Some Issues in Finite-Time Thermodynamics

Peter Salamon
Department of Mathematical and Computer Sciences
San Diego State University
San Diego, CA 92182-7720

ABSTRACT

The article responds to recent criticisms of finite-time thermodynamics. The issues concern a difference in viewpoint between analyses that seek in-principle physical insights and analyses that seek an efficient engineering solution to current problems with current technology and prices. The paper also highlights some of the achievements of the subject including recent implications for the design of distillation processes.

1. Introduction

The study of limitations to the operation of thermodynamic processes subject to finite time or finite rate constraints has been pursued by at least three groups of authors working in finite time thermodynamics [1], control thermodynamics [2] and minimum entropy generation [3]. These studies focused respectively on the physics of describing in-principle limitations to the set of possible processes [1] or on the control theory of what is achievable [2] or on the engineering implications of these kinds of considerations [3]. Despite the differences in the labels for their endeavors, the aims, results, and approaches of these three groups have a great deal in common. Important differences exist however. Notably, the *interpretations* attached to these results are often very different depending on whether one is interested in understanding in-principle limits to energy conversion [1], or physical controllability [2], or improving current engineering practice [3]. I argue in the present paper that understanding the *physics* leads (at least eventually) to engineering. The route is bumpy and the major purpose of the present manuscript is to smooth some of the bumps in the road caused by the inevitable difficulty of communication across disciplines.

2. Some Misunderstandings

My own interest concerns the goal of discovering new *physics* and that is the perspective that I try to impart in the present manuscript. I begin my narrative with a basic theorem of control thermodynamics -- the Orlov-Berry theorem [4]. It is really a special case of a general fact from optimization theory. The fact states that the optimum of a function f on a set A is at least as good as the optimum of f on a subset B of A. The implications of this fact for the analysis of finite time processes is our present concern. Analyzing the optimal performance of a system when we improve the control that we are able to exercise, can only improve the optimal value of our objective and can thereby give a bound on what is physically possible.

This was the spirit of the early papers on the finite-time thermodynamics of heat engines subject only to thermal resistance losses [5-7]. The formal proof came with Orlov and Berry's paper [4] and is striking in its simplicity and power. They begin by writing down the full dynamical equations for the working fluid, the heat baths, and the power source coupled to a heat engine complete with partial differential equations for the full distributed systems. The heat transfer to the working fluid is proportional to the temperature difference across a surface. They complete the careful formulation of their control problem by specifying an objective function f. Next, they switch to a problem in which the temperature at each position inside the working fluid and the heat exchangers is controllable, i.e. they discard the partial differential equation constraints changing the temperatures at the points inside the engine and heat exchangers from state variables to control variables. The optimum in the simplified problem bounds the optimum in the real problem since the simplified problem results from the real problem by effecting better, albeit possibly unrealistic, controls. Ignoring a great number of the dynamical equations converts state variables to control variables and enlarges the set of allowed processes. Of course this must be done carefully respecting the laws of thermodynamics -- these are constraints that we must not ignore.

Physically this is easy to ensure by counting these controls as reversible and taking the associated exergy cost as zero. Thus we assume reversible control over all but a few of the variables in our system. We then ask what is the least entropy production or maximum power output or the optimal value of various other possible objectives when we control the rest of the universe in an ideal way -- namely reversibly. This focuses the analysis on the limitations to energy conversion inherent in the part of the system or device which we did **not** assume to be reversibly controllable. The results bound the possible values of the objective in a more meaningful way than is provided by the comparative statics of classical thermodynamics. The Orlov-Berry theorem makes simple models interesting and able to say useful things about real processes. The simplified problems often lead to solutions which tell us to run the process infinitely fast or infinitesimally slow. The interesting domain is in between: well posed problems which ignore enough irreversibility to be tractible and yet count enough to keep the solution finite.

The results enable us to understand the exergy loss associated with a particular mode of entropy production and we have been making steady progress in doing such exergy loss accounting. The results must be used very carefully, however. Let us take as illustration the much celebrated equation of Curzon-Ahlborn-Novikov (CAN) [8, 9] for the efficiency at maximum power

$$\eta = 1 - \sqrt{\frac{T_c}{T_h}}. \qquad (1)$$

The striking simplicity of this equation, as well as its similarity to the well known efficiency of Carnot, has brought it rapid acceptance. Nonetheless, as pointed out in [10], this efficiency is surpassed in real power plants! The explanation is that this equation does **not** represent the maximum efficiency but rather the efficiency at maximum power. This associated maximum power

$$P = \frac{\kappa}{4}\left(\sqrt{T_h} - \sqrt{T_c}\right)^2 \qquad (2)$$

must be more than the power delivered in any process which corresponds to the CAN calculation augmented by additional dynamical equations. This much is mathematical fact. Note that it does **not** imply anything regarding a comparison between the efficiency obtained at this power and efficiencies in real processes -- even when the real processes are also designed to maximize power albeit with additional constraints!

One of my goals in the present paper is to respond to certain criticisms of my approach to the analysis of thermodynamic processes [3, 10, 11]. The discussion above regarding the CAN efficiency is one such issue. A second issue also concerns unwarranted conclusions based on the above formalism. Finite-time thermodynamics makes no claims to the effect that *every* process approaches reversible as the rate is slowed down. Thus Professor Gytopoulos's examples concerning 1000 spark plugs and batteries attack a non-existent claim. Certainly, unless we are able to exercise a great deal of control over the process, slowing it down does not help. The strongest correct statement along these lines which one can make is as follows: Finite process time is a very real constraint and forces any process to produce entropy provided some transport is required and conductivities are finite. When the process time constraint is increased, it is *possible* to use more time although it is *not necessary* to do so unless we assume further restrictions on our controls. Thus we are free to use the same optimal control that was allowed for constrained time τ even after this is relaxed to a larger constrained time $\tau' > \tau$. It thus follows that increasing the allowed process time cannot make the optimal process perform worse by any measure since all we have done is allow additional possibilities. Thus the issue is whether one understands time as a constriant for a control problem or as a traditional physical variable.

Whether or not additional time actually helps improve a process depends on many factors. Transport processes through a finite conductance can proceed closer to reversibly, provided we have adequate control which can take advantage of the longer time. Systems which have an exergy leak, [10] such as electrochemical cells, certainly do not do well when operated very slowly. This is an essential feature of a finite-time thermodynamic analysis for these systems [12].

My final issue related to repairing the road of communications between science and engineering concerns the idea that there can only be one "freely variable reservoir". Bejan, foremost among authors, has advanced this unfortunate point of view. I begin with a quote from his referee report on one of my papers [1].

> "In my 1996 Am. J. Phys. paper I [Bejan] explained why the Curzon & Ahlborn constant is unrealistic, and why related claims are unfounded. The reason is that the optimization performed by Curzon & Ahlborn is based on the unrealistic assumption that the heat input (amount of fuel) to the engine is a true degree of freedom in the design, i.e., a quantity that varies as freely as the rejected heat. This assumption would hold only in a world with two environments, or two atmospheres ..., certainly not in today's power plants on earth.
>
> My 1996 paper [11] was a challenge to modelers such as Curzon and Ahlborn to explain specifically (or graphically) where their free input comes from. This challenge was sidestepped by the present authors."

Let me not sidestep the issue any further. As I hope was made clear in the discussion above, this challenge comes from a mistaken conception of the physical subject of finite-time thermodynamics which by its nature seeks bounds through the use of very limited counting. This is also the answer to Bejan's similar challenge issued in this same 1996 paper [11]

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[1] He chose to disclose his identity in the report.

> "Whether the entropy generation estimate of Salamon et al. accounts for all the irreversibilities of the power plant is a topic I would like to open for discussion."

Let me reiterate; there is no attempt to count *all* the irreversibility but simply to *bound* the performance by counting only *some* of the irreversibility in order to understand the intrinsic limitations set by the effects of these modes.

Bejan's idea is that we need to count the complete process from the burning of the fossil fuel to the equilibrated combustion gases at atmospheric temperature. According to Bejan "Any other 'entropy generation rate' calculation is incomplete, i.e. irrelevant and useless." I now argue that this statement is completely untenable from a physical, an engineering, and an economic point of view.

Let us begin with the physics. Here the debate is perhaps moot since Bejan has admitted in print that if one is talking about a heat engine operating between the atmospheres of earth and another planet, one can consider both reservoirs to be freely varying. Thus the idea of a single freely variable reservoir is terracentric at best. To focus our analysis on the effects of a particular mode of irreversible interaction, it helps to ignore the irreversibilities of the other processes. This is the essence of the program I outlined above. Thus we are free to treat the combustion process and the residual cooling of the exhaust gases as reversible. Is there something physically sacred about combustion and exhaust (as opposed to, say, the inside of the engine compartment) that we are allowed to take one as reversible and the other not? We can focus our irreversibility analyzer on any mode that we choose and there is no physical grounds for limiting what irreversibilities one chooses to count. Recall that the physics we are talking about understanding is used for the analysis of processes from the molecular to the cosmic scales. There are many more thermodynamic systems than the ones commonly met in mechanical engineering and thermodynamics applies to them all. In fact, some of the finest accomplishments of finite-time thermodynamics have been at the molecular level [13]. The idea of only one freely variable reservoir is irrelevant for a beam of molecules undergoing interactions with a buffer gas and a laser beam.

Are there good engineering grounds for insisting that one must count the irreversibilities in the combustion of the fossil fuels and the exergy thrown away with the exhaust gases? After all, both of these represent very significant exergy costs in most real power plants. In the analyses of these plants for engineering purposes I certainly agree that it is reasonable, nay even crucial, to count the irreversibility of the discarded exhaust. This is not the same as discounting calculations that do not count this irreversibility as "irrelevant and useless". This would discard the engineering study of solar and geothermal power plants not to mention devices such as James Senft's icewater powered heat engines. This is an unaffordably narrow view of engineering. Are we to be forced to count the fossil fuel burned in producing the ice for the icewater engine? Of what relevance is this for the *engineering* problem of how best to design an engine that is to be powered by the temperature difference between a glass of icewater and the atmosphere? The icewater in this engineering problem *should* be counted as a "freely variable" reservoir.

Bejan dismissed the geothermal power plant example by saying that "in the end the hot stream becomes a very expensive per-unit commodity, not a freely varying flow rate as assumed in ...". Let us therefore examine a possible economic basis to the idea of a single freely variable reservoir. Once we let prices become thermodynamic variables we enter the domain of what has been called thermoeconomics [1]. A careful examination then reveals that no reservoir is free. Pumping river water to cool process streams or building cooling towers is not free but has a very real price associated with amortizing the capital costs of the heat exchangers, pumps, etc.. Thus the atmosphere is not exactly freely varying either. Is it a useful approximation to take heat exchange with the atmosphere as free? Sometimes. In a more careful economic analysis, heat from each reservoir has a shadow price and these prices will be of both signs and none of them will equal zero.

3. Some results from finite time thermodynamics

In the domain of well posed problems there is a veritable plethora of possible optimizations and analyses by varying the system, the constraints, or the objective. This fact has brought some indignation from various editors flooded with papers working out these various and sundry cases. This argues all the more in favor of a physics which could serve to unify these sundry results. I now cite a few of the steps in the direction of such a physical theory.

One beautiful result in this direction is the theorem of Tsirlin and Rozonoer [2] concerning a process in which the objective and all the constraints can be written as time integrals over the process. Physically, this corresponds to a control process in which the objective and the constraints depend only on net effects. Their theorem says that in such a problem the optimal control uses at most a finite number of constant values [2].

A second important result is a folk theorem that Bejan attributes to Gouy and Stodola [14, 15] and was rediscovered several times by various authors [16] which guarantees that entropy production is always just the exergy loss divided by the atmospheric temperature; thus minimizing loss of exergy is always equivalent to minimizing entropy production. The atmosphere is certainly a unique heat bath in defining this constant of proportionality for us.

A similar result regarding the equivalence of minimum entropy production and maximum power also holds provided one specifies the initial and final states of all participating systems except the atmosphere and a work reservoir. Once one has committed to a certain change in the exergy of all the participating systems except one (note that any change in thermal energy of the atmosphere carries exergy zero), any uncaptured work is perforce released into the atmosphere and so maximizing power is equivalent to minimizing entropy production. If one includes the possibility of saving some of the exergy for later use, e.g., burn less fuel, use waste heat for cogeneration, etc., the final states can be allowed to vary and minimum entropy generation and maximum power become opposing objectives; minimum entropy production generally means opting for conservation while maximum power means opting for rapid comsumption. For example, in a heat engine working between two heat reservoirs with a given entropy excursion[2], $\int |ds|$, where s is the entropy of the working fluid, there is a range of interesting optima with extremes at maximum power and at minimum entropy production [6]. There is interesting new physics at either end and thermoeconomics in between.

For linear heat exchange, simple results abound. The minimum entropy production ΔS^u_{min} goes as the square of the entropy excursion of the working fluid, i.e., is given by

$$\Delta S^u_{\min} = \left(\int_0^\tau |ds| \right)^2 / \kappa\tau \qquad (3)$$

where κ is the conductance to the working fluid and τ is the cycle time [5]. The maximum power from a working fluid in a periodically changing environment $T^{ex}(t)$ is given by

[2] For a simple cycle, the entropy excursion of the working fluid is just twice the width of the cycle in a T,S diagram. See references [5].

$$P_{\max} = \kappa \operatorname{var}\left(\sqrt{T_{ex}(t)}\right), \qquad (4)$$

where var indicates the variance in time [7]. If the conductance to the working fluid can vary between the two heat exchange branches, the optimal allocation of area is inversely proportional to the square root of the conductivity [17].

These early results have been worked and reworked, extended and applied many times to many different systems [1-3, 18-20]. So far the early results have served most importantly as a paradigm for how to calculate and reason. As argued above, the reasoning involved is delicate. For building a physical theory of such processes, reworking and reformulation is a necessary step toward coming up with a useful and general formalism. Such reworking brings the proper mathematical structure to the surface and allows us to give all of these problems a synthesis within one framework. Such a synthesis is hinted at in [21] and is pursued further in my upcoming talk for ECOS 1998.

4. The Horse-Carrot process and related theorems

One particularly important and general problem concerns controlling a system to follow a prespecified sequence of states. This has been termed a horse-carrot process by analogy since it requires coaxing a system (the horse) to move toward equilibrium with a controlled sequence of baths (the carrots). Here the coupling between the system and its environment is the mode of irreversibility considered -- the environment with which the system interacts is assumed reversibly controllable. For the process in a (sufficiently large) constrained time, the optimal solution is to control the system so the rate of entropy production is constant [22, 23]. The resulting entropy production is bounded by

$$\Delta S^u \geq L^2 \varepsilon / \tau \qquad (5)$$

where L is the thermodynamic distance traversed in the state space of the system and ε is a mean relaxation time [24].

The theorem is perhaps more interesting for a staged process in which the system proceeds by a sequence of equilibrium stages. For this case, the horse-carrot inequality takes the form

$$\Delta S^u \geq L^2 / 2k \qquad (6)$$

where k is the number of stages. Furthermore these stages should be equally spaced in thermodynamic distance ΔL=L/k=constant [25].

The discrete theorem has been extended to steady flow processes including fractional distillation [26]. In this analysis, the irreversibility comes from the equilibration of the material that moves to the next tray with the material on that next tray, the latter acting as the bath. This result has very real implications for column design: *Distribute the heating so the temperature profile along the column is in steps of equal thermodynamic distance.* Economic use of the design requires a heat pump which can work efficiently between many temperature stages. I would put before the present audience the important mechanical engineering problem of designing and constructing such a heat pump.

5. Conclusions

The message I hope to have conveyed to this audience is that there is an important distinction between physics and engineering studies of simple thermodynamic models. Rather than hindering each others' efforts, the engineering and physics groups interested in these problems would do well to work together. The road is frought with potential misunderstandings which are the inevitable hallmarks of cross-disciplinary work. Nonetheless, making the effort to understand each other can have substantial rewards.

6. References

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