RAFAEL JARAMILLO: Right. So what we're going to do today is we're going to finish our coverage of statistical thermodynamics, and then we're going to do a couple lectures, starting Monday. Friday's a holiday. So we'll do a couple lectures, starting Monday on reacting systems, and that includes oxidation processes.

And that's mainly to have chapter 11, and then that'll be it. Then we're going to have one more hour on social and personal, then we're going to have a game show, which I don't know how to run over Zoom. We're going to try it. And then the last exam, which is noncumulative.

So let's pick up where we left off, max entropy and the Boltzmann distribution. And this is continued, continued from the last lecture. So I don't like to do this, where I continue a derivation of something across two lectures, but that's how I broke.

So from last time, just at a high level, we decided that we wanted to optimize entropy for an isolated system. And we had Boltzmann entropy formula, so we could do some math. And we could write down the S equals 0 subject to constraints. And the constraints being conservation of energy and conservation of mass.

And we're going to do this using the method of Lagrange multipliers. And we had two of them because we had two constraints, alpha and beta. And we ended up with an expression like this, some stuff, so coefficient, independent variables. And in order to get our max entropy condition, I should say optimize entropy, we have to set these coefficients to zero. So it was a very familiar thermodynamic thing that we did, and what? We determined the first multiplier by normalization.

So this is where we left off. Where we left off was the following. We had ni over n total. So this is a distribution function of fractional distributions of particles in state I normalized by the total number of particles. And it was like this, this multiplayer beta as yet undetermined, energy of state I normalized by Boltzmann's constant. And that whole thing normalized by Q, which was the partition function. And this was the sum of all possible states e to the beta epsilon i over Boltzmann's constant. And so this is where we left things.

So now what we're going to do is we're going to determine beta. We're going to determine beta by considering a microscopic, reversible process where some of the particles change their shape. So we're going to do this. We're going to analyze ds for a process of some state changes. And I'm going to just go ahead and write down the equations that we've been using and developing for this. ds equals log n of i over n total. dn of i, you can pull that from the last two lectures. But now we actually have an expression for this distribution, so we're going to use that expression, kb sum over i.

The distribution is e to the beta epsilon i over Boltzmann constant over Q, then we have some logs of exponentials and things. So we can simplify this a little bit. And this equals minus beta sum over i epsilon i dn of i plus k beta log of Q sum over i dn of i. And taking our definitions, this equals minus beta du plus kb log of Q dn total.

So first thing to note, this is zero by construction. This is the Lagrange multiplier working, because we wanted ds to be 0 under conditions where du was 0 and dn total were 0. And we see that for this distribution, it works out. So Lagrange multiplier worked. The method worked. So I'm going to say 0 by construction. I really like this orange pen, but life is too short for fading sharpies.

So by construction, this is zero. If you'd like, you can convince yourself that if you have a different distribution function here, if you have a different distribution function, not this distribution, let's say a flat distribution function, a distribution function that doesn't depend on energy or has some other functional dependence of energy, I don't know what polynomials, you can put anything in there, you can show that that in that case, ds will not be 0. So again, Lagrange multiplier method works.

But here's the takeaway. We want to compare this to what we have derived two months ago from the combined statement, which is that ds equals 1 over t du plus p over t dv minus mu over t dn. And this is really the important thing here. We are comparing the coefficients. We're comparing the coefficients. And if you remember, this is almost like general strategy stuff. If you compare coefficients, you can buy inspection, set like coefficients to like.

So what is ds, du at fixed volume and fixed particle number? Well, from our statistical method, that's minus beta, but from the classical method, that's 1 over temperature. And so we can simply conclude that beta equals minus 1 over temperature. So now with that identified, we have the Boltzmann distribution. Oh, there's more paper. So with beta equals minus 1 over temperature, we have the Boltzmann distribution.

Number of particles in state I normalized by the total number of particles equals e to the minus Ei over kbT normalized by the partition function, where the partition function equals the sum over all states e to the minus Ei over kbT. And this generally has a falling exponential form with state energy. So state e of i, occupation n of i, all right, so falling exponential function.

In words, this is the distribution that maximizes entropy for an isolated system with n total particles distributed over states with fixed energy levels, so unchanging energy levels, according to that set of occupation numbers. And what is the state of maximum entropy for an isolated system? We have a name for that. What's the state of max entropy for an isolated system? Think way back to late February even.

STUDENT: Maybe equilibrium?

RAFAEL JARAMILLO: Yeah, equilibrium. So this is an equilibrium distribution. So we have an equilibrium distribution of single-particle energy levels, or single-particle energies. And again, you knew this already, but equilibrium does not mean everything is at the lowest energy. All semester, we've been exploring that consequence.

So if you were at zero Kelvin, if you're at zero Kelvin, or you're a physicist, which means you have a frigid heart, you're zero Kelvin, this is your distribution function. Everything's piled up, has zero energy. But in any real temperature, you get energetic particles, and you get them with a distribution function.

So a couple of observations here. The first observation is maximum distribution-- sorry, said maximum-- Boltzmann distribution and likelihood. Again likelihood, this is a stealth class on statistics. That's what statistical thermodynamics is. It's like a stealth class on statistics. So we'll ask, how much less likely is it to find a particle in state with energy, let's say, Em-- that's an ugly epsilon-- equals El plus delta e then in state with energy El?

So that's a typical thing that you might need to analyze. So let's see. nm over nl, that's how you turn the word problem into a math problem. How much less likely is it to find this distribution and this distribution? Within the equilibrium distribution, how much smaller is this number than this number? And you'll find the partition functions cancel out, and you get the following, El plus delta e over kt over e to the minus el ovet kT.

And so the e to the minus Els cancel, and you get e to the minus delta e over kT. Right. So this depends on delta epsilon over kT, clearly. It becomes less likely with increasing energy splitting delta e, and it becomes more likely with temperature. All right. So you're going to explore this a little bit on the p set and the context of semiconductors.

Another point, the thermal energy. This quantity is really important. It shows up in the natural sciences over and over and over again. And we're starting to see why. The why is what we've just shown, but the implications are really broad. You're going to see this all over the place. So let's remind ourselves what Boltzmann constant is. It's R over Na-- oh, that's funny-- RNa. So it's ideal gas constant divided by Avogadro's number. We have that from before. And this is something-- let's see, 1.380e to the minus 23 joules per Kelvin. So it has units of entropy. But that's not a number that I remember. Here's the number I do remember.

And if you work on the molecular systems, or semiconductor systems, pretty much-- well, gee, a lot of systems that we work on in DMSE. This is a useful number to have memorized, Boltzmann's constant and units of eV per coulomb, 8.617e-5. Why on earth would you memorize that? It sets the energy scale for likely fluctuations.

And we have-- all these words have meaning, likely fluctuations. Those words carry a lot of weight. So fluctuation, single-particle fluctuations with energy on the order of KbT are they're likely. That's something you're going to find, naturally occurring, as opposed to fluctuations, which are much, much larger than the thermal energy. Those are unlikely.

We have all sorts of language for this that comes up in all sorts of contexts. For example, these fluctuations might be called thermally activated processes. You need a little bit of thermal energy to activate it. All right. So not only is this a number you should know, but the thermal energy at room temperature is a number you should know.

A 298 Kelvin KbT equals-- well, in joules, it's not a number that I know because it's kind of unwieldy, but in eV, it is a number I know. So that's the natural energy scale of molecular processes. So it's 0.0257 electron volts, or 25.7 millielectron volts. So approximately 25 millielectron volts is the thermal energy at room temperature.

So if you have a molecular system or an atomic system or an electronic system, processes with that energy are likely to be happening spontaneously at ambient temperature. Processes with much, much higher energy are not likely to be happening spontaneously at ambient temperature. So you can see how powerful this is. For example, it's the foundation for the Arrhenius rate equation.

The Arrhenius rate equation-- and I'm going to use the notation from a chemistry class here-- a rate k equals a pre factor times e to the minus activation energy divided by Boltzmann's constant times temperature. All right. Now, this is a rate. This is an activation energy, rate and activation energy. And we are going to say hello to 3091 here. Actually may have seen that there. So that's another context, where you're going to see these exponentials, say why, where. Where does that come from? It comes from this Boltzmann distribution that we just derived.

More. Let's talk about-- and for one slide on this, a little dense, but this is to help you with later Let's talk about the Maxwell-Boltzmann distribution. And I posted the wiki entry for this on website. So it's a good article to read, and I think that the lab instructors refer to it as well. So we're going to consider particles with kinetic energy. Kinetic energy is momentum vector modulus squared divided by 2 times a mass. That's kinetic energy of a particle of mass.

And we're in three space, so this is px squared plus py squared plus pz squared divided by 2n. So that's the energy per particle and state of momentum p. So what we want to do is we want to figure out the distribution of particles as a function of energy. So this distribution in energy, I use f of v for consistency with Wikipedia.

It depends on both the Maxwell-- sorry-- the Boltzmann distribution-- I had an error in my notes there-- the Boston distribution n of 1 over n total equals Q to the minus 1 exponent. And it's going to be minus momentum of state I modulus squared over 2 MkT. So it depends on that, the Boltzmann distribution, and also it depends on the density of states in momentum.

This concept of density of states is not something that we've covered in this class. If you are in 029, you've discussed this. You're going to see it in the lab, but this really is a preview of what comes in the fall when density of states becomes kind of-- will be second nature for you in the context of quantum mechanics. But density of states means, well, this is the Boltzmann distribution for a given state I with this energy. How many such states are there? How many such states are there?

So 3d differential, 4 equals 4 pi p quantity squared dp. We get the 4 pi there because they integrated the spherical coordinates, 4 pi radians all around the sphere. And that equals 4 pi m root 2 mE dE. So this is a distribution of states in energy E. And you combine these two things, you combine the density of states and the Boltzmann distribution, and you get the Maxwell-Boltzmann distribution, distribution of energetic particles zipping around on the kinetic energy included as a function of energy. And it is 2 E over pi, 1 over kT to the 3/2, e to the minus e over kT.

So this is the Maxwell-Boltzmann distribution. And if you plot for example particle speed over probability, here's a low temperature, you have something that's pretty sharply spiked here, intermediate temperature, and then an high temperature. This is a series of increasing temp.

And so this has the feature that-- there are more particles that go faster at higher temperature. You can see that coming from this exponential. And there's also a vanishingly small number of particles at zero speed. And there's going to be some mean speed that characterizes the distribution. And that mean moves with temperature. So I haven't derived this in detail because we haven't spent time on density of states, but we're just exploring implications of that Boltzmann distribution. There's another implication.

The last thing I want to cover with only a couple of slides to go is the concept of ensembles, which is really just 3030 readiness. We're doing this just to show you that some concepts, which you're not going to use in this class, but you will use in kinetics and microstructure in the fall. So before we move on to discuss ensembles, I want to pause and take questions on the Boltzmann distribution, or Maxwell-Boltzmann or anything else, Arrhenius or anything else related.

Who is seeing the Boltzmann distribution or this-- who's seen the Arrhenius rate law? There's not a lot of participation on Zoom, so I understand that. I'm guessing that a large number of people raised their hands. And then if I ask you about the Boltzmann distribution, there'd be a small number. And if I ask you about the Maxwell-Boltzmann distribution, they'd probably be an even smaller number. But I bet that everyone's seen something of this form somewhere before. So I hope it's a little bit satisfying for you to see where it comes from and to understand the principles behind it, maximum entropy.

So let's talk about ensembles. Ensembles are-- what? I looked at the different definition of the Cambridge dictionary, says-- a group of things or people acting together or taken as a whole. So this is a concept, and we're going to use it a lot in statistical thermodynamics, if not necessarily in this class. But like, I said this is 3030 readiness here. If I didn't tell you about this, I've got in trouble with Professor Hu. All right.

So we're going to start with the microcanonical ensemble. And this is something that you've seen before, microcanonical-- something called the microcanonical ensemble. This is the set of all possible microstates. So this type of stuff that we've been doing, set of all possible microstates of a system with fixed energy, volume, and particle number. So a system with fixed energy, volume, and particle number, that is that's an isolated system.

For an isolated system equilibrium is state of max entropy. That's what we were just analyzing. All right. So this thing, which we've been doing for the last 2 and 1/2 lectures, this is called the microcanonical ensemble. Just gave a name to it. And so the partition function that we've been analyzing is actually better known as the microcanonical partition function, normally written as Q, as we've been doing. And it is a sum over single-particle energy states sum over all possible single-particle state.

And we know that we're at equilibrium with S maximize for what? For the Boltzmann distribution. So the probability of finding particle in state I equals caused number of particles in state I at that distribution over the total number of particles equals e to the minus el-- you are getting sick of seeing me write this by now all right-- prob of finding a single particle in state I with energy hereby.

So this is a repeat of everything we just did. I just gave it a new name. I called it microcanonical. So again, that name is kind of highfalutin, but there you have it. But we can generalize. So now I'm going to tell you about a different type of ensemble. So we've been analyzing microcanonical. Now, I'm simply going to tell you about the existence of a canonical ensemble. And please, don't ask me where these names come from.

A canonical ensemble is the set of all possible microstates of a system with fixed volume and n but not energy. So now we're allowing the system to exchange energy. The system is closed. It's rigid and closed. So volume and mass are conserved. System is rigid and closed but can exchange energy and form of heat with surroundings. And the system energy, which we're now going to give a label to, u sub nu, the system energy can fluctuate.

So I want to draw for you a representation of the micro of the canonical ensemble. So we're going to imagine-- I grab a fine tip marker-- we're going to imagine system labeled I with energy u sub I, but this thing is in thermal contact with a lot of other systems. So we're going to imagine a whole population, or, if you like, an ensemble of systems all with fixed volume and fixed particle number but with diathermal walls.

So if heat is like sound, you have to imagine this is an apartment building that's really noisy. Here are all your neighbors. So the volume is fixed and the particle number is fixed, but you're exchanging energy through the walls. But this ensemble as a whole-- so I've drawn an ensemble. I've drawn a set or a group considered as a whole. I've drawn a bunch of subsystems now that can exchange energy with each other. Each have the same volume. Well, that's how I've drawn it, but you can imagine they each have the same volume, each have the same particle number, but the ensemble as a whole is isolated.

So all of these ensembles, you have to imagine this being a very, very large number here, not just 4 by 6 or whatever I've drawn, is isolated. And so this is an ensemble, and this is an ensemble that has its own partition function. It's known as the canonical partition function. And that's typically written a z, and this is now sum-- as before-- sum over states. But we're not summing over single-particle states. We're summing over system energy states, sum over all possible states of the system. So it's distinct from before when we were coming over single-particle states and equilibrium Hold on.

When we had equilibrium in an isolated system, it was max entropy. Now, think back two months ago. When we had equilibrium for fixed temperature and fixed pressure, that was minimum Gibbs, but there was another case, which we haven't spent a lot of time on. It was equilibrium at fixed volume and fixed temperature. Do you remember what thermodynamic potential we use when we have a system at fixed volume and fixed temperature?

STUDENT: Is it Helmholtz?

RAFAEL JARAMILLO: Helmholtz. Equilibrium at minimum F, again, we haven't used that, this course basically, is minimized for the distribution probability of finding system and state nu equals e to the minus u nu over kT over Z. So has the same functional form as the bottom distribution except, instead of single-particle energies is energy of the system as a whole, and instead of maximizing entropy, it minimizes how much free energy.

So there's something very similar That's happening here, similar to when we started with entropy, and then we move to Helmholtz energy, and then we moved to Gibbs energy as we change the boundary conditions of the system. And I think you'll remember in problem set 2, we really delve into this. So there's something very similar that happens in statistical thermodynamics, where you start with the microcanonical ensemble and its partition function, and then you go to the canonical ensemble and it's partition function, and there's more. There are other ensembles.

The next one is called the grand canonical ensemble, and that corresponds to situations with fixed pressure and temperature. We're not going to bother to introduce that. So this is the Boltzmann distribution, but is for the canonical ensemble now.

STUDENT: So in this case, what was it that you held constant?

RAFAEL JARAMILLO: So this is equilibrium at fixed temperature. When you have an ensemble of systems that can't exchange volume and they can't exchange particle number, but they can exchange heat energy, they reach equilibrium when the temperature becomes constant. That's thermal equilibrium. So that's what we've done here. We've set up a system, a collection and ensemble of subsystems, that reach thermal equilibrium with each other because they can exchange heat energy.

It all works out. You end up getting minimum F for this distribution. This is the probability of finding system in state nu with energy u of nu. That's what that probability is. So I want to leave you with some final words on partition functions. We've seen some partition functions, Q and Z. And there are others, which we won't cover in this class. We haven't really covered this. This won't be on the exam. This is just commenting on what comes next. Again, this is in service to later classes in our curriculum.

So the partition functions, they describe equilibrium and fluctuations. The partition functions really describe the entire thermodynamic properties of a system. So for instance, they are the basis for calculating thermodynamic properties and expectation values. That is, most likely quantity. So for example, the mean energy of a system can be shown to be this derivative, d log z, d 1 over kT.

That's a little bit formal, can't necessarily calculate anything yet, but in principle, if you know the partition function, you can calculate the mean energy. heat capacity of a system is 1 over kT squared d squared log z d 1 over kT squared. The entropy of a system can be shown to be mean energy divided by temperature plus kb log z. The Helmholtry energy of a system is minus KbT log z. And it's not just equilibrium properties, it's properties of fluctuations.

So this gets really fun in a later class and has a lot of implications. So for example, the root mean squared energy fluctuation of a system is another quantity that can be calculated from partition functions. So I'm just showing you things, but if you have the partition function for a system, you can calculate the entire thermodynamic properties of that system.

So another example is in the textbook. If you look into Hoff, they calculate the partition function for a couple of different systems, a two-level system and then a system of a monatomic gas. And then by applying formula such as these, they derive the ideal gas law. So it's the ideal gas law from first principles. It's no longer empirical. So I'm going to leave you with some thoughts.

At this point, often students say, ah, this is the real stuff. This is somehow the most fundamental knowledge of thermodynamics, is a partition functions. So why did we mess around with all that classical thermodynamics? If the partition functions are the keys to the kingdom, why not just start there? And the answer is that, although this approach is beautiful and elegant and very powerful in instances, it also is extremely limited because we don't know and we can't calculate the partition functions for all but the most toy problems.

And you can see that. If we take thermodynamics in a physics department, you start from this approach. You start from the statistical thermodynamics approach because physicists love to write problems, things as intellectually rich but may or may not apply to the real world. We're a little bit more applied. So I'll give you an example. There's a toy model of magnetism known as the Ising model. And the Ising model says that you can have spins on a lattice, or magnetic moments, I should say, on a lattice, and they can face up or down. That's it.

So you have a one-dimensional chain, and each spin can face up or down. And the energy of a system depends on the orientation of the nearest neighbor. It's a very simple model of a magnet. And so if you take a course on magnetism, or you take a thermodynamics course in physics department, you'll probably calculate the partition function for 1D Ising chain. It's not that hard. It's kind of fun.

However, if we simply make it a two-dimensional Ising system-- and I'm drawing the direction of the arrows at random here, just showing you. All right. So we've just made this from one dimensional, which is definitely an imaginary thing, to a two dimensional, which is still imaginary, but we're getting there. We're at least getting close to real space. Calculating the partition function for this model is one of the grand intellectual achievements of 20th century physics and, it won Lars Unger a Nobel Prize.

It's horrendously complicated mathematically. I've never been able to follow even the first page of that. It's not in any textbooks. It's too long. So let's say I want to model a real magnet in three dimensions. Forget it. Unless you're Nobel Prize quality, that's an open problem you have at it. But basically, the point is that for real systems that we care about as engineers, this is a magical construct. In theory, this exists.

In theory, it allows you to calculate all the properties of the system from first principles, but in practice, it just remains an intellectual exercise. In practice, we have to-- if you go with a much more powerful route, which is the route of classical thermodynamics with its postulates and observations and data and models.