The need for entropy in Finite-Time Thermodynamics and elsewhere

Bjarne Andresen

Niels Bohr Institute, University of Copenhagen
Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

Abstract. Carefully specifying the entropy flow and entropy generation in a system is essential when optimizing its performance. Here we mention that in an ensemble some copies may seemingly violate the second law of thermodynamics, which is OK if on average entropy is produced. We focus on which quantity is being optimized and the need for controls to achieve an optimum. And we emphasize the importance of the defining boundary of what is considered the system; vastly different optima will result for different definitions. Finally, we show the effect of different heat transfer laws as well as the type of working fluid on the entropy production and thus the optimal performance of a system.

There have been many fights about the second law of thermodynamics and about definitions of entropy. Really, it is very much like a colleague from New Zealand told me that there are many ways of slicing a kiwi (Fig. 1). It is still my belief that entropy survives as a concept, and that it applies equally in chemistry, to quantum computers, to black holes, to everything. A well known quote from Albert Einstein is that "classical thermodynamics ... is the only physical theory of universal content that, within the framework of applicability of its basic concepts, will never be overthrown". That is quite a statement. However, I do not see any signs of contradiction so far.

FIGURE 1. One way to slice a kiwi. (From a New Zealand T-shirt)

Having just been at a meeting on cooling of atoms and molecules a month ago, I feel compelled to mention that the cooling of atomic systems is not really a question of removing their energy, but removing the last bit of entropy from these systems. The temperature getting closer and closer to that absolute zero is a matter of removing the entropy associated with mixed quantum states. Now, any real process generates entropy, including a cooling process. If the system is an ensemble of particles, we observe an increase of entropy not of each individual particle, but on average for the ensemble. This means that some particles may experience a decrease of entropy as long as more experience an increase. Fig. 2 illustrates this point [1]. It shows the measured probability of a certain change of entropy of a tiny nano sized system in a random process. Most of the bulk of that distribution is in the area of entropy generation, but there is a small tail which shows that a few systems actually decreased their entropy during this process. This is not a violation of the second law of thermodynamics. You cannot extract energy from that, because more often than not, you are going to lose. So let's keep in mind that just a single atomic system violating the second law of thermodynamics is not a violation of the principle because it is a rare occasion.

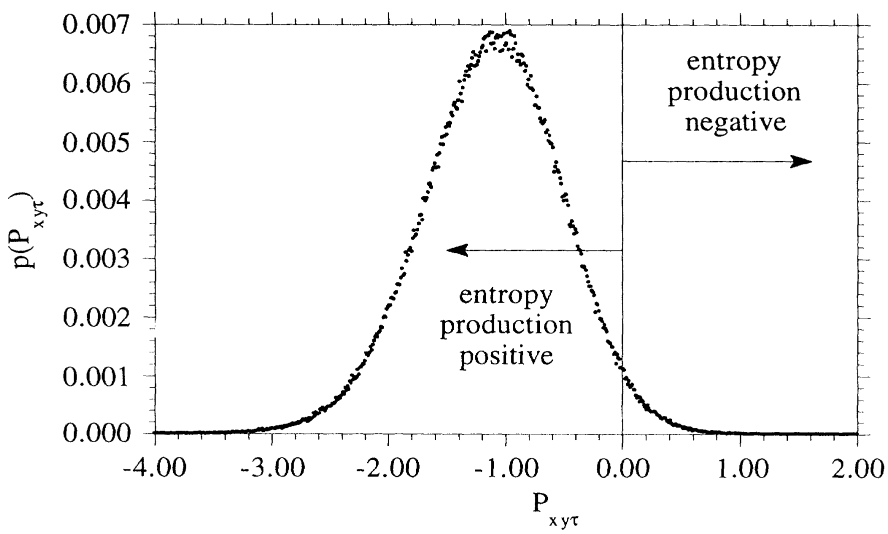

FIGURE 2. Frequency of entropy production $-P$. (From [1])

Bounding the performance of dynamic systems, one can make good use of the many ideas that have been put forward in finite-time thermodynamics [2]. One of the important lessons is that you have to specify carefully precisely what you want to optimize. Is it efficiency? Is it the power of the system? Or something else? These objectives all require different modes of operation (Fig. 3) [3].

The same distinction is apparent in the recent concept of thermodynamic geometry [4] where the bounds derived on the entropy production and on the loss of availability for a given type of process look very similar, but the optimal paths are different. Thus unless you carefully specify what you want to maximize, you will continue getting into these unproductive fights about my system is better than your system [5].

The next general observation is that in order to achieve any optimum, you need to have controls. Nothing happens by itself. It is the operator, not nature, that decides what is the desired path. Those controls could be on the rate, temperatures, and conductances for a piston system as shown in Fig. 4. Once again the path will be different whether you you want to maximize power or you want to maximize thermal efficiency. Such optimal

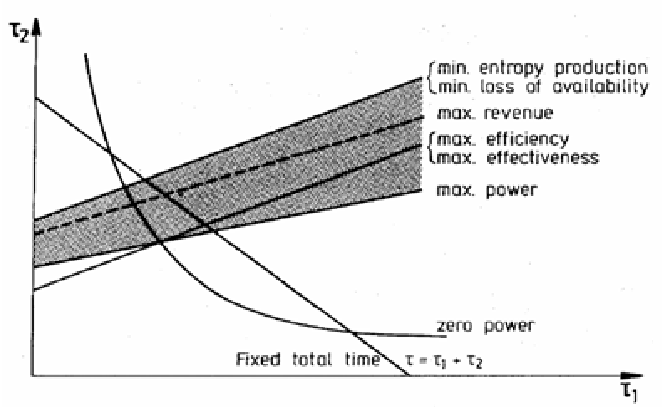

FIGURE 3. Time allocation on the hot/cold branch of an endoreversible engine for different objective functions.

paths are shown in Fig. 5 [6].

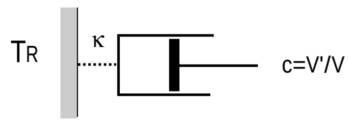

FIGURE 4. Control variables for a piston arrangement: reservoir temperature T_R, heat conductance κ, relative piston speed c.

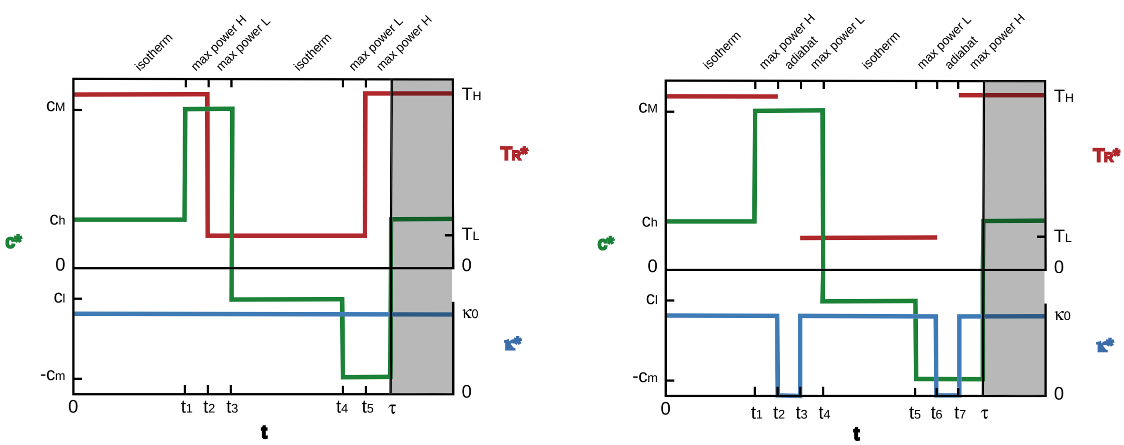

FIGURE 5. Optimal controls of the piston system when maximizing power output (left) and thermal efficiency (right).

Similarly, one can optimize the performance of distillation columns. Instead of traditionally heating at the bottom and cooling at the top, one can gradually heat or cool along the column in such a way as to increase the thermal efficiency of separation (Fig. 6) [7]. Optimal sequences are equally important for something as abstract as simulated annealing [8].

Another important lesson is that you need to be very careful in defining your system, e.g. how you carve it out of the environment. In the setup of Fig. 7, consisting of a heat engine coupled to its hot reservoir through a heat exchanger, it makes a major difference

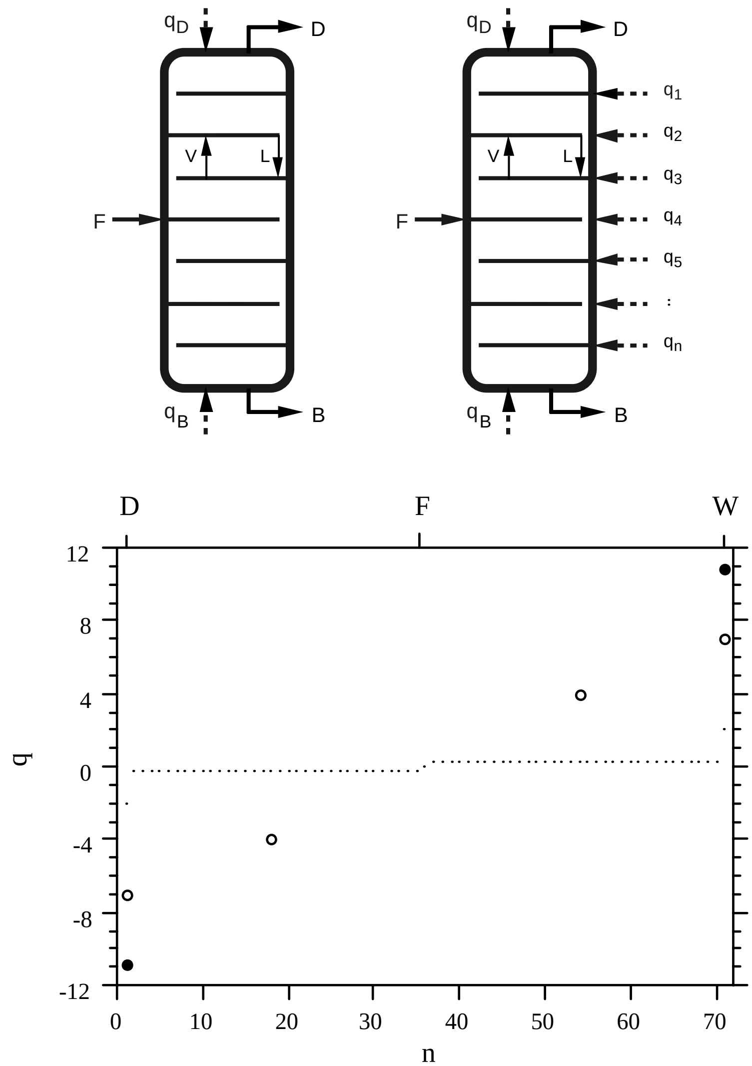

FIGURE 6. Conventional adiabatic distillation column (left) and diabatic column (right). Optimal rate of heat addition on each tray for a fully diabatic column (dots), for a conventional adiabatic column (2 solid circles), and for a column with just 2 additional heat exchange points (4 open circles) (lower frame).

for the optimization whether you define your system as boxed by the dotted line in the frame to the left or by the dotted line in the frame to the right. That is whether you include the depository of heat from the heat exchanger at T_2 in your system or not. In the former case useful availability remains at T_2 while in the latter, being inside the system, it has no use and can only be discharged to the environment [5].

Likewise, the mode of heat transfer affects the optimal path. In Fig. 8 the optimal paths for heating a system from 300 K to 900 K with the least generation of entropy are shown when the heat is transfered by thermodynamic force ($n = -1$), by normal conduction ($n = 1$), and by radiation ($n = 4$) [9].

Finally, you get different performances whether you work with a Bose gas or with a

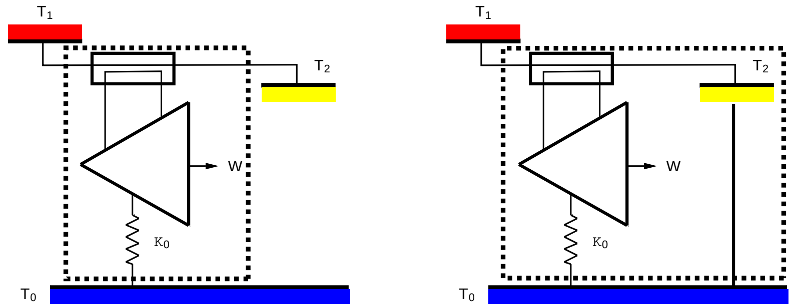

FIGURE 7. Heat engine supplied through a heat exchanger. The “system” is delimited by the dotted box. Optimizing the engine by itself (left) and including the exhaust reservoir (right) yield very different optima.

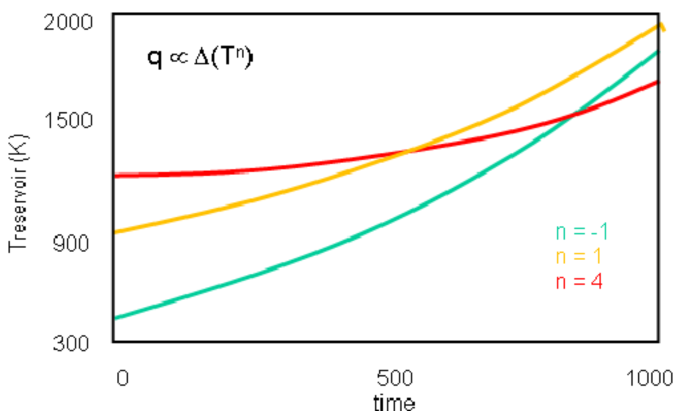

FIGURE 8. Optimal temperature paths for heating a system from 300 K to 900 K when the heat is transfered by thermodynamic force ($n = -1$), by normal conduction ($n = 1$), and by radiation ($n = 4$).

Fermi gas. Of course the thermal efficiency can never become better than the Carnot efficiency, but how much power is produced per stroke depends on the working fluid as illustrated in Fig. 9 [10].

REFERENCES

1. D. J. Evans, E. G. D. Cohen, G. P. Morris, *Phys. Rev. Lett.* **71**, 2401–2404 (1993).
2. B. Andresen, "Minimizing losses – Tools of finite-time thermodynamics", in *Thermodynamic optimization of complex energy systems*, edited by A. Bejan, E. Mamut, NATO ASI Science series 3/69 (1999), pp. 411–420.
3. P. Salamon, A. Nitzan, *J. Chem. Phys.* **74**, 3546–3560 (1981).
4. P. Salamon, R. S. Berry, *Phys. Rev. Lett.* **51**, 1127–1130 (1983).
5. P. Salamon, K. H. Hoffmann, S. Schubert, R. S. Berry, B. Andresen, *J. Non-Equil. Thermod.* **26**, 73–83 (2001).
6. M. H. Rubin, *Phys. Rev. A* **19**, 1277–1289 (1979).
7. B. Andresen, P. Salamon, "Optimal distillation using thermodynamic geometry", in *Thermodynamics of energy conversion and transport*, edited by S. Sieniutycz, A. De Vos (Springer, 2000), p. 319–331.
8. J. Nulton, P. Salamon, *Physical Review A* **37**, 1351–1356 (1988).
9. B. Andresen, J. M. Gordon, *Int. J. Heat Fluid Flow* **13**, 294–299 (1992).

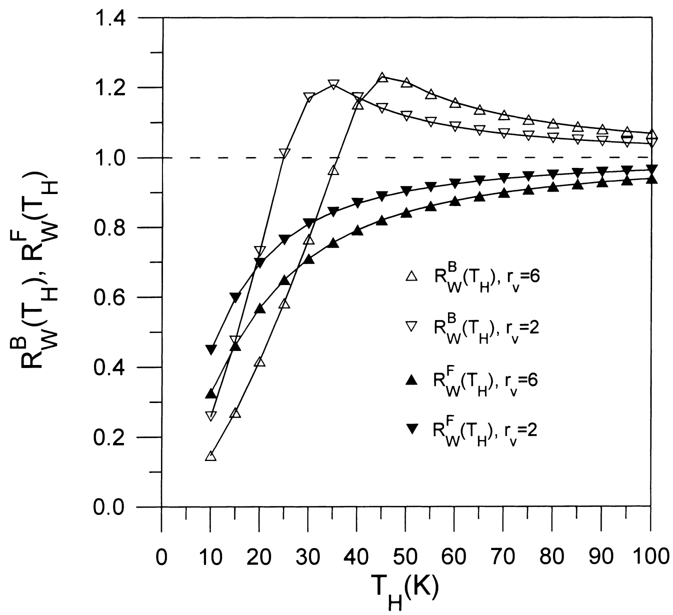

FIGURE 9. Work output per cycle for a Carnot engine using a Bose gas (open triangles), Fermi gas (filled triangles), and a classical gas (dashed line) as working fluid. (From [10])

10. A. Sisman, H. Saygin, *Applied Energy* **68**, 367–376 (2001).