Recent Developments in Finite Time Thermodynamics

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Finite time thermodynamics is a non-equilibrium theory. Its aim is to provide performance bounds and extremes for irreversible thermodynamic processes. Recent developments in different areas of this theory are presented. First it is shown how irreversible processes between reversible systems can be described by the endoreversible theory. Then maximum power and minimum entropy production processes are introduced. And finally the extension of finite time thermodynamics to the realm of quantum theory is demonstrated.

1 Introduction

Thermodynamics started in 1826 when SADI CARNOT, a French engineer, published his famous article 'Reflexions sur la puissance motrice du feu' (On the motive power of heat). He reported the results of the first systematic study on the physical processes governing steam engines. Building on this one of the earliest successes of thermodynamics was the formulation of bounds and optima for thermodynamic processes. Carnot showed that any engine which produces work taking heat from a heat reservoir at temperature T_H has to deposit part of that heat in a colder reservoir at temperature T_L and moreover no engine can convert more than the fraction

$$\eta_C = 1 - \frac{T_L}{T_H} \tag{1}$$

of the heat taken from the heat reservoir to work. η_C is the well-known Carnot efficiency and it is an upper bound for the efficiency of any heat engine running between two heat baths. In the subsequent development of thermodynamics the emphasis changed over to equilibrium concepts like entropy and energy. The past 30 years, however, have seen again a shift to process quantities and the development of non-equilibrium thermodynamic theories. Why is it that the non-equilibrium character of thermodynamics has again gained the importance it has today?

To understand this renewed interest in the conversion of heat into power let us look at a real life example. In a recently built brown coal power station near Lippendorf close to Leipzig the temperature T_H of the burner is roughly 900 K and the corresponding cooling tower temperature T_L is about 300 K. The observed efficiencies are little higher than 40%. From the temperature data follows that in a reversible process the achievable efficiency is about 66%. This efficiency exceeds the observed efficiency by a factor larger than 1.5. To emphazise this discrepancy I like to call it the science–reality gap in power conversion. It shows that between the observed efficiencies and the efficiencies which are provided by the often used reversible theories in thermodynamics a wide gap remains open which needs to be explained.

One possible explanation could be that the design which is currently used by the engineers for building power stations is not optimal for the purpose desired. In other words: a better design could be possibly used to increase efficiency further. To explore this possibility we look at the primary energy usage in power production (in SKE/kWh) as a function of time in Germany: 0.569 (1953), 0.361 (1973), and 0.347 (1993). The figures show that between 1953 and 1973 the primary energy usage decreased by about 30%, but between 1973 and 1993 the usage did not drop much further. From this we can conclude that most probably technology does not have much potential for further improvement. That means that the physical theory using the Carnot efficiency to determine the efficiency of power stations misses important effects of real life power stations and needs to be improved.

The realization of this science–reality gap led to the development of new non-equilibrium thermodynamics theories. One of these is finite time thermodynamics (Andresen, 1984; Andresen, 1983a). It developed starting from a number of simple but important questions:
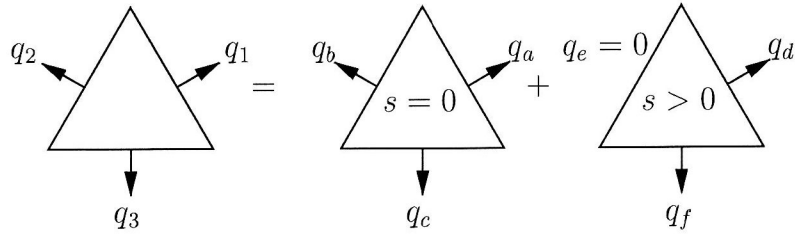
Figure 1: Tricycle decomposition of the general heat flows q_1, q_2, q_3 of a process into a reversible part and a totally irreversible part.

- Is there a price to be payed in terms of efficiency to operate a power station in finite time or at finite rates?
- How large is that price?
- Which kind of process leads to the minimal price?

Starting from these questions finite time thermodynamics developed into several directions.

2 Early Concepts in Finite Time Thermodynamics

One of the earliest concepts in finite time thermodynamics is the tricycle formalism (Andresen, 1977). It is a very convenient way to access the cost of a finite time operation for a heat exchange system, making use of the conversation laws for the process in question.

A system which is in contact with 3 heat reservoirs or 2 heat reservoirs and a work reservoir, e.g. a flywheel, is graphically depicted as a triangle, with heat flows q_1, q_2, and q_3 into the reservoirs at temperatures T_1, T_2, and T_3. In the case of a work reservoir the corresponding temperature is infinite and the energy flow is not accompanied by an entropy flow. The idea behind the tricycle is that it represents a cyclic or continuously operating energy conversion system, which does not produce energy itself, thus

$$q_1 + q_2 + q_3 = 0 \tag{2}$$

where for a cyclic operating system the q's are cycle averages. Using $\tau_i = T_i^{-1}$ the entropy production s is given by

$$s = q_1\tau_1 + q_2\tau_2 + q_3\tau_3 > 0. \tag{3}$$

One now decomposes the tricycle process into a reversible part and into a totally irreversible part as shown in Figure 1. To make the decomposition unique, q_e is set to zero. Such a decomposition becomes useful if by specifying the loss mechanisms the dependencies of the irreversibilities on the reversible flows or rates are determined. Once that has been achieved the objective (like power, efficiency, minimum entropy production etc.) for the optimization must be chosen and then the optimal flows and thus the corresponding size of the irreversibilities can be determined. One advantage of the tricycle formalism is that it allows to treat several loss mechanisms simultaneously, for instance the interplay between friction and heat leak losses have been analyzed. The formalism also allows to separate the most serious losses and concentrate on them. And finally it may be convenient for processes which have unavoidable losses, to split the tricycle into three parts: one for the reversible operation, one for the unavoidable losses, and one for the excess losses.

Another early concept of finite time thermodynamics is the finite time potential (Salamon, 1977). As pointed out above, thermodynamics started out as a practical science dealing with energy conversion, and throughout its development one basic question remained of interest at least from a practical point of view: How much work or heat can one get out of a system undergoing a thermodynamic process from one state to another?

The answer to this kind of question is given for certain reversible processes by the appropriate thermodynamic potentials. For irreversible processes these could provide only bounds on the process variables

which might be far from being realistic. The usually known potentials for reversible processes are characterized by the constancy of some state variables like volume, pressure or temperature. This is, however, not necessary, and Salamon, Andresen and Berry (Salamon, 1977) presented an extension of the Legendre transformations used in classical thermodynamics which allows to handle a much wider class of constraints including those which depend on time.

These extended potentials are called finite time potentials. They can handle finite rate and finite time constraints and provide a bound for process variables in the form of the difference of their value between final and initial states. For certain processes they can explicitly depend on time. The bounds provided by finite time potentials contain the losses by the irreversibilities and are thus more realistic than those for ordinary potentials. The same applies to bounds derived from finite-time availability, which is an extension of the usual availability to irreversible processes (Andresen, 1983a; Andresen, 1983b).

3 The Quest for Principles

The early concepts presented above already show the main idea behind the development of finite time thermodynamics. Even though it is a theory of irreversible processes, the systems are still described by equilibrium variables like pressure or temperature. The underlining reason why this description is still possible is a time scale separation, which is observed in nature in very many circumstances. Looking at thermodynamic systems one sees that even though parts of the system are not in equilibrium, large parts can be considered to be very close to equilibrium because their internal relaxation time is much smaller than that of the total system (Hoffmann, 1997). Thus the subsystems can be described very well by equilibrium terms. The resulting picture one has of a non-equilibrium system is therefore a picture of a collection of near equilibrium subsystems which interact in an irreversible manner.

The ideas developed in finite times thermodynamics have been applied in a variety of situations, for instance, in the field of heat engines the performance of internal combustion engines has been studied while in the field of chemical reactors the optimal type of fuel gas production has been considered. In the area of solar cells the efficiencies have been the goal of investigation while in the field of chemical distillation the question of diabatic columns is of recent interest. In all these cases the goal has been to find realistic process limits and to determine the corresponding optimal process.

Of course the optimization of the thermodynamic processes in these applications is an important goal in its own right. However, behind the treatment of these special problems lies the hope that in this way underlying principles can be discovered. It is this quest for principles (Salamon, 2001) which has led to a large number of very interesting investigations into special systems. In some of these areas more general principles have been uncovered.

In the following we will present four areas in finite time thermodynamics, in which recent progress has led to a deeper understanding of non-equilibrium thermodynamic processes.

4 Endoreversible Systems

Endoreversible thermodynamics (Rubin, 1979; de Vos, 1992; Hoffmann, 1997) look at a thermodynamic system in the specific way presented already above: The thermodynamical system is considered to consist of a number of equilibrium subsystems which interact in a highly irreversible way, as shown in Figure 2(a). The advantage of the equilibrium subsystems is that the well known relations from equilibrium thermodynamics can be used while all the entropy production occurs during the transport between the subsystems.

The transport between the subsystems is characterized by so called 'interactions' which are usually given by irreversible transport equations. Very simple examples are for instance the Newtonian heat conduction $q = \kappa(T - T')$ or $q = \kappa'(T^4 - T'^4)$ for radiative energy transfer, while for interactions exchanging particles one might use $j = \kappa(\mu - \mu')^\gamma$ with μ being the chemical potential and γ some appropriate exponent.

The reversible subsystems which are connected by the interactions described above can of course be equilibrium systems described by the usual intensities. The classical example is a heat bath described by a temperature T. Other examples are reservoirs of chemical substances with given chemical potential.
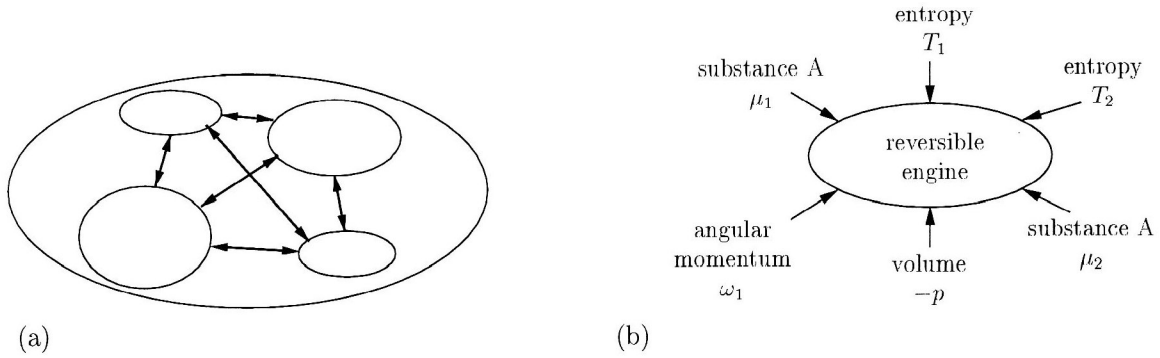
Figure 2: (a) Endoreversible thermodynamics views a thermodynamic system as a collection of reversible subsystems interacting in an irreversible manner. (b) Reversible engines receive extensities at different values of the corresponding intensity, thus allowing a very effective system endoreversible description.

Generally a subsystem i is described by its extensive thermodynamic variables X_i^α, for instance the volume V_i, or particle number N_i, all of which are counted by α. We note that there may be thermodynamic variables like the surface of the subsystem, which are not truly extensive, but for the sake of simplicity are here called 'extensive' too. The entropy S_i of subsystem i is a well defined state variable due to endoreversibility and belongs to the set of extensive variables. Thus the state of the subsystem is uniquely described by the set of its extensities $\{X_i^\alpha\}$. We then have

$$E_i = E_i(X_i^\alpha). \tag{4}$$

Note that (4) *defines* the properties of subsystem i, i.e. specifying E_i as a function of the X_i^α determines what the thermal behavior of that subsystem is. The energy E is not confined to be the internal energy, it can in addition include for instance the translational kinetic energy or the elastic energy. In each case the proper 'extensive' (or more common 'dynamical') variables must be included in the set of extensities. Even pure mechanical systems are within the scope of this description, which is very convenient for instance in the combined treatment of dynamic and thermodynamic systems.

Due to endoreversibility all the standard equilibrium relations hold within a subsystem. We obtain the respective conjugate intensive variables Y_i^α from (4):

$$Y_i^\alpha = \frac{\partial E_i}{\partial X_i^\alpha}. \tag{5}$$

The Gibbs equation becomes $dE_i = \sum_\alpha Y_i^\alpha dX_i^\alpha$ and in each subsystem the extensive and the intensive variables are related via the equations of state (5). Due to the Gibbs equation each influx of an extensity dX_i^α into the system carries an accompanying influx of energy dE_i^α (Falk, 1976):

$$dE_i^\alpha = Y_i^\alpha dX_i^\alpha. \tag{6}$$

For instance any heat flux q is carried by an entropy flux q/T, see figure 3(a). Figure 3(b) shows that in an irreversible interaction some of the energy switches from its original carrier to entropy as the carrier,
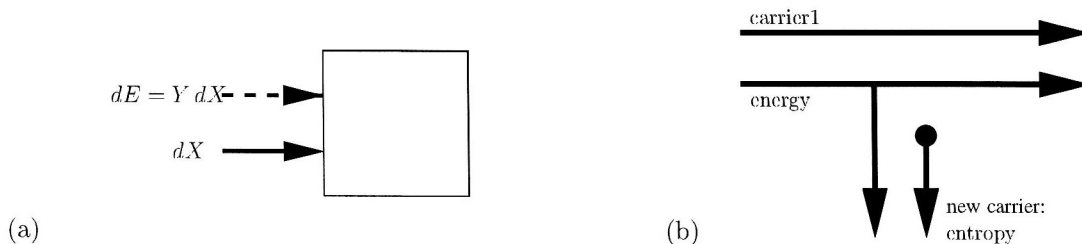

Figure 3: (a) Any influx of a 'carrier' dX into a system is accompanied by an energy influx dE. (b) In an irreversible interaction between systems part of the energy is transferred from its carrier to the new carrier entropy, which is created by the dissipation.
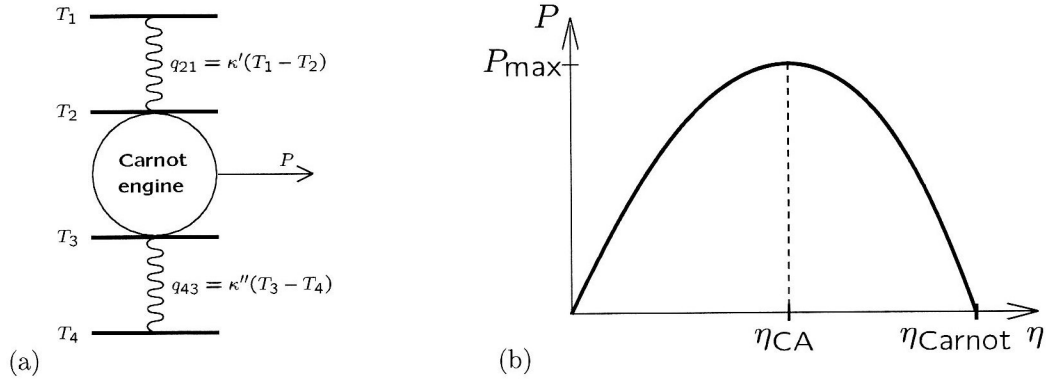
Figure 4: (a) shows a Curzon-Ahlborn-engine, consisting of a Carnot engine coupled to two heat baths by finite heat conductances. (b) shows the power of the Curzon-Ahlborn-engine as a function of the efficiency of the engine, indicating the interplay between the degree of irreversibility and the power output of its operation.

i.e. the dissipated energy becomes heat.

A large step forward in the description of endoreversible systems is the insight that the reversible subsystems should not only be reservoirs but can also be reversible engines, for instance Carnot engines or even more general systems which interact with each other due to many interactions. The new feature in reversible engines is that it has an exchange of extensities at different intensities at the same time. This is shown in figure 2(b) where for instance the substance A enters the system at a chemical potential μ_1 and could leave the system at a chemical potential μ_2. A more familiar system is a Carnot engine where entropy and heat enter at temperature T_1 and leave the system at temperature T_2.

Such a description using reversible engines allows to determine process quantities like entropy production or work very effectively in dependence on the manner in which a thermodynamic process is executed. The process can usually be controlled by certain control variables, for instance temperature differences or other quantities describing the states of the equilibrium subsystem. Thus endoreversible thermodynamics provide a unified description for non-equilibrium processes to determine performance bounds and extremes. Due to the introduction of reversible engines for the use as reversible subsystems the power of the theory has increased by much and provides nowadays a network description to simulate the dynamics of thermodynamic systems. One example for the power of this description is provided in the next chapter which deals with maximum power processes.

5 Maximum Power Processes

Maximum power processes have been at the center of interest of finite time thermodynamics from the very beginning. Maximum power processes have been studied for different types of heat engines ranging from the well-known Novikov and Curzon-Ahlborn engines to the optimization of internal combustion engines like Otto and Diesel engines (Mozurkewich, 1982; Hoffmann, 1985; Burzler, 2000) to the study of light driven engines (Watowich, 1985). They are of very great interest because they are of technological importance. In the following we present as an introduction the Curzon-Ahlborn engine (Curzon, 1975) which shows in a very simple way what type of results can be achieved.

As shown in Figure 4 (a) a Carnot engine operating between its two internal temperatures T_2 and T_3 is linked to two external heat baths at temperatures T_1 and T_4. Heat flows only from the hot bath to the engine and from the engine to the cold bath if there is a finite temperature difference between the respective temperatures T_1 and T_2, as well as T_3 and T_4. In this example it is assumed that heat transport occurs proportional to the temperature difference. Due to the finite heat conduction the produced power is limited. The efficiency of the engine at the operating point of maximum power is

$$\eta_{CA} = 1 - \sqrt{\frac{T_4}{T_1}} \quad . \tag{7}$$

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This is the well known Curzon-Ahlborn-efficiency which is smaller than the Carnot efficiency for the same temperatures. It is worthwhile to note that it does not depend on the values of the heat conductances κ.

In the following table taken from (Curzon, 1975), a comparison between the Carnot efficiency and the Curzon-Ahlborn-efficiency is shown for a number of power stations:

power station	type	T_L	T_H	η_C	η_{CA}	η_{real}
West Thurock	coal	25	565	0.64	0.40	0.36
CANDU	nuclear	25	300	0.48	0.28	0.30
Landerello	geothermal	80	250	0.32	0.17	0.16

The table shows that η_{CA} is much closer to the observed efficiency than η_C. Thus the Curzon-Ahlborn-efficiency is a first step forward towards a more realistic description of energy conversion processes.

In a number of studies it has been shown that the Curzon-Ahlborn efficiency occurs in several instances and is always connected to the case where the heat conduction in and out of the engine is proportional to the temperature difference which the heat has to cross. It does for instance not apply to engines for which the energy is transported by radiation. These results suggest that the applicability of the Curzon-Ahlborn efficiency is restricted to the case of Newtonian heat conduction.

In a recent work (Burzler, 2001) it was shown that that is not the case. In that paper heat engines with polytropic cycles are considered. Polytropic processes are used to describe the state change of the working fluid in a generalized way and include common standard branches, such as isotherms, isochors, and isobars, as special cases. A polytropic process of a working fluid is characterized by a constant product pV^n where p is the pressure and V is the volume of the working fluid. The constant exponent n refers to the *polytropic degree* of the heat transfer process. The concept of polytropic processes was taken into the realm of finite time thermodynamics by Pathria, Nulton and Salamon (Nulton, 1993).

The polytropic degree n can in principle take any value between $-\infty$ and ∞. Common standard processes correspond to $n = 1$ for isothermal, $n = 0$ for isobaric, $n = \pm\infty$ for isochoric, and $n = \gamma$ for adiabatic processes. The quantity $\gamma = C_p/C_V$ is the ratio of the heat capacities C_p and C_V of the working fluid at constant pressure and constant volume, respectively. In practice, a desired polytropic process can be achieved by controlling some of the state variables, for instance the volume or the pressure of the working fluid. The polytropic degree n is directly related to the polytropic heat capacity which is defined as

$$C_n = C_v \frac{n - \gamma}{n - 1} \tag{8}$$

The polytropic heat capacity C_n is not a material parameter but a *process parameter* and may in principle take any value between $-\infty$ and ∞, if no restrictions on n are imposed. A negative polytropic heat capacity C_n is not unrealistic. It could for example occur in a system where the working fluid receives heat and at the same time is very rapidly expanded such that the temperature of the working fluid decreases with time and the polytropic heat capacity C_n becomes negative even though the heat capacity of the working fluid has a finite positive value.

The thermodynamic cycle of the endoreversible engine investigated by Burzler et al. is made up of two polytropic and two adiabatic branches, like the example depicted in Figure 5(a). The engine operates between heat reservoirs at constant high and low temperatures, T_{0H} and T_{0L}, respectively. During the upper (lower) heat transfer process the entire working fluid is in thermal contact with the hot (cold) reservoir. Thus the model is capable of describing technologically important cycles like the Brayton cycle and Otto cycle and accounts for the finite time character of the heat transfer processes.

For engine cycles with arbitrary, non-equal polytropic heat capacities C_H and C_L the maximum power output is not easily obtained analytically. Thus numerical optimizations of the heat engine have been performed. The interesting and not expected result of the numerical calculations was that the efficiency of the polytropic engine differs significantly from the Curzon-Ahlborn efficiency if the branches are of a different type, i.e. have different polytropic heat capacities $C_L \neq C_H$.

A plot of the efficiency versus the polytropic heat capacities (in dimensionless units) is shown in Figure 5. The efficiency η of the optimized cycle is equal to the Curzon-Ahlborn efficiency $\eta_{CA} = 1 - \sqrt{T_{0L}/T_{0H}}$
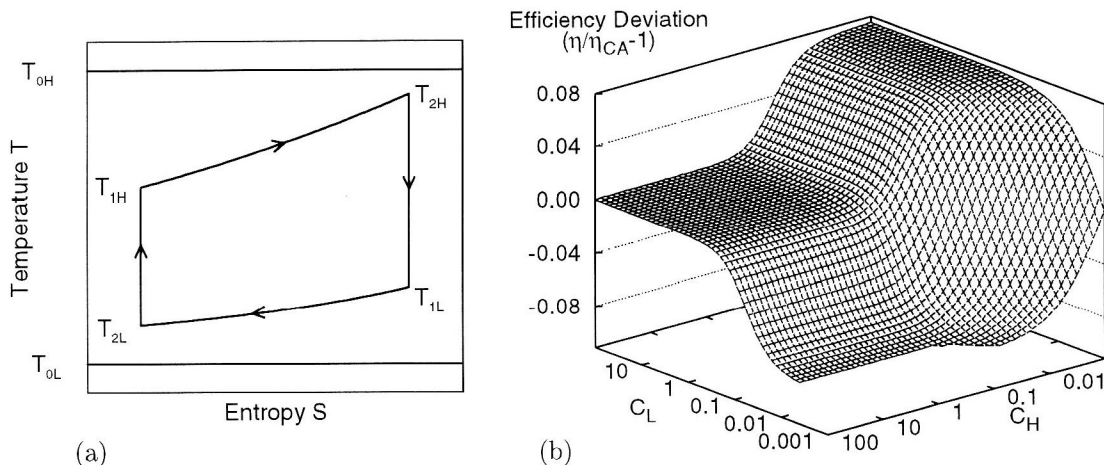
Figure 5: (a) Sketch of a polytropic engine cycle. (b) Deviation of the efficiency from the Curzon-Ahlborn value as a function of the polytropic heat capacities.

only if both polytropic heat capacities are equal. For all other cases the efficiency deviates up to about 8% from the Curzon-Ahlborn efficiency.

The above results show that the Curzon-Ahlborn efficiency can not be used as a universal figure for heat engines optimized for maximum work output although it still can serve as a rough estimate of the efficiency for such engines. This is quite surprising since the existing literature suggested that the linearity of the heat conduction law is the main criterion for an applicability of the Curzon-Ahlborn efficiency. But instead it turned out that the exponents of the polytropic branches are crucial in this context.

6 Minimum Entropy Production Processes

Minimum entropy production processes are often believed to be more or less the same as maximum power processes. It is very important to understand that they are not equivalent. This can be demonstrated in a very simple example. Assume that a person wants to drive in his car to the airport. If he is in a hurry, then he is interested in a maximum power process for his car engine, because that will provide the fastest transport. If on the other hand he is low on fuel, he is interested in minimum entropy production processes, because that will give him the best mileage. The difference between the two cases is obvious.

Being different from maximum power processes, the analysis of minimum entropy production processes has developed its own tools (Sieniutycz, 1990; Hoffmann, 1997). One of these is the concept of thermodynamic length or distance (Salamon, 1983). Its definition starts out from thermodynamic stability, which guarantees that the second derivative matrix of the entropy with respect to the other extensities is positive definite. Thus one can use that matrix to define a thermodynamic distance in the space of the equilibrium states of a system. The thermodynamic length $\mathcal{L}$ of a process is given by the line element (Salamon, 1998).

$$d\mathcal{L} = \sqrt{-d\vec{\mathbf{Z}}^{\mathrm{t}} \, D^2 S \, d\vec{\mathbf{Z}}} \,, \tag{9}$$

where $\vec{\mathbf{Z}} = (U, V, \dots)$ is the vector of extensities and $D^2 S$ is the matrix of partial derivatives $\partial^2 S / \partial Z_i \partial Z_j$. An important result of finite time thermodynamics is that this length can be used to bound the entropy production of that system. The nature of this bound becomes much clearer in the following application to the diabatic distillation in chemical separation processes.

While an adiabatic distillation column uses just one heat source (reboiler) and one heat sink (condenser), a diabatic column uses a heat exchanger at each tray of the column (see Figure 6). The idea goes back to the work of Z. Fonyo in the early seventies (Fonyo, 1974), but has recently been explored by a number of authors (see (Schaller, 2001) and literature therein.) The additional heat exchangers add or remove
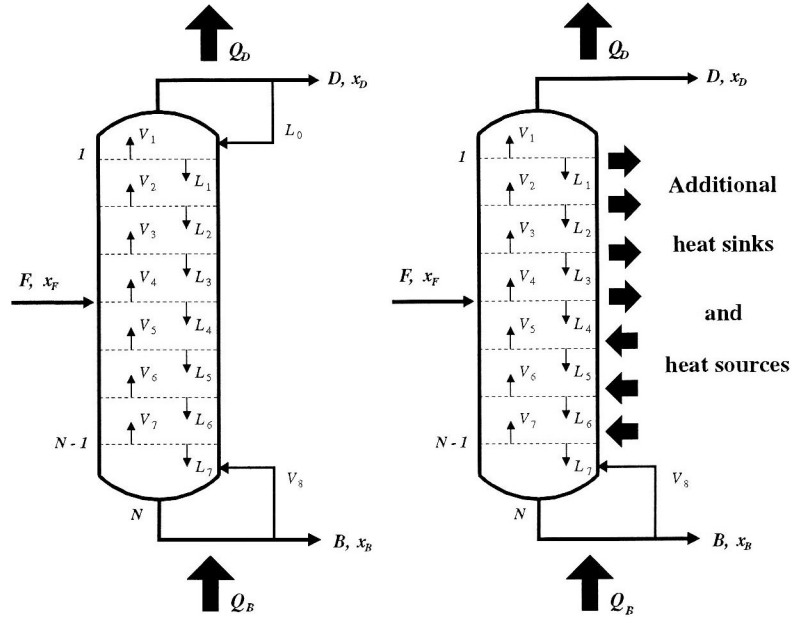
Figure 6: Sketch of a conventional adiabatic distillation column and a diabatic column with additional heat exchange. Both columns have $N = 8$ trays including the reboiler as tray 8.

heat to maintain a particular temperature profile inside the column.

The distillation process is modeled as an N-step process (Nulton, 1985), with N corresponding to the number of trays in the distillation column. Asymptotically in the limit of $N \to \infty$, the total entropy production ΔS^{u} of an N-step process is bound by $\Delta S^{\mathrm{u}} \geq \mathcal{L}^2/(2N)$ (a result from the horse-carrot theorem (Salamon, 1998; Nulton, 1985)). The thermodynamic length of an N-step process can be written as

$$\mathcal{L} = \sum_{n=1}^{N} \Delta \mathcal{L}_n \,, \tag{10}$$

where $\Delta \mathcal{L}_n$ is the length of the n-th step. A process where the lengths of the steps are equal, i.e. $\Delta \mathcal{L}_1 = \ldots = \Delta \mathcal{L}_n = \ldots = \Delta \mathcal{L}_N$ is called an equal thermodynamic distance (ETD) process. For the distillation model described in the previous section, the thermodynamic length element (9) is given by (Salamon, 1998) $d\mathcal{L} = \sqrt{C_\sigma}\, T^{-1}\, dT$ where C_σ is the total constant pressure coexistence heat capacity of the binary two-phase mixture in equilibrium.

As an ETD process minimizes the entropy production only asymptotically (Salamon, 1998; Andresen, 2000) in $1/N$ the question is how good is ETD for columns with few trays?

In order to answer this question, Schaller et al. (Schaller, 2001) investigated in a recent study the entropy production associated with distillation on shorter (small N) columns. They chose benzene/toluene as their system to be separated. The mixture to be separated is introduced as feed F usually near the middle of the column and the separated components are removed at the top as distillate D and at the bottom as bottoms B. The column is considered to be operating at steady-state so all extensive quantities are per unit time. For convenience, only binary mixtures are considered and the pressure is assumed to be constant throughout the column. The reflux is taken equal to zero. In order to calculate the heat required at each tray to maintain the desired temperature profile, the energy and mass balance has to be maintained for each tray. Constant heat capacities, a noninteracting mixture of ideal gases for the vapor phase, and an ideal solution for the liquid phase were assumed.

The entropy production for the separation of a 50/50 mole fraction benzene/toluene mixture is minimized by applying a fully numerical, multidimensional optimization routine as well as ETD. The number of trays and purity requirements were varied to show differences in the performance of ETD and numerical optimization. The comparisons are always between columns with the same material flows in and out. Notably the feed, bottoms and distillate flows match not only in magnitude but also in composition
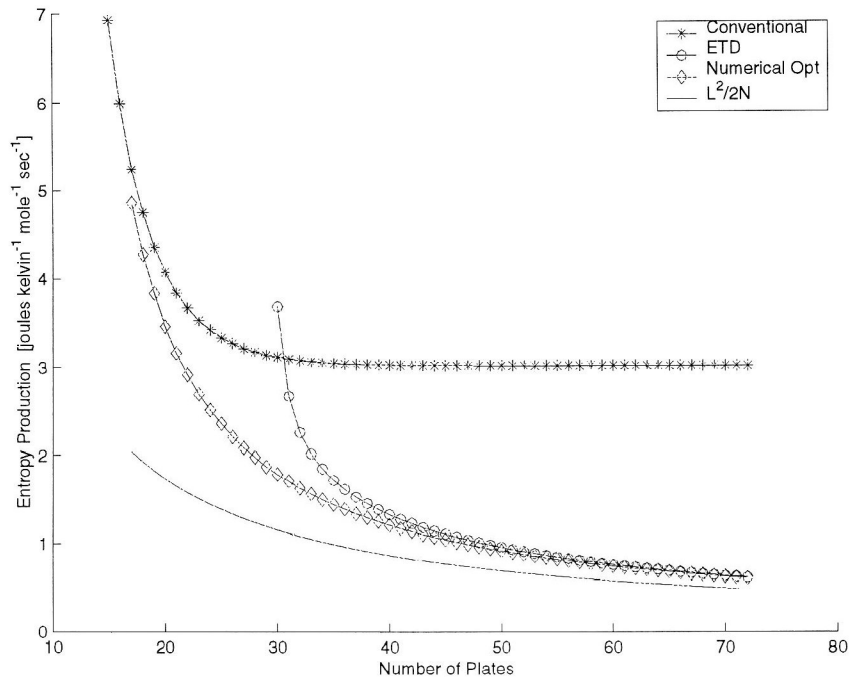
Figure 7: Entropy production for the separation of a benzene/toluene mixture.

Notably the feed, bottoms and distillate flows match not only in magnitude but also in composition and temperature in the columns compared. Because of its asymptotic nature, the minimum entropy production calculated with ETD should be higher than the true minimum for fewer trays.

Figure 7 shows the entropy production associated with the separation as a function of the number of trays for (i) a conventional column, (ii) the ETD column, (iii) the numerically optimized column, and (iv) the asymptotic lower bound $(\mathcal{L}^2/2N)$ for the entropy production based on the ETD calculation.

Interestingly the $\mathcal{L}^2/2N$ values are surprisingly far from the ETD curves. The good match between $\Delta S^u_{\text{optimal}}$ and ΔS^u_{ETD} led later to a deeper explanation. It turns out that the match between these two quantities is always of order $1/N^3$ (Salamon, 2001).

For all purity requirements considered, the optimal columns are far more efficient than their conventional adiabatic counterparts. The optimal results also are above the ETD lower bound, but approached the ETD bound as N was increased. The large N simulation for the 99/01 purity requirement has the closest values to the ETD bound as was expected due to the asymptotic nature of the ETD theory. The numerical optimization results predict slightly less entropy production in the small N regions, but agree very well with the ETD results for larger N values.

Finally we remark that similar studies comparing a different optimization algorithm to an isoforce criterion have appeared elsewhere (see Koeijer, 1999 and literature therein). From a technological point of view it is very promising that the optimal profile calls for a nearly constant heat demand which works well with the Rivero implementation of diabatic columns (Rivero, 1993).

7 Quantum Finite Time Thermodynamics

The ideas of finite time thermodynamics can be taken over into the regime where one needs to use quantum theory. In that regime the interactions are no longer described by phenomenological transport laws, but are derived from a quantum mechanical coupling of the system to the baths.

In the following a simple system in which the dynamics is given by quantum mechanical considerations (Geva, 1994) is presented. The system is shown in Figure 8. It consists of a number of atoms with three energy levels E_1, E_2 and E_3, where levels 1 and 3 are coupled to a hot temperature bath and levels 1 and 2 are coupled to a cold temperature bath. The dynamics is given by a quantum master equation. Such
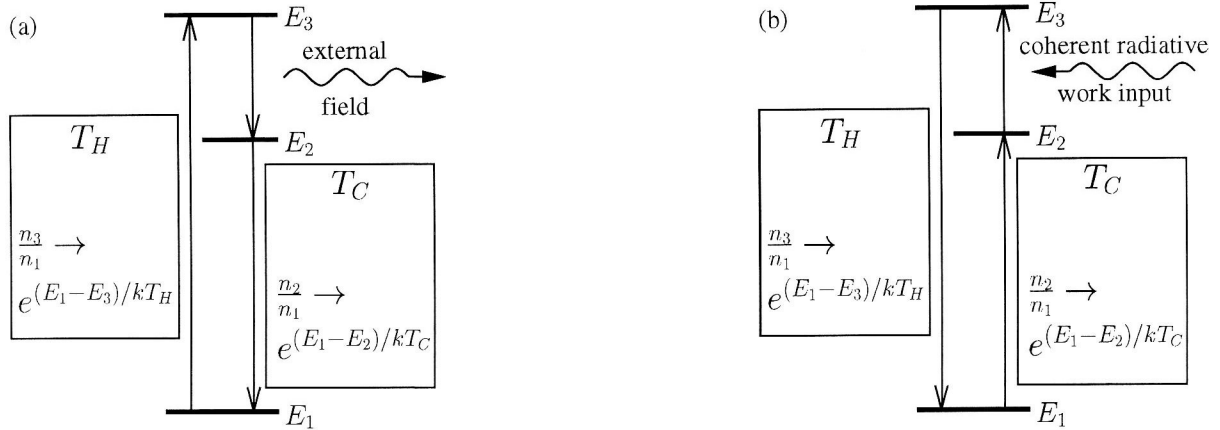
Figure 8: A three level quantum system is shown, coupled to two heat baths. The coupling tries to establish a certain population ratio between the respective levels. Work is delivered or taken from the system by coupling to an external field. (a) shows a quantum amplifier, (b) a quantum refrigerator with the arrows indicating the cycle taken by the system.

dynamics aim at establishing an appropriate population density of the levels so that the population ratio between level 3 and 1 moves towards

$$\frac{n_3}{n_1} \rightarrow e^{-(E_3-E_1)/kT_{\mathrm{H}}} \tag{11}$$

while the population ratio between levels 2 and 1 moves towards

$$\frac{n_2}{n_1} \rightarrow e^{-(E_2-E_1)/kT_{\mathrm{C}}}. \tag{12}$$

For this system the definition of an internal temperature is simple: the internal temperature of the hot side of the system is given by the actual population ratio of levels 1 and 3, and the internal temperature of the cold side is given by the actual ratio between levels 1 and 2.

Based on these internal temperatures it can be shown that the dynamics given by the quantum master equation lead to a heat transport law which differs markedly from the well known Newtonian heat transport. A surprising result is that even though the interaction and the transport law between heat bath and system are no longer Newtonian the efficiency at the maximum power output goes in the high temperature limit to the Curzon-Ahlborn-efficiency

$$\eta \longrightarrow \eta_{\mathrm{CA}} = 1 - \sqrt{\frac{T_{\mathrm{C}}}{T_{\mathrm{H}}}} \quad . \tag{13}$$

Thus the result from classical finite time thermodynamics reoccurs in quantum theory even though only in a limiting case.

Another interesting application of the system is to run it backwards as a three level quantum refrigerator (Kosloff, 2000). Here a coherent radiative work input in form of a radiation field leads to a heat transport from the cold temperature reservoir to the hot temperature reservoir as is shown in Figure 8. The cycle works as follows: The incoming radiation increases the population of level 3 compared to level 2. The resulting population ratio between levels 3 and 1 is now too high compared to the desired population ratio from the heat bath. Thus a number of atoms loose their energy to the hot temperature heat bath and make a transition into level 1. On the other hand level 2 is depleted due to the incoming field and its population is too low compared to level 1. Thus energy from the cold heat bath will be taken to increase the population in level 2 and the combined result of these changes is a heat transport from the cold temperature bath to the hot temperature bath by the use of coherent radiative work input.

For this system one can show that the cooling rate can be varied by changing a control parameter which in this case is the energy difference between E_2 and E_1. The cooling rate shows a maximum very

similar to the power of the Curzon-Ahlborn-engine. It turns out that the maximum of the cooling rate is proportional to the temperature of the cold heat bath. This result is, for instance, of interest for cooling at temperatures close to absolute zero.

The two examples show that quantum theory now provides the means to investigate important thermodynamic questions also for systems which are far from equilibrium and which need a quantum mechanical treatment. The ongoing miniaturization of devices as well as the fact that larger systems are showing quantum effects too will increase the demand for such treatments in the future.

8 Summary

Recent developments in four different areas of finite time thermodynamics have been presented. For the irreversible interaction between a network of reversible systems endoreversible thermodynamics provides a highly effective tool to analyze performance bounds and extremes. Especially the use of reversible engines as subsystems make this tool very powerful. In the area of maximum power processes the range of validity of the Curzon-Ahlborn efficiency is analysed. The surprising result is that even though there is a linear heat conduction the well-known Curzon-Ahlborn formula no longer holds for the efficiency at the maximum power point. In the area of minimum entropy production processes the quality of ETD solutions based on the thermodynamic length were studied for the case of diabatic distillation. For columns with many trays the agreement between ETD and numerically obtained optimal operation is good, while for shorter columns there are significant deviations. And finally the extension of finite time thermodynamics into the realm of quantum mechanics was shown presenting a three level amplifier and refrigerator. All these examples show that finite time thermodynamics is a powerful theory for the description and analysis of non equilibrium thermodynamic processes.

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