

[SQUEAKING]

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OK, here we are. Good afternoon. So we have done chemical kinetics. And today, again, with chemical kinetics, we are going to approach the truly non-equilibrium thermodynamics topics, including Onsager relations, that we will introduce today from the chemical kinetics point of view.

So let me remind you of where we were. And also, it will allow us to introduce some new ideas on things that we already know. So consider a single chemical reaction mechanism, which we have learned to represent by this equation here, stoichiometric coefficients and the symbols for the chemical compounds. And this is the way we have written the reaction rates or more precisely, the rates of change of the reaction coordinates.

And just as a reminder, these are the concentrations, stoichiometric coefficients of the forward and backward half reactions. These are the reaction constants, and for the reaction constants, we have developed two equivalent ways of writing them, one in terms of the Arrhenius activation energy and the other in terms of these equilibrium constants of the forward and backward reactions, half reactions.

And of course, the net reaction rate is the difference between the forward and the backward. We define this ratio, and the logarithm of this ratio we call the degree of this equilibrium. And we have seen examples in which this degree of disequilibrium builds up as the chemical dynamics isn't fast enough to catch up and maintain equilibrium, for example, in the nozzle expansions that we have seen.

Now, we can write this difference, also, by using this ratio. In this way, we factor epsilon plus out, and inside remains epsilon minus over epsilon plus, which is  $e$  to the minus the affinity. Or we can factor, also, epsilon dot minus, and this is the equivalent expression. Clearly, this shows that the reaction rates are functions of the affinities of-- each reaction is a function of its own affinity through this exponential, but it is also a function of a bunch of other stuff, which is included in here and in these concentrations. So it is not correct to say that the reaction rates are functions of the affinity, period. They are also function of the affinities.

This is important because in a moment, we will see that you may want to construct other relations between rates and affinities. You can also do the following. You can divide the reaction rate by the affinity of that reaction. And therefore, this would look like-- and if I write  $\epsilon \cdot j$  equals  $L_{jj} Y_j$ , it looks like a linear relation. But it is not linear because the  $L_{jj}$ 's depend on the affinities and depend on a bunch of other stuff.

Nevertheless, this ratio, this  $L$  proportionality constant between-- which constant is not-- between the rate and affinity, can also be viewed as-- if you do a substitution, except for the gas constant at the denominator-- this is the logarithmic mean of the forward and the backward reactions.

Now we are interested in seeing what happens if we are near equilibrium. We know that, at equilibrium, the affinity is equal to 0. So if we approach equilibrium, so the affinity is small, positive or negative, but small, then we can linearize these expressions here,  $e$  to the minus  $x$ . The first linear approximation is  $1 - x$ , or  $e$  to the  $x$  is  $1 + x$ . In either case, these linearizes-- becomes just the affinity.

And so we get an expression like this one, but with the coefficient now being the value at  $Y$  equals 0. In the Taylor series expansion, you have to take the constant terms and evaluate them where you do the expansion about. In this case, it's when the affinity is equal to 0.

And when the affinity is equal to 0, the epsilon plus and minus tend to the same value, which is epsilon 0, the equilibrium value, which is also-- so since they are equal, also their mean, even the logarithmic mean, is equal. And you can also express that if you use this definition down here and what we have done in the previous lectures. You can also connect it to the concentration at equilibrium of the activated complex.

So we've linearized. Now we have a linear relation. And if we substitute this linear relation in the expression for the entropy, rate of change of the entropy, which for a closed system, is also the entropy produced by reversibility. So it has to be greater than 0. You see that it becomes the square--

It's a constant, this  $L$ , times the affinity-- I mean, yes, the affinity squared, or the inverse of  $L$  times the rate squared. This is why we can identify the inverse of this ratio  $L$  as a sort of a chemical resistance to going back to equilibrium. The higher this, it means the lower the  $L$ . And therefore, for a given disequilibrium, because the affinity is disequilibrium, for a given disequilibrium, you have a lesser rate towards equilibrium.

Now, in practice, we have seen, like in this example that we've discussed a few times, hydrogen, the detailed kinetic mechanism contains a lot of chemical reactions. And you need them in order to describe the dynamics. However, you may notice that these reactions are not all independent of one another.

Just for an example, here, if you take the 11 and the 14 reaction and subtract them, it gives you the same result as if you take the first and the third reaction and you subtract them. So they are linearly combined. They are not independent. And there may be-- there are many other linear dependencies here.

So let's go back. So up to here, it's the same slide that we were on a minute ago. This is the new part. So the idea is that now we have a complex chemical detailed scheme or a reaction network. And it contains a lot of linearly-dependent reactions. That means that we can identify a subset of linearly independent ones, with respect to which you can write all the others.

So let's suppose that the stoichiometric coefficients-- now, here, I'm running out of symbols. So instead of new, I'm using this other letter that I wish your Greek colleague was here today, because I forget what the name is. In any case, this is the stoichiometric coefficients of the linearly independent mechanism, with respect to which I can write all the other ones.

So all the other schemes, for example, in the 24 for hydrogen, are linear combinations. So these  $x$ 's are the linear combination coefficients of the independent ones. And due to the linearity of the way the affinities are defined, also, the affinity of the  $j$ -th reaction is the same combination with the same linear coefficients of the affinities of the independent ones.

And so when you substitute these into the expression for the rate of entropy change, which for many reactions is the sum of the products of the rate times the affinity for each reaction, that substitution plus a change of-- a switch of summation symbols and recognizing that this one-- I'm sorry, that this linear combination of the rates is also the rate of the independent reaction, it turns out that this summation, which before had the 24 terms, now has the minimum number of terms, which is the number of independent reactions, their rates and their affinities. It's the same product of a rate and an affinity. That's what we just got.

And above is just a reminder what was the essential of the previous slide. So if we keep going and substitute, again, the expression for the affinities of the  $j$ -th reaction in terms of this other affinity of the independent ones, you come up with this. And therefore, you have a quadratic form in the coefficients of the linear combination that couple and combine the  $L$ 's, so the ratio rate to affinity of the single non-independent reactions.

So this linear combination, if you notice-- not linear, this is a quadratic combination of the  $L$ 's-- If you notice, is symmetric. Because if you change  $k$  and  $\ell$  it doesn't change. So we come up with the fact that the entropy production is a quadratic form in the affinities of the independent reactions.

And the matrix of the quadratic form is non-negative. That's required by the fact that you need that to be non-negative to satisfy the principle of entropy nondecrease. And it is also symmetrical.

You take this matrix and take its inverse. You can rewrite this double summation-- instead of in terms of the quadratic form in the affinities, it's a quadratic form in the rates of the independent reactions, where the coefficients are these. And these  $R$ 's are some sort of generalized resistance.

Now, these independent mechanisms are coupled via these linear combinations. So if you try to write the rate of each one, it is not any longer just dependent on its affinity. It depends also on the others. And this coupling is important and is typical of non-equilibrium behavior.

And we will see more about this because that's a good introduction to what happens in many other phenomena for non-equilibrium. Of course, I mean, so far, we didn't linearize yet. But of course, we can linearize.

Again, we can assume that we go near equilibrium, where all the affinities go to 0. So that's the linearization that we did before. And this is the linear combination of the rates. So the rate of the independent reactions becomes summation, like this. And if you keep going, in the end, you find that it is a summation of those affinities times these generalized inverse resistance. So let's call it the generalized conductivity matrix, symmetric.

And again, the rate of entropy production is a quadratic form either in the affinities or in the rates. This time, it is a real quadratic form. Up here, I was a bit sloppy in saying it is a quadratic form. But these coefficients may also depend on the affinities when you're far from equilibrium. So it's not really a quadratic dependence when you're off equilibrium. Whereas, when you linearize, then it becomes a quadratic form.

And these properties here, since they are evaluated at equilibrium, they are equilibrium properties. So if you want to measure them, for example, in a molecular dynamics simulation, you will have to go and wait for identifying an equilibrium state in order to evaluate this. Which makes it easy because equilibrium is reached quickly because of collisions. And so these are easily measurable properties. Or since we know if we have the full reaction mechanism, like the 25, 24 reactions for hydrogen, then you can infer these values from those rates.

So now let's step back one moment and assume we don't have developed a theory for the reaction rates. And all we know is, from the entropy balance, this expression, which is one of the first that we derived when we did chemical reactions. Because remember that the affinity is the derivative of  $S$  with respect to  $\epsilon$ . So this is simply the rate of change, the derivative of  $S$  with respect to  $t$ , which here is taken to be the entropy produced by reversibility because we are considering the isolated system.

So that is our constraint. It's part of our model with which we like to describe properties, even far from equilibrium, from chemical equilibrium, but assuming a pseudo equilibrium. We also know that at maximum entropy, which is stable equilibrium, chemical equilibrium, the affinities must be equal to 0.

And now suppose that our theory, we want to develop a theory in which the rates are functions of the affinities and nothing else or maybe some other parameters that can be kept constant while you change the affinities. Clearly, when you are at equilibrium, the net rate must be 0. So you want this function to be 0 when the argument is 0. And this argument is a vector. So that's why it's boldface. So this is 0. This is a list of conditions, so that you can substitute that into the expression for the entropy. And you get that the entropy, the rate of change is also a function of the affinity.

Now you linearize, linearize around equilibrium, these postulated constitutive equation, which presumably, should represent our rates. So we do the linear Taylor series. And we will stop at the first term that is on 0.

So the first term is 0. This should be a boldface 0. Then we have plus the first derivative evaluated at 0. This is also another bold and that multiplied by  $Y$ . So this is the linear term plus dot, dot, dots, because, in fact, this is already different from 0.

I'm going to call these partial derivative as  $L$ , our generalized conductivity, the inverse of the resistance matrix. It's a matrix. And it's a matrix that we can also write as the Jacobian matrix of the various rates as functions of the various affinities, big matrix to be evaluated at  $Y$  is equal to 0.

Then you take this expression, substitute it into the expression for the entropy production, and get that the entropy production is a quadratic form in the affinities, with the matrix of the generalized conductivity set to serve as coefficients of that form that requires that, being this, the dominating term in your expansion, this matrix must be non-negative in order to satisfy the principle of entropy nondecrease.

You may also do the linear expansion of this expression here for the entropy with respect to, again, to  $Y$  around the equilibrium. If you do that, so you get the term at equilibrium is 0 because the affinities are 0. You put 0 here. You get 0.

The first derivative of  $S$  dot with respect to  $Y$  at equilibrium is also 0. When you evaluate it, here is the evaluation. See-- you have to take the derivative properly of this expression here with respect to the  $Y$ 's, and it's better to do them with the indexes. Otherwise, you will miss some details.

So it's  $dS$  with respect to  $Y_j$ . it picks up from this summation the  $\epsilon_j$  plus the summation of the  $Y_i$ 's times the derivative of  $\epsilon_i$  with respect to  $Y_j$ . And at equilibrium, the  $\epsilon$ 's are 0. The  $Y$ 's are 0. So this is 0. That is why this first term, the linear term in the entropy disappears, showing that indeed, we are at the maximum or a minimum. The derivative is 0.

And then we go to the second term in the Taylor expansion. So this is the general one. But then you remember that the coefficient has to be evaluated at 0. So you have to evaluate this Hessian of the matrix of the second order coefficients, second order derivatives. And so you take its derivative with respect to  $Y_k$  of this first derivative. So you get the derivative of  $\epsilon_j$  with respect to  $Y_k$ .

Then from the summation corresponding to the  $Y_k$ , you pick up the coefficient that multiplies  $Y_k$  is partial of  $\epsilon_k$  with respect to  $Y_j$ . And then the summation, also has some leftovers, which are the second derivatives of the  $\epsilon$ s.

However, when you evaluate them at equilibrium, these are 0. So the summation disappears. But these ones do not. And notice that this is not equal to that, because the one is derivative of  $j$  with respect to  $k$ . The other is derivative of  $k$  with respect to  $j$ . So, essentially, you are left with this matrix here plus its transpose. When you switch the  $j$  with  $k$ , you get the transpose.

And so clearly, the sum of the matrix plus its transpose is a symmetric matrix, which satisfies the fact that we know like the Schwartz theorem of second derivatives, that they're symmetric. It doesn't depend on the order. So that is OK. So we get the same expression here.

However, in addition to non-negativity, there is an additional constraint that was proved. And we will try to see how we get there as we go on, was proved by Onsager in 1931, for which he got the Nobel Prize in '68. And he used the statistical considerations to show that this matrix needs to be symmetric.

And this symmetry is not a trivial result. It's actually the basis for a number of rationalizations of coupled non-equilibrium phenomena that are used in a variety of applications, of which we will touch a few as we go on and until the end of the course. A few lectures that we are left are going to be all around seeing the consequences of these important result, in addition to seeing how you could prove it.

Now, this is just a reminder of the simple mathematics of when you have a system, like for a 2 by 2 matrix  $L$ , what is the consequence if the matrix is symmetric and positive and positive semi-definite or non-negative. And also, by seeing these more explicitly, we will return to these relations not only for chemistry, like here, but later on, also, we will have coupled effects.

And we will typically take them 2 by 2. Because it's already complicated with two. And going with more, you have to first have understood the two, and then you go to more complicated.

So that's the linear relation. So it says that the rate of reaction 1 is proportional to the-- is partly due to the fact that the reaction one is in disequilibrium,  $\epsilon_1$  (I meant,  $Y_1$ ). But also, it's coupled with the disequilibrium of reaction 2. So in some extreme cases, you might have a reaction 1 that advances not due to its own degree of disequilibrium, but due to the degree of disequilibrium of another reaction.

And you may rewrite this system of equations in various ways. You can solve it. So you can write the affinities as functions of the rates. Or you can do something in between, in which, say, the rate of 1 is given by its own-- a coefficient times its own affinity, plus something that relates it to the rate of the other equation, of the other reaction.

Now, when a matrix is positive semi-definite, it means that the elements on the diagonal are non-negative. It means that the eigenvalues are non-negative. Therefore, also, the product of the eigenvalues, which is the determinant, is non-negative. The sum, which is the trace of the matrix, is non-negative, and so on.

And the rate of entropy production is a quadratic form of this matrix. And the quadratic form is written in general, this way. However, if you write it in this way, you notice that this double product in the middle may not have a definite sign, because the affinities can be positive and negative. So suppose  $Y_1$  is positive and  $Y_2$  is negative. This is negative, and so you have a negative term.

So there are ways, like we did, also, for the LeChatelier Brown theorem, to write a quadratic form in canonical forms either in terms of the affinities or in terms of the rates, so that it's, essentially, a sum of squares multiplied by positive coefficients. And so you make sure that you-- I mean, if you can manage to write it this way, you have proved that you are in shape in terms of non-negativity of the entropy production.

Sorry. So the proof that Onsager gave requires some statistical mechanics. And I might be able to give some hints about it later on. But hopefully, it will be given in some later versions of this course, when Professor Hadjiconstantinou will join in.

But for the moment, let us prove it from this principle of maximum entropy production rate, proposed by Ziegler around 1957, '58, which is simple enough and doesn't contain a lot of physics, except the idea that when a system is in a non-equilibrium state, we already know that it tends to reach equilibrium, developing entropy, until this entropy gets to the maximum allowed by the constraints, for example, the energy, if the system is isolated.

But this is not about the fact that the entropy increases. It's the fact that the system, when it is in non-equilibrium, searches for the path of steepest ascent in the entropy allowed by the constraints. So it's like you need to climb a mountain and go to the maximum of the entropy. And there are many paths that you can choose in order to climb that mountain.

It turns out the systems like to go there in the most direct way as possible. Of course, there are constraints, like the internal structure of your system or the molecules, the collisions, and all that. So here, the idea is the following. What are the constraints for a chemically reacting system?

We'll take as a constraint this equation, which comes from the entropy balance, plus our model for the properties. And then we make an assumption, like we did before, where OK, we want a theory in which the rates are linearly related to the affinities. So you want a linear theory. That means that the entropy production is given by this quadratic form.

And when we take the derivative with respect to the affinity, we have this expression here. Notice  $L_{ij}$  and  $L_{ji}$ , I do not know if they're equal or not. I'm not assuming. I want to prove that if you assume that this rate of entropy production is maximal, subject to that constraint, then we prove the symmetry.

Now, the method for maximizing is simple. We know it. It's the Lagrange multipliers method. We have only one constraint, which is this one. So in order to take the constrained maximum, you take the unconstrained maximum of your function minus the undetermined Lagrange multiplier multiplied by the constraint, written in the form, something is equal to 0. So this is equivalent to that equation set equal to 0. So it's the left-hand side of that equation.

And then all you do is to take the derivative of this with respect to the affinities and set it equal to 0. And so the affinities are in here, in here, and in here. So you get three terms. One is multiplied by 1 and one by minus  $\lambda$ . So  $1 - \lambda$ , the derivative of  $S$  with respect to  $Y$ ,  $S$  dot with respect to  $Y$ , plus this last term, which contributes an  $\epsilon$  dot times  $\lambda$ .

So you set that equal to 0. You get this relation, which says, OK, then if you want to do that maximization, your rates must be equal to  $\lambda - 1$  over  $\lambda$  times this derivative. This is called Ziegler orthogonality principle. And we'll try to interpret that in a while.

For the moment, this is the result in terms of the Lagrange multiplier. Then, as typical in the method, you substitute this back into the constraints in order to find the value for the Lagrange multiplier. So you take this one, substitute it back into the constraint, which is here, and do the things carefully. So when this derivative is written up here, and it has the  $L$ 's plus the transpose of  $L$ -- but now these are multiplied by the  $Y_i$  and  $Y_j$  under a double summation.

If you switch the  $i$ 's and  $j$ 's here, things don't change, because of the double summation. Therefore, this is twice, this double summations here with just one  $L$ . But this double summation written this way is the entropy production rate. So we've got entropy production rate is equal to  $\lambda - 1$  over  $\lambda$  times twice the rate.

So that imposes that this combination must be equal to 1. And therefore,  $\lambda$ , you get it when  $\lambda$  is equal to 2. So we found the Lagrange multiplier,  $\lambda$  is equal to 2. And we can substitute it into the result. And so the result of the maximization is this expression here. The orthogonality coefficient is  $1/2$ .

Finally, we can substitute into here our assumption for  $\epsilon \cdot$ . So this is for the left-hand side, and this is for the right-hand side. And you get these expression.

Then you move things left and right, so to keep the summation of the  $L_{ij}$ 's together and leave the  $L_{ji}$ 's on the other side. And here is the final result, that this summation must be equal to 0. And it has to be equal to 0 wherever your theory applies. That means in any of the non equilibrium states.

So for arbitrary choices of the affinities-- and remember that here, the affinities are many because you have several reactions that are coupled, like we've seen in the example. So among the various choices, you can select one, for example, in which only one of the reactions is off equilibrium, and the others are at equilibrium. That, therefore, picks up only one term in this summation and imposes that the coefficients must be 0. And so that proves the symmetry of the matrix.

So we proved that, at least, you get Onsager symmetry, if you accept the principle of maximum entropy production rate. It's-- I'm not sure you can do it also in reverse. In other words, is this an "if and only if" theorem? I'm not so sure. In other words, does Onsager reciprocity prove that the principle of maximum entropy production rate? Well, I think you'd probably need a little more.

This is Ziegler. And this is a pictorial representation of his orthogonality relation. So suppose we have two reactions. And this plot wants to represent on a plane the affinities. So for example, suppose you are in this point here. It represents a non-equilibrium state in which the affinity of reaction 1 is this much. The center is 0, and that's equilibrium. And the affinity of the second reaction is this much.

Here, the rate of entropy production, so the quadratic form, has a certain value different than zero. And these contour plots represent all other non-equilibrium states that have that same value of the entropy (production). As you move further from equilibrium, the entropy (production) goes up. As you move towards equilibrium, the entropy (production) goes down. So you may think of those contour lines as those of an ellipsoid that is touching 0 at equilibrium.

The red curves represent the gradients of these contours. So these curves are everywhere orthogonal to the constant entropy (production) contour lines. The expression for the gradient, the gradient is like a generalized derivative. So the derivative of  $S$  dot with respect to  $Y$  vector, this is the gradient.

And if I plot the gradient, it is a vector which is orthogonal. And I plot it here. So it's orthogonal to the (contour) curve for which it is the gradient.

Now, what the Ziegler principle orthogonality relation says is that you take this vector, which is the gradient, take half of it, and that gives me the rate vector. The epsilon dot is the rate vector, is just a half of-- the red is a half of the black. And this vector here, let me now, the last step, move it back to here, to the 0.

So then on the same plot, I am now reading on this axis, the one component. So that is the rate of the first reaction and on this other axis, the second component. So that's the rate of the second reaction.

And what this shows is that if you had only one reaction and one affinity, the proportionality is typically that the rate and the affinity have the same sign. So if  $Y$  is positive, epsilon (dot) 1 is positive. And the relation is, like this system here, but instead of having 2 by 2, it's just 1 by 1. It's simply the proportionality  $L_{11}$  is the direct proportionality. And it says that the rate of 1 is proportional to the affinity of 1.

And also, if you had only 2, reaction 2, the rate of reaction 2 is proportional to its degree of disequilibrium, same sign. Because we said that these  $L$ 's are positive. But here, you see, the coupling makes it so-- so the cross-- off diagonal terms-- makes it so, in this particular region of states, that-- look at reaction 2. It has a positive affinity, but as a result of the coupling, it gets a negative reaction rate.

So these off-diagonal terms may actually drive the system in a somewhat unexpected direction, something that if it were by itself, would violate the entropy non-decrease principle. Because if I didn't have, also the other terms and only this one, so if I have only one reaction, it is impossible that the rate be in the opposite sign of the affinity.

So that is, at least in the business of reactions, chemical reactions, the importance of this coupling terms. And it is, actually, for things like these, for many aspects of this chemistry off equilibrium, that also Ilya Prigogine has gotten a Nobel Prize-- I forget now what year.

But I want to-- just that I mentioned him, I want to also mention that if you're doing your PhD thesis in the field of thermodynamics, whatever field of thermodynamics, make sure you apply for the Ilya Prigogine prize for thermodynamics, which is held every two years. And it's a prestigious thing. It doesn't bring a lot of money, but it gives you some prestige. And you may look up the website of the prize and see what the previous winners are, very diverse and very high level set of guys, most of which are now renowned professors worldwide. Because it's an international prize.



So let's do a little switch. First of all, it sounds like a switch back, and then it will be a switch forward. So let's go back to heat transfer. And this is a slide that, more or less, we've already seen, maybe not exactly in this fashion.

You take a one-dimensional fluid element subject to a gradient of temperature. So it's a fluid element. On one side, there's one temperature. So there's a heat interaction at one temperature with the fluid element on its left and another heat interaction at a different temperature, slightly different temperature, with the element on the right. And for the moment, let's assume that this is in a steady state.

So let's do the energy balance. And we do the energy balance per unit of area of the surface of interaction between these adjacent elements. So 0, because we are at steady state, so there is no accumulation of energy. Otherwise, here it would be the derivative of the energy per unit volume with respect to time. But it's 0 because we are assuming steady state, is equal to the heat flux.

I'm using here the notation of heat transfer. So  $q''$  is the typical notation for heat transfer. And then we have heat flux at  $x + dx$ . So you may recognize this is the incremental-- the increment of the function  $q''$  as a function of  $x$ . So this is the partial of  $q''$  with respect to  $x$  times  $dx$ . And it is equal to 0.

And then we do the entropy balance. Remember, we are doing the balance for this element in the center. So here, we have to account for-- here, I've multiplied by  $A$ . So we have to account for the entropy coming in from the left, which is  $q \cdot / T$ . And  $q''$  is  $q \cdot / A$ , is the flux, so is the heat rate per unit area, minus the entropy that goes out on the other side.

And this is  $q''$  divided by the temperature, which prevails there, which is different, slightly but different, and then plus the entropy produced by irreversibility. So here, I'm denoting this lowercase  $s$  with the triple prime is entropy generated by irreversibility per unit volume. And the dot is the rate, so-- Soon we will go, actually, over here. We'll give a special symbol for that.

So from now on, when you see  $\sigma$ , it's not the stress tensor. It's not the surface tension. It's the rate of entropy production per unit volume. Sometimes, different fields use the same symbol for different purposes. But there is only one Greek alphabet.

So from this one, if you do properly this-- you recognize the incremental ratio  $T_{x+dx} - T_x$  divided by  $dx$ , that's the derivative of  $T$  with respect to  $x$ . In the denominator, here you can neglect the difference of-- so this denominator, you can simply call it  $T^2$ . That's why the approximate symbol.

So we like to write this as-- so the entropy production rate, you like to write it as the heat flux times this gradient of the inverse temperature. This is analogous, and this is why we are doing it now. It's analogous to the chemical idea that entropy production rates are given by a product of a reaction rate times an affinity.

If you interpret this gradient of the inverse temperature as the affinity or the degree of disequilibrium with respect to heat transfer, then you have a similar concept. And we have already discussed this in a previous lecture, so I will not do it now. But I simply remind you that this part of the slide was to show that you cannot be at equilibrium if this is different from 0. And therefore, when we actually adopt a local equilibrium model for our fluid element, we are neglecting this difference.

And you will see-- hopefully, today, we will see what accounting for that difference makes and how things change if you do account for that. But for the moment, if you want to, just go back to that previous lecture to find more discussion about this graph.

What we may also add is the following. Now, this fluid element in the middle of two things that are at different temperatures, although minute differences, could be, in principle-- you see, that heat transfer, direct, with no useful effect, is dissipated. And in fact, you have entropy produced by irreversibility. And we have learned that whenever you have entropy produced by irreversibility, if you can avoid that entropy production, you can do something useful with it.

So here, what you would need to do is to replace your fluid element by a small heat engine, a local something, maybe bacteria-- because here, it may be a small system-- in any case, a heat engine that while exploiting this temperature difference, extracts some work, like a Carnot engine.

We have learned that in order to compute the maximum work, you have to do energy balance and entropy balance. And you have to assume that the entropy produced by irreversibility is equal to 0. If you do that-- so you start from the entropy balance and impose that the entropy that goes out here is equal to the entropy that comes in, that gives you one relation. Then if you substitute it back into the energy balance, it gives you that maximum work.

And of course, the answer, we could have done it even without redoing the energy and entropy balance. The answer is that the maximum work you extract there is equal to the temperature that prevails around there, more or less it's the same, so  $T$ , times the entropy-- times  $\sigma$ -- times the entropy that you would have produced by irreversibility if you didn't do that work. So you get these relations here.

If your fluid element is three dimensional instead of-- here, we've discussed a one-dimensional case. But you can make it also three dimensional. So you have a nice fluid element of the kind that you consider in 3D heat transfer. Then of course, you have to account for exchanges of heat. The heat flux is a vector that has the three components.

And the equivalent of the energy balance here, this derivative of  $q$  with respect to  $x$ , is equal to 0, becomes the divergence of the vector  $q$  double prime is equal to 0. Or in this other problem, it becomes the divergence of  $q$  over  $T$ , of the vector  $q$  over  $T$ , which is the entropy flux, is equal to 0. And this expression for the entropy production rate per unit volume, from this which is just the  $x$  component of the heat flux times the  $x$  component of the gradient in  $1$  over  $T$ , it becomes the dot product, the scalar product of the heat flux into the gradient of  $1$  over  $T$ , which is a vector.

So this is why I like to put the underline under the nabla symbol because nabla is a vector operator like  $q$ . I'm sure you are familiar with that. So nabla is this operator here. It's a vector which has as components the partial derivative symbols.

So we have seen the analogy in the structure for the rate of entropy production with the chemical formalism, affinity times rate, affinity times rate, the rate of heat exchange. And so the affinity is the gradient in the temperature. So let's do the same procedure.

Let us assume, like we did, that the epsilon dot is a function of the affinity, with the function being 0 at equilibrium. Let's assume the same here. So let's assume that the heat flux vector is a function of the gradient of the inverse temperature. And it is equal to 0 if there is no gradient. Because we know that if the temperature profile is flat, and there's no gradient, there is no heat flux.

And we linearize this expression here, like we did here. So you take this derivative. And so the derivative of a vector with respect to another vector becomes a tensor. We call it  $L$  double underline. That's for a tensor. And so you're linearizing in gradient of  $1/T$ . So that multiplies gradient of  $1/T$ .

And of course, this tensor is to be evaluated at equilibrium. So this is an equilibrium property. You would evaluate this when there is no gradient, so when the temperature is flat.

Well, if you call that  $L$   $k$  tensor times  $T$  squared, you obtain the Fourier's law of thermal conduction, on which most of the heat transfer is based. So this is a fundamental step. Then from this, you construct all the applications.

Notice that  $k$  is a tensor, first of all. And only in some special cases, that tensor is isotropic. So you need only one variable to represent it.

And so for an isotropic material, then you can write that  $q$  double prime-- I'm sorry,  $q$  double prime is equal to minus  $k$  gradient of  $T$ . That's because, of course, the gradient of  $1/T$  is equal to minus  $1/T$  squared times the gradient of  $T$ .

So that is the standard Fourier law of proportionality (between) heat and (gradient of temperature) that says that the heat flux is indeed in the direction of the vector gradient. And that's true for an isotropic material.

But for an anisotropic material, you may have that the gradient is in one direction, and the heat flux is in another direction. For example, here, suppose you have a two-dimensional problem in which you have a two-dimensional anisotropic material. So the two dimensional means that whatever-- that nothing changes with the  $z$  direction, neither the temperature, nor the heat flux, nor the boundary conditions. In that case, every partial derivative with respect to  $z$  is equal to 0. That's condition for 2D symmetry.

So for example, the temperature field depends only on  $x$  and  $y$ . That's to simplify. And here, so this is the expression. The Fourier law becomes this linear expression here. And how do you build non-isotropic materials? For example, by sandwiching layers of different materials. For example, you could have a highly conductive layer of a material like carbon sheet sandwiched between an epoxy or some other material with low conductivity. That makes the anisotropy.

So these are the equations. Let's see how you would-- so in order to characterize this material, you don't just have one thermal conductivity. You need to measure three parameters. But actually, there are four entries in the matrix.

But thanks to Onsager principle, the off-diagonal ones must be equal because of his reciprocity, general reciprocity theorem, which applies also in this business. And therefore, you need only to measure three. And here are the three measurements that you could make.

You cut the sample of your material thin in the  $x$  direction, and assume that things in the  $y$  direction do not change, or set up an experiment in which they don't change. And then so that you are set up to use the first equation here, with no component of the gradient in temperature in the  $y$  direction. This is 0, and you have only this direct relation.

So you measure the heat flux. You measure the gradient in temperature across the small thickness of your sample. And you take that ratio. And so this ratio gives you the conductivity, the  $xx$  component of the conductivity tensor. That must be positive because this tensor is an Onsager matrix. So it needs to be positive semi-definite.

Do the same for the  $y$  direction, and you measure  $k_{yy}$ . Now, to measure the off-diagonal terms, one way is to put your sample. You squeeze it between insulating materials in the two faces in the  $y$  direction, with the normal in the  $y$  direction. So this is an insulation. This is an insulation. And you subject your sample to a gradient in temperature in the  $x$  direction.

Now, since the insulating material-- since this wall is insulated, the heat flux component in the  $y$  direction here is 0. And also, here is 0. So you can assume that it is 0, also, not really precise-- but that it is 0, also, in between because this is supposed to be a small thickness of your sample.

However, in spite of that, so there is no heat flux in the vertical direction. Yet, you're going to build up a gradient in temperature in that direction. Because of this equation here, which is rewritten here, the insulation sets this equal to 0 and therefore, makes these two terms equal to one another, I mean, equal and opposite to one another.

So by measuring the gradient in temperature that builds up in the  $y$  direction and dividing it by the imposed gradient in temperature in the  $x$  direction, you get this ratio of the off-diagonal coefficient versus the direct coefficient. And in fact, you notice that in this case, the  $x$  direction component of the heat flux  $q'_x$  is less than it was in this other example, in these other situation. Because you see there is still proportionality between the flux and the imposed gradient in the  $x$  direction, but the coefficient of proportionality is smaller.

Physically, you can realize that this sandwich makes it so that the heat flux finds it easier to run through the high conductivity layers. And since those layers are inclined, as hinted by these inclined lines here, the heat flux enters here. But it likes to go up, following the high conductivity materials. That's why you build up temperature gradient in the direction where there is no net heat flux.

So this is also called Righi-Leduc effect, which was discovered before Onsager theorem. Many of the things that are rationalized by the Onsager reciprocity theorem were actually discovered independently-- and sometimes, not even connected to one another-- by various researchers in the 19th century. And it's only later on that you could connect them. And so somehow, you had four different effects that, thanks to Onsager, were related and become only three independent ones.

And notice also that, for example, using this idea, you can construct a sensor, a non-disturbing heat flux sensor, because in here, by putting the thermocouples across the sample, which are off the way where the heat flux goes, by measuring this temperature difference, you measure the heat flux. And therefore, you don't have to put thermocouples in the way of a small sample, because typically, if you put the thermocouple, that will disturb the measurement because the thermocouple has its own size. And therefore, it alters the actual situation.

Of course, in the Fourier equation of the complete energy balance for a continuum with no motion, no velocity, so not a gas or a fluid, but, say, a solid or maybe a static fluid, this is the equation. And if you have, for example, a gas-- OK, this  $u$ ,  $\rho u$  is the-- OK, let's say that  $\rho u$  is the energy per unit volume. So you could write it as  $m$  over  $V$  times  $U$  over  $m$ .

And so by seeing that, you see this is  $\rho$ . And this is  $u$ . Here, I'm using  $u$  without the star, the asterisk. But that's the energy per unit mass, the specific energy per unit mass. And for example, for a gas, that would be  $\rho c_v$  times  $T$ . Or at least, the derivative with respect to time of  $\rho u$  can be written as this derivative here.

And if the density is constant, and the specific heat is constant, it goes out of the derivative, and you get only  $\rho c_v dT$  over  $dt$  minus the gradient (I meant, the divergence) of  $q$ --  $q$  is-- the Fourier equation, if you have an isotropic material, if it is-- OK, let's keep it isotropic just for simplicity.

So I have to substitute here, minus  $k$  times the gradient of  $T$ . So that makes it, if  $k$ -- this requires that  $k$  be independent of space-- of temperature. So if  $k$  is a constant, it goes out of this. Otherwise, you have to keep it inside.

So if  $k$  is constant-- because the conductivity of materials does change with temperature. So this step may not be always allowed, but if you do that, this becomes the Laplacian of the temperature. Because the gradient dotted into the gradient gives the Laplacian operator.

If you dot this vector into another vector equal to itself, the dot product gives you the products of the components of the vectors. And so here, you have the partial of  $x$  times another partial of  $x$ . So that's the second derivative with respect to  $x$  twice. And those are the various ingredients, the three that represent the Laplacian.

In any case, this is the equation of Fourier, the Fourier energy balance. If you have a non-isotropic material, there is an interesting change of coordinates. And we've seen that the heat flux and the gradient in temperature are not in the same direction.

And there is a change of coordinates that you can do. So define non-orthogonal coordinates instead of the usual orthogonal  $x$  and  $y$ , the small  $x$  and  $y$ . You can define capital  $X$  and  $Y$ .

Here, actually, this is wrong. There is no equal sign here. This is just the multiplication. So that's the linear combination of the original coordinates to give these coordinates, which are at a certain angle between one another. And if you write it that way, then the equation, the Laplacian in terms of the new coordinates becomes like that for a uniform material.

And where  $k$  is equal, the effective conductivity, uniform conductivity, is equal to this linear combination of the various terms. So this is the square root of the determinant of the conductivity tensor. And also, the heat flux vector in the original coordinates, it becomes a linear combination. Also here, I have to correct this. It shouldn't be an equal sign, just a multiplication sign.

And it gives the flux components in this new non-orthogonal coordinates. And they are related through that conductivity directly. So there are no off-diagonal terms. So this is just a useful change of coordinates.

But there is one last item that I wanted-- I promised I would discuss, which has to do with this problem, that if you are dealing with a heat transfer, there is this conundrum of the fact that the entropy-- that you cannot be at equilibrium. And in fact, so the entropy of your sample, of your material, is off the equilibrium. So assigning it the equilibrium entropy introduces an error.

And it's interesting to see how you now solve that problem by assuming, instead-- assigning to the fluid element or continuum element, not the equilibrium entropy, but an entropy which is less than equilibrium. And it departs from equilibrium more the higher the heat transfer. So you make it through a proportionality constant, which I, for convenience, call  $b$  over  $2$ , proportional to the modulus of the square of the heat transfer.

So clearly, if you're at equilibrium, there is no heat transfer. And this difference-- so the entropy is that of equilibrium. But the higher the heat transfer, the farther you are from equilibrium.

So if I take the differential of this one, it gives me the differential of the equilibrium state plus the differential of that, which is-- so the  $2$  goes away. It's  $b \dot{q}$  plus--  $q \dot{dq}$  plus  $dq \dot{q}$ . So it's twice  $q \dot{dq}$ .

Now, this is important because if we do the entropy balance, like we wrote the energy balance here, we should write also the entropy balance. And that is given by the divergence of the entropy flux, which is  $q$  over  $T$ , plus the rate of entropy production per unit volume, which is  $\sigma$ .

Now, usually, these two are related through the Gibbs relation. The Gibbs relation you can write it as  $d\rho s$  equals  $1/T$   $d$  of  $\rho u$ . And the reason I like to write it in terms of entropy per unit volume is that in this way, from the Gibbs relation-- we'll see more later about this-- the pressure disappears. The pressure is always a bit problematic to treat. So if you find a way that it disappears, it's better.

So if this is true for the differential, it means all possible changes in all directions. It's true, also, if you take the derivative with respect to time. So just move only with respect to time. So this can also be written as partial with respect to  $t$ , and it's  $1/T$  times the partial with respect to  $t$  of  $\rho u$ .

And this is shorthand for the partial derivative with respect to time. And so the Gibbs relation couples the energy and the entropy balance. And so in that way, this is actually what I just wrote. Yes, I should-- this is true. Because the Gibbs relation is valid for equilibrium. So this is true for the  $e$ , for the equilibrium entropy  $s_{sub e}$ , or  $s_{sub SES}$  stable equilibrium state. Here, I should just unify the notation.

Anyway, so if you do this substitution, you can obtain the expression for the entropy production, which is the product of the heat flux, times this thing-- so this is not only the gradient in  $1/T$ , but there is also  $b$  times the derivative with respect to  $t$  of  $q$ , which comes from here. So this term in square brackets is now the affinity.

So the affinity changes, the expression for the affinity has changed. And if we assume a linear relation between flux and affinity through a positive constant  $L$ , what we obtain is a correction to the Fourier's law of conduction, which was proposed by Cattaneo, which gives rise to the Cattaneo heat equation, 1948.

Cattaneo didn't start from these premises. He wanted to fix another problem that I'm describing in a second. But so let's take this one and then substitute back into the energy balance equation. So we have an expression for  $q$  double prime. You can take the divergence of that, and that gives you this term, which is like typical Fourier.

But also, it's the gradient, I mean, the divergence of the partial derivative with respect to  $t$  and the divergence of this contribution. You can switch the partial derivative with respect to time with the partial derivatives with respect to space. And so this also appears. And again, using the energy balance, this is the partial with respect to time of  $\rho u$ .

So you have the double partial with respect to time, which if you then substitute this expression for the specific heats and the density then can be rewritten in this way. So in other words, you obtain an equation with double-- second derivative with respect to time of the temperature, first derivative with respect to time, and then the usual Laplacian.

If you didn't have that term, you would have the standard Fourier equation. But with that term, things change, and it becomes a damped wave equation. And it actually fixes a problem. I'm sure you're familiar with this problem from heat transfer, in which you have a semi-infinite solid, which is initially at a certain temperature  $T_0$ .

And at time equals 0, you suddenly change and keep, from then on, the temperature here on the surface. As a result, you obtain temperature profiles that look like that, given by the error function distribution. And as time goes on, the distribution goes like that, so as time proceeds.

But what is the problem? The nonphysical problem is that already starting from time 0 plus, when the error function sets on, it turns out that since the error function is non-zero everywhere, it turns out that-- may be minute-- but you still have an infinite propagation rate of what you have done here, which is unphysical, because there is no infinite-- if you do something here now, it is unphysical to think that it is felt immediately at infinite distance.

So the Cattaneo equation solves this problem. And in fact, this equation has been used to represent the early times of this sharp change of temperature problem or situations in which you will change the boundary conditions very quickly and therefore, you need to account for a propagation speed, which is this coefficient here becomes now the wave celerity. And the gamma becomes the damping coefficient. So time is up, and I think we should stop here for today.