Discussion on “Teaching the Second Law”

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Abstract. This article reports an open discussion that took place during the Keenan Symposium “Meeting the Entropy Challenge” (held in Cambridge, Massachusetts, on October 5, 2007) following the short presentations – each reported as a separate article in the present volume – by Joseph Smith Jr., Howard Butler, Andrew Foley, Kimberly Hamad-Schifferli, Bernhardt Trout, Jeffery Lewins, Enzo Zanchini, and Michael von Spakovsky.

All panelists and the audience were asked to address the following questions

- Why is the second law taught in so many different ways? Why so many textbooks on thermodynamics? Why so many schools of thought?
- Some say that thermodynamics is limited to equilibrium, others that it extends to nonequilibrium. How is entropy defined for nonequilibrium states?

ROBERT SILBEY : I’ve been asked to moderate this session on Teaching the Second Law. I have taught thermodynamics in the Chemistry Department here at MIT for about 40 years. And I have to say that whenever we get to the second law I am always very nervous. And so I’m anxious to hear from the panelists their views on this. And I think it’s a little bit like the old story of Toscanini when he had to conduct Beethoven’s Ninth Symphony,he always said to the orchestra "courage, have courage". And I think when you do the second law it’s the same thing.

So, everybody on the panel has had their say. So now let’s have courage and begin the discussion. I think the range of the participants remarks are rather interesting, from Boltzmann’s soul to an analogy of thermodynamics to a Mint all the way to the unified theory of quantum mechanics and thermodynamics. I expect that this has caused some

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provocation, so I am looking forward to the questions.

UNIDENTIFIED VOICE: Boltzmann's didn't believe in soul but he definitely had the blues.

SILBEY: That's right, Boltzmann had the blues. There's no question about that. And headaches. Go ahead.

LIN-SHU WANG: Well, I certainly agree with Professor Trout that, of all the scientific laws, the second law has especially a strong philosophical content. But the main point I want to make here is one which, since this is a session about teaching the second law, is perhaps mroe appropriate here. It is this: There is only one mention of spontaneity in the panel presentation, but I believe spontaneity as a concept should be emphasized more in the teaching of the second law. After all, the Clausius statement and the Kelvin statement are the paradigmatic examples of spontaneity. And I think if we don't emphasize spontaneity as a central concept of the second law, we really fail in our teaching the second law to the students.

I want to back up the point with two examples, of which I have direct personal knowledge. One is this mechanical engineering professor at the University of Buffalo who years ago invented a perpetual motion machine of the second kind. He even got a patent. In the patent he described a system that intakes the atmospheric air, which undergoes through a series of processes converting some of the energy of the air into work. Finally after a long sequence of processes, the air exiting from the system to the atmosphere is actually at a lower temperature than the intake air temperature. (He said that there is a drawback to his invention: making the atmosphere in Buffalo cooler in the winter.) But he forgot to check the value of the exit pressure of his system, which is lower than ambient pressure. His system cannot work until a suction pump is added!

Naturally, the suction pressure work required is more than the "work" his inoperative system would have produced. The saddest part of the story is that he wrote a research report, in which he acknowledged many prominent specialists in thermodynamics and heat transfer. Now, isn't that almost like an example of a real-life Maxwell demon trying to cheat spontaneity.

The second example is very much a similar case. Recently, I met an engineer who, again, wants to do the same sort of things. And he paid me good money to examine his work. Basically, he is trying to "create" the spontaneity out of thin air to produce work output. An understanding that the entropy production being always non-negative leads directly to the conclusion that spontaneity cannot be created out of nothing, would have prevented this kind of waste of human fertility.

THEO NIEUWENHUIZEN: Sorry, with all respects, but I'm a bit shocked by the MIT view on thermodynamics. As far as I have learned in my courses and so on, an electron is some object which has a charge, a mass and a spin. But if I should now view this electron as a part of an ensemble, and because of that ensemble we have entropy. Now we are here, brought to the point of view that electron has a charge, mass, spin and intrinsic entropy. And, well, this is an interesting scenario, but I can inform you that I don't share this hope, let's put it this way. On the other hand, the field is open because we don't know what is an electron. I think it's one of the most outstanding questions of today's science, as it has been already for the last two centuries. That is basically a remark I just want to make. Because it was presented here as a breakthrough, I also want to say that there are counter opinions.

As another item, I want to pay some attention to the Gibbs paradox because sitting there and hearing the discussion, it came up to me this is an old paradox. If you mix two systems, then somehow you get a log 2 in entropy. But this log 2 is absent if you mix two identical gases, so there is a physical discontinuity when you go from "non identical" to "identical" gases. This old question can be answered if you go to quantum thermodynamics, but then not from the MIT quantum thermodynamics but just thermodynamics you get when you have a very small quantum system coupled to a big bath and a big work source. In that case, it appears that the first law still holds. And what about the second law, that's then the big question. And now you have a problem because you don't have a thermodynamic limit for your small system. And, therefore, the many formulations of the second law all do not agree with each other. They are all different statements about your small quantum systems. Some may be right, others may be wrong and so on. And so since you have all these formulations of entropy, entropy itself doesn't make sense anymore. And you have to go one step back. You have to undo Clausius and go back to work. So, work is your primary variable. Fortunately, that's exactly the thing which you can measure so that's a good thing. And if you look at this work and you take the limit in which your two gases become more and more similar to each other, then there is no discontinuity, there is not a jump of log 2. You have a continuity and the Gibbs paradox is resolved in that sense [A.E. Allahverdyan and Th.M. Nieuwenhuizen, "Explanation of the Gibbs paradox within the framework of quantum thermodynamics," *Phys. Rev. E* **73**, 066119 (2006)].

Now, of course, I have to put a question so I can ask the panel what is a question you think I should put here? Thank you.

SILBEY: Thank you. I should, I mean for your information and for the audience, calling the Hatsopoulos-Gyftopoulos-Beretta formulation, the MIT School of Thermodynamics, I think, reaches too far. I mean there are plenty of physicists and chemists at MIT who have a different view about it. So, I would say it's the odd part of the institute, that's where all the engineers are, in the odd numbered buildings.

NIEUWENHUIZEN: I am willing to accept this point, but can you please direct this to your neighbor (Michael von Spakovsky) and not to me?

ELIAS GYFTOPOULOS: We are fully aware that what we have developed differs from everything that is in the literature. So, by telling us that what we are saying is different is not enough. What you have to do is go through our works and find the errors that we have made, and none of you, both at this Institution or at others, especially at this Institution, who have opposing views like you do, have come up with a concrete scientific argument. That is a very bad aspect of the situation.

SILBEY: Elias, I agree with you completely. That's what we have to do.

NIEUWENHUIZEN: No, I'm not sure. Because if there is a new proposal the charge is on the people who bring the new proposal, because they have to ask themselves what does Nature think of this, either by just asking themselves questions or, better of course, coming with experiments. Either it is proven and then we have really a big step forward or where it is disproven and we can move onto other things. But until then the charge is on the authors.

SILBEY : Well, I would be more even-spirited about it. It's on the charge of anybody interested in this particular scientific area. And I agree with Elias that it should be considered and discussed, absolutely. And if I gave you the impression that I didn't believe that, I apologize.

MICHAEL VON SPAKOVSKY : My response is that it behooves both sides to look at this. I mean this is not my theory. I started looking at this out of curiosity several years ago, in 1998. I happened to have a number of discussions with Elias Gyftopoulos and I was thinking about what I was going to teach at a graduate level. It is not my theory. I said "MIT school" simply to give credit to the people who at MIT developed this. I was curious about this theory. I didn't simply accept it when I first looked at it, but I spent a number of years—even though my background is not quantum mechanics; I'm a mechanical engineer—I spent time, quite a bit of time teaching myself kinetic theories, statistical mechanics, statistical thermodynamics and quantum mechanics in order to try to understand these papers. And at the end I came to the conclusion that the mathematics is there, that the physical reasoning is there. And I think it does behoove our community, not just the authors but others in our community to look at it. Now, on the part of the authors, I agree with the gentleman who raised the question that it needs to be proved. Yes, there needs to be experiments set up in order to prove or disprove the theory in order to justify whether or not the assertion that entropy is an intrinsic property of matter, just like momentum and inertial mass is in fact the case. But the paradigm is there, it is a single theory. It is not a cobbling together of multiple theories. It's not a set of ad hoc theories. And it is there, the publications are there. They should be looked at by other people. If you have any curiosity about this discipline it is laid out there. And, as I said, I have spent quite a few years looking at it, and I'm convinced, at least within reason, that the arguments are correct.

GEORGE HATSOPOULOS : I just want to mention a very simple concept. The gentleman before (Theo Nieuwenhuizen) said: " you have a new theory and you should prove it and you should show whether it holds or not." Let me tell you what actually happened. There were a lot of inconsistencies that were bothering Joe Keenan for several years because nothing really explained, no theory at that time explained, say, the statistical mechanics together with quantum mechanics didn't seem to explain many things. And he had questions about it. And so we came with something that would answer these questions. As a matter of fact, one of my first paying jobs was when Joe Keenan asked me, when I first came to MIT and I took his course, he asked me to work for him. Three or four firms would engage him every year to see whether an invention was violating the second law, whether it was a perpetual motion machine of the second kind. And some of these inventions were very complicated. It would take Joe several months to figure out what the flaw was. And eventually he did, but he had to charge. And he got tired of that. He said would you take that job for me? And I worked with him for two years for pay, which was very welcome to me because I didn't have any other sources of income. And some of these things were very complicated, believe me. And eventually you would find what the flaw was. Now, let me tell you what that led to. We got involved, two or three years later, with the patent office. And the patent office told Joe Keenan "we have a lot of problems with inventions that violated the second law. Maybe what we should do is set up a rule that anything that violates the second law, regardless of whether we find what the flaw is, is not patentable until the inventor demonstrates a working model." So, about some 40 years ago the patent office adopted that rule. And from there on there was no job to try and find where the flaws were.

SILBEY: You lost your job. Thank you, George. OK. Maybe we can get back to teaching of thermodynamics.

GIAN PAOLO BERETTA: I thank very much Theo Nieuwenhuizen because he made the point that the physical community is not accepting the unified theory yet. However, I should remind him that he himself published a paper [A.E. Allahverdyan, R. Balian and Th.M. Nieuwenhuizen, "Maximal work extraction from finite quantum systems," *Europhys. Lett.* **66**, 419 (2004)] which develops ("rediscovers") the concept that he and his coauthors rename as the "ergotropy" where both the concept and the proof used are exactly what you find in the Hatsopoulos-Gyftopoulos papers in 1976 [pp. 136-138 of G.N. Hatsopoulos and E.P. Gyftopoulos, "A Unified Theory of Mechanics and Thermodynamics," *Foundations of Physics* **6**, 15, 127, 439, 561 (1976)].

Regading the "school". At the times of Prigogine, we used to call that the *Brussels School*, and I think no one in Brussels showed up and said "well, I don't agree, you shouldn't call it that way." But, anyway, since we received the statement that MIT takes distance from this approach, maybe we should just call it the *Keenan School*. I hope you agree with that, Keenan was the starter. Also because the quantum theory is not just the only contribution of this School. There is, I think, a more important contribution: the development of a rigorous exposition of thermodynamics, forget about the quantum [started by G.N. Hatsopoulos and J.H. Keenan, *Principles of General Thermodynamics*, Wiley, 1965; and finalized by E.P. Gyftopoulos and G.P. Beretta, *Thermodynamics. Foundations and Applications*, Dover, 2005 (first edition, Macmillan, 1991)]. That is also what Enzo Zanchini was trying to present in his five minutes, in which he found a way to give you our definition of entropy (valid for nonequilibrium states). I think he is the only person who has defined something here in regard to thermodynamics. That's what we must try to do. That's what I have enjoyed doing for 20 years, also in the teaching to undergraduates. And they are satisfied with this exposition and they do not find it confusing, no philosophy. It is simply engineering, and it provides a rigorous and general, yet easy introduction to energy balances and entropy balances.

JEFFREY STEINFELD: One question for anybody on the panel who wishes. One term I've heard a fair amount, particularly in Europe is exergy. Is that a useful concept or does it just confuse things? That's for anybody who wants to take it. But then one question up there that I have not heard addressed, actually, so far is why are there so many textbooks on thermodynamics? And that is specifically directed to Professor Silbey.

VON SPAKOVSKY: The response is that Europeans and the rest of the world call what Joe Keenan came up with—namely, availability—exergy. Now, in american textbooks, we talk about availability. You find some of the undergraduate textbooks that say availability and some that say exergy. But they refer to a concept that is not as broad as the available energy that is defined in the unified theory, which applies not only to stable equilibrium states but also to non-equilibrium states. So, is it a useful quantity? Yes, of course. It is a useful quantity because it is used, for instance, in exergy balances in order to do design, in order to guide the design, to improve the design by looking at where the imperfections (i.e., irreversibilities) in the machinery are.

HATSOPOULOS: May I comment on the word exergy? The first time I heard the term was when Myron Tribus came to MIT and told me "availability is too incomprehensible to students so why don't we come up with another word?" I said, well, Myron, what do you think? He said what about exergy? I said, sure. So then, from there on, he went back to teaching exergy. By the way, what exergy covers evolved with time. Originally it was intended to be another word for availability, but as Myron developed it during his teaching it took certain other forms.

STEINFELD: Thank you. The other, part two of the question is still on the floor.

SILBEY: Well, the question was why are there so many thermodynamic texts? I think it's, seriously, I think the reason is exemplified by the panel here and probably half the members of this audience, which is when you have to teach thermodynamics to students, either as undergraduates or graduate students, you have to first teach it to yourself because it is a very deep and complicated subject. And, when you teach it to yourself, you end up with a vision of how it should be taught and then you write a book.

NOAM LIOR: Addressing the objective of the panel to try and teach entropy to students, it wasn't mentioned that there is a completely different approach that was proposed by my precious and late friend Herb Callen at the University of Pennsylvania where he simply includes it as one of the axioms [H.B. Callen, *Thermodynamics*, Wiley, 1960]. He says that entropy exists and has certain properties, and then goes from there. So, as long as we're dealing with axiomatic thermodynamics, you might as well start with that approach and go from there. I use his book frequently. It's not completely satisfactory because it doesn't integrate the physics into the mathematical derivations early enough, but it is an intellectually interesting approach. And, by the way, exergy, the word exergy was not coined by Tribus, it was coined by Rant in 1956 [Z. Rant, Exergie, ein neues Wort fur "Technische Arbeitsfahigkeit" (Exergy, a new word for "technical available work"), *Forschung auf dem Gebiete des Ingenieurwesens*, Vol. 22, 36 (1956)].

ENZO ZANCHINI: Well, I have a different opinion on this kind of approach. I think that when you introduce a new quantity, in a physical theory, you should present, first of all, the definition of this quantity. So, you should not say that a quantity called entropy exists and becomes maximum under some condition if you did not present a definition of entropy. Every quantity, in a physical theory, should be introduced by means of an operative definitions, i.e., a definition which allows one to associate a number with this quantity, for every state of any system to which the definition applies.

ANDREW FOLEY: Can I just say something? Sorry. If it was up to me, I would quite happily drop entropy. It is kind of a nasty thing. You cannot visualize it. If instead we could just talk about good energy and bad energy that would be great, but there are situations when that can happen, and entropy kind of drops in as an indicator that is not quite energy but it gives us the indication of the quality of that energy. And that is why we kind of live with it. But it is also unfortunate that we have exergy, energy, entropy, I mean [could we?] use something else a little different from the e___py's. I think that causes confusion for students. They all sound the same.

SILBEY: Well, I'll add my own view here. Gibbs was very clear in reversible processes, what the entropy is and how you measure it. There's heat and temperature and so on. And so it's very clear in reversible processes what the change in entropy is. All the real issues that are all floating around here are in irreversible processes. And that's where we all go off in different directions.

YUNUS CENGEL : First, I would like to thank the panel members for sharing their experiences and ideas on teaching the second law. One thing I noticed is that there is little in common in their presentations, which means we have a long way from finding a unified approach in teaching the second law. I was particularly pleased to hear that MIT is team teaching a combined energy-philosophy course, which, I think, is very interesting. I wish Professor Trout the best of luck in this undertaking, and I hope this becomes a fruitful experience. My suggestion on teaching the 2^{nd} law is to relate the subject matter to students' experiences. Research on learning shows that if the students can relate the new material to what they already know then they have a better chance of learning it and also retaining the information. The primary difficulty with the teaching of the second law is that entropy, exergy, 2^{nd} law efficiency, etc. are not household words, and incoming students have no idea on what these concepts are. Also, the semester goes by very fast, and the students are exposed to these concepts for only a couple of months. Then they are gone, and most never revisit these concepts. They retain little unless they develop some kind of familiarity and passion for those concepts. Most often, the concepts just evaporate, and we need to find ways to increase retention. One way to remedy the situation is to strip the 2^{nd} law concepts off thermodynamic content, and to show that the core concepts are related to what they already know and even apply to non-technical areas that they are familiar with. It is just like what we do when teaching the Carnot cycle: We derive the equation for Carnot efficiency, which is $1 - T_L/T_H$, and just state that although this equation does not apply to real cycles quantitatively, the message conveyed by the functional form does: When designing an actual cycle, the source temperature must be as high as possible and the sink temperature as low as possible to maximize efficiency. Likewise, we can express the 2^{nd} law efficiency as what is actually done under specified circumstances relative to the best that can possibly be done under the same circumstances. So, the 2^{nd} law efficiency is a measure of how close we come to perfection. Also, we all are familiar with waste, and appreciate the importance of minimizing waste. This awareness has risen to a new level after the publicity on global climate change. The primary objective of a 2^{nd} law analysis is really to minimize waste and to better utilize the available resources. Entropy generation is a quantitative measure of waste during engineering processes, and a process with zero entropy generation is, from thermodynamic point of view, "waste-free". As another example, mixing of streams at identical or nearly identical states causes little or no entropy generation or exergy destruction, but mixing streams at very different states generates large entropy and results in large exergy destruction. Likewise, in social, political, and business life, unity among compatible things will be a source of strength but forced unity of incompatible people, nations, or companies will generate only waste and inefficiency, and result in fast degeneration. Any relevance to daily life will help the 2nd law concepts stick to the minds of students. Also, when writing general purpose articles for the public, we should not limit ourselves to the 1st law concepts. Such communications are opportunities for exposing the public to the 2nd law concepts like entropy, exergy, and 2nd law efficiency. Such exposure will help incoming students to view the 2nd law concepts as more relevant to real world, and increase their level of interest and curiosity in the subject matter.

JEFFERY LEWINS : I have a lot of sympathy with that attitude in the sense that the mechanical engineer needs concepts which he or she thinks they can measure. When we say that entropy measures the degradation of energy we haven't put it into units that the student can relate to energy. I would like to recommend you to think about William Thomas, Baron Kelvin, Lord Kelvin's use of the term dissipation where the entropy generated is multiplied by the temperature of the environment, and this is the lost work or energy or work dissipated. That gives a very clear idea to students, and it doesn't involve defining the temperature of the system, so we are not necessarily at equilibrium in the system. It does, of course, involve saying that we are surrounded by an environment that is at equilibrium at a defined temperature T_o.

KECK: I have a very simple question which I have often been asked by students and for which I would like to get an answer from this audience: Does the validity of the Second Law depend on the validity of Quantum Mechanics?

SILBEY : The question is does the validity of the second law depend on the validity of quantum mechanics? Anybody have an opinion? How many people? I think I am going to make an ad hoc decision. This will be very good for discussion at lunch. And I would like to end this session, and let's thank everybody.