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Nonlinear models for mechanical energy production in imperfect generators driven by thermal or solar energy

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Abstract

In this paper we show how the nonlinear kinetics of energy transfer in propelling fluids and imperfect (non-Carnot) thermal machines can be imbed into the contemporary theory of irreversible energy generators and heat pumps. We quantitatively describe effects of nonlinear heat transfer assuming that heat fluxes are proportional to the difference of temperature in certain power, T^a. We also show that the energy and particle transports can be treated either in a conventional way or as peculiar chemical reactions. In the latter case a recent approach distinguishes in each elementary transfer step two competitive (unidirectional) fluxes and the resulting flux follows as their difference. Nonlinear imperfect systems are investigated in the context of efficiency, heat flux, entropy production and mechanical power, for steady and unsteady operations.

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1. Introduction

When a hot fluid interacts indirectly with an environment through an engine mechanical power is produced. The mechanism of heat transfer between the fluid and the medium circulating in the engine has the significant influence on the efficiency of power production. The heat transfer is not necessarily linear. Gutowicz–Krusin et al. [1] derived a performance bound of a Carnot engine with the heat transfer law $q \propto (\Delta T)^n$. De Vos [2], Chen and Yan [3], Chen et al. [4], Gordon [5], Wu [6,7] and Chen et al. [8], have investigated the effect of the heat transfer law on the performance of irreversible heat engines. Yet, the works quoted above were restricted to steady systems (infinite reservoirs) and ignored the effect of internal irreversibility within the energy generator by considering Carnot engines and "endoreversible" systems. Our approach here extends our previous results [9,10] towards abandoning endoreversibility and providing nonlinear theory for imperfect unsteady processes that arise due to the finiteness of the resource propelling the engine (hot reservoir). Associated with the work delivered from a finite resource interacting with the environment in a finite time is the problem of a an exergy function. It is considered in the last section of the paper. The exergy considered here refers to a finite-time minimally irreversible process and, moreover, includes an imperfection factor of the energy generator, thus it represents a finite-time (irreversible) generalization of the classical exergy. We show that the generalized exergy provides suitable bounds on the energy production (consumption) that are stronger than classical thermostatic bounds.

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Nomenclature

A^{∞}	generalized exergy of a continuous process
A^{class}	classical available energy (exergy)
c	molar heat capacity defined as the derivative $\mathrm{d}h/\mathrm{d}T$
G	molar flux of fluid, total flow rate
g_1, g	partial and overall conductances
H_{TU}	height of transfer unit
h	molar enthalpy
n	stage number
P, p	cumulative power output and power output at a stage
Q_1	cumulative heat
q_1	driving heat power
$R(\boldsymbol{x}, t)$	optimal work function of cost type in terms of state and time
r_1, r_2	resistances, reciprocals of conductances g_1 and g_2
S	entropy of controlled phase
$\Delta S_{1'}$	entropy change of the circulating fluid along the isotherm $T_{1'}$ in Fig. 1
$\Delta S_{2'}$	entropy change of the circulating fluid along the isotherm $T_{2'}$ in Fig. 1
S_{σ}	specific entropy production
T	temperature of controlled phase
T_1, T_2	bulk temperatures of fluids 1 and 2
$T_{1'}$, $T_{2'}$	temperatures of circulating fluid (Fig. 1)
T^{e}	constant equilibrium temperature of environment
T'	Carnot temperature, temperature of controlling phase
t	physical time, contact time
$\dot{T} = \mathrm{d}T/\mathrm{d}\tau$	rate of temperature change as the control variable
$V = \max W$	optimal work function of profit type
$W = P/G$	total specific work or total power per unit molar flux of fluid
x	transfer area coordinate

Greek symbols

α'	overall heat transfer coefficient
$\eta = p/q_1$	first-law efficiency
Φ	factor of internal irreversibility
σ_{s}	cumulative entropy production
τ	nondimensional time, number of the heat transfer units (x/H_{TU})

Subscripts

i	i-th state variable
mp	maximum power point
1, 2	first and second fluid

Superscripts

e	environment, equilibrium
f	final state
I	initial state
N	total number of stages

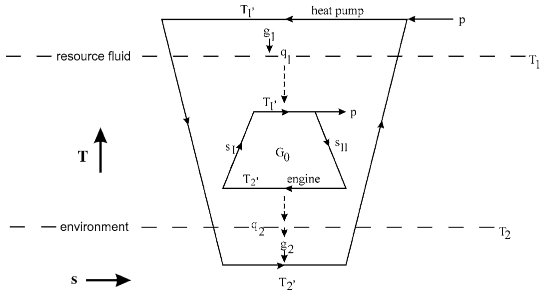

Fig. 1. Principle of designations for two basic modes with internal and external dissipation: power yield in an engine and power consumption in a heat pump. The primed temperatures characterize the circulating fluid.

In this research energy limits for imperfect cycles producing or consuming mechanical energy are investigated in the framework of finite time thermodynamics by taking the maximum power as the objective. Since the heat transfer law has a strong effect on the performance of the cycle an approach is pursued that aspires to derive a relatively large number of basic equations in the form independent on the mode of energy transfer between the circulating fluid and reservoirs. In the nonlinear modeling which is the methodological extension of that known for the linear case the heat transfer is assumed to obey the power law T^a (heat flux proportional to the difference in T^a) instead of Newton's linear law. A more recent approach is also briefly considered in which one distinguishes in each elementary transfer process two competitive (unidirectional) fluxes and the resulting flux being their difference. The unidirectional fluxes are equal in the thermodynamic equilibrium and their difference off the equilibrium constitutes the observed flux representing the resulting rate of the process. In this approach nonlinear resistance and a related affinity play important role. In most general situation when the particle transfer is included the non-equilibrium transports are described by equations containing exponential terms with respect to chemical potentials of Planck and temperature reciprocal, that simultaneously are analytical expressions characterizing the transport of the substance or energy by the energy barrier. We show how the kinetics of this sort can be imbed into the contemporary theory of thermal energy generators.

2. Thermodynamic issues

The classical exergy defines bounds on the common work delivered from (or supplied to) slow, reversible processes [11]. Such bounds are reversible as the magnitude of the work delivered during the reversible approach to equilibrium is equal to the one of the work supplied, after the initial and final states are inverted, i.e. when the second process reverses to the initial state of the first. Our research is towards generalization of the classical exergy for finite rates. During the approach to the equilibrium the so-called engine mode of the system takes place in which the work is released, during the departure the so-called heat-pump mode occurs in which the work is supplied. The work W delivered in the engine mode is positive by assumption. In the heat-pump mode W is negative, which means that the positive work $(-W)$ must be supplied to the system. To find a generalized exergy, optimization problems are considered, for the maximum of the work delivered [max W] and for the minimum of the work supplied [min $(-W)$]. We show that while the reversibility property is lost for such exergy, its (kinetic) bounds are stronger and hence more useful than classical thermostatic bounds. This substantiates role of the extended exergy for evaluation of energy limits in practical systems.

With functionals of power generation (consumption) at disposal we can formulate the Hamilton–Jacobi–Bellman theory (HJB theory) for the extended exergy and related extremum work. The HJB theory is the basic ingredient in variational calculus and optimal control [12–14]. A HJB equation extends the classical Hamilton–Jacobi equation [15] by addition of extremum conditions, and it is essential to develop numerical methods in complex cases (with state dependent coefficients) when the HJB equation of the problem cannot be solved analytically. Due to the direct link between the HJB theory and dynamic programming the associated numerical methods make use the Bellman's recurrence equation. These methods are complementary with respect of the Pontryagin's principle [16], as both are effective seeking methods of functional extrema. Yet, in spite of its power, Pontriagin's principle does not yield the principal function V which is in our case a general work potential describing the change of the extended exergy, the main result being sought. Otherwise, when a HJB equation is known, the exergy (or work) is explicit, and the discrete numerical problem leads to Bellman's recurrence equation, solvable by dynamic programming [17]. Our problem of generalized exergy falls into the category of finite-time potentials, an important problem of contemporary thermodynamics [18]. In this paper we solve the problem of extremum work by using the concept of multistage energy production or consumption, where each stage is the so-called Curzon–Ahlborn–Novikov process [18,19]. The concept of single irreversible stage is illustrated in Fig. 1 that presents the temperature-entropy diagram of an arbitrary irreversible stage. Each stage can work either in the heat-pump mode (larger, external loop in Fig. 1) or in the engine mode (smaller, internal loop in Fig. 1). Fig. 1 describes the principle of designations used for two basic modes with internal and external dissipation: power yield in an engine and power consumption in a heat pump. The primed temperatures characterize the circulating fluid.

Our unsteady analysis here extends the previous analyses of the problem [18–21] by taking into account internal irreversibilities within the thermal machines at each stage of the operation following the recent method that applies the factor of internal irreversibilities, Φ [22]. By definition, $\Phi = \Delta S_{2'}/\Delta S_{1'}$ (where $\Delta S_{1'}$ and $\Delta S_{2'}$ are respectively the entropy changes of the circulating fluid along the two isotherms $T_{1'}$ and $T_{2'}$ in Fig. 1) equals the ratio of the entropy fluxes across the thermal machine, $\Phi = J_{s2'}/J_{s1'}$. Due to the second law inequality at the steady state the following inequalities are valid: $J_{s2'}/J_{s1} \geqslant 1$ for engines and $J_{s2'}/J_{s1} \leqslant 1$ for heat pumps; thus the considered ratio Φ measures the process irreversibility. In fact, Φ is a synthetic measure of the machine's imperfection. The quantity Φ satisfies inequality $\Phi \geqslant 1$ for engine mode and $\Phi \leqslant 1$ for heat pump mode of the system. Our purpose is to derive in terms of Φ suitable formulas describing power produced or consumed in steady systems (infinite reservoirs) and a generalized exergy in dynamic systems with the finite resource reservoir. Fluids with constant molar heat capacity c are usually treated.

3. Entropy produced and efficiency

We shall follow here a shortest possible way of finding the real work W and work limit (extremum of W) by using the so-called Gouy–Stodola law that links the lost work with the entropy production [11]. In the analysis we shall make use of the fact that the thermal efficiency of any real thermal engine can always by written in the form $\eta = 1 - \mathrm{d}Q_2/\mathrm{d}Q_1$. By evaluating *total* entropy production at the stage (the sum of external and internal parts), S_σ, as the difference between the outlet and inlet entropy fluxes we find in terms of the first-law efficiency η

$$\mathrm{d}S_\sigma = \frac{\mathrm{d}Q_1(1-\eta)}{T_2} - \frac{\mathrm{d}Q_1}{T_1} = \frac{\mathrm{d}Q_1}{T_2}(1 - \eta - T_2/T_1). \tag{1}$$

This is a general equation as there was not any special assumptions involved in its derivation. It states that the entropy production in an arbitrary thermal engine is directly related to the deviation of the engine's efficiency from the corresponding Carnot efficiency. This conclusion leads us to an important analytical formula for the total entropy source that will enable its direct optimization. The entropy balance of the thermal machine contains the internal entropy production as the source term in the expression

$$\frac{\mathrm{d}Q_2}{T_{2'}} - \frac{\mathrm{d}Q_1}{T_{1'}} = \mathrm{d}S_\sigma^{\mathrm{int}}. \tag{2}$$

In terms of the coefficient

$$\Phi = 1 + T_{1'}\mathrm{d}S_\sigma^{\mathrm{int}}/\mathrm{d}Q_1 \tag{3}$$

called the internal irreversibility factor the entropy balance of the internal part of the system takes the form usually applied for thermal machines

$$\Phi\frac{\mathrm{d}Q_1}{T_{1'}} = \frac{\mathrm{d}Q_2}{T_{2'}}. \tag{4}$$

One can evaluate Φ from the average value of the internal entropy production that describes the effect of irreversible processes within the thermal machine. Clearly, in many cases Φ is a complicated function of the machine's operating variables. In those complex cases one applies the data of $\sigma_\mathrm{s}^{\mathrm{int}} = \mathrm{d}S_\sigma^{\mathrm{int}}/\mathrm{d}t$ to calculate an averaged value of the coefficient Φ. In the analysis of the operation considered the quantity Φ is treated as the process constant. In other words, it is an average value of Φ , evaluated within the boundaries of operative parameters of interest that is used in most of the analyses of thermal machines including the present one. For chillers and energy generators experimental data of $\sigma_\mathrm{s}^{\mathrm{int}} = \mathrm{d}S_\sigma^{\mathrm{int}}/\mathrm{d}t$ are available that allow the calculation of Φ; see Ref. [22] for more information.

Consequently, the efficiency η can be evaluated in terms of the parameters characterizing the thermal machine

$$\eta = 1 - \frac{\mathrm{d}Q_2}{\mathrm{d}Q_1} = 1 - \Phi\frac{T_{2'}}{T_{1'}} = 1 - \left(1 + T_{1'}\frac{\mathrm{d}S_\sigma^{\mathrm{int}}}{\mathrm{d}Q_1}\right)\frac{T_{2'}}{T_{1'}}. \tag{5}$$

After eliminating η from Eqs. (1) and (5) we conclude that, quite generally, the total entropy production can be written in a transformed form

$$\begin{aligned}\mathrm{d}S_\sigma &= \frac{\mathrm{d}Q_1}{T_2}\left(\Phi\frac{T_{2'}}{T_{1'}} - \frac{T_2}{T_1}\right)\\ &= \mathrm{d}Q_1\left(\frac{(\Phi-1)}{T'} + \left(\frac{1}{T'} - \frac{1}{T_1}\right)\right).\end{aligned} \tag{6}$$

Apparently the first term in the resulting expression of Eq. (6) describes the internal entropy source (within the thermal machine) and the second one the external entropy source (within the reservoirs). However the division of S_σ into the two parts is actually different, see Eqs. (10) below. Eq. (6) only states that in the "endoreversible" case (Φ = 1) the external entropy production is the same as that in the case of the contact of two bodies with temperatures T_1 and T'. Equivalently, after using in (6) the internal irreversibility factor (3)

$$\mathrm{d}S_\sigma = \frac{T_{1'}}{T'}\mathrm{d}S_\sigma^{\mathrm{int}} + \mathrm{d}Q_1\left(\frac{1}{T'} - \frac{1}{T_1}\right). \tag{7}$$

In the last two equations the structural quantity called the Carnot temperature T' was introduced that satisfies the thermodynamic relation

$$T' \equiv T_2T_{1'}/T_{2'}. \tag{8}$$

In terms of the Carnot temperature T' and factor Φ the efficiency η, Eq. (5), assumes the simple, pseudo-Carnot form

$$\eta = 1 - \Phi\frac{T_2}{T'}. \tag{9}$$

The efficiency decrease is caused by finite flows. The associated power of entropy production per unit time follows from Eqs. (6) and (7)

$$\begin{aligned}\sigma_\mathrm{s} &= q_1\left(\frac{(\Phi-1)}{T'} + \left(\frac{1}{T'} - \frac{1}{T_1}\right)\right)\\ &= \frac{T_{1'}}{T'}\sigma_\mathrm{s}^{\mathrm{int}} + q_1\left(\frac{1}{T'} - \frac{1}{T_1}\right).\end{aligned} \tag{10}$$

The true internal part of the quantity σ_s is the direct consequence of Eq. (3)

$$\sigma_\mathrm{s}^{\mathrm{int}} = \frac{q_1(\Phi-1)}{T_{1'}}. \tag{11a}$$

Whereas the true external part is

$$\sigma_\mathrm{s}^{\mathrm{ext}} = q_1\left((\Phi-1)\left(\frac{1}{T'} - \frac{1}{T_{1'}}\right) + \left(\frac{1}{T'} - \frac{1}{T_1}\right)\right). \tag{11b}$$

While Eq. (10) can be applied immediately either of Eq. (11) call for a function $T_{1'}(T_1,q_1)$ such as that in the first term of Eq. (13). When the upper heat exchange rate in both reservoirs depends on the difference of temperatures in the power a (a = 4 for radiative energy exchange and 1 for Newtonian one) i.e. for

$$q_1 = g_1(T_1^a - T_{1'}^a) \tag{12}$$

then, since $T_{1'} = (T_1^a - q_1/g_1)^{1/a}$, Eq. (7) yields the following formula for the power of entropy generation

$$\sigma_\mathrm{s} = \frac{(T_1^a - q_1/g_1)^{1/a}}{T'}\sigma_\mathrm{s}^{\mathrm{int}} + q_1\left(\frac{1}{T'} - \frac{1}{T_1}\right). \tag{13}$$

This means that only in the "endoreversible" case, i.e. when the internal entropy production vanishes, the external entropy production is simply related to the product of heat q_1 and the suitable difference of temperature reciprocals, $(T')^{-1} - (T_1^{-1})$. as in the two-body contact. In the general case of a finite internal entropy production the external part of σ_s follows in terms of its internal part in the form

$$\sigma_\mathrm{s}^{\mathrm{ext}} = \left(\frac{(T_1^a - q_1/g_1)^{1/a} - T'}{T'}\right)\sigma_\mathrm{s}^{\mathrm{int}} + q_1\left(\frac{1}{T'} - \frac{1}{T_1}\right) \tag{14}$$

so that the sum of both parts of the entropy production agrees with formula (13).

The definition (8) may also be derived from the invariance of the entropy production with respect to variables transformation when passing from constrained traditional controls $T_{1'}$ and $T_{2'}$ to the unconstrained control T'. We conclude that the analytical description of thermal energy converters in terms of the Carnot temperature is particularly simple.

The efficiency worsening caused by the dissipation is described in a general way by the transformed formula (1)

$$\eta = \eta_C - T_2\sigma_s/q_1. \tag{15}$$

Of course, the pseudo-Carnot formula, Eq. (9), also belongs to the class of imperfect efficiencies of the type (15) as it can be given the form

$$\eta = \eta_C - T_2\left(\frac{\Phi}{T'} - \frac{1}{T_1}\right) \tag{16}$$

which implies the ratio σ_s/q_1 consistent with Eq. (6) and (10). Various equations that describe the entropy production σ_s, presented above, are helpful in definite situations when one wants to evaluate the efficiency worsening. Yet the knowledge of the entropy production σ_s is also necessary in calculations of generalized exergies considered in the final section of this paper. But in the dynamical cases essential is also the best time behavior of σ_s.

4. Heat flux and power in steady operations

Consider steady thermal machines driven by fluids exhibiting nonlinear properties.

We begin with the symmetric nonlinear case in which the heat transfer rate is proportional to the difference of absolute temperatures in certain power a. The case of $a = 4$ refers to the radiation, $a = -1$ to the Onsagerian kinetics and $a = 1$ to the Fourier law of heat exchange. (In the Onsagerian case the quantities g_i are negative in the common formalism considered.)

Next we consider the "hybrid nonlinear case" in which the upper-temperature fluid is still governed by the kinetics proportional to the difference in T^n whereas the kinetics in the lower reservoir is Newtonian.

4.1. Symmetric nonlinear case

We assume that the energy exchange process in the upper reservoir satisfies Eq. (12), and that an equation of the same type and with the same coefficient a is valid for the energy exchange in the lower reservoir, namely

$$q_2 = g_2(T_{2'}^a - T_2^a). \tag{17}$$

To express the internal balance equation for the entropy

$$\Phi g_1(T_1^a - T_{1'}^a)/T_{1'} = g_2(T_{2'}^a - T_2^a)/T_{2'} \tag{18}$$

in terms of T' and $T_{1'}$ we substitute $T_{2'} \equiv T_{1'}T_2/T'$ into (18). Next we solve the result obtained with respect to $T_{1'}$. This leads to an equation describing the upper temperature of the circulating fluid $T_{1'}$ in terms of T'

$$T_{1'} = \left(T_1^a - g_2\frac{T_1^a - T'^a}{\Phi g_1(T'/T_2)^{a-1} + g_2}\right)^{1/a}. \tag{19}$$

From this expression and Eq. (12) the heat flux q_1 follows in terms of T'. This heat flux is obtained in the form

$$q_1 = g_1g_2\frac{T_1^a - T'^a}{\Phi g_1(T'/T_2)^{a-1} + g_2} \tag{20}$$

which represents the "thermal characteristics" of the system. An expression for $T_{2'}$ corresponding with (19) follows from the thermodynamic definition of Carnot temperature, $T_{2'} \equiv T_{1'}T_2/T'$. Also, $q_2 = q_1(1 - \eta)$, where η is defined by the pseudo-Carnot expression (9). Thus all necessary quantities are found. We observe that in the case of $a = 1$ the kinetics of heat exchange depends on the difference of two temperatures $T_1 - T'$, as in the case of direct two-body contact. Yet, in nonlinear processes the heat flux (20) emerges as function of three (not merely two) temperatures, T', T_1 and T_2. This means that the analogy with the two-body contact (satisfied when $a = 1$) is invalid in the case of nonlinear processes. Still we can evaluate associated power limits by maximizing power p related to Eq. (20) with respect to the free Carnot control, T'; see Eq. (23) below.

For $a = 4$ the model describes the radiation engine usually called the Stefan–Boltzmann engine. In spite of the model's simplicity, its two "resistive parts" take rigorously into account the entropy generation caused by simultaneous emission and absorption of black-body radiation, the model's property which some of FTT adversaries seem not to be aware of. This entropy generation is just the external part of the total entropy production that follows as the "classical" sum:

$$\sigma_s^{\rm ext} = q_1(T_{1'}^{-1} - T_1^{-1}) + q_2(T_2^{-1} - T_{2'}^{-1}), \tag{21}$$

where each q_i uses the Stefan–Boltzmann law.

For the "symmetric" kinetics governed by the differences in T^a, the T'-representation of the total entropy production in the system follows from Eqs. (10) and(20)

$$\sigma_s = g_1g_2\frac{T_1^a - T'^a}{\Phi g_1(T'/T_2)^{a-1} + g_2}\left(\frac{(\Phi - 1)}{T'} + \left(\frac{1}{T'} - \frac{1}{T_1}\right)\right). \tag{22}$$

The superiority of Carnot control T' over the heat flux control q_1 may be noted here. Since the heat–flux expression (20) cannot generally be inverted to get an explicit function $T'(q_1)$, the explicit formula for the heat–flux representation of the entropy production or associated mechanical power p cannot generally be found in an analytical form. Still we can express the entropy production and related power p in terms of Carnot control, T', and then evaluate a limiting power by maximizing p with respect to the free Carnot control, T'. The appropriate power expression is

$$p = q_1\eta = g_1 g_2 \frac{T_1^a - T'^a}{\Phi g_1 (T'/T_2)^{a-1} + g_2}\left(1 - \Phi\frac{T_2}{T'}\right). \tag{23}$$

In the case of analytical difficulties that may occur for a different from the unity the maximization can easily be performed graphically by making the chart of $p(T)$ at all remaining variables kept constant. Thus, in general, the maximization can be performed analytically or graphically using the Carnot T' as the free control.

4.2. Hybrid nonlinear case

We consider now the case when the radiation law ($a = 4$) governs the heat flow only in the upper reservoir, whereas it is the Newtonian model that governs the lower one

$$q_2 = g_2(T_{2'} - T_2). \tag{24}$$

Again, the efficiency of the imperfect unit is satisfied by expression $\eta = 1 - \Phi T_{2'}/T_{1'}$. To express the internal balance equation for the entropy

$$\Phi g_1(T_1^a - T_{1'}^a)/T_{1'} = g_2(T_{2'} - T_2)/T_{2'} \tag{25}$$

in terms of T' and $T_{1'}$ we substitute $T_{2'} \equiv T_{1'}T_2/T'$ into (25). This leads to T' in terms of $T_{1'}$

$$\Phi g_1(T_1^a - T_{1'}^a) = g_2(T_{1'} - T') \tag{26}$$

and then to the mechanical power p in terms of $T_{1'}$ The thermal efficiency of the engine can be obtained in the form using the temperature $T_{1'}$ as an effective control variable

$$\eta = 1 - \Phi\frac{T_2}{T'} = 1 - \frac{\Phi T_2}{T_{1'} - \Phi g_1(T_1^a - T_{1'}^a)/g_2}. \tag{27}$$

This leads to the mechanical power expression with the explicit control T_1,

$$p = q_1\eta$$
$$= g_1(T_1^a - T_{1'}^a)\left(1 - \frac{\Phi T_2}{T_{1'} - \Phi g_1(T_1^a - T_{1'}^a)/g_2}\right). \tag{28}$$

Since from Eq. (12) $T_{1'} = (T_1^a - q_1/g_1)^{1/a}$, the heat flux representation of the above equation is obtained in the form

$$p = q_1\eta = q_1\left(1 - \frac{\Phi T_2}{(T_1^a - q_1/g_1)^{1/a} - \Phi q_1/g_2}\right). \tag{29}$$

Eqs. (28) or 29) allow analytical or graphical maximization of power with respect to a single control variable, $T_{1'}$ or q_1. This leads to the steady limits on power production in imperfect units.

We note that in general a suitable control may be the Carnot temperature itself, a function or an operator of the remaining variables. The operator structure of T' is frequent in dynamical problems. These occur in the case when the thermal potential of one of the reservoirs changes (decreases in the case of an engine) due to its finite capacity.

5. Dynamical theory for finite resources

When resources become finite and/or the propelling fluid flows at a finite rate the driving temperature and other intense parameters decrease along the process path. The above analysis needs to be generalized to take into account the decay of the thermal potential of resource in time or space. This means that the previous (steady) analysis need to be replaced by a dynamic one and the mathematical formalism transferred from the realm of functions to the realm of functionals. Here the optimization task is to find an optimal profile of the driving temperature T' along the resource path (fluid's path) that assures the minimum of the integral entropy production and—simultaneously—the extremum of the work consumed or delivered.

In dynamical systems differential forms of expressions are necessary. For a suitably defined time variable τ (associated with the resource fluid; see Eq. (33) below) and an arbitrary type of heat transfer (Newtonian or not) the total entropy production can be obtained in an exact form as the sum of two apparent contributions, external and internal. Each apparent expression describes the contribution to the entropy source only approximately (hence their individual use is not recommended), yet their sum provides an exact expression for the total entropy source. The apparent internal entropy production is

$$\sigma_s^{\mathrm{int}'} = -\int_{\tau^i}^{\tau^f} G_c(T)\frac{\Phi - 1}{T'(T_1, \dot{T})}\dot{T}_1 \mathrm{d}\tau_1 \tag{30}$$

whereas the apparent external part

$$\sigma_s^{\mathrm{ext}'} = -\int_{\tau^i}^{\tau^f} G_c(T)\left(\frac{1}{T'(T_1, \dot{T}_1)} - \frac{1}{T_1}\right)\dot{T}_1 \mathrm{d}\tau_1. \tag{31}$$

Here the essential nonlinearities are caused by the temperature dependence of the quantity $G_c \equiv Gc$ or the product of the molar fluid's flux and its molar heat capacity. The total entropy production (exact expression), which determines the lost work in equations of extended availabilities is the integral

$$\sigma_s = -\int_{\tau^i}^{\tau^f} G_c(T)\left(\frac{\Phi}{T'} - \frac{1}{T_1}\right)\dot{T}_1 \mathrm{d}\tau_1. \tag{32}$$

The limiting production or consumption of mechanical energy is associated with extremum power or the minimal sum of functionals (30) and (31) or minimum of the overall entropy production (32). These equations assume that it is possible to determine explicit form of functions describing the Carnot temperature T' in terms of the current fluid's temperature T and its time derivative. Such functional structure would allow to apply the variational calculus in the optimization analysis. If this function is impossible to find in an explicit form then Eqs. (30) and (31) should be written in the form in which T' and T_1 are two separable variables in the Pontryagin's algorithm of the optimal control. In this case a differential constraint must be added that limits the changes d $T_1/\mathrm{d}t$ with the state variable T_1 and control T' (see Eq. (35) below).

We shall now specialize to what we called the *symmetric nonlinear case*. It involves the radiative heat transfer ($a = 4$) in both upper and lower reservoirs and corresponds with the form (22) of the intensity of total entropy production.

In the first approach following some literature indications (e.g. Refs. [23] and [24]) we include the variable heat capacity flux $G_c(T)$ into the definition of τ_1 We then exploit heat exchange formula (20)

$$q_1 = g_1 g_2 \frac{T_1^a - T'^a}{\Phi g_1 (T'/T_2)^{a-1} + g_2} \tag{20}$$

to define the nondimensional time τ_1 with the help of the equality

$$q_1/g_1 = -G_c(T_1)\mathrm{d}T_1/(\alpha_1 a_v F_1 \mathrm{d}x) \equiv -\mathrm{d}T_1/\mathrm{d}\tau_1, \tag{33}$$

where $G_c \equiv Gc$ is the product of the fluid's flow and its molar heat capacity. This equation describes the energy balance for the propelling fluid. The non-dimensional time τ_1 is simultaneously the number of heat transfer units related to the fluid in the state 1. Eq. (33) means that the driving heat flux can be measured in terms of the temperature drop of the propelling fluid per unit of the non-dimensional time τ_1. However, the time τ_1 defined as above includes the variable flux of heat capacity $G_c(T)$ and possibly other temperature dependent quantities such as α_1. This causes the problem of passage from time τ_1 to the usual residence time t or length x requiring the integration with respect of τ_1

$$x = \int_0^{\tau_1} \frac{G_c(T_1(\tau_1))}{\alpha_1 a_v F_1} \mathrm{d}\tau_1 = \int_0^{\tau_1} H_{\mathrm{TU}}(T_1(\tau_1))\mathrm{d}\tau_1 \tag{34}$$

after the temperature profile $T_1(\tau_1)$ is found. Still one can effectively proceed this way. Comparing formula (33) with the expression describing q_1 in Eq. (20) we obtain a differential equation

$$\mathrm{d}T_1/\mathrm{d}\tau_1 = -g_2 \frac{T_1^a - T'^a}{\Phi g_1 (T'/T_2)^{a-1} + g_2} \tag{35}$$

which is the differential constraint in the problem of minimization of total entropy production (32) by the Pontryagin's maximum principle. This minimization leads to optimal profiles $T'(\tau_1)$ and T_1 (τ_1) that assure the extremum work produced by an sequential engine system or consumed by a sequential heat pump system. As this is the multistage system in which the resource fluid is applied to produce or consume the extremum work, the work so obtained is the finite-time exergy of the resource fluid. However, it should be noted that the method of variational calculus cannot effectively be applied to Eq. (35) except the Fourier–Newton case when $a = 1$ since only then the control T' can easily by expressed in terms of the time derivative of temperature T_1 and the result substituted to (32) to get a Lagrange functional.

In the second approach (novel and not less suitable than the first one) we don't include the variable G_c into the definition of the non-dimensional time τ_1. Rather we use therein a constant G_{c0} (of the same units as G_c) that appears in an equation describing the variability of G_c with T. In the case of the radiation fluid ($a = 4$) the variability of G_c with T accounts for the variable flux of black photons along the fluid's path. With the heat expression (20) and the energy balance (33) the definition of the height of the transfer unit (H_{TU}) rests now on a constant quantity G_{c0} The constant appears in a formula describing the heat capacity flux G_c in terms of T_1

$$G_c(T_1) = G_{c0} T^{a-1}/T_0^{a-1} = G_{c0} T_0^{1-a} T^{a-1} \tag{36}$$

where T_0 is a reference temperature. In our case T_0 is the initial temperature by assumption. When the cross-sectional area F_1 is variable the above equation needs to be generalized to the form

$$G_{cF}(T) = \frac{G_{c0}}{F_{10}} T^{a-1}/T_0^{a-1} = \frac{G_{c0}}{F_{10}} T_0^{1-a} T^{a-1} \tag{37}$$

which describes the flux density of the product of molar flow G and c rather than the flux itself. In the theory of transport phenomena it is customary to assume the constancy of H_{TU}. In nonlinear processes this constancy must be associated with the assumption of the consistent change of the heat transfer coefficient

$$\alpha(T) = \alpha_0 T^{a-1}/T_0^{a-1} = \alpha_0 T_0^{1-a} T^{a-1}. \tag{38}$$

Applying the constant quantity $G_{c0} \equiv G_0 c_0$ in the H_{TU} defined in terms of the initial value G_c

$$(H_{\mathrm{TU}})_0 \equiv \frac{G_{c0}}{\alpha_{10} a_v F_{10}} \tag{39}$$

and introducing the nondimensional time based on the properties of first fluid

$$\tau_1 = \frac{x}{(H_{\mathrm{TU}})_0} \tag{40}$$

yields

$$\begin{aligned} q_1/g_1 &= \mathrm{d}^2Q_1/\mathrm{d}t\mathrm{d}\gamma_1 = -G_{\mathrm{c}}(T_1)\mathrm{d}T_1/(\alpha_1\mathrm{d}A_1) \\ &= -\frac{G_{\mathrm{c}0}T_0^{1-a}T_1^{a-1}\mathrm{d}T_1}{\alpha_{10}T_0^{1-a}T_1^{a-1}a_{\mathrm{v}}F_{10}\mathrm{d}x} = -\frac{\mathrm{d}T_1}{\mathrm{d}\tau_1}. \end{aligned} \tag{41}$$

Yet, if the proportionality assumption between G_{c} and α_1 cannot be assured, we don't generally obtain the equality of q_1/g_1 and $-\mathrm{d}T_1/\mathrm{d}\tau_1$ for the simple definition of τ_1 given by Eq. (41). For example, when α_1 is a constant equal to α_{10} and G_{cF} still varies according to (37) we obtain

$$\frac{q_1}{g_1} = -\frac{G_{\mathrm{c}0}T_0^{1-a}T_1^{a-1}\mathrm{d}T_1}{\alpha_{10}a_{\mathrm{v}}F_{10}\mathrm{d}x} = -T_0^{1-a}T_1^{a-1}\frac{\mathrm{d}T_1}{\mathrm{d}\tau_1}. \tag{42}$$

The multiplier term $T_0^{1-a}T_1^{a-1}$ is the price of using the same simple definition of dimensionless time given by Eq. (40) in the complex situation. Still the expression considered assures that for the special case of a Newtonian medium the following formula

$$q_1/g_1 = \mathrm{d}^2Q_1/\mathrm{d}t\mathrm{d}\gamma_1 = -\mathrm{d}T_1/\mathrm{d}\tau_1 \tag{43}$$

(equivalent to Eq. (33)) is valid. Comparing (20) and (42) yields in the general case of a non-Newtonian fluid

$$-T_0^{1-a}T_1^{a-1}\mathrm{d}T_1/\mathrm{d}\tau_1 = g_2\frac{T_1^a - T'^a}{\Phi g_1(T'/T_2)^{a-1} + g_2} \tag{44}$$

or

$$\frac{\mathrm{d}T_1}{\mathrm{d}\tau_1} = -g_2\frac{T_0^{a-1}}{T_1^{a-1}}\frac{T_1^a - T'^a}{\Phi g_1(T'/T_2)^{a-1} + g_2}. \tag{45}$$

This is a general dynamical equation of state for a non-Newtonian fluid. For $a = 1$ we recover from it the appropriate Newtonian formula. Yet the equation contains the reference temperature T_0 which is, again, the price of using the simple definition of τ_1 (Eq. (40)) in the complex situation.

We shall now specialize with what we called the *hybrid nonlinear case*. It involves the radiative heat transfer ($a = 4$) in the upper reservoir and the convective heat exchange in the lower one ($\dot{T}_1 \equiv \mathrm{d}T_1/\mathrm{d}\tau_1$). We find both apparent components of the total entropy production σ_{s}

$$\sigma_{\mathrm{s}}^{\mathrm{int}'} = -\int_{\tau^i}^{\tau^f} G_{\mathrm{c}}(T_1)\frac{\Phi - 1}{(T_1^a + \dot{T}_1^a)^{\frac{1}{a}} + \dot{T}_1\Phi g_1/g_2}\dot{T}_1\mathrm{d}\tau_1 \tag{46}$$

and

$$\sigma_{\mathrm{s}}^{\mathrm{ext}'} = -\int_{\tau^i}^{\tau^f} G_{\mathrm{c}}(T_1)\left(\frac{1}{(T_1^a + \dot{T}_1^a)^{\frac{1}{a}} + \dot{T}_1\Phi g_1/g_2} - \frac{1}{T_1}\right)\dot{T}_1\mathrm{d}\tau_1. \tag{47}$$

To obtain an optimal path associated with the limiting production or consumption of mechanical energy the sum of the above functionals i.e the total entropy production in the form of a Lagrange functional

$$\sigma_{\mathrm{s}} = -\int_{\tau^i}^{\tau^f} G_{\mathrm{c}}(T_1)\left(\frac{\Phi}{(T_1^a + \dot{T}_1^a)^{\frac{1}{a}} + \dot{T}_1\Phi g_1/g_2} - \frac{1}{T_1}\right)\dot{T}_1\mathrm{d}\tau_1 \tag{48}$$

has to be minimized for a fixed duration and defined end states of the fluid. The most typical way to accomplish the minimization is to write down and then solve the Euler–Lagrange equation of the variational problem. Analytical solutions are seldom, thus one has to rest on numerical techniques.

6. Other nonlinear approaches

In general equations of nonlinear macrokinetics a recent approach considers coupled transfer of particles (m) and heat (h). Introduced are potentials $F_{\mathrm{i}} = (1/T,-\mu_{i/\mathrm{T}})$, $i = 0,1 \ldots n$, which are the thermodynamic conjugates of the extensive variables in the Gibbs equation for the system's entropy

$$\mathrm{d}S = T^{-1}\mathrm{d}E - T^{-1}\mu_\alpha\mathrm{d}c_\alpha \equiv \sum_{i=0}^{s}F_i\mathrm{d}C_i \equiv \mathbf{F}.\mathrm{d}\mathbf{C}. \tag{49}$$

The process kinetics is described by the *general exchange equation* for the net flux J_i

$$J_i = I_j^0\left\{\exp\left(-\sum_i v_{ki}^* F_k^f/\mathrm{R}\right) - \exp\left(-\sum_i v_{ki}^* F_k^b/\mathrm{R}\right)\right\} \tag{50}$$

whose equivalent form in terms of deviations from equilibrium is

$$J_i = I_i^{\mathrm{eq}}\Delta\exp\left(-\sum_i v_{ki}^*(F_k^f - F_k^{\mathrm{eq}})/\mathrm{R}\right) \tag{51}$$

with

$$I_i^{\mathrm{eq}} \equiv I_i^0\exp\left(-\sum v_{ki}^* F_k^{\mathrm{eq}}/\mathrm{R}\right) \tag{52}$$

as the common value of the absolute current at equilibrium.

In the case of pure heat exchange the corresponding kinetic set reduces to just one equation that describes the nonlinear heat flux. The set of equations describing the exchange of heat between each reservoir and the thermal machine involves two equations. The first one describes the heat flux driving the engine

$$q_1 = I_1^{\mathrm{eq}}\Delta\exp(-E(T^{-1} - T^{-1^{\mathrm{eq}}})/\mathrm{R}) \tag{53}$$

where

$$I_1^{\mathrm{eq}} \equiv I_1^0\exp(-ET^{-1^{\mathrm{eq}}}/\mathrm{R}) \tag{54}$$

and the symbol Δ in (53) refers to the suitable difference of temperatures T_1 and $T_{1'}$. The constant E is the activation energy for thermal transfer. Analogous equation holds for the second fluid. Close to equilibrium, a linear approximation of the nonlinear exchange equation follows as

$$\begin{aligned} q_1 &= I_1^{\mathrm{eq}} E \mathrm{R}^{-1}(T_{1'}^{-1} - T_1^{-1}) \\ &\cong I_1^{\mathrm{eq}} E \mathrm{R}^{-1}(T_1 - T_{1'})/T_1 T_{1'}. \end{aligned} \tag{55}$$

Comparing this expression with the classical Newton's structure $q_1 = g_1(T_1 - T_{1'})$ we find that the conductance in the present model can be evaluated in accordance with the equation

$$\begin{aligned} g_1 &= I_1^{\mathrm{eq}} E \mathrm{R}^{-1}/T_1 T_{1'} \\ &= I_1^0 \exp(-E T^{-1^{\mathrm{eq}}}/\mathrm{R}) E \mathrm{R}^{-1}/T_1 T_{1'}. \end{aligned} \tag{56}$$

This also shows that the correspondence with classical equation of heat exchange can be assured. Above equation may serve to estimate the value of the exchange current provided that the heat exchange coefficient α, constant E and the common equilibrium temperature of two bodies is known. It should be realized that E characterizes the temperature dependence of the heat conductivity.

We can now write down the kinetic equations for both reservoirs. For the known process coefficients the heat exchange equation for the first reservoir has the form

$$q_1 = I_1^0 \{\exp(-E_1/\mathrm{R}T_1) - \exp(-E_1/\mathrm{R}T_{1'})\} \tag{57}$$

whereas that for the second one is

$$q_2 = I_2^0 \{\exp(-E_2/\mathrm{R}T_{2'}) - \exp(-E_2/\mathrm{R}T_2)\}. \tag{58}$$

On this ground one can develop the nonlinear theory in which thermal conductivities and related conductances are variable i.e. are state functions.

7. Classical Newtonian fluids

Analytical solutions are possible for linear problems in particular. For the Newtonian heat exchange in both reservoirs ($a = 1$) formulae (46) and (47) simplify to the forms

$$\sigma_{\mathrm{s}}^{\mathrm{int}'} = -\int_{\tau^i}^{\tau^f} G_{\mathrm{c}} \frac{\Phi - 1}{T_1 + \dot{T}_1\left(1 + \frac{g_1}{g_2}\Phi\right)} \dot{T}_1 \mathrm{d}\tau_1 \tag{59}$$

$$\sigma_{\mathrm{s}}^{\mathrm{ext}'} = -\int_{\tau^i}^{\tau^f} G_{\mathrm{c}} \left(\frac{1}{T_1 + \dot{T}_1(1 + \frac{g_1}{g_2}\Phi)} - \frac{1}{T_1}\right) \dot{T}_1 \mathrm{d}\tau_1. \tag{60}$$

Their sum constitutes the exact functional of the total entropy production that is the basics for the linear theory developed earlier [23,24]. Still the linear theory presented here is more general than the cited previous theory since the latter is here generalized to the imperfect energy generators (consumers) associated with Φ different than the unity.

Eqs. (46)–(48) contain expressions representing the Carnot temperature T' in terms of the upper reservoir temperature T_1 and the time derivative of this quantity. In fact, these equations prove that the success in achieving Lagrange functionals (necessary when one wants to apply the classical method of calculus of variations) is crucially dependent on the possibility of getting Carnot temperature T' in the form of an explicit analytical function of T' and $\mathrm{d}T'/\mathrm{d}\tau$. In the case of the symmetric nonlinear model (radiative exchange on both sides of the engine) such explicit function was impossible to find, yet as we have shown in Eq. (48) the possibility exists in the case of the hybrid nonlinear model. For the latter model one can therefore write down explicit Euler–Lagrange equations of the variational problem and perform extremization of functionals describing either the entropy production or produced (consumed) power. In fact, our earlier work [23] shows that such functionals yield the same optimal trajectory whenever fixed end states are assumed at the beginning and the end of the process.

In the case of the Newtonian fluid ($a = 1$) the already known result is obtained from Eq. (35) or (45)

$$\frac{\mathrm{d}T_1}{\mathrm{d}\tau_1} = -g_2 \frac{T_1 - T'}{\Phi g_1 + g_2}. \tag{61}$$

In this (Newtonian) case we usually work in terms of overall conductances and their associates

$$q_1 \equiv \frac{\mathrm{d}^2 Q_1}{\alpha_1 \mathrm{d}t \mathrm{d}A_1} g_1 = (T_1 - T_{1'}) g_1 = \frac{g_1 g_2 (T_1 - T')}{\Phi g_1 + g_2} \tag{62}$$

whence, after defining an overall $g'(\Phi)$

$$g' \equiv \frac{g_2 g_1}{\Phi g_1 + g_2} = (g_1^{-1} + \Phi g_2^{-1})^{-1} \tag{63}$$

one obtains

$$q_1 = g'(\Phi)(T_1 - T') \tag{64}$$

which is a well known result [22]. On the other hand

$$q_1/g' = \mathrm{d}^2 Q_1/\mathrm{d}t\mathrm{d}\gamma = -u = -G_{\mathrm{c}} \mathrm{d}T_1/\alpha' \mathrm{d}A \tag{65}$$

that yields a result linking q_1 with the change of T

$$q_1/g' = -G_{\mathrm{c}} \mathrm{d}T/(\alpha' a_{\mathrm{v}} F \mathrm{d}x) = -\mathrm{d}T_1/\mathrm{d}\tau. \tag{66}$$

For the Carnot temperature we shall obtain an operator formula. Using the transformed form of Eq. (61)

$$g_1 \frac{\mathrm{d}T_1}{\mathrm{d}\tau_1} = -\frac{g_1 g_2}{\Phi g_1 + g_2}(T_1 - T') \tag{67}$$

along with the definition of g' (Eq. (63) above) we find

$$T' = T_1 + \frac{\mathrm{d}T_1}{\mathrm{d}\tau_1}\alpha_1 \mathrm{d}A_1\left(\frac{1}{\alpha_1'\mathrm{d}A} + \frac{\Phi}{\alpha_2'\mathrm{d}A}\right) \tag{68}$$

or

$$T' = T_1 + \dot{T}_1\alpha_1\frac{\mathrm{d}A_1}{\mathrm{d}A}\left(\frac{\Phi\alpha_1' + \alpha_2'}{\alpha_1'\alpha_2'}\right). \tag{69}$$

The bracket term of this equation contains the reciprocal of the overall heat transfer coefficient α'; hence

$$T' = T_1 + \dot{T}_1\frac{\alpha_1\mathrm{d}A_1}{\alpha'\mathrm{d}A} = T_1 + \frac{\mathrm{d}T_1}{\mathrm{d}\tau} \tag{70}$$

where $A = A_1 + A_2$ and the last derivative is with respect of τ not τ_1. Thus, all suitable equations of the Newtonian fluid operate with the variable τ (overall number of heat transfer units modified by the presence of Φ), instead of the "partial" quantity τ_1.

In the case of Newtonian fluid the minimization of the entropy production integral for the dynamical problem involves the extension of the established endoreversible formula [23] to the case taking the internal dissipation into account. The extension has the form

$$\sigma_s = \int_{\tau^i}^{\tau^f} G_c\left(\frac{\dot{T}}{T(T+\dot{T})} - \frac{\Phi - 1}{T + \dot{T}}\right)\dot{T}\mathrm{d}\tau. \tag{71}$$

The optimal solution can be obtained by the variational calculus; it proves that an unconstrained extremal is an exponential curve satisfying the optimality condition

$$\frac{\mathrm{d}T}{\mathrm{d}\tau} = \xi(\Phi)T. \tag{72}$$

The modified non-dimensional time τ, or the ratio of pipeline length x and the height of the transfer unit H_{TU} related to overall g' of Eq. (63), is identical with the (Φ dependent) overall number of transfer units. $\xi(\Phi)$ is the rate indicator which is positive for the fluid's heating and negative for fluid's cooling. From the problem boundary conditions of the problem the numerical value of the ξ follows.

As it follows form the definition of Φ contained in Eq. (3) the following equality is valid

$$\sigma_s^{\mathrm{int}} = T_{1'}^{-1}q_1(\Phi - 1). \tag{73}$$

This equation can be used to show that the second term in (71) does not represent the sole effect of the internal dissipation. Of course this statement also holds for the general non-Newtonian model. For the general model we find

$$\sigma_s^{\mathrm{int}}/q_1 = \frac{(\Phi - 1)}{\left(T_1^a - g_2\frac{T_1^a - T'^a}{\Phi g_1(T'/T_2)^{a-1} + g_2}\right)^{1/a}} \tag{74}$$

and

$$\sigma_s^{\mathrm{ext}}/q_1 = \left(\frac{1}{T'} - \frac{1}{T_1}\right) + (\Phi - 1)\times\left(\frac{1}{T'} - \frac{1}{\left(T_1^a - g_2\frac{T_1^a - T'^a}{\Phi g_1(T'/T_2)^{a-1} + g_2}\right)^{1/a}}\right) \tag{75}$$

In fact, each of two additive parts of functional (71) or the additive parts of nonlinear functionals discussed can contribute to the external and internal dissipation.

8. Example of generalized exergy for Newtonian fluid

The Carnot temperature control ensuring the extremum of work associated with the Newtonian functional (71) is

$$\begin{aligned} T'(\tau) &= T(\tau)(1 + \xi(\Phi)) \\ &= T^i(T^f/T^i)^{(\tau-\tau^i)/(\tau^f-\tau^i)}(1 + \ln(T^f/T^i)/(\tau^f - \tau^i)) \end{aligned} \tag{76}$$

It corresponds with the power expression (29) in the case $a = 1$. Its integration along the optimal path with respect to time yields the generalized availability

$$\begin{aligned} A^{\infty} &= A^{\mathrm{class}} + c(1 - \Phi)T^{\mathrm{e}}\ln(T/T^{\mathrm{e}}) \\ &\quad \pm cT^{\mathrm{e}}\Phi\frac{[\ln(T/T^{\mathrm{e}})]^2}{\tau^f - \tau^i \pm \ln(T/T^{\mathrm{e}})} \end{aligned} \tag{77}$$

The properties of this function are depicted in Fig. 2. It illustrates the effect of internal irreversibilities Φ on limiting finite-rate work generated in engines and consumed in heat pumps. Example for non-ideal heat pump with $\Phi = 0.5$ and non-ideal engine with $\Phi = 1.5$, working with finite resources.

Generalized exergy of limiting continuous process, A^{∞}, prohibits processes from operating below the heat-pump mode line for $\Phi = 0.5$ (the lower bound for work supplied) and above the engine mode line for

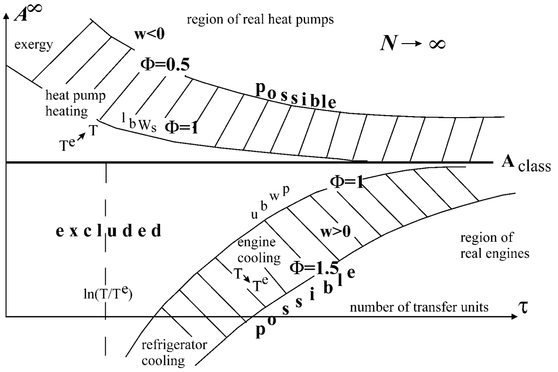

Fig. 2. Influence of internal irreversibilities Φ on the limiting finite-rate work.

$\Phi = 1.5$ (the upper bound for work produced). Weaker endoreversible limits correspond with curves for $\Phi = 1$; still weaker limits of classical exergy are represented by the straight line $A = A^{\text{class}}$. Dashed lines mark regions of possible improvements when imperfect thermal machines are replaced by those with better performance coefficients, terminating at endoreversible limits for Carnot machines.

The classical thermal availability contained in this equation is defined in the standard way

$$A^{\text{class}} \equiv c(T - T^{\text{e}}) - cT^{\text{e}} \ln(T/T^{\text{e}}). \tag{78}$$

The classical availability is the potential or the state function whose change between two arbitrary states describes the reversible work. On the other hand, generalized availability functions are irreversible extensions of this classical function including minimally irreversible processes. Due to the internal and external irreversibilities the limiting work estimates made with the help of classical function (78) are too weak and often insufficient; the function (77) assures stronger work limits.

Note that the mean process efficiency or the ratio A^{∞}/Q_1 is lower than the pseudo-Carnot efficiency (9) due to the finiteness of the resource flow and the corresponding decrease of the resource temperature as the process advances in time.

9. Conclusions

The obtained exergy functions are irreversible generalizations of the standard (reversible) exergy for the case of imperfect stages. The generalized exergy in processes departing from the equilibrium (upper sign) is larger than the one in processes approaching the equilibrium (lower sign). This is because one respectively adds or subtracts the product of T^{e} and entropy production in equations describing the generalized availability. We observe that the limits for mechanical energy yield or consumption provided by exergies A^{∞} are always stronger than those defined by the classical exergy. Thus, in both modes the generalized exergies provide enhanced bounds in comparison with those predicted by classical exergy. Our modeling shows that both internal and external dissipation increases the minimum work that must be supplied to the system. Likewise, both internal and external dissipation decreases the maximum work that can be produced by the system. Therefore functions A^{∞} provide work limits which take into account limitations resulting from finite rates of external transports and internal irreversibilities.

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