Coupled heat devices in linear irreversible thermodynamics

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Full analytical models of heat engines and refrigerators in linear irreversible thermodynamics can be defined by means of a chain of coupled heat devices. In this way it is possible to derive results and techniques of finite-time thermodynamics, like endoreversible efficiencies and the usual models of irreversible heat devices, in terms of an endoreversible energy converter plus a heat leak between external reservoirs. Also, a counterintuitive relationship is found between the global behavior of the chain and the individual performance of the devices: it is not necessary nor generally possible to impose the same operation regime on every device to achieve a desired overall performance.

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I. INTRODUCTION

One of the best-known results in equilibrium thermodynamics is Carnot's theorem [1], which states the upper bounds of energy conversion processes. Carnot showed that, for a heat device between two reservoirs at temperatures T_a and T_b ($T_a < T_b$), the maximum efficiency in the conversion is $\eta_C = 1-\tau$ ($\tau = T_a/T_b$) when working as a heat engine, while the maximum coefficient of performance (COP) when working as a refrigerator is $\epsilon_C = \tau/(1-\tau)$. These upper values have little practical relevance, since they refer to processes cycling along reversible paths which involve infinitely slow energy transfers. Real heat devices, on the contrary, work at nonzero power and evolve along irreversible paths coming from finite-time and finite-size unavoidable constraints.

Linear irreversible thermodynamics [2] focuses on the irreversible evolution of macroscopic systems, thus extending the scope of equilibrium thermodynamics. This theory, after a careful analysis of entropy sources of systems in local equilibrium, defines thermodynamic forces and fluxes that are related to each other by means of linear relationships governing the macroscopic evolution. But the identification of entropy sources in real energy converters is by no means obvious, and applications of the theory to real processes usually lead to complex equations from which it is hard to extract useful information. Because of these difficulties the theory has been up to now almost limited to the analysis of simple isothermal energy converters [3].

The limitations of both equilibrium and linear irreversible thermodynamics in describing the behavior of real heat devices and formulating useful criteria describing their performance has motivated the development of a new field known as finite-time thermodynamics (FTT) [4–10] which, while keeping the formalism as close as possible to that of equilibrium thermodynamics, introduces simple modifications to take into account the main sources of irreversibility observed in real devices. For example, the so-called irreversible Carnot-like models have a relative analytical simplicity and are able to account for irreversibilities due to finite-rate heat transfers between the working fluid and the external heat sources, internal dissipation of the working fluid, and heat leaks between reservoirs (see Refs. [9,10] for a recent review). Simplified, limiting models are those based on the endoreversible approximation [8,11] where the only sources of irreversibility are the heat transfers between the external reservoirs and the working system. A paradigmatic model in this context is due to Curzon and Ahlborn [11] (see also [12]), who studied a Carnot heat engine cycle coupled to external reservoirs and assumed that the heat transfers obey a Fourier law. They showed that the efficiency of this engine at maximum power is given by $\eta_{CA} = 1-\sqrt{\tau}$, known as the Curzon-Ahlborn efficiency. This expression, though subject to some controversy [13], provides a surprisingly good approximation to the observed efficiencies of very different power plants [8–10,14,15] suggesting that it represents a "universal" behavior rather than a model specific feature.

The analysis of Curzon and Ahlborn is not bound to devices working near equilibrium; hence it does not seem easy to reproduce within the framework of linear irreversible thermodynamics. Any attempt should first substitute simple FTT models by an exhaustive macroscopic description of the heat device, and then one must integrate involved differential equations describing the local behavior of such systems to get information about its performance. However, this program has been carried out recently, showing that the Curzon-Ahlborn efficiency and other endoreversible features discovered in FTT models of heat engines and refrigerators can be derived without approximations from the principles of linear irreversible thermodynamics [16–19], thus supporting their validity and generality. The starting point is the analysis of a chain (or "cascade") of coupled heat devices working between small temperature differences. Similar systems have attracted attention in FTT and also played a prominent role in the development of some of the most basic results of equilibrium thermodynamics, like the definition of the absolute temperature scale. Here in this paper they are considered from the point of view of linear irreversible thermodynamics to construct full models of heat devices working between arbitrary temperature differences. Unlike FTT models of heat devices (which are characterized by means of a reduced number of parameters), the systems considered in these works involve an infinite number of parameters like transport coefficients and thermodynamic forces, yet they can be tackled analytically.

The cascade construction was first introduced in [16], where the Curzon-Ahlborn efficiency was derived under the

assumption that the unit devices work individually at maximum power. Similar reasoning can be applied to analyze different working regimes of refrigerators [18]. In a subsequent work [19], we considered a chain of coupled heat engines placed along a monotonic temperature profile and proved that these derivations are particular cases of a much more general result: because of the couplings between adjacent devices in the chain, the thermodynamic forces and fluxes must satisfy a nonlinear differential equation whose solution depends on an integration constant. This constant can be viewed as a control parameter that fixes the operation regime of the whole chain. Quite surprisingly, the "global" operation regime of the chain does not generically coincide with those of the individual devices: for instance, when the chain works at maximum power, the individual devices generically do not work individually at maximum power (except for a very special form of the transport coefficients [19]), yet the Curzon-Ahlborn efficiency and other endoreversible features can be derived without the *a priori* assumption of a particular working regime for the individual devices. It suffices to introduce a certain delicate balance among the transport coefficients, which indeed implies that the thermodynamic fluxes are perfectly coupled along the chain.

With the present work we give details and extend our previous Letter and discuss some of its implications. Our main goals are (i) to extend the above study [19] for arbitrary temperature profiles (not necessarily monotonic), (ii) to develop a unified description within linear irreversible thermodynamics of nonisothermal energy converters including heat engines and refrigerators, (iii) to analyze for each device class some optimum operation regimes, comparing the results with those obtained in FTT for endoreversible and irreversible Carnot-like models, and (iv) to provide an interpretation within linear irreversible thermodynamics of heat leaks, which play a prominent role in the formulation of irreversible models of FTT [9,10]. The paper is organized as follows. In Sec. II we introduce a general formalism which describes chains of generic heat devices working along arbitrary temperature profiles in linear irreversible thermodynamics. The main result will be presented in Sec. III: a nonlinear differential equation linking the thermodynamic forces and transport coefficients in the steady state. Though its solution in the most general case is unknown to the authors, it can be fully worked out when the thermodynamic fluxes are perfectly coupled for otherwise arbitrary temperature profile and transport coefficients (Sec. III A). In any other case it is always possible to find a special temperature profile (Sec. III B) which allows us to decompose the system in terms of a chain with perfectly coupled thermodynamic fluxes plus a heat leak; such a decomposition could be viewed as the linear irreversible thermodynamics equivalent to some irreversible FTT models where an endoreversible heat converter is supplemented with a heat leak between external reservoirs. Also, various particular models for specific choices of the transport coefficients are considered in Sec. III C; they provide additional intuition about the behavior of the system beyond the perfectly coupled limit. In Sec. IV we perform a systematic analysis of several operation regimes when the chain works as a heat engine or as a refrigerator, and compare the results with those coming from FTT. We analyze in Sec. V the behavior of the individual devices when a collective working regime for the chain as a whole has been selected. Finally, the summary and discussion of our findings are presented in Sec. VI.

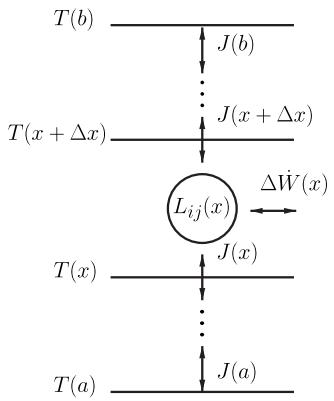

FIG. 1. Chain of coupled heat devices. If the unit device works as an engine and $T(x+\Delta x)>T(x)$ the heat fluxes $J(x+\Delta x)$ and $J(x)$ point downward and the power $\Delta\dot{W}(x)$ points outside the device. The direction of these fluxes is reversed when the unit works as a refrigerator.

II. BASIC FRAMEWORK

Let us consider a chain of coupled energy converters, each working between different heat reservoirs with well-defined temperatures. These reservoirs are labeled by the coordinate $x\in[a,b]$ and form a temperature profile $T(x)$ which varies from $T(a)=T_a$ to $T(b)=T_b$. The devices operate in a stationary state where all the magnitudes are time independent (we could also consider periodic states for devices evolving cyclically; in this last case the relevant averaged magnitudes per period eventually become time independent.) Moreover, the device units are coupled in the following sense: the heat output (input) per unit of time (or per period, in the case of cyclic heat converters) from the device unit at $T(x+\Delta x)$ is exactly equal to the heat input (output) to the next device unit at $T(x)$. Hence, the complete chain can be considered as a single energy converter whose overall behavior is determined by heat exchanges with the reservoirs at $x=a$ and $x=b$.

To see this, consider the generic unit device sketched in Fig. 1: heat is allowed to flow at rates $J(x+\Delta x)$ and $J(x)$ at the reservoirs $T(x+\Delta x)$ and $T(x)$, respectively, and the difference between these fluxes is exchanged with the surroundings as work at a rate $\Delta\dot{W}(x)$. This work is done via a force $f(x)\Delta x$ with conjugate flux $v(x)$; hence $\Delta\dot{W}(x)=f(x)v(x)\Delta x$. Conservation of energy in the device implies that $J(x+\Delta x)=J(x)+f(x)v(x)\Delta x$. Therefore in the limit $\Delta x\to 0$ the heat flux is a continuous function of the variable x and its derivative $J'(x)$ with respect to x has a form prescribed by the conservation of energy:

$$J'(x)=f(x)v(x). \tag{1}$$

Integrating this equation gives the net power exchanged by the chain in terms of the heat fluxes $J_a=J(a)$ and $J_b=J(b)$ at the reservoirs T_a and T_b, respectively,

$$\dot{W} = \int_a^b dx\, f(x)v(x) = J_b - J_a. \tag{2}$$

Since the devices operate in a stationary state, all the entropy they produce must be eventually transferred to the heat reservoirs. Hence, the rate of entropy production at the device unit working between temperatures $T(x)$ and $T(x+\Delta x)$ can be written in terms of the heat exchanged with the corresponding reservoirs: $\Delta\dot{S}(x) = J(x+\Delta x)/T(x+\Delta x) - J(x)/T(x)$. Taking into account the conservation of energy [Eq. (1)] we get at first order in Δx

$$\Delta\dot{S}(x) = \left(v(x)\frac{f(x)}{T(x)} - J(x)\frac{T'(x)}{T(x)^2} \right)\Delta x + O(\Delta^2 x). \tag{3}$$

This last equation implies in the limit $\Delta x \to 0$ that $\dot{S}'(x) = [J(x)/T(x)]'$. An integration from a to b gives the following expression for the total rate of entropy production of the chain:

$$\dot{S} = \frac{J_b}{T_b} - \frac{J_a}{T_a}, \tag{4}$$

which says that only the reservoirs at $x=a$ and $x=b$ experience net changes in the entropy.

So far we have written the main overall thermodynamic quantities of the chain in terms of the heat fluxes J_a and J_b. Now we go a step further and try to relate these heat fluxes to the specific properties of our chain. To this end a physical model of the energy conversions taking place at each device unit must be proposed. We realize that Eq. (3) suggests considering $f(x)/T(x)$ and $[1/T(x)]' = -T'(x)/T^2(x)$ as generalized thermodynamic forces with conjugate fluxes $v(x)$ and $J(x)$, respectively. For small values of the thermodynamic forces and under the assumption of local equilibrium, linear irreversible thermodynamics [2] allows us to write the following relationships:

$$v(x) = L_{11}(x)\frac{f(x)}{T(x)} + L_{12}(x)\left(\frac{1}{T(x)}\right)', \tag{5}$$

$$J(x) = L_{21}(x)\frac{f(x)}{T(x)} + L_{22}(x)\left(\frac{1}{T(x)}\right)', \tag{6}$$

where $L_{ij}(x)$ are Onsager coefficients. They depend on intensive parameters (like temperature and others) defining the state of local equilibrium [2] at each point of the chain; therefore these coefficients are functions of the coordinate x that labels the heat reservoirs. In addition they satisfy

$$L_{11}(x) \geq 0, \quad L_{12}(x) = L_{21}(x), \quad L_{22}(x) \geq 0,$$

$$L_{11}(x)L_{22}(x) - L_{12}(x)^2 \geq 0. \tag{7}$$

These properties ensure the positivity of Eq. (3) and therefore that of the total entropy production [Eq. (4)]. Moreover, the coefficients $L_{ij}(x)$ can be combined into the so-called coupling strength parameter,

$$q(x) = \frac{L_{12}(x)}{\sqrt{L_{11}(x)L_{22}(x)}}, \tag{8}$$

which measures the degree of coupling between the fluxes $v(x)$ and $J(x)$. As a consequence of Eq. (7) this parameter is bounded, $q(x) \in [-1,1]$.

III. THE COUPLING CONDITION

Once the temperature profile $T(x)$ and the Onsager coefficients $L_{ij}(x)$ are fixed, the force profile $f(x)$ cannot be chosen at random. The reason is that conservation of energy in every device unit expressed by Eq. (1) together with the transport equations (5) and (6) implies a Ricatti differential equation for $f(x)$:

$$[L_{12}(x)f(x)]' = L_{11}(x)f^2(x) - T(x)\left[L_{22}(x)\left(\frac{1}{T(x)}\right)' \right]'. \tag{9}$$

For simplicity we will frequently assume that the coupling strength parameter is independent of x $[q(x)=q]$; then we can make use of Eq. (8) to eliminate $L_{11}(x)$ in Eq. (9):

$$[L_{12}(x)f(x)]' = \frac{[L_{12}(x)f(x)]^2}{q^2 L_{22}(x)} - T(x)\left[L_{22}(x)\left(\frac{1}{T(x)}\right)' \right]'. \tag{10}$$

Obviously, these differential equations can be numerically integrated, but it will prove to be useful to consider some analytical solutions. The first difficulty is that in the most general case there is no way of writing the general solution of Eq. (9) or (10) by using some quadratures. However, one can integrate it completely if some extra information is added.

For instance, let us suppose that some particular solution $f_0(x)$ of Eq. (10) is known. Then it can be reduced to an inhomogeneous first-order linear differential equation and the general solution is found by two quadratures [20]. It is easy to check that the force profile can be written as

$$f(x;\lambda) = f_0(x) - \frac{\lambda\theta^2(x)}{L_{12}(x)[1+\lambda h(x)]}, \tag{11}$$

where λ is an integration constant and $\theta(x)$ denotes a positive function defined in terms of the particular solution $f_0(x)$,

$$\theta(x) = T_a \exp\left(\int_a^x ds \frac{L_{12}(s)f_0(s)}{q^2 L_{22}(s)} \right). \tag{12}$$

Finally, $h(x)$ is a positive, increasing function of x:

$$h(x) = \int_a^x ds \frac{\theta^2(s)}{q^2 L_{22}(s)}. \tag{13}$$

Clearly, in order to avoid divergences in Eq. (11), it is necessary that $\lambda > -1/h(b)$, otherwise the linear relationships (5) and (6) would be difficult to justify.

Once the general form of the force profile [Eq. (11)] is known we can proceed to calculate the relevant thermodynamic quantities. But we should notice that the particular solution $f_0(x)$ in Eq. (12) usually cannot be found in a systematic way.

A. Case $|q|=1$: Perfectly coupled fluxes

There exists an interesting class of functions $L_{ij}(x)$ which allows us to find a particular solution $f_0(x)$ of Eq. (10) quite easily by physical arguments. Let us consider the force profile that cancels the flux $v(x)$ [Eq. (5)]:

$$f_{\text{stop}}(x) = \frac{L_{12}(x)}{L_{11}(x)} \frac{T'(x)}{T(x)}. \tag{14}$$

This force profile is not acceptable, since in the most general case it does not represent a solution of Eq. (10). However, when the coupling strength parameter is $|q(x)|=1$ for all the device units along the chain, $v(x)$ and $J(x)$ are related by $J(x)=L_{12}(x)v(x)/L_{11}(x)$, and if one of them vanishes the other flux must vanish also. Taking into account that $L_{11}(x)=L_{12}^2(x)/L_{22}(x)$ when $|q(x)|=1$, Eq. (14) can then be rewritten as

$$f_{\text{stop}}(x) = \frac{L_{22}(x)}{L_{12}(x)} \frac{T'(x)}{T(x)} [|q(x)| = 1]. \tag{15}$$

This expression cancels Eqs. (3), (5), and (6), thus ensuring an equilibrium state in which the fluxes and the entropy production vanish. We mention that Eq. (3) together with Eqs. (5) and (6) defines a quadratic form in the thermodynamic forces that becomes degenerate for $|q(x)|=1$; in this situation it can be canceled by nonzero forces. Equation (1) is also satisfied, which implies that we can take Eq. (15) as the particular solution $f_0(x)$ in (12) so that Eq. (10) is fully solved for $|q(x)|=1$. Actually the function (12) is $\theta(x)=T(x)$ and together with $q^2=1$ fixes $h(x)$ [Eq. (13)], thus the force profile (11) is determined up the integration constant λ:

$$f(x;\lambda) = f_{\text{stop}}(x) - \frac{\lambda T(x)^2}{L_{12}(x)[1+\lambda h(x)]}. \tag{16}$$

Equation (16) together with the temperature profile $T(x)$ and the transport coefficients completely fixes the thermodynamic behavior of our system. For instance, the heat flux [Eq. (6)] crossing each reservoir is simply

$$J(x;\lambda) = \frac{-\lambda T(x)}{1+\lambda h(x)}, \tag{17}$$

and the total power exchanged by the array [Eq. (2)] is given by

$$\dot{W}(\lambda) = J_b(\lambda) - J_a(\lambda) = -\lambda \left(\frac{T_b}{1+\lambda h(b)} - T_a \right). \tag{18}$$

Equation (17) provides a direct physical interpretation of the parameter λ: substituting $x=a$ and taking into account that $h(a)=0$ one finds $\lambda=-J_a/T_a$, that is, the rate of entropy production at reservoir T_a.

B. Case $|q|<1$: Heat leaks

When $|q(x)|=1$ the situation could be summarized by saying that both thermodynamic fluxes are canceled by a force profile $f_{\text{stop}}(x)$ defined in terms of the temperature profile and the transport coefficients [Eq. (15)] so that it is a solution of Eq. (10). However, for $|q(x)|<1$, the entropy production Eq. (3) is not degenerate and vanishes for $[1/T(x)]'=0$ and $f(x)/T(x)=0$ only. Therefore outside equilibrium the thermodynamic fluxes do not simultaneously cancel and we cannot follow a similar line of reasoning as for $|q(x)|=1$ to find a particular solution $f_0(x)$ of Eq. (9). However, there exists a different possibility which reduces the solutions of Eq. (9) to those obtained in the previous section at the cost of assuming a very special temperature profile.

Let us consider a chain with transport coefficients $\{L_{ij}(x)\}$ and $|q(x)|<1$. We first realize that the linear dependence of Eq. (9) with respect to the Onsager coefficients suggests performing a decomposition of the system into two auxiliary chains working in parallel, with transport coefficients $\{L_{ij}^*(x)\}$ and $\{L_{ij}^{**}(x)=L_{ij}(x)-L_{ij}^*(x)\}$ subjected to the same temperature and force profiles. The coefficients $\{L_{ij}^*(x)\}$ are chosen so as to give a coupling-strength parameter $|q^*(x)|=1$ for the first chain. In principle, there are many ways to satisfy this condition, and we look for those that correspond to a direct thermal contact between the reservoirs T_a and T_b by means of a heat leak J^{**} across the second chain. Since in such a case no work is consumed or extracted from this chain, the heat flux J^{**} does not depend on x. Therefore Eq. (1) implies that $f(x)v^{**}(x)=0$, where $v^{**}(x)$ denotes the flux conjugate to $f(x)$ along the second chain. This constraint can be satisfied if

$$v^{**}(x) = L_{11}^{**}(x) \frac{f(x)}{T(x)} + L_{12}^{**}(x) \left(\frac{1}{T(x)} \right)' = 0, \tag{19}$$

which defines a relationship between the thermodynamic forces: different forces $f(x)$ will generally entail different temperature profiles $T(x)$.

It would be highly desirable that our analysis could work for a fixed temperature profile irrespective of the force $f(x)$. This is indeed the case if the transport coefficients of the two auxiliary chains are defined by

$$L_{11}^*(x) = L_{11}(x), \quad L_{12}^*(x) = L_{12}(x), \quad L_{22}^*(x) = L_{12}^2(x)/L_{11}(x) \tag{20}$$

and

$$L_{11}^{**}(x) = 0, \quad L_{12}^{**}(x) = 0 \quad L_{22}^{**}(x) = L_{22}(x) - L_{22}^*(x). \tag{21}$$

Equations (20) and (21) together with the properties (7) ensure that $L_{22}^*(x)$ and $L_{22}^{**}(x)$ are non-negative functions. On the other hand, Eq. (8) implies that the first chain has a coupling-strength parameter $|q^*(x)|=1$ whose properties are thus known in detail (Sec. III A). Moreover, the condition $v^{**}(x)=0$ holds for any force profile so that the heat flux J^{**} across the second chain constitutes a heat leak. We see from Eqs. (6) and (21) that it must satisfy

$$J^{**} = L_{22}^{**}(x) \left(\frac{1}{T(x)} \right)'. \tag{22}$$

Therefore the price we have to pay to perform the decomposition amounts to assuming a monotonic temperature profile $T(x)$ given by

$$\frac{1}{T(x)} = \frac{1}{T_a} + J^{**}\int_a^x \frac{ds}{L_{22}^{**}(s)}. \tag{23}$$

The condition $T(x=b)=T_b$ fixes the value of the heat leak. It can be expressed in the form of an effective linear law,

$$J^{**} = -\kappa(T_b - T_a), \tag{24}$$

where κ is the effective thermal conductance across the second chain,

$$\kappa = \int_a^b ds \frac{T(s)^2}{L_{22}^{**}(s)}, \tag{25}$$

or in the form of an effective inverse law,

$$J^{**} = \tilde{\kappa}\left(\frac{1}{T_b} - \frac{1}{T_a}\right), \tag{26}$$

where $\tilde{\kappa}$ is given by

$$\tilde{\kappa} = \left(\int_a^b \frac{ds}{L_{22}^{**}(s)}\right)^{-1}. \tag{27}$$

In any case it is clear that the heat leak flows toward the colder reservoir.

In order to check the consistency of the decomposition, we first note that for the temperature profile given by Eq. (23) the derivative in the second term of the right-hand side of Eq. (9) can be written as

$$\left[L_{22}(x)\left(\frac{1}{T(x)}\right)'\right]' = \left[L_{22}^{*}(x)\left(\frac{1}{T(x)}\right)'\right]', \tag{28}$$

where we have used the definition $L_{22}(x)=L_{22}^{*}(x)+L_{22}^{**}(x)$ and the fact that the right-hand side of Eq. (22) does not depend on x. Because of Eqs. (20) and (28) the differential equation (9) then reduces to the equivalent one for the first auxiliary chain:

$$[L_{12}^{*}(x)f(x)]' = L_{11}^{*}(x)f^2(x) - T(x)\left[L_{22}^{*}(x)\left(\frac{1}{T(x)}\right)'\right]'. \tag{29}$$

Therefore the original chain and the first of the two auxiliary chains share the same force profiles $f(x)$, while the second auxiliary chain gives rise to a heat leak.

C. Case $|q|<1$: Some particular models

As a final group of analytical solutions of Eq. (9) we consider specific models with constant $|q|\leq 1$ for which (i) the temperature profile strictly increases from T_a to T_b so that we can use the temperature $T\in[T_a,T_b]$ to label each reservoir and the corresponding quantities, and (ii) the transport coefficients are of the form

$$L_{ij}(T) = l_{ij}T^n, \tag{30}$$

where l_{ij} are constants such that the properties (7) are satisfied. In this way the existence of particular solutions of Eq. (10) of the form $f_0(T)=\alpha/T$ is guaranteed for a wide class of models with constant $q\in[-1,1]$.

To see this, let us substitute the transport coefficients (30) and the force profile $f(T)=\alpha/T$ in Eq. (10). Taking into account that the derivatives must be performed with respect to T, we get an equation of second degree in α whose solutions are of the form

$$\alpha = \frac{q^2 l_{22}}{l_{12}}\beta, \tag{31}$$

where β is a coefficient which solely depends on n and q,

$$\beta = \frac{1}{2}[(n-1) \pm \sqrt{(n-1)^2 - 4(n-2)/q^2}]. \tag{32}$$

The function $\theta(T)$ [Eq. (12)] is therefore

$$\theta(T) = \frac{T^\beta}{T_a^{\beta-1}}, \tag{33}$$

and the integral defining the function $h(T)$ [Eq. (13)] can be performed analytically:

$$h(T) = \frac{T_a^{(3-n)}}{(2\beta - n + 1)q^2 l_{22}}\left[\left(\frac{T}{T_a}\right)^{(2\beta-n+1)} - 1\right]. \tag{34}$$

The force profile (11) is then given by

$$f(T;\lambda) = \frac{\alpha}{T} - \frac{\lambda T^{(2\beta-n)}}{l_{12}T_a^{2(\beta-1)}[1+\lambda h(T)]}, \tag{35}$$

where α, β, and $h(T)$ are defined in Eqs. (31), (32), and (34), respectively.

According to Eq. (32), the existence of particular solutions of the form $f_0(T)=\alpha/T$ is guaranteed for $n\leq 2$ and also for $n>2$ when $|q|$ is not too small. The simplest situations correspond to $n=1$ ($\beta=\pm 1/|q|$) and $n=2$ ($\beta=0,1$); the case $n=0$ (constant L_{ij}) was considered in [19]. Irrespective of the value of n, the coefficient β is real for $|q|=1$. In such a case, one of its two possible values is $\beta=1$, so that $\theta(T)=T$ and Eqs. (34) and (35) correspond to the force profile (16) for the specific set of transport coefficients defined by Eq. (30). These models cannot be generally reduced when $|q|<1$ to the simple scheme discussed in the previous section of a chain with $|q|=1$ plus a heat leak. The reason is that Eq. (22) cannot be satisfied for a constant (T-independent) heat leak except for $n=2$.

IV. COLLECTIVE OPERATION REGIMES

The integration constant λ in the solutions Eq. (11) of the Ricatti differential equation determines which kind of energy converter we have. Let us assume that $T_a<T_b$: when $|q|=1$ a closer inspection of Eqs. (17) and (18) shows that the system works as a refrigerator ($J(x)>0$, i.e., heat flows up the temperature gradient and the power $\dot{W}>0$ is consumed by the array) for $-1/h(b)<\lambda<0$, while it works as an engine [$J(x)<0$ and $\dot{W}<0$] only for $0<\lambda<(1/\tau-1)/h(T_2)$ (Fig. 2). Finally, when $\lambda>(1/\tau-1)/h(b)$ heat flows down the temperature gradient and work is dissipated into the reservoirs.

But λ can be furthermore viewed as a control parameter which allows us to select different operation regimes when

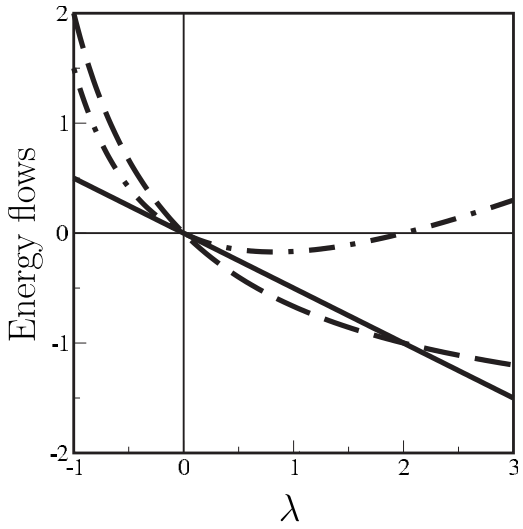

FIG. 2. $J_a=J(a)$ (solid line), $J_b=J(b)$ (dashed line), and $\dot{W}$ (dot-dashed line) vs λ [Eqs. (17) and (18)] in a model with Onsager coefficients given by Eqs. (30)–(35) with parameters (in arbitrary units) $n=2$, $l_{11}=l_{22}=1$, $T_a=0.5$, $T_b=1$, and $q=1$.

the chain works as a heat engine or as a refrigerator. In both cases two natural figures of merit can be proposed immediately: an efficiency defined as the ratio between the useful energy extracted from the device and the input energy, and the useful energy extracted from the device. These figures of merit correspond to the thermodynamic efficiency and the output power in the case of heat engines, and to the COP and the cooling power (that is, the heat extracted from the colder reservoir per unit of time or per cycle) when the device works as a refrigerator.

In addition to efficiencies and useful energies, one can consider different figures of merit. Since "one can't have it all" [21] some compromise-based criteria have been proposed [4–7,9,10], some of them inspired by economic [6] or ecological [22] considerations. Here we consider the so-called Ω criterion [23], which is based on a figure of merit that does not depend on particular derivations of the entropy production nor on external parameters to the heat device. It represents a trade-off between useful energy delivered and energy lost by any energy converter that is specially easy to implement. When the chain works as a heat engine this figure of merit (the Ω function) can be written as

$$\Omega(\lambda) = 2\dot{W}(\lambda) - (\eta_{\max} + \eta_{\min})J_a(\lambda), \tag{36}$$

where $\eta_{\max}$ and $\eta_{\min}$ denote, respectively, the maximum and minimum efficiencies of the chain upon variation of the parameter λ. On the other hand, when the chain works as a refrigerator the Ω function now reads

$$\Omega(\lambda) = 2J_a(\lambda) - (\epsilon_{\max} + \epsilon_{\min})\dot{W}(\lambda), \tag{37}$$

where $\epsilon_{\max}$ and $\epsilon_{\min}$ represent the maximum and minimum COPs of our system. The Ω function gives a performance regime placed between those of maximum efficiency and maximum useful energy which has been been found in macroscopic FTT models [23], in mesoscopic systems rectifying thermal fluctuations [24–26] (Brownian motors [27,28]), or even in quantum heat devices [29]; we will consider it in the following together with efficiencies and useful energies as a figure of merit to be optimized.

A. Heat engines

The most popular performance criteria for heat engines is the thermodynamic efficiency. When the chain works as an engine (Fig. 2 $\lambda>0$) and assuming that $T_a<T_b$, it can be written as

$$\eta(\lambda) = \frac{\dot{W}(\lambda)}{J_b(\lambda)} = 1 - \frac{J_a(\lambda)}{J_b(\lambda)}. \tag{38}$$

The power is also a commonly considered figure of merit in engines. The parametric plot of efficiency versus power is an open curve typical of endoreversible Carnot-like models for $|q|=1$, while for $|q|<1$ the plot becomes loop shaped where maximum efficiency and maximum power are close but noncoincident points [Fig. 3(a)], in agreement with results of real heat engines and with predictions of irreversible models in FTT [8–10].

1. Maximum efficiency

The maximum efficiency regime usually corresponds to a value of the parameter $\lambda=\lambda_\eta$ determined by the equation

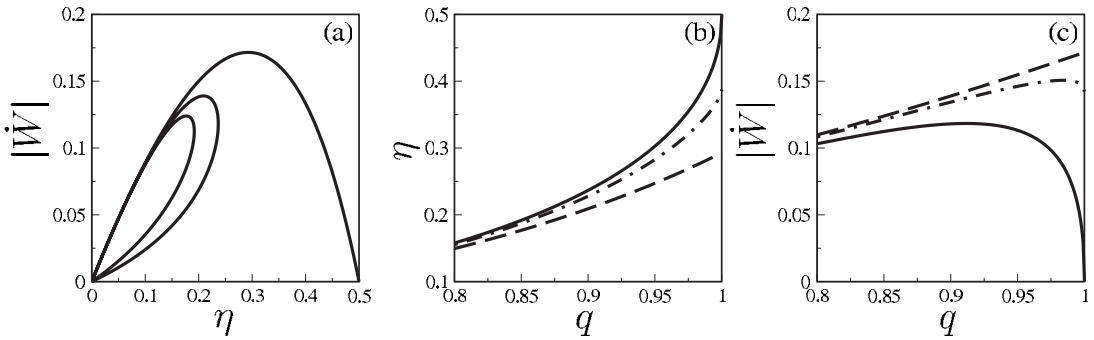

FIG. 3. (a) Power output vs efficiency in an engine model based on Eqs. (30)–(35) with parameters (in arbitrary units) $n=2$, $l_{11}=l_{22}=1$, $T_a=0.5$, and $T_b=1$. From top to bottom: $q=1$, 0.9, and 0.85. (b) Efficiency vs the coupling strength parameter q for the same engine model at maximum efficiency (solid line), maximum power (dashed line), and maximum Ω (dot-dashed line). (c) Power output vs q for the same model and operation regimes.

$\partial\eta(\lambda)/\partial\lambda=0$. Figure 3(b) shows that the maximum efficiency is an increasing function of the coupling strength parameter which attains the Carnot limit at $|q|=1$.

This limit can be easily analyzed, since for $|q|=1$ the efficiency (38) is a strictly decreasing function of λ,

$$\eta(\lambda) = 1 - [1 + \lambda h(b)]\frac{T_a}{T_b}, \tag{39}$$

and therefore the maximum efficiency is reached at the beginning of the engine interval, $\lambda_\eta=0$. Such a result is not surprising, since for $\lambda=0$ we have $f(x)=f_{\text{stop}}(x)$ [Eq. (15)], so that every engine unit in the chain is in equilibrium and works with an efficiency given by the Carnot value $\eta(x)=\Delta T(x)/T(x)$. Because of the invariance of the Carnot efficiency under the coupling of engines [16], the whole chain amounts to a single equilibrium engine working between the temperatures T_a and T_b with $\dot{W}=0$ and its efficiency is given by the Carnot bound. We mention that, due to the reversible behavior of engines near equilibrium, the sign of the heat fluxes and the power changes upon variation of λ in the neighborhood of $\lambda=0$ (Fig. 2).

2. Maximum power

The maximum power regime of the chain is characterized by means of the equation $\partial\dot{W}(\lambda)/\partial\lambda=0$. Figures 3(b) and 3(c) show that in this regime both the efficiency and the output power are increasing functions of the coupling strength parameter for $q>0$. In addition, the efficiency attains the Curzon-Ahlborn value in the limit $|q|\to 1$.

We will show in the following that the Curzon-Ahlborn efficiency is a fundamental result in linear irreversible thermodynamics for chains of coupled heat engines working at maximum power along arbitrary temperature profiles with no other restrictions imposed on the Onsager coefficients than that the coupling strength parameter (8) satisfies $|q(x)|=1$. Solving the equation $\partial\dot{W}(\lambda)/\partial\lambda=0$, we get after some algebra a second-order equation with two roots of opposite sign. The negative root must be discarded, since it lies outside the allowed interval $(-1/h(b),+\infty)$. Substituting the positive root

$$\lambda_{\dot{W}} = h(b)^{-1}\left(\sqrt{\frac{T_b}{T_a}} - 1\right) \tag{40}$$

in Eq. (18) gives the maximal power output [Fig. 3(c)],

$$\dot{W}_{\max} = -h(b)^{-1}(\sqrt{T_b} - \sqrt{T_a})^2, \tag{41}$$

which mimics familiar results in FTT with the factor $h(b)^{-1}$ playing the role of an averaged thermal conductance between T_a and T_b [8,9,14]. Finally, Eqs. (39) and (40) give the Curzon-Ahlborn result for the efficiency at maximum power,

$$\eta_{\text{CA}} = 1 - \sqrt{\frac{T_a}{T_b}}. \tag{42}$$

3. Maximum Ω

To define the Ω function when the chain works as an engine [Eq. (36)], we must first find the maximum and minimum values of the efficiency ($\eta_{\max}$ and $\eta_{\min}$) upon variation of the control parameter λ. The value of $\eta_{\max}$ follows from the analysis of the maximum efficiency regime discussed in Sec. IV A 1, while for the minimum efficiency one must take $\eta_{\min}=0$, since $\dot{W}(\lambda)\le 0$ when the chain works as an engine and $\dot{W}(\lambda)>0$ for λ large enough. Because of the continuity of $\dot{W}(\lambda)$, there is a special $\lambda>0$ which cancels the power output while $J_b\neq 0$ so that $\eta_{\min}=0$. Equation (36) is therefore completely determined and the solution of $\partial\Omega(\lambda)/\partial\lambda=0$ allows us to identify the regime of maximum Ω which, as Figs. 3(b) and 3(c) show, corresponds to a performance placed between those of maximum efficiency and maximum power.

We found in Sec. IV A 1 that the value of $\eta_{\max}$ in Eq. (36) is given by the Carnot efficiency for $|q|=1$. In this case the maximum $\Omega(\lambda)$ is reached at

$$\lambda_\Omega = h(b)^{-1}\left(\sqrt{\frac{1+\tau}{2\tau}} - 1\right), \tag{43}$$

where $\tau=T_a/T_b$. The efficiency (39) prescribed by (43) is

$$\eta_\Omega = 1 - \sqrt{\frac{\tau(1+\tau)}{2}}, \tag{44}$$

a well-known result of some ecological endoreversible models in FTT [9,10,22,23].

B. Refrigerators

When the chain works as a refrigerator a heat flux $J_a(\lambda)$, also known as the cooling power, is extracted from the cold reservoir at temperature T_a at the cost of an expenditure of power $\dot{W}(\lambda)$. The coefficient of performance, defined as

$$\epsilon(\lambda) = \frac{J_a(\lambda)}{\dot{W}(\lambda)}, \tag{45}$$

plays therefore a similar role to that of the thermodynamic efficiency in the case of heat engines.

The parametric plot $1/\epsilon$ versus $1/J_a$ is shown in Fig. 4(a). At $|q|=1$ a hyperboliclike behavior is observed, typical of endoreversible models in FTT just accounting for external, finite-time heat transfer losses. As $|q|$ decreases the contribution of the smaller cooling powers J_a progressively transforms into a monotonic increase, showing that the COP is optimized at nonvanishing cooling powers, in agreement with FTT models incorporating additional losses [9,10,30].

An interesting feature of the refrigerator models based on Eqs. (1)–(8) is that the cooling power [Fig. 4(c)] is bounded: since J_a is a monotonically decreasing function of λ, the maximum cooling power is reached at the lower limit of the physical interval, $\lambda=-1/h(b)$. At this point the power [Eq. (18)] diverges to infinity while the cooling power J_a remains finite so that the COP [Eq. (45)] drops to 0. Because of this simple behavior of J_a, we will focus on two working regimes only: maximum COP and maximum Ω.

1. Maximum COP

The analysis of the COP as a function of λ follows similar lines as for the efficiency in the case of engines. The solution

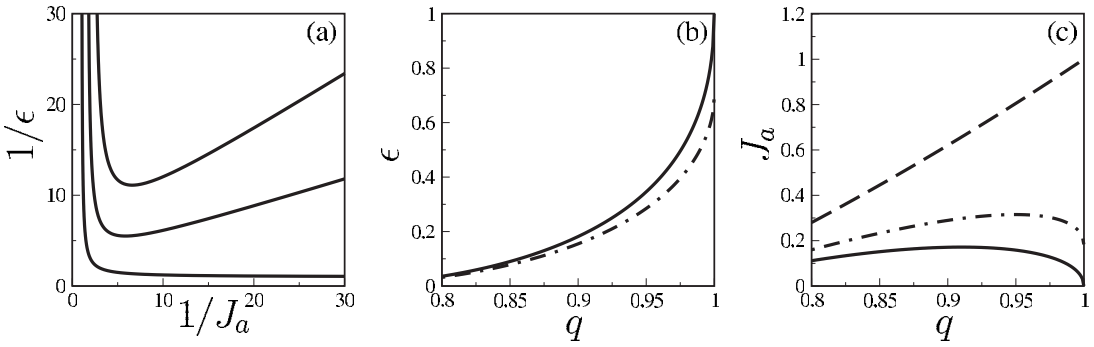

FIG. 4. (a) Parametric plot of $1/\epsilon$ vs $1/J_a$ in a refrigerator model based on Eqs. (30)–(35) with parameters (in arbitrary units) $n=2$, $l_{11}=l_{22}=1$, $T_a=0.5$, and $T_b=1$. From top to bottom: $q=0.85$, 0.9, and 1. (b) Maximum COP (solid line) and COP at maximum Ω (dot-dashed line) as functions of q for the same model. (c) Cooling power vs q at maximum COP (solid line) and at maximum Ω (dot-dashed line) for the same model. The dashed line is the maximum theoretical cooling power (see the text).

of $\partial\epsilon(\lambda)/\partial\lambda=0$ fixes the parameter $\lambda=\lambda_\epsilon$ associated with the regime of maximum COP of the whole chain. This maximal COP, as Fig. 4(b) shows, is an increasing function of the coupling strength parameter $|q|$ which attains the Carnot bound at $|q|=1$.

This fact is easily corroborated by a direct analysis of the COP when $|q|=1$. In such a case the COP is a strictly increasing function of λ:

$$\epsilon(\lambda)=\frac{[1+\lambda h(b)]\tau}{1-[1+\lambda h(b)]\tau}, \tag{46}$$

where $\tau=T_a/T_b$. Therefore the maximum COP is reached at the top of the refrigerator interval, $\lambda_\epsilon=0$. The force profile is then given by $f(x)=f_{\text{stop}}(x)$ [Eq. (15)] and the chain attains the Carnot COP for a reversible refrigerator,

$$\epsilon_C=\frac{\tau}{1-\tau}. \tag{47}$$

The individual units work also as reversible refrigerators with a COP given by the Carnot COP for the respective working temperatures for the very same reasons as those discussed in Sec. IV A 1 for the case of chains working reversibly as heat engines.

2. Maximum Ω

The definition of the Ω function when the chain works as a refrigerator [Eq. (37)] makes use of the maximum and minimum COPs $\epsilon_{\max}$ and $\epsilon_{\min}$ upon variation of the parameter λ for a given temperature profile $T(x)$ and a set of transport coefficients. The value of $\epsilon_{\max}$ follows from the kind of analysis described in the previous section. On the other hand, as mentioned above one can take safely $\epsilon_{\min}=0$; therefore the Ω function is fully characterized and it only remains to solve the equation $\partial\Omega(\lambda)/\partial\lambda=0$ to find the value $\lambda=\lambda_\Omega$ that corresponds to the optimum regime.

This task is much easier when $|q|=1$, since the maximum COP is given by the Carnot bound and λ_Ω can be derived in full generality:

$$\lambda_\Omega=h(b)^{-1}\left(\frac{1}{\sqrt{2-\tau}}-1\right). \tag{48}$$

The COP at maximum Ω is then found to be

$$\epsilon_\Omega=\frac{\tau}{\sqrt{2-\tau}-\tau}, \tag{49}$$

which coincides with the known value in FTT [23].

V. INDIVIDUAL OPERATION REGIMES

In this section we consider the behavior of the individual devices when different collective working regimes of the chain have been selected. To this end we compare the force profiles which optimize a certain figure of merit for every single device in the chain with those associated with the corresponding optimum working regimes for the chain as a whole. The procedure to find the force profile for such individual optimum regimes is sketched in the case of maximum efficiency; we only quote the result for other regimes.

A. Heat engines

1. Maximum efficiency

Let us consider the maximum efficiency regime of the generic unit device depicted in Fig. 1. At first order in Δx we take as thermodynamic forces $F_1=f(x)\Delta x/T(x)$ and $F_2=[1/T(x)]'\Delta x$ with conjugate fluxes $\mathcal{J}_1$ and $\mathcal{J}_2$, respectively. We also define transport coefficients $\bar{L}_{ij}(x)$ such that $\mathcal{J}_i=\bar{L}_{i1}(x)F_1+\bar{L}_{i2}(x)F_2$ for $i=1,2$. Therefore this engine delivers a power $\Delta\dot{W}=T(x)\mathcal{J}_1F_1$ with an efficiency given by $\eta=T(x)\mathcal{J}_1F_1/\mathcal{J}_2$. Solving the equation $\partial\eta/\partial F_1=0$ gives the force F_1 which maximizes the efficiency of the engine, and substituting then the above definitions of F_1 and F_2 one gets in the limit $\Delta x\to 0$ the force profile $f_{\eta,\text{loc}}(x)$ that locally maximizes the efficiency of every device in the chain. If we furthermore assume that $\bar{L}_{ij}\to L_{ij}(x)$ as $\Delta x\to 0$, the result is

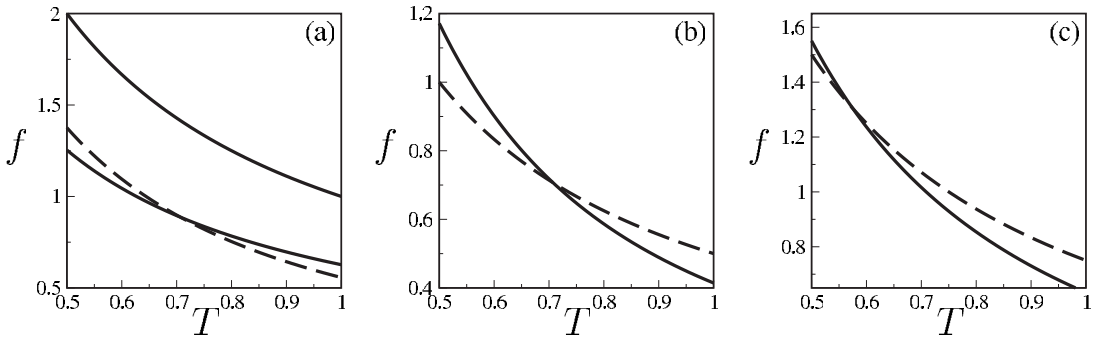

FIG. 5. (a) Force profile at maximum efficiency in an engine model based on Eqs. (30)–(35) with parameters (in arbitrary units) $n=2$, $l_{11}=l_{22}=1$, $T_a=0.5$, and $T_b=1$ for $q=1$ (top solid line) and $q=0.9$ (bottom solid line). The dashed line represents the force profile which maximizes the efficiency of every engine unit separately [Eq. (50)] when $q=0.9$. (b) Force profile at maximum power in the same model for $q=1$. The dashed line represents the force profile that maximizes the power of every engine unit separately [Eq. (52)]. (c) Force profile at maximum Ω in the same model for $q=1$. The dashed line represents the force profile that maximizes the Ω function of every engine unit separately [Eq. (53)].

$$f_{\eta,\mathrm{loc}}(x) = [1 - \sqrt{1-q^2(x)}]\frac{L_{22}(x)}{L_{12}(x)}\frac{T'(x)}{T(x)}, \tag{50}$$

and the maximum efficiencies of the individual devices are given by

$$\eta_{\max}(x) = \left(\frac{1-\sqrt{1-q^2(x)}}{q(x)}\right)^2 \eta_C(x), \tag{51}$$

where $\eta_C(x)=\Delta T(x)/T(x)$ denotes the Carnot efficiency for the working temperatures of the infinitesimal heat engines.

However, the force profile (50) does not satisfy Eq. (9) in the most general case. This fact is apparent in Fig. 5(a), where the force profiles that maximize the efficiency for the whole chain and for every engine unit are compared. The surprise is that, in contrast to the case $|q(x)|=1$, the engine units work in different regimes. This observation is at first sight quite paradoxical since at the end Eq. (9) is a consequence of the conservation of energy expressed in the form of Eq. (1) and of the transport equations (5) and (6), the very same ingredients that we have considered to perform the analysis of the maximum efficiency regime of a generic unit device.

The solution to this apparent paradox is that the force profile (50) is the result of the analysis of a single engine which does not take into account the couplings with neighboring devices. On the contrary, the force profile (11) which solves the differential Eq. (10) implicitly assumes the existence of the couplings in the form of a heat flux $J(x)$ which continuously varies along the chain as Eq. (1) predicts. As a consequence of such couplings, when we put one unit to work at maximum efficiency by means of a suitable force (50), the forces upon the rest of devices are automatically prescribed by Eq. (1) or equivalently by the differential equation (9), and these forces do not correspond in general to local maximum efficiency regimes for every device. An exception is the case $|q(x)|=1$, where at maximum efficiency regime every engine unit works also at maximum efficiency as mentioned above and therefore the force profile Eq. (50) is a solution of Eq. (9). The conclusion is that the analysis of optimum operation regimes for the whole chain must be performed globally in terms of the parameter λ, but not by means of a local analysis of the behavior of the individual units which leads to force profiles as Eq. (50) which, except for the maximum efficiency regime when $|q|=1$ or for special choices of the transport coefficients [19], are generically incompatible with the couplings among the individual devices.

2. Maximum power

The force profile that maximizes the power output $\Delta\dot{W}(x)$ of every engine unit along the chain can be obtained by means of the analysis of a generic device which is entirely analogous to the one performed in the previous section to study the maximum efficiency regime of the individual units. The result is

$$f_{\dot{W},\mathrm{loc}}(x) = \frac{L_{12}(x)}{2L_{11}(x)}\frac{T'(x)}{T(x)} = \frac{q^2(x)}{2}\frac{L_{22}(x)}{L_{12}(x)}\frac{T'(x)}{T(x)}, \tag{52}$$

which in general does not satisfy Eq. (9) and differs from the force profile prescribed by Eqs. (16) and (40) even for $|q(x)|=1$. In Fig. 5(b) we have plotted this last force profile and the one that maximizes the power output of every engine unit [Eq. (52)] with the result that both profiles coincide only for a single engine unit.

3. Maximum Ω

Let us construct the "local" Ω function for the device working as a heat engine between temperatures $T(x)$ and $T(x+\Delta x)$. Taking into account Eq. (36) and the above definitions of thermodynamic fluxes for an infinitesimal device placed at x the objective function now reads $\Omega=2\Delta\dot{W}-(\eta_{\max}+\eta_{\min})\mathcal{J}_2$. By means of a suitable force F_1 it is always possible to make $\Delta\dot{W}=T(x)\mathcal{J}_1F_1=0$; hence $\eta_{\min}=0$. On the other hand, we already know the maximum efficiency $\eta_{\max}$ of the device at x [Eq. (51)], therefore Ω is completely determined. The maximization of this function with respect to the thermodynamic force F_1 implies a force profile which in the limit $\Delta x\to 0$ is

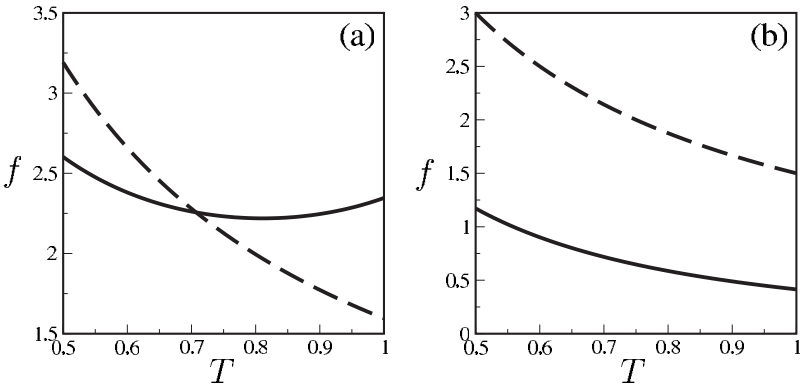

FIG. 6. (a) Force profile at maximum COP in a refrigerator model based on Eqs. (30)–(35) with parameters (in arbitrary units) $n=2$, $l_{11}=l_{22}=1$, $T_a=0.5$, and $T_b=1$ for $q=0.9$ (solid line). The dashed line represents the force profile which maximizes the COP of every refrigerator unit separately [Eq. (54)]. (b) Force profile at maximum Ω in the same refrigerator model for $q=1$. The dashed line represents the force profile that maximizes the Ω function of every refrigerator unit separately [Eq. (56)].

$$f_{\Omega,\mathrm{loc}}(x)=\left[\frac{1}{2}+\left(\frac{1-\sqrt{1-q(x)^2}}{2q(x)}\right)^2\right]\frac{L_{12}(x)}{L_{11}(x)}\frac{T'(x)}{2T(x)}. \quad (53)$$

This expression also gives at $|q(x)|=1$ a force profile which in general differs from the one prescribed by Eqs. (16) and (43); see Fig. 5(c).

B. Refrigerators

1. Maximum COP

The analysis of a generic refrigerator working between temperatures $T(x)$ and $T(x+\Delta x)$ gives the force profile which locally maximizes its COP, $\epsilon=\mathcal{J}_2/\Delta\dot{W}$. In the limit $\Delta x\to 0$ the result is

$$f_{\epsilon,\mathrm{loc}}(x)=[1+\sqrt{1-q(x)^2}]\frac{L_{22}(x)}{L_{12}(x)}\frac{T'(x)}{T(x)}. \quad (54)$$

The maximum COP is then given by

$$\epsilon_{\max}=\left(\frac{q(x)}{1+\sqrt{1-q(x)^2}}\right)^2\epsilon_C(x), \quad (55)$$

where $\epsilon_C(x)=T(x)/\Delta T(x)$ denotes the Carnot COP for the working temperatures of this infinitesimal refrigerator. Again, the force profile (54) in general does not satisfy Eq. (9) and, except for $|q(x)|=1$, does not coincide with the force profile that maximizes the COP for the whole chain [Fig. 6(a)].

2. Maximum Ω

In order to apply the Ω criterion to the infinitesimal refrigerator working between temperatures $T(x)$ and $T(x+\Delta x)$, one has to consider the function $\Omega=2\mathcal{J}_2-(\epsilon_{\max}+\epsilon_{\min})\Delta\dot{W}$, where $\epsilon_{\max}$ is given by Eq. (53) and $\epsilon_{\min}=0$. The maximum Ω corresponds to a force profile $f_{\Omega,\mathrm{loc}}(x)$ which in the limit $\Delta x\to 0$ reads

$$f_{\Omega,\mathrm{loc}}(x)=\left[\frac{1}{2}+\left(\frac{1+\sqrt{1-q(x)^2}}{q(x)}\right)^2\right]\frac{L_{12}(x)}{L_{11}(x)}\frac{T'(x)}{T(x)}. \quad (56)$$

Figure 6(b) shows that the force profile given by Eq. (16) together with the integration constant $\lambda=\lambda_\Omega$ [Eq. (48)] differs from the one maximazing Ω for every individual refrigerator [Eq. (56)] even for $|q(x)|=1$.

VI. SUMMARY

We have developed a theory that allows the detailed analysis within linear irreversible thermodynamics of a wide general class of nonisothermal energy converters: chains of coupled heat engines and refrigerators working along arbitrary temperature profiles. The main result of our work is summarized in Eq. (9), which represents a differential equation linking thermodynamic forces and transport coefficients. If the temperature profile and the transport coefficients are known the force profile $f(x)$ is determined up an integration constant λ which fixes the kind of energy converter we have and its operation regime.

In the limit of perfectly coupled fluxes ($|q(x)|=1$) the general solution of Eq. (9) has been presented (Sec. III A) in terms of simple expressions involving the temperature profile and the transport coefficients so that the thermodynamic quantities along the chain can be reduced to analytic form. In Sec. IV we found that these chains share relevant features with endoreversible models of FTT. Specifically, we have derived from first principles of linear irreversible thermodynamics known endoreversible efficiencies and coefficients of performance, thus giving strong support to their validity and generality. In view of these findings it seems plausible to argue that a real device could approach such efficiencies or COPs if the processes taking place in it are strongly coupled and the global performance is optimized.

The general solution of Eq. (9) when $|q(x)|<1$ is unknown to us. However, we have found some solutions for special choices of the temperature profile or transport coefficients (Secs. III B and III C) which reproduce the qualitative behavior of irreversible FTT models of heat devices (Sec. VI). This observation is reinforced by the analysis presented in Sec. III B, where we showed that chains with $|q(x)|<1$ can be decomposed into two auxiliary chains working in parallel under the assumption that their common temperature profile is given by Eq. (23). The first chain has a coupling-strength parameter $|q(x)|=1$ so that its properties are known in detail (Sec. III A), and the second chain amounts to a purely thermal contact between T_a and T_b that gives rise to an irreversible heat leak which does not depend on the working regime of the system. This kind of decomposition closely reproduces the usual formulations of irreversible FTT models of heat devices. As in FTT, the heat leak does not alter the net power $\dot{W}$ delivered or consumed by the system but modifies the heat fluxes exchanged with

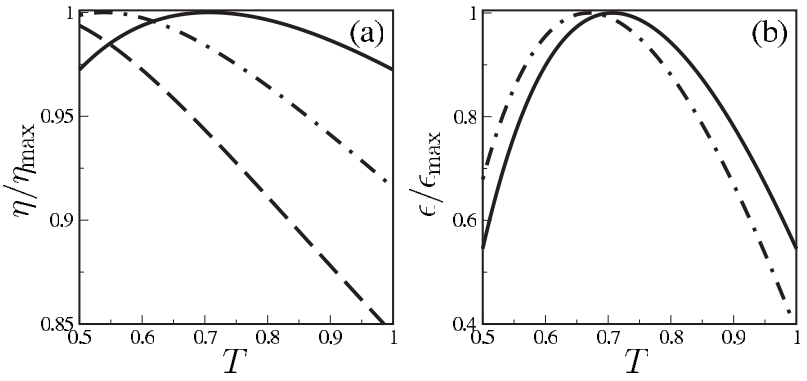

FIG. 7. (a) Normalized efficiencies of individual heat devices (see the text) for an engine model based on Eqs. (30)–(35) at maximum efficiency (solid line), maximum work (dashed line), and maximum Ω (dot-dashed line). Parameters in arbitrary units are $n=2$, $l_{11}=l_{22}=1$, $T_a=0.5$, $T_b=1$, and $q=0.8$. (b) Normalized COPs of individual heat devices for a refrigerator model based on the same equations and parameters as the previous one at maximum COP (solid line) and maximum Ω (dot-dashed line).

the reservoirs, thus implying a poorer performance concerning the efficiency or the COP of the whole chain. The conclusion is that chains with $|q(x)|<1$ are intrinsically irreversible, since the irreversibilities cannot be attributed exclusively to the operation regime. This is the case of chains with $|q(x)|=1$, where the reversible mode of operation is always accessible for any temperature profile.

Finally, we realized that, in contrast to the assumptions made in [16,18], the relationship between the overall and individual behaviors in chains of coupled energy converters is far from obvious in the most general case. Clearly, they both are fixed by means of a single parameter (λ), but at first sight it seems difficult to infer the overall working regime in view of the behaviors of the device units. General exceptions are the maximum efficiency and maximum COP regimes for $|q(x)|=1$: In such cases the individual devices and the chain work in the same operation regime, but this coincidence is due to the special conditions of the reversible mode of operation. In any other situation, at least one could substitute in the differential equation (9) some of the force profiles obtained in Sec. V for local optimum regimes to obtain conditions among the temperature profile and the transport coefficients ensuring that collective and individual behaviors coincide [19].

Besides these very particular cases, the rule is that we will observe intricate individual behaviors which apparently have nothing to do with the overall working regime. For instance, it could happen that no device unit works in the same regime as the one globally selected [Fig. 6(b)]. Moreover, we mentioned previously that there exist some order relationships among different working regimes: the power delivered at maximum efficiency is usually low and the maximum power regime has a poor efficiency so that the performances at maximum efficiency and maximum power can be considered as natural bounds to intermediate working regimes of heat engines. In the case of chains working at maximum Ω we can write the inequalities $\eta_{\dot{W}} \leq \eta_\Omega \leq \eta_{max}$ and $\dot{W}_{max} \geq \dot{W}_\Omega \geq \dot{W}_\eta$ [Figs. 3(b) and 3(c)]. These inequalities do not hold necessarily at the individual level, that is, a single unit device could work with greater efficiency when the chain works at maximum power (or maximum Ω) than when the chain works at maximum efficiency. That is what is observed in Fig. 7(a), where we have plotted the normalized efficiency η/η_{max} of the units for different collective working regimes: η are individual efficiencies in these regimes and η_{max} denotes the maximum efficiencies of the devices [Eq. (51)]. Obviously, for $|q|=1$ the maximum efficiency regime of the chain implies that $\eta/\eta_{max}=1$ and the efficiency of every device will be lower when the chain works in any other regime, but if $|q|<1$ a much more intricate behavior is possible, which indeed depends on the detailed properties of the system. Similar remarks apply to refrigerators: in Fig. 7(b) we have plotted normalized individual COPs [with respect to maximum individual COPs, Eq. (55)] to show that the COP of a single device can be lower when the chain works at maximum COP than when it works at maximum Ω.

To sum up, not only does the force profile along the chain in a certain collective working regime not generically optimize the performance of any particular device, but even the natural order relationships among different working regimes can be violated at the individual level. The reason is that the collective and individual behaviors, as well as the bridge between these two levels of description, are mediated for the specific set of transport coefficients and the temperature profile we choose. In spite of these complex behaviors, we have shown that when $|q(x)|=1$ the overall efficiency or COP exhibits a kind of universality: they become functions of $\tau=T_a/T_b$ which are independent of the detailed structure of the system [i.e., of the specific form of the temperature profile and transport coefficients $\{L_{ij}(x)\}$] in several operation regimes. These observations could be of interest in various problems which arise in natural and social sciences, where a variety of agents must cooperate to accomplish some task: organelles within the living cell, division of labor within an insect colony, or assembly-line workers in a factory, to name but a few. One fundamental problem in analyzing such systems is to assess how the specific agents' behaviors affect the overall performance and how to define a unified thermodynamic principle governing these complex, nonequilibrium systems.

ACKNOWLEDGMENTS

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[1] S. Carnot, *Réflexions sur la Puissance Motrice du Feu, et sur les Machines Propres à Développer cette Puissance* (Bachelier, Paris, 1824).
[2] S. R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics* (Dover, New York, 1984).
[3] S. R. Caplan and A. Essig, *Bioenergetics and Linear Nonequilibrium Thermodynamics* (Harvard University Press, Cambridge, MA, 1999).
[4] B. Andresen, P. Salamon, and R. S. Berry, Phys. Today **37**(9), 62 (1984).
[5] R. S. Berry, V. A. Kazakov, S. Sieniutycz, Z. Szwast, and A. M. Tsirlin, *Thermodynamic Optimization of Finite-Time Processes* (Wiley, Chichester, U.K., 2000).
[6] *Finite-time Thermodynamics and Thermoeconomics*, edited by S. Sieniutycz and P. Salamon (Taylor & Francis, New York, 1990).
[7] A. Bejan, J. Appl. Phys. **79**, 1191 (1996).
[8] A. De Vos A, *Endoreversible Thermodynamics of Solar Energy Conversion* (Oxford University Press, Oxford, 1992).
[9] C. Wu, L. Chen, and J. Chen, *Advances in Finite-Time Thermodynamics: Analysis and Optimization* (Nova Science, New York, 2004).
[10] A. Durmayaz, O. S. Sogut, B. Sahin, and H. Yavuz, Prog. Energy Combust. Sci. **30**, 175 (2004).
[11] F. Curzon and B. Ahlborn, Am. J. Phys. **43**, 22 (1975).
[12] I. I. Novikov, J. Nucl. Energy **7**, 125 (1958); P. Chambadal, *Les Centrales Nucleaires* (Armand Colin, Paris, 1957).
[13] D. P. Sekulic, J. Appl. Phys. **83**, 4561 (1998); B. Andresen, *ibid.* **90**, 6557 (2001).
[14] A. Bejan, *Advanced Engineering Thermodynamics*, 2nd ed. (Wiley, New York, 1997).
[15] S. Velasco, J. M. M. Roco, A. Medina, J. A. White, and A. C. Hernández, J. Phys. D **33**, 355 (2000).
[16] C. Van den Broeck, Phys. Rev. Lett. **95**, 190602 (2005).
[17] C. Van den Broeck, Adv. Chem. Phys. **135**, 189 (2007).
[18] B. Jiménez de Cisneros, L. A. Arias-Hernández, and A. C. Hernández, Phys. Rev. E **73**, 057103 (2006).
[19] B. Jiménez de Cisneros and A. C. Hernández, Phys. Rev. Lett. **98**, 130602 (2007).
[20] H. T. Davis, *Introduction to Non Linear Differential and Integral Equations* (Dover, New York, 1962).
[21] N. S. Greenspan, Nature (London) **409**, 137 (2001).
[22] F. Angulo-Brown, J. Appl. Phys. **69**, 7465 (1991).
[23] A. C. Hernández, A. Medina, J. M. M. Roco, J. A. White, and S. Velasco, Phys. Rev. E **63**, 037102 (2001).
[24] N. Sánchez Salas and A. Calvo Hernández, Europhys. Lett. **61**, 287 (2003).
[25] S. Velasco, J. M. M. Roco, A. Medina, and A. Calvo Hernández, J. Phys. D **34**, 1000 (2001).
[26] N. Sánchez Salas and A. C. Hernández, Phys. Rev. E **68**, 046125 (2003).
[27] P. Reimann, Phys. Rep. **361**, 57 (2002).
[28] J. M. R. Parrondo and B. Jiménez de Cisneros, Appl. Phys. A: Mater. Sci. Process. **75**, 179 (2002).
[29] N. Sánchez Salas and A. C. Hernández, Phys. Rev. E **70**, 046134 (2004).
[30] J. M. Gordon and K. C. Ng, *Cool Thermodynamics* (Cambridge International Science, Cambridge, U.K., 2000).