

Discussion on “Frontiers of 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 4, 2007) following the short presentations – each reported as a separate article in the present volume – by Adrian Bejan, Bjarne Andresen, Miguel Rubi, Signe Kjelstrup, David Jou, Miroslav Grmela, Lyndsay Gordon, and Eric Schneider.

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

- Is the second law relevant when we trap single ions, prepare, manipulate and measure single photons, excite single atoms, induce spin echoes, measure quantum entanglement? Is it possible or impossible to build Maxwell demons that beat the second law by exploiting fluctuations?
- Is the maximum entropy generation principle capable of unifying nonequilibrium molecular dynamics, chemical kinetics, nonlocal and nonequilibrium rheology, biological systems, natural structures, and cosmological evolution?
- Research in quantum computation and quantum information has raised many fundamental questions about the foundations of quantum theory. Are any of these questions related to the second law?

GEORGE HATSOPOULOS: I just want to point out that there has been a lot of discussion trying to explain why entropy of an isolated system increases, how it increases, why some equations of motion are reversible and some are not and which ones are right. I just want to point that as far as I know there is no argument in thermodynamics that says

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the second law implies the increase of entropy. The second law only says that the entropy cannot decrease but there's nothing wrong with the entropy staying constant. Now, there's no question that we have evidence that in some cases it appears that the entropy of an isolated system increases but that's not required by the second law. The second law says that entropy cannot decrease. And we have to think about it because maybe the reason we observe such entropy increases is that our system is correlated with some other unknown system.

The point is that we don't have to state that any equation of motion has to show an increase of entropy by virtue of the second law. All it has to show is that there is no decrease of entropy. A decrease of entropy will violate it. That's all.

ELIAS GYFTOPOULOS: In fact, I would like to express exactly what George said in a different way. If you approach the definition of entropy the way Professor Keenan would ask us to do, you conclude the following: *If* a process is reversible the entropy remains constant, *if* a process is irreversible the entropy increases. That "if" is of great value and proof of that is that we started with engines some 350 years ago with an efficiency less than one tenth of a percent and today we have achieved in combined cycles and with gas turbines thermodynamic efficiencies that exceed 90% (with respect to the availability of the combustion gases). The means that thermodynamics did not impose from the beginning that our processes be irreversible. It simply predicts what the consequences of irreversibility are.

GIAN PAOLO BERETTA: I like what George said, but I want to say this fine point which has to do of course with the quantum theory. If you take unitary evolution and you take the equilibrium states according to unitary evolutions, then for a given value of the energy you find many states that according to that dynamics are stable equilibrium. If you want to make it in such a way that for a given value of the energy only one of these states is stable equilibrium, and by stable I mean according to dynamical theory, Lyapunov stability [G.P. Beretta, A theorem on Liapunoff stability for dynamical systems and a conjecture on a property of entropy, *J. Math. Phys.*, Vol. 27, 305 (1986)], then you do need to have irreversibility in your equation of motion if you want to derive the uniqueness of the stable equilibrium state for the given value of the energy [as we prove in our G.P. Beretta, E.P. Gyftopoulos, J.L. Park e G.N. Hatsopoulos, Quantum thermodynamics. A new equation of motion for a single constituent of matter, *Nuovo Cimento B*, Vol. 82, 169 (1984)]. So that would be my addition to your statement.

HATSOPOULOS: Well, I think it's a good point we should discuss further.

LLOYD: Very Keenan-esque.

SAM MILLER: As we all know, thermodynamics deals with real physical systems. Real physical systems typically involve boundary systems. For example, most gaseous systems are bounded by some sort of cavity wall, which is a real physical interface. My understanding of the H-theorem is that it is derived by making certain fundamental assumptions regarding those boundary conditions. One has to include the boundary conditions in the derivation. So the question is, what is the physical basis for the gas-surface boundary conditions for real physical systems that then lead to the H-theorem?

MIROSLAV GRMELA: The time evolutions taking place in the bulk and on the boundary are coupled by boundary conditions, i.e., by the boundary values of the bulk state variables and their derivatives (their number depends on the order of the derivatives appearing in the bulk time evolution equations). In the time evolution of the boundary state variables, the boundary conditions play the role of external forces. The requirement that the total (i.e., both the bulk and the boundary) time evolution be compatible with thermodynamics then determines admissible boundary conditions.

In the particular case when the boundary time evolution is much faster, an asymptotic analysis of its governing equations provides the boundary conditions and the governing equations of the total time evolution reduce to the bulk time evolution equations equipped with the boundary conditions.

Unfortunately, the complexity of the physics involved in the boundary time evolution makes this type of analysis very difficult. To the best of my knowledge, even the very familiar no-slip boundary condition used in classical fluid mechanics have not yet been derived in this way.

MILLER : Yes, I understand that gas surface interactions are very complex sorts of critters. Gas-surface interaction assumptions are essential for a number of derivations. It is important because if you make certain assumptions regarding the gas surface interaction and then very rigorously derive a mathematical result, then the validity of the result is only as good as those assumptions. One other thing that I would point out is it can be shown for a molecular flow cavity (i.e. where the mean free path is much longer than the dimensions of the cavity) the gas in equilibrium is isotropic and homogenous only if the outgoing angular flux distribution leaving the surface at all points is proportional to cosine theta. Now, you would expect that for a rough surface or a randomizing type of surface. However, technology has allowed us to create engineered surfaces with nanoscale structure. For example, there exists reduced dimensionality surfaces that are known to have many fundamentally anisotropic properties, including optical, phonon, and electrical properties. I would be surprised to expect that gas surface interactions, even for reduced dimensionality surfaces, have to be cosine. So that to me is a very fundamental issue associated with gases in real cavities; the issue is resolving the cosine angular distribution issue even for reduced dimensionality surfaces.

SIGNE KJELSTRUP: I can't answer your comment on the H-theorem, but when you mentioned the surface boundary problem I would like to point out that a two-dimensional surface can be perfectly well described using Gibbs excess variables when the system is in equilibrium, but also in a non-equilibrium situation. You can then define dynamic boundary conditions using non-equilibrium thermodynamic theory as developed for surfaces. I agree with you completely that it is important to match the experimental situation. This branch of non-equilibrium thermodynamics is developed to do so, with focus on transports along and across surfaces [see D. Bedeaux, *Adv. Chem. Phys.*, Vol. 64 47-109 (1986)]. A book on the method will appear in March 2008, S. Kjelstrup and D. Bedeaux, *Non-Equilibrium Thermodynamics of Heterogeneous Systems*, Series on Advances in Statistical Mechanics, Vol. 16, World Scientific, 2008.

MIGUEL RUBI: There is another example in the heat conduction between two nanoparticles. So in this case new physics appeared in the sense that you calculate the

conductivity between the nano-particles. It turns out that it depends on the distance, whereas for macroscopic objects it doesn't. So there are some properties that emerge at the nano-scales, that are completely different to what's going on for macroscopic systems.

ZHUOMIN ZHANG: My question is for Professor David Jou. Actually I read your book on nonequilibrium heat transfer and liked it very much. But then there is a problem. Based on the Fourier law, heat transfer and thermodynamics are very much related. The Fourier law says that the heat flux is proportional to the temperature gradient, and the Fourier law turned out to follow the equilibrium thermodynamics or basic thermodynamics principle very well. There have been discussions about the deviation of the Fourier law at very short timescale. It says that the temperature gradients not only depend on the heat flux but also depend on the time derivative of the heat flux, which gives the hyperbolic heat equation. However, the hyperbolic equation violated the second law of thermodynamics and so it doesn't work. It looks like that your theory, which redefines the nonequilibrium entropy, can be consistent with the hyperbolic equation or the modified Fourier law. However, I do not know whether you have any evidence or fundamental proofs. Normally, thermodynamics goes first, then using thermodynamics principle we derive the Fourier law. The hyperbolic equation to me has some problem. A lot of other people have showed contradictory experimental results, but your theory seems consistent with that. Does it really prove anything or not?

DAVID JOU : In fact in our theory we must redefine the entropy in order that this hyperbolic thermal conduction becomes compatible with the second law. Without our generalization, the entropy production may indeed become negative, and this is the reason for the contradictions you have mentioned. Furthermore, the expression for the entropy I have presented may be obtained from the kinetic theory of ideal gases or quantum ideal gases, of radiation, of polymers, or of some other different systems, and it has always this kind of form I have shown, with the additional term quadratic in the heat flux and proportional to the relaxation time. Thus, consistency with theory and experiment is achieved at the level of the Maxwell-Cattaneo equation. But more delicate experiments demand more elaborate transport equations, that we have worked out but I have not shown. I agree with you in that consistency with thermodynamics is a necessary but not sufficient criterion for having a successful transport equation able to describe experimental results.

ZHANG: But there does not exist a foundation for the entropy definition that you have given.

JOU: Yes, our entropy has several independent foundations. One of them is purely phenomenological because it gives a positive entropy production for hyperbolic heat transport. The second one is the physical interpretation of the additional extra term which comes from the integral of the entropy production when we suddenly isolate the nonequilibrium system and let it decay to equilibrium. This yields a small entropy production which is incorporated in our extra term quadratic in the heat flux. A third derivation comes from microscopic grounds, from Boltzmann's definition and the nonequilibrium distribution function obtained from the Boltzmann equation in Grad's approach or in Chapman-Enskog's approach. Still another foundation is based on projection operators

when the state of the system is projected onto an extended phase space incorporating the fluxes. Therefore, there are several different kinds of justification of our entropy, going from purely phenomenological, to microscopic nonequilibrium approaches.

HOWARD BUTLER: Dr. Hatsopoulos, you just stated that the second law of thermodynamics does not allow the entropy of the system to decrease. Did I hear you correctly?

HATSOPOULOS: That in an isolated system the entropy cannot decrease.

BUTLER: That is a very important restriction that must be put on that statement since the entropy may decrease during an irreversible process with adequate cooling.

LLOYD: I thought what George said is, let's talk some more. I thought we were going to disagree with that.

DUSAN SEKULIC: My question goes to both Adrian and Eric and it is inspired by a few things that I saw on your slides. Adrian promotes a statement of "evolution of configuration in time." This leads to the statement that "thermodynamics becomes a science of systems with configuration." Eric considers biological systems as well as global eco-systems, hence "interjecting thermodynamics in biology" and identifying the "ecological successions directional processes that directly tie to Darwinian evolution." If one accepts it as feasible to extend these statements to the domains of the applications mentioned (social and/or global ecological systems and evolutionary trends), the tools of Thermodynamics (say the ones related to entropy) may be applicable for not necessarily "physical" systems (but, say, for various population systems). Most of us came to Thermodynamics fields from engineering or physical/chemical sciences, looking at what we call just "physical systems." Such systems must be "well defined" to be prone to analysis, and if you take the definition of a system as it is given by Keenan's-MIT school of Thermodynamics [say, as rigorously formulated in E.P. Gyftopoulos and G.P. Beretta, *Thermodynamics: Foundation and Applications*, Dover, 2005], there is nothing there that would exclude non-physical systems if their constituents and descriptions of constraints, complexity and interactions are rigorously defined (and if the properties and the applicable Laws can be used). However, the students of Thermodynamics tend not to like to see the non-physical systems (like the ones from social sciences, say economics and other fields) being modeled by Thermodynamics tools. Such efforts may be considered as an unjustified intrusion of those fields into thermodynamics or viceversa. So my question would be, could one properly define a system to be prone to the thermodynamic analysis if it is not necessarily a traditional physical system? The analysts in remote fields tend to promote a set of analogies, and if one defines the properties of systems (and if the system under consideration is well defined) the implementation of Thermodynamic Laws may potentially agree with the empirical evidence? Do you see a fundamental flaw in such extensions?

ADRIAN BEJAN: The three examples that I gave, the inanimate which is the river basin flow architecture, the animate which is a river basin of animals flowing on the same landscape and the societal, which is our mass sweeping and scouring the same landscape are not because of an "analogy". I defined each of these systems in the thermodynamic sense, to be brief. Each of these systems is a heat engine powering a vehicle, and the power output of that vehicle is eventually dissipated by rubbing against the environment.

That's all there is. That is the model and it works for all those things that I listed. And if you invoke the constructal law then you discover, with your eyes closed really, the configuration of that flow system, end of story. And, from the principle, the unification. Human taste is a different thing, it applies to the individual but this is not what I've been discussing. I have been predicting the flow configuration.

SEKULIC: Yes, we do agree about an inherent character of the outcomes of an analysis that starts with a thermodynamic system definition (which is, by definition, a "physical system") My position was somewhat rhetorical because I myself am ambivalent about the systems that I intentionally did not name as "thermodynamical," but that may potentially become "thermodynamical" – if properly defined? I noticed presence of some very clever approaches to "non physical systems" like the "populations of hawks and doves" studied by Müller [I. Müller, Socio-thermodynamics – integration and segregation in a population, *Cont. Mech. and Thermodynamics*, Vol. 14, pp. 389-404 (2002)]. We agree that converting a non-physical system by using a system of analogies does not make the system more "physical" for Thermodynamics to be applied, but at least some of these currently used analogies may offer hints of a deeper coherence between such systems and of a potential analysis that would require a promotion of a generalized (even new) discipline involving such extended systems with defined properties and Laws similar to the ones we know exist within the field we call thermodynamics. So, I am asking whether we would be more comfortable with using the tools of thermodynamics in analyzing broader phenomena than what we presently name as "physical systems" if we would be able to identify this underlined coherence more clearly.

BEJAN: That is an old field in which other disciplines have tried to use our mathematical constructs, those of Gibbs if you wish. Now that is not what we've been discussing. In fact, I have to give credit to Professor Gyftopoulos for the little story with the evolution of the efficiencies of heat engines. Today it was illustrated by Gian Paolo Beretta with his original graph [G.P. Beretta, World energy consumption and resources: an outlook for the rest of the century, *Int. J. Environmental Technology and Management*, Vol. 7, 99 (2007)]. This is a story Professor Gyftopoulos told me almost ten years ago at the NATO Advanced Study Institute and it landed on my head at the right time because that's when the constructal law was taking shape. The evolution of the heat engines is not required or predicted by the second law. It's a different thing, it is a different phenomenon. It is evolutionary like the unseen evolutionary patterns of Darwin; it is evolutionary like the visible patterns of river basin development right after a downpour. Earlier today Bernard Guy spoke of needing principles of constructing the space or principle of the existence of the construction or of the drawing. This is a subject that requires separate attention, serious discussion.

ERIC SCHNEIDER : My work on the thermodynamics of biological and ecological systems is based on accepted empirically derived theory and observations; and to me, are only analogous to social and economic systems. We can parse ecosystems, rather precisely; using energy flow information derived from organism to organism interaction. Like economists who tally economic flows in an economy, ecologists tally energy pathways through ecosystems. In particular ecologists have borrowed the method of analysis that won Harvard economist Wassily Leontief a Nobel Prize for analyzing flow

of money through economic systems. Leontief not only measured the input and outputs in goods, services, and money but also measured money that cycled *through* the system. Leontief is known for calculating the gross national product (GNP) of an economic system and suggesting that this capital flow is a measure of the size of the economy. The enumeration of ecosystem energy flows allows one to uncover the partitioning of energy in the ecosystem. In ecosystems the total system throughput is a measure of the size of a system in terms of energy flow, as the GNP is a measure of the “size” of the economy. With such data we can calculate many types of system intricacies, like cycling, hierarchal structure, diversity of flows, etc. Generally economics and the social sciences have evaded the net of thermodynamics, however it is interesting to note that the basic economic “deal” is an equilibrium seeking process.

CHARLES BENNETT: I think there’s some problem with both of the engines presented by Lyndsay Gordon. In the one, the osmophoretic engine, it had a left side which was the osmophoretic apparatus that generates a fluctuating motion of the piston rod and then a right side that was rectifying those fluctuations in order to lift weight. There’s nothing wrong in my opinion with the left side. You can get fluctuations like that, no problem. The right side has a problem which was analyzed by Feynman in his ratchet and pawl story and essentially what you drew there was a somewhat more complicated version of a ratchet and pawl. That is, a device that should take a fluctuating motion and convert it into a steady rotation. What happens in that kind of device, as Feynman showed, is that if the temperature of the ratchet is lower than the temperature of the fluctuating element, in this case your osmophoretic engine, then it will run indeed in the direction that you say. But in the course of doing that the ratchet will warm up and when the two come to the same temperature there will be no net motion and if the ratchet is warmer it will work in the opposite direction from the intended direction and so it never manages to violate the second law. Similarly with your rotary–

LYNDSAY GORDON: You’re quite mistaken in the sense that I haven’t got a ratchet and pawl on the right hand side. The ratchet and pawl of the macroscopic world has been changed in design so that the osmophoretic engine can overcome the problem that Feynman envisaged and indeed this design does not resemble a ratchet and pawl at all. The action of the pawl is partially associated here with the solute. If the engine and converter were disconnected, the weight would fall for there is no pawl of macroscopic or microscopic design in the converter to prevent such motion.

BENNETT: I’m not saying you have a ratchet and pawl. You have another device that like a ratchet and pawl aims to impose a directionality on the output from a fluctuating input. And I believe your right hand side of your device is susceptible to the same analysis that Feynman did of his ratchet and pawl.

GORDON: Right. So the right hand side of the device was the converter. It jiggles away in Brownian motion. It moves as it wishes under thermal disturbance but there’s no ratchet and pawl there. The modified part is in the left hand device.

BENNETT: The left hand I have no problem with. I believe it works as you say.

GORDON: Then we haven’t a problem at all.

BENNETT: Yeah, the problem’s only in the rectification on the right hand side.

GORDON: I don't have any pawl or ratchet on the right hand side. It is true that rectification is addressed by the converter but the action of the solute carries the responsibility of Feynman's pawl.

BENNETT: But you have something that is supposed to convert a fluctuating motion into a steady motion in one direction in order to lift the weight.

GORDON: No, not steady. Fluctuating.

BENNETT: Fluctuating, but more one direction than another.

GORDON: Well, why not? The left and right sides are intimately connected and one side can not move without the other producing a corresponding movement. That is why the solute can inhibit total movement when crossing the membrane. The engine causes the rectification. Why wouldn't this work.

BENNETT: Because, as Feynman showed, it doesn't work.

GORDON: Ah. Rectification of motion of the piston and blockage of the reverse movement of the weight are two independent processes.

Please, the other question about the Centrifugal valve device then.

GORDON: The Brownian rotation of the enzyme is produced by the statistically uneven bombardment of a multitude of solvent molecules. The effect of one solute molecule contributing to this rotation is insignificant and if it did it would be to produce a wobble (or libration about the enzymic centre) instead of rotation. No rotational momentum is transferred from the solute molecules to the enzyme. However, momentum is transferred from enzyme to the solute providing the calculated free energy during the transfer.

BENNETT: If they have some finite temperature they have momentum.

GORDON: They've got Brownian momentum and act in the manner described by Onsager (1931) where he describes the action of a centrifugal force in the molecular domain.

BENNETT: Yeah, Brownian momentum, that's what I'm talking about, yes. OK, this is enough for now. We can settle it afterwards.

LLOYD: You can punish him by not investing in his company, Charlie.

NOAM LIOR: Actually I had a similar question to Dr. Lyndsay Gordon. I think the best way to prove what you're doing is to perform an experiment because all these speculations are not too fruitful. But my main point is more to Eric Schneider. Perhaps I misinterpreted your strong statement at the end that you are not going from order to chaos but the reverse. One operational interpretation of entropy that also easily interprets why we can't get so much work is that it takes much less work to make a mess or a chaos than to make order. So perhaps natural systems move in the way that you are saying, that they're decreasing, they're doing some kind of optimization as also Adrian Bejan says. But anthropogenic effects do increase the chaos. What we do is increasing the chaos. Anthropogenic effects are slowly overwhelming what nature is trying to correct. One last brief comment. There is some kind of implicit assumption that nature is ideal and is a highly efficient system and it's not. Many natural processes, including photosynthesis for instance, are very inefficient in fact.

LLOYD: The collection of energy from photons is extremely efficient. It's like 95 or 96% efficient but the actual transfer of that energy into usable energy biomass is very inefficient.

LIOR: One of my questions was, why don't you do an experiment?

GORDON: I'll answer that. Sometimes theory precedes experiment. At present, it appears that nanotechnology is not sufficiently advanced for the production of Maxwellian valves. However, experiments are being done and perhaps in the very near future will be the time for celebration.

LLOYD: One last question and then it's going to be time to adjourn.

DEREJE AGONAFER: I just want to ask this community why is not an exergy analysis more widely used in applications, especially stuff like electronics cooling? I know Eric mentioned it. I thought maybe, Adrian, you might want to start.

BEJAN: On the use, you should pose that question to the panel tomorrow which is about the teaching and the like. But I don't think there is any reason for avoiding that method as there is no reason to avoid availability and other good lessons from very basic thermodynamics based on minimum words.

KJELSTRUP: I think that's a very appropriate perspective that you gave to this panel. In my view a major reason to work with the entropy production of a system is to be able to understand better where exactly the exergy is lost, or where the entropy production is, if you want [A. Zvolinschi, S. Kjelstrup, O. Bolland and H. van der Kooi, *J. Industrial Ecology*, Vol. 11, 1 (2007)]. The next step is then to see how we eventually can minimize it [E. Johannessen and S. Kjelstrup, *Chem. Eng. Sci.*, Vol. 60, 3347 (2005); E. Johannessen and S. Kjelstrup, *Energy*, Vol. 29, 2403 (2004)]. This is what the panel is going to be about tomorrow.

SCHNEIDER: Thermodynamic-exergy analysis is lacking in energy policy decisions at many levels in government today. Corn based ethanol fuel is just one national energy policy devoid of basic thermodynamic analysis. I believe that any of us that have the thermodynamic knowledge and access to any levels of government, should put these analytical procedures forward in issues from building design to national energy policy.

LLOYD: OK, we've now reached the end of our allotted time. I'm sure this has engendered lots of discussion. I urge you to take it outside and duke it out there. Or even better, as George wants us to do, the original meaning of symposium means drinking together so have a glass of wine together this evening and then I'm sure that tongues will be loosened and thoughts will flow.

HATSOPOULOS: Cheers.