

[SQUEAKING]

[RUSTLING]

[CLICKING]

**GIAN PAOLO BERETTA:** So where do we stand? We've gone a long way, not yet done heat, but we've done temperature. And we introduced this diagram, energy versus entropy, that allows us to represent most of the results that we have discussed so far.

So I want to do a little more with this diagram. Notice that it took us a while to get to temperature because in order to define temperature, we need the state principle and the fundamental relation for the stable equilibrium states. Because it's only for those states that we can define the slope of this curve, which is the temperature.

In other words, states that are inside the region, these are non-stable, in general, non-equilibrium states. There is no temperature defined there. Although, we will see as we go on that we may be able to represent the system as a composite of several smaller systems that are close to equilibrium, so that somehow, we can assign temperatures. That's what we do in fluid mechanics. That's an interesting application of what we're doing.

We have seen that with this diagram, if I have a generic state here and I want to represent what I can do-- the best I can do in a weight process, best in the sense of trying to extract as much energy as possible from our system in such a way that we make something useful, like lifting a weight, the maximum we can do in a weight process is the adiabatic availability of that state, which is represented here by the difference in energy on the vertical line.

And in fact, the final state, when we do this maximum, we have done the process reversibly. Otherwise, you get less. And in a reversible weight process, the entropy remains constant. We've seen that as one of the theorems that we had cited. And so the process that extracts-- the weight process that extracts the adiabatic availability, moves vertically down until you reach the lowest energy state with that entropy. You cannot go below, so you cannot extract more energy because there are no states below that one.

We've discussed the fact that the thermal reservoir has a constant temperature. And you actually had in the homework this discussion to try to reproduce it, the definition of temperature for a reservoir. So for the reservoir, the stable equilibrium state curve is just a straight line.

The allowed states are on the left. Also, reservoirs can have non-equilibrium states. But most of the time, we are interested in their stable equilibrium ones.

And then we also constructed the available energy. And I want to somehow do this again on the blackboard, just so that we can see together this construction. And I'm going to do it in a slightly different way, so that we can-- so, say that this is our system A, and this is its E versus S diagram.

And this time, let's do-- you see in the viewgraph, state A1 is to the left of the final mutual equilibrium state with reservoir R, which is AR. So I'm going to do it just for a change differently. So I assume now that the state is here, A1, and that the final state, when I will reach mutual equilibrium with the reservoir, it's going to be here.

That means that the temperature of the reservoir is this one. Because when they are in mutual equilibrium, the system and the reservoir have the same temperature. We haven't proved that yet, but we will do it, hopefully, today just after this example.

So let me draw below here, also, the E versus S diagram for the reservoir. So you see that in order to go from here-- from this state, to this state, the system must decrease its entropy. Definitely, it cannot do it in a weight process, because in a weight process, the most you can do is keep the entropy constant. But if you're not doing things reversibly, you generate entropy. So you're going to move to the right, not to the left.

So in order to do that, this is the reason why I wanted to-- we can use the reservoir because we are considering-- we are starting the adiabatic availability. The available energy is the adiabatic availability of a composite system in which there is a reservoir. So my initial state is here. I have a reservoir, and what I want to do is lift the weight as much as possible.

So the reservoir is available to do this job. We need to remove entropy from the system. So we can transfer that entropy from system A to the reservoir. So the system must decrease its entropy from  $S_1$  to  $S_R$ .

The reservoir can take it. OK, so the reservoir has a stable equilibrium state with this slope. So it's this. It must take entropy so its entropy will increase. So the initial state will be here,  $R_1$ , and the final state will be here,  $R_2$ . And the entropy of the reservoir will go from  $S_{1R}$  to  $S_1$ , to  $S_{2R}$ .

Now, so you would like to give just entropy to the reservoir. Because, look, so far-- suppose you consider here this is the initial energy of A, and this is the final energy of A. And we call  $\omega_{1R}$  the energy that we transfer to the weight.

So if we could do that process without the need of the reservoir, it would be a weight process for system A. And we would extract this much energy. But we cannot do it in a weight process, because we cannot subtract entropy. We cannot destroy entropy. So we need to transfer it to the reservoir. So we need to give it to the reservoir.

And the reservoir, in order to accept entropy-- you see, we want to move this initial state of the reservoir to the right. But there are no states to the right, because that's the maximum entropy for that value for the energy. You need to give it also some energy. And that energy is the difference between  $E_2$  and  $E_1$  for the reservoir.

So  $E_2$ , you must subtract that. And so you take this segment, and you put it up here, if you want. And it's this much. It's not precise in scale, but this much is that much. So you subtract from this energy difference, this energy difference, and what you are left with is, again, you see from this point to that point. And that's  $\omega_{1R}$ .

Notice that this point is equal to a geometrical construction. It doesn't correspond to a state, because it's below the stable equilibrium state curve. It's just the construction of bringing from-- translating this energy difference into there. So that I subtract it from the segment that represents the difference in energy for the rest.

And then all I have to do is remember that the stable equilibrium state curve for a reservoir is a straight line. So I can rewrite this as  $TR$  times  $S_2R$  minus  $S_1R$ . And then I also remember that the amount of entropy that the reservoir must take is equal to the decrease in entropy that I need for my system. So  $S_2$  minus  $S_1$  is equal to  $S_1A$  minus  $S_2A$ . And so we finally get the expression for the available energy that we have-- we started with, we wanted to represent graphically. OK.

So this brings us to a very important concept for applications, for applications in engineering, where you want to extract, convert energy from systems. And often, the systems you start with are in stable equilibrium states, maybe hot, but still stable equilibrium states.

For example, when you-- in a steam power plant, you just heat up water. You make steam, and that steam is some sort of a high temperature stable equilibrium state. So here is the state. And you would like to extract as much energy as possible. So you would like to go down. But going down on the diagram, it would be an impossibility, I mean, a perpetual motion machine of the second kind. So it's impossible.

In order to go down in energy, you need to subtract also some entropy. But then you need a system that takes up that entropy. And usually, that role is played by the environment, or maybe the nearby river, or lake, or the sea, or the air. That is the system in which you dump the entropy that you must extract from your system.

So it's like you use the environment as an entropy sink. But the environment has its own needs. It does not take entropy for free. It takes entropy only if you give it, also, enough energy so that it can climb in the stable equilibrium state curve.

So that energy that you are giving to the environment in a typical energy systems application is not a waste. Sometimes, you say, well, I'm wasting energy. No, no, it's not waste. You're using the environment for a very important function. You're using the energy there. That's not where the inefficiency of your power plant is. The inefficiencies come from the internal irreversibilities that are in your machinery.

Instead, the role of the reservoir here is important because otherwise, you wouldn't be able to do anything useful. We'll come back to this when I do a quick review of heat engines and exergy stuff in a couple of lectures.

But today, I want to go into some details on how we show that for systems to be in mutual equilibrium, you need equality of temperatures when they can exchange energy. You need equality of pressures when they can exchange volume. You need equality of chemical potentials of the various constituents for those constituents that can be transferred from one system to the other.

And the way we prove this is by means of the maximum entropy principle. You remember that we proved that the stable equilibrium state is the maximum entropy one among those states that have the same energy and amounts and parameters. I'm not going to repeat amounts and parameters. Let's keep them fixed for the entire day.

So how does the proof work? You say, all right, let's start from two systems, A and B, that are in mutual equilibrium. Therefore, the composite system C, this is the E versus S diagram of the composite system of the two. So the composite system is on the stable equilibrium state curve because by definition of mutual equilibrium, it's when the two systems-- the composite, is in stable equilibrium.

So now what we do is, all right, let's construct another state. We'll call it  $C_1$ , with the same energy, but a different state. Being a different state with the same energy, it necessarily has lesser entropy. We have many choices for this other state  $C_1$ . So we are going to choose one that is easy for us in some sense.

So for example, here is my system A. Here is my system B. In the mutual equilibrium state-- so now these are the partial-- the local energy-entropy diagrams. Sometimes I forget to write the ES because I give it for granted, but I shouldn't. So let's say that this is temperature  $T_0$  of system A, and this is temperature  $T_0$  of system B. And we want to prove, so I'll build it in already in this construction, that the two temperatures must be equal.

So I start from for them being in a stable equilibrium state. And then I consider another state, which is this one, with the same energy for the composite, but different for the parts. So let's see.

Let me arbitrarily choose a small amount of energy,  $dE$ , and therefore, assume that my system A-- I'll make it bigger so as to represent it-- has an energy higher by an amount  $dE$ . And B has an energy smaller by the same amount, so that since energy is additive, the total energy remains constant. And therefore, the composite system is still at the same energy.

Plus, I mean, I have many choices on how to do this, but I'm going to choose the easy way, easy for our proof, so that both system A and system B change their energies, but remain in stable equilibrium states. So this is how I construct state  $A_1$  and  $B_1$  so as to make up the composite  $C_1$ .

Since I want to do, also, equality of pressure, I want to prove also that. Think also of the volume that changes. So this becomes a three-dimensional surface. I'm not going to represent it. Otherwise, it gets too messy.

But imagine that in addition to changing the energy, I'm also going to change the volume. So the partition between system A and B is movable. And let's move the partition slightly to the right so that A gains a little volume  $dV$ , and B yields a little volume  $dV$ . OK.

So now we constructed this state  $C_1$ , that has the same energy and also, the same volume for system C. And what we want to make use of is the fact that-- the maximum entropy principle-- so that the entropy of C in state 0 is greater than that in, say, in  $C_1$ . So that I can write it this way.  $S_{1C} - S_{10}$  must be less than 0.

So we start. We want to compute this. And we end up imposing that it must be negative. Then the next steps are simply using the additivity of entropy. So in state initial and final state, the entropy of C is the sum of the entropies of A and B. We just rearrange, so that it's the additivity of the entropy differences.

And then because of our construction, because we selected this particular state that still belongs to the stable equilibrium state curve, we can use a Taylor series expansion of the fundamental relation, which describes this curve, to represent how the entropy changes for the subsystems. You remember-- let's see-- yeah, we had  $S$  for stable equilibrium is a function like that. And if I want to compute the value of-- so this represents this curve.

So if I want to compute the difference of, say,  $S_2 - S_1$ , this being state 1 and this being state 2-- or actually, sorry, let's make it 0 and 1, so  $S_1 - S_0$ . That's what we want. Yeah. I can do a Taylor series expansion around the initial state, the initial point of the function, so around  $E_0$ .

So let me do it only as if it were only a function of energy. So forget about these ones for the moment. So that would be  $S$  of  $E_0$  plus  $S$  prime of  $E_0$  times  $E_1$  minus  $E_0$  plus  $S$  double prime divided by 2, or 2 factorial, whatever-- it's the same-- times  $E_1$  minus  $E_0$  squared plus dot, dot, dot. And the series continues.

And of course, in the limit, as  $E_1$  minus  $E_0$  is small, the dominant terms are the first ones that you find in the expansion. So that's what we are doing here, with the notion that this  $S$  prime is what we call the inverse temperature. And when you do this, also, in terms of the second variable, which is the volume, that's what we call the pressure over temperature.

So here is that expansion for system A. The second derivatives, let me write them as  $d^2$  because it contains several terms. Since I'm doing that in terms of two variables, subsequent slide will have the details. And we'll do the same for system B.

Then we use the fact-- well, then we combine terms. And here is what we get,  $1$  over  $T$  minus  $1$  over  $T$  for A and B times  $dE$ ,  $P$  over  $T$  minus  $P$  over  $T$ , A and B,  $dV$ , plus the second differentials of  $S$  plus dot, dot, dots.

So what can we infer? And this must be a negative, strictly negative. Of course, notice and remember, that when you do a series expansion, the terms here, like this one, are evaluated at the initial state. So they do not depend on how much you move around. So these terms in parentheses, and that term in parentheses, is fixed by the initial state, state 0. It's independent of how you move around to another state. So it's independent of  $dE$  and  $dV$ .

On the other hand, you see here, I could have chosen another state of A with higher energy, but also, one with lower energy. So I could have chosen  $dE$  to be positive or negative, large or small, positive or negative, whatever, as long, of course, B gets the opposite, equal and opposite. So that means that  $dE$  and  $dV$  can be chosen arbitrarily, positive or negative.

And if these terms in parentheses were different than 0, suppose they were positive, then I could choose a positive  $dE$ , and this would be a dominating term in the series, violating the fact that that sum must be negative. So the only possibility, due to the arbitrariness of the choice of  $dV$  and  $dE$  is that these terms in parentheses be equal to 0.

And of course, then the burden to keep the inequality satisfied is going to be shifted to the second order terms in the expansion, which are going to be negative. So, essentially, what we proved here is that in order for that system here to be in a stable equilibrium state, the two temperatures must be equal and also, the two pressures must be equal.

So above here is the same as before. I simply wrote more explicitly the expression for the second order differential, which must be non-positive. So it's either 0 or negative. If it is 0, it's the third order terms and fourth and go on, that must obey, must take up and satisfy this inequality.

For example, see, if I have a reservoir, the second derivative is equal to 0 of the fundamental relation. So for this reservoir, I need that somewhere along the line, there is a derivative which is negative. And since a straight line isn't like that, it means that this straight line in practice is really an approximation.

So in other words, a real reservoir with a true straight line as a stable equilibrium straight curve cannot exist. It would violate this. So the reservoir is an approximation, extremely good approximation if you make it like water at the triple point, with sufficient amount of water. But if you go to small, very small amounts, then you may have difficulties constructing a real reservoir.

So we proved equality of temperature and equality of pressure, and we proved, also, the sign of the second derivatives of the fundamental relation. The reason why I have drawn the  $E$  versus  $S$  diagram this way and not the other way, so with the concavity upward, is now proved here. The second derivative of  $S$  with respect to  $E$  is negative or 0, negative or 0.

The same, you can prove. Since this form, differential form, must be negative for all possible values, you need that it's a quadratic form, and you need that the coefficient, the matrix of coefficients, be positive-- I mean negative definite-- or actually, non-positive definite, meaning that, for example, not only the terms on the diagonal, which are these two, but also, the determinant must be non-negative-- I mean non-positive, which gives us, also, this expression here. OK.

Now, we can do, also, but more quickly the proof for when, instead of putting the movable piston-- I must change this drawing. So this should be replaced with a porous material, non-movable. So this is going to be a porous material that would allow the transfer of constituent  $i$ , so of molecules or atoms of type  $i$ , only one type.

So they are in mutual equilibrium in state 0. And we construct another state with the same energy by shifting some energy from  $A$  to  $B$  and also, some amounts. So I take  $A$  with some more particles of that type and  $B$  with less particles. So it's like moving them from  $B$  to  $A$ .

Well, exactly the same procedure, I'm going to exploit the fact that the entropy of  $S_1$  must be less than that of  $S_0$ . Only that when I do the series expansion for the energy, it's still the same. But now I'm not I'm not changing the volume. I'm changing the amount.

So instead of  $P$  over  $T$ , the partial derivative with respect to amounts is minus the chemical potential over  $T$ . Combine in the same way. And this term by the arbitrariness of our choice of state  $C_1$ , so the amounts  $dn_i$ , the difference are arbitrary, like the energy. And therefore, we find the same conclusion, that these coefficients must be 0.

And of course, also, that second order differential must be non-positive. We prove, therefore, that we need equality of temperature and equality of the chemical potentials of that constituent in the two systems for mutual equilibrium. And we prove some other convexity or concavity relations.

In fact, if you do it for several variables, you end up with the fact that all these second derivatives must be 0. But more than that, this matrix, which is the  $S$  matrix of partial, all the possible second order partial derivatives, must be negative definite or negative semi-definite. And therefore, you can apply all that you know about positive definite matrices, and so on, and obtain a number of inequalities.

For example, from some of these-- one of these inequalities that is well-known is that the specific heat of a substance, which is related to the second derivative of  $S$  with respect to  $E$ , must be positive. But as you see here, that's only one result. You could obtain several.

Now, by the same technique to prove the inequalities, we can also prove another interesting relation, which is known as the Young-Laplace equation for surface tension. So let me do this because it's also useful for those of you who are in fluid mechanics or mechanics of interfaces. For example, take the system which contains a drop-- so  $D$  stands for drops, say-- of one phase immersed or surrounded by another phase.

And there are many examples here. I just put three of them. Let's start with the last one. It could be liquid and vapor, so a drop of liquid, and outside, you've got vapor, like water vapor or a vapor of any substance. Or you could have air on the outside, which is partially dissolved.

Here is a drop of water in which there is some air dissolved. Or if it's not air, like  $\text{CO}_2$  or some other substance. Or you could have two liquids, like oil and water, that are not miscible. So in the bulk of each one, you don't find any of the other.

But in the interfacial region, they must live together, these different molecules. So in this region, the properties of this layer, which is generally very thin, and therefore, these properties of the substance feel the different forces, intermolecular forces, than any of the two bulks. Because here, you have just forces between the same gray molecules. Here, you have just intermolecular forces of the dark molecules. And here, you have some and some.

So they are really different systems. And the fact that the interface is-- or interfacial region is generally very, very thin, allows you to model it. You can model it, of course, in a continuous way. But here, we're going to do it like when you do a Young-Laplace equation. You model it in a much simpler way, as if it was just another very thin system, which can exchange molecules on both sides.

But on the right, it can exchange only dark molecule, on the left, only gray molecules. Whereas, a situation in which you have coexistence of the two can only move along the surface in a 2D geometry. So it's only by moving along this circle here, if it is a spherical geometry, that you can find this coexisting situation.

And it's the same kind of idea when you have phase separation, when the system in order to reach a stable equilibrium, doesn't find the maximum entropy state by remaining homogeneous, but it separates. So molecules like to bump to each other and become a liquid on one side. And on the other side, you've got a water vapor.

The interface, interfacial region, is a very, very thin region in which the density changes drastically. Now, the factor of 1,000 is the density difference between the liquid and the vapor, like, for example, for water. So the density drops in a matter of few-- what is it? Nanometers. It drops by a factor of 1,000.

So if we have a system like that, it's confined on a layer. So its extension is not measured in terms of thickness, but it's only in terms of the surface area where it can develop. So for that system, the parameter of the geometrical container, or let's say, mental container, where those molecules are confined, is not the volume, but it's the surface area. Or if you want, it is still the volume, but the volume can be split in the surface area and a very thin layer.

So area of the surface becomes a parameter for that system, which plays a parallel role of that played by volume for bulk systems. And like we define the partial derivative of fundamental for the stable equilibrium state with respect to volume, we call it  $P$  over  $T$ , for this particular system, the derivative of  $S$  with respect to  $A$ , we call it  $\sigma$  over  $T$ .

And if we invert the function, we see that you can see, for the bulk system, the pressure is minus the derivative of the energy with respect to volume of the energy form of the fundamental relation. And for the interface system, it's  $\sigma$ -- we call it surface tension-- is the partial of the energy with respect to  $A$  without the minus sign. That's why one is a pressure, the other is a tension. OK, so that is for the definition.

So now we can play the same role, the same trick, of applying the maximum entropy principle, to see what happens at mutual equilibrium between those three phases, those three systems,  $B$ ,  $D$ , and the interface  $C$ . And the trick is to construct another state. We call it  $F_1$ . Because now I'm running out of letters.

So  $F$  is the composite system of  $BCD$ . So this overall system is  $F$ . I'm not using letter  $A$ , because now,  $A$  is the area. So that's used up. So we need to construct another state.

And the way we do it is by changing-- we do it in a particular way-- by changing the shape, perturbing the shape of the original drop. And then we proceed in the same way. We want to prove that this thing is negative-- yeah here is the minus, the negative sign.

We apply additivity. We now have three systems. So the one,  $B$  and  $D$ , are like we've done before. But now we have, also, system  $C$ , for which the Taylor series expansion in the first terms in the expansion contain the surface tension. Of course, it's the value, like the pressure evaluated at the stable equilibrium state  $F_0$ .

Here the dots represent many things. I should have written also, but I didn't have space enough on the viewgraph, the derivative with respect to the amounts and the second-order terms. But in order to focus on the interesting part, new part, let me choose a particular situation in which-- this very particular value-- state  $F_1$ , in which I have already satisfied the temperature equality condition.

I already satisfied the chemical potential equality. And so all I am interested in is changing the volume. So that allows us to, essentially, concentrate on these three terms, this one, that one, and that one.

And by getting rid of-- yeah, there shouldn't be  $1/T$  here that disappeared. I have to fix also that on the viewgraph because these temperatures are assumed to be equal. So I'm left with this equation. And this equation has to be negative, strictly negative.

But as we will find out, is that, again, because of the arbitrariness of the choices of the change in the geometry, in the volume, it will turn out to have to be 0. And so the burden for the inequality will be carried by the extra additional terms.

So yes, again, also here, I have to fix the viewgraph. So this is just in order to make room for something else. So now there is an easy way of proceeding here, is assume a geometry. If we assume a geometry, just to see what comes out-- so we assume, for example, spherical geometry of the drop, and we assume that we change the volume. So we consider a perturbed state with a volume slightly increased by an amount.

If  $R$  was the radius of the drop, it becomes  $R + dR$  or  $d\epsilon$ ,  $\epsilon$  to stress the fact that it's small. OK. So the area of the interface of the surface of the sphere is  $4\pi R^2$ . The volume that is-- if I increase this sphere from this solid line to the dashed line, the increase in volume is equal to the surface area times the shift in-- so times  $d\epsilon$ . So that's  $dV$ , and that's what happens to what appears in this part of the equation.



Also, since I am going from small to large, also the area changes. Now, the area changes because the radius has changed. So I go from  $4\pi R^2$  to  $4\pi(R + d\epsilon)^2$ . And if I forget about the  $d\epsilon^2$  because it's small with respect to  $d\epsilon$  put into the others, what I'm left is-- so one of these cancels with that. I'm left with  $8\pi R d\epsilon$ .

And this is the change in area that I put here. Still, the  $d\epsilon$  is arbitrary. So that expression now becomes this expression. And it should be equal to 0-- I mean, negative, for arbitrary values of the  $\epsilon$ . I could have chosen, also,  $d\epsilon$  negative instead of positive, and still that should be satisfied. So essentially, it's just what multiplies  $d\epsilon$  that has to be 0.

So the  $4\pi R$  cancels, and you get this expression here. There is a 2 that emerges from the 8 divided by 4. And so you find that the condition for mutual equilibrium between those three systems is that the pressure inside the drop must be greater than the pressure of the outside by the surface tension multiplied by  $2/R$ .

Now, if you repeat that for a cylindrical shape, we just skip that. But here are the details. You get a similar expression, only with  $1/R$ . But a true story is that we don't know this shape. So we shouldn't, in principle, assume that shape, because in principle, who tells us that the shape should be spherical or geometry or cylindrical?

That is also a result of this maximum entropy principle and the Young-Laplace. It's a bit complicated, so it took me days to construct these pictures. So I'm not going to spend too much time on them. But simply, I assume that you know that if I have a surface in space, I can define principal radii of curvature.

And like in a sphere or in an ellipsoid, you could have the centers of curvature on the same side of the surface. But in a saddle point of your surface, you could have the centers of curvature on the two opposite sides. So for example, suppose this is the drop. In this situation, you have one center of curvature inside the drop and one outside. Whereas here, they are both inside.

But, you see, this is a local picture. If you have an arbitrary shape, if you have a drop of arbitrary shape, like, for example, when you have a drop of water in gravity field, you know this is the shape. So the local curvature and the surface must be represented somehow by running over the entire surface with local variables and integrating.

So in order to calculate the entire area, you have to do an integral of these local areas. So here is a lot of expressions that I hope are correct that allows you-- that describe these geometrical situations, one for the system when the two centers are on the two sides of the surface and one for this, the case in which they are both on the same side.

The difference, you see, locally, the purpose of this formula here is to compute the ratio of the area change to the volume change. As you shift to C, remember that we were talking about this situation. We want to perturb the shape of the drop and go to another state. And we want to compute the volume and the area.

So what is important is the ratio of the area change over the volume change. And that's why here, we compute it for locally. So as I perturb, move the surface, that entails a change in volume,  $\Delta V$ , and a change in surface area,  $\Delta A$ . And this ratio is related to the inverse. It's called the mean local curvature. It's the sum of two contributions, but it is an algebraic sum. Because one of the-- when the radius is on the other side, it has a negative in front.

So if we go back to our picture here and try to compute these areas and these change in volume, we have to integrate somehow over the entire surface. That's why you need a double integral over some variables. So  $\theta_1$  and  $\theta_2$  maybe is a way to describe local angles.

And then if you go on and do all the math, you calculate, again, the change in area, it's, again,  $R + d\epsilon$  and  $R$ . Now it's plus or minus  $d\epsilon$  because when you move the surface on one side, in this case, one radius of curvature increases, and the other decreases by the amount  $d\epsilon$ .

And so in the end, you get a double integral over the surface coordinates. And the  $d\epsilon$ , now you can choose arbitrarily the  $d\epsilon$  at every location in the surface. And that's arbitrary. So that integral must be equal to 0 for arbitrary choices of how you want to distribute the  $d\epsilon$ s. Which says that, therefore, it's the integrand that must be equal to 0.

And so you find that you can rewrite it this way. And you find that therefore, the sum of the inverse of the radii of curvature, so the mean curvature, which, in principle, could be different locally from point to point, must be equal to this ratio of difference in pressure and the surface tension. Which is something that doesn't depend on location of the surface.

So this result means that the average curvature must be uniform, must be equal everywhere on the surface when you are in mutual equilibrium, like in a sphere, like in a cylindrical situation. There are some other interesting surfaces-- if you look up in the Wikipedia, Surfaces of constant mean curvature, you find that somebody has found a very interesting shape where it's more complicated than a sphere, plus, of course-- so this is the main result, the uniformity of the mean curvature. And this is the standard Young-Laplace equation for a surface with the two different radii of curvature.

So now we are ready for the next move. We want to prove the Clausius statement of the Second Law. We want to capitalize now on the fact that systems can exchange energy and entropy. And we would like to consider this particular situation, two systems A and B, initially in stable equilibrium states. For simplicity, for the moment, we just consider fixed volume, fixed amounts. And we want to transfer some energy from one to the other.

The question is, Is it always possible, or when is it possible? Do I need to transfer, also, some entropy in order to make it possible? So that's the question answered by the Clausius-- the inequalities that we will prove right now.

So, look, it's, again, the same story as we started with. If my system A starts in a stable equilibrium state here, and I want to extract the energy so that I give it to system B, I need to go down in energy. But in order to go down in energy, I also need to go down in entropy.

So already from the picture, we see a geometrical proof. We will have viewgraphs that do that more in detail, but also more complicated. But first, let's do it with equations. So how do we model a system? We make energy balances and entropy balances.

And let's consider a small change in-- a small amount of energy transferred. So if I make the energy balance for system A simply says that the rate-- I mean that the change in the energy of A is equal to minus the amount that I gave to B, that I extracted from A. And for system B, its energy change is equal to the amount that it received.

Notice the arrows. The arrows tell you, when these symbols are positive, it means that the flow has been in the direction of the arrow. Entropy balance. The change in the entropy of system A as it goes to the left is equal to two contributions. One is the entropy that has been transferred out of system A, and the other, if any, is the entropy that has been produced by irreversibility within system A, if the process is irreversible. If you do it reversibly, this one isn't there. But if you do it irreversibly, this one, this term, must be greater than 0.

For system B, the entropy balance says that the change in the entropy of B is equal to the entropy that it received from A plus, if any, the entropy that was generated within B by irreversibility. Now, again-- this state A1-  
- Yeah. And we extracted this much energy. I call it  $\delta E_A$  out of A and goes into B.

I do not necessarily have to go to the stable equilibrium state. I could go to any of these states, in principle. Well, maybe I cannot go all that far. But that will depend. Because if I want to go this far, I need a system on the other side. Since I reduce the entropy, I need a system that picks up that entropy. So it has to have the ability to do that.

So at a certain stage, we will see that we cannot go too far to the left. But in any case, these are the possible changes of state of system A. What I know is that the stable equilibrium state for the new value of the energy is the one that has the highest entropy, so again, maximum entropy principle.

So the entropy  $S_2$ , I'll define it. The entropy of state A2, suppose that's this one, is less than the maximum entropy corresponding to that value of the energy, which is the entropy of the stable equilibrium state corresponding to the new value of the energy. So here is the inequality, and here the fundamental relation, for which we can do, as usual, a Taylor series expansion around state 1. It will have a linear term. And let's keep, also, the second order term, plus dots, dots.

So you see this expression. It's  $S_2$ ,  $S_1$ , but  $S_2$  is  $S_1$  plus  $dS$ . So we can take the  $S_1$  on the left-hand side here. It becomes  $dS$ . And here is the rewriting. So  $dS$  is equal to  $dE$  over  $T$  plus the second derivative plus dots, dots, dots.

What do we know about the second derivatives? Well, we just proved that they are negative. So if this is a negative number, and this is a squared number, this thing will subtract. Therefore, this will be less than just  $dE$  over  $T$ .

There is an exception, though. If the system is a reservoir, that second derivative is equal to 0. So here, we would have an equal sign if A is a reservoir. And the same identical treatment goes for system B.

So now we can put these all together. Just to shuffle things around, up to here, it's the same that we've seen so far. Now let me combine those equations. We have 1, 2, 3, 4, 5, 6. And we can eliminate four variables and remain two equations.

I'll let you do the algebra. It's easy enough. And since I want to concentrate on the energy and entropy transfers, so the  $\delta E$  and the  $\delta S$ , these are the variables that I keep. I eliminate the other four, the changes. So this is for system A, from the balances from system A, and this is from system B.

They both contain  $\Delta S$ , so I can combine these two in a single train of inequalities, where  $\Delta S$ , the entropy exchanged, is at the center. And it's less than if I add entropy produced by reversibility. And this must be less than  $\Delta E$ , the energy over  $T_1B$ . And on the other side, this is greater than if I subtract something positive, and it is, in turn, greater than the energy over  $T_1A$ .

So this is interesting by itself because it says-- all right, remember, we started from our two systems in two different stable equilibrium states with different temperatures. So  $T_1A$  and  $T_1B$  are different.

And here, we find that if we forget about-- if you look only at the central and the two extremes of these inequalities, it says that definitely, if you want to have a finite-- I mean, not a finite, but a non-zero transfer of energy from A to B, you need an entropy change, an entropy transfer, with some value that stays within this interval of the energy transfer divided by the two temperatures of the two systems.

So let me do it. So it says, What is it? I could write that inequality this way. Take things on the left-hand side. And am I right if I do this? Yeah. I'm taking this all the way to the other side.

So what does that tell me? If I want  $\Delta E_{AB}$  positive, in other words, if I want to transfer energy from A to B, if this is positive, that has to be negative. If this has to be negative, it means that the second term must be bigger than the first one. So that means that the denominator must be smaller.

So that implies  $T_1A$  greater than  $T_1B$ . Is that what we expected? Yeah. We can transfer energies only in the direction from the hot to the cold. That's Clausius's statement of the Second Law. Of course, if you want this negative, it can do it only in the opposite situation.

So by looking at the two end parts, we proved the Clausius statement of the Second Law, that energy cannot flow spontaneously. And spontaneously is, well, while there are no other external effects. You're considering a system in which this composite A and B is isolated. So, it can only occur from hot to cold, from high temperature to low temperature.

If the two systems initially are at different temperatures, it says that there must be also an entropy transfer between the two. And this entropy transfer must be contained between these two extremes. It doesn't have to have a specific value as long as it is within that interval.

And clearly, if the temperatures are positive, as they are for most systems, that entropy transfer occurs in the same direction as the energy transfer. So the sign of  $\Delta S$ , I mean, if this is positive, temperature is positive. So this is a positive number, and  $\Delta S$  must be greater than a positive number. So it's positive, too. So I need, also, to transfer entropy, which is also the geometrical idea here.

**AUDIENCE:** I have a question.

**PROFESSOR:** Yeah?

**AUDIENCE:** Under the inequalities, what do a  $2A$ ,  $3A$ ,  $1A$ ,  $1B$  means at that?

**PROFESSOR:** Yes. Yeah, let's discuss that. This is just a way to identify the inequalities. Because I'm interested, also, in, When are the strict equalities valid in these various situations? And so I kept track of where they came from. For example,  $1A$  comes from here.

If system A undergoes a reversible process, so that there is no entropy produced in A, this becomes a strict equality. And so here's 1A, so this becomes a strict equality when this is 0; that also for system B.

Then we have 3A-- and I'm sorry, 2A is here. When is the strict equality valid? OK, remember, there is where we did the Taylor series expansion. So if we remain on the curve for the stable equilibrium state, so if state 2 of system A is stable equilibrium, we have strict equality because we are in the maximum entropy state here.

If you, instead, go somewhere inside, then you have an inequality, a strict inequality. So in other words, that inequality measures how distant you are from equilibrium. So that means that if system A ends up in a stable equilibrium state, you have the equality here in 2A, idem for 2B.

3A and 3B are, when do I have equality there? We said it. If we have a reservoir. If we have a reservoir, the second derivatives are 0. And therefore, this is equal. So in order for  $dS_A$  to be strictly equal to  $dE_A$  over  $T_1$ , I need both these inequalities to be strict equality. So I need system A to end in a stable equilibrium state and system A to be a reservoir, idem for B.

Now, it's clear, also, that since these two extreme values are different, if I started from different temperatures, it's impossible that all the strict equalities apply at once. Otherwise, I would have a situation in which one number is equal to a different number.

But for example, suppose system A is a reservoir. And suppose it does end in a stable equilibrium state. And suppose that there is no entropy produced by irreversibility within A. That is enough for this strict equality to apply and that strict equality to apply. So that means that the amount of entropy that is extracted from A is equal to the amount of energy extracted divided by the temperature of A.

And we are converging to the idea of a heat interaction. Because that will be a heat interaction. When the ratio of the energy to the entropy exchange is equal to the temperature of the system that gives the energy.

So if A is a reservoir and ends up in an equilibrium state, then either this one or the other one must not be strictly equal. It cannot be strict equality. So if system B, if you insist that system B also ends in a stable equilibrium state, and maybe it's also a reservoir, so now we are having two reservoirs, it means-- so this one is equal. So it means that this one cannot be equal.

And therefore, it means that you need to generate some entropy by irreversibility in system B, which we can picture this way. Oh, no, sorry, reservoirs. We'll do it here, system A, system B. So just say A and B. And you know what we mean, energy versus entropy.

So if I extract energy from A, it ends up in a stable equilibrium state and no entropy production by irreversibility here. Now, system B must take that same energy. So somehow, I should take a segment of this match.

It receives an entropy, which is equal to this. So it goes here. So the effect of the interaction with A is to transfer this much energy and this much entropy to B. B ends up in a non-equilibrium state. And if you wanted to go to an equilibrium state, it needs to generate this entropy by irreversibility.

So this is a complicated picture. It's another couple of days of playing with PowerPoint. But it does provide a geometrical explanation of this train of inequalities, essentially showing that the entropy change, or actually the entropy transferred is between a minimum and a maximum value that is related to the slopes, the local slopes of the stable equilibrium states of the two systems A and B.

And I think there is, also, an even more complicated one. You see, Clausius's statement. We proved it for infinitesimal amounts of energy transferred. But what about you want to extract a finite amount of energy?

Well, finite amount of energy, again, we can reason this way. I'm starting from system A in state  $A_1$ , and I want to extract this much energy. So as I said, it could go in any of these states. System B starts from here. It receives that energy. And in principle, it can go in any of these states.

So that means that if you give to B this much energy, it is able to accommodate only this much entropy. It cannot go off to the right, because there are no states there. So this is the maximum amount of entropy that we can accommodate. And therefore, that's the maximum amount of entropy that A can decrease.

So that means that somehow, A can only go down to here. And that is the meaning of these constructions. So there is a limited range of possible values. And here is the analytic expression for the Clausius inequality. Let's call it Clausius inequality for this. OK.

We have five minutes. I think it's enough. Oops. No, next, yeah, sorry. I decided that I couldn't get this far. So I don't have viewgraphs anymore. So next time, we'll do work and heat. But let me anticipate the idea.

First of all, we define work as an interaction in which there is no entropy transfer. See that we shifted the order of typical presentation, usually we define-- so here, we are using entropy to define work.

And the other, anything that transfers entropy is a non-work interaction. And if there is an entropy transfer, it's not necessarily always heat. We're going to call heat a very special limiting situation. Essentially, that limiting situation that is captured by this train of inequalities here, when you squeeze the interval in which the entropy transfer values are confined, and you squeeze that interval, it becomes just a single possibility.

Now, how do you squeeze that interval is by having the two systems begin at temperatures close and close. Or actually, in the limit in which the two systems have the same temperature, the entropy transfer has a precise value. It doesn't have any more a range, just a precise single value, which is equal to the energy transferred divided by the temperature of the two systems.

We call it heat. And so energy, we will call it  $Q$ , so  $Q$  over  $T$ . So the entropy transfer will be the heat over the temperature, which I'm sure is the way you have seen probably the definition of entropy in previous courses. So, yeah, I think we can stop here for today.