

[SQUEAKING] [RUSTLING] [CLICKING]

**GIAN PAOLO
BERETTA:**

OK, so good morning. Well, we finally got to the heat interaction. So we are almost comfortable with the old ideas of thermodynamics being the theory of heat and work. We did temperature. Usually, there is also another thing that maybe I didn't stress enough.

Usually, you are taught that thermodynamics deals with large amounts of substances, many particle systems. But you see that, if you went to the seminar yesterday, I suggested-- if you are going to the seminar by Professor Howard Stone, who is a very important name in fluid mechanics, and you'll see today that much of current interest is in small devices-- microfluidics, bacteria floating on solutions, trying to find food or other things-- few particles, in some extremes, like in the quantum thermodynamics, only very few particles, maybe one, whereas in the fluid mechanics of small systems, it's few, but not so few.

Nevertheless, it's not many. So these are not macroscopic systems. So you would wonder, well, does thermodynamics apply? OK, this is precisely the reason why I'm postponing the part that deals with many particles. In other words, all that we have done so far, if you noticed, didn't require any assumption about the number of particles.

So all the things that we do also today, until maybe the next-- or the next, other lecture does apply to microscopic and macroscopic systems, all right? So this is important because if you work downstairs in the Hatsopoulos Microfluidics Lab, or if you do research in biology, at some point, you're going to have to-- even if you are an experimentalist, you're going to have to make a model of your experiments.

If you are a theorist, you start from the model. If you are an experimentalist, you want to correlate your data. And you need a model usually to do that. And therefore, what we are doing, which is, of course, a lot of theory, a lot of equations, but is exactly what you need to do this modeling. So that's the motivation for this course. It's timely also because it's one of the few ways of presenting thermodynamics in such a way that it starts from generalities that hold not only for macroscopic systems.

OK, let me just review quickly what we did last time. We defined heat interactions. So a heat interaction was defined as one in which a system-- two systems, A and B-- initially at stable equilibrium states exchange energy and entropy. But they do so in such a way that even if you put in between them some machinery that tries to separate the energy transferred into two streams, one of which is work-- so it's pure energy and no entropy-- that machine will not succeed. So no fraction of the energy exchanged can be recognized as work.

So heat is the extreme, the farthest non-work interaction, farthest from work, most distinguishable from work. And that definition leads to the condition that the two systems, to have a heat interaction, must be at almost the same temperature, if not the same temperature, because only in that limit the Carnot ratio between the two temperatures, which represents the fraction of the energy that could be identified as work, goes to 0.

We also mentioned that, in spite of the usual understanding that heat is the energy transferred between bodies at different temperature, and therefore seems to contradict our definition, we noticed that, if the standard model that we adopt in heat transfer is a local equilibrium or quasi-equilibrium model, whereby the system is divided in smaller systems that are modeled as being near equilibrium-- not at equilibrium, like highlighted here-- near equilibrium.

And therefore, in that way, first of all, you could assign the temperature of the equilibrium state that these elements would reach if you isolate them from the rest and just let them relax to equilibrium. And second, on the E versus S diagram-- we notice also this is important and we'll return to this-- the heat interaction on one side pulls the system in a direction that--

So on the E versus S diagram, if I'm here and I'm going to inject both energy and entropy, that's the direction in which my state will move. And if another interaction injects the same energy but takes away-- I'm sorry, takes away energy, same energy, but takes away more entropy, then it goes that way. And the two are not aligned.

So in order to align them to keep the state at steady state so that the state doesn't move, you need also something. And that something is another vector, which is representing the entropy produced by irreversibility. So you need irreversibility to keep a fluid element or a solid element in steady state when subjected to a gradient in temperature, that means a temperature difference between one side and the other side.

OK. So let's do something new now. Not very new, but it's another-- it's similar to what we have done when we proved the conditions for mutual equilibrium between systems. This time, though, we are not applying the maximum entropy principle, but we are applying the principle of entropy nondecrease in weight processes.

And let me say it again. The principle of entropy nondecrease is for weight processes or for systems that are isolated. In other words, it's impossible to decrease the entropy of an isolated system or a system that undergoes only a weight process. Otherwise, it is possible to decrease the entropy, like we do here. Like, the heat interaction is precisely the kind of interaction that allows to extract entropy from a system.

All right. So here, the idea is that we start from a composite system of two systems, A and B, at different temperatures. This time, they are different. And we ask ourselves, is it possible-- when is it possible for them to exchange energy and volume through a movable partition?

So here is the initial state. And on the E versus S diagram for the composite system, I denote it by this point here. And here is the final state-- same energy and same volume. So it's on the same energy line for the composite system. But internally, some energy has gone from A to B.

So for example, if dE is greater than 0, the energy of A is increased. So the energy has flown from B to A. Or if dV is greater than 0, the volume has increased. So again, system B has lost volume for the gain of volume of system A.

What we apply here is the condition that, since this system is isolated-- this is the particular case of a weight process with no external effects-- the entropy can only increase or remain 0 if the process is reversible. So the final entropy of the composite must be greater than the initial. And so we have this inequality here-- S_2 greater than S_1 , which we write this way, which we write this way. Then the tools are the same that we already used. We use additivity. We use the fundamental relation.

Remember now, here your systems, system A starts from a stable equilibrium state. We want to extract or to, let's say, change with a negative dE the energy. And so at the new level of energy, there are many states that can be obtained. So I'm trying to explain the reason for this less than or equal to. The change in entropy for system A is either this one, but it can also be less-- I mean, I'm sorry, more and the same for B.

So we end up with this relation here. And so these things must be greater than 0 because these are all connected. So now, we can still choose some special cases. For example, suppose we don't change the volume. So the piston is-- it's blocked by a stop or there is no piston. This is just a wall.

Then dV is equal to 0. So this contribution isn't there. And suppose we want to transfer energy from B to A so that dE is greater than 0. Here it is. So if this is greater than 0, then this term in parentheses must be greater than 0. And that hopefully will say that T_{1B} must be greater than T_{1A} if in a process without external effects, some energy is transferred in the direction from B to A.

We say this in words by saying that the temperature-- or better somehow or equivalently-- the minus-- the negative of the inverse of the temperature can be understood as an escaping tendency for energy. So if you have two systems that have different escaping tendencies, the one who manages to give energy to the other is the hotter one, the one that has a higher escaping tendency.

Suppose we choose that the two systems, A and B, are initially at the same temperature. So this term in parentheses isn't there. And we want system A to acquire volume at the expense of system B. All right, so the denominators here are equal. And so we find that p_{1A} must be greater than p_{2B} -- sorry, this should be also 1. These should be 1's. I have to correct that. So you can interpret pressure, as we all have the typical idea as a capturing tendency for volume.

Now, we can do the same when instead of exchanging energy and volume, these two systems exchange energy and particles. And let's say particles of one type. I see here again another 2 that slipped. Fine, I'll need to remember to correct that.

So it's the same story, only that instead of energy and volume, it's now energy and amount of constituent i . Still, the system is isolated. The entropy can only increase. And we end up with these inequalities. The first one still confirms that the minus 1 over T is escaping tendency for energy.

Regarding chemical potentials, again, suppose that you choose the initial temperatures T_{1A} and T_{1B} to be equal. So the denominators here become equal. And this is going to be 0. So the only term is this. It must be greater than 0. So And also, this dV -- sorry for the slide. This was a cut and paste. This should be a dn_i and also this one. I wanted to see if you are-- if you are attentive.

Well, anyway, the result is that if dn_i must be greater than 0, if you want, therefore that system A acquires particles of type i through this semi-permeable membrane that allows it to get it from system B, you need the chemical potential of A to be greater than the chemical potential of B.

Is that correct? I'm not so sure anymore because of all these mistakes. And in fact, it shouldn't. It should be because there's a minus sign here. And so I either put a minus sign there or I invert A and B, the positions of A and B because, in order for constituent i to flow from B to A, I need that the chemical potential of constituent i in system B be higher than that in A because chemical potential. At least the title I got right. It's an escaping tendency for constituents.

So this gets a feel of what the chemical potentials are. If you have a feel of what the temperature is, you also have a feel of what chemical potentials are. Temperature works for energy. Chemical potentials works for molecules and atoms and so on.

And in fact, again, if you visited the talk today by Professor Stone, you'll see a lot of chemical potentials. The chemical gradients, they call them, for short. Instead of saying chemical potential gradient or gradient in chemical potential, they simply say chemical gradient.

And since the chemical potential goes with the logarithm of the concentration, we'll see-- so a gradient in the chemical potential goes with the gradient of the log of C . And that's $1/C$ gradient of C . Usually, people don't talk a lot about this $1/C$ in front. And they simply say, well, for example, diffusion processes depend on the gradient in concentrations. True. They also depend on the gradient in concentration.

But there is this C at the denominator. And when you have a number at the denominator and it is small, this enhances things. So the gradient in chemical potential has two contributions. One is also this C at the denominator. So for dilute systems, this gets amplified.

And it's very nice to see how many experiments they are able to do in which this is the driving force. But it's also very nice to see how the modeling part is still a bit, I would say, primordial. And very few people really care about checking if some of the non-equilibrium phenomena that we will talk in particular Onsager reciprocity, cross-coupling effects that we will discuss in the third part of the course, whether they do play a role or not, whether they are small or not.

Usually, they are neglected, but just neglected because you want a simple model, not because you know the effect isn't there. So that's why there is still a lot of research. And you find lots of very interesting papers on these subjects.

OK, talking about experiments, last time, we also talked about-- we made a quick survey of the methods that we have in order to measure properties of substances or properties of systems. So one is measuring the temperature with the thermometer, measuring the pressure with the manometer, measuring the chemical potentials through a measurement of the partial pressure of a constituent.

When this constituent is in mutual equilibrium with the system of interest through a semi-permeable membrane, permeable only to that constituent, when you reach chemical equilibrium that defines the partial pressure of the constituent in the mixture. And that's how you measure that.

And I skipped all the other slides, but just to remind you that we said that, eventually, if you are an experimentalist and you like to characterize properties of substances, or maybe you discover a new substance and you want to characterize it, what you have to measure in the lab, and what you have to publish and eventually gets listed in like the *Handbook of Chemical Physics* or the NIST website, where you can find properties of substances-- in the old times, you would buy the book, the *CRC Handbook of Chemical Physics*.

Now, books are disappearing. So you're all virtual. And so you go to the websites and look for these properties. Or you buy softwares. You probably use some software that has built-in correlations for many substances. And these correlations give you values for these quantities. The specific-- I'm sorry, yeah, the heat capacities of your substance, the compressibility, κ , isothermal, or sometimes also another kind of-- the isentropic compressibility, which is equivalent or connected to this one.

And also here, it's either the heat capacity at constant pressure or the heat capacity at constant volume because, through the Mayer relation, they are related, and the coefficient of expansion of your substance. For example, the compressibility, if you are in solid mechanics, you remember the Young modulus of elasticity. Well, this is a sort of Young modulus in the bulk.

So in elasticity, you do stretching in one direction. If you do it in all three directions, you get the compressibility coefficient. No? That's because V , for a specimen of-- like a parallelepiped is given by that. And if you have $1/V$ times the partial of V with respect to p at constant T times minus, that's κ_T . That's the isothermal compressibility.

So you could write that as minus the partial of the log of V with respect to p . And because of the additivity of logarithms, this, you could write it as the partial of L_1 with respect to p times partial of L_2 . Is that correct? Yeah, no, plus, not minus, not minus, minus L_3 .

OK, so this. And that's also-- sorry, oh boy, that's more than a senior moment. Let's do it again. $\log L_1$ partial dT minus $\log L_2$ and so on. And each one of these is the Young modulus. It's $1/L$ dL over p . So it's the percentage stretching, change in distance, for an increase in pressure.

And that's the thing that you measure with the compression machine. It's the Young modulus in that direction. All right, what we proved is that once you have these functions here-- you don't just need one point, you need the entire function, so how they vary in temperature and pressure at given composition-- then, using these formulas, you can integrate these formulas and obtain the values for energy and entropy.

And therefore, you can reconstruct the fundamental relation. So that's how you measure the fundamental relation, somewhat indirectly, through its derivatives, temperature, pressure, and derivatives of derivatives, like the specific heat or the heat capacities.

So that introduces to the subject that I started, just barely started last time, which is, again, a bit boring because it's like a mathematical game played on the fundamental relation. But it is part of the traditional topics that we do in thermodynamics. It's certainly things that are needed when you do measurements and you want to correlate the data, you want to make sure that these relations are satisfied. So let's do it. I'll do it as quickly as possible.

So the idea of a Legendre transform is to describe a curve, this curve, instead as the direct description, F equals F of y -- so this is F and y -- in a more indirect description, in terms of the family of the tangent lines to the curve so that the curve becomes the envelope of this family of lines.

And this family of lines is described in such a way that you choose a value for the slope of the line. And then you shift the line until you find the point in which your curve is tangent to that line with that slope. And then you mark the value of the intercept at y equals 0 here. We call it L of λ . So this L of λ is the Legendre transform of your original function.

When I have more time, but I don't here, I like to play this game. This is a game in which you can-- the Legendre transform has applications also in mechanics. So for example, it allows you to design, in a bridge-- you know those bridges with lots of wires? You want to have the wires be distributed in such a way that they make this envelope. And you want to decide which shape of envelope you want, for example.

So here is my bridge. And suppose I want the envelope of these things that sustain the bridge-- from a distance, you want it to have a certain shape, maybe a circle, or maybe an ellipse, or whatever. So you fix that shape. And then by doing the Legendre transform, you find the points where you have to pull or attach your wires.

So by construction here, essentially L -- if you look at this triangle, you realize that L is simply F minus y times the tangent of this angle, which is λ . So L is F minus λy , F minus λy . So that's how you construct it.

You can play-- these are some examples. For example, e to the y , the Legendre transform is λ minus $\lambda \log \lambda$. Or the Legendre transform of $1/2$ of y squared, like the parabola, is exactly the same function and so for quadratic forms. If you put the $1/2$, the $1/2$ is important.

What is also interesting is-- if you like this game, I'm not going into the details, but here is the proof that when you do this kind of transformation-- and this is why Legendre does it-- you don't lose information about your original function. And so if you do again the Legendre transform of the Legendre transform, you get back your original function.

And this is similar to what we have done here because we describe this function here in a smart way, which was devised by Gibbs in the late 1800s, by tangents. You describe this function by its partial derivatives. So temperature is the slope in one direction and pressure is the slope in the other direction. So this is why this transformation matters.

And here, in fact, is that transformation done, starting, for example, from the fundamental relation based on energy, in energy form, for which, you remember, this is the form of the differential. So dE is TdS minus $p dV$ plus chemical potentials times dn .

And this line reminds you of what we just saw. So it's the definition of-- the generic definition of Legendre transform for a function F of y . So L is F minus λy . And here is the application. So if I take that function-- now, it is a function of many variables. So I have to choose one at a time and do a Legendre transform of 1.

For example, I want to substitute S with T . So I want to find an equivalent function that contains the same information of the fundamental relation, but in which the independent-- I change the independent variable S to its slope, T . So it's F , the new function, the Legendre transform, is the original function minus the product of λ times y . So λ , in this case, is T and y is S . This function is called the Helmholtz free energy.

And you can also write very easily the-- let's do it only-- forget about the amounts. So we have this one up there. Now, we have defined a function F equals E minus TS . We want to compute dF . So this is dE minus d of TS .

And then we can use the, I think it's called Leibniz rule, that this is equal to-- so for dE , we have it up there. It's TdS minus $p dV$. And here, this is minus TdS minus SdT . So one of these will cancel that. And we are left with minus SdT minus $p dV$, which I hope is what is written there. Yeah, OK.

So in a sense, from the practical point of view, what have we done here? We gained the fact that we have a new function that contains the same information. And it is in terms of properties easily measurable-- temperature, volume. I could have done it also with respect to the second variable. So change the volume with pressure. It's the conjugate variable. So the slope in that direction is the conjugate value to the volume. It's the pressures-- minus the pressure.

Then the Legendre transform is E , the original function, minus the slope, which is minus p , times V . So that's E plus pV . That's called the enthalpy. And you have used it for bulk flow interactions. We'll review that extremely quickly, probably next time. No, later because it needs to-- it needs the macroscopic, the simple system model.

All right, so you take this one. It still has the-- see, this is now a function-- becomes a function of S , p , and n . You can compute, as we did, the differential. And it still has entropy. So now, we can take the Legendre transform of this one with respect to entropy, so substitute S with its conjugate, which is T .

It's not always that T is the conjugate of S because previously here you prove, by looking at the differential, that T is also the partial of H with respect to S . So by doing that differential, we found that T , which is from the fundamental relation up there, is the partial of E with respect to S when the other variable is V . I forget the n for the moment.

Now, we also proved-- well, we didn't prove it. But that form of differential says that this is the partial of H . What is it? Partial of H with respect to S when the other variable is p . So I do the Legendre transform of this one. So H minus the slope, which is T times the original variable, independent variable. So that's H minus TS . That's E minus TS plus pV . That's the Gibbs free energy, very important.

And you compute this differential. Yeah, because, you see, by looking at-- by looking at the form of a differential, like this one, and look at the coefficients, it is clear that this that I circled is the partial derivative of F with respect to T when V is the other variable. So from this one, I immediately can see that minus S is the partial of F with respect to T when V is the other variable. And the other says that minus p is the partial of F with respect to V when T is the other variable.

We could also go on. Usually, nobody does this because you're not interested in small systems. But we do it because we are. So if I take the Gibbs free energy and transform with respect to one of the amounts-- so I want to substitute now amounts (I meant, the amount) n_i with its conjugate, which is the chemical potential, the slope because the chemical potential is the partial of G with respect to μ at constant n .

All right, so I have $G - n \mu$, $n \mu_i$. I was short of letters for this game. So since eventually the last one I want to call Euler free energy, and this one maybe could be called osmotic free energy because it plays a role and because some colleagues who are working on nanothermodynamics are beginning to introduce these names. So I just call it $E_{sub i}$.

And if I do this not just for one but for all-- so I keep going until I've exhausted all the constituents-- I have this function that I call the Euler relation-- Euler free energy. It's G , the Gibbs free energy, minus μ times n . If you remember-- yeah?

STUDENT: Oh, sorry.

**GIAN PAOLO
BERETTA:**

STUDENT: Just, I might have missed this. Should the F in the Gibbs free energy row be something else, or is it meant to be F ?

**GIAN PAOLO
BERETTA:**

STUDENT: In the second example row, yeah. F equals $F(T, V, n)$.

**GIAN PAOLO
BERETTA:** Ah. Yeah, this is also probably a cut and paste problem, I guess. Oh, no, no, no. No, no. This is still OK because if you start from the Helmholtz free energy and you transform, you get rid of the volume to get pressure, then you also get the Gibbs free energy because, for the Gibbs free energy, you transform with respect to S and V . And you can do it doing first the S and then the V or first the V and then the S . And you get the same result.

STUDENT: Sorry, I think I was getting confused. So F is Helmholtz free energy.

**GIAN PAOLO
BERETTA:**

STUDENT: Oh, OK. All right. That's what was confusing me because it was also used as the general function, I guess.

**GIAN PAOLO
BERETTA:** Ah, the F up there. You're right. Yeah. Yeah, yeah. It's difficult to find letters. Even if you use the Greek alphabet and so on, there's still not enough.

OK, I wanted to emphasize this one. We'll go back to this one. And I call it Euler because some of you might object, well, but this is 0. And the answer is yes, this will be 0 for the macroscopic systems.

But for microscopic systems, it is not. And that's why I want to give it a name and let it play some role until we introduce the idea of many particles because this-- so in a sense, we will see that, in the limit of many particles, which means negligible wall rarefaction effects because the key will be that, this will turn to 0. Yeah?

STUDENT: Does that apply to the microscopic systems?

**GIAN PAOLO
BERETTA:** This one is not 0. And therefore, it's something that you can measure. It will depend on how many particles you have.

STUDENT: I just mean like for-- because Gibbs-Duhem relation is [INAUDIBLE].

GIAN PAOLO BERETTA: Gibbs-Duhem is in this realm. It starts from the Euler relation. It requires the condition that E_u equals 0. And so you get all those, like the phase rule that comes out of the Gibbs-Duhem relation. That applies in this domain of macroscopic systems.

But here, let's say that it's still a bit open. There is a book by Terrell Hill, *Thermodynamics of Small Systems*, long ago-- I forget now the exact date-- who did care about this thing. But I'm not sure that he went far enough to talk about phase transitions in that domain.

So this is still a pretty open subject. But it's becoming important because of the enormous advances in, I would say, experimental technologies that allow you, with microfluidics or quantum dots and all that stuff, to deal with very small systems, few particles.

Well, math, and math, and math, and math. All right, I told you, when we have a function, we can play as much math as we want forever and ever. So I'm concerned here to tell you only about the useful math. And apparently, also the second derivatives are useful, at least if our project is that of measuring properties because, again, we don't have the entropy meter and we don't have the energy meter. So we have to rely on these tangents to measure properties.

So each one of the functions that we have defined through the Legendre transform has first order derivatives, but also second order derivatives, for which we have the Schwarz theorem of symmetry that says that the order of derivation doesn't matter.

So for example, if I take the second derivative of just the fundamental relation in energy form with respect to S and V , that's equal if I do first S and after V and vice versa. So since the partial of E with respect to V is minus the pressure, this one can also be viewed as minus the derivative of minus the pressure with respect to the entropy when the other variables are V and n .

The right-hand side can be viewed as the partial of E with respect to S . That's T , the temperature. So the partial of the temperature with respect to V at constant-- I mean, when S and n are the other variables. So we get a relation here. This relation is still not fully practical because, yes, it does have measurable properties almost all places except entropy here and entropy there.

Let's do the same game. These are called Maxwell relations, by the way. And there are many. Anything that derives from the Schwarz theorem becomes a Maxwell relation. If you play that on the Helmholtz free energy, here is what we get. This is a bit more practical because, you see, we have just the entropy here. And the rest is easy, measurable stuff-- pressure, volume, temperature.

So that means that if you take your substance and want to know how much the entropy varies with volume at constant temperature, you could measure it indirectly using this relation, by measuring how much-- by taking the substance, increasing the temperature a little bit, seeing how the pressure increases at constant volume. And once you've measured that, you've measured that indirectly. So this is one way to-- it's like an entropy meter. It's an indirect measurement of entropy. You could build an entropy meter based on this relation.

If you do the same with the enthalpy, you get this one-- not very useful because it has S on both sides. It's not easy to keep S constant because keep S constant-- yes, you could do a weight process. And you could make sure that it is reversible. But usually, reversible processes are not easy to do. And often, you have to extrapolate to some zero velocities or some very high velocities, so not easy to make sure that-- to be sure in the lab that your process is reversible.

The last one, if you play the Maxwell relations game on the Gibbs free energy, is also useful. It could also be a basis for an entropy method because it has entropy only on one side. So you can see how the entropy changes as a function of pressure at constant temperature by measuring how the volume changes if you change the temperature at constant pressure.

You can also have Maxwell relations when you take some derivatives, second order-- I mean, second-- yeah, second order derivatives with respect to a pair of variables, of which one is the amount of one constituent. So if I do that, temperature and one constituent, here is the relation.

The derivative of G with respect to n is the chemical potential. So this is the derivative-- is minus the chemical potential. No, sorry. No, it is the chemical potential. Then I moved the minus sign on the other side. So this one is the derivative of μ with respect to T , whereas the derivative of G with respect to T is minus S . And so this is the derivative of S with respect to n . When the other variables are T , p , and the other amounts of constituents.

This is important because, as we do mixtures starting soon, the second part of the course, we will call this the partial entropy of constituent i in the mixture. In the limit of large amounts, the partial entropy contributes to the properties of the mixture in proportion to the amount. So you multiply the amount times the partial entropy, sum up, and you get the entropy for your mixture. That's why it's called partial entropy. This is true only in the limit of Euler going to 0.

You do the same-- instead of T , you do it for the pressure. And you get this other derivative of the chemical potential with respect to p . And this is what we will call the partial volume of the constituent in the mixture. Again, if you take this one, multiply it by the amount, sum over all constituents, that gives you the volume in general, as long as Euler is equal to 0.

You could also take the double derivative with respect to two different amounts of constituents. And you have this sort of reciprocal relation that says that the derivative of potential of constituent 1 with respect to the amount of constituent 2 is equal to the derivative of potential of 2 with respect to the amount of constituent 1. We will use this in one of the proofs related to the Duhem-Margules relation.

Yeah, you could also-- play the same game starting with the relation-- I don't have it. Well, starting not with the fundamental relation in energy form, but in entropy form. And here is the result of the game. Let me skip the details. One of the functions is called the Massieu free energy. It's S minus E over T .

This entropy-- or say, entropic formulation-- becomes more and more important. And so you will find in the literature often if you go-- yeah, people that do small systems or quantum thermodynamics, S minus E over T , you find it a lot. Some of them recognize that this is due to Massieu. Some just call it free something or free entropy.

So this is-- following them-- I'll call it Massieu free entropy, although I think the term might be a bit confusing because I'm not sure what free entropy means. Sometimes, the wrong words are confusing and cause a lot of damage.

So if I do that, I'm sorry about this, but I needed a name because instead of giving it this kind of name, for example, in the book with Professor Gyftopoulos, we were very careful not to use names that were misleading. And so we called them characteristic functions, characteristic stable equilibrium state functions. It's a more aseptic way of defining the same thing.

Planck also has its own. And again, if I do the transform with respect to all the variables, including also the-- yeah, including also all the amounts, I end up with the equivalent of the Euler relation here-- how did I call it-- S_u , which is equal to minus E_u over T .

Notice that also the others are very-- for example, Planck is minus G over T . So it's like a Gibbs free energy divided by the temperature. And Massieu is Helmholtz over T . So they are related. And of course, you can play also the game of double derivatives here.

Well, by the same token, these derivatives are useful if you want to construct an energy meter. The first one, not so much because you have energy on both sides. But this one, yes, I can measure how the energy varies with respect to volume at constant temperature by measuring pressure, temperature, and how the pressure varies as a function of temperature at constant volume.

So you could build an energy meter based on this equation. This one, no, because it has both sides. But the last one, yes, although it's not so simple. You have to realize that you have to here change the temperature of your system and see how the volume will change while you keep p over T constant.

So if you double the temperature, you also have to double the pressure in order to keep that ratio constant. And then you measure how the energy varies with this function of p . All right, so we have ways to measure stuff and, therefore, to characterize the stable equilibrium, stable states of substances.

All right, so now, we go back to one of the characteristic questions for which thermodynamics was born, how much useful things or how much work, now that we've defined it, can we do by exploiting a change of some system from one state to another-- for example, by cooling a hot object.

Or also, what is the minimum amount of work that is necessary in order to obtain a certain change in the state of some system? For example, in material processing, I transform-- I've got a bunch of raw materials coming in. And I want to produce my product, like steel. Steel is a product. You have to put in iron ore and carbon and lots of other stuff, energy. So what's the minimum requirement to produce a unit of your product? That is also the typical question.

We have already seen the answer for the case of a system that varies in-- now, select your system. You want to have a change from A_1 to A_2 , which could be heating or cooling. If it is cooling, it means that you are extracting energy out of your system. And then maybe you want to know how much of that energy can be used in order to lift the weight. So how much is it useful?

Or it could be instead an increase in energy. You want to heat up your system. And then maybe you want to know how much do I need to lower my weight. So what's the minimum lowering? So what's the minimum work I need to spend in order to heat up something?

And here, we do it with a reservoir. If we have a reservoir available, we can do a lot of stuff that we cannot do in an adiabatic or a weight process without the reservoir. So the reservoir plays a role, as we know. So all these questions about maximum and minimum work that can be done, useful stuff that can be done get solved. And this is the basis of all the homework problems that you have in our book, but also in any course in thermodynamics.

You solve these problems by, one, defining the system, choosing a system for which to make an energy balance and an entropy balance. And the choice of your system depends on the question of the problem. The energy balance here is easy. And so it's the difference between the final and the initial energy on the left-hand side must be equal to the net energy input of your system.

So here, since I'm interested in the work done in order to lift the weight-- or maybe, the work received if the weight goes instead down-- the system I'm doing the energy balance for is the composite system, A and R. The entropy balance says the final entropy, which is the sum of the entropies of the two systems, minus the initial entropy must be equal to the entropy exchanged plus the entropy generated within the system.

But since this is a work interaction only, there is no entropy exchange. So there is 0 here. And then there is entropy generation. And then I also have to remember that, at least for the reservoir, I know an easy-- I mean, the fundamental relation is easy enough that I can write it as the equation of a straight line, so a linear relation between the change in energy and the change in entropy, the slope being the temperature of the reservoir.

All right, so now you solve that. So we have three equations. You can use them to eliminate two variables. So let's eliminate the change in energy for the reservoir and the change in entropy for the reservoir. You combine. And this is what you obtain. You are left with one equation, the initial energy of A minus final energy of A minus the temperature of the reservoir times initial entropy of A, minus final entropy of A minus S generated multiplied by TR.

So you could write this as $W_{rev} - TR S_{generated}$ because when S generated is equal to 0, the work corresponds to the reversible process. You could also write this in terms of what we already defined as available energy, so the work done in the reversible case.

So this first part of the right-hand side is equal to the difference of the available energy of system A in the initial state and that in the final state. And this is the formula for the available energy that we have seen just after the definition of entropy. If you go back, you can find that.

OK, there is still another interesting way of writing this, by defining-- We can call it an availability function, another function. I'll call it canonical availability function, just because later we need to define other similar things. And we need the names. But soon, we will get short of letters and names also in this business here.

In any case, we call $\gamma E - TRS$. And notice, therefore, that the available energy is equal to γE minus γR . γR is the evaluation of this function at the state AR, where the system A is in mutual stable equilibrium with the reservoir.

So the available energy is the difference between the availability function at the generic state of your system and the value of that availability function at the mutual equilibrium state with the reservoir. Notice that when I am in equilibrium with the reservoir, the temperature of-- by the conditions for mutual equilibrium-- the temperature of my system, A , is equal to the temperature of the reservoir.

And so this T_R , in that state, is also the temperature of your system. So in that mutual stable equilibrium state, γ_R takes up the value of one of those Legendre transforms that we call the Helmholtz free energy. We called it F . It's E minus TS . But this function is not E minus TS for other states. It's E minus $T_R S$. So it's different.

We can do the representation on the E versus S diagram. So γ is E minus $T_R S$. So let's see. E is this much, from here to here. No, sorry. Let's say that we set this is equal to 0 is here, the origin. So E_1 is this length.

And then I need to subtract T_R times S_1 . So T_R is the slope of this line. So I take a line with a slope equal to T_R starting from the origin. So T_R times S_1 is this segment dashed. So γ is represented by this distance, between this and that, because it's this length minus this length.

This is for the generic state, A_1 . For the state in which the system is in mutual equilibrium with the reservoir, its temperature is T_R , we are here. And that same construction, so the distance from the line with slope T_R originating at the origin, is this much. So this is γ_R .

And now, you may see that this γ_R is the minimum value that that characteristic function can take-- I'm sorry, the availability function can take. Any other state, whether it is stable equilibrium-- so if you go along this curve, either side of A_R , or if you go inside the region of non-equilibrium-- of course, here, we are talking about fixed values of n and V -- the values of γ are greater than γ_R . So γ_R is minimum.

So that means that if I start from here and go anywhere else, I must decrease γ -- I'm sorry, I must increase γ . So I start from state A_R , go to any other state. Then the Δ , so the change in γ , is positive.

That condition gives rules about-- it's the generating inequality for inequalities regarding the second order derivatives. And therefore, they have to do with stability and the concavity or convexity of curves. In particular, this is, in a sense, a review because we already encountered these particular ones. But this is just to give the idea. So I apply this principle that, as I move away from this state, no matter where I go, I always increase γ .

So let me apply it to one particular change. So I decide to go to-- just a small change, a small amount of entropy change, dS , d for infinitesimal. And also, I choose to move along the stable equilibrium state curve. So I'm going this side. But dS could also be negative. So I can go the other side, but along the stable equilibrium state curve.

So if I change the entropy and I move along the stable equilibrium state curve, the energy changes according to the fundamental relation. So I move from E_R to another energy, which is given by the fundamental relation. It's given by this one. And I can use a Taylor series expansion around the original point.

And it's there. Yeah, OK. So the Taylor series expansion has a value, which is equal to A_R , which cancels with that. And I have a first order term, which is the derivative of E with respect to S , which is the temperature, which, at the point where I started, is the temperature T_R times dS plus the second order terms in the Taylor expansion. And remember that here, V and n are fixed. So this, we could call it the second differential of at fixed n and V . So that's ΔE .

Now, I substitute into ΔG to compute-- so ΔG is going to be-- since G is $E - TS$, ΔG is $\Delta E - T\Delta S$. So I substitute. And this $T\Delta S$ cancels with that one. So I'm left with the second order differential only. And since these plus signs, dots, dots must be strictly greater than 0, it requires that this term must be greater than or equal to 0. So that gives us one condition.

I could also have chosen to move to a state in which I instead I change-- I decide how much I change the energy. I still move along the stable equilibrium state curve. But now, I decide the value of dE . Well, then the Taylor series expansion gives me this. And the ΔG becomes minus the second-- Lots of things cancel, as before. And so I'm left with ΔG is minus the second differential of S .

And for this to be greater than 0, it requires that to be-- oops, this is wrong. This should be-- I have to correct that, too. This should be less than or equal to 0. I'll correct it in the slides. So remember when we talked about concavity, we had quickly passed this slide where we took the fundamental relation and took, in full glory, the matrix of second order derivatives, which is the Hessian matrix of the relation.

If you keep fixed some of these variables, it becomes a function of fewer variables. So the Hessian becomes smaller. And if I keep n and V , as we did in the previous thing, fixed, this becomes just-- the Hessian becomes just the second order derivative.

So let's call it the partial Hessian. And what we proved is that d^2S should be-- and here it is correct-- less than or equal to 0. So d^2S is equal to the second derivative times dE squared because here d^2S , in general, is the Hessian matrix that gets multiplied on the left and also on the right by the dE . So you get the dE squared and all the combinations.

This is in general. In the particular case, this is just dE squared. And since it is squared, that simply requires that this derivative be negative. And therefore, we get the concavity of the S versus E relation, which justifies our drawing the E versus S diagram that way.

But for example, recalling that the partial of S with respect to E is $1/T$, this derivative can be written this way because it's the derivative with respect to E of $1/T$. So it's minus $1/T^2$ times derivative of T with respect to E .

And if you go back to what we defined, we called heat capacity at constant volume-- this is just the inverse of C_V . So this second derivative is equal to minus $1/T^2 C_V$. And that requires therefore that C_V -- since it has to be negative, it requires that C_V is greater than or equal to 0. So for your models, if you have a substance with a negative C_V , you are in trouble. You have no substance. You made a mistake.

Also from the other equation that we have-- condition that we have here, d^2E greater than or equal to 0, we can remember that the partial of E with respect to S is the temperature. This is also written, also equal to the partial of T with respect to S , which is greater than 0. And this also is related to the one above. It gives the same practical result.

These inequalities give an interesting-- give rise or are manifestations of a general principle that is called the Le Chatelier or Le Chatelier-Braun theorem or principle that, if we combine it with the idea that we have seen today, that temperature is an escaping tendency for energy, you see what this says.

If, at fixed n and V , I give some energy to my system, it increases its temperature. Well, we all know that. Did we need so many lectures to get to this result? All right. This also says that if you give some entropy, the temperature will increase. But the temperature is the escaping tendency for energy. So that means that if I give energy to my system, in a sense, it reacts by heightening its willingness to give away energy.

So it is as if it counteracts-- it wants to counteract what you're doing. So if you externally heat up the system, you give energy, and then it reacts by shaping things, so as soon as it can, it gives that energy away. So for example, if you start with your system in mutual equilibrium with your thermal reservoir and externally give some energy to your system, it will get off equilibrium, off mutual equilibrium, higher temperature than the reservoir.

That higher temperature will make up a difference in temperature that will drive an energy exchange back to the reservoir. Thereby, your system will try to reestablish equilibrium. So you can see this natural tendency of reestablishing equilibrium here as a theorem that also emerges from the stability conditions and the concavity of the fundamental relation.

The Le Chatelier-Braun theorem, of course, is more general. And we'll see a little more the next time about this. It's not just when you do this with respect to these variables, but also when you do it with respect to many other variables. And also, it has an additional little other twist that we will see when we do two variables. But for today, I think that, yeah, we are done. And we are just in time. So I'll see you next time.