InterPore Time Capsule Interview with Professors Signe Kjelstrup, Dick Bedeaux & Alex Hansen

In this InterPore Time Capsule, Professor emeritus Dick Bedeaux and Professor emerita Signe Kjelstrup (Signe Kjelstrup - NTNU) are interviewed by Professor Alex Hansen, all at PoreLab – Centre of Excellence (SFF), Department of Physics (Hansen) and Department of Chemistry (Kjelstrup), Norwegian University of Science and Technology. Professors Bedeaux and Kjelstrup are presently active members of PoreLab. They have both served as Principal Investigators since the start of the Center where Hansen is the director.

Alex Hansen
This interview is in the Interpore Time Capsule Series, where people behind important contributions to porous media science tell the background history. And I'm here with Signe Kjelstrup and Dick Bedeaux, who have done important contributions to irreversible thermodynamics on transport phenomena, across surfaces and interfaces. They have more recently developed the thermodynamics of confined fluids in nano-porous media based on the Hill approach. Before we get into what these contributions are, let's delve into their respective backgrounds.

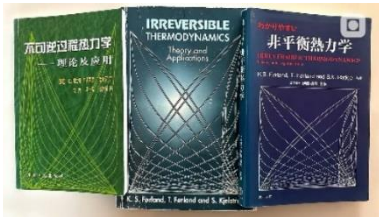
Signe, we start by your background. So why science, why chemistry and why irreversible thermodynamics?

Signe Kjelstrup
As you know Alex, I was growing up in the north of Norway and to do that makes a spectacular impression on a child because nature and everything is so dramatic: the midnight sun, the polar light, you name it. So, I was always interested in nature and my father fostered that. He had radio lectures on astronomy, and I thought that this was fascinating when I looked at the Northern light. He also encouraged me to study science. He advised me to come to the Norwegian University of Sciences and Technology.

But when I came here and about to start in physics, there were no female professors and there were only a few out of the about thousand students starting in physics that were women, 2, I think. The advice from friends of my father was no, "*She will not get a job*". So, I started chemistry, but there is such a thing as physical chemistry where I ended.

Then, I was only in my second year when there was a big event in the campus and that was on the occasion of the Nobel Prize to Onsager in 1968.
I could not enter the lecture, but my coming thesis advisor did, and he was very enthusiastic. So, when I eventually found him (Tormod Førland) as a teacher, he said to me: "*Let us do something in this field*". Then, we decided to seek for applications in chemistry.

Alex Hansen
Thank you. I note that your first book, Signe, was *Irreversible Thermodynamics* 'without tears' from 1988. Who did you write it for?



Signe Kjelstrup
Irreversible Thermodynamics 'without tears', the 'tears' were what we hoped to avoid with the chemists. Big efforts were put into writing the book as clearly or simple as possible. My co-author, professor Kathrine Seip Førland, should be mentioned in that respect.

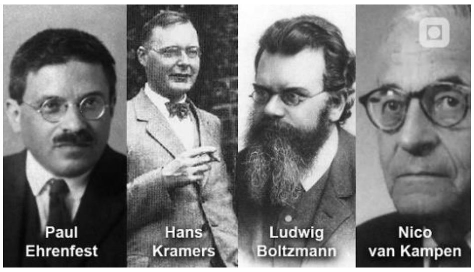
Alex Hansen
Why is it that irreversible thermodynamics is part of the field of chemistry much more than physics?

Signe Kjelstrup
What is essential in irreversible thermodynamics compared to the simple transport laws we had before, like Fick, Fourier, Ohm and Darcy, is that irreversible thermodynamics introduces coupling, and coupling is much more important in chemistry. You can't have a process across a membrane of an ion without it dragging along water, so you immediately have coupling. There is also coupling to charge, and to chemical reactions. To describe this, the full matrix (of coefficients) is actually needed, for example to describe a lithium battery like we have just published. So, I think that the physicists are not so much in need of this coupling, that's why there is a difference.
But when that is said, I really wish that the subject should be taught, because it has also other aspects. It gives a precise definition of the second law, not as an inequality but as a precise analytical expression. The world is needing that, in its effort to obtain better energy efficiency of processes.

Alex Hansen
Dick, your background, you originate from the strong Dutch tradition in statistical mechanics.

Dick Bedeaux

The tradition for me in a sense started by Ehrenfest who is, scientifically, my great grandfather and my grandfather was then Kramers. And my scientific father, Nico van Kampen, was my thesis advisor. He was a person that was extremely clear in his lectures, defining concepts properly, clearly, and so that attracted me. That made that I ended up being his graduate student. Now, that was not quite as easy as you would like. I mean it was difficult to get to talk to him, and in that sense, he was a difficult thesis advisor, but he made me strong because I had to explain things to him very well whenever I then got the opportunity. By the time I had my thesis kind of nearing the end, he disappeared for sabbatical to the USA. In that time, he clearly never read what I was sending him because when he came back, he had, according to his notes in what I had sent him, read it until page 14. Then he asked me: "*Is the rest also correct?*". I was by that time hard enough to say: "*Of course otherwise I wouldn't have written it"*. Then he said: "*Well, you rewrite it a bit and then you should make an appointment for your defense*", which I then did.

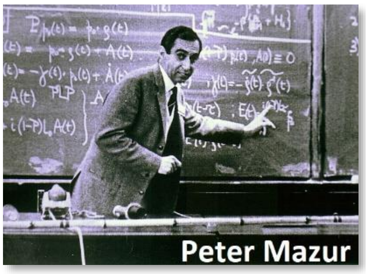


Alex Hansen

I remember meeting Nico van Kampen once and he was clearly quite a character. How was it to be a graduate student with him?

Dick Bedeaux

Van Kampen was very clever and in that sense a wonderful thesis advisor. However, he was also difficult. He, himself, got his degree with Kramers, who got his degree with Ehrenfest, who got his degree with Boltzman. My scientific heritage is, in that sense, very much into statistical mechanics. Of course, van Kampen was very good in statistical mechanics. He was a little bit strange in the sense that he would tend to not believe anything that other scientists in the field would do. He would explain us that the Kubo relations were wrong, and why they were wrong. Of course, that was very stimulating because I immediately studied the Kubo relations and I saw that they were perfectly OK. In that sense, it taught me to disagree with him. In addition to that, he had of course much against the work of Prigogine. I also studied that, and I fear that, there, I agreed to a large extent with him.



After my thesis I went to America. When I came back, I worked with Peter Mazur. Of course, Peter Mazur was a very good friend of Prigogine. He also disagreed with Prigogine on these things but that was all extremely interesting.

But Nico van Kampen was, in a sense, interesting because he always tried to not see me. If I would ask him to talk to me, he would say *yes* but then he would run away. So, I taught myself to corner him such that he could not run away. When he would say *yes*, I would say: "*What about this afternoon*?" Then he would - kind of - say *yes* again, and then run away again! But then I had an appointment.

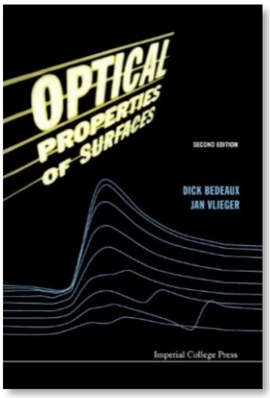
He had a very clear tendency to do everything using differential equations. After his advice trying to do that did not work, I went other ways. I used linear perturbation theory of operators which is an extremely interesting field. Van Kampen did not like it. But I used it to prove what I had to prove. That was the reason, I think, when I got my thesis ready, why he escaped to America for a sabbatical. When he came back, he had read the first 14 pages, and said to me: "*You have to rewrite it, but is the rest also correct?*" and I said: "*Yes, otherwise, I would not have written it*" and he said: "*After you have re-written it, you can make your appointment for a defense*". That was Nico van Kampen!

Alex Hansen

Dick, you have written a book on light scattering from rough surfaces. Where does that fit into your career?

Dick Bedeaux

That was in fact a very important moment and it related to the observation that in order to describe surfaces you need excess densities, and in that particular case, it was the polarization. You had an excess polarization along the surface and an excess polarization parallel to the surface. The excess polarization parallel to the surface causes actually the dielectric constant to have a singularity at the surface. The parallel dielectric constant causes the electric field not to be continuous across the surface. In the normal direction, there is a polarization normal to the surface, but that finds its origin in the inverse dielectric constant which has to have a singularity. And that causes the displacement field to be discontinuous at the surface. After all the work I did with Jan Vlieger on the subject, we wrote a book about that subject.



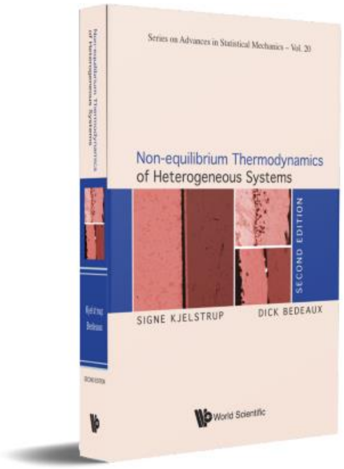
But meanwhile I had also realized the work that Gibbs had been doing, in which he defines excess densities. He had only been doing that for equilibrium systems and you could extend that. In addition to have excess densities of variables, you could also have excess fluxes along the surface and that makes it possible to develop non-equilibrium thermodynamics for surfaces where quantities like the normal fluxes (i.e. fluxes normal to the surface) are all the sudden scalar. They are no longer vectorial, and they can therefore directly couple to the reactions at the surface. Also, the temperature difference across the surface can drive the reactions at the surface.

I started to work with Albano and with Mazur on formulating non-equilibrium thermodynamics for surfaces. That drove the attention of for instance Majid Hassanizadeh, an important person in Interpore. He came to Leiden to discuss exactly this work about non-equilibrium thermodynamics and transport for surfaces, along and through surfaces. (This was).. in his quest to derive equations on the macro level - the Darcy level - for porous media, starting with the description in the pores. In the pores of course, the surfaces and lines are important, therefore he consulted me. That was a very interesting discussion, but it took I fear, another 15 years before you, Alex, personally, got me and Signe going into doing non-equilibrium thermodynamics for porous media.

Alex Hansen

Your first common book was on Irreversible Thermodynamics of heterogeneous systems. Please explain.

Signe Kjelstrup



When we first met and discussed, it was clear that we didn't understand each other. I came from the chemistry background, and he came from the statistical mechanical background, but we *did* understand that there was something to gain by combining our experiences, because everything in chemistry happens at interfaces. The catalyst interface, the electrode, the membrane, the interfaces are crucial. And here he was with all this knowledge about how things should be properly written for the interface.

Dick Bedeaux

The work for this book made me realize that one needed excess densities and fluxes for a proper description of transport through and along the surface. The reason I wanted to talk to Signe about this issue was that in order to derive Maxwell's equations for the surface, you have to use the Maxwell equations in vacuum, which are Lorentz invariant. However, the description for the surface is Galilean invariant. That implies that you have to neglect certain things and I was seeking advice on what would be important or not. Now, it was clear that this question was not a question to put to chemists. But I did listen to her, and it was clear that she understood what she was talking about, and that made me eager to get closer to experimental interpretation of matters at the surface, and then to talk again. And the book is the result!

Signe Kjelstrup

Yes, so the book is an extension of the irreversible thermodynamics for bulk phases, like everybody had been doing it after Onsager. We extended it such that we could deal with the dynamic surface. That is the extension, the combination of the two things: the bulk and the surface. And this is our big contribution, I think, to transport.

Dick Bedeaux

The surface can move, and the fluxes on both sides have velocities that are different from the velocity of the surface. The whole theory has to deal with that and not in the barycentric frame of reference as de Groot and Mazur typically do. You have to do it in the frame of reference of the surface. That's an important ingredient in getting an excess entropy production for the surface that makes any sense.

Signe Kjelstrup

So, then you have a precise description of the entropy production at the surface, and you also have a dynamic boundary connection. But it's only transport perpendicular to the surface that we have treated. So, there is still the transport along, that is waiting, of course.

Alex Hansen

Trondheim has an interesting place in the history as far as irreversible thermodynamics goes. Can you elaborate on this?

Dick Bedeaux

Well, I have a lot of contact with Trondheim because I was appointed to be a professor in Theoretical Physics in 1981. The reason that they appointed me was because of my work on statistical mechanics and in particular on the description of surfaces, and also the non-equilibrium thermodynamics of surfaces. So, I went to Trondheim and there I had a lot of contacts with Per Christian Hemmer and Eivind Hiis Hauge who were both very good colleagues in that field. They were also very much connected to the Netherlands where they were good friends of Hans van Leeuwen and Matthieu Ernst, and they would visit the Netherlands to visit these people. Matthieu Ernst and Hans van Leeuwen would also come here in Trondheim, and they would write papers together. In that sense Trondheim was clearly a center in which statistical mechanics was very actively done.

Signe Kjelstrup

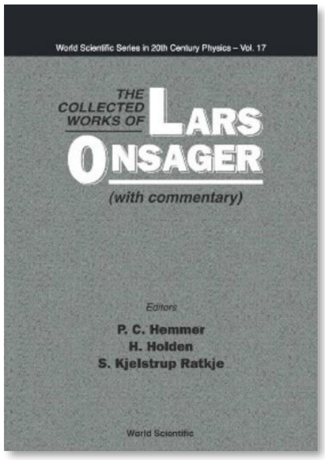
And Alex, you, yourself are a part of that group and tradition. So, you are the flag carrier right now.

Alex Hansen

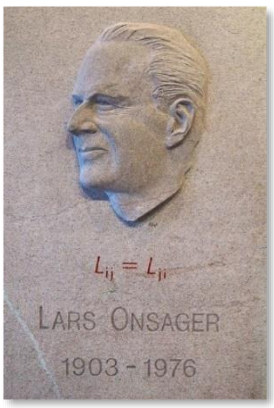
Thank you!

Signe, you have co-edited *The Collected Works of Lars Onsager*. What's his place in history or in this field?

Signe Kjelstrup



The Collected Works! That was obvious (to do). We celebrated his birthday in '93 and then people said to us: "*Why don't you make his collected works*?". And of course we should do that! And we have since then collected all his things and papers here (at NTNU). The aim or the purpose is of course to show the younger generations that we have this ideal role model, I would say, in science right here at his alma mater! He never got a job in Norway, but he came back every year and with his stature in the field that makes even us a bit visible.

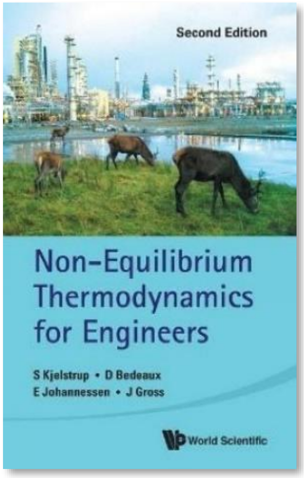


Onsager has a tremendous important role in many fields, but he got the Nobel Prize for irreversible thermodynamics. Everybody asked: *For what did he get it*, but it was for irreversible thermodynamics. This university is his alma mater, but he did not get a job in Norway. Nevertheless, he always kept contact and came every year back to Norway. So, it was logical for the group (of editors), my colleagues in physics, mathematics and me, to celebrate that we had

Onsager as an ideal for this school of science. When we did that in 93, Onsager's birthday, and we were asked "*Why don't you make the collected works?*". They were not done yet at that point. Everybody meant that this was important because of his contribution to many fields. We could do it with some confidence because there has always been a strong group in statistical mechanics in this university. You, Alex, are one of them who can lift that flag high. So, I think, all together, I am happy to have that role model so strongly present for younger generations, here, now.

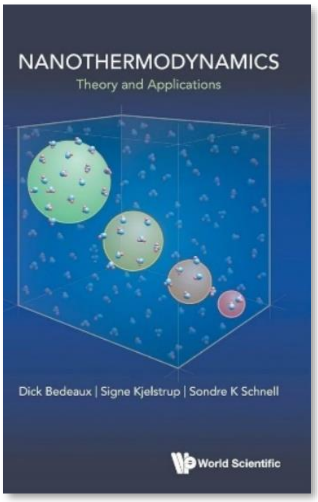
Alex Hansen
Where do you see this field is going? Irreversible thermodynamics is applicable in many settings. You wrote a book which recently came in a second edition, namely, *Irreversible Thermodynamics for Engineers*. Is this something that engineers can use in their daily work?

Signe Kjelstrup
Well, this is my dream or vision you could say, that such a book could be the standard textbook for teaching thermodynamics in a modern way in universities world over. And the reason is obvious. Equilibrium thermodynamics has to do with equilibrium and states. You can compare different states, but non-equilibrium thermodynamics includes the dynamics going from one state to the other, and it computes precisely the entropy production along the way, which you don't compute in another way. And speaking about the need for energy efficient processes and precise models for what is the interaction of phenomena in electrolytes and wherever, I think that, if we want to improve what is already there in the industry, this theory is needed. So, that is my hope! We, and the world, could benefit in using this.



Alex Hansen
You also have several books behind you. The latest one being *Nanothermodynamics*. Can you say a few words about it?

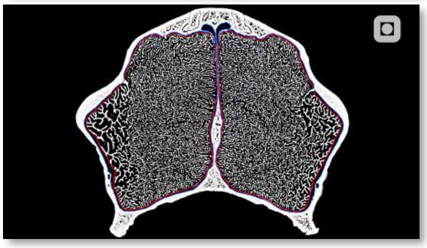
Dick Bedeaux
Yes, *Nanothermodynamics* is an extremely interesting field because it goes into a spectrum of systems that cannot be properly described with thermodynamics. And the reason for that is that they are too small. One of the reasons we got ourselves entangled in that, was that we had this feeling that when we were doing simulations, which by nature is not an infinitely large system (it is always a relatively small system), the question came up: *how do we use the data there to obtain results for the large system*? Well, that did not work so well until we discover the book by Hill about thermodynamics of small systems. Hill is very clever in the sense that he extends the theory that was developed by Carnot, Clausius, and Gibbs, by introducing an additional term. That additional term describes the smallness of the system, and it comes in by looking at an ensemble of small systems. The ensemble of small systems together forms a big system. So as a function of the number of small systems of the number of replicas, the system is again Euler homogeneous of the first order and you can go through the whole analysis. And then you obtain new equations and important quantity what is found in terms of what is called the sub-division potential. This actually measures the energy that you need to subdivide a given amount of internal energy, entropy, or number of particles, over a larger subset of replicas. That, of course, gives you a measure of the energy difference, that depends on the size of the replicas. That aspect we have used and expanded on in the book. And we have done, contrary to what Hill, I fear, is doing, he tends so say: *well, you know, when you control the volume, you need two pressures, not one*. Then he comes to another case where he controls the number of particles, and makes the observation that: *well, this is exactly the same as when you control the volume, you do not control the number of particles*. With this, you have to do everything yourself. For an uninitiated person in the field, this is not easy. That is why we wrote the book: We do it explicitly for six ensembles, expanding on Hill and extending Hill also, because we actually bring forward the importance of the subdivision potential. We just wrote the paper on how to measure it.



Signe Kjelstrup
In short, the hope is that it could serve as an alternative path to get the continuum equations that we do need for the complicated porous media. A path that you, Alex, also are pioneering an effort to find. So, I hope in the end that we will be able to more directly compare and see and learn what the assumptions behind each systematic approach are, and how they can complement each other. So, there is a lot to do in the future.

Alex Hansen
Signe, you have recently published papers with biologists on the structure of the seal nose. Elaborate!

Signe Kjelstrup
Yes! And that was extremely fun because the seal nose has a very interesting labyrinthic structure. And why is that? It is, we think, because it has a very efficient system for saving heat (body heat) and water in the Arctic climate where it lives. That structure function relationship is fascinating, and I would really like to explore it in other contexts as well. Because, what if nature has invented porous structures that are so efficient, shouldn't we then try and copy them in technology? That is a question I could pose to many people, including myself.



Alex Hansen
Looking back at your long careers, any advice to young scientists?

Dick Bedeaux
Yes! The important thing is to be independent, to trust yourself and to not believe was all the established older people are telling you as the truth about the world.

Signe Kjelstrup
And I would like to add: Follow your heart and find a group where you can enjoy working … one person … it doesn't have to be many in the group. It could be only you and one more.

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Professor Alex Hansen

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Video editing
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