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Minimal rate of entropy production as a criterion of merit for thermal engines

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Abstract. The optimization of a motor and a refrigerator, performing a Carnot-type cycle, is considered under the criterion that in their best mode of operation they should produce the minimum possible entropy per cycle. Time is introduced assuming heat transfers through walls with finite conductivities. These engines turn out to work optimally only in the quasi-static limit. Then the special case of constant rate of cooling for this refrigerator is analyzed, with the result that there now exists a regime of operation where the optimal condition is fulfilled in finite time. In this case minimal rate of entropy production, minimal loss of availability and maximum efficiency are all equivalent as criteria of merit.

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1. Introduction

In recent years, following the pioneering work of Curzon and Ahlborn [1], attention has been given to the study of thermal engines taking into account the finite duration of their cycles. The objetive of this 'finite time thermodynanmics' is to optimize the performance of machines according to a given criterion of excellence. For example, Curzon and Ahlborn optimized their engine making it run in such a way that the power it delivered was maximal. Another method employed has been to maximize the efficiency of work-producing cycles [2]. Yet another criterion has been to optimize processes by requiring that their rate of entropy production should be minimal. This approach has its analogue in a theorem of Prigogine according to which under stationary conditions, the fluxes in an open system not too far from equilibrium minimize the rate of entoropy production [3]. As a complement to these criteria, the concept of thermodynamic potentials has been generalized to finite time processes and used to obtain bounds on the work provided by open stationary processes [4]. The method consists of identifying some constriction of the form $g(\{\chi_j\}) = 0$, with $\{\chi_j\}$ state variables, satisfied along the process under consideration, and using it to make $\bar{d}W$, the work differential element, into a complete differential along this path. The bounds obtained through this approach are consistent with those coming from other methods.

Finite time thermodynamics has entered a dormant period lately, as the original wave of interest lost its momentum, in the absence of general principles and laws to guide research. The initial hope of generalizing the second law of thermodynamcis to finite times through the optimization of cycles, just the way it happened last century with the work of Carnot, remains unfulfilled. This lack of fundamental principles has also impeded meaningful comparison with the methods and results of other approaches to finite-time processes, such as irreversible [3] and extended [5] thermodynamics, for example.

Two main attempts have been made to provide a theoretical basis for finite time thermodynamics. The most recent one [6] generalizes the concept of availability to finite times, extending an earlier proposal by Tolman and Fine [7]. When considering a finite-time process $i \to f$ undergone by a given system in contact with a reservoir at temperature and pressure T_0, P_0, instead of Gibbs's inequality $W \leq -\Delta A$, where W is the work performed and $A = U + P_0V - T_0S - \sum_j \mu_{0j}N_j$ the available energy, Tolman and Fine write an equality:

$$W = -\Delta A - T_0 \int_{t_i}^{t_f} \dot{S}\, dt \tag{1}$$

where the integral is evaluated along a trajectory of equilibrium states chosen such that $\dot{S}$ is known explicitly along it. S being a state function, the choice of trajectory does not affect the value of W.

Andresen *et al.* [6] propose again an upper bound for the work provided:

$$W \leq \max W(\Sigma_0, \tau) \tag{2}$$

where $\max W$ denotes the maximum work $W(\Sigma_0, \tau)$ performed by a different, or "model" system Σ_0 that changes its parameters from their values at i to those at f in a time τ:

$$W(\Sigma_0, \tau) = -(\Delta A)_{\Sigma_0} - T_0 \int_0^{\tau} \dot{S}(\Sigma_0, t)\, dt \tag{3}$$

W is then calculated according to the Tolman-Fine prescription, and its extremum calculated varying some internal parameters of Σ_0, usually employing the technique of optimal control theory.

The weakest link in the chain of reasoning leading to the bound (2) on W is the choice of a "model" system Σ_0. Each system under study requires one, and no general rules are given to identify it. Thus it becomes an art to pick a good Σ_0, and this has greatly reduced the usefulness of the method just described to generalize the concept of change in availability when calculating bounds on the work performed in finite-time processes.

An earlier attempt to put the conceptual basis of finite-time thermodynamics on a firm foundation was made by Berry *et al.* [8], who employed minimal rate of entropy production as a criterion of merit for cyclic and general processes. In fact, when mechanical friction, turbulence, chemical reactions and other sources of entropy are neglected, leaving only heat transfers as irreversible processes, minimal rate of entropy production coincides with minimal loss of availability (*cf.* Appendix A in Ref. 8).

This criterion of minimal rate of entropy production has led to some general results about the performance of processes. For example, it implies that for an optimal n-branch cycle the entropy produced must be a constant along each branch, and this allows the calculation of bounds for the work provided by the cycle [8]. Nevertheless, the proof of these results normally employs the involved techniques of optimal control theory, which render the physical considerations of the problem somewhat obscure: eliminating unphysical solutions and determining the allowed ranges of parameters like conductivities, friction coefficients and reservoir temperatures in terms of the convexity of manifolds and the like, rapidly gets very complicated as the number of variables increases, making it difficult to grasp the physical meaning of the results.

In this article the simplest possible cycle is studied: the Carnot-type isothermal-adiabatic-isothermal-adiabatic process generalized to finite times by Curzon and Ahlborn. The aim is to discuss the implications of minimal rate of entropy production with a minimum of mathematical detail in order to emphasize the physical arguments.

The conclusions reached are: i) this criterion is fulfilled only in the quasi-static limit, both when the cycle works as a motor and when it does as a refrigerator; ii) If one restricts the refrigerator to the regime of constant rate of cooling the condition of minimal rate of entropy production can be satisfied in finite time, and this permits the type of analysis mentioned in the above paragraph.

2. Curzon and Ahlborn motor

This engine functions between two heat reservoirs, at temperatures T_1 and T_2 ($T_1 > T_2$), exchanging heat with them through walls at temperatures T_h (with the hot reservoir) and T_l (with the cool one), and describing a Carnot-type cycle (see Fig. 1a).

In our case the relevant function is $\dot{S} = \Delta S/\tau$, *entropy produced per cycle/duration of cycle*, and we will attempt to determine the internal temperatures T_h and T_l that minimize it.

As the working fluid of the engine goes through a cycle, assumed reversible ('endo-reversibility' requeriment), entropy will be produced only at the reservoirs, in the two isothermal branches. This hypothesis of endo-reversibility disregards turbulence, chemical reactions and other entropy producing mechanisms as the dominant sources of irreversibility. It is the usual assumption and serves the purpose of freeing the analysis from the details of the working substance. One then has:

$$\frac{Q_1}{T_h} - \frac{Q_2}{T_l} = 0 \qquad \text{(endo-reversibility)} \tag{4}$$

$$\Rightarrow (\Delta S)_{\text{cycle}} = Q_1\left(\frac{1}{T_h} - \frac{1}{T_1}\right) + Q_2\left(\frac{1}{T_2} - \frac{1}{T_l}\right) = \frac{Q_2}{T_2} - \frac{Q_1}{T_1} \tag{5}$$

(All Q's are taken positive). Time is introduced as a variable through finite conductivities at the walls where heat transfers take place,

$$Q_1 = \alpha t_1(T_1 - T_h) \tag{6}$$

$$Q_2 = \beta t_2(T_l - T_2) \tag{7}$$

where α and β are thermal conductivities, t_1 and t_2 the times during which heat flows, and a linear conduction law has been assumed: $dQ/dt = \sigma\Delta T$, with ΔT the temperature difference across a given diathermal wall, and σ its conductivity. The duration of the cycle is $\tau = t_1 + t_2$, *i.e.*, the adiabatic branches are taken to last negligibly compared to the isothermal ones. This is again the usual hypothesis and it amounts to neglecting the masses of pistons and other moving parts, and disregarding mechanical friction. Otherwise, their equations of motion would have to be included, complicating the problem. Inertial effects were considered in Ref. 9.

Using equations (4), (6), (7) and $\tau = t_1 + t_2$ to eliminate Q_1 and Q_2 one obtains for the rate of entropy production

$$\dot{S} = \frac{(\Delta S)_{\text{cycle}}}{\tau} = \left(\frac{\alpha\beta}{T_1 T_2}\right)\frac{x^2 y T_2 + x y^2 T_1}{\alpha T_2 x + \beta T_1 y + (\alpha - \beta) x y} \tag{8}$$

with $x = T_1 - T_h$ and $y = T_l - T_2$, the temperature differences across the walls. For a motor, $x \geq 0$ and $y \geq 0$ define the right directions of heat flow.

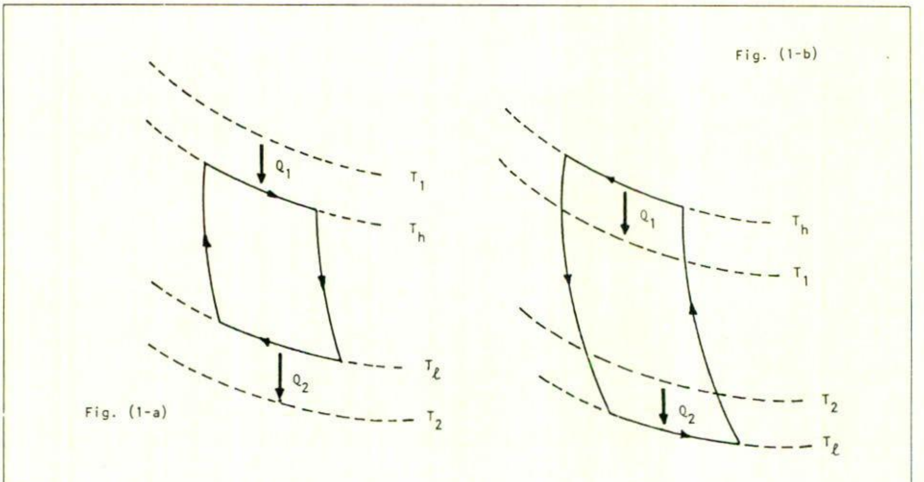

FIGURE 1. Cycles performed by the Curzon and Ahlborn motor [Fig. 1a], and its analogous refrigerator [Fig. 1b]. Non isothermal branches are adiabatic ones. Dashed lines denote isotherms and thick arrows indicate directions of heat flow.

Now, keeping the reservoir temperatures T_1 and T_2 fixed, the extrema of $\dot{S}$ will be sought varying x and y. Combining the extremal conditions $\partial\dot{S}/\partial x = 0$ and $\partial\dot{S}/\partial y = 0$ leads to $T_h/T_1 + T_l/T_2 = 0$, and this can only be satisfied in the trivial case $T_h = T_l = 0$. In fact examination of $\partial\dot{S}/\partial x$ and $\partial\dot{S}/\partial y$ shows that they are both positive for $x, y \geq 0$, and so $\dot{S}$ attains its minimal value ($\dot{S} = 0$) for $x = y = 0$, *i.e.*, for $T_h = T_1$, $T_l = T_2$, the quasi-static limit.

3. Curzon and Ahlborn-type refrigerator

It performs the cycle in Fig. 1b, where T_2 would correspond to the body being cooled and T_1 to the atmosphere. The endo-reversibility condition (*cf.* eq. (4)) leads to the same expression for $\dot{S}$ as in the case of the motor (eq. (8)), but now with $x \leq 0$ and $y \leq 0$ defining the right directions of heat flow. Both partial derivatives of $\dot{S}$ turn out to be negative for negative values of x and y (*i.e.* $\dot{S}$ positive and decreasing as we approach the origin from the left), and so the minimum of $\dot{S}$ is again attained in the quasi-static limit $x = y = 0$.

4. Refrigerator with fixed rate of cooling

Let us consider now the special case of fixed rate of cooling (*cf.* Fig. 1b): $Q_2/\tau = \text{const.} \equiv \lambda^{-1}$. The entropy produced per cycle becomes

$$\dot{S} = \left(\frac{Q_2}{\tau}\right)\left(\frac{T_h}{T_1 T_l} - \frac{1}{T_2}\right) \tag{9}$$

As Q_2/τ, T_1 and T_2 are constant, the minima of $\dot{S}$ will coincide with those of $f \equiv T_h/T_l$. Using $Q_2/\tau = \lambda^{-1}$ and $Q_1 = \alpha t_1(T_h - T_1)$, $Q_2 = \beta t_2(T_2 - T_l)$, $\tau = t_1 + t_2$ to eliminate T_h,

$$f = f(z) = (T_1)\frac{1 - \beta\lambda z}{\beta\lambda z^2 - \left(\beta\lambda T_2 + 1 - \frac{\beta}{\alpha}\right) z + T_2} \tag{10}$$

with $z = T_2 - T_l$.

This function has its extrema at $z = (1/\beta\lambda)[1 \pm (\beta/\alpha)^{1/2}]$. The solution with the minus sign will now be eliminated on physical grounds: one must have $z = T_2 - T_l > 0$, so $z = (1/\beta\lambda)[1 - (\beta/\alpha)^{1/2}]$ implies $\beta < \alpha$. One must have, too (*cf.* Fig. 1b), $T_h > T_1$, and this implies, using results from the former paragraph,

$$T_2 < -\left(\frac{\alpha}{\beta}\right)^{1/2} z\left[\beta\lambda z + \left(1 - \frac{\beta}{\alpha}\right)\right] \tag{11}$$

which is impossible to satisfy with $\beta < \alpha$. It is proved in a similar way that $z = (1/\beta\lambda)[1 + (\beta/\alpha)^{1/2}]$ is a physically acceptable solution, and calculating the second derivative of $f(z)$ one shows that it indeed corresponds to a minimum if

$$T_l > \frac{1}{\beta\lambda}\left(\frac{\beta}{\alpha}\right)^{1/2}\left[1 + \left(\frac{\beta}{\alpha}\right)^{1/2}\right] \tag{12}$$

The internal temperatures T_l and T_h that minimize entropy production per cycle are then readily obtained:

$$T_l = T_2 - \frac{1}{\beta\lambda}\left[1 + \left(\frac{\beta}{\alpha}\right)^{1/2}\right] \tag{13}$$

$$T_h = T_1 \left[1 + \frac{\frac{1}{(\alpha\beta)^{1/2}\lambda}\left[1 + \left(\frac{\beta}{\alpha}\right)^{1/2}\right]}{T_2 - \frac{1}{\beta\lambda}\left[1 + \left(\frac{\beta}{\alpha}\right)^{1/2}\right]^2}\right] \tag{14}$$

The physical condition $T_l < T_2$ is automatically satisfied in eq. (13), and $T_h > T_1$ implies

$$T_2 > \frac{1}{\beta\lambda}\left[1 + \left(\frac{\beta}{\alpha}\right)^{1/2}\right]^2 \tag{15}$$

From T_l and T_h given by equations (13) and (14), $(\dot{S})_{\min}$ can be written in terms of the fixed parameters of the system: λ, T_1, T_2, α, β. The resulting expression is not very informative and will not be reproduced here.

Consider now the work spent by the refrigerator,

$$\frac{W}{\tau} = \frac{Q_2}{\tau}\left(\frac{T_h}{T_l} - 1\right) \tag{16}$$

For fixed rate of cooling (Q_2/τ = const.) the minima of W/τ are again those of $f = T_h/T_l$, and the conditioin for minimal entropy production coincides with that for maximum efficiency, which is given by

$$\eta_{\max} = \frac{W_{\min}}{Q_1} = \left[1 - \frac{T_2}{T_1}\right] + \frac{Q_2/\tau}{\beta T_1}\left[1 + \left(\frac{\beta}{\alpha}\right)^{1/2}\right]^2 \tag{17}$$

This reduces to the Carnot expression in the limit $Q_2/\tau \to 0$, as required. The deviation from the Carnot value comes through an additive term, and so a refrigerator with fixed rate of cooling does not give rise to anything resembling the famous square root in $\eta = 1 - (T_2/T_1)^{1/2}$, the efficiency of a Curzon and Ahlborn motor working at maximum power.

5. Conclusion

- Minimal rate of entropy production is only attained in the quasi-static limit both for a Curzon and Ahlborn motor and for its analogous refrigerator. In the case of constant cooling rate, a refrigerator can be constructed that minimizes the entropy produced per cycle: its internal temperatures are given by equations (13) and (14), and conditions (12) and (15) must be satisfied for physical consistency.

In this regime of operation minimal rate of entropy production, minimal loss of availability and maximum efficiency are all equivalent as criteria of merit.

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Resumen. Se aplica el criterio de mínima razón de producción de entropía a un ciclo del tipo de Carnot funcionando en ambos sentidos, como motor y como refrigerador. El tiempo se introduce suponiendo transferencias de calor a través de paredes de conductividades finitas. En los dos casos el ciclo funciona de manera óptima sólo en el límite cuasi-estático. Se considera a continuación el caso especial de razón de enfriamiento constante para el refrigerador, encontrándose un régimen de operación óptimo con duración finita. En este régimen, mínima razón de producción de entropía, mínima pérdida de energía utilizable y máxima eficiencia son criterios de mérito equivalentes.