[SQUEAKING]

[RUSTLING]

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GIAN PAOLO BERETTA: Good afternoon. So we've been studying properties of stable equilibrium states, relations that can be extracted from the fundamental relation of any system and, therefore, if the system is, for example, a substance of a pure substance or mixtures of substances. And yes, it is a lot of math and mathematical manipulations. And today we will have a little more of that. And then we'll stop about the mathematics, at least for this part.

But I wanted to stress the fact that we are extracting a lot of information out of just the idea that there exists a fundamental relation for stable equilibrium states from which we can extract properties. And it's precisely the mathematical manipulations that is not just by itself but with proper physical interpretation. And that's the important aspect. It's not just the mathematics. It's also to interpret the mathematics and see what the useful part of it is. It's from these that you can extract a lot of information.

For example, in economics, manipulations of this sort have earned the Nobel Prize to Paul Samuelson, who was a professor here at MIT, because he realized that, essentially also in economics-- don't ask me what part of economics-- but in any case, in economics, there are functions like that that can be manipulated by the tools that we are developing from which you can extract a lot of information about economics in that case. So mathematics is a powerful tool, a way that allows you to think straight.

So, right, we've done the Legendre transform. And we have applied it to derive the Helmholtz free energy, the Gibbs free energy, the enthalpy, and also this Euler free energy that we'll return to also today and the next time. Also we developed this Maxwell relations coming from the reciprocity of the second order derivatives of the various functions.

Today I want to introduce quickly, or review quickly if you've seen it already, this other tool which is Jacobian determinants. So if you have a system of two functions and you take the matrix in which you put all the partial derivatives in that fashion, the determinant of that matrix is called the Jacobian determinant. The matrix is the Jacobian.

And the determinant of the Jacobian is we call it the Jacobian anyway, just for short. And we use this symbol, which resembles a partial because somehow it's a partial of a vector of functions with respect to a vector of independent variables.

And it has these properties, which you can infer easily by the properties of determinants. You exchange row, exchange a column, you change the sign, and so you can easily prove these relations. You can also notice that if one of the functions like, for example, g is the simple function g equals y, then the second row is just the derivative of y with respect to x. Since y and x are independent variables, that's 0. And the derivative of y with respect to y is 1. So that's 0 and 1, which leaves for the determinant just this term here, which is the partial derivative of f with respect to x.

So this is a useful identity because you can pass from partial derivatives that might be want to evaluate to an equivalent Jacobian. And then we will see that we can manipulate that further. Of course, if also f is equal to x, then this becomes simply the identity, I mean 1.

OK. The other theorem about Jacobians is that if you consider a function of a single variable and you invert the function so you have f as a function of x, and you invert it as x as a function of f, you know that the derivative of this inverted function is equal to the inverse of the derivative of the original function.

And the equivalent for a system of two functions of two variables is that the Jacobian of the inverted system, when you solve the system, this system of equations, to put in evidence x and y as a function of x and g. So if you change the independent variables, and so you invert-- well, the Jacobian of the inverted system is equal to the inverse of the Jacobian of the original system.

And that also shows that if you prove-- if you choose the function g of y as before, g equals y as before, you can prove by this relation the fact that the inverse-- I mean the partial derivative of the inverse with respect to f, at fixed y, is equal to the inverse of the original partial derivative. So formally, you see this is x over y, at constant y. Let's read it loosely. Well, you can just put it-- consider the x and the y. And consider it as a fraction and put it under a denominator and you get this function. And it is fair. In other words, this proves that you can do that easy manipulation.

All right. And the other item is that if you have a function f of x, so x is your independent variable, but suppose you want to represent your independent variable in parametric form. So x is a function of another variable, say a, x of a. So you substitute in the function. And so you have a function of a function. This a function of a. Now a has become the independent variable.

So the chain rule for derivatives says for single variables that the derivative of f with respect to a is the derivative of f with respect to x times the derivative of x with respect to a. The equivalent for our system of two variables-- so when you change your system f and g, instead of as a function of x and y, but as a function of a and b, so the x and y are in turn functions of a and b, then you have a situation similar to that. And the derivative actually, the Jacobian of f and g with respect to the new variables, is equal to the Jacobian with respect to the old variables times the Jacobian of the old variables with respect to the new ones.

Informally, you can write this result-- suppose you delete these two. So we view this result as simply the Jacobian of f with respect to a. So you write it this way. And then you have empty spaces here where you can put anything that cancels out. So for example, you can put the Jacobian of x, y with respect to x, y, which is equal to 1, the identity. We just proved it before. And thus the formal manipulation becomes easy now because then you interpret this one as the Jacobian of f with respect to x, y. And this is the Jacobian of x, y in respect to a, b.

Let's give an example that brings us to a useful relation useful identity for two properties that are among the list that we have seen are measurable. So take the Hess determinant, the determinant of the Hess relation-- of the Hess matrix of the fundamental relation with respect to entropy and volume. So it's the matrix of the second order derivatives of energy with respect to entropy and volume.

Now since this second derivatives are derivatives of, for example, we remember that the derivative of the first derivative of E with respect to S is the temperature, you can also write them in this way in terms of the conjugate variables, temperature for entropy minus the pressure for volume.

OK. So this is just applying those definitions. And then here you recognize that, apart from the minus sign here that can be taken outside of the determinant, this is just the Jacobian of temperature and pressure versus with respect to S and V. So now let's do this trick of shifting the denominator, leaving the empty spaces. And let's put here whatever we want. So I'll do it in two ways. I put S and p here and there.

And then I notice that I have chosen my-- made my choice so that in each of these determinant-- I mean Jacobian, there is a repeated pressure above and below. So that is the derivative of T with respect to S at constant p. And this other side has S, which is repeated. So that is the derivative of p with respect to V at constant S.

But then if you look up-- and let me remind it here. We define the heat capacity at constant pressure, a few days ago. And that was defined as the derivative of the enthalpy with respect to temperature at p. But if you look at how the differential for the enthalpy is, if you keep p and n constant, dH is equal to TdS.

So you can substitute the dH with the TdS here at constant p and n. So Cp, or actually, you see here that the derivative of S with respect to T at constant p is Cp over T. This derivative is therefore the inverse of Cp over T. Why the inverse? Because we just proved that these derivatives here is equal to the inverse of its reciprocal, so to speak.

Also this other one we can recognize as one of the properties that we have defined or almost. It's the derivative of V with respect to pressure with the minus in front. And so it's the compressibility. Actually, the other day, we defined the isothermal compressibility, so when you compress a material at constant temperature, but you could also compress it at constant entropy. That defines the isentropic compressibility. And so here you recognize the inverse of the isentropic compressibility.

OK. So first result is that since the determinant of the Hess matrix has to be non-negative by the conditions of stability that we have already proved, we have this inequality. But that's not the main object here. I want to do now the same but by substituting here in the empty spaces, another pair of variables, again in such a way that numerator and denominator have one same variable like here the temperature and here the volume.

Then this becomes the partial of p with respect to volume with constant temperature. And this becomes a partial of T with respect to S at constant V. And by the same definitions that we just reviewed, you can show that this is equal to T over the heat capacity at constant volume and this other is 1 over the volume times the isothermal compressibility. Also this group must be greater than or equal to 0.

But since they came from the manipulation of the same stuff, these groups must also be equal to one another. And that by eliminating T and V, which cancel if you equate that to this, you obtain this result, that the ratio of the heat capacities, constant pressure and volume, is equal to the ratio of the compressibilities, at constant temperature versus at constant entropy.

For example, if you remember like for air or for a diatomic gas, how much is Cp over CV? Anybody remembers? For air, it's 1.4. It is 7/5, 7 over 5. So that means that also the ratio of this compressibility is 1 point 4.

We will see in a while that this gives us-- this has some importance in a practical application, which is the air springs that are used in many transport devices-- I mean transport systems like trains, trucks, cars, and so on, even bicycles, air springs. But before we get to that, let's keep going with another relation that we can prove by, again, using the properties of Jacobians.

And here is a situation in which you have a surface. For example, a function of x, y, and z equals 0, represents a surface that you can represent in three dimensions x, y, z. So of course, you can view that surface from various points of view by choosing what your base reference frame is and what the independent variable is.

So you can represent that surface also in these three alternative ways, x as a function of x, y. No. You see what I'm saying? If I have this surface here which is f of x, y, z equals 0, I can represent it. Suppose this is x, y, and z. OK. So this is also-- For every x and y, I have a value of z so I can view it as a function z of x and y. But I can also view it also from here. I fix x, I fix z, and that gives me a y. So that's y function of z and x and so on.

So these are alternative ways of representing, in thermodynamics, the typical surface that is treated this way is the pVT relation. The equation of state. That particular equation, that, for a class of states, like single phase states, is equivalent to the fundamental relation. And so it's useful because it's in terms of easily measurable properties like volume, temperature, and pressure.

So here we do-- what do we do? We take, essentially, ratios of stuff that are equal to 1 or actually say minus 1. So say x, z, and z, x in the denominator. By the properties of determinants, that's equal to minus 1. If I switch one column, it changes sign. So I write this, which are easy identities, then I rearrange them in a more interesting way so that, again, I have the same variable numerator and denominator.

So for example, this is the partial of x with respect to y at constant z. This is the partial of x with respect-- I'm sorry, y respect to z at constant x. And this is partial of z with respect to x at constant y, which is written here. And if you multiply minus 1 three times, you get minus 1. So this is called the cyclic relation. And if you apply it to the pVT relation, equation of state, here is what you get.

And for example, you could apply it-- remember that one of the Maxwell relations that we said could be useful to measure entropy because it gives entropy changes that you can measure by measuring volume changes, pressure changes, temperature changes at constant temperature and constant volume. So this is somehow the basis of an instrument that you could call an entropy meter.

Well, by applying this cyclic relation-- and I'm not going to the details but I'll let you show that-- you prove that this derivative is equal to the ratio of alpha p over kappa T. So it's the isobaric coefficient of expansion alpha over the isothermal compressibility of your material. For example, for a gas, I mean, if I can write the ideal gas relation, you can view that as a V as a function of T, and p, and n.

So it's nRT over p. So it's easy to compute, for example, alpha p. alpha p is 1 over V, the derivative of V with respect to T at constant pressure. So it's how much the expansion for a given increase in temperature. All right. So it's 1 over V. The derivative of V with respect to T is easy. It's nR over p. And if you use that again, this is 1 over T. kappa T is minus 1 over V, the derivative of V with respect to p at constant T.

All right. We can also do that derivative. The derivative of this with respect to p is minus nRT over p squared. I apply that again. And the minus goes away with the minus. One V goes away. And I'm left with 1 over p. So alpha and kappa for ideal gases are relatively simple. And so this gives that the derivative here is equal to p over T for a gas.

There is another interesting relation that you can prove not so easily but relatively straightforward by using the Jacobians. It's the Mayer relation which relates Cp, CV, alpha p and kappa T, and, of course, temperature and volume. And here you see this is just the definition of Cp.

We write this derivative in terms of a Jacobian with the property that is kept constant, repeated numerator and denominator. Then we shift, leave the empty space, and then we search. And now the choice of what to put there is sort of a smart-- you have to use just trial and error or some experience on how to choose it. But here if you, for example, we choose to select T and V, the second one has a repeated variable numerator and denominator so it is a partial derivative. And again, we find that it's related to kappa T.

The first determinant has four different variables. So we write it here in terms of its definition. And then these various entries can be recognized as those properties. For example, this is CV over T. This we just proved is alpha over kappa T.

This is the same because of the symmetry of the Hess determinant or because of the Maxwell relations, which is the same. And this is one over kappa T. So now we compute the determinant. You get that. You place it here. And out comes the Mayer relation. OK. Yeah. So what's the Mayer relation for a gas? What's the relation between Cp and CV for the ideal gas? No?

How about R, the gas constant? Usually, you don't do heat capacities. We do specific heats. So that's CP. Small c is capital C over n. And cV, small c, heat capacity. I'm sorry, specific heat, is the CV over n. And then the Meyer relation is that CP equals CV plus the gas constant, but let's prove it because we said that we have it there. So we have to compute V-- what is it-- the VT alpha squared over kappa T, all right, which is this term here, which is the difference between the two capacities.

So alpha. So that's VT. Alpha is 1 over T. So we got T squared here. And kappa is 1 over p. So I've got the p there. So that goes with that. And hopefully, since pV is equal to nRT, divided by T gives nR.

I see a lot of rust in your mind about previous thermo. That's OK. All right. So done with these properties. I want to go back to the subject of available energy. You remember what we've done I forget now if it was the previous lecture or the one before.

Available energy. This is the setup in which I have a system and the reservoir. And they undergo a weight process. And we know that if the process, the weight process is reversible, we can extract the maximum amount of energy when the system ends in a mutual equilibrium state with the environment, with the reservoir.

Here instead we are going to adopt two different states, two arbitrary states, initial and final. And you ask yourself, well, if my system has to go from A1 to A2, and it has available the interaction with this thermal reservoir, what is the maximum weight lift that it can do, or if it cannot lift the weight, what is the minimum weight lowering that is required so as to achieve that change?

And we have seen that-- I mean this class of problems-- what's the maximum work, what's the minimum work-- Are always solved by writing an energy balance, an entropy balance, and also inserting as much as we know about the properties of the systems involved. In this case, we have a reservoir for which we know the fundamental relation is this linear relationship between energy and entropy.

And by the way, usually in-- often, especially in physics language, what we call thermal reservoir is called a heat bath. OK. Now you realize that we defined the heat interaction so that from heat from A to B so that if you want how much entropy is transferred, you get it because the ratio between energy and entropy transferred in a heat interaction is equal to the temperature at which that transfer occurs.

OK. Now the reservoir-- you can write the fundamental relation for the reservoir this way. So you see why they call it heat bath because the heat reservoir is ready to provide the heat interaction. If you extract energy at its temperature, then it provides also the entropy and in the right ratio so that you have a heat interaction at the temperature of the reservoir.

So it's a heat bath in the sense that it can provide heat so that at least justifies-- that's the reading of-- my justification of that language. It is not a reservoir of heat, though in the sense that heat is not a form of energy. It is a form of energy transfer. You cannot store heat. You store energy. OK. You transfer energy in the form of heat when you have an interaction of that form.

So the language is important. And loose language is OK if you understand what you're doing. If it is too loose and if you assign to this language too popular a meaning, then you get a lot of confusion. This is why one of our objectives here is to try to be as careful as possible with the language. And by the way, my sincere congratulations for how good you're doing in your homeworks.

OK. So the work that-- by solving this system of equations, we already said that we find an expression for the work which has a term related to irreversibility-- entropy produced by irreversibility, which is not there if the process is reversible. And that's typically the best you can do.

Whether you have to spend energy or produce a mechanical energy, you get the best always when you do it reversibly. So if you have to extract energy, if you can extract energy, you extract the maximum if you do the reversible process. If you have to spend energy in order to obtain a change of state, for example, heating up some water, that's a task that requires spending energy, you can ask yourself, what is the minimum work that you need to spend in order to heat up that water. And if you do that, maybe when we do the next time they review on exergies, we'll see how efficient are certain ways we have to heat up water.

OK. Now the maximum, the reversible work, is the difference between the available energies of the two states of your system. It's also the difference in this availability function gamma that is energy minus entropy multiplied by the temperature of the reservoir. We called it canonical availability function. And that we have seen that if you try to represent it graphically, it acquires an absolute minimum at the state in which the system is in mutual equilibrium with the reservoir.

So by exploiting this idea that this is a minimum, we extract information about, for example, the concavity of the fundamental relation by devising changes. You start from this mutual equilibrium state. And you move anywhere else in one of the possible states of your system A. Wherever you move, gamma must increase.

And so, for example, we chose a particular changes. And we proved that with those particular changes, you can find that the second differential of the energy at fixed n and V, second differential, so the concavity here is positive. You can view it also from the other point of view. So you find that the second differential of S at fixed V and n is negative. OK.

Now, yeah, we also applied that to prove that, for example, the specific-- I mean the heat capacities are non-negative. And we proved the first part. This is just the first part of the theorem by LeChatelier and Braun.

Today we'll do also a second part, which is even more interesting. So the first part was, anyway, that if you perturb the state of your system, which is initially in mutual equilibrium with the reservoir, you put it off the mutual equilibrium by, for example, giving energy, the system will react by increasing its temperature.

And the temperature, as we know, is the escaping tendency for energy. So it increases its willingness to give away energy. And since the reservoir is there, the increasing in temperature prepares for a heat interaction in which the system gives energy to the reservoir, thereby contrasting the change with which you took it away from equilibrium. It tries to spontaneously return to equilibrium by increasing its temperature. So that's one thing.

All right. So to see a little more, let's broaden our class or category of systems that we call thermal reservoirs or, say, heat baths because, in practice, we often have also reservoirs that are variable volume. Often, the atmosphere where we live is the environment. And it's something that would accept a change in volume.

If the change in volume is reasonably small and also the changes in energy are reasonably small, you can add or subtract the volume and energy to the environment without changing its temperature and pressure. So if the system is large enough, like the air in the environment of a town, or the water in the sea, or in the lake, or in the river, with respect to-- if it is large enough with respect to the amounts of energies, entropies and volume that you exchange, then you may consider that as a thermal reservoir, so a system that maintains fixed values of the temperature and the pressure.

In this case, we consider a system which has variable volume but still the amounts are fixed. Then the fundamental relation for a system is also linear except that now-- OK. Before we had energy, entropy, and this is the temperature, TR. Now we add volume as a possibility to change then,

we have an equation of the plane of which the slopes are TR when you take the slope at constant V and minus pR when you take the slope at constant S. So this is the equation of a plane. And that's the fundamental relation for that thermal reservoir at variable volume.

So we ask the same question now. OK. What if I'm changing state for my system but it exchanges volume with the reservoir. So maybe the system changes also the volume. And where does it take that volume? From the reservoir. Or where does it give it? To the reservoir.

You want to ask the maximum work or the minimum work requirement for doing that change. Well, energy balance, entropy balance, fundamental relation for the reservoir. And here you also have to do a volume balance because you have an additional variable that has to be kept fixed for the composite system. The overall volume is conserved in order to have no other external effects like in a weight process.

So when you do the-- when you solve this problem by eliminating the variables that relate to the reservoir, here is the result. It is almost like before except that there is now an extra term here, which is PR times the difference in volume of your system. And again, it's a reversible term minus a term related to irreversibility.

The reversible term can be seen as the difference in two properties. You could consider this as a definition of another property that we still call, for short of names, available energy with respect to that particular reservoir at variable volume. It's like the one before plus this additional PR times delta V. And also this one, if you notice, may be written as a difference in an availability function E minus TRS plus PRV, which we are going to call just with the name capital Psi.

And we may notice that this is not-- that it looks like but it's not the Gibbs free energy except when the system is in mutual equilibrium-- in the state of mutual equilibrium with the environment. In that case, TR is also the temperature of your system A and therefore this is the Gibbs free energy, whereas in any other state, this TR and this PR may not be the temperature of your system A.

And actually, if the state is not an equilibrium state, the system A might not even have a temperature defined. Actually, it does not if it is not stable equilibrium. Yet this availability function is defined. And it gives you these answers to questions of minimum or maximum work to do or to obtain.

Yes. Exactly with the same procedure that we have done to obtain these conditions for the stability. You can do it also here. Now, since I have several variables, it's not-- I'm sorry. Let me go back one moment here. So you should think of a similar procedure only in a three-dimensional setup in which you start from a mutual equilibrium state and you move away from it. And then you apply the condition that gamma must increase if you move away.

Now whereas here you could move away only on the S plane, in the new setup, where also the volume can be changed, yes, you can move at constant V or constant E, but you can also move in any other direction so you have more choices. And whatever choice you make, you still have to have this property to increase.

So here, I'll let you, if you're interested, watch the details. I chose, for example, to move by changing the entropy and the volume, keeping the n fixed. And it turns out that when you compute the change in the variable Psi, it is exactly equal to 1/2 the second differential of E. And therefore you prove that this is greater than or equal to 0. Or if I choose instead to change the energy and the volume and therefore-- and to move along the stable equilibrium state curve so that the entropy is determined by the fundamental relation, then delta Psi becomes equal to minus the second differential of the entropy. And since that must be greater than 0, it gives again that the d2S at fixed n (is negative).

Now this d2S if you want to represent it, it's not just the second derivative because you see when we have d2S at constant V and n, this was equal to the second derivative of S with respect to E times dE squared. But this other d2S at constant n only, you can vary both E and V. Then it's given by d2S with respect to E squared times dE squared plus twice the second derivative of S with respect to E and with respect to V times dE dV plus the second with respect to V twice times dV squared. So it's a quadratic form which you can express also in this form using matrices, dE dV.

Here, you put the Hess determinant, which is the determinant made up of the second derivatives. And this is equal. And then you multiply this by this other vector made up of two elements dE and dV. If you do matrix multiplication of this-- let's be more elegant here-- you get the above result. OK. And the fact that this has to be negative for arbitrary choice of your vector dE dV, which means no matter what direction you want to move, this has to be negative, that requires that the matrix inside be non-negative definite. And the matrix is a non-negative definite. When? Sorry. Non-positive. So it's negative semidefinite.

OK. When is a matrix-- let's start with positive. When is a matrix positive definite? I have a matrix a11, a12. And let's make it symmetric. OK. So this, if it is positive semi-definite, the diagonal entries must be non-negative. The determinant must be non-negative. So a11 a22 minus a12 squared because it's a symmetric must be greater than or equal to 0.

You want to make it-- if the matrix, instead of being positive semi-definite is negative semidefinite, so this is less than or equal to, so the entries on the diagonal should be non-positive. How about the determinant? Should I change the sign? Not for a 2 by 2 matrix because you see also, the more fundamental property of a non-negative-- of a non-positive-- of a negative semi-definite matrix is that its eigenvalues are all negative. So it means-- let's call them lambda. So lambda 1 is less than 0. Lambda 2 is less than 0.

And for a 2 by 2 matrix, the determinant is equal to the product of the two eigenvalues. So this is also equal to lambda 1 times lambda 2. So if you multiply two negative numbers, you get a positive number. And so you get the determinant is greater than zero. If instead you had a 3 by 3 by 3 matrix, then you have three negative numbers that multiply to give the determinant in that case with an odd number of entries.

Negative times negative times negative makes negative. So the determinant of a negative semi-definite matrix is positive for odd number of rows and columns and negative for-- what did I say? Positive for even number and negative for odd number. OK. We'll need that in a short while.

Here-- oh yeah. Let me just go back to a simple question about-- all right. Suppose you have a vacuum. So we have a piston. You have a container in which you manage to have nothing. Vacuum. Vacuum means no particles, nothing. OK.

So the question is, is that a situation-- and this vacuum is in an environment which I can model as a reservoir at pressure pR, also temperature TR but the temperature doesn't play much of a role here. So it's like I have this container in the environment here. I managed to make vacuum. What's the minimum work required to make that vacuum? Or if I have that vacuum, can I do something useful? Can I lift a weight? What's the maximum lift?

Well, let's apply this formula here. Assume that we do things the best thermodynamic way. So that means without generating entropy by irreversibility. And suppose I want my initial state, state one. So let me say that I started with my piston down below here. And this is my state 1 and this is my state 2 and I pull.

Here I have the pressure of the environment. So if I pull, how much work do I have to do? I have to-- if you look at the piston on one side, you have zero pressure because nothing here. On the other side, you have PR. So if the volume change is V2 minus V1, you can view that as-- let's call x this--

OK. Let's go call z the location of the weight-- I'm sorry, of the piston. And let's call little a the area of the piston. So the force that you have to apply is equal to the pressure times-- which is force per unit area times the area. So that's the force. The work is f times x. I'm sorry. z. So that's pR times a z. But a z is the volume so that's pR times V. But actually, it's V2 minus V1 because this is V2 and this is V1 is equal to 0 in our case.

So it seems that the work that you need to spend in order to go from 1 to 2 in a reversible way is equal to that, which is written here except that now it has the wrong sign because this represents the work with the arrow out instead if we change the direction of the arrow so let's say that this is the work that I need to spend.

And of course, this I could also write the same thing by changing the arrow. If I change the arrow, I change also the sign. So essentially, the minimum work required to produce the vacuum is equal to the pressure of the environment times the volume of that vacuum. That's an easy result. We could have-- I mean, we actually got to that result without all the complicated long story that we're telling. But that's just to show the consistency of this relation with what we know.

So now let's think of another kind of reservoir which, again, can be typically-- is a typical model of the air in the environment or some natural environment. So here is a particular reservoir that can exchange through a semi-permeable membrane only one type of substance with your system. We may call it an osmotic reservoir or a thermal reservoir or we just don't give any names but just define it by just these words. All right.

You run the same machinery, energy balance, entropy, balance. Now you also have to make a balance for the amounts of constituents of the kind of substance that can be transferred. For example, you may be interested in-- some people are devising methods or plans that want to extract CO2 from the atmosphere.

All right. So you want to ask, well, what's the minimum amount of work I need to spend if I want to extract CO2 from the atmosphere because that minimum defines the target. Defines also the way in which you determine the efficiency, the second law efficiency of that particular equipment.

And it's a question very similar to this one because one way to do that, not saying it's the reversible way, but I'm saying that one way to do it is first you do vacuum. And then you open up the permeability of the piston to just CO2. And so CO2 will fill this region. And you'll have just CO2 because the other parts, oxygen and nitrogen, cannot go through this particular semi-permeable membrane. And that way you have separated. So one way is produce vacuum. And we know how much work it requires. Use a semi-permeable membrane and there you have your CO2. Your CO2 eventually will reach mutual equilibrium with the reservoir.

At that stage, I have blocked my piston. Cannot go up and down. And I change the reservoir. Instead of having a reservoir at variable volume, I have a reservoir that can exchange-- at constant chemical potential of that substance, CO2.

The final state will be that, instead of vacuum, I will just have CO2 pure. Let's say that this will have a chemical potential that we will call mu double i. And it will have a pressure that corresponds to what we defined when they are in mutual equilibrium, equality of chemical potentials defines the partial pressure. So the CO2 will be at the partial pressure that it has in air viewed as a mixture. OK.

This second part of the process from after I made the vacuum, and I stopped the piston, and I opened the pore, the second part of the process is spontaneous because, initially, you are in a nonequilibrium state because here you have no CO2, whereas, in order for equilibrium, you need to have chemical potentials to be equal. So this is an irreversible process.

There will be entropy produced by reversibility. So this is not the best way to do it. You could also evaluate how much is the efficiency, if you could compare it with what's the minimum work that is required. And the minimum work that is required is given here by this formula here. I'm sorry. By this formula here.

So there is, again, another available energy function-- I'm sorry, available energy property for this particular kind of osmotic reservoirs, the difference of which tells you the minimum or the maximum works for producing or exploiting a situation. So we will return later on to this question of minimum work for separating a substance from, say, the atmosphere.

Here this combination that appears in the expression for this new version of the available energy, namely E minus TRS minus the chemical potential times the amount of that substance that can cross between the system and the reservoir, we may give it a name or not, simply an availability function. Maybe we could call it osmotic availability function. Maybe we could use this letter or another letter. It's just a matter of choice.

As for the other availability functions, there is also this minimum. So also from this one, you can derive by the same method as before, same procedure, conditions for stability of equilibrium. For the second differential of the energy, now it will be like this but not with volume but with n i that substitutes. And that's the expression for these second order differentials.

And finally, we could have a grand situation, so a grand reservoir with which your system can exchange anything it wants-- amounts, volume, energy, and entropy. OK. So you have to run again the same machinery-- energy balance, entropy, balance. Fundamental relation for the reservoir.

Notice that-- of course, in the previous case, maybe I didn't emphasize it enough, but what changes from reservoir to reservoir is the expression for the fundamental relations. These terms are new, peculiar to this reservoir, that acts as a reservoir not only for exchanges of energy and entropy but also for if you change volume, it doesn't change the pressure. If you change the amounts, it doesn't change the chemical potentials.

And then you have to remember also to do the volume balance and the balances for all of the amounts of the various constituents that are conserved. No chemical reactions here. Again, eliminate the terms that relate to the reservoir. And you get this expression, which is another generalization of the available energy with respect to this completely open reservoir. And this is the available energy, the expression, which can also be written as a difference in two values.

So the work, the maximum or minimum, the reversible work is the difference in the values of this new availability function, which I like to call Euler availability function for the reason I already explained the other time. And that will be also clear later on. So this E minus TRS plus PRV minus mu Rn. This availability function is defined for all states, equilibrium and nonequilibrium.

When your system is in mutual equilibrium, so it is in the state at temperature TR, pressure PR, and with the chemical potential, so complete equilibrium between system and reservoir, then this availability function corresponds to that characteristic function that we call the Euler free energy that I just reviewed at the beginning of today. OK.

And from this one, this also is minimum at mutual equilibrium. And you can do the same again to extract conditions for stability. This time, this expression d2E is with respect not to just two variables, so this matrix, the Hess matrix will not be just 2 by 2 but will be 2 plus r because it also can change all the constituents. And if you have r constituents is like 2 plus r by 2 plus r. So it's this matrix that we have already anticipated a while ago. And this therefore proves-- I mean the details here prove in more detail also these expressions that we had anticipated.

But you can also choose-- since now you-- think that you are in a mutual equilibrium state, and then you can move your state in various directions. And one way is that you choose another state that still has the same temperature and pressure of your reservoir but you change the amounts.

So you choose to move away from mutual equilibrium because the conditions for mutual equilibrium with the reservoir not only now that it can exchange not only energy but also amounts. It's not only the temperature equality. It's also the pressure equality for the volume change and the chemical potentials, all chemical potentials. So I can move away from mutual equilibrium while keeping some of the mutual equilibrium conditions satisfied, like same temperature and same pressure, and moving only the amounts.

If you do that and move along the stable equilibrium state surface, constant temperature and pressure, the condition that delta-- that this Euler availability function must increase along that path turns out to be the change in this variable Xi is equal to the second differential of the Gibbs free energy.

You can prove it by remembering that the Gibbs free energy is E minus S minus TR. And here TR and PR remain constant. So it remains defined. So this proves that the Gibbs free energy has a minimum if you move-- so the second differential is non-negative. Yes. It is non-negative if you move at constant-- if you change the composition at constant T and P.

If you keep only temperature fixed and change the volume instead of keeping the pressure constant, you get a similar relation. This is not the Gibbs free energy. It's the Helmholtz free energy at constant T.

So remember that we have seen the-- that from these conditions here, we obtain a first part of the LeChatelier-Braun principle. Now, yes, another little piece of math. Sorry about that. But that will get us to the second part of the Le Chatelier-Braun principle, which is a more general statement which requires a little brush up or maybe first-time-you-see math.

So let's say we have a function of two variables. I put also the other z here just to say that the z's are going to be constant. So I have several variables but I keep constant all except two of them, which are x and y. And then, for example, I have that function. I can write the differential. So that's the partial of A with respect to x times dx plus the partial of A with respect to y times dy. I'm going to use the notation comma x for partial with respect to x, which is often used in fluid mechanics so maybe you've seen it already or elsewhere.

And for example, comma double x is the second derivative with respect to x twice. comma xy is the derivative with respect to x and with respect to y. OK. So this is the partial derivative with respect to x. And here is the full glory of the representation of the derivatives where these subscripts, as you remember, mean the other variables of the original function that you're taking the partial derivative of. OK. Good.

Then we have, like we've seen there for d2S, here's d2 of this variable A. Can think of S but it could be also others like the Gibbs free energy, or the Helmholtz free energy, or whatever you need. And this is the quadratic form that represents the explicit form of the second differential.

OK. So now that we have a quadratic form, the trick is to put it in the so-called canonical form because, you see, this quadratic form has a square here, a square there, and then it has a product dx dy. This doesn't have a definite sign. But let's try to rewrite this quadratic form into a form in which you have something squared and dy squared.

So a combination of dx and dy, if you choose the proper combination of dx and dy-- and this is the proper combination. I've already built in the answer. So if you want to check it, you just substitute. If you take this expression and work it out, you will prove to yourself that it's equivalent to that one. And this ratio, this coefficient here is the ratio of the second derivative with respect to xy divided by the second derivative with respect to xx.

And then if you substitute, by comparison you find that what you need to put in front of the dy squared is this lambda, which is not-- sorry that I used lambda here. It's not the eigenvalues. But this lambda is given by this expression. Again, in terms of the original. You can do it in this way, where in your summation, you keep the square of-- dy squared, or you can do it also in this other way. This is another canonical form in which you keep dx squared. They are two equivalent ways. Of course, here the lambda is different and the lambda x is given by this one. OK. Now do I have more space?

Now let's look at-- suppose that our function A is such that its second differential must be positive. OK. So positive means that this matrix is positive definite or semidefinite. And as we remember-- yeah. I took away the wrong. So if we remember, positive definite for a matrix implies all these things are positive or non-negative.

So we have to have that A xx is greater than zero. And in fact, here is just what I have written. A xx is greater than 0-- is greater than something else and greater than zero. And also A yy is greater than zero. But here we have written also something more strong than that. We have written that A xx or A yy is greater than lambda.

Let's see. The lambda-- for example, lambda y-- let me rewrite it this way. It has at the denominator A xx squared and at the numerator A xx times A yy minus A xy squared. That is the determinant of the Hess matrix, that numerator.

So since the matrix is positive, the numerator is positive, the denominator is positive, so this is also positive. OK. So this explains why lambda-- you can do that for y, but also for x. The lambdas are also non-negative. And now you can also see here why lambda-- for example, lambda y is smaller than A yy because look here. This is lambda. This is A. And then you subtract something positive. So if from A you subtract something positive, it means that lambda is smaller than A yy. OK.

All right. So this is the mathematics that stands behind the Le Chatelier-Braun principle that we are going to do in a second. Of course, you can do exactly the same that I've done here for positive semidefinite. You can also do it for negative semidefinite. OK.

These steps help understanding the various steps on the previous slide. And the bottom line is here, you can rewrite that A double x-- this is equal to the partial of A (with respect to) x, which is the conjugate potential to variable x. So yeah.

So suppose our function is S. And S is a function of energy. And so S EE, which is the equivalent-- so our function is the entropy and the x variable is the energy. So S EE means partial of S with respect to E twice. But since the partial of S with respect to E is 1 over T, this is equivalent also to-- you can write it as S comma E, which is the inverse of the temperature, again comma E.

And of course, you can do also the other like that. So this is the meaning of partial of A comma x, again comma x, done at constant y. The point is that, by doing this math here that I want to skip, I prove that the lambda also, the lambdas can be written as partials of these potentials-- so of the first derivative with respect to x but not while keeping constant y but while keeping constant the other potential conjugated to y.

So what changes in these two terms is what is kept constant. Here I keep constant y. Here I keep constant the potential conjugated to y. And that's the key to the practical consequences of this mathematics. So for example, let's change once more variables so that we get even more confused. But we just have five minutes so it's OK.

So we start from the function E from this fundamental relation, this form of the fundamental relation. Keep the n fixed and look at what happens by applying what we've just seen. This is the train of inequalities that is implied by one of the forms, by this form, and by the second form is written here. You can do the substitutions.

You see I put here what the variable x and y is, what A sub x, A sub y, the temperature and the pressure in our case. And here is the result. Now, by the way, by looking at these derivatives, you find old friends. And you can see that, for example, you can rewrite this as CP is greater than or equal to CV, which is greater than or equal to 0, or that one, the compressibility at constant temperature is greater than the compressibility at constant entropy.

So what's the reading that Le Chatelier-Brown does? What's the difference here between these two derivatives? It is what is kept constant. I change the entropy and measure what temperature change occurs when I keep volume or when I keep pressure fixed. You see, volume is the original variable. Pressure is the conjugated potential. It has to do with the tendency to escape, to gain volume. So minus pressure is the tendency to yield volume.

So the idea is that the interpretation of these derivatives being positive is that the system reacts if you move it away from the mutual equilibrium state of the environment. If you add some entropy, for example, it will increase its temperature-- this is positive-- so as to increase its tendency to return energy to contrast your change by giving energy away to your environment.

So the system responds by trying to spontaneously reestablish equilibrium. But it does more so if you do it at constant volume than if you do it at constant pressure. So the reaction of the system is stronger if what? So what's the difference? The difference is that, here, the system has a smaller reaction if you keep-- keeping the pressure constant means keeping your system in equilibrium with your reservoir at least as for the condition that requires pressure equality. So you're not touching that condition for mutual equilibrium. You're touching only something else.

So if you do it there, the system says, all right, well, after all, you're moving me away but not so much so its reaction is softer. If you move it away so that also its pressure changes and therefore like you do when you keep the volume constant, then it will increase not only-- so essentially, you are touching two conditions of mutual equilibrium, touching equality of temperature and touching equality of pressure. And therefore the system reacts stronger. Wants more to come back to equilibrium.

This is the-- this is the idea. And since I wanted to-- give me two more minutes. I wanted to show you the application here. This is an air spring. So it's a piston with air inside. And it acts like a standard mechanical spring. You can compute the spring constant. Here are the details. It's kind of easy mechanical engineering, so to speak.

This k is the spring constant that relates, the increasing reaction or force of your spring to a change in its compression. And this is also a similar situation. This acts as a spring. And you can compute the dF over dx. And if you go down here, you see it's related to how much the area, little a, of the piston, the volume. And this thing at the denominator is the compressibility.

So you could have-- so if you act your spring while keeping the temperature constant-- so if your spring is in contact with the thermal reservoir and therefore, it has the time to exchange energy to remain in mutual equilibrium, which typically is when you push it, but push it slow enough so that the system has time to exchange heat with the environment and remain in equilibrium, then you get one spring constant. If instead you push the spring fast, like when the car goes on a bump, the system doesn't have time to exchange energy or heat and the entropy remains constant.

So that's the isothermal compressibility-- I'm sorry, the isentropic compressibility that appears. And so you see that the ratio of these two spring constants is equal to CP over CV, which for air is 1.4. We just reviewed. So that means that if you act on the spring fast, you get the spring constant that is 40% higher than if you act on the spring slow.

And these devices, if you look up air springs, you can see that it's an enormous business because, as I said, trains, buses, bicycles, and cars use spring constants combined also with the damping system to give you suspension systems that are allowed to absorb vibrations and make it more comfortable. OK. So sorry if I went a little bit late.