Discussion on “The Second Law and Energy”

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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 Thomas Widmer, Ernest Geskin, James Keck, Noam Lior, Debjyoti Banerjee,[1] Richard Peterson, Erik Ydstie, Ron Zevenhoven, Zhuomin Zhang, and Ahmed Ghoniem.

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

- Current state-of-the-art efficiency of combined-cycle energy conversion technology is about 60%. Based on the trend of historical data, some forecast that second-law efficiency of energy conversion will reach 80% by the end of the century. What technologies are at sight that might hold this promise?
- Nanotechnologies and microtechnologies point towards the development of microscopic heat engines? How do second law limitations map down to these scales?
- Combustion is the principal way of converting the chemical energy of fossil fuels to thermal energy, but it is highly irreversible. Are there promising ways to reduce combustion irreversibility? Are fuel cells the only alternative to combustion?

GIAN PAOLO BERETTA :[2] I think this is a very particularly happy time in the long and cyclic history of thermodynamics. Many of you may remember that two or three decades ago, many engineers and scientists used to be convinced that thermodynamics is a “dead subject”. Well, your presence today proves that we are not yet out of business.

[1] Unfortunately Dr. Banerjee was unable to finalize his contribution to the proceedings.
[2] This statement was made in the introduction of Dick Bedeaux’s lecture. It is inserted here because Figure 1 is relevant to the present discussion.

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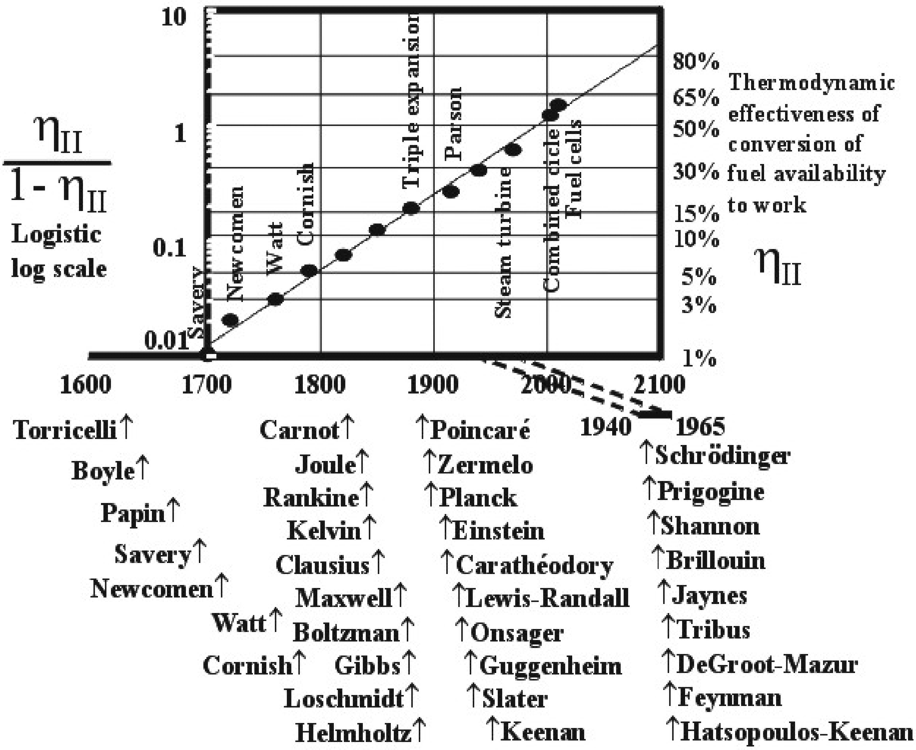

FIGURE 1. Regular growth during the last 300 years of the *thermodynamic effectiveness*† η_{II} of the best available technology for converting fossil fuel availability to work (right scale). The linear "logistic" growth of the logarithm of $\eta_{II}/(1-\eta_{II})$ (left scale) is typical of many learning processes. On a linear scale, η_{II} follows a typical S-shaped learning curve, i.e., the historical data are very well fitted by $d\eta_{II}/dt = \eta_{II}(1-\eta_{II})/\tau$, with $\tau \approx 60$ years. The names of important contributors to the history of thermodynamics are shown in chronological order on the same time scale. †Here, η_{II} is what many (somehow misleadingly) refer to as the "second-law efficiency".

And to see where my enthusiasm originates, I would like you to look at the graph in Figure 1, which shows a very important practical impact of the development of thermodynamics [G.P. Beretta, "World energy consumption and resources: an outlook for the rest of the century," *Int. J. Environmental Technology and Management* **7**, 99 (2007)]. Over the past three centuries, the graph shows (right scale) the evolution of the effectiveness of the best available technology for converting fossil fuel availability into useful (mechanical or electrical) work. It is plotted on a particular scale. On the left side you see on a log scale the ratio of the effectiveness over the margin of further improvement (1 minus the effectiveness). The fact that on this log scale it is a remarkable straight line over the past three centuries, is a typical feature of a learning process, a well-known feature of all learning processes. Here, I added at the bottom of the slide a good crowd of important names in the history of thermodynamics. What I find exciting is that your presence here, the discussions we will have, the ideas that each of us will try to communicate—however theoretical and abstract they might be–are going to constitute the scientific background for the development of new technologies that by the end of the century, according to this graph, will bring the thermodynamic effectiveness of the best power production technology from the current 65% to over 85%. That means that we are still just past half of our learning process about understanding and mastering the laws of thermodynamics. That is why we thermodynamicists are still going to remain in business for a long while.

ELIAS GYFTOPOULOS : I have a comment about Professor Peterson's presentation and a question for Professor Banerjee. There exists no engine that has ever been built for land, sea, air and space application which satisfies the nonexistent theory of finite-time thermodynamics. Now, my question. I am intrigued by the possibilities of nanotechnology. And I want to ask you whether there is a possibility of controlling the nanosystem you create in such a way that you can use it while it is still in nonequilibrium or an equilibrium state which is not stable equilibrium and, therefore, is relatively far from the stable equilibrium condition. What motivates me to ask you this question is my wristwatch. The little batteries that we have in our wristwatches have two time constants. One is of self-discharge and the other the work producing part. It so happens the self-discharge constant is much longer than the five or six years that our watches work. I am puzzled and intrigued as to whether, with nanotechnology, we can repeat that kind of operation in a more general way. Because if we have systems working from a state that is not a stable equilibrium, for the same energy we are going to get more work out.

DEBJOYTI BANERJEE : Regarding the nanoscale processes, I did not get into the details of phase change phenomena. Whenever we say there is a stable boiling process, if you look at the micro and nanoscale processes, it is not really stable. It is a highly unstable situation that is going on in a repeated cyclic manner. And it is not exactly a cyclic process. It is a chaotic process which does not come back to the same position at fixed intervals. That interval varies. My point of telling this is that, if you look at that scales, some papers from European labs working on boiling have shown that every time a bubble departs, fresh liquid comes and hits the heater surface, and you have a peak in the transient heat transfer, which is estimated to be of the order of MW/cm^2. But these are really tiny flow phenomena and they are operating over a very small surface area. If you can somehow increase that frequency or if you can increase the area over which it is occurring, you can actually harness much higher amounts of heat transfer in phase change than you can currently do, and those are non-equilibrium processes.

SETH LLOYD: If I may comment on your talk about how when you try to scale down heat engines, you seem to be saying that scaling down doesn't work: there's no room at the bottom. But then I look at Professor Zhang's talk. If you actually scale down further then you can get strongly enhanced heat transfer due to near field effects. So, maybe you just didn't go far down enough to the bottom.

RICHARD PETERSON: Well, when you form a model of an operating heat engine for the purpose of scaling, you must consider the cycle and the heat transfer into and out of the cycle. It is not sufficient to consider a single component of the cycle or just the working fluid of the heat engine. What I am implying here is that there are certainly phenomena that occur at the micro and nanoscales that expand, contract, emit energy and potentially produce work, but from my survey of the small-scale heat engine area, and keeping tabs on who is doing what in the so-called micro engine area, there is nothing that would be classified as a complete thermodynamic heat engine that operates efficiently close to what the theoretical limits are; say, in the one millimeter size range and below. Now, you can make thermoelectric conversion elements much smaller than that. But the efficiency is not high and the operating device doesn't approach what finite rate, finite time thermodynamics tells us. If I understood your comment correctly about that particular area in terms of its applicability to reality, I view finite rate, finite time thermodynamics as a step closer to a description of reality, a step closer than the Carnot ideal. But there are certainly problems with it. I would tend to disagree with the statement that finite rate thermodynamics is a nonexistent theory. For example, when you analyze the temperature difference of actual, practical heat engines, and place the appropriate thermal resistance between the engine and the heat source, you get very close to what finite rate, finite time thermodynamics tells you for their thermal efficiency. You don't get the Carnot ideal. You find engines operating near their maximum power point.

SAMUEL MILLER: My question also pertains to nano- and micro-technologies. I am just going to ask a question that was listed as a panel discussion question in the program, but was not addressed by any of the panelists. How do second law limitations map down to those size scales? That's just one of the formal panel questions that no one addressed. At what point does the second law break down, what are the requirements, do you deviate from the second law, is it rigorously valid all the way down to the microscales? Just any comments or discussion regarding how the second law relates to small scales would be helpful. It is clear to everybody that the second law applies to large macroscopic systems where you have large numbers of interacting chaotic particles. If there's somebody that could describe the nature of the second law at small scales that would be useful.

ZHUOMIN ZHANG: Let me make a comment. There are some recent publications in the Physical Review Letters about the violation of second law. Maybe someone earlier yesterday discussed that. What it looks like is that, if you have a truly, truly small system at a truly, truly short timescale, you only take one shot. Therefore, there is a possibility that if you talk about the entropy it will decrease in an isolated system.

LLOYD: Let me comment since I've actually built heat engines that operate at the scale of single molecules at the level of nuclear spins. There, I mean, if you take the entropy to be minus trace rho log rho then the second law never gets violated for the simple reason that these engines are operating in a unitary fashion. A good example of a very tiny heat engine is a single atom laser, like the kind that has built by Jeff Kimball at Caltech, that takes thermal energy and converts it into radiant energy. These atomic engines perfectly obey the second law. Entropy does not increase. They operate as a kind of a cycle that is not the Carnot cycle but still works pretty well. Theo, were you commenting on the same question?

THEO NIEUWENHUIZEN: Yes sure. I want to answer, to rectify another point, that we already heard yesterday. There may be configurations, single configurations, which go against the direction of the second law, but if you do the average, and we saw this yesterday in one of the talks, you get out pretty well the second law. To be specific, the second law and work are about averages, about ensemble averages, and they say nothing about individual realizations [Th.M. Nieuwenhuizen and A.E. Allahverdyan, Comment on "Experimental demonstration of violations of the second law of thermodynamics for small systems and short time scales," *Fluctuation and Noise Letters* **5**, C23 (2005)].

LIHONG WILLIAMSON: Because this meeting is about meeting the entropy challenge and I think we're talking about nano scale heat engine. But I think in the real world, the biggest challenge of entropy is in the power plant. Actually, if I can call this the Rankine demon because in America alone we have more than 80% of our electricity generated by the Rankine Cycle based power plant, in which efficiency is less than half. That means we are wasting more than 50% of our precious resources. And I think we should concentrate on this issue. We have to do something to improve the Rankine Cycle efficiency.

Actually, I have an idea for how to improve it, which involves redesigning the steam generator to utilize heat pipe technology. It involves a series of heat pipe units tailored to the temperature in each segment of the combustion area. Those units are arranged so that the working fluid temperature of the heat pipe in those units matches the combustion temperature of the flue. By doing so it also breaks down the Rankine Cycle's chaotic steam generator into numerous heat pipe micro steam generators which are separated from the combustion flue gas passing route. I would like to receive comments as to whether this idea works. Please contact me for further information.

PETER SALAMON: A couple of quick questions here, one for Richard Peterson. For the one millimeter range, it's probably more useful to look at refrigerators than heat engines. Have you done that?

PETERSON: Yes. I've applied a similar analysis to refrigerators and cryocoolers and ended up, instead of the maximum power point, calculating the point where the heat load to the cold side is equivalent to the heat lift performed by the refrigerator. From this type of analysis, a length scale can be determined.

SALAMON: Have you looked at minimum entropy production operation instead of maximum coefficient of performance or power?

PETERSON: That's on my list of things to do in the future, but thanks for the suggestion.

SALAMON: For Ernest Geskin, you said the most efficient energy conversion device is a gun? I mean we should be generating power with it then, right? What does that mean? I don't understand it so if you could elaborate. What are you comparing it to? In what sense is it most efficient?

ERNEST GESKIN: It means that 2 g of explosive have approximately the same internal (chemical) energy as 2 g of coal. While a powder can accelerate 8 g of metal up to several hundreds meters per second, what amount of work can you extract from 2 g of coal? However the direct manufacturing use of bullets is not possible. We cannot control solid-solid impact. At the same time, as it was shown by our experiments, the manufacturing applications become feasible if a solid projectile is replaced by a liquid one.

JAMES KECK: I think you have just described the internal combustion engine.

GESKIN: It is an example of when you have direct conversion of heat to work without intermediate electrical power station and so on. Like in a mine and in destruction, we use explosives because they are the best when we do not need to control the result. But using the device we developed, it seems that you can control explosive. Liquid projectiles can be controlled precisely, so they can be used as a manufacturing tool, as opposed to bullets which you can use only to kill.

ADRIAN BEJAN: I have two brief comments. They are based on the questions raised by Professor Ghoniem.

First, the slide with the line showing efficiency of power plants versus size. You asked does size matter? It does. You have size plotted on the abscissa, and such alignments of designs are found everywhere, particularly in animal design. If you multiply the efficiency by size and you put it on the ordinate, you have the allometric metabolic rate. And so the sharpness of these lines, these very thin clouds of data, suggest that there has been a lot of evolution before these champions, which are now lining up on this podium. The same is found in inanimate flow structures such as the river basins. And so the answer is yes.

The second comment is an answer to your question on the next slide. If you look at this sketch in the upper left-hand corner, how to make the power plant better, it is about improving efficiency, which means to minimize entropy generation in the power plants. This means more power to us, a bigger red arrow. And that, of course, is the basis for the question used as a headline for this entire workshop. However, the bigger picture contains the answer to the question of what happens to the red arrow. The power that is generated is not eaten or stored by any of us. It is destroyed by us.

In the final analysis, the red arrow is rubbed against the ambient and dissipated. What was entropy generation minimization in the drawing that you made becomes the maximization of entropy generation (exergy destruction) in the drawing that we did not see. Look at the whole picture then, and ask why we need red arrows? We need them for the reason that Professor Hatsopoulos said in his example at dinner last night. There is a correlation between the use of fuel or energy and the economic activity in a country. The red arrow is us, moving on earth because of what goes on in our fire filled bellies and engines. That also holds true for all the animals, and for the big wheels of atmosphere and oceans of the earth.

AHMED GHONIEM: Absolutely, the scale matters, but not indefinitely. In other words, if you look at small power units, the reason why they are less efficient is, in my opinion, because of the economy. It is because the fuel is cheap. If you want to really extract more power out of them, that is, more availability, you could. For instance, you could do polygeneration. You could do cogeneration, “waste heat recovery,” etc. You know, that is the concept of distributed power. Also, if you hybridize, you will get better overall efficiency. A hybrid car has a little engine, but it is hybridized with a storage system for optimal utilization, and so on. I just brought that up to bring us back to reality. And the connection is the economy ....

The second point, absolutely, you are right. I mean, it depends on what you are going to do with what you are getting out (of the conversion process). But I also put up that picture (entropy generation during combustion) because it is not obvious that our current combustion technology is optimized for the designs for the engines. Improvements will require changing the engine design as we change the combustion processes to reduce entropy production. So, you will have to discover different engine designs that are compatible with novel combustion processes that minimize entropy production. And there, we will also have to worry about other issues such as the materials because first order analysis will tell you that we will have to burn at higher temperature, and higher pressure. (Novel fuels will also have to be discovered.)

NOAM LIOR: I have a comment about this, just a short one. I think what Adrian brings up is a very important element. Sustainability hasn't been mentioned for one moment in this whole conference. I don't think we can design any kind of energy systems without considering overall sustainability. And we should adopt our laws of thermodynamics to consider not only the power generation, the isolated benefit that we have, but also the entire impact. And that's the way the things are going now, so I think we better catch up with what the world is doing.

TIMOTHY GUTOWSKI: Thank you for the introduction, Noam, because that's exactly where I wanted to go. There have been a lot of comments about the hope of nano-engines, but you have to make these things. Now, I don't know all the techniques. I certainly don't know how to make the single atom laser, but I do know the variety of techniques that we have out there, for example, chemical vapor deposition, plasma etching etc., the things we use right now for microelectronics. Well these are also what we frequently use to make our nano-engines. Now if you do a life-cycle energy analysis on the products made by these processes, you will see that the energy consumed shifts from the use phase to the manufacturing phase. You can see this, for example, if you compare an automobile which consumes energy and emits carbon at the use phase, to the computer which is dominated not by the use phase but by the manufacturing phase. So, there is something else going on here. And our attention may be in the wrong spot on nano-engines.