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**GIAN PAOLO
BERETTA:**

Good afternoon. OK, so the last time, we defined diffusive and convective fluxes. I want to review this definition with some graphics. The idea is that we have a continuum with all the assumptions that go under this description.

And suppose that anywhere, somewhere inside your continuum, you set up a small surface area with an oriented normal, $\mathbf{n}$. And then you look at what properties-- and here we are talking about the extensive properties, those that we said that can be described as integrals over volume of densities of that property like energy, entropy, mass, momentum.

So this is how much of that property crosses that area and with which speed. So how much it transfers, it goes across, divided by the area of this surface that we call $d\Omega$ and divided by the time interval during which we measure the amount that crosses. That defines the flux.

So let's consider first the flux, the measurement, in terms of the reference frame of the laboratory. And that we call it J_0 . I also call it Lagrangian, but maybe the term Lagrangian is not really appropriate. But in any case, it's the flux with respect to the laboratory reference frame.

And once I have done that and I know the density, which means the property per unit volume that prevails in that position, that defines also a velocity, which is the velocity of transport of that property which is this vector here. So multiply-- I'm sorry-- the long vector is the flux. The short vector is the velocity.

One of the properties is mass. So if I do that same measurement for mass, I get the flux of mass which is what we call momentum, momentum density. And the velocity associated with that flux, we call it barycentric velocity of the flow. It's the velocity of fluid mechanics.

Then we define also a-- for property A, we go back to property A, and we define a relative velocity. So the difference between $\mathbf{v}_A$ and the velocity with which the fluid parcels cross that surface, which is the barycentric velocity. So the difference you compute, since these are vectors this way, like the typical vector construction. So this blue vector is the difference between the two.

It's the relative velocity. It's the velocity of transport of property A relative to the barycentric velocity. And then you multiply by the same factor that goes between the short and the long vector here. So the density of property A, and that gives you the diffusive flux of property A. The difference between J_0 and the diffusive flux, is the convective flux, which is this vector, red vector, which, of course, by construction is directed in the same direction as the barycentric velocity.

And so you can take it also as the barycentric velocity times the density of property A. So it's this vector here. Then we have defined this extension or generalization of the idea of a heat interaction to when-- in the same way as we did heat, we approached the interactions between systems that are almost in mutual equilibrium, so exactly or almost exactly the same temperature and the same chemical potentials.

And they exchange not only energy but also amounts of constituents. And the relation Q/T for heat generalizes to this relation between the flux of entropy, the flux of energy, the flux of constituents. Here we are introducing also these variables that are shorthand. And instead of carrying all the times one over the temperature, we just call it τ , which I know it's a bit unfortunate nomenclature because then we will use τ double underline also for the stress tensor.

But that double underline will keep the difference. And also λ_j denotes minus the potential over T . So we use λ or λ_{tot} for the chemical potential or the total potential. And so the relation between energy, entropy, and n can be written this way. So once we have this relation between vectors, we are going to use it, for example, in the balance equations where there is a divergence of the fluxes.

Well, we can take the divergence of these, and that's how it goes. It's typically a product. So the divergence of a product of a scalar times a vector is given by these two terms. The gradient of the scalar dotted into the vector times the scalar times the divergence of the vector.

Now, remember that energy in our model has several components. One is the internal energy, proper of the stable equilibrium state that is underlying, that is there. That would be the only thing if we view our fluid element from a reference frame that moves with the barycentric velocity, and therefore, with respect to that reference frame, there is no kinetic energy. And also an accelerated frame where you don't also see the potential gravitational energy.

And then here you have the additional contribution for the electrostatic energy. And if you multiply this by ρ -- and I put all the stars just to be pedantic, but at least we know what we're talking about. We get this expression here.

The total potential, therefore, is defined this way. It's the derivative of E with respect to n , is given by these contributions to the chemical potential plus this potential for kinetic, gravitational, and electrostatic potentials. So this is where we were, I guess. And, of course, the next step is to substitute these assumptions about the interactions between fluid elements into the energy, entropy, and constituent balance.

And here, I've also done, although I'm not going to talk too much about it, but I've also written the momentum balance, that bases the fluid mechanics part, for reference. And as you remember, I have written the balance equation in the two equivalent forms that we have derived. One in terms of the Lagrangian fluxes with the partial derivative of ρe with respect to time, the other with respect to the diffusive fluxes with the material derivative of the mass specific properties.

We proved the last time that these are equivalent. From these equations here and possibly-- well, no. From these equations here, you can obtain also these other equations below that, I am skipping the details. But it's simply, for example, the equation for the conservation of mass which derives from this one of the amounts multiplied by the molecular masses.

This is the so-called continuity equation of fluid mechanics which you can also write this way. And so this is the divergence of v represents the rate of change of the volume of your fluid element as you follow it during the motion, during the flow along its path. And typically, unless the flow is very speedy and unless the Mach number is high, you can assume incompressible flow. And so this divergence is equal to zero.

But, for example, from the momentum balance equation, if you dot it into $\mathbf{v}$, the velocity, you can obtain a balance for the kinetic energy. And then you can also get a balance for the gravitational potential energy and a balance for the electrostatic potential energy, so that you can subtract from the overall energy of your fluid the internal energy. And so that difference is made up of just kinetic, potential, gravitational, and electrostatic.

So the sum of these three gives you this. And it's the rate of change of the mechanical energy content of your fluid. And now we can put them all together. So we have assumed the local simple system equilibrium so that we can write the energy this way that we just described.

The simple system model includes the Euler relations so that together, it allows you to write the Gibbs relation in this way-- remember, τ is $1/T$, and λ is $-\mu/T$ -- which, as you recall, gets rid of the pressure. So that if you need the pressure, you need to go to the Gibbs-Duhem relation to get you the pressure from the concentrations and temperature gradients.

So we are going to assume this relation between the properties of the particles. And notice that this is the internal energy, just this part of the energy. So we assume this relation holds as you follow the fluid particle along its path. So we assume that it is valid for the material derivatives.

That means that the left hand side of the balance equations that we have in the previous slide where we have these material derivatives, they are related. We can essentially substitute the balance equations into this one, and we get an extra relation. Plus, we are going to assume the mode of interaction that we call heat and diffusion to be valid and holding between fluid elements as they move along.

So it's the diffusive fluxes that are related in that way that we have discussed with the exclusion, though, of the flux of energy, which is related-- which is work. Because when you have the fluid element that deforms, especially it changes in volume, that change in volume against the normal components of the stress imply work. And that is a kind of interaction between adjacent fluid elements that is not of the heat and diffusion kind.

So we exclude it. That's why I call these $\mathbf{v} \cdot \mathbf{T}$ non-work. So the non-work component of the heat transfer between the fluid elements as they move along the path line is related to entropy flux, and constituent flux, as in the heat and diffusion mode of interaction. But energy has an additional contribution, which is the work component, given by the stress tensor dotted into the velocity.

This one, as we said, we take-- since in the balance equations there appear divergences, so all this stuff, all these fluxes, we can combine those with the divergence of this relation, which is here. And a few things will cancel out, and here are the terms that survive. And we write what survives as an expression--

We took on the left hand side only the rate of entropy production, the density of entropy production, so the rate of entropy production per unit volume, σ . And we have on the right hand side all the terms that contribute to that entropy production. And this is the most general form. It includes all sorts of terms. One is an old friend from chemical kinetics.

This term here will give rise, as you will see, to the dissipation function of fluid mechanics, which you will see in a moment. The first term is the one that gives the Fourier expression when you have only heat and not also diffusion. And these are terms that we have to see what they do because they do important effects for many applications.

Now, the other time we also have seen how to recognize in the heat-- sorry, energy, in the energy flux, a portion of the energy flux that we can still recognize and call heat, or we call it the measurable heat, more properly. But essentially, it's the part that we can identify with the heat of heat transfer so, again, with this q double prime notation.

So if we take the non-work part of the energy flux, it's given by the heat plus a portion, which is related to the flux. So this is the energy which is carried by the particles just because they are diffusing. This is not convective because this is a diffusive part. So this is particles that are moving at a different velocity than the barycentric velocity. So they diffuse away or into our fluid element.

And as they do so, they carry with them their backpack of internal energy. And plus, they also have to advance and face the pressure that is present. And therefore, there is also this-- there is this pulsion work, which is p times the partial volume, which is hidden here because remember, the enthalpy is u plus $p v$. So this is partial enthalpy.

So it's partial energy plus p times partial volume. And that p times partial volume is the pulsion work equivalent to what you would have in a bulk flow situation. But here we are in diffusion. So we can substitute these terms here into our expression. And this is a very typical procedure that we like somehow to express, to rewrite.

Every time you formulate a problem in non-equilibrium thermodynamics, you typically start-- and it's the safest way to do it-- start from the entropic point of view. So you write it in this way. You identify these gradients as the degrees of non-equilibrium related to the various transport of the various properties. But then you like to translate this into a more common and familiar language.

And since we consider more familiar, talking about heat because it's related to Q and Q over T , we often go back to these and then also the fluxes of particles and the chemical potentials. So we substitute this into there. We also use a relation that I think we've discussed that you can write. When you write a differential of the chemical potential, you can separate the part that depends on temperature and the part that changes at constant temperature.

So it depends on pressure and concentrations. And so we keep that part written this way. And so the bottom line is that we can write the entropy production density σ in this way. So here, we have more explicitly, the Fourier kind of entropy production. Here, you have a similar term related to diffusion.

Here, we still have the usual term related to chemical kinetics. And what is left here is the dissipation function-- 1 over the temperature times the dissipation function. And here are the details of the dissipation functions, if you like, if you are a fluid mechanician. It has two contributions.

It's not just the deviatoric part of the stress tensor and the deviatoric component of the strain tensor. But it has also this term, which is related to the divergence of v . And it's true that for most flows like low Mach number flows, this is zero. So this is really not important.

But in principle, this is one of the dissipative terms. And in fact, notice also that in our doing the procedure here, there was a pressure which came in here. And there is a p_m , which is the mechanical pressure. That is the trace over one-third of the trace of the stress tensor. They are not necessarily the same.

And so their difference gives rise to this entropy production term. You can still view each of these terms as a product of a rate and an affinity or a degree of disequilibrium. So the gradient in temperature, more properly minus $1/T^2$ times the gradient in temperature, can be interpreted as the degree of disequilibrium associated with heat transport.

Similarly, minus $1/T$ times the gradient of the chemical potential done at constant T is the degree of disequilibrium with respect to diffusion of particles. The affinities in chemistry-- $1/r$ (I meant, $Y_{sub k}$) have already been recognized as the degrees of disequilibrium. And here for the fluid part, we have a degree of disequilibrium which is related to the rate of strain, just the symmetric part of the rate of strain of the local stress tensor-- I'm sorry, of the local

gradient of the velocity field. And whereas, the conjugated flux is the flux of momentum, which is related to the stress tensor. But then there is also this one. So the divergence of velocity, which, as we said, is the rate of change of volume as you follow the fluid element. That is also an affinity for a dissipation for which the flux is given by this difference between the thermodynamic pressure and the mechanical pressure.

If we also have charged particles-- so if some of the constituents of our fluid are charged particles, and we're talking electrostatics, not-- electrodynamics is even more complicated because, of course, then you get the Maxwell equations, the magnetic field, the vector potential, and so on. Too complicated to cover. But in any case, so here we have just electrostatics.

And so ϕ is the electrostatic field. J_q is the diffusive component of the electric current density. Because if this fluid element contains charges, and these fluid elements moves with the barycentric velocity, there is a convective part of the charge which produces an electric current. We're not talking about this part.

We are talking about the part of charge exchange between adjacent fluid elements due to the fact that they have-- the diffusion with respect to the barycentric velocity. So this is a diffusion flux of charge. And in fact, so the total current density may be denoted with I double prime. And it is the flux of charge with respect to the laboratory frame.

So it's the flux with a zero on top. And it's made up of the diffusive plus the convective term. And ρq is the density of charges, the local density of charges. So the non-work part of the diffusive energy flux is related to heat, to the diffusion of particles, and to the diffusion of charge.

So we have this extra term, which we can single out in here when you do the same procedure as before to write this expression in terms of the familiar variables. So here, the entropy production is related also to minus $1/T$ times the gradient in the electrostatic field is the degree of disequilibrium with respect to moving charges. And the associated or the conjugated flux is this difference here, which is just the diffusive flux of charge.

That's, again, the same equation. Now, the next step to introduce the next notion is to group these terms in order of increasing tensorial character. So some of these are scalars like chemistry. And also inside the dissipation function, there is a scalar term, which is the one that we described before, and then there is a tensorial term, which is the one related to the contraction between the deviatoric parts of stress and (rate of) strain tensors.

And the rest are vectorial terms-- heat, flux, electric current, flux of particles. These are vectors. Why is that important? All right, now, so I started with some coloring here just to single out the-- the degrees of disequilibrium are the red stuff, and the fluxes are the blue. And so you see each one is written as a product of a degree of disequilibrium times a flux.

And if we recall what we said about exergy, you can also read this expression as a representation of how locally your fluid or continuum is dissipating exergy. Multiply that by the temperature of the environment with respect to which you want to-- or the reservoir with respect to which you want to measure exergy. And so these terms tell you that you have dissipation whenever you drive, like I read here, you drive a chemical reaction down the direction of a decreasing affinity.

And that gives you entropy production. You drive a heat flux down a temperature gradient. Also you drive a diffusion flux down a chemical potential gradient. Or an electric current down a voltage drop. Or a momentum flux down a velocity gradient, which is the rate of strain.

You may find, if you look into papers that deal with non-equilibrium thermodynamics, that expression up there-- this one with all these terms-- written in a compact form in this way as a sum of products of fluxes and-- instead of degrees of disequilibrium, they are called forces-- fluxes and forces. So this is a force flux representation of the same or shorthand notation.

And this symbol here is whatever is appropriate to use when you have to multiply a scalar flux times a scalar degree of disequilibrium. It's just a simple multiplication like here. When you have to multiply a vector times another vector, it is the dot-- it's the vector product. I'm sorry, the dot product, because the vector product is something else.

And if you have to multiply the tensor, two tensors, and get a scalar, it's the contraction. So if you take the two matrices of the two tensors, you multiply them, and then you take the trace. And that's the equivalent of this double dot operation. So we will proceed now for a while-- I mean, for today, for the rest of today, I guess, with these more abstract and shorthand notation.

Because we want to discuss some geometry of the relations that we can write in order to model how a flux is related to a force or vice versa. Yeah, actually, maybe you should go back for a moment. I mean, there was one slide that I don't know where where it went. But in any case, maybe it will come up later.

But what I need to say at this moment is that this relation is what I call an extrinsic relation. Extrinsic means that it has been obtained using only assumptions about the continuum, the balance equations, things that hold in general. It doesn't contain anything that has to do with how the material behaves. It doesn't yet contain any property of the material.

For example, here, the property of the material, when you do heat transfer, comes in when you write the Fourier law. And therefore, you insert the thermal conductivity tensor, which is the description of-- which contains how your system behaves. And so that takes me here. In other words, once we have written the extrinsic general relation for sigma, then we have to go into the detail of the particular problem and the particular material or materials that we are dealing with.

And each material has its own way of reacting to fluxes and forces. The principle in general is that the material tends to spontaneously go, if it can, towards stable equilibrium. But sometimes, if it is subjected to permanent forces, it will reach a steady state. Because those fluxes and forces that are imposed by the exterior or by the adjacent fluid elements-- by the flow situation, by the boundary conditions-- those prevent the system from relaxing spontaneously to equilibrium.

So it will keep the state off equilibrium. And typically, boundary conditions, most of the times, impose either the forces or the fluxes. But sometimes you also impose a relation between force and flux. Like when you do convective heat transfer, that is a boundary condition of Robin type.

In any case, you can view-- there is a dual point of view. You can describe your material resistance to flux by saying how it reacts when you impose some fluxes in it. And the material typically reacts to a flux by building up a degree of disequilibrium. Remember, Le Chatelier-Braun theorem-- degree of disequilibrium that will enhance its tendency to contrast that flux and return to equilibrium.

So your model for the material will be a relation that gives you the force as a function of the flux. And the gammas are the other properties, like equilibrium properties, if you are near equilibrium, like temperature, chemical potentials, electrostatic field. But of course, you can also view it in the opposite way. It's just the inverse function or the dual point of view.

You impose a force, for example. You impose a gradient in temperature on a specimen of a piece of metal. And the material reacts by building up a flux which will try to go in the direction of re-establishing a flat-- of killing that temperature gradient that you are imposing. Again, in this case, you write the relation flux as a function of force.

And clearly, then, you have-- you put it into the extrinsic formula for the entropy production that we just obtained, and here comes a relation in this picture. The entropy production is related to the fluxes that you have imposed, or this one is related to the forces that you have imposed.

And then you start (with) particular models-- particular, but pretty general. For example, here, if you want to model the relation between force and flux in heat transfer, you adopt the Fourier law, which for an isotropic material, doesn't have a tensor here. This is just a scalar. But if it is anisotropic, we have seen that this should become a tensor-- a symmetric tensor-- due to the Onsager reciprocity.

The relation between the difference between mechanical and thermodynamic pressure and the divergence of the velocity is called the Lamb law for a Newtonian fluid. And the constant between the two-- I mean, the-- the constant of proportionality between the two is called the bulk viscosity. In fluid mechanics, the relation between the deviatoric part of the stress tensor and the deviatoric part of the rate of strain tensor is what we call-- is this linear relation.

And the proportionality relation is called the shear viscosity. We typically just call it viscosity. And with this plus Lamb, you may rewrite the stress tensor in this way where, notice here that I'm using the thermodynamic pressure, not the mechanical pressure, because that difference between the two has been shifted on this side to use the Lamb law.

And so here you have the standard stuff, and here you have the stuff that you usually neglect because this is typically zero. But this is the second coefficient of viscosity. And then, if you have electricity conduction, diffusion, you have Ohm's law. The coefficient of proportionality between the charge diffusive flux and the-- minus the gradient in the electrostatic field is the electric field.

So this is-- you could also write it as E . And in any case, this is the inverse of the electrical resistivity of your material. And this is one way of proceeding, and it has-- it has been the way for most of the applications. However, there is some arbitrariness in saying, as we've seen here, that, for example, the heat transfer is not related to some other degrees of disequilibrium.

And in fact, there is this possibility, and the matrix of possibilities is this one. Here is all your degrees of disequilibrium, possible ones, and here is all the fluxes. And those laws that we have seen in the previous slide are just the diagonal terms in this matrix of coupling. They presume a direct coupling between-- I mean, a chemical reaction rate and the affinity of the reaction, a coupling between these mechanical rate of change of velocity-- I'm sorry, of volume of the fluid elements and this difference in pressures or these and the heat transfer and so on.

But as you see, at least part of this matrix is filled with other possibilities that have names. So they correspond to effects that have been observed. And long ago, as you see. We're talking about the 19th century still. These are typically called cross effects because they happen in the off diagonal terms of this coupling matrix.

And also you may have noticed that I haven't put anything in these parts. So why don't I fill completely this matrix? Well, in principle, you should, except that there are many applications in which your fluid is isotropic. If the fluid is isotropic, if the symmetry of your problem, the material, as well as the boundary conditions are isotropic, then there is this principle.

Symmetry takes-- it's saying and it implements what Pierre Curie described with this words, that the symmetry of the cause must be preserved into its effects. So what this means is that if you are in isotropic conditions, there is no way you can couple a phenomenon which is of, say, a vectorial character with one which is of a different character, like a scalar or a tensor.

So tensors can couple only with tensors and scalars only with scalars-- and sorry here are the scalars-- and vectors only with vectors. But remember also that this is true only for isotropic conditions. Because, for example-- there is an important aspect of when you have, for example, an interface. So this is supposed to represent an interface between two phases, for example, let's say f on one side and g on the other side-- two different phases separated by an interface.

In an interface,-- ok, let's view it also in this other point of view-- f -- and let's plot the density. Now, as we know, if we plot the density of a liquid and the density of a vapor, there is a big difference. The vapor is about-- for water, is about 1,000 times less dense than the liquid.

So in the interface, things are not sharp. Things are smooth. There is this smooth interface. There is a layer-- there is a small layer in which there is this huge gradient in density. And this is at equilibrium, so this is not the kind of gradient that would cause fluxes. It's not a degree of disequilibrium. This happens at equilibrium, But still, you have a gradient there.

And the description of this situation can be done in several ways. Gibbs did it by assuming a sharp equivalent jump from this value to that value, which is a good approach. And I will direct you to a very nice (1976) paper by Bedeaux, Mazur and (Albano) another author-- I forget the name now-- that writes exactly the equations that we have written here, these extrinsic relation for sigma in the case of a jump description between two phases.

In this situation here, definitely there is no isotropy because one thing is to move across this interface, and one thing is to move along the interface. So if you sit on the interface and move on the interfacial region, maybe that is isotropic in the tangent direction. But it's not in the orthogonal direction.

So for example, in this case, the stress tensor which is-- you can represent it as a 3 by 3 matrix-- splits. And so you have a pressure, an orthogonal pressure and a tangent pressure-- and a tangent tensor field. So you have a two dimensional tensor field, which is isotropic, and it represents the stress component in the tangential part plus a scalar-- a scalar for-- the orthogonal pressure becomes a scalar.

And so in this situation, this is very interesting because that scalar now, since it is a scalar, it can couple with all these scalars here. So you may have the possibility at interfaces to couple chemistry and the flow field, and the pressure field, the orthogonal pressure. And that is I think used in models also for biological systems because that coupling is important.

So it's mechanical and chemical coupling. But you need to break the isotropy in order to have this kind of, let's say, exotic couplings. Now, we have already talked about Onsager relations. And you remember that we did it in the context of chemical reactions, and we did it-- we proved the reciprocity-- Onsager reciprocity theorem. We have shown that in the linear regime, we could prove it as a consequence of the principle of maximum entropy production by Ziegler.

Here, I'm not discussing this slide a lot because, essentially, it is exactly the same slide that we had then where I changed some of the symbols. Here, instead of sigma, we had entropy production-- $S \dot{\text{irreversible}}$. Here, we had the reaction rate, so the epsilon dots. And here, we had the affinities of the reactions.

And instead of these super dot symbol, we just had nothing because they were scalars. And the procedure was just the same. We proved-- we assumed that the material in the linear regime-- so we assume a linear relation-- and the linear relation is, therefore, in terms of this tensor here, L . It's actually a super tensor because it has as many entries as that matrix that we just had in the previous slide with some zeros around.

But it's not a full because of the Curie principal, but it's still-- OK, so this is what we assume, a linear relation. The bottom line will be that these super tensor has to be symmetric. And the assumption, in order to obtain this result, is that the entropy production should be maximal subject to the constraint given by the extrinsic relation. And in passing, we obtain this orthogonality-- Ziegler orthogonality relation that we also described graphically in one of the previous lectures.

So fine, you can proceed this way. Ziegler actually introduced this idea of maximum entropy production because his objective was to-- he was a material science, I guess, person. And he wanted to be able to describe things like plasticity. And plasticity doesn't have a linear regime. So we wanted to extend Onsager reciprocity to nonlinear regimes.

And in fact, here is how you do it, again, just to skip the details, but just to give you a flavor. All it takes is to-- instead of assuming, like we did in the previous slide, a linear relation between forces and fluxes, we assume a generic relation and still apply the principle of maximum entropy production. So maximize σ subject to the extrinsic relation between the forces and fluxes.

And you come up with an orthogonality condition in terms of the Lagrange multiplier, which is still only 1 because it's only one constraint. The only problem is that now-- remember, when you have-- in the method of Lagrange multipliers, in order to find the value of the Lagrange multiplier, you have to substitute back into the constraint.

So you take this orthogonality relation this way, put it back in the constraint-- and this is done here-- and then solve for λ . In the case of linear case, we found that λ is equal to 2. Here, it's more complicated because λ is this function of whatever functional form you have chosen for your relations between forces and fluxes, which is non linear, in general. So you can substitute these into here, and you get this complicated stuff, which nevertheless, is an orthogonality.

It's a condition that must be satisfied by the functional relation of your-- that you have chosen here. So it tells you that you don't have complete freedom in choosing these functions. They have to satisfy this. For example, if you choose the linear relation, which is this one, this expression reduces to the one that required the symmetry of the Onsager conductivity tensor.

In a general case, you get something else, which is a generalization to the nonlinear case of Onsager relations, à la Zeigler, so to speak. There is another way of viewing things. They are all sort of equivalent. And let me try to explain it in this heat transfer example.

They are all equivalent, and there's so much. And as you see-- I'll say a little bit later about this-- I collected this point of view in a paper a couple of years ago. And let's do it for the heat transfer case. So consider this an anisotropic material made of-- so that the microstructure is made of layers sandwiched of high conductivity and low conductivity materials.

And so suppose you subject these material to a-- you impose a gradient in temperature. The material, then, is under a-- I shouldn't say stress-- but in any case, it has to decide. All right, how do I react to that gradient in temperature that you impose? Definitely I want to react in a way that will allow me to, like Le Chatelier-Braun says, to reduce that gradient in temperature and try to reestablish equilibrium.

But you see here, what I am showing is that there are many possibilities. It could decide to move heat in one direction or in another. And how come it chooses this particular direction? In some sense, it's like, suppose you are in a crowd. You're in the middle of a lot of people, maybe at a concert or going into or out of a soccer stadium.

Lots of people, and everybody wants to reach or get next to the podium or to the entrance or go to your car. But you have a crowd in front of you. And so even though the direct path could be apparently shorter, but it would require less effort for you to move in another direction where you see less resistance to your motion.

So this is what happens here. So there is-- you evaluate, and the material does a local evaluation sensing-- OK, how much would it cost me to move in terms of effort or in terms of-- yes, effort in order to move in the crowd? How much would it cost me to go in this direction or in that direction?

And so there is this tensor G , which I would call a metric. It's the driver of that logic. It measures how dissipative is moving in the various directions. And if you write an equation like this, the quadratic form with that G for given heat fluxes and set it equal to some constant. That gives you an equation of an ellipsoid.

And that ellipsoid represents the locus of all the tips of the vectors that would cost the material the same effort, so the same dissipation. And so it turns out that the entropy production is the scalar product between the blue vector and the red vector. And the scalar product here, between two vectors, is given by the projection of one vector onto the other one.

So for example, this blue one, you see that this blue one, the actual full, not the dotted ones, is the one that has the maximum projection onto the red vector. So it maximizes-- Among all these possibilities that have equal effort, the one that maximizes σ is this blue one, and that's the one that the material chooses.

It turns out that G is the inverse of the conductivity tensor. So you can read Fourier law for an anisotropic material in this way, that the material is choosing the direction of maximal entropy production for a given effort. Like in your crowd, you choose the direction with which you feel that you are moving farther away with a given effort, for a given amount of effort that you put into that movement.

So these are words just to explain what I just said. And so if you-- so you could have an isotropic material. For an isotropic material, that ellipsoid becomes a sphere, a hypersphere. All directions are equivalent.

And if all directions are equivalent, which one is the direction of steepest entropy ascent? It's the same as the gradient of T because the vector q , has the maximal projection on the red vector when they are co-linear. And so here is the construction in that same diagram for which we have seen the orthogonality Ziegler relation.

So we have an x and y or 1 and 2 versors. So think of it as x and y . I impose a gradient in temperature, which has two components. And that places me-- the two components places me somewhere, not at equilibrium. If they are zero, I'm at the center. So I'm already in an equilibrium state, and nothing happens.

But if I'm off equilibrium, these are the lines of contours of constant entropy. So the higher the gradient, the further I am, and the highest is the entropy. I'm sorry-- the highest is the degree of disequilibrium. This is the maximum entropy. So the entropy goes decreasing as I go farther.

So if I am here and that degree of disequilibrium has been generated at one instant of time, and then the system is allowed to evolve by itself, as if it were isolated-- nothing else, no constraints, just you can go to equilibrium-- it doesn't go to equilibrium in the straight path. It follows the path that is dictated by its local metric.

Now, true, the isotropic material is-- doesn't favor any direction. So these, although it doesn't show exactly as a sphere, it should be a circle. In any case, it has to evolve, though, in a scenario in which the entropy contour lines may not be also circles. If they were also circles, you would go down straight.

But if they are not-- like here, they are ellipses-- then it would choose, among the ones that are all equivalent effort, it chooses the one that takes you to the highest entropy possible. So it's the one that is tangent here, and that is also for this other metric. And then, of course, you can proceed and go on as you-- at each point, you insert, stop, and pause.

It doesn't happen, of course, but you stop and consider which one is the direction in which it should go the next step. And that's how it gets to equilibrium. They all get to equilibrium, of course, but along different paths. And if I start even from this exactly same state, but with a material that is oriented differently, and therefore, for it the metric and these ellipsoids of equal dissipation, of equal effort is oriented in a different way.

And therefore, it would move there, and then it will search again. And it will move, maybe even overshoots a little bit, and then goes back to equilibrium. So this is the role of the metric that describes-- This is for a heat transfer problem, but you can also view it in a more general context. And that is what-- I like to call it the Fourth Law, simply because it is something that has emerged.

Let me see, do I have-- I think I had-- keep missing slides today. There will be a slide sometime with a list of many different theories of non equilibrium over the last 40 years in which people in different languages, different mathematics, different frameworks. Often, they don't talk to each other. They completely ignore each other. They wouldn't admit that they're doing the same thing, but they are doing the same thing.

And that is what I was trying to point out to the community here by calling it the Fourth Law. And why do I-- why do I dare elevating it to such a high level in the hierarchy of physical laws? That's because of the generality. Remember, the great conservation principles are great-- the greatness comes from the generality. It should hold for every model of physical reality.

Well, it turns out that in every model of non-equilibrium dynamics, there is something that, maybe you don't call it a metric, but it is. It has the properties of a metric. And therefore, it appears to be an essential feature of any model. And also, I like also the fact that it is a statement of existence.

Like, the first law is a statement of existence of energy. The second law is a statement of existence of entropy. This is a statement of existence of a metric in non-equilibrium states. And it's a property, like this thermal conductivity, that has to be defined at every state, every non-equilibrium state of your system for it to decide in which direction to move when you let it alone and want to let it go towards equilibrium.

Yeah, here, this is to show that the same construction can be also done more formally and mathematically, again, with the method of Lagrange multipliers. You see-- you maximize the scalar product between the X and the J , subject-- so that's the Lagrange multiplier-- to the constraint given by an equal effort ellipsoid. So if-- so it expresses exactly mathematically the word description that I gave.

There is a metric that describes this ellipsoid. It tells you, for a given distance I want to move, which one is the best direction. And best is in terms of maximizing the rate of entropy production. From this one, using the method of Lagrange multiplier, setting the derivative equal to zero, substituting back into constraint, and so on, you get a relation between forces and fluxes.

You can always write it in this way, which looks like a linear relation, but it's not because these R , which is a resistance, is not a constant, in general, but it's just a function of the fluxes which is given by the solution of this problem here. So this is a non linear relation.

And of course, you can do the exact same in the force picture, and impose the X . And there is a metric also from that point of view, and the two are related to one another. They are the inverse somehow. So you also maximize these projections subject to these other blue ellipsoid, which also represents the effort.

At this time, it's the effort for the system to set up a gradient in temperature so as to contrast the flux of heat that you have imposed in it. And of course, when you get close to equilibrium, then you go to the linear regime, you get Onsager relations. And of course, these two are-- the metric becomes the Onsager generalized conductivity for the L s or resistivity for the R s. One is the inverse of the other.

OK, here is the list of theories that converge to the Fourth Law. Of course, I've-- we contributed to it. But in the same period, already you have Grmela, Morrison, Kaufman, who did the-- completely-- from completely different point of view. So, in fact, I met Miroslav Grmela only maybe 30 years later.

And so these all are independent contributions. GENERIC has become very popular because some communities are more effective than others into propagating and publishing. I will say a few words also about the constructal law of Bejan. Although, he would be unhappy if I say that he belongs here because I think he believes that his point of view is more general, and I think I agree with him.

I'll explain in a moment, I mean, later, why. This other also-- some mathematicians, from the point of view of certain classes of partial differential equations, have developed-- now it's already 25 years ago-- this theory of gradient flows. They-- in order to do that, they have introduced a particular metric-- pretty complicated mathematical-- but it is a metric that regularizes those differential equations and makes them fit into this same scheme.

So that's very interesting. Then there is also more modern stuff like large deviation theory. And not only that, but also there is some people that are applying this notion to solve in original way complicated problems in a much simpler way than the traditional descriptions. Because this view, geometrical view, you know, the power of mathematics and of geometry, is if you can view something from a geometrical point of view, you have captured the essence.

And you have also often simplified even the numerical solutions of your problem. I'll give you some references here just for fun, if you're interested in this. Now regarding Bejan constructal law, if you haven't come across, Adrian Bejan was a graduate of this department two or three years before me, I guess. He did a PhD in mechanical engineering here.

And his-- you see, his focus is on design and evolution in nature, the role of design. Design, for example, the structure of-- the tree structure of lungs or even the structure of trees, which are sorts of the result of optimization of two contrasting tendencies. And the system is trying to find the best direction in which to build and to-- but in which to make things flow.

And things flow, to me, is also translated into choose the way in which you can produce as much as possible your entropy at the fastest rate compatible with the constraints. And so for this part, I think that we're saying the same thing. So it's also fitting into the Fourth Law. But what's beyond that, and I think he's right, is that he's saying that in nature, things evolve.

And also the design of natural things, including the design, for example, of the wings of animals and how they are related to evolution, so how from the-- I forget the names of the ancient birds when you had the T-Rex and how that evolved. And that evolution is an evolution in the design of how structures are built in nature.

They always have the purpose of favoring flows. That means favoring entropy generation and making it as effective as possible. Because as you know, life is impossible without entropy generation, and we need that. That is the driving force. While you produce entropy, you also produce useful things.

So entropy production is not completely negative. It's not just a waste of exergy. You need it, because if you didn't have it, nothing useful would happen. But what Bejan says is that also structures evolve, and the choice-- there is some randomness in how a particular structure is given birth.

It was nonexistent, and then all of a sudden, perhaps because of a fluctuation or of perturbation, it becomes possible. Now, regarding structure, though, for example, there is this problem of the-- it's called Benard conduction. It's a problem in which you heat-- you have a fluid-- like-- you have a pan with some oil, and it's heated from below and cooled from above.

Now, typically, if your heating is not strong enough, you would have just conduction. But then, there is also the possibility, because of the instability, due to the fact that the stratification-- since you get hot stuff below and cold above, and they like to switch. So this movement, which requires moving a flow, therefore, it involves a friction. So if you have enough motivation for doing it, eventually, that flow will start.

And therefore, you'll get convective-- it will switch from conductive heat transfer to convective rolls of heat conduction, which will enhance the heat conduction. It's more effective. So you see, here, it is a situation in which structure gets built in order to make the entropy production more effective. And in this paper, you view it from the point of view of maximum entropy production.

So you see, for example, here you have a situation in which you are-- for example, you have the rolls. So you have the high non-equilibrium situation, high flux, in which you have the Rayleigh Benard rolls. And that structure is the one that maximizes the entropy (production). So among all the possibilities, the system chooses that one, maximizing the entropy production.

But as you turn the heat off, and here, as time goes on, you reduce the heat from below. That tendency goes down until it becomes comparable or even less efficient than the direct simple conduction. And then what happens, the system switches. And the convection gets stopped, and the system switches to another maximum.

So this is also a jump in configuration. So it's a construction of-- it's a design, so to speak. It's a design choice that your system has made in order to move from one maximum to another maximum. And this, of course, corresponds to critical a value of the Rayleigh number that is the onset number for this Rayleigh-Benard instability. It is a very famous problem in fluid mechanics and heat transfer.

And by the way, Adrian Bejan has written hundreds of papers, but also many books, including one at the beginning, which is entropy production in heat transfer which is very good. So let me conclude today with this last idea just to add to the confusion, if you want.

The idea that-- there is a theorem, famous theorem, proved by Glansdorff and Prigogine called the minimum entropy production principle. So many people facing simply the words in a superficial way, they say, well, is it minimum, or is it maximum? All right. So the difference and the key is local and global.

So the system locally chooses-- the material locally, chooses to react in a direction that goes towards the steepest entropy ascent. So it's the local maximum entropy production. This theorem instead looks at a global situation like an integral over a volume of many pieces of material. And it does the integral not of σ , which is the rate of entropy production, but of the rate of change of σ .

And it proves that the rate of change of σ under a broad set of boundary conditions and assumptions that are listed there-- very large set of conditions-- is negative. So that means that σ , if you start-- like in the previous slide, if you start from a situation in which in your control volume, there is a lot of entropy production, and you let it go. If it is not already in a steady state, it will change, evolve, towards a lesser and lesser entropy production situation until it gets to zero.

And the zero will be either a steady state, if it is sustained by the boundary conditions, or the equilibrium state. Instead of doing the details here that are not really essential for us, let me give you this example. Consider a one dimensional heat transfer problem. And suppose that at time equals zero, you have imposed this temperature profile.

And your boundary conditions are that the temperature here is given and fixed. So you fix the temperatures left and right. Of course, that is not a steady state. The system will evolve. You can solve this with the Fourier equation or any software that does this solution.

And you see it will evolve and at the end, it will reach the steady linear solution of the typical heat transfer problem. Now, if you compute the entropy production rate here, it's this much. If you compute it here, it's this much. It's a half. So the system, as it moves from here to there, has an overall global entropy production that goes down in time until it reaches a minimum at steady state.

If you start-- this is another example in which you have different boundary conditions that would allow an equilibrium state. So you start from this one, and you have an entropy production rate, which is given by this. You let it go, it will reach a flat temperature profile, which is equilibrium, zero entropy production, again, a minimum.

So globally, it has gone down. But locally, at every instant, at every local, each material element here has followed Fourier's law. And therefore, has at any time chosen the direction of flow is compatible with the gradient imposed. All right, so we're just on time and just finished.