Hamilton-Jacobi-Bellman theory of dissipative thermal availability

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We analyze a steady-state problem of maximum work delivered from a finite resource fluid and a bath, as the dissipative, finite-time generalization of the evolutionary Carnot problem in which the temperature driving force between two interacting subsystems varies with the contact time. The thermal capacity of the bath is very large, so its intensive parameters do not change. At the classical, reversible limit, the instantaneous rates do vanish due to the reversibility requirement, whereas in the generalized problem some inherent, rate-related irreversibilities are inevitable, in particular those occurring in boundary layers at interfaces. Methods of the optimal control and variational calculus are suitable to optimize nonlinear dynamics of the process. An analytical formalism, strongly analogous to those in analytical mechanics and optimal control theory, is effective in thermodynamic optimization. A variational theory treats an infinite sequence of infinitesimal Curzon-Ahlborn-Novikov processes as the theoretical model pertinent to develop the theory of a finite-resource fluid interacting with a bath in a finite time, when the active exchange of the energy occurs through the working fluid of participating engines, refrigerators, or heat pumps. The main application is the extension of the classical availability (exergy) beyond the class of reversible processes. The generalized exergy is next discussed in terms of the finite intensity and finite duration of the process. Optimality of a definite irreversible process is an essential feature for a finite duration. A link is shown between the process duration and the optimal intensity measured in terms of a dissipative Hamiltonian. An interesting approach, based on the Hamilton-Jacobi-Bellman equation for the irreversible availability and underlying work functionals (HJB theory), is developed. The HJB formulation is suitable for generation of numerical data of the work potentials, by the standard recurrence equation of Bellman's dynamic programming. Such an equation is, in fact, the sole solving algorithm for functionals with constrained rates and states and with complex boundary conditions. It will certainly be inevitable in the case of the problem generalization to mass transfer and chemical reactions. An essential decrease of the maximal work received from an engine system and an increase of minimal work added to a heat-pump system is shown in the high-rate regimes and for short durations of thermodynamic processes. The results prove that the limits known from the theory of the classical availability should be replaced by stronger limits obtained for finite-time processes, which are closer to reality. Hysteretic properties are effective which cause the difference between the work supplied and delivered, for the inverted end states of the process. The significance of these results for the theory of the structure creation and destruction is underlined. [S1063-651X(97)12910-5]

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I. INTRODUCTION

Considerable progress has recently been achieved in understanding the thermodynamics of finite-rate and finite-time systems, including the theory of the Curzon-Ahlborn-Novikov engine or CAN engine [1,2]. This progress makes it possible to accomplish the basic task of this paper: a finite time extension of the theory of a resource interacting with a bath, as the irreversible extension of the corresponding reversible problem [3]. A good review of various single-stage CAN systems was presented by de Vos [4]. However, for the purpose of the extension mentioned above, in which the thermal parameters of the (finite) resource change in time, one needs to deal with sequential CAN processes. In particular, dynamical models of infinite sequence of infinitesimal CAN processes arranged sequentially in order to accomplish the active (work producing) exchange of heat between two fluids (in particular fluid and bath) were worked out [5,6]. It was underlined therein that the sequence is the basic theoretical tool to define a rate- and duration-dependent function of available energy (exergy) which generalizes the classical thermal exergy for finite-time processes with dissipation occurring in associated resistances. Some works on the finite-time exergy published to date [7–9] suffered from the absence of associated time evolution and particular functional formulations which could comprise (in a single expression) the potential property of the classical reversible component and the path-dependent property of the irreversible component, in addition, these works did not make a distinction between the finite-time availability of processes approaching and leaving equilibrium. This property was first emphasized only recently [10,11]. The property disappears in the reversible case of quasistatic processes, when the effect of resistances does vanish, and the extended available energy simplifies to the classical exergy, inherently associated with infinite durations.

The standard thermodynamic reasoning which leads to the classical exergy is based on the theory of a macroscopic body immersed in a bath, as known from various books [12–14]. This classical exergy can also be obtained as the limiting work received from the sequence of a finite number of Car-

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not cycles, at the limit when the number of these cycles tends to infinity [3]. For the purpose of the classical exergy, which is the reversible quantity, the commencement of the theoretical scheme with a finite-stage model [3] is unnecessary; the traditional model of infinitesimal stages is sufficient. Indeed, the presence of *reversible* cycles, such as those used in Ref. [3], fixes automatically the first-law efficiency of each infinitesimal stage at the well-known (Carnot) level, $\eta = 1 - T^e/T$, where T is the instantaneous temperature of a finite resource and T^e is the temperature of the environment or an infinite bath. Since the unit mass of the resource releases the heat $dq = -c dT$, where c is the specific heat, the classical thermal exergy E_x follows by integration of the product $-c \eta dT = -c(1 - T^e/T) dT$ between the limits T and T^e. The integration yields the well-known classical expression, Eq. (13) of the present paper, in a quite trivial way. However, the problem becomes nontrivial in the case when a finite-rate process is considered, since the efficiency differs in this case from the Carnot efficiency. That efficiency should be determined before the integration of the product $-c \eta dT$ can be made. The integration then leads to a generalized available energy associated with the extremal release of the mechanical work in a finite time. Such generalized availability is the main task of this paper.

We shall distinguish two classes of active (work exchanging) nonequilibrium systems. When the system is approaching equilibrium the work is released, and the system plays the role of an engine. This case is called the engine mode of the system. The delivered work W is then positive by assumption. Otherwise, when the system is departing from the equilibrium the work must be supplied, and the system plays the role of a heat pump. This is the so-called heat-pump mode of the system. The work W is then negative, which means that the positive work $(-W)$ must be supplied to the system. To obtain the generalized exergy, optimization problems are considered in this paper, which involve the maximum of the work delivered (max W) and the minimum of the work supplied [min$(-W)$]. The boundary states of the system at the engine mode are inverted boundary states of the system at the heat-pump mode.

The classical thermal availability is the non-negative quantity. It is reversible in the sense that the magnitude of the work delivered during the reversible approaching of the system to equilibrium is equal to the magnitude of the work supplied, after the initial and final states are interchanged. The first case corresponds with the engine mode of the system, the second with the heat-pump mode the system. The classical exergy is the quantity which defines bounds on work delivered from (or supplied to) very slow, reversible processes. Our research is directed toward generalization of this classical idea for the finite-rate transitions. We show that while the reversibility property is no longer valid for the generalized (nonclassical) exergy, the thermokinetic bounds formed by this generalized exergy are stronger and hence more useful than classical thermostatic bounds. This substantiates the role of the generalized exergy for evaluation of the energy limits in practical systems [15]. It is quite essential that these limits depend on the direction of the finite-time process, i.e., the limit corresponding with the change of the thermodynamic state from A to B is not the same as the limit associated with the change of the thermodynamic state from B to A for the same, finite, duration of the process.

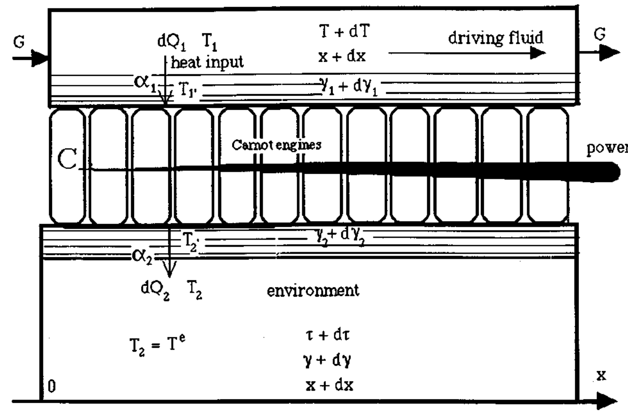

FIG. 1. Model of power production and dissipative availability of flowing fluid accomplished in an infinite sequence of infinitesimal Curzon-Ahlborn-Novikov engines.

In the present work we first briefly recapitulate some basic issues associated with derivation of basic work functionals, and then direct our analysis toward an aspect which is the derivation of the Hamilton-Jacobi-Bellman theory (HJB theory) for functionals of dissipative exergy and work. The HJB theory is known as a basic ingredient of variational calculus and optimal control [16–20]. The HJB formulation is important to find data of the generalized available energy and/or related work potentials by numerical methods. These methods, along with the associated Pontryagin's maximum principle [21], are the main effective extremum seeking methods for functionals in cases of constrained rates and states [22]. They will certainly be inevitable in the case of the problem generalization to include the mass transfer in separation units and chemical reactions. However, Pontriagin's maximum principle, in itself, does not generate an optimal performance function (principal function) which is in our case the generalized work potential or the dissipative exergy, the main result which is sought. Otherwise, when the HJB equation is known, the exergy (or work) function is explicit therein, and a discretization approach can transform the problem into Bellman's functional equation which can be solved by standard solving techniques of discrete dynamic programming [23]. This is not in contradiction with the fact that we restrict ourselves here to systems which are continuous from the physical viewpoint. Systems which are discrete by nature will be considered in a separate publication.

II. DIFFERENTIAL MODEL AND IRREVERSIBLE GENERALIZATION OF CARNOT FORMULA

It is important to realize that no analysis of a single CAN unit is sufficient for the purpose of generalization of the available energy to finite durations; rather a treatment of a complex system composed of infinite number of infinitesimal CAN units is necessary. The corresponding abstract scheme, which is shown in Fig. 1, depicts an infinite sequence of the infinitesimal CAN processes. As its classical, reversible prototype, it is still a highly abstract, work-producing system in which active heat exchange occurs between the two real fluids of finite thermal conductivities and containing their own boundary layers as dissipative components of the system.

The mass flux of the first fluid (subscript 1) G is finite; otherwise the amount or mass flux of the second fluid (subscript 2), which plays the role of a bath or an environment, is infinite, which results in the constant temperature of the second fluid, $T_2=T^e$. The differential Carnot engines are located continuously between two separated boundary layers of the fluids, so that they work between their interfaces. This abstract model of the active energy exchange, associated with the power production, is a finite-rate, irreversible generalization of the corresponding classical model of the available energy released from two fluids. In both cases (reversible and not) the second fluid plays the role of the bath [12].

Let us derive a mathematical model of infinitesimal CAN process at the steady state [6]. In the steady process the conservation balances refer to the fluxes rather than to stocks. The finite-mass flux G of the first fluid, whose constant specific heat capacity equals c, is in the direction parallel to x axis. Between the working fluid of the Carnot engine and each of two fluids (each of a finite thermal conductivity) the differential conductances $d\gamma_1$ and $d\gamma_2$ are present, as the system dissipative elements.

Changes of various physical quantities are measured as functions of the horizontal length coordinate x between its initial value $x=0$ and any current value x. The (partial) conductances γ_1 and γ_2 link the heat sources with the working fluid of the engine at high and low temperatures, and their differentials can be expressed as $d\gamma_1=\alpha_1 dA_1$ and $d\gamma_2=\alpha_2 dA_2$, where α_1 and α_2 are the heat transfer coefficients and dA_1 and dA_2 are upper and lower exchange surface areas. The areas A_1 and A_2 are components of the composite area A whose differential dA satisfies the equality $dA=dA_1+dA_2$. The heat powers Q_1 and Q_2 are the cumulative heat fluxes flowing respectively from the upper reservoir and to the lower reservoir. For the differential length dx (the differential composite area dA) the fluid delivers the driving heat power $d\mathsf{Q}_1$ to the working medium of the infinitesimal Carnot engine. The temperature of the driving fluid (fluid 1) decreases slightly along its path since this fluid releases the heat to run the engine. In the range $T_1>T^e$ the differential dT_1 is negative for the engine and positive for the heat pump. The differential of the driving heat flux, $d\mathsf{Q}_1$, describes the heat power subtracted from the flowing driving fluid when its temperature decreases from T_1 to T_1+dT_1. (Later the symbol T_1 will be simplified to T and the driving fluid temperature will be identified as the single state variable T of the process.)

We designate by $T_{1'}$ and $T_{2'}$ the upper and lower temperatures of the working agent which circulates in each differential Carnot engine. The high-grade heat $d\mathsf{Q}_1$ reaches the engine part at $T_{1'}$. In the simplest case of the Newtonian heat exchange which we consider here, this heat is proportional to the temperature difference $T_1-T_{1'}$. Otherwise, the low-temperature part of the Carnot subsystem releases the pure heat to an environment (or fluid 2) through another conductance, $d\gamma_2$. The flux of the released heat is proportional to the difference $T_{2'}-T_2$. This low-grade heat flows between the low-temperature part of the engine (at $T_{2'}$) and the environmental fluid, and reaches this fluid at the low temperature $T_2=T^e$. We are dealing with the case when the temperature of the bath fluid is constant and equal to that of an environment (infinite bath of the second fluid, $T_2=T^e$).

Let us first note that the local efficiency of an infinitesimal unit of the process is $\eta=d\mathsf{W}/d\mathsf{Q}_1$. While this local first-law efficiency is still described by the Carnot formula

$$\eta=1-\frac{T_2'}{T_1'} \tag{1}$$

this efficiency is nonetheless lower than the efficiency of the unit working between the boundary temperatures T_1 and $T_2=T^e$, as the former applies to the intermediate temperatures $T_{1'}$ and $T_{2'}$. The intermediate temperatures are unknown, but they can be expressed in terms of the boundary temperatures T_1 and T_2 and the efficiency η. By solving Eq. (1) along with the reversible entropy balance of the Carnot differential subsystem

$$\frac{d\gamma_1(T_1-T_{1'})}{T_{1'}}=\frac{d\gamma_2(T_{2'}-T_2)}{T_{2'}}, \tag{2}$$

one obtains the primed temperatures as certain functions of the variables T_1, $T_2=T^e$, and η. Such an approach may be regarded as the differential version of the finite-stage approach which was developed earlier and applied to the single-stage and multistage systems [4,10]. The associated driving heat flux $d\mathsf{Q}_1=d\gamma_1(T_1-T_{1'})$ is then found in the form

$$d\mathsf{Q}_1=d\gamma\left[T_1-\frac{1}{(1-\eta)}\,T_2\right], \tag{3}$$

from which the efficiency-power characteristic follows in the form

$$\eta=1-\frac{T_2}{T_1-d\mathsf{Q}_1/d\gamma}. \tag{4}$$

In Eqs. (3) and (4) γ is an appropriately defined *overall* conductance of the traditional heat transfer theory [6]. The symbol $\mathsf{Q}_1(\gamma)$ refers to the function describing the driving heat flux along the conductance coordinate γ. The associated differential conductance $d\gamma$ may be expressed as the product $\alpha' dA$, which further leads to the expression

$$d\gamma=\alpha' dA=\alpha' a_v F\ dx=\alpha' a_v F v\ dt. \tag{5}$$

Here α' is an overall heat transfer coefficient referred to the total differential area dA, a_v is the total specific exchange area per unit volume of the system, and F is the system cross-sectional area for the driving fluid, perpendicular to x. The symbol v refers to the linear velocity of the driving fluid, and t is the contact time of this fluid with the heat exchange surface.

Now one can introduce the spatial scale of the process or the quantity

$$\frac{G_c}{\alpha' a_v F}=H_{\mathrm{TU}}, \tag{6}$$

which has the length dimension and is known from the heat transfer theory as the so-called height of the heat transfer unit (H_{TU}). In Eq. (6) it is referred to the driving fluid (fluid 1).

A nondimensional length $x/H_{\mathrm{TU}}=vt/H_{\mathrm{TU}}$ can next be defined, which is known as the number of transfer units. Since it measures the extent of the system and it is proportional to the contact time of the fluid with the energy exchange area, it plays also the role of a nondimensional time, and this is why it is designated by τ,

$$\tau\equiv\frac{x}{H_{\mathrm{TU}}}=\frac{\alpha' a_v F}{G_c}x=\frac{\alpha' a_v F v}{Gc}t. \tag{7}$$

In what follows the subscript 1 designating the first fluid (driving fluid) is no longer needed, and it will be omitted for simplicity of equations. From the energy balance of the driving fluid, the heat power variable Q_1 satisfies $d\mathsf{Q}=-Gc\ dT$, where dT is the differential temperature drop of the first (driving) fluid, and c is its specific heat. With the above definitions and the differential heat balance of the driving fluid, the control term $d\mathsf{Q}_1/d\gamma$ of Eq. (4), may be written in the form

$$\begin{aligned} d\mathsf{Q}/d\gamma&\equiv-u=-Gc\ dT/\alpha' dA=-Gc\ dT/\alpha' a_v F\ dx\\ &=-GcdT/\alpha' a_v Fv\ dt=-dT/d\tau \end{aligned} \tag{8}$$

(subscript 1 omitted). The negative of the derivative $d\mathsf{Q}/d\gamma$ is the control variable u of the process. In short, the above equation says that $u=\dot{T}$, or that the control variable u equals the rate of the temperature change with respect to the *nondimensional* time τ. The control u has the temperature dimension.

With the help of Eqs. (5)–(8), the efficiency formula (4) becomes the simple, finite-rate generalization of the Carnot formula

$$\eta=1-\frac{T^e}{T+\dot{T}}. \tag{9}$$

When $T>T^e$ the derivative $\dot{T}$ is negative for the engine mode. This is because the driving fluid must release the energy to the engine to assure the work production. Similarly $\dot{T}$ is positive for the heat-pump mode. In the engine case $\eta\leqslant\eta_C$, whereas in the heat-pump mode $\eta\geqslant\eta_C$. When $T<T^e$ the efficiencies (as the first-law efficiencies do) become negative, nonetheless *in each case the efficiency of a finite-time process deviates adversely from the Carnot efficiency*. The simplicity of Eq. (9) is its great advantage when analytical studies are in question. With the help of Eq. (9) work functionals can easily be formulated, as shown in Sec. III.

III. WORK FUNCTIONALS FOR INFINITE SEQUENCE OF INFINITESIMAL CAN PROCESSES AND LINK WITH ENTROPY GENERATION

It is suitable to work with the vector $\mathbf{T}=(T,\tau)$ composed of the temperature and the number of heat transfer units in order to describe finite-time thermal processes in which the temperature T is the state variable and τ is the nondimensional time or the number of the heat transfer units. We also designate by W the cumulative power input (output) for the system at time τ (the length coordinate between 0 and x). For any process mode, the cumulative power delivered per unit fluid flow, W/G, is obtained by integration of the product of η and $d\mathsf{Q}/G=-cdT$ between an arbitrary initial temperature T^i and an arbitrary final temperature T^f of the fluid. (In all designations that follows, the superscripts f and i refer to the final and initial states, respectively.) This integration yields the specific work of the *flowing* fluid in the form of the functional

$$W_{I\mathbf{T}\cdot\mathbf{T}^fI}\equiv\mathsf{W}/G=-\int_{T^i}^{T^f}c\left(1-\frac{T^e}{T+\dot{T}}\right)\dot{T}d\tau. \tag{10}$$

The notation $[\mathbf{T}^i,\mathbf{T}^f]$ means the passage of the vector $\mathbf{T}\equiv(T,\tau)$ from its initial state $\mathbf{T}^i$ to its final state $\mathbf{T}^f$. For the above functional, the work maximization problem can be stated for the engine mode of the process

$$\begin{aligned}(W)_{\max}&=\max\left\{-\int_{\tau^i}^{\tau^f}L(T,\dot{T})d\tau\right\}\\ &=\max\left\{-\int_{\tau^i}^{\tau^f}c\left(1-\frac{T^e}{\dot{T}+T}\right)\dot{T}\ dt\right\},\end{aligned} \tag{11}$$

whereas for the heat-pump mode (an inverse process), one states the minimization problem

$$\begin{aligned}(-W)_{\min}&=\min_{dT/d\tau}\int_{\tau^i}^{\tau^f}L(T,\dot{T})d\tau\\ &=\min_{dT/d\tau}\int_{\tau^i}^{\tau^f}c\left(1-\frac{T^e}{\dot{T}+T}\right)\dot{T}\ d\tau.\end{aligned} \tag{12}$$

For each process mode, a dissipative exergy of the finite-time process is obtained as the extremal of the related functional with the appropriate integration limits ($T^i=T$ and $T^f=T^e$ for the engine mode of the process, and $T^i=T^e$ and $T^f=T$ for the heat-pump mode of the process).

The above Lagrange functionals represent the total power per unit mass flux of the fluid which is the quantity of the specific work dimension, hence their direct relation to the specific exergy of the fluid at flow. In the quasistatic limit of vanishing rates, $dT/d\tau=0$, the above work functionals represent the change of the *classical exergy*

$$W_{(dT/d\tau\Rightarrow0)}=-\int_{T^i}^{T^f}c\left(1-\frac{T^e}{T}\right)dT=\Delta h-T^e\Delta s. \tag{13}$$

This functional leads to the classical exergy for appropriate boundary temperatures, $T^i=T$ and $T^f=T^e$. Consequently, Eq. (10) represents the dissipative exergy change for the finite-time processes in which irreducible dissipative phenomena occurring in the boundary layers are essential. For the engine mode of the process, the dissipative exergy itself is obtained as the *maximum* of functional (10), with the integration limits $T^i=T$ and $T^f=T^e$, for the heat-pump model—as the minimum of the negative of this functional, with the integration limits $T^i=T^e$ and $T^f=T$.

An alternative form of the specific work, Eq. (10), can be written as the functional

$$W_{IT^i,T^fI} \equiv \mathsf{W/G} = \int_{T^i}^{T^f} \left[-c\left(1-\frac{T^e}{T}\right)\dot{T}\right] d\tau - T^e \int_{T^i}^{T^f} c\,\frac{\dot{T}^2}{T(T+\dot{T})}\,d\tau = -\int_{T^i}^{T^f} c\left(1-\frac{T^e}{T}\right) dT - T^e S_{\sigma I\mathbf{T}^i,\mathbf{T}^fI}, \quad (14)$$

in which the first term is the classical ''reversible'' term and the second term is the product of the equilibrium temperature and the entropy production,

$$S_{\sigma I\mathbf{T}^i,\mathbf{T}^fI} = \int_{T^i}^{T^f} c\,\frac{\dot{T}^2}{T(T+\dot{T})}\,d\tau. \quad (15)$$

This has been shown at some length elsewhere [6,11]. The entropy generation rate is referred here to the unit mass flux of the driving fluid, hence the specific entropy dimension of the quantity S_σ. The quantity S_σ should be distinguished from the specific entropy of the driving fluid, s. The entropy generation S_σ is the strictly quadratic function of the process rate, $u = dT/d\tau$, only in the case when the work is not produced, corresponding with the vanishing efficiency $\eta = 0$ or the equality $T + \dot{T} = T^e$ in Eq. (15). For the active heat transfer (nonvanishing η) the entropy production appears to be a nonquadratic function of rates, represented by the integrand of Eq. (15).

IV. BASIC PROPERTIES OF EXTREMAL TRAJECTORIES

Applying the maximum operation for the fundamental functional (14) at the fixed end temperatures and times, it is seen that the role of the first (potential) term is inessential, and the problem of the maximum released work, max(W), is equivalent with the associated problem of the minimum entropy production. Similarly, performing the minimum operation for the negative of this functional (the role of the first term is inessential again) it is seen that the problem of the minimum supplied work, min($-W$), *with the inverted thermodynamic end states*, is also equivalent to its corresponding problem of the minimal entropy production. This confirms the crucial role of the entropy generation minimization in the context of the extremum work problems, for each mode of the process. The consequence of this conclusion is that a problem of the extremal work and an associated fixed-end problem of the minimum entropy generation have the same solutions. Yet considerations involving the entropy production are unnecessary when the work functionals are given.

For each process mode, the work extremization problems can be broken down to variational calculus for the Lagrangian

$$L = c\left(1-\frac{T^e}{\dot{T}+T}\right)\dot{T}. \quad (16)$$

The Euler-Lagrange equations for the problems of extremal work and the minimum entropy production lead to the same-second order differential equation

$$T\ddot{T} - \dot{T}^2 = 0, \quad (17)$$

which characterizes the optimal trajectories of all considered processes. It has been proven [6] that the extremal rate $\dot{T}$ satisfies the Legendre condition for the minimum work supply in case of the heat-pump mode and for the maximum work delivery in the engine mode, and that each of these two situations is associated with the minimum entropy generation. For a given duration and the prescribed end temperatures T^i and T^f, the extremal function $T(\tau)$ which satisfies Eqs. (17) is described by the equation

$$T(\tau,\tau^f,T^i,T^f) = T^i(T^f/T^i)^{\tau/\tau^f}. \quad (18)$$

One also obtains a momentumlike quantity, a formal analog of the mechanical momentum

$$z \equiv \frac{\partial L}{\partial \dot{T}} = c\left(1-\frac{T^eT}{(\dot{T}+T)^2}\right), \quad (19)$$

and the first integral

$$E \equiv \frac{\partial L}{\partial \dot{T}}\dot{T} - L = c\,\frac{T^e\dot{T}^2}{(\dot{T}+T)^2}, \quad (20)$$

which is a formal analog of the mechanical energy. For the quasistatic state changes, when the rates $dT/d\tau$ vanish, E vanishes too, hence E is a dissipative quantity. An equation for the optimal temperature follows from the condition $E = h$

$$\dot{T} = \frac{\pm T\sqrt{h/cT^e}}{1-\pm\sqrt{h/cT^e}} \equiv \xi T, \quad (21)$$

and the integration of this equation for the fixed-end boundary conditions leads to Eq. (18). The coefficient ξ is a process intensity constant, which can be determined from the boundary conditions of the fixed-end problem,

$$\xi = \frac{\ln T^f/T^i}{\tau^f - \tau^i}, \quad (22)$$

ξ is positive for the fluid heating process, and negative for the fluid cooling process. In what follows we shall assume $\tau^i = 0$, then the total duration will be represented by the time τ^f.

Equation (21) proves that, for the same h, the heat-pump heating processes run faster than the engine cooling processes (larger ξ and shorter durations in the engine case than in the heat-pump case). On the other hand, as shown by the function $E(\xi) = cT^e\xi^2(1+\xi)^{-2}$ obtained from Eq. (20), for the two values of ξ of the same magnitude but of opposite signs and for the same durations, the values $E = h$ are larger for the engine mode than for the heat-pump mode of a process with the same initial and final thermodynamic states. This property is valid in spite of the fact that the engine modes, which drive the process thermodynamic state from, say, A to B, and the heat-pump modes, which drive the inverse process from B to A, are described by the common work formula and share the same autonomous trajectory for the function $T(\tau)$.

V. TOWARD CHARACTERISTIC FUNCTIONS VIA DYNAMIC PROGRAMMING

The problem of generalized availability falls into the category of certain finite-time potentials, an evergreen problem of contemporary thermodynamics [24]. The power of the dynamic programming (DP) method as applied to problems of this sort lies in its important property: regardless local constraints on controls or state variables the *optimal* performance functions satisfy an equation of Hamilton-Jacobi-Bellman (HJB equation) with the same state variables as those for the unconstrained problem. Only *numerical* values of optimizing control sets and those of the optimal performance functions differ in constrained and unconstrained cases. Although in the case of pure heat transfer problem most components of the solution can be obtained analytically, even then there exist formulations in which the analytical solutions are not possible. These include free boundary conditions, non-Newtonian heat transfer and constraints imposed on the rate change of state, and the state itself (the rate change of the temperature and T itself in our one-dimensional case). Otherwise, the state function property of dynamic programming potentials should prove to be very suitable for more complex problems, such as those with mass transfer and chemical reactions. Therefore, any test of the HJB method in the context of the pure heat transfer problem and associated exergy is highly desirable. This test should initiate a systematic search toward properties and implications of HJB equations in thermodynamics. In particular, the test performed in this work shows that our problems may be correctly described by two kinds of HJB equations: a backward HJB equation and a forward HJB equation. The former is associated with the optimal work or exergy as an optimal integral function (I) defined on the initial states (temperatures), and accordingly refers to the engine mode or processes approaching the equilibrium. On the other hand, the forward HJB equation deals with the exergy (work) as the function ($-I$) defined on the final states, and accordingly refers to the heat-pump mode or processes leaving the equilibrium (see Sec. X). Frequently I is called the optimal performance function for the work integral.

Among the work extremization problems considered, the problem of the maximal work delivery (constrained or not) is governed by the characteristic function

$$I(\tau^f,T^f,\tau^i,T^i)\equiv \max W_{I\mathbf{T}^i\cdot\mathbf{T}^f I} = \max\left\{\int_{T^i}^{T^f}\left[-c\left(1-\frac{T^e}{T+u}\right)u\right]d\tau\right\}. \tag{23}$$

In Eq. (23), $u=\dot{T}$ is the rate control variable defined by Eq. (8). This equation refers to the engine mode or to processes approaching equilibrium. For the heat-pump mode and processes departing from equilibrium, one can define the optimal function as

$$-I(\tau^f,T^f,\tau^i,T^i)\equiv \min(-W_{I\mathbf{T}^i\cdot\mathbf{T}^f I}) = \min\left\{\int_{T^i}^{T^f}c\left(1-\frac{T^e}{T+u}\right)u\ d\tau\right\}. \tag{24}$$

Indeed, since for an arbitrary quantity W for the same change of the end states and times, the components of the vector $\mathbf{T}=(T,\tau)$, within the same mode of the system the following holds:

$$\max W_{[\mathbf{T}^i,\mathbf{T}^f]}=-\min(-W_{[\mathbf{T}^i,\mathbf{T}^f]}); \tag{25}$$

the common extremal function $I(\tau^f,T^f,\tau^i T^i)$ describes the two modes, yet, in order to satisfy the second law of thermodynamics, each mode is accomplished in different regions of the space $\mathbf{T}$. Clearly, the quantity I describes the *extremal* value of the work integral $W[T^i,T^f]$, Eq. (10). It characterizes the extremal value of the work released for the prescribed temperatures T^i and T^f when the total process duration is $\tau^f-\tau^i$. (The invariance of the integral with respect to the variation of one of the end times when the total duration is fixed is consistent with the existence of the energylike integral for the problem.)

Here this problem is transformed into the equivalent problem in which one seeks the maximum of the final work coordinate $x_0^f=W^f$ for the system described by the following set of the differential equations:

$$\frac{dW}{d\tau}=-c\left(1-\frac{T^e}{u+T}\right)u\equiv f_0(T,u), \tag{26}$$

$$\frac{dT}{d\tau}=u\equiv f_1(T,u), \tag{27}$$

$$\frac{dx_2}{d\tau}=1\equiv f_2(T,u), \tag{28}$$

The state of the above system is described by the enlarged state vector $\mathbf{X}$ which is composed of the three state coordinates, $X_0=W$, $X_1=T$, and $X_2=\tau$. The designation $f_0(T,u)$ is used for the work production intensity in the integrand of the work integral. The last equation of the set states that the state coordinate $X_2=\tau$ has been chosen as the independent variable of the system. The single control variable $u=dT/d\tau$ (the rate of the temperature change of the driving fluid in the nondimensional contact time τ) is the process control for the system in which the temperature changes in the space. Supposedly, more involved models describing extensions of this problem may exist, with a vector of control variables $\mathbf{u}$, hence the symbol $\mathbf{u}$ rather than u is used in our general formulas below, where $\mathbf{u}$ is the control vector of any generalized process.

While the knowledge of the characteristic function I only is sufficient for a complete description of the extremal properties of the problem, other functions of this sort are nonetheless very suitable for the problem characterization. We now introduce the optimal performance functions, respectively, for the initial and final work coordinates Θ^i and Θ^f. One of these functions, Θ^i, works in the space of one dimension larger than I, and involves the work coordinate $x_0=W$

$$\max_{\mathbf{u}} W^f\equiv\Theta^i(W^i,\tau^i,T^i,\tau^f,T^f)=W^i+I(\tau^i,T^i,\tau^f,T^f). \tag{29}$$

This structure is the consequence of the fact that the state variable W is not explicitly present in the rates of the state equations (26)–(28). In this paper we do not consider more general cases.

In still enlarged space of variables $(W^i,\tau^i,T^i,W^f,\tau^f,T^f)$ we also introduce the (nonextremal) wave-front function V defined as

$$V \equiv W^f - \Theta^i(W^i,\tau^i,T^i,\tau^f,T^f) = W^f - W^i - I(\tau^i,T^i,\tau^f,T^f). \tag{30}$$

Its two mutually equal maxima, at the constant W^i and at the constant W^f, are described by the extremal functions $V^i(W^i,\tau^i,T^i,\tau^f,T^f) = V^f(\tau^i,T^i,W^f,\tau^f,T^f) \equiv 0$, which vanish identically along all optimal paths. They are associated, respectively, with maximum of the free final coordinate W^f in the subspace of variables $(W^i,\tau^i,T^i,\tau^f,T^f)$ and minimum of free initial coordinate W^i in the subspace $(\tau^i,T^i,W^f,\tau^f,T^f)$.

Regardless the state variables are constrained or not, the partial derivatives of the extremal performance function Θ^i with respect to its ''working state'' [the initial enlarged state (W^i,τ^i,T^i)] and those of the wave-front function $V = W^f - \Theta^i(W^i,\tau^i,T^i\ldots)$ do coincide modulo to sign. One can therefore use the negative partial derivatives $-\partial V/\partial T^i$, $-\partial V/\partial \tau^i$, and $-\partial V/\partial W^i$, instead of $\partial \Theta^i/\partial T^i$, $\partial \Theta^i/\partial \tau^i$, and $\partial \Theta^i/\partial W^i$ in any equation of the backward DP algorithm (the standard algorithm in which the initial set of the coordinates W^i, T^i, and τ^i forms the state variables).

On the other hand, within the same mode, one can also formulate a dual problem of a minimal initial work coordinate W^i, when the final work coordinate W^f is fixed. This minimum is described by the extremal performance function

$$\min_u W^i \equiv \Theta^f(W^f,\tau^f,T^f,\tau^i,T^i) = W^f - I(\tau^f,T^f,\tau^i,T^i), \tag{31}$$

which is related to the wave-front function V as follows

$$V = \Theta^f(W^f,\tau^f,T^f,\tau^i,T^i) - W^i = W^f - W^i - I(\tau,^i,T^i,\tau,^f,T^f) \tag{32}$$

[compare Eq. (30) for V in terms of Θ^i]. Of course, the following equalities hold along an extremal path:

$$\max W^f - W^i - I(\tau^f,T^f,\tau^i,T^i) = W^f - \min W^i - I(\tau^f,T^f,\tau^i,T^i) = 0, \tag{33}$$

They can be written in terms of the wave-front function V as follows:

$$\max V = \max\{W^f - W^i - I(\tau^f,T^f,\tau^i,T^i)\} = 0, \tag{34}$$

The partial derivatives of the extremal performance function Θ^f with respect to its coordinates of the working state [the final coordinates (W^f,T^f,τ^f) which are varied in the forward DP equation] and those of $V = \Theta^f - W^i$ do coincide. One may therefore use the partial derivatives $\partial V/\partial T^f$, $\partial V/\partial \tau^f$, and $\partial V/\partial W^f$ instead of $\partial \Theta^f/\partial T^f$, $\partial \Theta^f/\partial \tau^f$, and $\partial \Theta^f/\partial W^f$ in any equation of the *forward* DP algorithm (the algorithm where the final coordinates W^f, T^f, and τ^f are the state variables). These properties are exploited below.

We search for a dynamic programming equation by applying Bellman's optimality principle [16,17] for a control $\mathbf{u}$, in an admissible set U, which makes the final work coordinate $\mathbf{X}_0(\tau^f) \equiv W^f$ a maximum or the initial work coordinate, $X_0(\tau^i) \equiv W^i$, a minimum. We use the enlarged state vector $\mathbf{X}$ as the vector including the work coordinate $x_0 = W$ and the coordinates T and τ, and the optimality principle in a relatively seldom form which links the original and dual optimization problem. This form states that the *optimal* final value of an optimized quantity is a function of the initial state, whereas the *optimal* initial value of the optimized quantity is a function of the final state. Accordingly, the ''original'' problem of the maximal final work coordinate is described by the function $\Theta^i(\mathbf{X}^i) \equiv \Theta^i(W^i,\tau^i,T^i)$, Eq. (29), and the ''dual'' problem of the minimal initial work coordinate by the function $\Theta^f(\mathbf{X}^f) \equiv \Theta^f(W^i,\tau^i,T^i)$, Eq. (31). In the first function the complete set of the initial coordinates must appear, in the second one the complete set of the final coordinates must be used. Taking this into account, we will occasionally omit for brevity of formulas the remaining variables in these functions, which can be regarded as parameters. We apply the original and dual form of the optimality principle respectively for the initial and final part of a path, to show that the conclusions obtained from DP equations can be read in terms of the single, common wave-front function $V(\mathbf{X}^i,\mathbf{X}^f)$ which treats the initial and final states in the enlarged space $\mathbf{X}$ on an equal footing. While the accepted independent variable can be to large extent arbitrary (its monotonicity property in time is the suitable limitation), we will assume the time coordinate τ as the independent variable. We also assume that the rate $dW/d\tau \equiv dx_0/d\tau$ is known in the form $f_0(\mathbf{X},\mathbf{u}) = -L(\mathbf{X},\mathbf{u})$, where L is the integrand in Eq. (12) with $\dot{T} = u$. By passing to the usual residence time t (in seconds) and taking into account the explicit presence of transfer coefficients in f_0, one could admit the possibility of ''aging'' of the system. However, this extension is omitted in this paper. While below we derive the DP equations for $\Theta^i(\mathbf{X}^i)$ or $\Theta^f(\mathbf{X}^f)$ only, the related equation for the integral work function $I(T^i,t^i,T^f,t^f)$ in the narrowed space of the coordinates (T,τ), which does not involve the coordinate W, follows immediately from the condition $V = 0$. Our main task is now to derive the HJB equations as the basic quasilinear partial differential equations of the considered optimal control problems.

VI. DYNAMIC PROGRAMMING APPROACH TO HJB EQUATIONS

The problem can be treated mathematically as follows. Let us write our system of the three state equations [Eqs. (26), (27) and (28)] with the state variables $X_0 = W$, $x_1 = T$ and $x_2 = \tau$ in a general form

$$\frac{d\mathbf{X}_\beta}{d\tau} = \mathbf{f}_\beta(\mathbf{X},\mathbf{u}) \quad \beta = 0,1,2 \tag{35}$$

$(f_2 \equiv 1)$. Let us assume differentiability of the optimal performance function $\Theta^i(\mathbf{x}^i)$ and consider the control $\mathbf{u}$ in intervals $\langle \tau^i, \tau^i + \Delta\tau \rangle$ and $\langle \tau^i + \Delta\tau, \tau^f \rangle$, where $\Delta\tau$ is a small quantity. In order to take the variations of the initial state in $\Theta^i(x^i)$ into account, we assume that the ''long,'' final segment of trajectory, for τ in the interval $\langle \tau^i + \Delta\tau, \tau^i, \tau^f \rangle$, is optimal. The performance index of this segment equals

$\Theta^i(\mathbf{x}^i+\Delta\mathbf{x})$. Therefore the optimal final work for the whole path in the interval $\langle\tau^i,\tau^f\rangle$ is the maximum of the criterion

$$W^f\equiv\Theta^i(\mathbf{X}^i+\Delta\mathbf{X})=\Theta^i(W^i+\Delta W,T^i+\Delta T,\tau^i+\Delta\tau). \tag{36}$$

The maximization is with respect to the control vector $\mathbf{u}^i$ at the constant $\mathbf{X}^i$, for the small initial (nonoptimal) part of the path. It is performed at the constant $\mathbf{X}^i$ subject to all constraints, i.e., including the differential transformations of state, Eqs. (26) and (28). Restricting to linear terms of expansion of Θ^i, Eq. (36), in Taylor series one finds

$$\begin{aligned}W^f&=\Theta^i(\mathbf{X}^i)+\frac{\partial\Theta^i}{\partial X^i_\beta}\,\Delta X_\beta+0(\varepsilon^2)\\&=\Theta^i(W^i,T^i,\tau^i)+\frac{\partial\Theta^i}{\partial W^i}\,\Delta W+\frac{\partial\Theta^i}{\partial T^i}\,\Delta T\\&\quad+\frac{\partial\Theta^i}{\partial\tau^i}\,\Delta\tau+0(\varepsilon^2).\end{aligned} \tag{37}$$

In Eq. (37) the symbol $0(\varepsilon^2)$ means second-order and higher terms. They possess the property $\lim[0(\varepsilon^2)/\Delta\tau]\to 0$ when $\Delta\tau\to 0$.

Similarly, one may consider variation of the final coordinates of the state vector $\mathbf{X}=\mathbf{X}^f$. One then assumes that a ''long'' initial segment of a trajectory is optimal. The performance index of this optimal segment equals $\Theta^f(\mathbf{X}^f-\Delta\mathbf{X})$. In this case the control $\mathbf{u}=\mathbf{u}^f$ should be properly adjusted along a ''short'' nonoptimal final part of the path. The optimal initial work coordinate W^i, for the whole path in the interval $\langle\tau^i,\tau^f\rangle$, is the minimum of the criterion

$$W^i=\Theta^f(\mathbf{X}^f-\Delta\mathbf{X})=\Theta^f(W^f-\Delta W,T^f-\Delta T,\tau^f-\Delta\tau). \tag{38}$$

Now the minimization is with respect to the control $\mathbf{u}^f$, at the constant $\mathbf{X}^f$ and subject to all constraints, i.e., including the differential transformations Eqs. (26)–(28). Restricting to linear terms of expansion of Θ^f, Eq. (38), in Taylor series one obtains

$$\begin{aligned}W^i&=\Theta^f(\mathbf{X}^f)-\frac{\partial\Theta^f}{\partial\mathbf{X}^i_\beta}\,\Delta\mathbf{X}_\beta+0(\varepsilon^2)\\&=\Theta^f(W^f,T^f,\tau^f)-\frac{\partial\Theta^f}{\partial W^f}\,\Delta W\\&\quad-\frac{\partial\Theta^f}{\partial T^f}\,\Delta T-\frac{\partial\Theta^f}{\partial\tau^f}\,\Delta\tau+0(\varepsilon^2).\end{aligned} \tag{39}$$

In Eqs. (37) and (39) the state changes are connected with controls $\mathbf{u}$ by the state equations (35); hence for small $\Delta\tau$,

$$\Delta\mathrm{X}_\beta=\mathbf{f}_\beta(\mathbf{X},\mathbf{u})\Delta\tau+0(\varepsilon^2). \tag{40}$$

After substituting Eq. (40) into Eqs. (37) and (39), and performing the appropriate extremizations in accordance with Bellman's principle of optimality, one obtains, for variations of the initial point,

$$\max_{\mathbf{u}^i}\,W^f=\max_{\mathbf{u}^i}\left\{\Theta^i(\mathbf{X}^i)+\frac{\partial\Theta^i}{\partial X^i_\beta}\,\mathrm{f}_\beta(\mathbf{X},\mathbf{u})\Delta\tau+0(\varepsilon^2)\right\} \tag{41}$$

and for the variations of the final point

$$\min_{\mathbf{u}^f}\,W^i=\min_{\mathbf{u}^f}\left\{\Theta^f(\mathbf{X}^f)-\frac{\partial\Theta^f}{\partial X^f_\beta}\,\mathrm{f}_\beta(\mathbf{X},\mathbf{u})\Delta\tau+0(\varepsilon^2)\right\}. \tag{42}$$

Equations (41) and (42) can then be simplified on the basis of definition of the optimal performance functions Θ^i and Θ^f, Eqs. (29) and (31), and using the property that these functions are independent of the control $\mathbf{u}$. After reduction of Θ^i and Θ^f and the division of both sides of Eqs. (41) and (42) by $\Delta\tau$, the passage to the limit $\Delta\tau\to 0$ subject to the condition $\lim[0(\varepsilon^2)/\Delta\tau]\to 0$ yields, respectively, the backward and forward HJB equations of the optimal control problem.

For the initial point of the extremal path, one finds, as the backward DP equation,

$$\begin{aligned}\max_{\mathbf{u}^i}\left\{\frac{\partial\Theta^i}{\partial\mathrm{X}^i_\beta}\,\mathrm{f}_\beta(\mathbf{X},\mathbf{u})\right\}&=\max_{\mathbf{u}^i}\left\{\frac{\partial\Theta^i}{\partial W^i}\,\dot W^i(T^i,\mathbf{u}^i)+\frac{\partial\Theta^i}{\partial T^i}\,\dot T^i(T^i,\mathbf{u}^i)+\frac{\partial\Theta^i}{\partial\tau^i}\right\}\\&=\max_{\mathbf{u}^i}\left(\frac{d\Theta^i}{d\tau^i}\right)=-\min_{\mathbf{u}^i}\left(\frac{dV}{d\tau^i}\right)\\&=\max_{\mathbf{u}^i}\left(\frac{dV}{d(-\tau^i)}\right)=0.\end{aligned} \tag{43}$$

On the other hand, for the final point of the extremal path, one finds the forward DP equation

$$\begin{aligned}\min_{\mathbf{u}^f}\left\{-\frac{\partial\Theta^f}{\partial\mathrm{X}^f_\beta}\,\mathrm{f}_\beta(\mathbf{X},\mathbf{u})\right\}&=-\max_{\mathbf{u}^f}\left\{\frac{\partial\Theta^f}{\partial W^f}\,\dot W^f(T^f,\mathbf{u}^f)+\frac{\partial\Theta^f}{\partial T^f}\,\dot T^f(T^f,\mathbf{u}^f)+\frac{\partial\Theta^f}{\partial\tau^f}\right\}\\&=\min_{\mathbf{u}^f}\left(-\frac{d\Theta^f}{d\tau^f}\right)\\&=\min_{\mathbf{u}^f}\left(-\frac{dV}{d\tau^f}\right)\\&=-\max_{\mathbf{u}^f}\left(\frac{dV}{d\tau^f}\right)=0.\end{aligned} \tag{44}$$

The properties of $V=W^f-\Theta^i=\Theta^f-W^i$ have been used in the second lines of the above equations. The rates $d\mathbf{X}_\beta/d\tau$ should necessarily be considered in terms of the state variables and control(s). One concludes that *the optimal motion of the wave always maximizes the speed of the advancing wave front $dV/d\tau^f$ or the speed of the retreating wave front $dV/d(-\tau^i)$.*

The partial derivative of V with respect to the independent variable τ can remain outside of the bracket of this equation as well. Taking this into account as well as using in Eqs. (43)

and (44), $\partial V/\partial W^i = -\partial \Theta^i/\partial W^i = -1$, $\partial V/\partial W^f = \partial \Theta^f/\partial W^f = 1$, and $\dot{W} = f_0 = -L$, one finds for the extremal work problem

$$\frac{\partial V}{\partial \tau^i} + \min_{u^i}\left\{ \frac{\partial V}{\partial T^i} u^i + L^i(T^i,u^i) \right\} = 0 \quad (\max W^f), \quad (45)$$

$$\frac{\partial V}{\partial \tau^f} + \max_{u^f}\left\{ \frac{\partial V}{\partial T^f} u^f - L^f(T^f,u^f) \right\} = 0 \quad (\min W^i). \quad (46)$$

In terms of the integral function of optimal work, $I = W^f - W^i - V$, these equations become, respectively,

$$\frac{\partial I}{\partial \tau^i} + \max_{u^i}\left\{ \frac{\partial I}{\partial T^i} u^i + f_0^i(T^i,u^i) \right\} = 0, \quad (47)$$

$$\frac{\partial I}{\partial \tau^f} + \min_{u^f}\left\{ \frac{\partial I}{\partial T^f} u^f - f_0^f(T^f,u^f) \right\} = 0. \quad (48)$$

In all equations of this sort the extremized expression are some Hamiltonians. In fact, they are Pontryagin's type, nonextremal Hamiltonians. The optimal control u which solves the optimal work problem is chosen in order to extremize a Hamiltonian at each point of the extremal path, which means extremizing the wave-front velocity $dV/d\tau$ in the considered HJB equation. As long as the optimal control u is found in terms of the state, time, and gradient components of the extremal performance function I, the passage from the quasilinear HJB equation to the corresponding nonlinear Hamilton-Jacobi equation is possible.

VII. PASSAGE TO HAMILTON-JACOBI EQUATION

The process Lagrangians are represented by the rate of the work production, f_0, or the rate of the work consumption, L, where $L = -f_0$. For these Lagrangians, the extremum condition of the Hamiltonian of the pertinent HJB equation (which is, in fact, the Pontryagin's Hamiltonian) links the derivatives of L or $-f_0$ with respect to the process rate $u = \dot{T}$ with the adjoint variable $z = -\partial V/\partial T = \partial I/\partial T$. For concreteness we will work with Eq. (47), in which the index i is omitted. The maximization of this equation with respect to the rate u leads to the two equations of which the first describes the optimal control u expressed through the variables T and $z \equiv \partial I/\partial T$,

$$\frac{\partial I}{\partial T} = -\frac{\partial f_0(T,u)}{\partial u}, \quad (49)$$

and the second is the original Eq. (47) without the extremization sign

$$\frac{\partial I}{\partial \tau} + \frac{\partial I}{\partial T} u + f_0(T,u) = 0. \quad (50)$$

With the momentum-type variable, $z \equiv \partial I/\partial T$, and using Eq. (49) written in the form

$$z = -\frac{\partial f_0(T,u)}{\partial u} = \frac{\partial L(T,u)}{\partial u}, \quad (51)$$

one can solve the above equation in terms of u to obtain the function $u(z,T)$. Next one substitutes this function into the two last terms on the left-hand side of Eq. (50). [This is just the maximal case of Eq. (47).]. One obtains then the energy-type Hamiltonian of the extremal process,

$$H(T,\tau,z) = zu(z,T) + f_0(z,T). \quad (52)$$

With this Hamiltonian and using $z \equiv \partial I/\partial T$, one obtains from Eq. (50) the Hamilton-Jacobi equation for the integral I,

$$\frac{\partial I}{\partial \tau} + H\left(T, \frac{\partial I}{\partial T} \right) = 0. \quad (53)$$

(In our example both functions f_0 and H do not contain time explicitly.) This equation differs from the HJB equations as it refers to extremal paths only, and H is the *extremal* Hamiltonian. In Sec. VIII we apply the above formulas to our concrete Lagrangian $L = -f_0$, where f_0 is the intensity of the mechanical work production.

A brief heuristic approach to derivation of Eq. (53) for a fixed but otherwise arbitrary mode along the lines of reasoning first introduced to variational calculus by Caratheodory is insightful [25–27]. As follows from the definition of the maximum performance function I for the work functional (23) in which the final state is subject to variations (while I still includes a fixed initial state)

$$\max_{\{u(\tau)\}}\left\{ \int_{t^i}^{t^f} f_0(T,u)\, d\tau - I(T^i,\tau^i,T^f,\tau^f) \right\} = 0. \quad (54)$$

The path differentiation of this equation with respect to the final time τ^f proves that the total time derivative of I satisfies the equation

$$\max_u\left\{ f_0^f(T^f,u^f) - \frac{dI(T^i,\tau^i,T^f,\tau^f)}{d\tau^f} \right\} = 0, \quad (55)$$

whereas for the free initial state of the dual problem and the same mode of the process

$$\min_u\left\{ -f_0^i(T^i,u^i) - \frac{dI(T^i,\tau^i,T^f,\tau^f)}{d\tau^i} \right\} = 0. \quad (55')$$

Equation (55) describes the vanishing maximum of the power f_0 gauged by the total derivative of the optimal performance function. Expanding in Eq. (55) the total time derivative and changing signs (associated with change of the extremum operation) yields

$$\min_{\mathbf{u}^f}\left\{ \frac{\partial I}{\partial \tau^f} + \frac{\partial I}{\partial T^f} u^f - f_0^f(T^f,u^f) \right\} = 0. \quad (56)$$

In view of the equalities $\partial I/\partial \tau^f = -\partial I/\partial \tau^i$ and $\partial I/\partial T^f = -\partial I/\partial T^i$ the above equation reads in terms of the initial state quantities as follows:

$$\min_{\mathbf{u}^i}\left\{ -\frac{\partial I}{\partial \tau^i} - \frac{\partial I}{\partial T^i} u^i - f_0^i(T^i,u^i) \right\} = 0, \quad (56')$$

which is identical to with Eq. (55′) and equivalent with Eq. (47). The latter leads to the Hamilton-Jacobi equation (53).

VIII. HAMILTON-JACOBI EQUATIONS FOR EXTREMAL WORK AND GENERALIZED AVAILABILITY

Now the general procedure described in Sec. VII is applied to the basic integral (10) written in the form

$$W_{I\mathbf{T}^i\cdot\mathbf{T}^fI}=\int_{T^i}^{T^f}\left\{-c\left(1-\frac{T^e}{T+u}\right)u\right\}d\tau, \tag{57}$$

whose extremal value is the function $I(T^i,\tau^i,T^f,\tau^f)$. The momentumlike variable (equal to the temperature adjoint) is then

$$z\equiv-\frac{\partial f_0}{\partial u}=c\left(1-\frac{T^eT}{(T+u)^2}\right). \tag{58}$$

Hence the rate control u in terms of T and its adjoint $z=\partial I/\partial T$,

$$u=\left(\frac{T^eT}{1-z/c}\right)^{1/2}-T. \tag{59}$$

The energylike function $E(T,u)$ of the problem is the rate representation of the extremal Hamiltonian,

$$E(T,u)=-\frac{\partial f_0}{\partial u}u+f_0=\frac{\partial L}{\partial u}u-L=cT^e\frac{u^2}{(T+u)^2}. \tag{60}$$

The extremal Hamiltonian itself is E expressed in terms of the adjoint z,

$$H(T,z)=cT^{-1}(1-z/c)\left[\left(\frac{T^eT}{1-z/c}\right)^{1/2}-T\right]^2, \tag{61}$$

from which the extremal Hamiltonian is described by the simple formula

$$\begin{aligned}H(T,z)&=cT^{-1}[\sqrt{T^eT}-T\sqrt{(1-z/c)}]^2\\&=c[\sqrt{T^e}-\sqrt{T(1-z/c)}]^2.\end{aligned} \tag{62}$$

Accordingly, the Hamiltonian in terms of the derivative $\partial I/\partial T$ is

$$H(T,\partial I/\partial T)=c[\sqrt{T^e}-\sqrt{T(1-c^{-1}\partial I/\partial T)}]^2. \tag{63}$$

By changing signs at the adjoint variables one could obtain a negatively-defined H which could reflect the energy dissipation; however, we retain the Hamiltonian (63) positive. Such a quantity H is still a well-defined property of the dissipative process.

The Hamilton-Jacobi partial differential equation for the maximum work problem (the engine mode of the system) deals with the initial coordinates, and has the form

$$\partial I/\partial\tau+c[\sqrt{T^e}-\sqrt{T(1-c^{-1}\partial I/\partial T)}]^2=0. \tag{64}$$

Equation (64) is valid not only for the engine mode but also for the heat-pump mode. Indeed, for the heat-pump mode one has to minimize the time integral over the Lagrangian $L=-f_0(T,u)$, and that procedure leads to the extremal function $-I(T^i,\tau^i,T^f,\tau^f)$. The adjoint variables and the Hamiltonian change their signs ($\lambda=-z$, where $\lambda=-\partial I/\partial T$. Consistently, the new Hamilton-Jacobi equation takes the form of the equation given above. See our complementary work [10,11] for related information about the canonical equations and the role of the Legendre condition.

IX. HAMILTON-JACOBI APPROACH TO MINIMUM ENTROPY GENERATION

Our analysis based on Eq. (14) has shown that the variational fixed-end problem of the maximum work W is equivalent to the variational fixed-end problem of the minimum entropy production. Let us, however, compare the Hamilton-Jacobi equations of these two problems. The specific entropy production is described by the functional [11]

$$S_\sigma=\int_0^{\tau^f}L_\sigma d\tau\equiv\int_0^{\tau^f}c\,\frac{u^2}{T(T+u)}\,d\tau. \tag{65}$$

Assume that the minimum of this functional is described by the optimal function $I_\sigma(T^i,\tau^i,T^f,\tau^f)$. We shall find the Hamilton-Jacobi equation for this function. For an extremal path the partial derivative $\partial I_\sigma/\partial T$ satisfies the maximum condition for the corresponding Pontryagin's Hamiltonian. This condition yields

$$z_\sigma\equiv\frac{\partial I_\sigma}{\partial T}=\frac{\partial L_\sigma}{\partial u}, \tag{66}$$

where $\partial L_\sigma/\partial u$ is the adjoint variable of the entropy generation problem, or the momentum-type variable $\partial L_\sigma/\partial T$. In our case

$$\frac{\partial L_\sigma}{\partial u}=\frac{c}{T}\left[1-\frac{T^2}{(u+T)^2}\right], \tag{67}$$

from which

$$\frac{T}{u+T}=\sqrt{1-Tz_\sigma/c}. \tag{68}$$

It follows from the Legendre necessary condition for a minimum of the functional (65) that the sum $T+u$ must always be positive, the condition which limits considerably the values of z_σ whenever u is negative as in the case of the engine cooling. From Eq. (67) the positive values $\partial L_\sigma/\partial u=z_\sigma$ correspond to the heating of fluid (heat-pump mode when $T>T^e$) and the negative values of z_σ correspond to the cooling of fluid (engine mode when $T>T^e$). From Eq. (68), one finds the rate control $u=dT/d\tau$ in terms of the temperature T and its adjoint $z_\sigma=\partial I_\sigma/\partial T$,

$$u=T\left(\frac{1}{\sqrt{1-Tz_\sigma/c}}-1\right). \tag{69}$$

This equation is valid for every mode of the system. The energylike integral for the entropy production functional, Eq. (65), is

$$E_\sigma = \frac{\partial L_\sigma}{\partial u} u - L_\sigma = c\,\frac{u^2}{(T+u)^2}. \tag{70}$$

Moreover, from Eqs. (60) and (70) the following equation holds:

$$E = T^e E_\sigma. \tag{71}$$

The equation means that the equality $E = E'_\sigma$ is valid, where $E'_\sigma \equiv T^e E_\sigma$, and the equations $E(u) = h$ and $E'_\sigma(u) = h$ have the same solutions with respect to the rate $u = dT/d\tau$. This is, of course, the formal consequence of the physical equivalence between the problem of the minimum entropy generation and the problem of the extremum work. This equivalence can be stated in the form of equality (71) for each mode of the system.

The entropy production Hamiltonian H_σ is the representation of E_σ in terms of T and z_σ,

$$H_\sigma = c\,\frac{u_2}{(T+u)^2} = c\left(\frac{T}{\sqrt{1-Tz_\sigma/c}} - T\right)^2 \left(\frac{T}{\sqrt{1-Tz_\sigma/c}}\right)^{-2}, \tag{72}$$

from which

$$H_\sigma = c\left(1 - \sqrt{1-Tz_\sigma/c}\right)^2. \tag{73}$$

Clearly, from Eqs. (66), (67), and (70), the case of vanishing z_σ and u implies $H_\sigma = 0$ identically. This case refers to the reversible quasistatic processes.

The Hamilton-Jacobi partial differential equation for the minimum entropy generation problem (each mode of the system) is

$$\partial I_\sigma/\partial\tau + c\left(1 - \sqrt{1 - c^{-1} T \partial I_\sigma/\partial T}\right)_2 = 0. \tag{74}$$

This equation can be compared with Eq. (64), which describes the extremal work problem in terms of the work Hamiltonian H, Eq. (63). In spite of the equality $E = E'_\sigma$ the partial derivatives of both extremal functions with respect to T, $\partial I/\partial T$ and $I'_\sigma/\partial T$, differ. Since, however, the two functionals (that of the work and that of the entropy generation) yield the same extremal, the connection between them should exist. This connection is determined in Sec. X.

X. AN ANALOGY WITH A PARTICLE IN A VECTOR FIELD AND GAUGING THE ENERGY DISSIPATION

An interesting formal analogy can be observed between the thermodynamic system considered and a microscopic system which contains a particle in a vector field, say, an external electromagnetic field. In the latter case, the addition of the vector potential term $\mathbf{A}\cdot\mathbf{v}$ to the particle Lagrangian does not change the value of the energy of the particle in the electromagnetic field. Since, hovever, the term $\mathbf{A}\cdot\mathbf{v}$ changes the canonical momenta, the Hamilton-Jacobi equation of the particle contains the vector potential $\mathbf{A}$, and thus it differs from the corresponding equation of the particle when the field is removed.

In the thermodynamic case considered, the role of the $\mathbf{A}\cdot\mathbf{v}$ term is played by the product $-c(1-T^e/T)\dot{T}$, which appears in the first line of Eq. (14), as the term representing the ''reversible'' thermodynamic power. From the formal viewpoint the thermodynamic case is more special than the electromagnetic case, not only because the former is one dimensional but also because a thermodynamic counterpart of the the electric potential ϕ does vanish and the classical thermodynamic work acquires the potential (path-independent) property. Leaving aside these differences, however, the formal consequence of the linearity of the reversible term $-c(1-T^e/T)\dot{T}$ with respect to $\dot{T}$ is that this term does not influence the dissipative energies E and E_σ, Eqs. (60) and (70); hence the equality $E = E'_\sigma$ described by Eq. (71) is valid. Yet the considered term of Eq. (14) influences the definition of the canonical momenta, and this is why it causes the different forms of the Hamilton-Jacobi equations for the work and entropy generation, Eqs. (64) and (74). Moreover, the potential nature of the classical work integral, Eq. (13), causes the identity of the extremal trajectories for the work extremization problem and those for the entropy generation minimization problem. The potentiality of the classical work integral (13) is the property which renders the analogy considered trivial, since the thermal counterparts of the electric and magnetic fields E and H vanish identically in the thermodynamic problem.

The canonical transformation theory can be applied in this case which leads to the conclusion that the lost power $L'_\sigma \equiv T^e L_\sigma$ can be gauged by addition of the total time derivative $d\Omega/d\tau$ of a gauging function $\Omega(T)$. Taking into account the change in the type of the extremum operation, in order to preserve unchanged equation of the extremal curve, the following general equation must link the momentum-type variables:

$$\frac{\partial f_0}{\partial u} = \frac{\partial \Omega}{\partial T} - \frac{\partial L_\sigma}{\partial u}. \tag{75}$$

When the above equation is applied to our thermodynamic problem, the result is

$$-c\left[1 - \frac{T^e T}{(\dot{T}+T)^2}\right] = \frac{d\Omega(T)}{dT} - \frac{cT^e}{T}\left[1 - \frac{T^2}{(\dot{T}+T)^2}\right]. \tag{76}$$

This relationship links the Lagrangians of the entropy generation and work. The equality $E'_\sigma = E$ proves that we are dealing with an autonomous gauging function Ω, hence the time independent derivative $d\Omega/dT$ in Eq. (76). The above equation yields

$$\frac{d\Omega(T)}{dT} = -c\left(1 - \frac{T^e}{T}\right), \tag{77}$$

from which after integration between T^i and T^f,

$$\Omega(T) = c(T^i - T^f) - cT^e \ln\left(\frac{T^i}{T^f}\right) = -\Delta B(T), \tag{78}$$

which is just the classical work or the *change* of the classical thermal availability, Eq. (13). Therefore the change of the classical available energy is just the Hamiltonian-preserving gauging function for the functional based on the entropy generation intensity, $L'_\sigma \equiv T^e L_\sigma$. Equalities (71) and (76) may be viewed as equations linking the two functionals, the entropy generation functional and the generalized availability functional, along an extremal. Extraction of the potential work ΔB from the total work of the process is that form of gauging which preserves the same extremal trajectories and dissipative Hamiltonians of the two fixed-end problems considered. This conclusion is also illustrated by the relation between the two available energy functions, generalized and classical, as described by Eq. (84).

XI. PRINCIPAL POTENTIAL FUNCTIONS FOR EXTREMUM WORK AND GENERALIZED AVAILABLE ENERGY

One can now discuss the solutions of the Hamilton-Jacobi equations for the considered problems. From Eq. (23), by integration along an extremal path, one finds the function which describes the optimal specific work,

$$I(T^i,T^f,\tau^i,\tau^f)=c(T^i-T^f)-\frac{T^e}{1+\xi}\,c\,\ln\frac{T^i}{T^f}. \qquad (79)$$

This is the expression which generalizes *changes* of the available energy to processes with a finite rate $dT/d\tau=\xi T$. In a finite-rate process this work depends explicitly on the process duration.

From the above equation and after using the end conditions to evaluate the intensity ξ in terms of the boundary temperatures and times,

$$\xi=\frac{\ln(T^f/T^i)}{\tau^f-\tau^i}=-\frac{\ln(T^i/T^f)}{\tau^f-\tau^i}\quad(\text{each mode}), \qquad (22')$$

the extremal specific work between two arbitrary states follows for every process mode in the form

$$\begin{aligned}I(T^i,T^f,\tau^i,\tau^f)&=c(T^i-T^f)-cT^e\ln\frac{T^i}{T^f}\\&\quad+c\left(T^e-\frac{T^e}{1+\xi}\right)\ln\frac{T^i}{T^f}\\&=c(T^i-T^f)-cT^e\ln\frac{T^i}{T^f}\\&\quad+cT^e\left(\frac{\xi}{1+\xi}\right)\ln\frac{T^i}{T^f}\\&=c(T^i-T^f)-cT^e\ln\frac{T^i}{T^f}\\&\quad-cT^e\frac{[\ln(T^i/T^f)]^2}{\tau^f-\tau^i-\ln(T^i/T^f)}.\end{aligned} \qquad (80)$$

The particular extremal work which describes the generalized availability should contain the environment temperature as one of the boundary states. The generalized availability function is the maximal work $W_{\max}=I(T^i,\tau^i,T^f,\tau^f)$ with $T^i=T$ and $T^f=T^e$ for the engine mode, and the negative minimal work $(-W)_{\min}=-I(T^i,\tau^i,T^f,\tau^f)$ with $T^i=T^e$ and $T^f=T$ for the heat-pump mode of the system. For $\xi=0$ the change of the classical thermal availability, a positive quantity, is recovered.

From Eq. (80), with $T^i=T$ and $T^f=T^e$, one finds the dissipative exergy of the engine mode

$$E_x(T,T^e,\tau^i,\tau^f)=c(T-T^e)-cT^e\ln\frac{T}{T^e}-cT^e\frac{[\ln(T/T^e)]^2}{\tau^f-\tau^i-\ln(T/T^e)}. \qquad (81)$$

E_x is the generalized (irreversible) exergy of mass unit which includes the effect of dissipation caused by finite rates in the boundary layers of the real fluids. It may be verified that this function satisfies the backward Hamilton-Jacobi equation, which is Eq. (64) with respect to the initial state and for $I=E_x$. Otherwise, one obtains the exergy of the heat-pump mode for the function $-I(T^i,\tau^i,T^f,\tau^f)$ with $T^i=T^e$ and $T^f=T$

$$E_x(T,T^e,\tau^i,\tau^f)=c(T-T^e)-cT^e\ln\frac{T}{T^e}+cT^e\frac{[\ln(T/T^e)]^2}{\tau^f-\tau^i+\ln(T/T^e)}. \qquad (82)$$

This function satisfies the forward Hamilton-Jacobi equation or Eq. (64) with respect to the final state and for $I=-E_x$. Taking into account that the last term of the above equation contains the minimal integral of the entropy production,

$$S_\sigma(T,T^e,\tau^i,\tau^f)=c\,\frac{[\ln(T/T^e)]^2}{\tau^f-\tau^i\pm\ln(T/T^e)}, \qquad (83)$$

the general formula for the dissipative exergy is

$$\begin{aligned}E_x(T,T^e,\tau^f)&=c(T-T^e)-cT^e\ln\frac{T}{T^e}\\&\quad\pm cT^e\frac{(\tau^f)^{-1}[\ln(T/T^e)]^2}{1+\pm(\tau^f)^{-1}\ln(T/T^e)}\\&=E_x(T,T^e,\infty)\pm T^eS_\sigma,\end{aligned} \qquad (84)$$

where $E_x(T,T^e,\infty)$ is the classical available energy of mass unit, B, and we have assumed without any losses in generality that $\tau^i=0$. In the above equations the upper sign refers to the heat-pump mode, and the lower sign to the engine mode.

An alternative form of the generalized available energy contains the *height of the transfer unit* $H_{\mathrm{TU}}=\mathcal{L}/\tau$ and the contact length $\mathcal{L}$

$$E_x(T^f,T^e,\tau)=E_x(T^f,T^e,\infty)\pm cT^e\frac{H_{\mathrm{TU}}[\ln(T^f/T^e)]^2}{\mathcal{L}\pm H_{\mathrm{TU}}\ln(T^f/T^e)}. \qquad (85)$$

This form shows that the classical availability yields an exact estimation of the extremal work for small H_{TU}, i.e., for the excellent transfer conditions, or for infinitely long contact times of the energy exchange. The generalized availability of the engine mode, the exergy function $E_x=(W)_{\max}$, which defines the upper bound for the mechanical work released in a finite time, is necessarily smaller that the maximal work of classical thermodynamics. Otherwise the generalized availability of the heat-pump mode, $E_x=(-W)_{\min}$, which defines the lower bound on the work consumption, can be significantly higher than the minimal work of classical thermodynamics. For state changes occurring in short times, this work may differ from the classical work substantially. These ''rate penalty'' effects are a consequence of nonvanishing entropy generation in all finite-time processes.

XII. ENHANCED BOUNDS FOLLOWING FROM SECOND LAW

The general thermodynamic result in the second line of Eq. (84) is in the complete agreement with the classical Gouy-Stodola law [13,14]. This law is, in fact, a formulation of the second law of thermodynamics, which links losses of the extremal work, finiteness of the process rates, and the related entropy generation, S_σ. However, the classical formulations of the second law (contained in the adduced works, for example), provide neither analytical expressions for the nonclassical component of the availability (and the related quantity S_σ) nor information about the time evolution of the system. For these purposes a dynamical model of the evolution and the solution of the related Hamilton-Jacobi equation [such as Eq. (64)] are necessary. Therefore the HJB theory becomes an important ingredient of nonequilibrium thermodynamics in which certain post-thermostatic (rate penalty) terms are sought for generalized thermodynamic potentials, i.e., when classical thermodynamic potentials are generalized to finite-time durations.

The irreversible or hysteretic properties of the generalized exergy as a finite-time work function are important. They are associated with different values of the work function obtained when processes which leave the equilibrium are compared with corresponding inverse processes, which approaches the equilibrium. The first sort of processes corresponds with the heat-pump mode, associated with the supply of the work to the system, the second sort of processes—with the engine mode, characterized by the delivery of the work from the system. Speaking in more general terms, processes departing from equilibrium may be regarded as those in which the creation of a (nonequilibrium) structure takes place. Otherwise the processes approaching the equilibrium may be regarded as those of the destruction of the structure.

While in the classical reversible thermodynamics the two modes can be accomplished with exactly the same magnitude of work, in the generalized theory, which includes the effect of dissipation, the works consumed and produced in the two modes operating between the two fixed states are no longer equal. A significant decrease of the maximal work received from the engine system and an increase of the minimal work added to the heat-pump system is shown in the high-rate regimes and for short durations of thermodynamic processes. These results show that limits known from the classical availability theory should be replaced by stronger limits obtained for finite-time processes, which are closer to reality. These limits are such that the structure creation processes consume in a finite time more mechanical energy than the mechanical energy which could be recovered in corresponding processes of the structure destruction. This is another manifestation of the asymmetry inherent in the macroscopic world, which is explained by the second law of thermodynamics.

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