Finite-time thermodynamics and thermodynamic length

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Summary — Finite-time thermodynamics is the extension of traditional thermodynamics to deal with processes which have explicit time or rate dependencies. In doing so the macroscopic measurable description of thermodynamic systems is preserved while irreversibilities, and hence entropy production, are introduced via empirical rate equations or imposed constraints such as friction coefficients, heat conductances, reaction rates and the like. However, the models remain simple in order to yield physically transparent reference points rather than detailed simulations. Some concepts of reversible thermodynamics, such as potentials and availability, generalize nicely to finite time, others are completely new, eg, endoreversibility and thermodynamic length.

1 INTRODUCTION

Finite-time thermodynamics was invented in 1975 by RS Berry, P Salamon, and myself as a consequence of the first world oil crisis. It simply dawned on us that all the existing criteria of merit were based on reversible processes and therefore were totally unrealistic for most real processes. That made an evaluation of the potential for improvement of a given process quite difficult [1].

Finite-time thermodynamics is developed from a macroscopic point of view with heat conductances, friction coefficients, overall reaction rates, etc, rather than based on a microscopic knowledge of the processes involved. Consequently most of the ideas of traditional thermodynamics have been assimilated, eg, the notions of thermodynamic potential (§ 2.1) and availability (§ 2.2). At the same time we have seen new concepts emerge, eg, the non-equivalence of well-honored criteria of merit, the importance of power as the objective, the generality of the endoreversible engine, and in particular thermodynamic length (§ 2.3). Several of these abstract concepts have been successfully applied to practical optimizations [2,8].

The model of Curzon and Ahlborn [9] has evolved into almost a classic paradigm of systems operating in finite time. This is a Carnot engine with the simple constraint that it be linked to its surroundings through *finite* heat conductances.

Figure 1 illustrates the slightly more general endoreversible system with the triangle signifying any reversible engine (the term endoreversible means internally reversible, ie, all irreversibilities reside in the coupling of flows to the surroundings; in this case, that means resistance to heat transfer and possibly friction). It turns out that the results derived by Curzon and Ahlborn explicitly for an interior Carnot engine are equally valid for a general endoreversible system. The maximum efficiency of their engine is of course $\eta_C = 1 - T_L/T_H$, obtained at zero rate so that losses across the resistors vanish, but these authors showed that, when the system operates to produce *maximum power*, the efficiency of the engine is only:

$$\eta_w = 1 - \sqrt{\frac{T_L}{T_H}} \qquad (1)$$

Besides the simplicity of the expression, it is remarkable that it does not contain the value of the heat conductances.

2. PERFORMANCE BOUND WITHOUT PATH

The smallest amount of information one can ask for concerning the performance of a system is a single
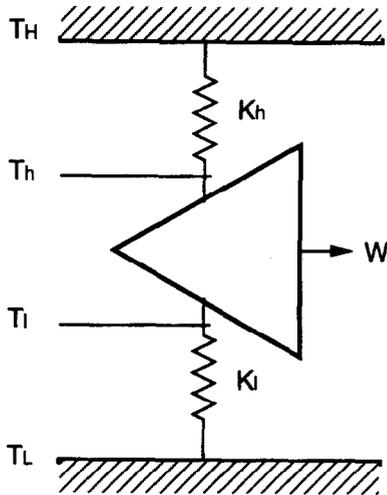
Fig 1. *An endoreversible engine has all its losses associated with its coupling to the environment, there are no internal irreversibilities. This is illustrated here as resistances in the flows of heat to and from the working device indicated by a triangle. These unavoidable resistances cause the engine proper to work across a smaller temperature interval, $[T_h; T_1]$ than that between the reservoirs $[T_H; T_L]$, one which depends on the rate of operation.*

number, eg, the work or heat exchanged during the process, its efficiency, or any other figure of merit. In most cases, this can be calculated without knowledge of the detailed path followed and is then computationally much simpler to obtain.

2.1. GENERALIZED POTENTIALS

In traditional thermodynamics, potentials are used to describe the ability of a system to perform some kind of work under given constraints. These constraints are usually the constancy of some state variables like pressure, volume, temperature, entropy, chemical potential, particle number, etc. Under such conditions, the decrease in thermodynamic potential Φ from state i to state f is equal to the amount of work that is produced when a reversible process carries out the transition, and hence is the upper bound to the amount of work produced by any other process:

$$W \leqslant W_{rev} = \Phi_i - \Phi_f \qquad (2)$$

In this section we will show that the constraints need not simply be the constancy of some state variable, and that the potentials may be generalized to contain constraints involving time [10]. The procedure will be a straightforward extension of the Legendre transformations [11] used in traditional thermodynamics [12,13], and we will start with such an example. In a reversible process, heat and work can be expressed as inexact differentials,

$$dQ = TdS, \qquad dW = PdV \qquad (3)$$

ie, they cannot by themselves be integrated, further constraints defining the integration path are required. Such a constraint could be that the process is isobaric, $dP = 0$. One can then add a suitable integrating zero-term, $x dP$ to make dW an exact differential. The obvious choice is $x = V$:

$$dW = PdV = PdV + VdP = d(PV) \qquad (4)$$

such that the isobaric work potential becomes $\Phi = PV$.

Now, the constraints need not be the constancy of one of the state variables. Consider a balloon with constant surface tension α. In equilibrium with an external pressure P_{ex} such a sphere of radius r has an internal pressure

$$P = P_{ex} + \frac{2\alpha}{r} \qquad (5)$$

which can be rearranged into:

$$(P - P_{ex})V^{1/3} = 2\alpha \left(\frac{4\pi}{3}\right)^{1/3} \qquad (6)$$

Since the right hand side of this equation is a constant, this means that $(P - P_{ex})V^{1/3}$ is an integral of motion for the fluid inside the balloon. We can then add a suitable amount of $d[(P - P_{ex})V^{1/3}](= 0)$ to dW to make it exact:

$$dW = PdV = PdV + \frac{3}{2}V^{2/3} d\left[(P - P_{ex})V^{1/3}\right]$$

$$= d\left[\frac{1}{2}V(3V - P_{ex})\right] \qquad (7)$$

Thus the work done by the coupled system, surface + fluid, is given by the decrease in the potential $\Phi = \frac{1}{2}V(3V - P_{ex})$, regardless of path followed.

This procedure of adding a suitable amount of a zero-quantity can be generalized to any differential constraint, even including time explicitly [10].

2.2. FINITE-TIME AVAILABILITY

One of the more powerful results in finite-time thermodynamics is the definition of a finite- time availability [14]. The traditional availability A of a system in contact with given surroundings is a state function with the quality that the decrease in its value in going from state i to state f is the maximum (and hence reversible) work that can be extracted during that process. The finite-time availability Ψ retains this property and simply adds that the process is restricted to operate (go to completion) during time $\tau = t_f - t_i$. Then:

$$\Psi = W_{max}(\tau) = \max \left[A(t_i) - A(t_f) - T_0 \int_{t_i}^{t_f} \dot{S}_{tot} dt \right] \qquad (8)$$

where the last equality uses the Tolman-Fine form of the Second Law of thermodynamics [15].

The maximum search in equation (8) can either be constrained to exactly reach a given final state at time t_f (the initial state is always considered known), in which case ΔA is fixed, and the optimization becomes one of minimizing the entropy production, or also the final state may be included in the optimization, in which case Ψ must be evaluated by optimal control. If the final state is specified, a solution may not exist if τ is too short, since only a certain set of states can be reached from a given initial state in time τ. In addition, the finite-time availability does not necessarily have ΔA as its limit for very long times, because the system may contain internal relaxation processes which remain irreversible even for very slow operations. If there is a direct heat leak from the system reservoir to the surroundings, then a long process time may even reduce Ψ to 0. On the other hand, losses are not always detrimental to the performance of a system if they open up new pathways. Actually some processes depend on irreversibilities for their very existence (eg, [16]).

2.3. THERMODYNAMIC LENGTH

For static purposes, Weinhold [17,18] defined a metric on the abstract space of equilibrium states of a system represented by all its extensive variables X_i as:

$$\mathbf{M}_U = \left\{ \frac{\partial^2 U}{\partial X_i \partial X_j} \right\} \tag{9}$$

where U is the internal energy.

Based on this metric, Salamon and Berry [19] found a connection between the thermodynamic length along a process path and the (reversible) availability lost in the process. Specifically, if the system moves via states of local thermodynamic equilibrium from an initial equilibrium state i to a final equilibrium state f in time τ, then the dissipated availability $-\Delta A$ is bounded from below by the square of the distance (ie, length of the shortest path) from i to f times ε/t, where ε is a mean relaxation time of the system. If the process is endoreversible, the bound can be strengthened to:

$$-\Delta A \geqslant \frac{L^2 \varepsilon}{\tau} \tag{10}$$

where L is the length of the *traversed* path from i to f. Equality is achieved at constant thermodynamic speed $v = dL/dt$ corresponding to a temperature evolution given by [20]:

$$\frac{dT}{dt} = -\frac{vT}{\varepsilon\sqrt{C}} \tag{11}$$

where C is the heat capacity of the system. For comparison, the bound from traditional thermodynamics is only $-\Delta A \geqslant 0$.

An analogous expression exists for the total entropy production during the process:

$$\Delta S^u \geqslant \frac{L^2 \varepsilon}{\tau} \tag{12}$$

The length L is then calculated relative to the entropy metric:

$$\mathbf{M}_S = -\left\{ \frac{\partial^2 S}{\partial X_i \partial X_j} \right\} \tag{13}$$

In statistical mechanics, where entropy takes the form:

$$S(\{p_i\}) = -\sum_i p_i \ln p_i \tag{14}$$

the metric $\mathbf{M}_S$ is particularly simple, being the diagonal matrix [21]:

$$\mathbf{M}_S = -\left\{ \frac{1}{p_i} \right\} \tag{15}$$

The same procedure of calculating metric bounds for dynamic systems has been applied to coding of messages [22] and to economics [23].

More recently [24], we have relaxed a number of the assumptions in the original work, primarily those restricting the system to be close to equilibrium at all times and the average form of the relaxation time ε. The more general bound replacing equation (12) then becomes:

$$\Delta S^u \geqslant \frac{1}{\Xi} \left(\int_{\xi_i}^{\xi_f} \frac{1}{T\sqrt{C}} \left| \frac{dU}{d\xi} \right| \sqrt{1 + \frac{\theta}{CT}\frac{dU}{d\xi} + \ldots} \, d\xi \right)^2 \tag{16}$$

with $\Xi = \xi_f - \xi_i$ being the total duration of the process in natural dimensionless time units:

$$d\xi = dt/\varepsilon(T) \tag{17}$$

and where we have defined:

$$\theta(T) = 1 + \frac{T}{2C}\frac{\partial C}{\partial T} \tag{18}$$

The equality (lower bound) in equation (16) is achieved when the integrand is a constant, ie, when:

$$\frac{dS^u}{d\xi} = \text{constant} \tag{19}$$

Consequently, constant rate of entropy production, when expressed in terms of natural time, is the path or operating strategy which produces the least overall entropy.

One can express the optimal path in a form similar to equation (11):

$$\frac{dT}{dt}\sqrt{1 + \frac{\theta(T)\varepsilon(dT/dt)}{T} + \ldots} = \text{constant} \times \frac{T}{\varepsilon\sqrt{C}} \tag{20}$$

The constant thermodynamic speed algorithm, equation (11), is thus the leading term of the general solution in an expansion about equilibrium behaviour.

3. OPTIMAL PATH

A knowledge of the maximum work that can be extracted during a given process, eg, calculated by one of the procedures described in the previous section, may not by itself be sufficient. One may also want to know *how* this maximum work can be achieved, ie, the time path of the thermodynamic variables of the system. The primary tool for obtaining this path is optimal control theory (eg, [25-27]).

Typical manipulation usually leads to a set of coupled, non-linear differential equations for which a qualitative analysis and a numerical solution are the only hope. Thus answering the more demanding question about the optimal time path rather than the standard question about maximum performance requires a considerably larger computational effort. On the other hand, once the time path is calculated, all other thermodynamic quantities may be calculated from it, much like the wave function is the basis of all information in quantum mechanics.

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