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OK, good afternoon. Let's start. All right. So we are talking about non-equilibrium. And this table summarizes a bit of what we have done. We talked about forces and fluxes. The forces can be thought of as the degree of disequilibrium of the various aspects, and the fluxes are the modes with which molecules transfer stuff, properties, the extensive properties.

In fact, this fact that molecules transport something gives rise to this language of phoretic, like thermophoretic, electrophoresis. Phoretic means-- the etymology of the word is transporting something. And we want today to introduce a couple of examples of these transport cross effects that emerge from this table from the fact that not only we find things on the diagonal, so we have processes like heat transfer, that follows Fourier's law, or mass transfer that follows Fick's law that we will derive, and electrostatics that provides Ohm's law.

And also fluid mechanics, the law that connects, with viscosity, the stress and the rate of strain of fluids. But there are also off diagonal terms. These are called cross effects. And in some cases, some of these cross effects are forbidden by symmetry reasons. In particular, if you have an isotropic fluid or continuum, the Curie principle forbids cross effects between phenomena of different tensorial character.

Although there may be other situations, like we said, for example, interfaces between phases, where there is isotropy is broken by the interface, and it's substituted by another kind of isotropy that will allow some additional coupling that would not be allowed in the bulk. OK, all right. So let's recall also that we have defined these relations that, yeah, this mode of interaction that is the extension of the idea of heat interaction, which we call the heat and diffusion, which is fundamental in that it brings in a relation, like the heat  $Q$  over  $T$  relation.

Here, it becomes a relation between heat and also additional terms like these ones in the flux for the energy, and also for the entropy. The language that you find in papers and books on this subject sometimes is varied. And so you have to be careful. Often, you find people calling this heat. And this is the measurable heat flux. I've tried to call heat flux only this. And that, I'll try to call it just the energy flux.

In addition, in some of the situations in which you have multiple phenomena occurring like heat and mass transfer simultaneously, or heat and electrical charge transfer, there are also languages like the heat of transfer in some particular situations. For example, if you have no gradient in temperature, which doesn't necessarily mean that  $q$  double prime is 0, but in that situation, the overall energy flux is sometimes called the heat of transport because it's the heat that is transported in the absence of the traditional cause of heat transfer, which is a gradient in temperature.

Nevertheless, it's a combination of these terms. So beware of the language. And if you ever have to write on this subject, be careful and be consistent. Now, when we define the heat and diffusion interaction, we did it for a situation in the absence of fluid flow. So these are the diffusive fluxes with respect to a non-moving bulk. And therefore, in the next slide, we'll have to do a little bit of additional job to introduce also the idea that typically, in fluids, there is flow.

And that, of course, is a complication. It complicates some of the equations. But this is the right moment to bring it in. And also, what else? It escaped. I'll come back. And so let's dig into this. Well, it's a little crowded slide, as usual. But it's full of things that we have already seen. So just to have a way to remember.

For example, you remember that we, as part of the local equilibrium assumption, and together with the simple system model, and like when we described bulk flow, we say that the energy of our system, including-- like a fluid parcel, is described by the energy typical of a stable equilibrium state with the amounts of entropy, volume, and constituents that are in that fluid element plus additional terms that are either mechanical or electrical, like the kinetic energy, the potential gravitational energy, the potential electrostatic energy.

And if you have also your fluid static in centrifugal field, you can add this negative potential energy. And of course, you remember that the mass is related to the concentrations, via the molecular weights. And the charge,  $q$ , is related to the concentrations via the individual charges of-- the  $z$  of your molecules.

So we have seen a few times that when you compute the derivative of the energy that enters in the conditions for mutual equilibrium, which is not the chemical potential, but the total potential, that picks up a contribution from just the stable equilibrium state property. And that's the chemical potential. But then, there are also additional contributions to the chemical potential, which makes it, for example, if you add this one, it makes it the electrochemical potential, the gravitational, the kinetic, and the centrifugal.

In a moment below, we will see that we can write this. These terms are highlighted in white as energy minus internal energy, specific, because indeed, that is what it turns out to be. In fact, you remember that in general, without-- before we make any assumptions about the mixture being ideal or non-ideal, in general, we define the partial properties. And this is the partial internal energy, which is related to the total internal energy by this summation, which you can also cast in terms of concentrations,  $c_i$ .

So if you substitute-- if you rewrite this expression for the energy in terms of-- right here-- specific energy per unit volume times the volume, and here, you substitute this for the internal energy, which is the first term here. So you see that the overall energy is given by a summation weighted on the concentrations of all these terms. All these terms somewhere have the concentration coming in either through the mass or the charge.

And so this term in parentheses can be called the specific energy, total energy. And it can be split like we have seen here. So let's see. Yeah, I get lost myself in my slides. Yes. It's sad. All right. OK, so yeah. We write it in terms of the  $e$  without is per unit volume. The  $e$  with the star is per unit mass. That is also some kind of source of confusion somewhere in the literature.

And all right. So this is one first equation. The second relation that we need to bring in is the fact that the fluxes, the fluxes of constituents, are not all independent, because these-- remember, they don't have the naught on the superscript. So these are the diffusive fluxes. Those-- so it's the flux relative to the center, the barycenter of the fluid element.

And with respect to that, the mass flux by definition of barycentric velocity is equal to 0. And therefore, the weighted sum of the-- molar fluxes of the various constituents weighted on their molecular weight must be equal to 0. That makes them not all independent. So we can recast the equations by writing, taking, for example, the last one. So the flux of the last constituent, this is the mass, is equal to the negative of the sum of the fluxes of masses of the remaining constituents.

And we can introduce this idea into the expression that we need for the heat and diffusion interaction, because there, we have the sum. And in this sum, we have all the fluxes playing. But we have to also make a system with this other relation between fluxes. So one way is to rewrite by subtracting this equation here. We first do it with the mass so that this is easier to subtract.

So here, when I see the summation, it goes from 1 to  $r$  to the total amount of constituents. Now, I substitute it with the summation that goes from 1 to  $r - 1$ . And the last one is written-- it comes inside the summation by virtue of this mass. Oops. What happened? Yeah, by virtue of this mass balance, so to speak, equation.

No, that's not a mass balance. It's simply the definition of barycentric velocity. OK, so now, once we have this expression here, it's the difference between the total potentials. But the difference between the total potentials, we've seen somewhere above. I got the mouse stuck a moment, but somewhere above, you find the relation that gives you here, this relation here and that one up there.

So this difference can be substituted with this one where the  $z$ 's stand out. And they bring in the charge, the charge flux. OK, and OK. So we've substituted. So now, this expression has the advantage of having all the fluxes that are independent because you are excluding the  $r$ . You go the summation only up to  $r - 1$ . Then we do the usual trick. We remember that the chemical potential can be written as  $h - T s$ .

And this is for the partial properties so it's partial  $h - T$  partial  $s$ , which is written here. And so you can split terms in these fluxes that are multiplied by the temperature and terms that are not. We can also go back to molar quantities, molar fluxes without the stars. And eventually, we recognize that this term that is multiplied by  $T$  is what we define the measurable heat flux, that is the heat flux of heat transfer.

So, the bottom line is highlighted here that we finally have written the fluxes of energy and entropy, which are needed to make the energy and entropy balances, of course, to the flux of heat transfer. So the measurable heat flux to the fluxes of constituents. But not all of them, only up to  $r - 1$ , and to the diffusive flux of electrical charge. So this is basic to analyze any of those cross effects that we need to do.

Now, just a little detour to mention that since we're talking about fluxes, and we are talking about heat and diffusion interaction, a legitimate question is, well, is there some interaction that is not like the heat and diffusion, it's not like heat? And one important example, which also gives me a chance to mention, is radiation. Electromagnetic radiation contains not only energy, the photons that come from the sun for example. They do not have only energy. They also have entropy.

And you can think of actually the-- if you remember probably from your physics courses, this idea of the black body radiation in a cavity, in a vacuum cavity, you have photons bouncing around and exchanging with the walls. Now, the electromagnetic field is an interesting subject because if those walls in your cavity were perfect mirrors, so they wouldn't absorb the photons, but they would simply bounce them away, these--

The modes of the electromagnetic field would not interact with each other. So in other words, you would have that photons with a certain frequency will remain-- will not exchange with photons with another frequency. It is only through the interaction with matter that radiation can move energy from one mode, namely one frequency, to another frequency.

OK, this is all described by Planck's theory of electromagnetic radiation. And these are the well-known spectra of the various items. One is energy, curve A is for energy, curve B is for entropy, P, the pressure is C, and then you get also-- yeah, we plotted here also the functions in terms of instead of frequency of wavelength. But what is important is that-- so the equivalent, if you have two bodies, yes-- two bodies at different temperatures,  $T_A$  and  $T_B$ , and there is vacuum in between, they exchange energy via the electromagnetic radiation because there are photons in each of the solid.

The solid is not-- you think it is full completely, but it's full of empty space. And in that empty space, the photon go in and out. OK, so the photon that emerge from one body go directly, ballistically, so to speak, in like a ray to enter, or to hit the other solid. And vice versa.

And if you take-- if the solids are at stable equilibrium and the electromagnetic radiation that leaves the solids is in equilibrium with that, it has the features of that temperature. So the photons that come out of body A have the temperature  $T_A$ . And then they arrive to system B. And that is a non-equilibrium situation. They have to interact and thermalize. And so by interacting, and being absorbed, and re emitted by the molecules of body B, there is a remesculation (I meant, redistribution) of the energy. It's like the collisions that we talked about that it is an irreversible fact.

that allows the thermalization of these photons. So the-- so  $\sigma T^4$ ,  $\sigma$  is the Stefan-Boltzmann constant, it's written down here, I'm sure you remember it. So this  $\sigma T^4$  is the amount of energy that goes out of body A. And this is the one that goes out of body B. So they exchange-- so the net exchange is the difference. And together with the  $\sigma T^4$ , which is very well known, there is also a  $\frac{4}{3} \sigma T^3$  for the entropy that goes with it.

So these photons do not carry only energy, they also carry entropy like the photons that come from the sun. The sun has photons that on the surface have a temperature of the order of, what is it, 5,700, 5,760K. And those photon leave the plasma that is on the surface of the sun that we've seen very well during the eclipse the other day. And they all the way travel to here, to the Earth. And they carry the features of energy and entropy proper of that temperature.

And the fact that they have entropy limits the amount of work that you can do with that energy. So it's not entirely-- you cannot extract 100% of energy because of that entropy. That's the-- do you remember that when we talked about, I think, in the allocation chapter, we talked about the exergy of solar radiation being around 0.93. That is where-- part of the story, comes from this entropy content.

But of course, you can also not only talk about the flux, overall flux of energy carried by these photons, but also, you can talk about the flux of energy carried by each mode of the electromagnetic field. So you do this per frequency. And you can do that energy wise, but also entropy wise. So this is the flux that is exchanged between body A and body B at temperature  $T$  via photons of that frequency  $\nu$ . Or if you want, you can write it in terms of the wavelength.

In this paper that we wrote long ago, and then it was republished recently, you find all these formulas that are useful if you are in the solar energy business. So let's go back now to the formula for the entropy production, which will be the starting point for our applications.

And we do-- also here, we want to introduce the fact that-- use the fact that these fluxes are not all independent and rewrite this expression in which-- that you-- I don't go over it because we talked about it so many times. But we now want to concentrate only on this term, which has to do with the diffusion of particles. And we want to rewrite it in a form that goes only up to  $r$  to the minus 1, or essentially, that it is written in terms of independent fluxes.

And one way of doing it is through these steps because now, we also have to remember that the gradient in the chemical potentials, which appears here, this is a gradient done at keeping the temperature constant, is-- they are not all independent either because of the Gibbs-Duhem relation. Remember, the Gibbs-Duhem relation is written here. It says that the weighted sum of those gradients of chemical potentials weighted on the concentrations of the elements-- of the constituents is related-- gives the gradient in the pressure.

Remember that the pressure, we managed to make it disappear somehow from-- by working in terms of properties per unit volume. But here, it's where it reappears via the Gibbs-Duhem relation.

And now, I'll let you play with the math. Here, it explains how. The fact that if you have a relation like this, you can rewrite it in this other form. It's just playing with summing and subtracting 0's. And the good thing is that if you-- that now, the right-hand side of this expression has differences between chemical potentials. And therefore, this summation, which goes still from 1 to  $r$ , but effectively goes to  $r$  minus 1, because when  $j$  is equal to  $i$ , this difference is 0.

So this is the first step that we make. We substitute this into here. And next, once we have this expression like this, again, I let you play with the math. It's an expression of this type in which it happens that the coefficients that multiply here are invariant upon exchange of  $i$  and  $j$ . And that symmetry allows you to add and subtract or to rewrite this term-- this summation by exchanging those indexes and then subtracting the two, and essentially, you can get this identity, which we apply there.

So now, we have this nice expression in which we have the summation, it's a double summation. But it has a number of 0 elements because every time-- it's all written in terms of difference between fluxes and differences between chemical potentials, which also has the advantage that makes it reference frame independent because those are fluxes with respect to the barycentric velocity.

So they depend on the reference frame, which is the barycentric one, the one that follows-- the Lagrangian local (frame) following your fluid element. But if you take the difference between the two, then the difference is independent of that frame. And that is also an advantage.

So finally, yes, we bring back the pressure here. And we-- but we have this summation, which is expressed in terms of these differences that we now rename. So  $J_{ij}$  is the flux of particles of species  $i$  with respect to particles of species  $j$ . So for example, if you have the water vapor that comes out of your shower and so those water molecules travel in the air and go and get your mirrors wet.

OK, so that's diffusion of particles of water vapor. And of course, the room that is made empty by those particles of water vapor that goes away are filled by the air molecules. So there is a crossing of flows. OK, so here, we are talking about-- so  $J_{ij}$  is the flux of particles of the water vapor with respect to the motion of the air molecules. So it's a relative flux. And also, this chemical potential differences that are also written here, we can think of them as the conjugate-- So there are relative forces.

So now, if we take this expression here, we substitute what we get here. So we get a term with the gradient in the pressure. And we also have the term with the dissipation function from fluid mechanics. Let's forget about those. So let's suppose we take no flow and no-- yeah, no flow. So we move with the-- perhaps we have a box with particles that are steady with respect to the laboratory frame.

And let's suppose we are at uniform pressure. And also, we have no chemical reactions. Then, we are left with these three terms. And these are the three terms that will allow us to define the thermodiffusion and the thermoelectric phenomena that we are interested in dealing with as examples of these cross effects. So this will be our starting point. Let's start with the thermoelectric effects as the more or less simple example of the procedure that we need in order to understand it.

We start from this expression of the entropy production that we just reviewed. And in this case, there is only one particle, which is the electrons in your conductor, or semiconductor, or the holes in the semiconductor. So charges. But a single constituent, it means that there is no diffusive flux with anything else. So the term that we had a couple of slides ago, so this one, this one does-- oops. Sorry. This one doesn't contribute because there is no relative motion with anything. There is only one type of particle.

And here, I have highlighted in blue and red the flux and the conjugated entropic force. You'll see in a moment why I suggest that when you do this, you always start from this entropic point of view because that's the only safe place in which you can apply Onsager relations without making too many mistakes. All right.

So the next step, remember, this is the extrinsic relation. It doesn't contain any feature yet of your material. Now, in order to bring in the features of the material, you have to model the relation between the fluxes and the forces. And if we assume a linear force flux relation because we assume that we are near equilibrium and so on, this is the most general linear relation between these fluxes and these forces.

And it has a matrix of coefficients, which is the Onsager matrix of coefficients. Actually, in this slide, these are tensors because as you remember, suppose we didn't have-- suppose we had only Fourier law. Fourier law is a linear relation between the heat flux, which is a vector, and the gradient in the inverse temperature, which is also a vector. And the most general relation is through a tensor, which is the conductivity tensor  $\underline{\underline{k}}$  that we have already discussed, and which is symmetric by the Onsager principle.

Here, we have added also relations with other tensors. So this would be instead the relation between electrical current, this is current density, so it's the flux of charge. Yeah, I'm calling it now  $i$  double prime. I should have probably more consistently called it  $J_q$ . So the diffusive flux of charge, because this is still diffusive.

But since our solid is a solid, it is not moving, there is no convective part of the charge. And so they are the same. So just to make it more appealing to the idea that we're talking about electrical currents, something that you measure in a wire. OK, so this is Ohm's law. If you take only this last term, the relation between current and the gradient in potential is the thing that you measure in volt, with the voltmeter, in volts.  $T$  is--  $\tau$  is  $1$  over  $T$ .

And  $L$  is the resistivity of your material, which you would measure in Ohm per meter, I guess. And it is a tensor also. So if your material is isotropic, that tensor to reduce this to just the one number, one scalar. But if it is anisotropic, exactly like we have seen for heat transfer, you would have different principal directions of-- where the electrical current likes to run easier than in other directions.

OK, so this is the first step. Assume linear flux relations. Next, what we typically do is to rewrite. So rearrange these equations by bringing in more familiar variables. And in this case, the more familiar variable is simply the temperature instead of  $\tau$ . So this is  $1/T$ . But we also want to rewrite it in a different way. So we want in the first equation to substitute this term here with the electric current.

So what we do is take the second equation and extract the gradient in  $\phi$  from the second equation that we will then substitute in the first one. So this is what we are doing. So we take this, we solve, of course, these are tensors. So in order to solve, you have to multiply to the right-- from the left with the inverse of this tensor, which exists because the tensor is positive definite because of the principle of entropy nondecrease.

So you do that, you get the gradient in  $\phi$ , you substitute up there. And here is what you get as a result. So you get now a relation between the heat flux, the gradient in temperature, and the electrical current. And of course, the substitution that you've made since the gradient in the electric field-- I'm sorry, in the electric potential, depends on the current, but also on the gradient in temperature.

When you substitute it up there, it gives its own contribution to the term that multiplies the factor, the prefactor, of the gradient in temperature. That's why you see this difference. So this is the direct, say, Fourier like kind of term. And this is the indirect due to-- due to the flow of charges, of electrons.

OK, so and then finally, we-- instead of carrying all these names with the  $L$ 's, we just give different names. So the term that multiplies in this equation, the gradient in temperature, we call it  $\epsilon$ . And that's called the Seebeck coefficient. This other term, we call it the electrical resistivity of the material. So the  $L$  was the conductivity, electrical conductivity. I misspoke before.

Now, this combination of  $L$ 's here with the minus-- the  $1/T^2$ , we call it thermal conductivity. And this last one, we call it the Peltier coefficient. And here, we repeat their definitions just for clarity. Next, we're not done yet, because these four numbers, these four properties, these are equilibrium properties. They are-- remember that this is a linearization around the equilibrium. So these are measured at equilibrium. And they are not all independent because there is the Onsager principle of reciprocity.

So  $L_{12}$  is equal to  $L_{21}$ . More precisely, since we're talking about tensors, you should think of this big-- this is a big system in which you have three equations here for the components of the heat flux and three equations here for the components of the current density. So you have-- so it's a 6 by 6, which you can cast in this more compact way. But this 6-by-6 matrix has to be symmetric by the Onsager reciprocity.

And so this symmetry requires that each of the groups, these blocks that we have defined of this matrix, are symmetric themselves, and also that these off diagonal are one equal to the other. So if you apply that symmetry, you may notice-- let's see. Yeah, you may notice that there is a relation between the Peltier tensor and the Seebeck tensor. If you take the transpose of the Peltier, the transpose of a product of matrices, when you do the transpose, you have to also change the order, the product of the transposed.

And then you apply Onsager symmetry. So the  $T$  goes away. And here comes something that is contained in Seebeck except the temperature. So essentially, you find that the transpose of Peltier is equal to the temperature times Seebeck. And of course, if the material is isotropic, these tensors simplify to simple scalars multiplied by the identity tensor, which is matrix with all 1's on the diagonal and 0's outside.

And so the Onsager reciprocity implies that the Peltier coefficient is equal to temperature times the Seebeck coefficient. Moreover, you can also rewrite in terms of these new properties of this material. You can rewrite the entropy production. And you would like to write it in a canonical form just to make sure that it is-- that your model does indeed respect the principle of entropy non decrease. So these are quadratic-- canonical form-- And these are quadratic forms, which as you see, they are.

And you can write it in this way or also in this other way. A single quadratic form. So let's see an example of where we use the Seebeck effect every day in the lab, which is the thermocouple. You see, we started from the general linear relations. And we ended up with these other relations.

Now, yeah. Let me go back one moment. Sorry. I want to show you this. Already at this stage, if I change  $1$  over  $T$  and write the equations in terms of temperature and not the inverse temperature, look what happens-- that-- just that little step makes you lose the symmetry because  $L_{12}$  is equal to  $L_{21}$ . But this coefficient here is divided by  $T$ . This is divided by  $T$  squared. So they are not equal to one another.

So if you by mistake started from-- Oh, say, well, who cares? I mean, temperature or inverse temperature. So you took the wrong-- so it's not the temperature, the witness of non-equilibrium, the degree of disequilibrium. It's the gradient of the inverse temperature. So that is minus  $1$  over  $T$  squared times  $\text{grad } T$ . So that is the-- so this is why I say, you better be careful and start always from the entropic point of view and the proper degrees of disequilibrium.

Otherwise, you may end up thinking that there are symmetries where there are not. And you get the wrong relations, of course. Even more so here. And the symmetry between this and that is-- there is a temperature in between-- because Peltier is Seebeck times the temperature.

OK, all right. So what is this example? So if we apply these equations to an electric current that runs in a wire in which there is a temperature gradient, then you have this expression here that relates the temperature gradient, the electric current, and the voltage drop along the wire.

Now, a wire is a one-dimensional thing. So you can describe it by a set of coordinates, which is like this. So a local set of coordinates where one versor is tangent to the axis of your wire. And the other two are orthogonal. And then you have these vectors. So these vectors are, let's say, the gradient in  $\phi$  that's a vector. But the important part, if you want to compute the difference in voltage between point 1 and point 2, you have to integrate the component of the gradient in  $\phi$  projected onto the  $\ell$ , onto the direction of the wire and integrate.

So you do the integral of  $d$  (read, nabla)  $\phi$  dotted into  $d\ell$  from 1 to 2. And that gives you the difference in voltage. What is it,  $V_2$  minus  $V_1$ . It turns out-- I don't know if you have seen this, but this is easy to do. So the gradient, remember what it is, it's this operator here. And  $d\ell$  is also a vector, which has components  $dx$ ,  $dy$ ,  $dz$ .



So now, what we are doing here is taking the scalar product of this applied onto the scalar  $\phi$ . So when you do the dot product of two vectors, you get the multiplication of these two. So the multiplication is going to be, the derivative of  $\phi$  with respect to  $x$  times  $dx$  from these two components plus the derivative of  $\phi$  with respect to  $y$  and  $z$ .

And what is this? Well, this is the expression for the differential of  $\phi$ . OK, so you can rewrite this term here as  $d\phi$ . And therefore, the integral is very easy. It's just  $\phi_2$  minus  $\phi_1$ . Which is what we do here. Now, we are doing it-- the thermocouple has to have two different materials, two different conductors.

And here we call it A and here we call it B, that are joined with a good conducting junction here and here. And at the other end in this place, they are not touching. So they are just-- it's an open circuit so that there is no current circulating. And you will measure a voltage difference if there is any.

Now, in order to compute that voltage difference, you need to do that integral three times, from 1 to 2 with metal A, from 2 to 3 with metal B and from 3 to 4, again, with metal A. And what are we integrating? Well, the governing equation is this one. But since we are at open circuit, there is no current. So there is no-- the current is equal to 0. So the remaining stuff is this simple relation between the gradient in  $\phi$  and the gradient in temperature. So you do those three integrals.

You cannot assume-- you should not assume that  $\epsilon$ , the Seebeck coefficient, is constant. And so it goes out of the integral. Yeah, you could, but that would be an approximation unless you use the proper average in that temperature range because Seebeck coefficients are functions of temperature. So let's keep them inside the integrals this way.

And then of course, since at the junctions, there is electrical continuity, the voltage, so the electrostatic potential, is always-- is equal. And so now, you can add these three equations. And what you are left with is this, that  $\phi_4$ , so voltage at 4 minus voltage at 1 is equal to this integral from 3 to 2. Yeah, because you're combining this and that, which are the integral of  $\epsilon A$  into a single integral from 3 to 4 and then from 1 to 2.

Why? Because at 4 and 1, you are assuming the same temperature. This is a laboratory temperature, the place where you put your thermometer (I meant, voltmeter). So you assume that  $T_1$  is equal to  $T_4$ . And therefore, you get this difference. And sometimes, you call this difference or actually each generic integral of this difference between reference temperature and a generic temperature is called the characteristic function of the thermocouple, or the couple of the materials.

And here are some plots of those types of thermocouples. That means-- at the end of this calculation, what's the final result? That we may have a difference in voltage measured by our voltmeter if there is a difference in temperatures between 2 and 3,  $T_2$  and  $T_3$ . And of course, in order to have this voltage, you need that the characteristic function of that thermocouple be different at these two temperatures.

This function here is the function that you do when you calibrate in your lab. When you buy a thermocouple, you should do calibration, or maybe you buy it certified so it comes with a calibration. And calibration is that somebody has actually measured this for your thermocouple because-- yeah, could do it theoretically, but small variations in the cross section of your material or some impurity along the wires, may result in different features and properties of your wires.

So you always work with-- you always need to do a calibration for your thermocouple. Now, the nice thing is that therefore, you have here something hot, here something cold, and you generate a voltage. So if I have a hot reservoir and a cold reservoir, and I want to produce electricity, the thermocouple can be made to function as a generator. This is the thermoelectric generator, which is exactly what I just said.

The difference is that now, it's a generator. So I don't want us to measure the voltage difference, but I want to do something useful like run an electrical engine, light up some light, or use that electricity. So I attach a load, an electrical load, to the two places where before, I was attaching the voltmeter. An electric current will start flowing, because that voltage will cause a flow of electrons.

But then that-- what does it do? If there is a current that goes from 4 to 1, there is also a current inside the wires that goes all the way around. So when I do the calculation for the voltage, I also need to take into account now the other part of the equation, the one that has to do with the electrical current. So I have to add up for the voltage drop, Ohm's law.

So the voltage goes down. The more current you have, the lower the voltage. And you could actually go all the way to short. If you short the thing, you have the highest current but it's all dissipated in Joule effect, in heating. OK, so now, I have a voltage, the actual voltage, multiplied by the current that goes through my device, the one that uses that electrical energy. Voltage times current is the electrical work, the power.

Volts, amperes, watts. OK, so that's the electrical power which is given by this expression here. And as you see, there is a Joule effect dissipation. So the the higher is this, the more inefficient is my engine. The problem is that if I want to make this 0, I have to make  $I$  0. So I also get 0 work. So there is a compromise. And one way is to compute the maximum power. And so the maximum power is just take the derivative of this with respect to  $I$  and set it equal to 0.

That gives you this value for the electric current. And you substitute in there and you get the maximum power, which goes, you see, as the square of the difference between the Seebeck coefficients of your two materials, these materials pair. Notice that also, not only for the thermoelectric generator in which there is a electrical current, but also for the thermocouple, let me go back one moment.

We focused a lot on-- in order to do this calculation on the first equation, but also, the second equation is in place. And in addition, we should also remember that this is an irreversible phenomenon. It's driven by entropy generation. And in fact, there is a heat  $q$  double prime that runs across, runs down from-- along the wire, because the wire is an electric conductor, but it's also a thermal conductor. It has a thermal conductivity. And it has a Peltier coefficient.

So it moves heat for two reasons. One is the gradient in temperature along the wire, and the other is the electrical current that, how do you say, carries with it some heat. That's the Peltier effect, which is this proportionality here. So that heat is dissipated and produces-- of course, it produces the effect. You can also think of it in the other way around. It's that the heat that flows drags also the electrical charges together with the flow of heat. And that is why electrical charges accumulate on one side of the thermocouple. And that's how you measure the voltage.

So it's the combination of-- so this same equation gives rise to the Peltier effect. The Peltier effect, you can see it here. It emerges from this second equation more directly. And the typical setup is that you have a junction between two different materials in which you run an electric current. So you-- they have to be conductors or semiconductors. And so you have to have a possibility to drive a current through this junction from material A to material B.

So that's the current  $I$ . And let's assume for a moment that you can-- that you are keeping no gradient in temperature. So the temperature is uniform throughout here. So this term in the equation is not there. And but you still have the equation. It says that the heat flux is proportional to the electric current. But the problem is that this proportionality Peltier coefficient is different for material A and material B.

So at the junction, whereas the electric current must be continuous because you cannot create charge, so at the junction, there is a continuity. So the electric current that comes from A is the same that goes into B. But this equation also says that the heat  $q_A$  is given by this. And here, I have another heat which is given by this. And it's different because the Peltier of B is different from Peltier of A. So there is a jump here in the heat flux.

Of course, jump in a heat flux wouldn't satisfy the energy balance unless there is energy coming from somewhere. So essentially, this jump calls in for the balance of energy that is needed for it to exist. And therefore, this junction transforms into either a cooler or a heater, depending on the difference of the Peltier coefficients and the direction of the current.

So if you choose a Peltier pair in which, say,  $\Pi_B$  is greater than  $\Pi_A$ , then-- and you run the electric current in this way so that this is positive, then  $q_B$  is greater than  $q_A$ . So that means you need to provide energy. So that means this junction becomes a cooler. This is the Peltier cooling effect. This is what you obtain when you buy a Peltier cell, something that you can buy on the internet now for a couple of bucks. And or you can make it simply if you have a thermocouple.

Also, a thermocouple is where you have a junction between two different materials. You have the possibility of using this effect. A nice aspect of the Peltier effect, and also a nice aspect, I forgot to say it, about the thermoelectric generator, is that they convert electrical energy into heat and vice versa without moving parts. So these are engines that do not have machinery.

So these are very important features for some applications. For example, for space applications, this is fundamental because once you have sent something in space, then it's very hard to provide maintenance. So moving parts are a problem. And so if you have these kind of devices, they're good.

Plus, also, in space, you have the availability of very large temperature differences because you have the photons coming from the sun that we just said, are at 5760 K. And on the other side, you have the dark space, which is maybe, what is it, 2.7 or 4K. So that-- through, of course, you need electromagnetic radiation because those-- you don't have a heat exchanger. The provider of those fluxes are the photons that we just talked about.

The problem with the development of devices based on these effects is the materials because standard materials have very small values of the Peltier or Seebeck coefficients. For example, here, I took the ones for copper. Copper has a Seebeck coefficient of 1.5 microvolt per kelvin against a very high conductivity,  $k$ .

And so the Peltier coefficient, which would mean-- in this case, if I have 1 millimeter cross section of my wire, and I run one ampere into it, and suppose I have on the other side an ideal material that has 0 Peltier, so the difference is only that of copper, I would be able to generate 1/2 of a milliwatt, 1/2 of a milliwatt per ampere. Ampere is a lot of current. Milliwatt is pretty little.

Yeah, you can also read this equation here in another situation. Suppose you have no current, sorry-- no heat flux. So no heat flux, 0 here. So that says that if you run an electric current through your wire with no heat flux, you have a buildup of temperature. This is, we call it also Thomson effect. But no, no. I think it's Peltier. OK, but so how much temperature gradient does it build up?

So again, see if I take my millimeter wire and I put 1 ampere into it, it does-- it builds up 1K, 1.2K over a meter of wire. So these are small effects, but people are developing materials for this purpose. So there is an entire literature, that you might be familiar with if you're working on the field, of scientists working on developing nanomaterials or special materials designed to maximize these Peltier and Seebeck coefficients.

Some of these materials are also semiconductors. So this is a typical setup. And you put many of these devices in parallel so as to produce a sensible amount of power. Each one contributes a little. But if you put a lot together, overall, you may obtain the effect that you need. And the typical design of these devices is the same, whether you're using the thermoelectric generator or, if you want, your solid-state thermocouple, or you want the Peltier cell.

So it's the same device that, depending on how you use it, performs in different ways. Now, regarding the thermoelectric generator, traditionally, people like to characterize the materials with this parameter here, which is called figure of merit for the thermoelectric material, which is the epsilon, so Seebeck squared, times temperature divided by resistivity and thermal conductivity.

You may-- we may see how this parameter comes out in our own language, or at least the language that we have developed in this course. If you accept that you can rewrite the work-- the power of the thermoelectric generator that we have developed in the previous slides as an integral of what happens locally. So as if everywhere in the wire, there is something that is the local contribution to the overall effect.

So you integrate that local contribution over the entire distance, and you get the overall effect. In a sense, this is a power density. Electrical-- useful power density of your device. OK, so if you accept that, and in fact, that power density is the product of the electric current. And the gradient in the voltage. So that's-- voltage times current is power. So this is the density, though.

So I take this one and then I'm going to-- in order-- so I want to define an efficiency, second-law efficiency, which is down here. So I want to take the work obtained and divide it by the maximum work I could obtain for that same temperature difference. Now, locally, the temperature difference is just the temperature gradient. And if you go back in the notes, and maybe this image reminds you where to go, you remember that when we did the elements of heat transfer, we said, yeah. We could substitute our material with a little engine.

And how much work would it be able to do? If you go back, you find that that maximum work, or work rate, is given by the heat times the gradient in  $1/T$  times  $T$ . So this is the expression. Therefore, the second law efficiency of your thermoelectric generator, locally, at least, the local contribution, is given by the ratio between this and that, which we can calculate because we have the equations for the gradient in  $\phi$ , for  $q$ . It's the same equations that we started with.

So let's do the substitutions and compute the work. Now again, here, the work can take a maximum value. I think there is an error here. This must be a minus sign here. Yeah, because there's a minus here. Yeah-- I don't see it right offhand, but this-- I think this should be a minus because this is a Joule effect that should detract from the work that is done.

So you maximize this by taking the derivative with respect to the current density and set it to 0, substitute, and you get the expression for the maximum power density. And this is the maximum that you should get. Ah no, OK. I see. They are different in signs because the gradient is negative because you get work when the current goes down, the negative-- you need a decreasing temperature gradient. Yeah. In fact, you get the maximum when  $I$  is minus gradient of  $T$ .

And so we take this, substituting the expression for the  $q$ , and obtain therefore the maximum reversible work. So at maximum power, the ratio of this to that, you see, they both depend on the square of the gradient. So they disappear. This cancels with that. And you are left with just a ratio of coefficients where this parameter of merit appears, this  $Z$ . This is not the standard way of presenting this parameter of merit.

But at least, it has some value of being local. The problem is that in practical applications, since the materials that you use are temperature dependent, and it is important that they be temperature dependent, often, in these kind of derivations of this parameter, you assume constant Seebeck coefficient, or constant thermal conductivity, or constant  $P_i$  which is only for the purpose of the derivation, in order to arrive to this expression.

OK, again, in the list of thermoelectric effects, we can also-- list this Thomson effect, which is, though, I think still the same thing, only said in a different language. So we have seen that the interplay between electric current and temperature gradient allows you to transform electrical energy into thermal energy, and vice versa.

So what we do here is to take-- to write the balance equation for the internal energy. And you can do this also for a flow situation. We've written-- if you go back where a couple of lectures ago when we did the general balance equations, we had an expression for the balance for energy. And today, in one of the previous slides, we've done the difference between the energy and the internal energy, which is all those terms, kinetic, potential, and so on.

So in order to obtain a balance equation for just internal energy, you have to subtract from the energy balance equation, the balance equation for the non-thermal aspects. So for the mechanical aspects, like the kinetic, the potential, and the electrical. And if you do that, this is what-- using the slide that I mentioned-- you can obtain this. Of course, in the balance for energy, there appears the energy flux. That's the overall diffusive energy flux, which we have broken into a non-work and a work part.

The non-work part is the one that now for a solid, in the absence therefore of other moving particles other than just the electrons in the conductor, is just given by these two terms. Otherwise, you would have the summation of the partial enthalpies. And for the work part, it's given by the stress tensor times the velocity. But if we are assuming that there is no velocity here, this is really going away.

So if you get to the end, the terms that survive are these. On the left-hand side of the balance equation, you have the material derivative of the internal energy of your fluid element. So that's the internal energy, that part of the energy of the fluid element as you follow its motion. That gets changed by what? By heat diffusion. This is Fourier thermal diffusion. So you should think of this as the equivalent of the Fourier law or Fourier equation of conduction.

So this would be  $\rho c_v$  times the  $DT$  over  $Dt$ ,  $D$  of the temperature over  $Dt$ . This is  $k$  times the Laplacian of the temperature, if  $k$  is independent of position, and therefore of temperature. Then you have this term here. This term here is the Joule effect. This is like a source term. It would be-- in heat transfer, you would put it as a  $q$  triple prime. So it's a source term of thermal energy.

And it actually is electrical energy that gets dissipated into thermal energy via the Joule effect. If you had written the balance equation for the mechanical and electrical parts, the same term would appear there with a negative sign. So it would detract, it would destroy, mechanical and electrical energy. So it would be a negative sign in those equations, and appears here with positive sign because it goes from electrical to thermal. And it's one way.

It has a definite sign, it cannot be negative. It goes only in that way. You can only kill electrical energy with the Joule effect. Like-- although we're in a solid, and this doesn't really make sense. But I just put it for our discussion. If you also have flow, the viscous dissipation also has the same feature. It appears with a negative sign in the equation for the kinetic energy, the kinetic plus potential energy, because it kills that kind of energy and it appears with the positive sign in the internal energy.

So that transforms. So this is always positive. But then there is also this term. This term is the Thomson effect. It's-- you see, there is a scalar product of the electric current and the gradient in temperature. This can be all signs, it could be positive and negative. And it allows you-- and it is that term which allows the effects that we explained in transforming thermal energy into electrical energy if it is negative because with a minus sign, I'm sorry, since it has a minus sign, if it is positive, it consumes internal energy. And where does that energy go? It becomes electrical.

Or vice versa, you use electrical energy for this becoming thermal energy. OK, so this adds a term. The Thomson coefficient is-- if you follow the various steps at a certain stage, we have-- since there is the divergence of the energy flux, it brings in the gradient of the Peltier coefficient. And the gradient of the Peltier coefficients can be written as the partial, as how it varies with temperature, partial of  $\Pi$  over  $T$  times the gradient in temperature.

And this Thomson coefficient, sometimes it's called with  $T$ . I used this epsilon  $T$ -looking Greek symbol. Just not to confuse it with so many  $T$ 's here that one more would be too many. So this is given by the difference between how the Peltier coefficient varies with temperature and the Seebeck coefficient. But since Peltier and Seebeck are connected via the Onsager relation, Peltier is epsilon times  $T$ , you can also write this coefficient as  $T$  times how Seebeck varies with temperature.

And recently, there have been people discussing the fact that there may be-- it may be more-- or at least it may be a good idea, to try to build thermoelectric generators, not so much on the basis of that parameter there, but on the basis of materials that have very high temperature dependence of the Seebeck coefficient. So as to enhance this gamma (I meant, epsilon), and therefore enhance the capability for a given gradient in temperature to produce the highest current.

OK, let me just mention before-- yeah, we have a couple of minutes-- I'm not going into the details here. Just want to mention that the range, the inventory, the catalog of effects that we have covered with that matrix that we started on today with the Curie principle, is not at all complete because for example, if you add one item, the magnetic field, you add another spot in that matrix, and actually, add another four spots.

And these are effects that belong to the same category. One is called-- and they also belong to the history-- one is called the Hall effect.  $H$  is the magnetic field. And the other is called-- the converse, or let's say the Onsager reciprocal effect is called Nernst effect. And they generate-- if you have an electric field and you have an electric current in one direction, the magnetic field produces an electric current also in the orthogonal direction. This is the Hall effect.

And Nernst does the same thing. Instead of having as driving force the electric field, you have as driving force the gradient in temperature, which we know that drives an electric current like we've just seen in the thermoelectric effect. But in the presence of magnetic field, it also drives an orthogonal current like the Hall effect.

And very recently, as you see, this is just a few years ago, people have been working on the equivalent of these effects also on spin currents. So they're not moving charges but are moving the spin that is internal into the atoms, or the nuclei of the atoms that you move around. And you look just at the current of spin. And they have found similar effects. And this is, I guess, a similar idea done with spin currents instead of charge currents.

And so this was only to say that this is a topic that is so broad and so full of applications that it's very difficult to cover in a sort of a systematic way. But it's also to show that it can be, it must be, regularized and understood in a systematic framework like we have done, starting with the entropic point of view and developing the linear force flux relations, and applying Onsager relations.

And often, this way of proceeding is what drives the search for new effects. You didn't think about it until you said, oh, I see. Ah. So by induction, there must be an effect like that because there is a spot in that matrix of phenomena that is related via the Onsager principle.

All right. So yes. I think we are done for today. And next time, we do the thermodiffusive effects. And then, we will be done. So next lecture will be the last one.