two states. And there's only one way for all six particles to be on the left-hand side. So this would be a macrostate called-- the volume is $1/2$. Let's just say this is a volume of 1. This macrostate would be defined as the volume is $1/2$.

There's only one way for them to all be on the left-hand side. Maybe you say there's two ways. The volume's $1/2$, it can be left or right. That's what we're doing. We're counting, right?

And then you can say, OK, let's say that I have a state where I have two regions, one with density 5 over $1/2$ and one with density 1 over $1/2$. How many different ways can that macrostate be instantiated by microstates? And you say, OK. 1, 2, 3, 4, 5, 6. There are six ways.

You can define a different macrostate, and you can count. So the baby book here is doing exactly what DeHoff is doing. So now we'll do a little bit more of a general case. Let's do a general case.

n particles distributed over r states. n particles distributed over r states. And we're going to introduce capital ω .

Capital ω is going to be number of microstates in the macrostate defined as n_1 particles in state 1, n_2 particles in state 2, and so forth.

So the macrostate is defined by a set, $n_{sub\ i}$. $N_{sub\ i}$, that set describes the macrostate. And sometimes those will be called occupation numbers.

So when you do probability and statistics or when you do quantum mechanics-- and especially, quantum statistics-- you spend a lot of time talking about occupation numbers. So now you've seen the occupation numbers. I mean, it's encountered in other areas as well.

I'm just thinking about-- what am I thinking about? I just came out of a talk about material science challenges for quantum computing, and so I was seeing a lot of that stuff. So that's what's on my mind.

All right. Anyway, here's the answer. The answer is this. And if there's time, we can come back to derive this. The book does not derive this. It's not hard to derive.

OK. So this is the number of microstates for n particles distributed as follows, with $n_{sub\ 1}$ in state 1, and $n_{sub\ 2}$ in state 2, $n_{sub\ 3}$ in state three, and so forth. So again, we can come back to that.

But I want to show you something qualitative about that function. For large systems, for large systems-- that is, n much greater than 1 and especially when r is much greater than n -- so a very, very large number of particles and an even larger number of places to put those particles.

This function becomes very sharply peaked around a particular macrostate. What does that look like?

Here, I'm going to plot ω , and it's going to be on a log scale. I'm not going to put tick marks on there, but I just want you to appreciate the orders of magnitude involved, so I'm going to tell you this is a log scale.

And the abscissa here are macrostates, macrostates-- let's say indexed somehow. And you're going to have some macrostates for which the distribution of microstates is overwhelmingly higher than for all other macrostates.

It's this area under the curve here. Let's draw that in orange so it's even possible to visualize it. This is a highly-peaked distribution function-- so again, another concept from probability and statistics.

And this state, we will see, is the most probable macrostate. It's the most probable macrostate. So we saw that a little bit at the beginning of class when we looked at ways of distributing six balls in two halves of a container.

And Fenney told us that the reason why this is a more common macrostate-- of course, he didn't use that term-- the reason why this is the most common macrostate is because it has the most number of microstates. So this is a macrostate with one microstate. This is a macrostate with six microstates. This is a macrostate with 15 microstates.

And this is a macrostate with 20 microstates. And that was the reason it was the most often seen. You could say it's the most likely. And we will see soon within a lecture and a $1/2$ that it is also the state with the highest entropy. So we're starting to see a connection between equilibrium and likelihood.

OK. So let's do some more counting. Let's work on defining-- I think I have too many letters in that-- defining-- or, that is, counting-- the macrostates for n particles in r states.

And again, you can think of these as boxes, places to put the particles. So we're going to do some more counting. I'm going to index these things just so we have an ordinate. And so-- let's say-- and I'm going to write sets of occupation numbers. These are going to define the microstates.

Let's start with all the particles in the first box, so n followed by a bunch of 0's. That is a good macrostate-- all the particles, let's say, on the left. That's what that would correspond to. Let's call that macrostate 1.

We could also have all the particles in the second box or all the particles in the third box and so on. Let's see. How many of these states are there going to be? How many of these sort of states are there going to be?

These states are defined as all particles on one box. How many of those are there going to be?

AUDIENCE: R?

RAFAEL JARAMILLO: R, right. There are r choose 1 of these. I'm using the parentheses notation for the binomial distribution. Some of you have seen this as r choose 1. It's a little more compact to write in parentheses. If you've never seen the binomial distribution, we should make time to talk about it.

But why is r choose 1? It's because you have r states and you're just choosing one of those states into which you're going to put all the particles, so r choose 1. And, by the way, r choose 1 is just r , right? You have r choices.

OK, all right. Next, what about states where you have n minus 1 particles in a box and one particle in another box? And the other box is, of course, empty. And then there's going to be a bunch of ways that you can do this, right?

Here, I put n minus 1 particles in the first box and the remaining particle in the second box. Here, I put n minus 1 particles in the first box and the remaining particle in the third box-- and so forth. OK, this is a challenge. Can somebody tell me how, in a compact way, to count how many states such as these are there? How many total macrostates such as these are there?

How do we think about it? I have r boxes. And out of those r boxes, I'm picking two of them. I'm choosing two of them. I'm choosing two of those boxes to have particles in them where the rest are empty.

So do we have an expression for how many ways can we choose 2 boxes out of r boxes?

AUDIENCE: r choose 2?

RAFAEL Our choose 2. Good. And this keeps going until you get to r choose minimum of r and n .

JARAMILLO:

AUDIENCE: Can I ask you a question?

RAFAEL Mm-hmm.

JARAMILLO:

AUDIENCE: Would it be r choose 2 regardless of how you distribute the particles within those two boxes? So, like, say you did, like, n minus 2 and then 2 in the next. Would it still be r choose 2?

RAFAEL n minus 2 and then 2. That would be--

JARAMILLO:

AUDIENCE: Or oh, OK. By definition, you can only have, like, max 1 or--

RAFAEL No, that's OK. That's going to be a different set, and that would also be counted this way. It's just not the way

JARAMILLO: that I've defined it here.

AUDIENCE: OK.

RAFAEL There are so many ways of doing this. I'm only giving you a very introductory example here how to start thinking through it. But we'd be writing all day if we were to write these all out. We'd be writing these all day. But that's a good way to think about it.

JARAMILLO:

So now, in principle, we now know how to identify-- or you could say count-- the macrostates. We know sort of a systematic way now to generate these sets.

And the result in DeHoff, we know how to count microstates for each macrostate. We have a systematic way of moving through all the macrostates and describing them and counting them. And we have an equation for the number of microstates for a given macrostate.

So we have this procedure. We have this algorithm. and so now we can calculate and plot the distribution function or log sigma or omega. So let me show very, very simple case, extremely simple.

So I wrote a little script that does this, and I ran the script for a couple of cases. And so as I move from left to right here, I'm changing r . I have three particles in five boxes, three particles in 10 boxes, three particles in 20 boxes, and three particles in 100 boxes.

The top and bottom plots are the exact same data set, I'm just distributing them differently. It's the exact same data set, distributions visualized with different sorting. And so with three particles and five boxes, the log of the number of microstates spends some time around 0-- that's 1, right? Log of 0 is 1. So these are conditions for which there's one microstate.

And then it jumps up and it spends some time around 1-point-something. And then it jumps up and it spends some time around 2-point-something. And what I want you to see is, as the number of boxes it gets higher, the distribution of microstate count gets more sharply spiked.

So what you're seeing is even at low numbers, three particles in 100 boxes, you're entering a situation where this distribution function is becoming very sharply spiked. And this is a very small number case, three particles in 100 boxes. I tried to run 10 particles in 100 boxes and I calculated that my computer would take about a year. So these numbers get really big really fast. If you typed in Avogadro's number here, I think your computer literally laugh at you.

But you're supposed to see, qualitatively, that this function is becoming sharply spiked. That has profound implications. That's why I'm spending time on it. So why does that matter? Why does it matter that that distribution is sharply spiked? Who cares?

It cares because of something called the ergodic principle. I'd never heard that word before I took statistical thermodynamics or stat max for the first time. So maybe you have. I don't know. Maybe you're more well-read than I was. But I've never seen that word outside of this context. It's, like, the weirdest word. Where does it come from? I don't know. If anyone knows where it comes from, I'd be curious.

Anyway, this is what it is. The ergodic principle is the following. It's a hypothesis, not always true. Here's the hypothesis.

All microstates, all microstates that are compatible with constraints are equally likely. That's the ergodic principle.

So we have a word here, which is, again, from another discipline. We have the concept of constraints, which we're familiar with, but here it is again. And we have this sort of funny new word.

So this gives rise to the concept of ensembles, ensembles of microstates-- going to use shorthand here-- ensembles of microstates that all satisfy given constraints.

So what's an ensemble? An ensemble is a collection. So here's an ensemble. Here is the ensemble of microstates that all satisfy the constraint that the volume is the full rectangle with solid lines. That's a constraint. The constraint is that the volume is the full volume, and this is an ensemble. It's an ensemble of different microstates that all satisfy some clearly-stated constraints.

And here is something a little bit profound. A corollary of this is that time averaging is the same thing as an ensemble averaging. Time averaging is the same thing as ensemble averaging.

And for those of you who like probability and statistics, this connection between time averaging and likelihood is known as frequentist probability-- as opposed to Bayesian. So what does that mean, that time average is the same as the ensemble average?

It means that if you can define, if you can write down the ensemble of all possible microstates that satisfy a given macrostate, if you can write down the ensemble of all microstates and you average over that ensemble, the average you get for any observable quantity-- be it pressure, or temperature, or magnetization, or density or what have you-- that average is the same as if you take a given system and evolve it forward in time and take a timeout average-- so, in other words, like this.

The average you get when you average over this ensemble is the same as you would get if you start with just that and then play forwards in time and average over the movie. That's what time averaging equals ensemble averaging means.

And the likelihood of finding a given macrostate is proportional to its number of microstates. The likelihood of finding a given macrostate is proportional to his number of microstates.

The probability of finding the macrostate j is equal to the microstate number for macrostate j divided by the microstate number summed over all macrostates, is number of microstates in state j - that's what that is.

This is total number of microstates within constraints. And this is the probability of finding macrostate j . That's what that is.

So let's go back to the baby book and to the plots. So if we have constraints that the particles just have to be somewhere inside of this gray box, we have one microstate here, we have six microstates here, we have 15 microstates here, and we have 20 microstates here. And then we're going to have another 15 with the particles weighted more to the right, another six with the particles weighted more to the right, and another one with the particles fully on the right.

So we have 1 plus 6-- that's 7-- plus 15-- that's 22. 22 times 2 is going to be 44-- and then 20-- is going to be 64. So we have 64 total microstates. And the most likely scenario is this one. Why is it the most likely scenario? Because its likelihood is 20 divided by 64.

You have a $20/64$ chance of finding something that looks like this. You have a $15/64$ chance of finding something that looks like this. You have a $6/64$ chance of finding something that looks like this. And you have $1/64$ chance of finding all the balls on the left.

So the balls not know what they are doing. They do not care about any of this. They move at random. But somehow, from their collective behavior, some simple rules emerge, that you're far more likely to find this scenario. And $20/64$ is not a very large number. That's only because we're dealing with six balls and two compartments. $20/64$ is not that large of a number.

But when you have a distribution function which looks like this, where this is now log of microstates and this is number of macrostates, you can see that this number, taking the exponent divided by this number is very, very large. That's the likelihood that you're going to find this macrostate instead of this macrostate.

And I think in the very first lecture, I referred to this as being the reason why we don't have to worry about suddenly suffocating because all of the oxygen molecules in the room have decided to go into one corner. The oxygen molecules move at random. Perhaps if you waited a very long time, you would find a snapshot in time for which all the oxygen molecules were in one corner. But none of us expect to find that.

Why is that? Because the likelihood of them being evenly distributed through the room is overwhelmingly close to 1. OK. So that is all following from the ergodic principle. All microstates that are compatible with constraints are equally likely. So likelihood follows microstate counting.

All right. So that's all I wanted to get through today. I want to leave you with a question, which is something we can discuss, and it gets to the P set. For what types of systems might the ergodic principle break down?

For what types of system might this break down? So we had this example, that ensemble averaging equals time averaging. And I said, what is the time average? Well, let's take a snapshot at time equals 0, call it. And we'll play the movie forward and we'll know the average over the time history of that movie.

That implies something. What does that imply about this system?

AUDIENCE: Maybe that it's closed and there are no additional particles being added?

RAFAEL Good. That's good. That's not what I was going for. You're talking about the boundary conditions and constraints.

JARAMILLO: There's something else, though, that is beyond the scope of this class. It's the title of a course you'll take in the fall. What does that imply about this system?

AUDIENCE: The kinetic energy is constant, maybe?

RAFAEL Kinetics. It's not quite what you said, but you said the keyword, which is kinetics. It implies the kinetics or

JARAMILLO: sufficiently fast that the movie will play. So if you're at 0 Kelvin and nothing is moving, if this is your starting point, this is pretty much where you will remain. So your time average will no longer be your ensemble average because the particles don't move anywhere.

So you only get this sequence of snapshots in time if the particles are moving at all. So systems that have sluggish kinetics violate the ergodic principle. What's something that we said about equilibrium way at the beginning?

Equilibrium is a state of rest. Equilibrium is what you get when you wait long enough. And we've never quantified long enough. We don't really do that in 020 because this is a course on equilibrium thermodynamics. We don't quantify long enough.

But the idea that you have to wait long enough for a system to evolve to equilibrium is equivalent to the concept that you have to wait long enough for the time average to become the ensemble average for any of this statistical thermodynamic stuff to work. Those turn out to be quantitatively the same thing.

OK. So we talk about kinetically-sluggish systems, kinetically-sluggish systems, systems that don't move very fast. They don't move fast enough to reach equilibrium. That might be an example of the types of systems in which the ergodic principle breaks down.

OK. I have four more minutes. And one thing which I could do with those four minutes is go back and show you how this comes about, because this is just stated in the text without proof. But I could also answer questions about this or anything else.

So let's start with questions about this material or even the material that we finished with Professor Olson's lecture or the problem set, which is due today. There's another problem set that goes out. Oh, I'll mention-- the problem set that goes out today is P set 9.

It's due Thursday because Friday is a student holiday. And it is shorter than I would otherwise give you because you have one less day to work on it. So don't forget that. Any other questions on any of this?

AUDIENCE: Could you go back to the counting macrostates page?

RAFAEL Sure.

JARAMILLO:

AUDIENCE: Yeah, this one. So for that one where you have r choose 2, will the n minus 1 always come before the 1? Because first you choose like which two boxes will be occupied, right? So there's r choose 2 ways to do that. But then don't you also have to choose which one has n minus 1 and which one has 1?

RAFAEL Yeah, you do. So that's another case that I don't draw out here. Thank you for that. So if you like-- so I'm not

JARAMILLO: being explicit here. I'm writing sort of suggestive cases and then putting ellipses, dot, dot, dots, right? So it's like, what on Earth is he talking about? You're getting to an ambiguity in the way I've written this out.

So it's the same ambiguity that you have here. Does this picture stand for one state, or does this picture stand for two states? It depends how you count. I imagine that Chris Ferrie-- He's a research physicist. He actually works at a quantum computing center in Australia. This is to say that he's a smart person, and I gather that he could do this accurately if he chose to, but this is the baby book.

So he wasn't explicit about, oh, there's actually two states and they're equivalent. that make does-- are you following me here with respect to the baby book?

AUDIENCE: Yeah. So basically, what you're saying is, if you were to write out, you would also have one where it would be, like, 1 comma n minus 1 that would be counted separately.

RAFAEL Right. Let's flip that. So if you want to say that we're counting those, we just double it--

JARAMILLO:

AUDIENCE: OK, that makes sense.

RAFAEL --in this case. But then the next case down, you can't just times 2 it. It becomes more complicated. So the

JARAMILLO: counting is not easy sometimes. So you can imagine that if I asked you to sit down and do this bookkeeping correctly, you could. And don't worry, this is not a case that's on the problem set. But you could do it, and other people have done it right.

I try to do it in a MATLAB script that I wrote to produce those plots, for instance. Yeah, good point. Good point. It all comes down to how you think about doing combinatorics.

AUDIENCE: My question was basically equivalent so I'm glad that you asked it. Thank you. But then for the slide before that, then-- or maybe it was two sides before, where you're counting states in the very beginning.

When you were doing two particles in state 1, two particles in state 2, just like you explained it here, that would mean that if you had, say, like AB state 1 and CD state 2, that would count separately, then, AB state 2 and CD state 1, right? Those would be two different cases.

RAFAEL Yes. Yeah, again, another case where I just put ellipses and I wasn't explicit. Yeah.

JARAMILLO:

AUDIENCE: OK. So basically, the type of particle matters. We're labeling these particles. It's not just labeling--

RAFAEL We're labeling these particles. We're labeling these particles, yes. We're labeling these particles.

JARAMILLO:

AUDIENCE: On the r choose 2 on that slide, could you talk a little bit more about how you draw that conclusion? I'm not super familiar with the way that you wrote it out.

RAFAEL Sure. So let me finish this comment on labeling these particles. This is all classical statistics. It's perfectly fine. It gets you a long way.

When you get to quantum statistics, you have to start dealing with indistinguishability. And you have to-- well, this might be much more than you want to know at the moment, but I'll share it because I think it's kind of cool.

Imagine that all of the grid squares are states, and I have two particles. And let's say they're the same isotope of an atom in the same spin state, same quantum numbers. In that case, they're indistinguishable, quantum mechanically. So I want the modulus squared of my system wave function to be unchanged if I exchange these particles, because they're indistinguishable.

That still gives me a choice of sign in the wave function, because a negative number squared gives you a positive number. And a positive number squared gives you the same positive number. And that's the difference between bosons and fermions. And it produces very, very different physical behavior, those statistics, quantum statistics.

And actually, there's a quantum computing scheme that uses anyons, where the phase is imaginary in any way. So you're getting somewhere which we don't have time for in this class. But right, OK. So that was a point on distinguishability versus indistinguishability. The other question was about combinatorics.

So here, I have r states. And two of them are special. Two of them are special because they have some particles in them. And one of them, I've put $n - 1$ particles, and the other, I put one particle. And all the other states are 0's.

So one way to think about defining such states is, I'm just picking two boxes out of all these boxes. So imagine again the grid square here are all the possible boxes. And I just have to pick two. I just have to pick two.

So the combinatorial expression r choose 2 does that for me. I'm picking two. All the rest are 0. So that's sort of funny. You think about have to write all these 0's down. Forget about writing all these 0's down. Just choose two that have some particles in them.

And, by the way, r choose 2 times 2 is r pick 2, right? So that's the difference between a pick distribution and a choose distribution. But anyway, so let's say I have three boxes of particles in them. Well, I didn't even draw that case, right? Then it's R choose 3. You choose 3 boxes that have particles, and all the rest you forget about.

And in general, a choose b , which is the same thing as-- sometimes it's written this way, a choose b , it's a factorial over b factorial a minus b factorial. So anyway, if this is unfamiliar to you, the wiki entry is a good place to start if you haven't seen this before. I hope that helps.