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GIAN PAOLO BERETTA: So good morning again. Lecture number 8. Today, we finally get to the macroscopic world and models. But let me just remind you what we've done-- the last topic.

We've seen the LeChatelier-Braun principle as a consequence of some interesting relations that emerge from the fact that stability conditions involve quadratic forms of some of the fundamental-of-- where the matrix is second derivatives of the fundamental relation or of some other characteristic function, like the Gibbs free energy or the Helmholtz free energy. And as a result of the mathematics of putting a quadratic form in canonical form, we obtain these inequalities that we have also interpreted in the sense of a theorem, because after all, this is a theorem.

We could call it LeChatelier-Braun theorem that has two assertions-- namely, the fact that the system responds to-- when you move it away from where it is comfortable-- so when it is mutual equilibrium, for example, with a reservoir. And we have seen that there are different types of reservoirs with which the system can be in mutual equilibrium. So the same idea apply for mutual equilibrium with all those kinds of reservoirs.

But the idea is that the system, if you do something to it from outside-- for example, put in energy, or put in particles, or change the volume, the system reacts trying to go back to where it was comfortable. That's the first assertion. So if you put in energy, it will increase its temperature so that it increases its willingness to give away energy and return to equilibrium with the reservoir.

But the second assertion, which is a consequence of this additional math from the canonical form of the quadratic forms, is that it depends-- the reaction of the system depends on which direction you take it away from equilibrium, and in particular, if you break conditions for mutual equilibrium.

So for example, if you have a-- if the system can exchange volume-- like in the example of the air springs, the system can exchange volume. And suppose that it is in mutual equilibrium also with the thermal reservoir, so at the same temperature.

So there are two conditions for mutual equilibrium-- equality of pressure and equality of temperature. If you change the volume while breaking both conditions, the system will react stronger than if you just break one condition. And that's the idea. And the difference is important. For example, in the case of the air spring, the difference in the-- you get the reaction makes this volume act as a standard spring. But the spring constant depends on how many conditions for mutual equilibrium you've broken while changing that volume.

And the change may be of the order of-- I mean, it's 40% if you do it slowly so that the system has the time to remain in the same temperature. So by exchanging energy with the reservoir, it remains in mutual equilibrium. Then you get a milder reaction than if you do it fast. And if you do it fast, you change both the pressure and the temperature. And so the system wants to-- has two reasons to go back to equilibrium.

So now we're finally to the question-- well, what's the difference between microscopic systems and macroscopic systems? What do we gain if we make some additional assumptions? It will involve having many particles.

So let me start with a few pictures, but also even a more simple idea, because there are several ways in which we can see the effect of what happens when we have few particles. For example, consider a single particle, and consider the most basic description, which is one-- the quantum mechanics description.

In quantum mechanics, you have that the particle at-- the position of the particle is described by a probability density function, which tells you that-- so it tells you what is the probability to find, for example, the particle when you make a position experiment in this small interval between x and x plus dx. And in fact, according to quantum mechanics, all you can predict is the probability. You cannot predict where the particle will show up in the next time you call for, where are you?

So essentially, the state in quantum mechanics is the probability distribution, or the set of probability distributions that allow you to describe all these measurement acts, but in a statistical sense.

You see, the important thing that I want to emphasize today, that is important for our discussion today, is the fact that you find-- in order to solve, in quantum mechanics, this problem, you write the Hamiltonian of your particle, or system, or particles. And you have to solve an eigenvalue problem to find the eigenfunctions of that Hamiltonian. And you have to face the boundary conditions.

So the walls of your system, the things that we call external forces, are represented by an infinite potential here on both sides, which forces the functions to go to 0 at the wall.

Then, of course, if you solve that eigenvalue problem, you find functions that-- you can look it up in any Wikipedia page. There is the various solutions and various eigenfunctions. And then when the system is in a stable equilibrium state, the overall probability is a mixture of those eigenfunctions.

For example, here, I took a paper in which there is not one particle, but four particles confined in a box like that and at very low temperature. Now, very low temperature-- that mixture of eigenfunctions makes the lower eigenvalue ones prevail. And you see here that-- so these are the distribution of probability to find the particles for various cases, going from a boson-- black line-- to a fermion, to things in between.

The common feature that is important to us is that at the wall, those go to 0. So there is a-- that means-- I would call it the rarefaction effect. You can think of it as a gas, a probability gas, but it's rarefied at the walls.

Here is another paper-- the review written by Professor Hadjiconstantinou, who is the mentor of this class. And in another realm-- this is not quantum mechanics. It's molecular dynamics-- the molecular fluid mechanics. So there is a solid wall probably made of carbon. And what happens is that the particles-- the interaction of the particles due to Van der Waals forces-- so this is repulsive and attractive forces, like Lennard-Jones.

And we will talk again about this, but for the moment, I presume that you have some ideas about that. Due to these forces, and due to the fact that the wall is a fixed layer, and it imposes-- forces that do not move, whereas on the side of the bulk of the fluid, the particles move. And so there is more random action of forces.

The ordering imposed by the wall implies an ordering-- a layering of particles at various distances. There is a first preferred distance, and then there is a second, third, and so on fading out as the randomness become more important away from the wall. So this is also a sort of wall. I would still call it the rarefaction effect because, yeah, in-- very close to between the first layer and the wall, there is nothing. The particles don't like to stay there.

These in fluid mechanics is important because it is related to the problem of the no-slip condition. If you are a fluid mechanicist, when you have few particles, you have to deal with this problem. And this is another example. Again, watching the density distributions of a gas.

Now, here, it's not few particles. It's, like, 10 to the 5th atoms. It's not very few. Still in these cases, you see density-- wall effects with a rarefaction very near the wall. And then there are peaks where the particles like to stay near the wall more than in the bulk.

Now, 10 to the 5th is not small, but it's not large. Why is this important? And so let's start with-- Suppose I have two particles like this. So I have the wall, but on the other side, I have a specular situation in which I have another particle in the same stable equilibrium state.

This is the meaning of this part of the figure. Think of just one particle on one side and one particle on the other side. That's OK. Now, suppose I find a way to make that wall that separates the two particles disappear.

So the moment it disappears, particles don't know yet. We just removed it. They're still there. Let's say, oh, hey, there's more room available. There is more volume we can fill.

So there will be a spontaneous process, whereby the particles will fill that volume. And eventually, we'll reach a new stable equilibrium state-- let's say something like that. If we look at it with the help of the E versus S diagram, which is very useful here-- I have drawn the E versus S-- the stable equilibrium state curves-- fundamental relation of the two systems that we have considered.

One is the system in which there is a partition that divides it into two. The other is the system without the partition. And that system without the partition, for that one, we are considering two states. The state we started with. When we just removed the partition, it's a non-equilibrium state, so much that we know that we'll evolve towards the stable equilibrium state.

So this point here represents for the system with the-- partition system as the initial stable equilibrium state. But it also represents the state of the system without partition, and it's the non-equilibrium state for that system. So here, we call system A the one without the partition. And system 2 lambda-- I mean, lambda plus lambda, so it's 2 lambda-- the system with the partitions.

The reason I draw them on this same spot, meaning that they have the same energy and entropy is a consequence of the idea that I have found a way to remove a partition without perturbing the system, without putting energy in, without any external exchange in no time so that, essentially, I don't change any of the properties. Ideally, you could do it. And the fact that I have put this state to the left of the final stable equilibrium state is that-- yeah, intuitively, we know that the particles will evolve by filling the entire space.

So that's the direction in which the system will evolve, not vice versa. If I put this state on the other side, it would mean that the system would separate spontaneously, which doesn't happen.

So the first consequence of this is that the entropy of the stable equilibrium state of the two particles that have the same initial energy because this system is-- it all happened in an isolated system. The entropy of the final stable equilibrium state is greater than the initial entropy of this state or also of this non-equilibrium state.

That is by the principle of entropy nondecrease. A spontaneous process goes only in the direction of increasing entropy for an isolated system. So what is that changes when you have many particles? Somehow, I have already used this idea here.

When you have many particles-- because here, I go from 1 to 2 particles-- the slope of this probability distribution at the wall becomes steeper. So in other words, the more particles you have, the smaller is the rarefaction layer next to the wall.

And as a result, you see here-- you see the difference with-- let me highlight where the differences are between the probability distributions of the two stable equilibrium states.

Here, they're remarkable. But as this distribution becomes sharp-- so eventually, you have an almost flat distribution in the bulk of your system and a sharp, very thin area-- we call it boundary layer, or wall layer, or rarefraction layer. So even at the center, this region is very small. That means that the two stable equilibrium state curves get closer to one another.

And in the limit of many particles, you can neglect this difference. So you can neglect this fact. You can approximate the properties of a system with the partitions with the properties of the system without the partition. Or if you are interested, you can model the system without the partitions as if it had the partitions.

This is very important. We will return to this when we go through the continuum hypothesis. It is very important for example in fluid mechanics-- because you have a big box, or boundary for whatever flow you are considering. And we want to work in terms of fluid elements, fluid parcels that are small.

Small enough with respect to the big system, but not small enough to have this kind of effects. Meaning you have enough particles inside here so that you can consider it--

consider the continuum hypothesis valid. We will return to the continuum hypothesis. But--

What I'm interested now in saying is that when I consider, my fluid element here, I am going to apply models, like the local equilibrium model. And we will assign to this-- the properties of a system in which the particles are closed by physical walls.

So we approximate this fluid element as if locally it has the properties of a fluid element that is separated from the rest by physical walls. How do you do that? Well, I insert a partition-- three-dimensional-- make this small three-dimensional box. Take this system outside. Study how it behaves when it has some temperature, some pressure, some energy, and so on.

And then I assign-- I say, well, the properties of this are the same as that, forgetting about the walls' effect. But this idea of physically inserting or removing partitions and the fact that it doesn't change the properties of your system is fundamental in our description of continua at the macroscopic level.

But in principle, we should know that if you-- in that fluid parcel, or fluid element, you have too few particles, then you may be in trouble playing this game. And so your assumption that you usually make, which involves local equilibrium and the continuum hypothesis, also should take care about the many particles hypothesis.

So let's see what we gain in the limit of many particles. Then we'll go back toward computing this effect we got within partitions. Let's see what we gain.

So here is a more schematic idea. So suppose we have our system A is this one, where we have whatever particles, a given volume. Volume here is important because, of course, it has to be-- we have to be able to partition the system.

Also, you see, when we are in this limit, since the rarefaction effects become unimportant to the boundary, essentially, the geometry of your container loses importance.

For example, here, where in this-- this picture here shows very well the geometry of your container does play a big role. So if you go to this paper, there are other geometries that are shown in nice pictures. You see that the way particles are layered out, they form layers near the walls depends, of course, on the shape of the container.

And therefore, the properties of stable equilibrium depend on the shape. But in the limit in which those wall effects become unimportant, only the overall volume of the container, not the details are important. Because in the bulk, the probability distribution becomes uniform. So it's uniform everywhere.

So here, suppose we have our system, and suppose we partition it into lambda partitions. Here, we call it lambda. Later, we'll call it n. So that means that on this side, this is a composite system.

It's still in a stable equilibrium state. Each one is in a stable equilibrium state. Like the system we started on here on the blackboard. And we assume that we have partitioned it in such a way that not only the volume, but also number of particles is exactly 1 over lambda. The volume is 1 over lambda of the overall, and the energy of 1 over lambda.

So now, remember what the fundamental relation means. For example, here, fundamental relation means that it gives us the properties of all the stable equilibrium states as a function of energy, volume, and the amounts. So it is valid.

It is a function-- the same functional form-- maybe E squared, E cubed, log of n, things like that. It's the same function for all values E, V, and n. I can compute it also for E, but also for E over lambda. The same function, if it is the same mixture of substances, for example.

For a lot of energy or small energy, large volume, small volume, many particles, few particles. As long as this few doesn't get too few, it's OK. I mean, it's OK what we are going to say. So at this stage, it's OK in general.

But what we said here is that these curves-- this is the partition curve. It's the summation-- it's this side, so it's this much for each subsystem. So if you have lambda of those, you multiply it by lambda, so lambda times S, because S is an additive property. The entropy of the overall is the sum of the entropies of the parts.

And so this composite system has an entropy lambda S. And this S sub lambda. Whereas system A has an entropy S sub A. In general, this has bigger entropy than that. But in the limit of many particles, this difference becomes unimportant. And so we can approximate that the two are equal.

That's what we call the "simple system model." You don't find it around with this name except in our book. Perhaps the choice of the name wasn't so fortunate, but it expresses what you find under the title of "thermodynamic limit." In physics, that's how it's called-- this idea.

Indeed, it is a limit because now look what we're going to do. Here, we choose a finite value for lambda. So we partition the system in a finite number of partitions. And it has to be finite in order for the number of particles inside each to become not too small.

Yet if lambda can be large enough for practical purposes--

You have many particles-- 10 to the 23-- that means that lambda could be, say, a million. And still, in each partition, you have 10 to the what, 17? So that means still a lot of particles.

So from the practical point of view, when you have so many particles, you can think that this lambda can be any number. Oh, yes, could be integer, but I mean, who cares? Between the integers, there are the reals, so let's just make it real. So you make this mathematical assumption. Essentially, take this formula here and make it valid-- make it as valid for any lambda, integer or real decimal.

So you formally assume that the fundamental relation has this property. And this property for a function in mathematics, is called the homogeneity of first degree. The fundamental relation is the homogeneous function of first degree in all of its independent variables.

Divide each one by the same lambda, then multiply the result by lambda. You get the value of the function for the original values of the independent properties. And this is an important assumption, of course. It's a heavy assumption which has this physics to support it.

And when you do it, we gain one relation-- We're going to prove it in a moment-- which is called the Euler relation And notice also-- I changed the letter for energy from E to U. And we're also going to call it internal energy for distinction.

So as soon as we say internal energy, we say, aha, we are within the simple system model approximation. So how do we prove that relation? Well, it's simple. One way is-since this has to be true for all lambdas. Take the partial derivative of this with respect to lambda.

Now, is it-- yeah, OK. I think there is something fishy in this-- there's something fishy in this viewgraph-- something missing. Sorry about that. So when you take the partial derivative with respect to lambda of this thing, you get U because of this lambda here.

And then you have to take-- you have lambda that multiplies the derivative of U with respect to S times the derivative of this with respect to lambda. So it's minus 1 over lambda squared and so on. So yeah, this is wrong viewgraph. Sorry. I'll correct it.

And then in the end of this derivative, you take lambda equals to 1, and here comes this relation. It's better done in the book than in this viewgraph. Sorry.

And what is another consequence of these derivatives? These are OK now. The main consequence of the Euler relation is that we can define-- it makes sense to define specific properties. For example, I have the energy. I'm not going to call it E. I'll call it U. And suppose I have n particles. Then n is the sum of all the particles that are present of different type. Those are the amounts.

So this I am going to call it specific molar energy. I do the same for the entropy, for the volume and for the amounts. Well, the amount of substance i divided by n is yi, the mole fraction of that constituent.

So now, I'm going to express. I want to see how the specific molar energy that is-- that represents how much energy I have per unit number of particles. Instead of n, I put at the denominator the m, the mass. That would be the specific energy per unit mass, the amount of energy I have per kilogram of substance.

So from the definition, U is a function of S, V, and n. But S can be written here as small s, specific entropy times the amount, n times s. Also the volume can be written as n times lowercase v, and the amounts can be written as n times the mole fractions.

So if I look at this expression here, I see that the specific energy does depend on the specific entropy, specific volume, the mole fraction, but it also depends on n because n appears in several places here. So that means, for example, if I have one kilogram, a given amount of substance, that has a certain specific energy.

But if have 2 kilograms, the energy per kilogram may not be the same, if it depends on n. It's like here. I have-- If I have one particle, it has this probability distribution. If I have two particles, their properties will not scale down to the same probability distribution per unit particle.

So for small systems, this dependence on n is there, and it is represented by the fundamental relation. So you need to measure it. But for small systems, you have to measure-- it's not enough to measure the unit of a substance, like 1 kilogram.

When you measure the properties of water for the steam tables, you measure 1 kilogram, and you're done. Because when you have 2 kilograms, you just multiply by 2. That's good in the macroscopic limit. But when you have 200 molecules of water, it's not just twice the properties of 100 molecules. You have to see how those properties depend also on the amount.

But in the limit of many particles, that dependence vanishes. So this proof, which takes again the partial derivative of U with respect to n. So you want to see how much is it. Well, that dependence is equal to-- if you do the derivatives-- and let you do it-- it's minus 1 over n squared times-- you remember what was this?

You should add there it's the Euler characteristic function. That term in parentheses is what we called the Euler characteristic function. But here, what we say is that the way the specific energy of the system at stable equilibrium depends on the number of particles. It is measured by the Euler characteristic function.

But in the limit as n goes to infinity-- so that's the simple system-- it goes to 0, because the Euler relation just says that this is equal to 0. That relation here, or what we call the Euler relation, is equivalent to saying Euler characteristic function equals 0.

So that's what we gain. We gain one more relation. And you know-- we have obtained already so many things from just watching the fundamental relation. Now we have another one. You can imagine that you can expect also a lot of additional information.

For example, one way which is now equivalent to the Euler relation is to take its differential and subtract from it the Gibbs relation, which is the differential of the fundamental relation. The result is called Gibbs-Duhem relation, and it is this one. It's a relation between-- in which you see the independent differentials are temperature, pressure, and the chemical potentials. So these are the properties that enter in the conditions for mutual equilibrium.

Once we have this idea, we can also proceed with defining another kind of interaction, which is the bulk flow interaction. Which uses this idea that now that I have a system of many particles, and I am within that model, I can consider a fluid element, and I can assign to it properties as if it were separated by physical walls.

Instead of doing it like a cube, I consider a sphere, but that's the same idea. So suppose that locally I have a fluid element, and it is in a stable equilibrium state. This little box, it contains enough particles so that the wall rarefaction effects are not important. This little box is in a stable equilibrium.

Now, if I look at that fluid element from a different frame of reference, for example one that moves, I look at it from the frame of reference that moves this way. It goes the other way. It acquires a velocity with respect to the new frame of reference.

And associated with that velocity is a kinetic energy. In addition, if I look at it from an accelerated reference frame that has the same acceleration as the gravity, g, then this applies also a potential energy. This is Mechanics.

So the idea is this. Now, in fluid mechanics we consider interactions in which particles cross the boundary between two systems, there is movement. If we choose as reference frame that of the boundary where the particles are crossing, then they have velocity.

But for each of these particles, I can always find the reference frame in which it is not moving. And even if it is in presence of a gravitational field, for each of these particles, you can find an accelerated frame where it is not moving. With respect to those frames there is no kinetic energy and no potential energy. So somehow, this kinetic energy and potential energy are effects that can be added or removed by just changing the reference frame.

Clearly, that doesn't change the internal properties of the stuff. It doesn't change the energy. Yes, it does change the energy, but it doesn't change the other properties like entropy. So this is the model that we make-- that we call bulk-flow state-- bulk-flow local-equilibrium state.

We assign to the fluid element, the properties of a local stable equilibrium. Or we assume that there is some reference frame with respect to which it is not moving and has no potential energy. We subtract, in a sense, the kinetic energy and the potential energy with respect to the laboratory reference frame, so that we get an energy which satisfies the fundamental relation of stable equilibrium.

In that sense, it has temperature. It has a pressure. It has all the slopes of the fundamental relation. So that's step one-- defines a local-equilibrium model. Step two is that if you have a boundary between two systems-- for example, you have a pipe that brings fluid elements inside your system-- well, usually, how do we-- this is an open system we call it in open system.

And we usually represent as a boundary-- a formal boundary-- we imagine-- in our mind-- there is a boundary between the pipe and the system, but this boundary isn't physical. Yet in order to model the interaction, we suppose it is physical. Suppose we can put a physical partition, which we are allowed because we are in the simple system model.

So let me put at time instant t-- let me put a partition that separates that amount of fluid that is going to cross this boundary in the next time interval delta t, or dt. So now it's here. Later, it's there. And it's physically separated by a partition. At no cost, I have put in that partition.

Then what happens? If I look from the fluid element, the fluid parcel that is crossing here, from a reference frame that moves with its velocity, I am assuming for simplicity here that there is a flat velocity profile, all the particles move with the same velocity. Or if not, you should make it for smaller parcels to also single out the velocity profile. But for simplicity, let's suppose we look at just one element.

And so that has its velocity. And we look at it from the reference frame from which you see it as not moving. This partition that you put in is a partition that separates two systems that are in mutual equilibrium. They have the same pressure and temperature.

In particular, the pressure is the same at partition. Even if it could move, it wouldn't move because all the fluids that are coming in the pipe here have the same pressure. But if you now make the energy balance-- and here is the details of making the energy balance for this composite system of-- the system which is receiving that amount of fluid plus this fluid that will eventually get in.

So now that we have separated it with a physical partition, this partition makes it a legitimate system. So the composite system, A plus B prime, is well-separated from the rest because it has a wall. And it's always satisfied our definition of system in which we get external forces with certain kind. So for these kind of systems, which are closed system now, we have already introduced the energy balance.

We can do the energy balance, which involves saying that the final energy minus the initial energy is equal to the energy exchanged via interactions. And here, there is only one interaction. It's the fact that there is a pressure acting on a moving piston-- moving boundary. And that is a work, but this is the work.

That means that now we play additivity. In the final state, we note that in system B prime, there is nothing left. The system B prime is now between this fixed boundary and the moving boundary.

If you want, we could say that-- to be more precise, I should say that at the initial time, at time t, in order for system B prime to be a system, I have to have introduced physical boundary here. Then I remove it. I let things go.

And in the end, I will put, again, a physical boundary here. But there is nothing between the two boundaries. So the energy and entropy there are 0. And again, in order to do the adding or removing partitions, I need to be within the simple system model.

So to make the long story shorter, here is the expression for the work. It's pressure times the area times the displacement. And you can show that it is proportional to the specific volume times the pressure times the amount of the fluid parcel that is being exchanged. And in the end of the story, you see that this work, which we usually call the pulsion work, adds a contribution to the energy that is brought into system A.

It's not only the internal energy of the fluid-- not only its kinetic energy and potential energy, but also this pulsion work. And that is why in a bulk-flow interaction, it's u, internal energy, plus pv, which, if we recall, it's called it corresponds to the definition of that characteristic function that we called enthalpy. That enters into the expression that says how much energy is transferred in this kind of interaction. Of course, you can do the same when the parcel is going from inside to outside.

And therefore, we get this summary of defining properties for the bulk flow interaction. It contributes mass to the system. And by the mass balance, you can write it this way. Energy gives the enthalpy and also entropy. The entropy is just the entropy that the fluid element simply translates from outside to inside-- translates. OK, in/out. You can also do this per unit time.

Therefore, now with these additional type of interaction, you can write balance equations for a system that is subject to all sorts of interactions. For example, here, we have heat at temperature Ta. Typically, we use the letter A or the letter 0 for the environmental conditions.

Here, we have a heat interaction at some other temperature-- maybe cold. This one at another temperature. We may have work interactions of various types, like a shaft bringing in mechanical energy, electrical wires bringing in electrical energy.

These are all work equivalent. Or a moving boundary against the pressure of the atmosphere, that is also a work interaction. And plus we may have many bulk-flow interactions. And as we have seen, in order to characterize a bulk flow interaction, we need to characterize the bulk-flow states of the fluid elements that are carried in and out.

So you need the enthalpy, the local enthalpy, the local entropy, the velocity of the fluid elements, and the local height in the gravitational field so that you can compute the potential energy.

Of course, subject to all these interactions, you're going to be-- it's not going to be easy to balance them so that you keep the energy the same, the entropy the same, the volume the same, the mass the same, which would be required to keep the system in a steady state.

But very often, that's exactly what you do. For example, this is a power plant, and you want to operate it in such a way that it doesn't consume itself. It simply processes stuff. So you need to balance what goes in with what goes out. And while you do that, definitely, most of the times, produce entropy by irreversibility.

These are the balance equations of mass. Rate of change of the mass is the net mass flow rates that go in and out. Here, to simplify the notation, I consider m dot with the arrow just in. So it's positive if it's in.

That means that if I want to represent something going out, I do need that negative. Or you could split the summation into two sums and put on one sum the masses that go in and minus the summation of the masses that go out.

So also this for the energy-- the rate of change of the energy is equal to the net amount of energy transferred by interactions. Here are the heats, works. Here are the bulk flows. And for the entropy-- the rate of change of the entropy of the system is-- first term here is the entropy exchanged either via the bulk flow interactions or via the heats.

And then, well, how about this sign? What do you think? That's an error! The entropy-- plus the entropy produced by irreversibility. That needs to be corrected.

I probably left it there to see if I'm awake enough and you are awake enough to spot it. So luckily we did. And once we have these balance equations, we can manipulate them, solve problems.

In a large community of engineers that have played with these equations, they developed this idea of exergy and exergy analysis of energy systems. It adds nothing to these equations except perhaps it helps in reading them.

It adds nothing because it simply-- it is based on a linear combination of these equations. So mathematically, all the information is contained in here. So this is it, basically. Definitely, we need to make an energy balance and an entropy balance. If you don't like working with entropy, and you prefer to work with a linear combination of energy and entropy, fine. Then you call it exergy balance.

And so one way to combine these equations is to take one of these forms that is still-- take the second equation, the entropy balance equation, multiply it by some temperature. And it is convenient to choose the temperature of one of your heat interactions. And it's even more convenient to choose the temperature of the heat interaction that is considered free of charge.

For example, if your machinery operates in an environment like air-- your air conditioning at home works in the air and dumps heat in the environment. I would use that temperature as the temperature that I use in this linear combination. If instead your power plant is cooled by the water of the river, I would use the temperature of the river.

In any case, you take that, multiply, and then subtract it from the energy balance. Yeah, see? Here also, you have to be a little-- I should have been a little more careful in making explicitly the work-- write separately the work related to the p times rate of change of volume. The pa times the rate of change of volume should have been singled out here.

Maybe I'll do it later on the slide-- just for the slides, when I correct also the minus sign here-- so that that work term can go on this side of the equation and make this pa times dV over dt. So here is an exergy balance equation. And the exergy is a topic that we need to discuss.

I will not make the story very long, but it's part of thermodynamics, so it is a good idea to discuss it-- also because it brings several useful ideas about how to define efficiencies of energy conversion devices. And so it is important in a mechanical engineering department.

We already have seen that combinations like that-- I think we use the letter capital Psi to represent this availability function-- E minus TRS sub plus PRV. So this says that's the rate of change of the availability. But exergy and availability are the same idea, same concept. There's two words for the same idea.

Heat times Carnot coefficient-- and the Carnot coefficient is between temperature of what I've chosen as my environment and the temperature at which the heat is exchanged.

This represents, for a given Carnot engine, the maximum work that you could extract by exploiting that heat interaction, having available an environment at temperatures T0. And so this is the exergy associated with that heat interaction at temperature Tk.

Work appears directly-- not multiplied, not corrected-- because work is already available to-- let's say if you have some work, you can do useful things directly. You don't have to convert. The work is already, in a sense, exergy, because the word "exergy" really means the essential part of the energy. So the useful fraction of the energy that-- it's either within your system or an energy transferred.

So the concept applies both for the additive properties of the system, like energy is, or the modes of energy transfer-- heat, work, and here is also the exergy expression for the bulk-flow interactions. And out of this-- do the proper sign here-- you get a minus-- and here's correct-- minus T0 times S dot irreversible.

This is the dissipation, the terms that represents the destruction of exergy. And like entropy cannot be destroyed, exergy cannot be created. You can only destroy it.

So they are related, so irreversibility. If you do things reversibly, you don't create entropy, and you don't destroy exergy. If you do things irreversibly, you create entropy and destroy some exergy. That's the idea.

And so since we are at the business of exergy, let's just do it. We have already done, a few lectures ago, the first-law and second-law efficiencies for heat engines, refrigerator units, and heat pumps. This is just a summary of the same equations that we have already seen up there.

Just notice that the first-law efficiencies are a ratio where you put at the numerator an energy, and at the denominator another energy. Typically the numerator is the useful effect that you want, and the denominator is the resource that you are using, energy-wise.

Instead, second-law efficiency, you put at the numerator, what you want to achieve, and at the denominator, the minimum expenditure that you need to pay in order to achieve that, which is typically done-- minimum in the sense of thermodynamics, of course. And so it's the reversible case.

Not saying this is the practical optimum. Because in practice, you don't want to operate reversibly. Your objective is rarely to operate reversibly. Because if you operate reversibly, most of the times, you have to do it in such limiting conditions that you get nothing. So in practice, what you want to optimize is power, or a combination of power and efficiency, depending on the cost of equipment.

Because of course, the more you put in, in terms of sophisticated equipment, you may achieve higher efficiencies. But the cost may kill you, so you have to compromise. Therefore, there are other terms in the equation of optimization in terms of practicality.

So here, we are just talking about the second-- this is the limitation of the second-law efficiencies that it gives in denominator, which is your term of comparison, the reversible process, which may be too far away from practicality. One sort of halfway solution would be to put there the work required by the best available technology to do that particular job.

In that way, at least you compare the efficiency of your device with the efficiency of the best available technology. And of course, if your device is better, your efficiency will be higher, higher than 1. And eventually, your technology will impact and will become the new best available technology.

So this viewgraph simply summarizes again the idea of first law, where energy associated with the useful effects divided by the energy associated with the resource that you have used, which could be burning a fuel or using solar energy.

And here, for the second law, for the second law efficiency, you can cast it by saying that I put the-- that also the exergy associated with the useful effect-- because the exergy represents the work equivalent of that useful effect.

And then you put at the denominator the exergy associated with the resource that you've used. If you reason it out. You realize that this is equivalent to putting here the energy of the useful effect, and below, the minimum resource you should use in order to obtain that, which is, I think, written here.

See, this form of the second law efficiency is also equivalent-- once you do the balance equations and obtain the expression for the reversible work-- as a ratio of exergies. So for example, for the heat engine, it's the ratio of the exergy of your product-- which is work, so just pure exergy-- divided by the exergy of the resource, which is the heat times the Carnot coefficient.

And notice that the Carnot coefficient has to be computed using the temperature-- as environment the temperature of the cold reservoir, which you are using as an environment or as the thing where you dump your entropy. And similarly, for a refrigerator, this definition is equivalent to the definition in which you have exergies numerator and denominator.

Now, for a refrigerator, this is the exergy of cooling with a cooling load QB times-- this is equivalent to a Carnot coefficient because minus signs becomes a Carnot coefficient.

But here, now you see the Carnot coefficient with the T at the numerator. So the T of the environment now is the hot, because in the refrigerator, you are pumping entropy to the environment, which is hotter than the refrigerator cell, and similarly here for the heat pump.

So going back to this idea of exergy-- so the word "exergy," or the word "availability--" in the old times, there were fights-- well, how should we call it?

I participated in conferences where people would really fight. Nowadays, I think everybody is more loose about the idea, and just use exergy or availability-- doesn't really matter. It's a generic concept, though. So exergy does not have one definition. You have different forms of exergy.

For example, we encountered many already. For example, the automatic availability is a form-- is one exergy. It's the exergy associated with when you restrict yourself to weight processes. Well, you can call that an adiabatic system. A system that undergoes only weight processes, so you can call it adiabatic.

Or we have seen that if your system is in combination with a thermal reservoir, the maximum you can do-- the maximum work you can do depends on the type of reservoir. If the reservoir has fixed volume, we have this that we call available energy, omega R.

But then we have defined, also, available energy with respect to other kinds of reservoirs, where the reservoir can change also volume; or maybe the osmotic reservoir, where it can exchange through a semi-permeable membrane, only one type of substance; or a completely open exchange in which your system can exchange volume and any of the amounts.

These are all exergies. Different formulas, same word. Work is just pure exergy. And heat interaction-- just said. So the exergy associated with the heat interaction at temperature TQ is given by the heat times the Carnot coefficient.

Exergy requires as before, here, requires a reservoir as reference in some cases. Not in here. For heat interaction, it does require that. And you need to specify what kind of-- so you need to specify-- you choose a temperature.

Exergy is relative to a choice of a particular reference or environmental temperature. Well, even that makes it a broad concept. So you can define the exergy for a heating/cooling interaction.

And, for example, suppose you have a machinery that operates like a Carnot engine. And this is simple case in which we have two reservoirs. But suppose that neither the hot reservoir nor the cold reservoir are environmental reservoirs. For example, this cold reservoir could be your house-- the house that you want to warm up.

You want to be at 70 Fahrenheit or 21 C in your house. And one way to heat up your house-- it's actually one of the best ways from the point of view of thermodynamics-- is to use cogeneration.

You use some costly heat source-- for example, ok, this is a reservoir, so it's not exactly a proper example. But usually, you buy gas to heat up water, and then you have your water circulating like here-- heating elements. And that hot water is going to heat up the air in your room.

So you're using gas with which you could reach very high temperatures. And all you do is, by a series of heat transfers, use it to produce something at the temperature which is very close to the environmental temperature. That's a very dissipative way of doing it.

We have been doing it for a long time like that. We are still doing it. That's the way it's done in my apartment building where I live right now. But that's not the good way. It's a very inefficient way.

Cogeneration is the idea that you take that high level energy, and before you and you do as much as you can with it. For example, to run a power plant, or run a plant, or run an engine-- for example, you could run a car engine-- this is our cold total energy modules, like car, or truck engines, or maybe ship engines, depending on the size-- where you burn your fuel, make mechanical energy. With that mechanical energy, you produce electricity.

And then since your engine needs to dump entropy somewhere, instead of dumping it directly into the environment, you dump it into the heating system of your house. And then your house takes care of dumping the energy that leaks to the environment. So you get this heating as a byproduct, or as one of the two products of your system, which is combined heat and power.

So it's called cogeneration, or CHP, solution. And in this way, you have used that energy at best. So this would be, say, the best-available technology. For example, in the town where I worked 30 years or longer, which is Brescia in Italy, this idea has been taken very seriously starting in 1973.

And now about 95% of the volume of the town-- and it's a town with the size of Boston-- it's heated in this way with cogeneration power plants that dump energy into a district heating system. So you get this hot water going around the town under the roads and reaching all the houses. And then with heat exchangers, you do the heating.

More recently-- 20 years ago-- they also added a more complex system in which you also-- not only use fossil fuels, but you use also waste. You burn the trash that is not recyclable. And they also integrated with, in a hybrid way with some solar. So it's an entire system aimed to efficiency for heating the homes.

I know that many are thinking about doing these things also in the States. But here, the problem has been that-- the problem-- the reason that these things have not evolved is the cheaper cost of energy than it should. One incentive for improving efficiency is the cost of the energy. Higher the costs, people will invest to spend less. Yeah.

OK. Good.

Glad to know it. Yeah, I thought that somebody was thinking of also doing it for the town. The problem is that it takes a lot of investment.

And the way it got started in Brescia was that the municipal company was-- the company that would run also the roads would run a lot of public services, including transportation. And so they could decide and move quickly about doing it, because they were the people working on the roads.

So put in pipes because you need to put very large pipes under the roads. If you do it internally, it is easier. And also, they did it in such a way that-- because another issue is people would want to get connected to the district heating system, but sometimes it's more efficient to start with big buildings and then go to smaller ones. So these kind of decisions, it's political. And so that is an issue.

OK. Sorry, we are late. So I'll see you next time.