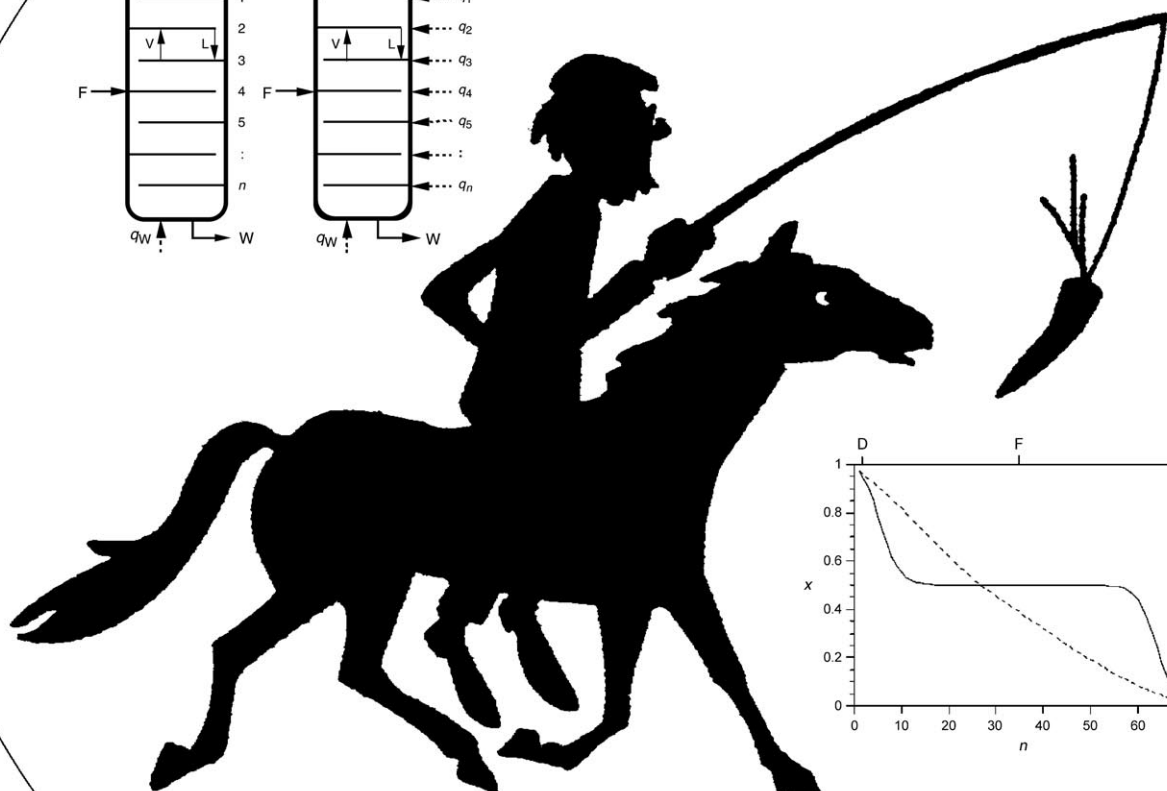
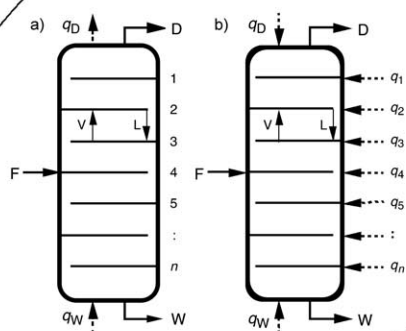


# Current Trends in Finite-Time Thermodynamics

Bjarne Andresen\*

## Keywords:

distillation · finite-time thermodynamics · heat engine · optimization · thermodynamics



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*The cornerstone of finite-time thermodynamics is all about the price of haste and how to minimize it. Reversible processes may be ultimately efficient, but they are unrealistically slow. In all situations—chemical, mechanical, economical—we pay extra to get the job done quickly. Finite-time thermodynamics can be used to develop methods to limit that extra expenditure, be it in energy, entropy production, money, or something entirely different. Finite-time thermodynamics also includes methods to calculate the optimal path or mode of operation to achieve this minimal expenditure. The concept is to place the system of interest in contact with a time-varying environment which will coax the system along the desired path, much like guiding a horse along by waving a carrot in front of it.*

## 1. Introduction

Finite-time thermodynamics is coming of age. A child of the 1973 oil crisis, it was conceived in 1975, and the first publication on this topic appeared in 1977.<sup>[1]</sup> To date, 597 papers have been published with “finite-time” in the title or keywords, and many more have appeared based on the same concept but without using the actual term. The subject has also made its way into textbooks.<sup>[2,3]</sup> The idea is really very simple. Reversible thermodynamics, with the Carnot efficiency as its most famous example, provides bounds on the performance of all thermal and chemical processes, but these may be achieved only when the processes are operating infinitely slowly. This is obviously unrealistic, so the pressing question is how much the performance must deteriorate so that the process is completed in a finite time: What is the price of haste? With this central question finite-time thermodynamics is clearly one version of irreversible thermodynamics.

The immediate inspiration for finite-time thermodynamics was the seminal paper by Curzon and Ahlborn<sup>[4]</sup> in which they showed that a Carnot engine with heat resistance to its reservoirs has a maximal power production, and at that maximum its thermal efficiency can be described by Equation (1).

$$\eta_{CA} = 1 - \sqrt{\frac{T_{low}}{T_{high}}} \quad (1)$$

This expression has three remarkable features: It is simple and generic; it is amazingly similar to the Carnot efficiency; and it is independent of the magnitude of the heat resistances. It turned out that this expression had been found twice earlier for similar systems and then forgotten.<sup>[5]</sup>

Most of the initial papers in finite-time thermodynamics analyzed heat engines and refrigerators with a number of different loss mechanisms, primarily located in their connections to the ambient, that is, endoreversible<sup>[6]</sup> machines. Because these were easy to analyze compared to for example, chemical reactions, a large body of papers on such endo-

## From the Contents

1. Introduction	2691
2. More Heat Engines and Refrigerators	2692
3. Thermodynamic Length	2693
4. Distillation	2694
5. Chemical Reactions	2695
6. Averaged Optimal Control	2696
7. Economics	2697
8. Mesoscopic Systems	2697
9. Quantum Systems	2699
10. Limits to Control	2699
11. Applications Inspired by Finite-Time Thermodynamics	2700
12. Inspiring Conferences	2700
13. Outlook	2700

reversible engines emerged to the point that some people thought that finite-time thermodynamics was only about endoreversible engines. That is not true. Finite-time thermodynamics covers all thermodynamic processes with the one added constraint, that they go to completion in a finite time. In recent years, studies have appeared in which chemical reactions and separation processes have been analyzed.<sup>[7–20]</sup>

Science and engineering to a large extent live in separate worlds with their own journals and conferences. It therefore took several years for finite-time thermodynamics to enter engineering circles; it was first picked up by Bejan in 1994<sup>[21]</sup> and subsequently redubbed “entropy generation minimization”. This is a most unfortunate name, because it limits the scope to just that, minimization of entropy generation, while its parent discipline, finite-time thermodynamics, covers irreversible thermodynamics much more broadly, considering all conceivable object functions. In the beginning, those were primarily maximizing power production and minimizing entropy production, but others have been introduced at times.<sup>[15, 20, 22]</sup>

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An important forerunner of finite-time thermodynamics in the quest for improving the efficiency of thermodynamic systems is found in availability/exergy/second-law analysis.<sup>[23,24]</sup> (A very nice review may be found in Ref. [25].) Typically, entropy production is minimized by varying specific system parameters (flows, transfer surfaces, temperatures, etc.) and not the entire process path. The method is still very much in practical use. While not providing the unrestricted optimal process path, exergy analysis is indeed a very important advance over older energy-flow analyses, and it was inspirational for the development of finite-time thermodynamics.

The choice of objective function is an important issue which clearly distinguishes finite-time thermodynamics from traditional reversible thermodynamics. In reversible thermodynamics, all objective functions are optimal at the same time. When the process is reversible, there are no losses and all descriptions are equally good. Not so in finite time. The optimal operation depends on our choice of maximizing the power production, maximizing the efficiency, minimizing the entropy production, etc. This is well known from driving a car where you adopt different strategies depending on whether you want to reach your goal as quickly as possible, whether you want to conserve fuel, or whether you want to make your passenger as comfortable as possible (minimum acceleration). Surprisingly, some authors have argued that the objective for example for a heat engine doesn't matter because any energy that is not extracted from the source ends up in the environment anyway. This is a case of an imprecisely defined distinction between the system and the environment.<sup>[26]</sup> As always in science, one must be very careful in defining the system under consideration.

In an analysis of an imaginary power plant optimized for profit, buying fuel, and selling electricity,<sup>[27]</sup> it was found that the optimal operation was a certain combination of maximum power and minimum entropy production, a balance which depends on the relative prices of the commodities. Subsequently a so-called "ecological function",  $E' = w - T_{\text{low}} \sigma$ , was suggested<sup>[22]</sup> as the "proper" objective for power-producing equipment. Like the power plant example, this is also a linear combination of the power  $w$  and entropy  $\sigma$  produced. There are an infinite number of such linear combinations, so unless there is a physical reason for picking a particular one, the choice becomes just a matter of taste. No single objective is more correct than any other. However, all relevant optima are in the range between minimum entropy production (as close

to reversible as possible) and maximum power (as much output as possible).<sup>[27]</sup> Those two, by contrast, are unique and extreme.

Irreversible thermodynamics seems to have fractionated into many devotions which compete for attention. I mentioned finite-time thermodynamics and entropy generation minimization above. The Brussels school and Onsager's reciprocal relations have been important players much longer. And then we have extended irreversible thermodynamics dealing with very fast reactions, field formulations for continuously distributed systems, evolutionary thermodynamics, and GPITT<sup>[28]</sup> just to name a few. Muschik very appropriately entitles one of his reviews of the selection "Why so many "schools" of thermodynamics?"<sup>[29]</sup>

Starting with Carnot, the emphasis of thermodynamics was on processes, in his case the process of converting heat into mechanical power, and on developing performance bounds for such processes. With Clausius and Gibbs the emphasis moved to state functions in equilibrium situations and thus less emphasis on the transformations. Now the focus is moving back to processes, and we are calculating bounds on the performance of irreversible processes as well as the complete paths which achieve these bounds.

A few reviews of finite-time thermodynamics have appeared over the years.<sup>[30,31]</sup> This review will therefore primarily cover developments from the past decade and focus on the methods I consider the most promising. It will contain a number of sections on quite disparate applications of finite-time thermodynamics—some operational, some more fundamental, and some in more detail than others—all in an effort to cover the topic as broadly as possible within the given format of a review. Thus each section is more or less self-contained.

## 2. More Heat Engines and Refrigerators

In the early years of finite-time thermodynamics, several simple engine and refrigerator models were analyzed, simply to explore the possibilities of the new methods. These systems were optimized for maximum power production, maximum efficiency, and minimum entropy production. They typically consisted of named engines (Carnot, Stirling, Otto, Diesel, etc.) connected to their reservoirs through simple heat-transfer mechanisms. These could follow the Newtonian law, radiation law, Dulong–Petit law, or similar simple power laws. Along the way important insight was gained about the qualitative difference made by the presence of a rate-independent loss and about the great similarity of the different transfer laws. However, nobody would base the design of a real engine or refrigerator on such simple models. For real designs much more elaborate models, developed hand in hand with experiments, are needed. Such a line of research was followed by Gordon and Ng,<sup>[32]</sup> culminating in a book on designing and maintaining coolers.<sup>[33]</sup>

A couple of very prolific groups are continuing the old tradition and are analyzing a series of named cycles in connection with a variety of heat-transfer power laws. These machines are run as engines as well as refrigerators, with and



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without a summary internal dissipation term, and with a fixed total heat conductance available for distribution between the hot and cold sides.<sup>[34]</sup> The tradeoff between power and efficiency is essentially the same for all. A certain novelty is embodied in a study using a complex number for the heat conductance, although we still need to learn what the imaginary parts of the conductance and the heat transferred really mean.<sup>[35]</sup>

Several other objective functions for the optimization of heat engines and refrigerators have been proposed. An “ecological function” was mentioned above. A related “ecological coefficient of performance”, defined as the ratio of the power production or cooling load to the rate of availability loss (or entropy generation rate),<sup>[36]</sup> has considerable intuitive merit; of course on the scale of haste this function is still situated between maximum power and minimum entropy production. Compactness is favored by the objective function “power density”, that is, power produced relative to maximum volume of the cycle.<sup>[37]</sup> Similarly, “power for the buck” is in focus with the thermoeconomic (see Section 7) criterion “cost density”.<sup>[38,39]</sup>

Solid insight into distributed systems was gained early on when Gordon and Zarmi treated the atmosphere as a heat engine driven by temperature gradients set up by the solar radiation in an attempt to find limits on the amount of energy that can be extracted from the wind.<sup>[40]</sup> Soon thereafter De Vos applied more general finite-time thermodynamic methods to the same problem.<sup>[41]</sup>

### 3. Thermodynamic Length

Thermodynamic length is one of the most important concepts introduced by finite-time thermodynamics. The concept starts out quite abstract but it delivers realistic bounds on performance [Eqs. (3) and (4)] and the paths in configuration space which achieve them. These bounds are much stronger and more telling than the traditional bounds of thermodynamics,  $\Delta A \geq 0$  and  $\Delta S \geq 0$ .

As far back as 1975 Weinhold<sup>[42]</sup> defined a thermodynamic metric at a point as  $\mathbf{M}_U = d^2U/d\mathbf{X}d\mathbf{X}$ , where  $U$  is the internal energy of the system and  $\mathbf{X}$  are all the other extensive variables (entropy, volume, particle number, etc.). Soon after, a thermodynamic length with this metric was calculated along a given path (e.g. adiabat or isotherm)<sup>[43]</sup> according to the standard expression in Equation (2),

$$L = \int_{\text{specified path}} \sqrt{d\mathbf{X} \mathbf{M} d\mathbf{X}} \quad (2)$$

but it took quite a bit longer to interpret this length. Salamon and Berry<sup>[44]</sup> found that the square of this length  $L$ , combined with an intrinsic relaxation time  $\varepsilon$  and the duration of the process  $\tau$ , provides a lower bound to the dissipation (lost exergy or availability)  $\Delta A$  in this process [Eq. (3)].

$$\Delta A \geq \frac{L^2 \varepsilon}{\tau} \quad (3)$$

Equality is achieved when the thermodynamic speed  $dL/dt$  is constant throughout the process. A similar expression was derived for the entropy metric  $\mathbf{M}_S = -d^2S/d\mathbf{X}d\mathbf{X}$ , bounding the entropy production in the process.<sup>[45]</sup> Even systems described statistically through their state probabilities can be treated this way<sup>[46]</sup> using the very simple diagonal metric  $\mathbf{M}_S = -[1/p_i]$ . For processes proceeding in steps from one equilibrium state to another, the bound of the dissipation is described by Equation (4), where  $N$  is the number of steps in the process.<sup>[47]</sup> Here equality is achieved when all steps have the same length,  $L/N$ .

$$\Delta S \geq \frac{L^2}{2N} \quad (4)$$

The starting point for calculating a thermodynamic metric is always the full equation of state for the system in question. For a simple ideal gas with just two degrees of freedom the equation of state would be Equation (5) in the energy picture or Equation (6) in the entropy picture ( $a$  and  $b$  are constants). Those give rise to the two metrics in Equations (7) and (8). As is apparent, these metrics are made up of quite normal thermodynamic quantities. The entropy metric is even conveniently diagonal.

$$U(S, V) = b e^{S/C_v} V^{-k/C_v} \quad (5)$$

$$S(U, V) = C_v \ln U + k \ln V + a \quad (6)$$

$$\mathbf{M}_U = \begin{pmatrix} \frac{\partial^2 U}{\partial S^2} & \frac{\partial^2 U}{\partial S \partial V} \\ \frac{\partial^2 U}{\partial V \partial S} & \frac{\partial^2 U}{\partial V^2} \end{pmatrix} = \begin{pmatrix} \frac{T}{C_v} & -\frac{P}{C_v} \\ -\frac{P}{C_v} & \left(1 + \frac{k}{C_v}\right) \frac{P}{V} \end{pmatrix} \quad (7)$$

$$\mathbf{M}_S = - \begin{pmatrix} \frac{\partial^2 S}{\partial U^2} & \frac{\partial^2 S}{\partial U \partial V} \\ \frac{\partial^2 S}{\partial V \partial U} & \frac{\partial^2 S}{\partial V^2} \end{pmatrix} = \begin{pmatrix} \frac{C_v}{U^2} & 0 \\ 0 & \frac{k}{V^2} \end{pmatrix} \quad (8)$$

If we introduce also quantities of material,  $n_i$ , so that we may describe chemical reactions, the equation of state becomes considerably more complicated [Eq. (9)].<sup>[48]</sup>

$$U(S, V, \{n_i\}) = b e^{\frac{S}{N C_v}} N \prod_i \left[ \left( \frac{n_i}{V} \right)^{\frac{k}{C_v}} \frac{1}{m_i} \right]^{\frac{N}{m_i}} \quad (9)$$

Here  $N$  is the total amount of material,  $N = \sum_i n_i$ , and  $m_i$  is the mass of particle type  $i$ . This is the unifying form of the better known partial equations of state,  $PV = NRT$ ,  $U = C_v T$ , and  $\mu_i = kT [\ln(n_i/V) - (C_v/k) \ln(m_i kT) + a]$ , each one a projection of Equation (9) keeping certain parameters fixed. However, the length calculations require the full form. For a mixture of ideal gases we then find the full metric [Eq. (10)], which will be used in Sections 4 and 5 below for the optimization of distillations and chemical reactions. The last row and column are really a condensed notation for all the participating particles  $i$  or  $j$ , and  $\delta_{ij}$  is the Kronecker delta function, meaning that that term appears only in the diagonal of the metric.



$$\mathbf{M}_U = \begin{pmatrix} \frac{\partial^2 U}{\partial S^2} & \frac{\partial^2 U}{\partial S \partial V} & \frac{\partial^2 U}{\partial S \partial n_i} \\ \frac{\partial^2 U}{\partial V \partial S} & \frac{\partial^2 U}{\partial V^2} & \frac{\partial^2 U}{\partial V \partial n_i} \\ \frac{\partial^2 U}{\partial n_i \partial S} & \frac{\partial^2 U}{\partial n_i \partial V} & \frac{\partial^2 U}{\partial n_i \partial n_j} \end{pmatrix} \quad (10)$$

$$= \begin{pmatrix} \frac{T}{NC_v} & -\frac{P}{NC_v} & \frac{\mu_i}{NC_v} - \frac{T}{N} \\ -\frac{P}{NC_v} & \left(1 + \frac{k}{C_v}\right) \frac{P}{V} & -\frac{k}{C_v} \frac{\mu_i}{V} \\ \frac{\mu_i}{NC_v} - \frac{T}{N} & -\frac{k}{C_v} \frac{\mu_i}{V} & \mu_i \left(\frac{\mu_i}{U} - \frac{1}{N}\right) - \frac{1}{N} \mu_j + \frac{1}{N^2} U + \frac{RT}{N_j} \delta_{ij} \end{pmatrix}$$

Immediate applications of this geometry to distillation and sequential chemical reactions are described in the next two sections. The optimization method has also found its way into economics (Section 7), mesoscopic systems (Section 8), and information coding theory.<sup>[49]</sup>

Further geometrizations of thermodynamics with different definitions have proven useful in many contexts like black holes,<sup>[50]</sup> material behavior,<sup>[51]</sup> fluctuations,<sup>[52]</sup> and basic thermodynamic theory<sup>[53]</sup> as well as those based on different definitions of the geometry<sup>[54]</sup> just to point to a few.

#### 4. Distillation

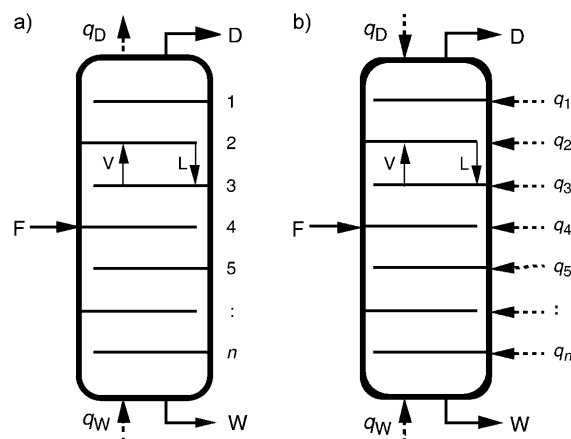
As a first example of geometric optimization, let us look at trayed distillation. It is a unit process in chemical engineering in serious need of improvement. It is used industrially on a grand scale, for example, in oil refineries, at great energy expense, and at the same time it is thermodynamically quite inefficient. Even under the very best of conditions, for the separation of an ideal 50:50 mixture into its two components, using an ideal distillation column of infinite length, the thermodynamic efficiency cannot exceed 69%. In real life it is much lower. The main problem lies in the construction of the distillation column itself: All heat is added at the bottom of the column and all heat is withdrawn at the top; thus the heat is degraded over the full temperature span of the column even though the largest heat demand is only in the middle around the feed point. Improvement can only be achieved with additional control of the process, requiring in turn more freedom in its construction. The obvious extension is to allow heat to be added and withdrawn on any tray in the column as the optimization may require. The concept of such diabatic distillation columns is not new (see e.g. Refs. [24,55]); the novelty is calculating the optimal heat distribution, and this is where thermodynamic length comes in.

A trayed distillation column is exactly a stepwise process where liquid and gas are in equilibrium on the  $N$  trays, whereas the space between the trays is beyond our control. Thus we can calculate the thermodynamic distance  $L$  from the top to the bottom of this column from the specified purity of the light and the heavy products. As stated in the previous section, the least dissipative path will be the one where all the steps are of the same thermodynamic length,  $L/N$ . The final component is to calculate backwards from thermodynamic length to, for example, the temperature of the mixture on each tray.

On each tray of the distillation column the energy of the mixture is a function of a large number of extensive variables:

volume, entropy, amount of light component, and amount of heavy component, all for the liquid as well as the vapor phase, that is, 8 variables, making the metric matrix from Equation (10)  $8 \times 8$ . Fortunately, a number of conservation equations can reduce that number dramatically. For example, we have mass conservation of both components, the column typically operates under constant pressure, and we have equilibrium between the gas and liquid phases on the trays. All combined, these constraints reduce the number of degrees of freedom to one, which for simplicity we may take to be the temperature on each tray.<sup>[11]</sup>

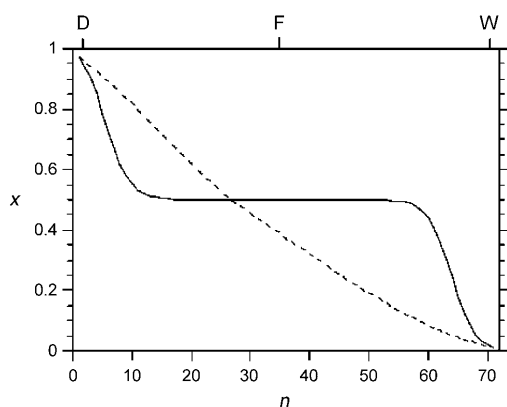
The example chosen to illustrate optimal distillation is the separation of an ideal 50:50 mixture of benzene and toluene into almost pure components (different purities were considered) in a 72-tray column. This diabatic column is compared with a conventional adiabatic distillation column in Figure 1.



**Figure 1.** a) Sketch of a conventional adiabatic distillation column with flowrates  $F$ ,  $D$ , and  $W$  for the feed, distillate, and waste, respectively, heating and cooling rates  $q_w$  and  $q_D$ , and tray number  $n$ . b) Sketch of a diabatic distillation column with heating or cooling on all  $n$  trays.

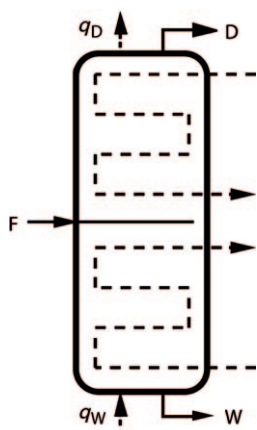
The absolutely best operation, just concentrating on the distillation process itself without worrying about how heat gets into and out of the fluid, reduces the exergy demand of this separation by a factor of 4 compared to the usual adiabatic operation.<sup>[11]</sup> Actually, if one allows the number of trays in the column to go to infinity, the thermal separation efficiency approaches 1, that is, reversible separation. The physical reason for this is that while energy and mass conservation between trays force large temperature steps around the feed point for a conventional column, the freedom to adjust the tray temperatures individually in the optimal diabatic column can split the burden of separation evenly among all trays, making it approach zero as the number of trays becomes infinite, as illustrated in Figure 2.

Subsequent papers introduced more reality in the optimization, first considering the losses in the heat transfer process in and out of the fluid.<sup>[12]</sup> The thermodynamic efficiency of course is reduced a bit when a new dissipation is introduced, but not by much, and the overall conclusion is the same: Distribute the heat load uniformly. Now, technically



**Figure 2.** The liquid composition profile  $x$  (mole fraction of light component) as a function of tray number, counted from the condenser, for conventional (—) and equal-thermodynamic-distance (-----) separation of an ideal benzene–toluene system. The separation effort is almost equally distributed among the trays in the latter setup.

it is not very convenient to have to pierce the distillation column at many locations, and it may be difficult to obtain heating and cooling sources at all those specified temperatures. The next idea therefore is to organize the heat exchangers such that the trays are daisy-chained from the top to the feed point and from the bottom to the feed point<sup>[10]</sup> as shown in Figure 3. In this way only four additional piercings of



**Figure 3.** Diabatic distillation column with sequential heat exchange (-----), thus requiring only one hot and one cold source.

the shell are required compared to the traditional column, and only one hot heat source and one cold heat sink are required. Obviously, this is not quite optimal, but the entropy reduction not obtained is only 12 %.

An argument arose about whether constant thermodynamic speed or constant thermodynamic force, calculated according to Onsager,<sup>[56]</sup> is better. While fewer assumptions are involved in derivation of the thermodynamic geometry bounds, in the end it was settled that both solutions reproduce the exact optimal solution for temperature-independent heat parameters (e.g. heat capacity). If the parameters vary, the constant thermodynamic speed calculation follows the exact

solution up to the order of  $N^{-2}$  in all cases with a fair number of trays  $N$ , whereas the constant thermodynamic force principle deviates further.<sup>[8]</sup> However, for most practical purposes at low to moderate speeds both methods are close to the true optimum.<sup>[57]</sup>

Other researchers have used more conventional entropy-minimization techniques to optimize diabatic distillation.<sup>[9,14,58–60]</sup>

## 5. Chemical Reactions

The first applications of finite-time thermodynamics beyond heat engines appeared in 1980<sup>[19]</sup> with emphasis on the rate of product formation in a reaction flow tube. A statistical mechanical version came in 1996.<sup>[17]</sup> Mironova applied optimal control to chemical reactions.<sup>[18,61,62]</sup>

The optimal temperature path for the industrially important reaction of ammonia synthesis,  $N_2 + 3 H_2 \rightleftharpoons 2 NH_3$ , was established using a Temkin–Pyzhev-type rate equation.<sup>[63]</sup> This optimal path runs counter to the standard temperature path in commercial ammonia reactors, indicating that the efficiency of a given amount of catalyst can be improved considerably. It is interesting to note that the optimal and equilibrium paths differ by an almost constant temperature of 35 K, very much resembling the optimal paths derived using constant thermodynamic speed in Section 3. Subsequently the generic reaction  $n A \rightleftharpoons m B$  was exhaustively analyzed for all possible stoichiometric coefficients  $n$  and  $m$  and activation barriers.<sup>[64]</sup> The optimal paths for maximum production of  $B$  from  $A$  are composed of explicit boundary branches as well as interior branches depending on these parameters.

The more delicate problem of finding the maximal production of the intermediate component  $B$  at a particular time for the consecutive reaction  $A \rightleftharpoons B \rightleftharpoons C$  with Arrhenius rate constants was solved in detail only quite a bit later.<sup>[15]</sup> This question actually goes back to the 1950s, but the tools were not available for a full solution at that time. In Ref. [15] the power of optimal control theory, alternating between state and co-state variables in the optimization, succeeded in finding the optimal time sequence of the reactor temperature which will maximize the intermediate product  $B$ . It is interesting to note that for certain combinations of activation energies for the four reactions the permitted duration may actually be too long; that is, the product disappears again unless the temperature is decreased to zero, thus halting all reaction and just wasting time. In such situations there are a multitude of possible temperature paths with identical results. The excess time may be wasted anywhere over the entire interval and be broken up into any number of smaller pieces. In 2009 Chen et al. applied this analysis to the slightly generalized reaction scheme  $x A \rightleftharpoons y B \rightleftharpoons z C$ .<sup>[16]</sup>

Another approach, devised by De Vos,<sup>[65]</sup> is to set up a chemical framework analogous to the endoreversible heat engine; that is, two chemical reservoirs are connected through a substance at two different chemical potentials (concentrations) to a “chemical converter” through transfer resistances, for example, diffusion. In the same vein, the objective is to maximize the mechanical power output like in a heat engine.

Realizations could be an engine powered by a difference in salt concentration between, say, a river and the ocean, making use of osmosis. The pump equivalent could be the opposite, making fresh water from seawater. A large number of papers were subsequently published based on this chemical analogy, describing all kinds of two-, three-, and four-reservoir systems with and without leaks as if they were heat engines and pumps.<sup>[66,67]</sup> Clearly, the performance characteristics of these chemical systems are very similar to that of their heat equivalents.

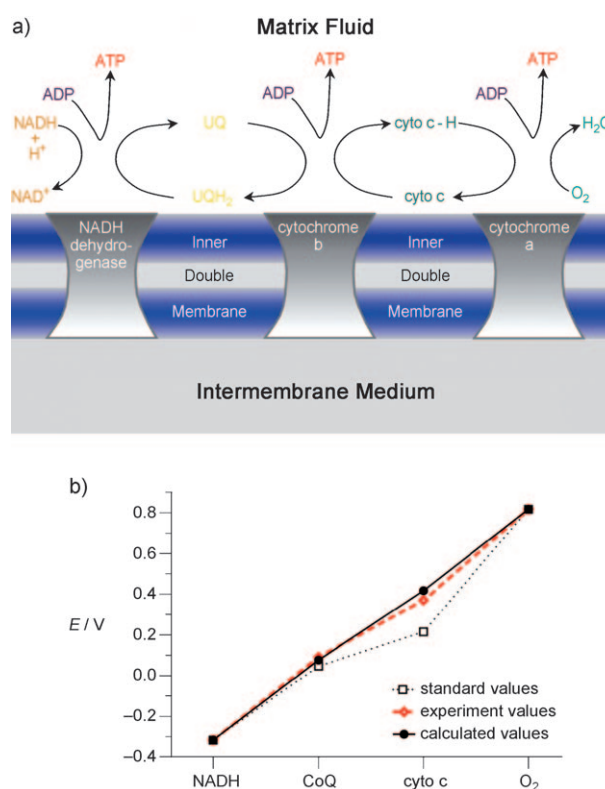
An unconventional “chemical reaction” is found in solar energy capture, be it in a semiconductor solar cell or in the chlorophyll of plants. In either case, one of the reactants is a photon, and in the subsequent reaction chain electrons are passed from one substance to another. The thermodynamics of the process is right out of a textbook,<sup>[68]</sup> and all the results of finite-time thermodynamics apply.<sup>[38,69]</sup>

As our second example of thermodynamic geometric optimization let me mention the cytochrome chain which recently has been optimized for the maximum conversion of chemical energy from hydrogen into the carrier ATP.<sup>[20]</sup> This is the primary energy source in mitochondria where essentially all hydrogen from the food of the cell passes through this three-step reaction to combine with oxygen to form water (Figure 4a). The technical equivalent is a fuel cell where the reaction  $\text{H}_2 + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{H}_2\text{O}$  proceeds in a single chemical step while producing electrical power. The analysis of the cytochrome chain, treated as a step process, proceeds as described previously for distillation; that is, the full equation of state is set up, the metric is calculated, and the dimensionality of the problem is reduced using all available constraints. Again the problem reduces to a single degree of freedom which most conveniently is taken to be the electrochemical potential at points along the path. This yields the optimal path shown in Figure 4b which is very close to the actual path of the cytochrome chain inside a real mitochondrion. Thus mitochondria are nicely optimized for efficient power production.

The take-home lesson is that finite-time thermodynamics optimization using thermodynamic length is indeed a good description of real systems. Next, we can learn from this chemical optimization that the natural system achieves its high efficiency without a fragile membrane to separate reactants but by relying solely on the chemical specificity of the enzymes. Another advantage of this feature is that the reactions in mitochondria can take place in its entire volume, whereas a surface-catalyzed reaction is only two-dimensional. Once again there is room for inspiration from nature.

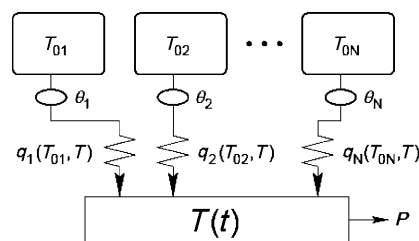
## 6. Averaged Optimal Control

One of the more powerful optimization methods introduced into thermodynamics is averaged optimal control. Traditional optimal control theory, used for example to find the optimal paths for the chemical reaction above and for the endoreversible heat cycle,<sup>[71]</sup> has been described<sup>[72]</sup> and is discussed in the first volumes of *Advances in Control Systems*.<sup>[73]</sup> Rubín also provides the essential background.<sup>[71]</sup> The traditional theory requires specification of the behavior



**Figure 4.** a) Illustration of the cytochrome chain. Three protein complexes imbedded in the inner double membrane of the mitochondrion act as catalysts for the redox reactions. Electrons are transferred in successive steps through ubiquinone and cytochrome c (cyto c) before the terminal product, water, is generated. b) The standard, calculated (optimized), and observed<sup>[70]</sup> values of the electrochemical potential of each electron-transfer unit in the cytochrome chain. The three redox steps are almost equal.

of the system at every point in time along the cycle. Averaged optimal control<sup>[74,75]</sup> relaxes that requirement and is satisfied fixing these quantities on average for the cycle as a whole. An example would be a system in contact with several reservoirs of different intensities at the same time. One very strong mathematical conclusion for such systems is that the optimal path consists of piecewise constant control variables where the control can take on at most  $n$  different values, where  $n$  is the number of constraints plus one, usually a very small number. A nice example is a heat engine coupled to a number of different temperature reservoirs, some hot, some tempered, and some cold<sup>[76,77]</sup> as shown in Figure 5. How should

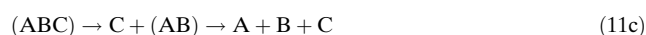
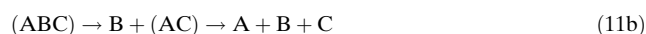
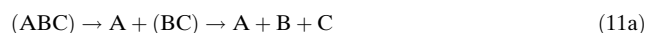


**Figure 5.** Model of an endoreversible heat engine connected to several heat reservoirs  $T_0$  and producing power  $P$ .

the engine make use of its selection of reservoirs in order to produce the most power? It turns out that for some combinations of temperatures and heat conductances it should only use the hottest and the coldest reservoirs, never touching the tempered ones even though there might be a temperature gradient to be captured there. The same surprising conclusion of course results if this thermal system is replaced by a chemical potential system.<sup>[67]</sup>

The method of averaged optimal control has been applied by Tsirlin and his group to a number of different optimizations, primarily in thermodynamics<sup>[14, 18, 59, 62, 75, 77–80]</sup> and economics.<sup>[79–83]</sup> In work related to Section 4, they applied the method to a distillation column, treating the throughput and the heat exchanges at different temperatures in an average way while minimizing the heat requirement of the column.<sup>[84]</sup>

More recently averaged optimal control was applied to the issue of how most efficiently to separate a multicomponent mixture by binary steps. For example, for three components A, B, and C, which sequence described in Equation (11 a–c) should be used?



The result obviously depends on the relative volatilities (for distillation) or permeabilities (for membranes) of the substances as well as their relative abundances in the mixture, but when these parameters are given, the optimized process emerges without explicit integration through all the stages of the separation process.<sup>[60, 85]</sup>

## 7. Economics

Next, let us look at the influence of the concepts of finite-time thermodynamic outside the traditional realm of macroscopic thermodynamics. It was realized quite early that the approach and the methods of finite-time thermodynamics are also applicable in economic theory<sup>[86–88]</sup> in two distinct ways. In the first instance, the ideas of finite-time thermodynamics were directly transplanted to economics, simply by changing the definition of the variables, such that the bounds on thermodynamic losses became bounds on economic losses. The case studied was the market situation where sellers and buyers are not equally up to date on the market conditions. This results in a loss, a foregone earning which the buyers could have had if they had possessed the full information, like lost work in an irreversible process. This time delay of information is akin to the relaxation time in a thermodynamic process, and prices in the market are like temperatures in thermodynamics. With this analogy, dissipation (foregone earning) is limited from below by the same formula as in Equation (3) for thermodynamics, just with parameters taken from the economic universe rather than the thermodynamic one [Eq. (12)].<sup>[87]</sup>

$$\text{foregone earning} \geq \frac{L^2}{\tau} \quad (12)$$

Now  $\tau$  is the duration of the trade. For the Cobb–Douglas utility function,<sup>[87]</sup>  $U(x,y) = x^a y^b$ , for example, the geometry is a spiral and thus flat in the corresponding circular coordinates  $(r, \theta)$  with the length between points  $(x_1, y_1)$  and  $(x_2, y_2)$  given by Equation (13).

$$L((x_1, y_1), (x_2, y_2)) = \sqrt{(x_2 - x_1)^2 + (y_2 - y_1)^2} \quad \text{if } |\theta_2 - \theta_1| \leq \pi$$

$$L((x_1, y_1), (x_2, y_2)) = \sqrt{x_1^2 + y_1^2} + \sqrt{x_2^2 + y_2^2} \quad \text{if } |\theta_2 - \theta_1| > \pi \quad (13)$$

A similar analogy between endoreversible thermodynamics and economics, but without the thermodynamic geometry, was also investigated by De Vos using a formalism identical to a thermal engine and to a chemical engine.<sup>[89]</sup> Related to this extrapolation to economic thinking, but still within the physical world, is the economic optimization of a heat engine, that is, maximizing the profit while selling the power (electricity) and buying the heat (coal).<sup>[27, 38]</sup>

Tsirlin and his group have also recognized this systemic similarity between thermodynamics and economics. They have reviewed this one-to-one relationship and in particular defined irreversibility and temperature in economic terms.<sup>[85]</sup> Elsewhere they have applied their powerful method of averaged optimal control to find, for example, the optimal time sequence of events in a market and the optimal distribution of intermediate traders.<sup>[79, 81]</sup>

As a second instance of contact between thermodynamics and economics, thermodynamic constraints may be introduced into traditional economic analysis. The simplest form is to recognize that the efficiency of all processes is reduced as speed of operation increases. Take a production function  $Q(E, L)$  of two substitutable input factors  $E$  and  $L$  which we may think of as energy and labor. In this simple universe, the relative price of  $E$  and  $L$  is the slope of the curve of trade-off between  $E$  and  $L$  for fixed production, a so-called isoquant. Now finite-time thermodynamics tells us that higher rates of production incur higher energy demands which translate the isoquants to still higher energy consumption as production is increased. This has an influence on the relative price: The importance (price) of energy goes up relative to that of labor in a predictable way.<sup>[88]</sup> More recently arguments from finite-time thermodynamic have been applied to improve economic assumptions.<sup>[90]</sup>

A variant of this way of thinking is the foundation of the field of thermoeconomics which has become very popular in engineering. Even though concepts and optimizations from finite-time thermodynamics are often used, this extensive area deserves a review of its own. A number of papers which explicitly acknowledge the connection to finite-time thermodynamics may be found in Ref. [91].

## 8. Mesoscopic Systems

Recently finite-time thermodynamics has made its entry into the mesoscopic world, dealing with systems that are neither classically macroscopic nor single particles. This domain poses conceptual as well as practical problems. Traditional thermodynamics basically assumes continuous



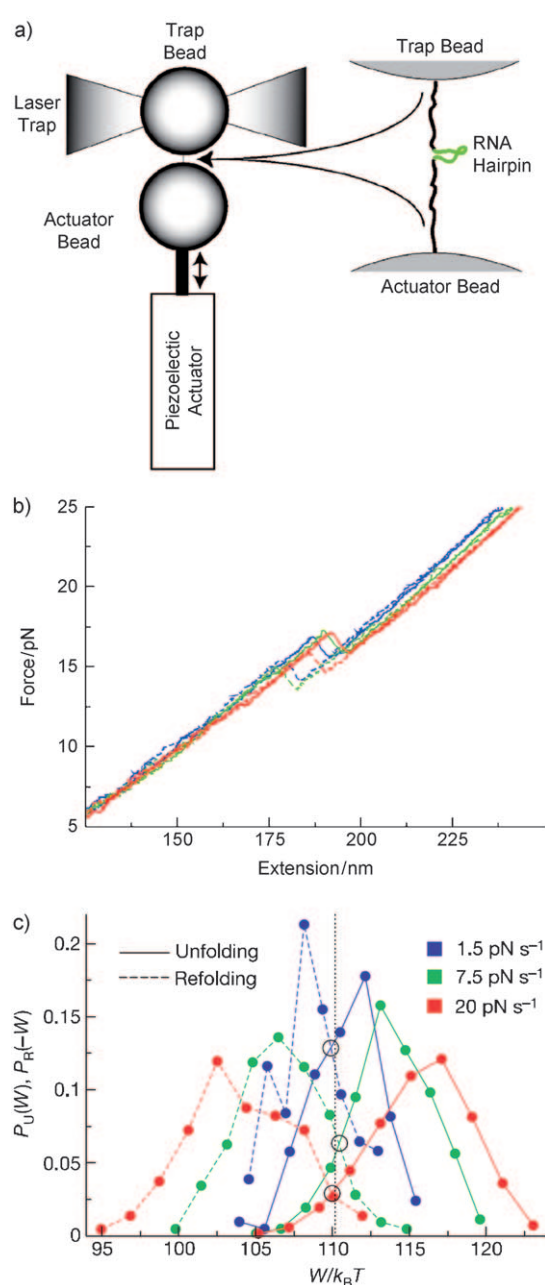


behavior of all variables. That means that they should be well defined at all times and at all points in space. For small systems this becomes a problem owing to natural fluctuations. A wonderful illustration of this random component of thermodynamic variables is the experiment by Evans et al.,<sup>[92]</sup> in which they repeatedly measured the entropy production of a single colloidal particle trapped in flowing water. Classically, of course, this entropy production must be positive at all times, but the experiment showed a Gaussian distribution of entropy productions with a tail extending into the negative range; that is, in a few of the experiments the particle actually lost entropy. Clearly, such a tail is not a violation of the second law as long as the mean is nicely positive, but it demonstrates that the mesoscopic world is different from the macroscopic one. Such size effects are of utmost importance for the miniaturization of, for example, electronics and will increase the relative energy requirements of very small components.

Nonetheless, most concepts and procedures from macroscopic thermodynamics also work in the mesoscopic regime, including finite-time effects. One such system that has been investigated extensively is the mechanical work associated with the untwisting and twisting of an RNA or DNA hairpin.<sup>[93–96]</sup> Hydrogen bonds make most RNA stretches twist up into segments of double-stranded structure for purely energetic reasons. 45 years ago it was standard to test the dynamics of this type of macromolecule by melting and recombining DNA double strands, that is, changing the equilibrium through the entropic component. These days, experiments have become much more sophisticated, and it is possible to grab the ends of a single molecule using optical tweezers (see Figure 6a). Thus the stretching force and the extension can be measured continuously during repeated untwisting and twisting of the same molecule. Some typical results are shown in Figure 6b.<sup>[94,95]</sup> Many experimental runs are required owing to natural fluctuations, but the trend is clear: Untwisting and twisting proceed symmetrically except that there is a difference in the mechanical work. Less work is recovered in the twisting than was expended in the untwisting, and this discrepancy increases with the rate of the reaction (Figure 6c). This finite-time effect is in nice agreement with the macroscopic finite-time thermodynamics bound of Equation (3).

Membranes are another class of mesoscopic systems of interest for finite-time thermodynamics. In particular Rubi and Bedeaux have made great strides toward understanding the detailed processes involved in transport through membranes and onto and from reactive surfaces. They find that substantial over voltages may build up next to the surface, that large amounts of water may be transported across the membrane along with the ion in question, and that the temperature (very) locally may be distinctly different from that of the bulk.<sup>[97]</sup> Most of their work is based on Onsager's reciprocity relations.

In principle, thermodynamic quantities are defined in a situation of local equilibrium. This leads to two problems when these quantities are needed in finite-time thermodynamics. The first one is that a finite-time thermodynamics system is obviously not in equilibrium, or it wouldn't be a



**Figure 6.** a) Experimental setup for folding and unfolding an RNA hairpin. A single RNA molecule is attached to two beads by means of linkers. One bead is captured in an optical laser trap that can measure the applied force on the bead. The other bead is attached to a piezoelectric actuator used to unfold and refold the hairpin (from Ref. [96]). b) Typical force–extension curves for the unfolding (—) and folding (----) of a RNA hairpin 20 base pairs in length. The area below the force–extension curve is equal to the mechanical work done on the RNA hairpin. Thus the enclosed areas are the hysteresis of the unfolding–folding cycles (from Ref. [96]). c) Work distributions for RNA unfolding (—) and refolding (----) at three pulling rates. The probability (ordinate) of a given work expenditure (abscissa) is recorded for a large number of experimental trials at these three different speeds. Unfolding and refolding distributions at the different speeds show a common crossing around  $\Delta G = 110.3 k_B T$ , indicating the reversible energy of folding. Unfolding–refolding asymmetry constitutes hysteresis (from Ref. [94]).

finite-time process. Usually this is sidestepped by the argument of a Taylor series expansion of the quantities from their equilibrium value to the “close by” non-equilibrium state. This is the case, for example, in the derivation of the dissipation bounds based on thermodynamic length mentioned earlier (Section 3).<sup>[44]</sup> Only the first nonvanishing term is retained. It is possible to include still another term in the expansion,<sup>[98]</sup> but then calculations become complicated.

The second problem is that non-equilibrium quantities generally are much more difficult to measure than equilibrium ones precisely because they are rate dependent. One way around this was suggested by Jarzynski<sup>[99,100]</sup> and involves ensemble averages for the small system [Eq. (14)].

$$\langle e^{-\beta W} \rangle = e^{-\beta \Delta F} \quad (14)$$

Here  $W$  is the work performed on the system and  $\Delta F$  is the change of Helmholtz free energy for the process, an equilibrium quantity. This equality is to be compared with the usual inequality  $\langle W \rangle \geq \Delta F$ . Thus on the one hand the Jarzynski equality has the power of being an equality, on the other it holds only on average. Any particular system may require more or less work, akin to the Evans experiment<sup>[92]</sup> mentioned above. The implications of this important relation have been extensively studied, in particular its relation to the second law of thermodynamics.<sup>[101]</sup> Jarzynski in a tutorial fashion has made the connection between this equality and the classical controlled stretching of a rubber band.<sup>[100]</sup> A very close link to the first interpretation of thermodynamic length<sup>[44]</sup> through the dissipation and lag in irreversible processes appeared just a few months ago.<sup>[102]</sup> Also Van den Broeck<sup>[103]</sup> has contributed important interpretations of thermodynamic length using the Jarzynski equality.

Crooks has elaborated on the interpretation of thermodynamic length far from equilibrium, relating it to equilibrium fluctuations<sup>[104,105]</sup> and to ensembles of paths.<sup>[106]</sup> The relationship between the thermodynamic length [Eq. (15)] and dissipation [Eq. (16)], where  $\mathbf{M}$  is the metric Equation (10) and  $\mathbf{X}$  are all the extensive variables of the system, appears through the general inequality in Equation (17).

$$L = \int_{\text{initial}}^{\text{final}} \sqrt{\mathbf{X} \mathbf{M} \mathbf{X}} ds \quad (15)$$

$$I = \int_{\text{initial}}^{\text{final}} \mathbf{X} \mathbf{M} \mathbf{X} ds \quad (16)$$

$$I \geq L^2 \quad (17)$$

Note that the only difference between  $I$  and  $L$  is the square root. While both are equilibrium quantities, the non-equilibrium component inherent in the dissipation comes about through the fluctuations around equilibrium. Thus it is possible to measure the dissipation of a system through a series of equilibrium measurements. Obviously, these are most pronounced for mesoscopic systems.<sup>[105,107]</sup> The hysteresis in RNA hairpin unfolding and folding mentioned earlier has been directly related to this.<sup>[104]</sup>

Brownian motion as well as ratchets have frequently been treated as heat engines, and with considerable success. Seifert

and co-workers are currently very active in such analyses, using a finite-time thermodynamic approach. In a recent study they surprisingly find an efficiency at maximum power production different from the Curzon–Ahlborn value [Eq. (1)].<sup>[108]</sup>

## 9. Quantum Systems

Even though thermodynamics is inherently a classical discipline, its application to quantum systems has been quite successful. The first paper in this field dates back to 1992<sup>[109]</sup> and is a faithful modification of standard finite-time thermodynamics ideas, also resulting in the now standard Curzon–Ahlborn efficiency [Eq. (1)]. The thermal reservoirs are still that, thermal reservoirs, while the work in/output is in the form of radiation. The working fluid is taken to be either a set of non-interacting harmonic oscillators or a set of non-interacting  $j$ -spins. These two engine types have remained the standard systems until today. They are both considered because their quantum behaviors are slightly different. The crucial—and most difficult—element of the calculation is how to introduce a dissipative element into a quantum calculation which inherently is time symmetric. Lindblad<sup>[110]</sup> devised a coupling operator between the system (“the engine”) and its reservoirs which removes any phase relationship between the two. Not only does that provide the finite-time element, but it is also essential for operation of the engine since otherwise all components would be described by a single wave function, and the reservoirs wouldn’t be reservoirs but parts of a grander total system.

The “standard” optimizations of finite-time thermodynamics like maximum power and minimum entropy production have been solved.<sup>[111]</sup> Further, the third law of thermodynamics was given a quantitative dynamical interpretation through the derivation that the fastest possible cooling rate to the absolute-zero temperature is proportional to  $T^{3/2}$ .<sup>[112]</sup> Recent endeavors have been to calculate the optimal schedule which will bring the oscillator and the spin system as quickly as possible from one given state to another.<sup>[113]</sup> The corresponding optimization of a classical oscillator amounts to the opposite of the fastest way of pumping a swing, an exercise most of us were quite good at as children without applying mathematics in any way.<sup>[114]</sup> Assuming that two frequencies  $\omega_{\text{low}}$  and  $\omega_{\text{high}}$  (thermal reservoirs) are available for the optimization, the energy can be lowered by the factor  $\omega_{\text{low}}/\omega_{\text{high}}$  in every cycle if the phasing can be done optimally, but only by the square root of this ratio if the phase is random or unknown, as for example, in an ensemble of identical systems.

A brief review of quantum thermodynamics appeared in Ref. [31].

## 10. Limits to Control

Let us briefly touch upon a more abstract question. A large part of thermodynamics is concerned with establishing limits to performance (efficiency, power, amount of product,

etc.). An even more fundamental issue is to delineate the set of final states that can be reached from a given initial state. A prime example is Callen's statement<sup>[2]</sup> of the third law of thermodynamics: "No reversible adiabatic process starting at nonzero temperature can possibly bring a system to zero temperature". The equivalent issue in finite-time thermodynamics is no less important, now in the form "which states can be reached within a certain length of time?" Tsirlin and Kazakov map out these limits for heat engines and for mass transfer<sup>[115]</sup> while Salamon et al. state nine principles that put stringent limits on finite-time processes.<sup>[116]</sup> Jou and Casas-Vazquez base their limits on the second law, applied to far from equilibrium, mesoscopic, and quantum systems.<sup>[117]</sup>

Related to limits to control is the dynamic stability of thermodynamic systems. Several authors<sup>[118]</sup> perturb the traditional steady state of a reaction, for example, the steady-state operation of a heat engine, and investigate the relaxation time for return to the steady state. Often these systems have two relaxation times, one of which will increase the other decrease as the driving force is increased (the outer temperature ratio in the case of an endoreversible heat engine). This implies a basically stable situation, just less so for strongly driven systems. However, this is not a general feature of all thermodynamic systems. Many chemical flow systems are in a metastable steady state and can easily be thrown out of that. Likewise, a distillation column with a vapor-rate-dependent tray efficiency has multiple steady states.<sup>[13]</sup> Such stability analyses are essential for industrial processes in order to avoid accidents. It is about time they also get a more fundamental basis.

### 11. Applications Inspired by Finite-Time Thermodynamics

It is always a pleasure to see a theory inspire developments in other areas than its own. This is evidence of the unity of science. One of the most important applications of finite-time thermodynamics ideas outside their own domain proper is in the general optimization algorithm simulated annealing. Each point in the abstract state space is visited at random but with a preference for the more favorable states, that is, states with the lowest value of the objective function  $E$ , usually called "energy". The preference is introduced through the Boltzmann factor  $\exp(-\Delta E/T)$ , where  $\Delta E$  is the change in objective function when the proposed iteration step is accepted and  $T$  is the only control variable in the procedure, usually called the "temperature". Since this Metropolis algorithm<sup>[119]</sup> is based on statistical mechanics, it is only logical to try to apply further results from thermodynamics to the algorithm. The most obvious concept to transfer is the optimal calculation of a temperature path for a given process calculated as the path of constant thermodynamic speed (see Section 3).<sup>[198,120]</sup> This addition to simulated annealing has been most successful and has increased the calculational speed substantially for very complex problems like seismic inversion and determination of molecular structure.<sup>[121]</sup>

Related to these abstract calculations are calculations of the potential energy surface on which molecules move during

chemical processes. Free energies are notoriously difficult to calculate with precision for large molecules. Even if you have a good value for the reactant molecule, that does not help in obtaining the value for the product molecule; it has to be generated from scratch. Reinhardt and co-workers<sup>[122]</sup> found a very clever way around that problem by artificially modifying the energy barrier temporarily while the transformation takes place and then reestablishing it when the system approaches the desired conformation. Not surprisingly, the optimal way to modify the barrier is to follow a path of minimal thermodynamic length and do so at constant thermodynamic speed.<sup>[123]</sup> This procedure is much more efficient than adiabatic switching and should be useful in many other situations of barrier crossing.

Closely related to this philosophy, the first-order gas-liquid phase transition has been modeled in finite-time thermodynamics. It was found that the least supersaturation needed for condensation in a finite time is along a path of shortest thermodynamic length.<sup>[124]</sup> In this connection I would also like to mention the design of structures of chemical substances (molecules or solids) and their optimal synthesis using finite-time thermodynamics and annealing procedures which is spearheaded by Schön.<sup>[125]</sup>

Fluid dynamics has long been the domain of the Navier-Stokes equation, based on tracing the motion of little parcels of fluid. A new perception of a flow is to think of these little parcels as moving around in phase space at random, whereby only a few boundary conditions like the walls and an overall flow are observed.<sup>[126,127]</sup> The rest is then a thermodynamic or statistical mechanical optimization. The calculations are vastly simpler than the solution of the Navier-Stokes equation, and the resulting flow profiles are amazingly precise. Once again, thermodynamics provides a good and simple description of continuous or fine-grained systems with fluctuations.

### 12. Inspiring Conferences

Major contributors to the advance of finite-time thermodynamics have been the *Telluride Summer Research Center* (now *Telluride Science Research Center*)<sup>[128]</sup> and a biannual series of Gordon conferences. Both events were carefully designed to be discussion meetings where new ideas could grow out of unlimited discussions and brainstorming among people of different backgrounds. The *Telluride Summer Research Center* just last year celebrated its 25th anniversary with an impressive lineup of science events. It is thriving very well. The Gordon conferences ran from 1994 to 2003 but unfortunately were terminated.

### 13. Outlook

Many people have declared thermodynamics a dead research field, fully explored and polished, a fossil. The new developments and results mentioned above as well as many others not included in this Review prove such a statement utterly wrong. But what is still left to discover? By definition,

of course we don't know. However, I will risk a short extrapolation.

I am confident that many more results will emerge at the mesoscopic length and time scales, sometimes referred to as the nanoscale. As briefly touched on, many traditional single-valued thermodynamic concepts and predictions break down at that scale but without being totally random. Thus many electronic, mechanical, and chemical products emerge which need further development of thermodynamic and optimization tools. Similar developments in mesoscopic statistical mechanics, for example, omitting Stirling's approximation, are beginning to emerge.<sup>[127,129]</sup>

A new field where I believe that thermodynamic ideas have great potential is a bird's eye description of ecosystems. Currently most descriptions of ecosystems contain detailed assumptions about who eats whom or what and about rates of growth for the many components in the ecosystem. Is that really necessary? In chemistry we are able to derive predictions of reactions with great accuracy without any mention of the detailed reaction mechanisms of the reactants and products. Only the relative free energies of the components matter, combined with an assumption of rapid reactions. The energetics and the statistics will then take care of the rest. An ecosystem is just a chemical soup with "large molecules", so why shouldn't thermodynamic concepts work there as well? Finite-time thermodynamics has been introduced to ecology in its more traditional form, but that is not what I have in mind here.<sup>[130]</sup> The surface has barely been scratched in this area.

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## Reviews

### Finite-Time Thermodynamics

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Current Trends in Finite-Time  
 Thermodynamics



The essential element of thermodynamic optimization is to coax a system (the horse) along the optimal path by interaction with a judiciously varying reservoir (the moving carrot). This is called a horse-carrot process. If the distance from the horse to the carrot is small the horse will not move very quickly; if the distance is too large, it will give up and not move at all. The goal of optimization is to find the right driving force under the given conditions.