[SQUEAKING]

[RUSTLING]

[CLICKING]

GIAN PAOLO BERETTA: OK, good morning. So we are still here in studying cross effects that emerge from the Onsager theory of non-equilibrium near equilibrium as a result of linear relations between forces and fluxes.

Just as a reminder, in this slide, we got these expressions that summarize the relation between energy flux and entropy flux and constituents flux, including current, electrical charge flux.

And these are diffusive fluxes. So they are relative to the-- if we have a motion, like in a fluid, they're relative to the barycenter of the fluid parcels.

And this other slide also, which we have reviewed the last time, allowed us to write this term in the expression for the rate of entropy production in terms of independent fluxes, or, actually, in terms of these Jij's. These are differences between fluxes of pairs of constituents that are present in our system.

And they go together. So the conjugated force to these diffusive relative fluxes are-- we could call them diffusive relative forces. And they are given by the difference in the gradients of the chemical potentials of the same two kinds of particles.

Notice that these by definition are antisymmetric. So you change-- you swap the indices, you change the sign, of course, because it's obvious from here.

And therefore, you see here we have 1/2 of the summation over ij. And you're supposed to sum over all the i's and all the j's. And that will pick each of these elements twice.

So the 1/2 will go away. And so, for example, if you have just one pair, you will have J12 plus J21, and they will end up-- this sum will end up being just one term-- J12 times X12.

You also should remember that we have to use the Gibbs-Duhem relation, which relates the gradient in pressure to the gradients in chemical potentials. For example, for a pure substance-- so there's only one constituent-- this also holds.

And it says that the gradient in pressure is equal to the concentration of the substance times the gradient in the chemical potential at constant temperature of that substance. We will use this today in one of the examples.

So here I've included up there-- here there's still the full expression. But now I want to focus only on the vectorial fluxes and forces-- so the fluxes of extensive properties that are of vectorial yeah, vectorial character.

So we exclude the scalars, chemical reactions. We exclude the tensorial fluxes. So we exclude the dissipation function.

You see here that we have many different terms. And then let's suppose we have only three kinds of particles in our system. That summation over the i's and j's ends up contributing only three of these products of forces and fluxes.

Only three of them are nonzero and independent. So this will be the interdiffusion of particle 1 with respect to 2, of particle 1 with respect to 3, of particle 2 with respect to 3.

And then we have the diffusion of electrical charge related to a change in electrostatic potential-- gradient in electrostatic potential. Of course, heat is in the gradient of 1 over T.

And then there is also this term with the pressure, which gives you a flux of particles driven by a gradient in the pressure.

So we have six terms, six different extensive properties that can be transported in our system, and six different degrees of disequilibrium which control and drive the system back towards equilibrium.

This is also related to the Le Chatelier-Braun principle. And if you remember, the more-- see, each one of these degrees of disequilibrium is related to a necessary condition for mutual equilibrium.

So if you have no gradient in temperature, you have equality of temperature. So from that point of view, you are OK for equilibrium. But that's not the only condition. You also need no gradient in pressure. That's pressure equality, if the systems can exchange volume.

This is part of the chemical potential, but it's the electrostatic. So if you-- so you are at equilibrium, at least from that point of view, from the electrostatics, if you have no gradient in the electrostatic potential. And here also you have the equality of chemical potentials of the various pairs.

If they are all equal to 0, then we are at equilibrium. The more you have of them that are different from 0, the further you are from equilibrium, the more they adapt to the degrees of equilibrium. And therefore, like Le Chatelier-Braun says, your system will have a stronger tendency to return to equilibrium.

And the way the system returns to equilibrium is described by this big matrix. In fact, I didn't put the tensor signs, but these are-- each of them is a tensor because the most general relation between a vector and another vector is through-- even linear, it's through a tensor.

So you see how rich the variety of phenomena that we can encounter and that we can model is So, of course, if you want to include all of them, you'll need a computer program to do it. This is done in simulations.

But even though nowadays we have computers and we have softwares that are very-- they're able to model very complex phenomena in fluids-- and not only fluids, because, of course, I'm talking with fluids, but also in solids, we have the same ideas, very seldom they are implemented to include all these off-diagonal terms.

Most of the times, you just keep the diagonal ones. For example, here I've already sort of shaded out these off-diagonal ones because most of the times, you assume that each pair-- so the relative flux of pair 12 is driven by the relative difference in gradient of chemical potentials of that pair and not the other ones.

But these are possible cross effects. And these possible cross effects may result in, for example, the possibility that concentration gradients-- you have two different--

you could have a flow upward of the concentration gradient of one constituent driven by the flow downward of two other constituents. And part of it could be captured by this. But I think that if you want the most general description of that, you would need to include also these off-diagonal terms.

OK, now, we have already done thermoelectric effects. And from this point of view, the thermoelectric effects cover these degrees of disequilibrium-- so a material in which you have a gradient in temperature and a gradient in electrostatic field. And so our system becomes just 2 by 2, two quantities, extensive quantities transported and two degrees of disequilibrium.

And since we are at it, I think I should-- there was something wrong in the viewgraph-- in the slide where I did this calculation last time. So I corrected it now because I was using the wrong expression for the work, the work triple prime.

So here I've taken a slightly different approach to correct that. First of all, I write what the reversible work is. And you remember in the situation like we have done when we did heat transfer, we had here, this is x. Here is T, and here is T plus dT.

And then we put in an engine that receives a heat flux, like a Carnot engine with the Carnot efficiency, because it's a reversible engine, produces a w-- let's call it th for thermal-- reversible, which is given by that minus q gradient in T over T.

Now, here, we also have a gradient in the electrostatic potential. So we can use that, by extracting, with an electric motor, for example, some work also this way.

And that will add an electrical work reversible, which is given by-- since the gradient in the electrostatic potential is driven by the Seebeck effect, this is given by minus I times the gradient in phi.

And that's minus I times epsilon gradient in T. Or maybe-- sorry, there is no minus here.

I drive a current down from high potential to low potential, and the power of the engine is current per voltage. The power is current per voltage. And so there is no I here. The minus sign comes from the relation for the Seebeck effect.

So that's what I've done here. And next, I say, well, the actual-- if I put my thermoelectric generator, and it does have some entropy produced by irreversibility, and that entropy produced by irreversibility is given by the Fourier term and the Joule effect term, of course, the actual work of the generator will be less. It will be the reversible minus T times sigma.

And since I was there, I just decided to keep also all the tensors that I know complicates the story, but since I haven't seen it done anywhere-- not that I looked everywhere, but-- so I said, well, why not working it out? And I hope I did the right thing.

So using that expression and substituting the thermoelectric relations, these ones, you find an expression for the actual electrical work. You can maximize it, so you find at which current density it has the maximum power.

So maximum power doesn't mean that the engine is reversible. It's a particular point of operation of the engine or generator.

And so if you compute this-- if you substitute this current density at maximum power into the expression for the work, you get this expression here, where there begins to appear-- now I highlight this parameter Z, which for an isotropic material takes this form.

And it's what is called the parameter of merit, the figure of merit for the thermoelectric material. And there are some materials that have that parameter of the order of 1, but there are also some nanostructured materials that go well above 1, maybe, I think, even 2, or even 3.

And this is why the fact that you can achieve, and that nowadays, you are actually engineering materials by layering. Exactly like we did for the nonisotropic heat transfer example, here you can cook up layered materials that have properties, alternate properties with high conductivity or low-- I mean, yeah, high Seebeck coefficient and low thermal conductivity.

And depending on how you structure them, you may obtain good aspects of this tensor, which, of course, relates to the properties of how much the directions come in, because you see the gradient in temperature dotted into the tensor means that the directions are important, the relative direction of your material and the direction in which you put the gradient in.

Then, once you have these, you can also substitute all the rest in all the rest and compute also the second-law efficiency. Second-law efficiency is the ratio between the work at maximum power and the reversible work that you could get with that current that you have at the maximum power.

And this is the generalized expression for that efficiency, which, for the isotropic material, becomes this one-- the figure of merit divided by 1 plus 2Z.

And if you look at this function-- l mean, Z and-- what is it-- Z divided by 1 plus 2Z. Well, it's a function that, of course, is 0 at 0, and then it goes up and eventually, it could reach 1.

Does it reach 1? Or does it reach 1/2? Ah, that's a good question, eh? Yeah, it looks 1/2, yeah. Yeah.

OK, all right. So this fixes that error that I made a while ago. But errors are instructive and stimulating so that you try to correct them. So that's good.

Here is another example somewhat similar to that one. Think of having, instead of the electrostatic potential, having the pressure. So you have two reservoirs, one at T and p and the other at T plus dT and p plus dp.

So here you could-- since you have-- suppose this is a fluid. Well, then, in addition to the thermal work, you could use the difference in pressure to drive a flow through a hydraulic turbine.

And the work of the hydraulic turbine is given by the difference in pressure times the volumetric flow rate, like in a pump, so that it's very analogous to the thermoelectric effect. And so with this pair of degrees of disequilibrium--

OK, so-- you treat exactly-- you take those two elements that survive in the expression for the entropy production. You assume linear relations. And now the flows are heat and, instead of charge here, now you have just particles.

And if you divide the flow of particles by the concentration, you get a volumetric flow rate. So this is cubic meters per second per square meter flowing.

So you can rewrite, because, usually, what we do is rewrite these expressions where we have been careful in using the entropic degrees of disequilibrium so that we know that that's where the Onsager reciprocity applies.

And so I can safely say that these coefficients, LQP, is equal to LPQ. Here Q stands for heat and P stands for pressure, of course. And so now at this level, I can apply Onsager.

But then we like to work with more familiar variables, which, in this case, are the volumetric flow rate and the gradient in pressure is already there, and the gradient in temperature instead of the inverse temperature.

So we introduce parameters, like the thermal conductivity, the other diagonal element is usually written as k over nu (I meant, eta), where nu (eta) is the viscosity, the shear viscosity of your fluid.

And k (kappa) is the Darcy permeability, because if you had only this diagonal term here, this is simply Darcy's law of flow in a capillary or in a porous medium driven by the gradient in pressure, which is what you would use, for example, to describe the flow in a porous material or a permeable membrane, like here, or in a capillary tube or in a microfluidic device or things like that.

But the off-diagonal terms are also there. And they give rise to two cross phenomena that are related to one another That sometimes go under the name of thermo-osmotic effect or mechano-caloric effect.

So the thermo-osmotic is this one. No, I'm sorry, thermo-osmotic is this one. You have a flow of material in the absence of a gradient in pressure driven by a gradient in temperature. We could actually have this flow go-- if the gradient in pressure is small but opposite to what the Darcy's law would drive the flow, you could go against that pressure gradient by using a thermal gradient, appropriate thermal gradient.

So that is one way in which you could somehow drive your material in a capillary or microfluidic device with a gradient in temperature against a gradient in pressure.

And the opposite or the conjugated cross effect is this one, where, without a gradient in temperature, you would have a gradient in pressure that drives a heat flux. But also, here, you could have-- depending on the relative differences, you could have a gradient in pressure drive heat against-- up a temperature gradient, so in the opposite direction of what you would expect if you just had Fourier.

So now let's move into the realm of diffusion of particles. The simplest is when we have two constituents, a pair of particles. So we have interdiffusion of one into the other.

And so this is a direct law case, which gives rise to Fick's law of diffusion. Or also, since we're talking about a pair, it belongs to-- instead of Fick, it's called Maxwell-Stefan law of diffusion.

And here is the story. Actually, see, on the left-hand side here I've just repeated all the various steps that took us to the relation I just said. So let's just look at what we have here on the right-hand side, which is the new aspect.

So we assume a linear force flux law and, as we have seen in the previous, just a direct effect. The degree of disequilibrium X_{12} drives a relative flux, J_{12}, through a coefficient that-- yeah, on the previous slide we call it L_{1212}, here, just drop the double 12.

Usually, there are a couple of ways in which this is typically rewritten. So there is no single familiar way of rewriting this.

We like to rewrite it in terms of diffusion coefficients, which are the things that we measure in the laboratory. Or we measure also, nowadays, with Monte Carlo or molecular dynamics simulations.

And so we rewrite-- we call this L12 this way, identify-- so these are the concentrations of the two constituents. And, of course, they are related to one another, because the mole fraction of the second species is 1 minus the mole fraction of the other one. So also between the concentrations, you have a similar relation because-- all right.

And the other aspect is that you somewhere-- yeah, here, yeah, here, you notice that you can prove that the X12 can also be written by virtue of the Gibbs-Duhem relation.

It can be written also in terms of either just one gradient-- X1 is just the gradient in chemical potential of substance 1.

So it's just is this one-- minus 1 over T times gradient of mu 1. And that's X1. But you can also define an X2, and these are all related to X12. So by substituting and expressing these in terms of the flux of particles 1, proportional to the gradient in chemical potential of that particle, you can rewrite it this way.

And then the gradient in chemical potential of particle 1 can be related, if you do properly the various derivatives, since the chemical potential is a function of the concentration.

You remember our usual expression here, for example, for an ideal mixture. For an ideal mixture, you can write this. And therefore, the gradient in the chemical potential done here at fixed temperature and pressure. So this doesn't enter into the gradient.

And so then you get that gradient in mu is RT times the gradient of the logarithm. So that's the gradient of y over y.

And, of course, since the mole fraction are related to the concentration, you can also rewrite it in terms of concentration.

So that is-- I mean, this expression is for the ideal. If you have a more general situation, you would have to do the partial derivative of mu with respect to n, which is written here. And that's what appears here.

So if you include all these, then you have a relation between the flux of particle 1 and the concentration of particle 1 times the gradient in the mole fraction. And then you can call this group the Fick diffusion coefficient, which you see is related to the Maxwell-Stefan diffusion coefficient.

And so it all depends on giving names to these diffusion coefficients. Typically, people measure Fick diffusion coefficients.

Notice also that you can also define a self-diffusion case. This is done, for example-- suppose you have just water in your box. But suppose that some of the oxygens, some of the water molecules, some percentage of water molecules, are doped. Well, actually, they're made with isotopes of oxygen. So instead of using oxygen-16, you use oxygen-18. So you have water molecules that have an isotope for the oxygen.

The isotope doesn't change the chemical properties. But that allows you to, with proper detection, to follow the diffusion of the heavy-- it's not really heavy water, because the heavy water is with deuterium, not with the oxygen-18, but in this case, it's a heavier water than the other one. So you can see the interdiffusion.

And, of course, this diffusion is related to the Brownian motion, the random motion generated by collisions and the kinetic energy that the particles always have at finite temperatures. So in that case, you measure the self-diffusion of water, which is an interesting subcase of this.

Now, if in addition to having gradients in concentrations, you have also gradient in temperature, this opens up to diffusion or thermo-diffusion effects.

And so the transport-- thermophoresis means-- remember, "phoresis" means "transport." So you generate flux of particles with a gradient in temperature, even if you don't have the driving force of the gradient of the chemical potential. So even if you don't have gradients in concentrations, just the gradient in temperature drives particles.

So that is-- this is written explicitly X12, which is minus 1 over T times the gradient in mu 1 minus mu 2.

We can write it also in terms like I've said here with the partial derivatives starting from the chemical potentials. You can write it this way, in terms of the concentration. Yeah, sorry, this should be a c1 over c1, not i. I'll correct that.

OK, so this is the setup. So that's the usual formula for the entropy production from which you infer what are the entropic degrees of disequilibrium, which are the ones that enter in the linear force-flux relations.

And so the force-flux relations are these. You therefore put in a matrix of coefficients, and the matrix has to be symmetric. So we will have that LQ12 is equal to L12Q.

And we rewrite it in so-called familiar variables, or the traditional ways, so as to single out the gradients in concentrations instead of the gradients in chemical potentials.

However, when you do that, your system of equations loses the apparent symmetry. So you see these off-diagonal terms are not identical.

But I have used, in order to put this DT here-- you see, DT is called the thermo-diffusive coefficient. And whereas D12 is the Fick-- so this is-- the Fick diffusion coefficient is the direct effect between-- so it drives a flow-- a flux of particles, the diffusion of particles, by the concentration gradient of one of them, whereas this drives the flow of particles, the flux of particles, the diffusive flux of particles, with a gradient in temperature.

And you can enter these equations in many different ways. For example, if you assume no gradient in concentration, then you have the heat flux that is simply given by Fourier law. Or if you choose to work at zero gradient in temperature, the second equation gives you Fick's law.

You could also consider, though, that when you work at no gradient in concentration, you don't have only the first equation. You also have the second equation. And that gives you a flux of particles driven by just the gradient in temperature.

That is the Soret effect. This is the effect whereby, for example, you have dust particles in the air that collect. You may have noticed, or you probably know that in your house, you often find dust near the cold walls.

It's the Soret effect, because, from the mechanistic point of view, suppose this is a dust particle. So it's a large particle with respect to the molecules of air. And let's say these are molecules of oxygen, nitrogen.

And so suppose you have a gradient in temperature this way. So you get cold here and hotter there. So the idea is simply that the particles on this side have a higher kinetic energy.

And when they bounce on the particle, of course, they exchange-- they exert a force on one side that is slightly less than the one exerted by the collisions with the particles that come from the cold side, which are a bit slower. So this pushes your dust particle towards the cold.

Notice also, yeah, and the opposite effect, the conjugate effect, is the Dufour effect. So when I have a Fick law at no gradient in temperature, so I have a flux of particles driven by concentration, but I also have a heat flux driven by the concentration.

So it's like the flux of particles that carries with it also a heat flux. And that's the Dufour effect. These effects were discovered separately, then only later they were linked by the Onsager theory of reciprocity.

Also, it's interesting to note this, that, for example, suppose you have no flux of particles. So you set this equal to 0.

OK, so if you set that equal to 0, you see that there comes a relation between gradient and concentration and a gradient in temperature. So if you impose a gradient in temperature, then-- and there is no way that-- and you don't allow this flux of particles-- then the gradient in temperature builds up a gradient in concentration, and that gradient in concentration has a play in the first equation up here.

And it reduces the effective conductivity. So the thermal conductivity at no concentration (gradient) is higher than the thermal conductivity at no diffusive flux.

Now, that simple picture that I have shown here on the blackboard is one possibility. And it's one mechanistic possibility that explains the Soret effect, or the thermophoresis for the transport of dust particles towards the cold side.

In part, that is due to the size of the particles. And so it belongs-- this nice article that summarizes thermophoretic mechanisms shows that there are many other mechanisms that drive the Soret effect, that control the Soret effect.

So, typically, the heavy particles like to get moved to the cold side, or the skewed particles, or the large particles. But then there are also more sophisticated actions, including some double layer effects on the surface of particles that have some charge on their surface.

So there is a whole realm of possibilities with which you can use Soret effect to drive things towards the hot or towards the cold, depending on how you engineer your materials and/or the properties of your materials.

This is another paper that shows how you can use a gradient in temperature to move particles against friction force in a small pipe. This is a carbon nanotube in which you have water molecules.

And so you manage, with a gradient in temperature, to win the friction forces, because one of the problems in moving stuff in small pipes is that you would need huge pressure drops if you wanted to do it with a pump. And the device will break because of the high pressures, whereas the thermophoresis or electrophoresis are more effective and more doable.

And this is also in a thermofluidic device, the idea that the gradient in temperature-- so you have a hot flow which keeps a hot side and a cold flow which keeps a cold side. And then you have your actual device with particles in it, and you want to separate the particles.

And that's what happens by the Soret effect, let's say, the particles go to the cold side, and so you reach a separation in your device.

Now, it is also important to realize that what we have covered here is only a very minor aspect of the phenomenology that goes with diffusing particles. And so what I'm doing with these slides is-- I don't pretend I can describe what happens, but I want just to suggest that the variety of phenomena that needs to be discussed, if we had, let's say, another course, but also by another teacher, because I'm not prepared on this topic.

But maybe the next teacher of this course will be. And so there are-- for example, we talked about the Knudsen number, the relative size of the mean free path relative to the dimension of your device.

So if the Knudsen number is very small, then your particles-- let's say that if they make at least 100 collisions before traveling a distance of the order of magnitude of your device, which could be the diameter of your pipe, then we are safe, and you can make the continuum assumption that we have made-- in what we have done.

But if the Knudsen number becomes larger, you may reach the other extreme, which is the ballistic extreme, in which a particle may travel all the way from one side to the other of your device without even having a collision.

So this is not dominated by collisions between particles, but it's dominated by collisions between particles and the walls of your device. Plus, there are surface effects. And so you see there is a variety of things that need to be considered.

Now, thermophoresis can also be-- is also used as a way to move particles around. This is called self-propelling particles. For example, here we have a PhD thesis and an article that talks about using a phenomenon that we have discussed, which is spinodal decomposition, in order to move around particles.

And there are two kinds of particles. This one, which has a double face, is called a Janus particles because Janus is the god with two faces, the Greek god with two faces. So this particle is gold-plated on one side and not on the other side.

And the gold surface layer guarantees-- since it has a high conductivity, guarantees a uniform temperature. And so then what they do is to shine some laser light to heat up that particle.

And therefore, a temperature profile builds up. And then they find a solution. So the particle is in a solution which is nonmiscible at high temperatures.

So we have studied spinodal decomposition in substances that have an upper critical point. Remember? And this is the spinodal curve. This is the unstable, and this is the metastable region.

So you could do that phenomenon, that thing if you could cool down the particle. But it's easier to heat up than cool. So they found it easier to develop mixtures that work the other way around.

From what I remember also, water and nicotine has a lower bound-- has a lower critical point like this. I don't know exactly what substances they use here-- water and 2.6-lutidine, OK, whatever that is.

In any case, the idea is that you start with the blue mixture, which is surrounding the particle at this point. So it's fully mixed.

And then, since you heat up the surface of the particle in this boundary layer around it, the temperature goes up, and you enter into the unstable region. And the unstable region creates-- let's say, frees the free energy. And that free energy, if properly directed, can be used to propel the particles in two ways.

You need asymmetries. So for the Janus particles, the asymmetry is on the fact that you have more heating on one side than on the other. And therefore, you generate a concentration gradient from this side to the other side. And that movement of particle in one direction propels the big particle in the other direction.

And so you get the particle move. Or here, they have still a gold-plated particle but all around. So it's not Janus. But it's not completely spherical. So it's a nonspherical particle.

And the nonspherical aspect here makes it so that the gradient in the concentration and the gradient in temperature cross. So that crossing means that these two gradients are not directed in the same-- so there is a component of the gradient in concentration that goes orthogonal to the gradient in temperature. And that will cause the movement of particles that will push your big particle, I think, downward.

So you can play also. You can play-- people are playing because this is recent work. There's a lot that people are doing using these methods.

Or another way to exploit or deploy nonequilibrium is-- what they are called-- molecular motors, essentially, are nanoparticles that develop motion at the expense of chemical reactions.

And here, for example, the particle, simply has a catalyst, or an enzymatic site which catalyzes the chemical reaction. So it lowers the Arrhenius activation energy only locally here.

So it promotes chemical reactions in this side of the particles. Of course, the chemical reactions change the composition. The change in composition creates a gradient in concentration. And that's how you get a flux of particles.

In fact, we said that the Curie symmetry principle prevents in an isotropic medium to couple chemical reactions, which are scalar transport, with vectorial transports.

But on the other hand, diffusion is sometimes the limiting aspect in chemically reacting system because it is by diffusion that particles go to the proper place where they're used up for reacting with the other reactants.

So indirectly, diffusion processes are very important in controlling chemical reactions. So they are effectively not coupled in the way of the Onsager kind, but they are coupled overall in order to feed the chemical reactions with the reactants where they need to be.

And then, if you have simultaneously diffusion, so many constituents, and also the electrostatic field, the charges play a role. They may play a role just locally like this kind of double layers around particles that have charges inside that can move to the surface.

And these effects are things that happen, for example, at the electrodes in a fuel cell or an electrolytic device. Or simply you have a thermoelectric effect coupled to diffusion.

So this is what you-- So, electrochemical systems belong to this kind of class. And these are the kind of equations that you need to consider if you model an electrochemical system with, say, three different particles.

And three different particles is very common because you may have the solvent and you have two solutes, but often you have many more. And these solutes could be the ions that travel in your electrolytic solution.

The typical models are done this way, with this interdiffusion taking up only the diagonal ones and often forgetting these other more complicated or second-order, maybe, cross effects.

But if you are interested in modeling electrochemical systems, then these are the references that you should not overlook. This book, *Non-Equilibrium Thermodynamics for Heterogeneous Systems* by Kjelstrup and Bedeaux, is an excellent starting point for doing properly things the way we've done, and also for realizing that-- so you can compute distributions in the heat.

They use the De Groot and Mazur notation. So what we call the q double prime, they call measurable heat flux. But other than that, they essentially use the same notation that we've done.

And also, a very important aspect here is the interfaces at the electrodes, where you have jumps from one substance to the other. And, yes, you could define continuous or diffuse interface theories, which is another aspect that needs to be covered.

But they do it with sharp interfaces, which is the Gibbs traditional method. But the reason why I urge you to go to their work is that they do it correctly and carefully. And in particular, also, regarding this role of interfaces and nonequilibrium thermodynamics at surfaces, there is this paper, again, by one of them, Dick Bedeaux, in 1986, which is really wonderful. And you should study that paper if you are in this business.

Now, of course, we are at the end of the course, so I'm not covering anything more. But I want to mention that there are many other directions in which you could go in the field of thermodynamics, which is related to the general principles that we have developed, but perhaps not the detailed models.

So, of course, the queen is statistical mechanics, which is behind-- we've used also some of it when we did the single particle in a box. But then you have also kinetic theory to deal with rarefied gas dynamics if your Knudsen number is not very small.

And, in fact, to cover that, the phenomenology of essentially the entire fluid mechanics is redone at the non- very small Knudsen number.

People have redeveloped. There's been a couple of decades of very active work on small-scale hydrodynamics-- still ongoing.

Then, on the side of developing the foundations even for continuum, we have this issue. Remember the local equilibrium, where we assume that we are at this state, but we're actually there. And so there is this difference in entropy that we are neglecting if you do local equilibrium, which is not neglected in these other theories, like rational extended thermodynamics or other nonequilibrium thermodynamics theories.

And there are not only papers but books about these approaches. And you've seen that by using these, we've seen one example, the Cattaneo heat transfer equation. Well, in that same idea, you can develop, and you should develop also, all the things that we've done, even including what we've done today. So there is a lot to be done also in that direction.

There is also-- OK, then there is quantum aspects. We talked already about that. And there is also these diffuse interface methods that, again, if you have two phases, you could consider them as sharp, like, for example, liquid and vapor. You could have-- this is the density of the vapor, and this is the density of the liquid.

You could consider it sharp. But if you enlarge this region, it's actually something like this.

And by assuming the fundamental relation for your states, for example, by assuming that s is not just a function of u, v, n, but it's also a function of the gradients in concentration, and, actually, since you need a scalar, you can take the square of the gradient.

And you put it in as an additional variable, which determines equilibrium. And now you're talking about equilibrium because that's a stable equilibrium state for equilibrium. That term there, which was present also in a paper by Van der Waals, which actually is a very nice paper-- it's been translated by Rowlinson later on. And I suggest that you go and see that paper if you are studying this.

Well, this theory here has been developed by Landau. It has now become known as Cahn and Hilliard models or diffuse interface methods. With that thing, you can predict the exact shape of this curve at equilibrium.

And actually, there is a very nice paper in *The Physical Review* by Antanovskii that I suggest that you read if you are interested in that kind of development.

Plus, of course, you have a list of-- an infinite list of other approaches, from statistical to numerical simulations-- the Boltzmann equation, approximations of the Boltzmann equation. This is a famous one, which allows you to compute the hydrodynamic quantities like heat flux, the fluxes of particles, but also the momentum and diffusive-- as moments of the Boltzmann distribution off equilibrium.

So we are talking about models that can cover also nonequilibrium and far nonequilibrium. Another approximation is one which derives the equivalent of the Navier-Stokes equations, but more complicated with more moments.

Then there's the Fokker-Planck, the stochastic equations. These are equations that have some random noise terms in it.

And then you're certainly familiar with molecular dynamics, Monte Carlo, and various types of molecular dynamics, various flavors of molecular dynamics that have been developed over the years to overcome some of the limitations.

So, with this, I think I'd like to end the course remembering that we have celebrated Carnot's 200th birthday with-- and I also, yes, I want to remind you of the Prigogine Prize.

So if you ever end up with a PhD thesis in the field of thermodynamics-- all aspects of thermodynamics, from applied to experimental to very theoretical-- don't forget to apply for this prize.

It is done every two years. The next deadline is February 1 next year. And for this call, it will cover PhD defended between January 1 of last year, 2023, and December 31 of this year.

It's a pretty international prize. In the last eight editions, we had 134 candidates from 28 different countries. You can click here for all the details.

And it is sponsored by a series of conferences called the Joint European Thermodynamics Conference but has become an international one. And the next one will be in Belgrade in Serbia next year, in May or June. The date has not been decided yet. As soon as it will be out, I'll put in a link here so that you can see what it is about.

All right, so I'd like to conclude, and I'd like to thank you for attending the lectures, which I dedicate to my mentors. But also, I thank you very much for the quality of your video homeworks, because they have been stimulating me for-- at least giving me some feedback that some of the messages I wanted to pass have been passed. So thank you very much.