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Optimal work flux in sequential systems with complex heat exchange

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Abstract

We extend here our earlier idea of a finite-time exergy [S. Sieniutycz, M. von Spakovsky, Energy & Conversion Management 39 (1998) 1423–1447; S. Sieniutycz, Open Sys. Information Dyn. 5 (1998) 369–390; S. Sieniutycz, Int. J. Heat Mass Transfer 41 (1998) 183–195] to fluids characterized by complex exchange of heat and to those with coupled heat and mass transfer. Functionals are formulated which express work delivered from (or consumed by) a non-equilibrium system composed of a complex fluid, a thermal machine and the environment (acting as an infinite reservoir). The complex fluid constitutes a resource of a finite flow or amount, and work production (consumption) takes place sequentially, in stages of "endoreversible" thermal machines. Boundary layers play the role of resistances for heat and mass transfer, and cause the entropy production at each stage of the operation. For the fluid at flow, total specific work is extremized at constraints which take into account dynamics of heat and mass transport and rate of work generation. Finite-rate model subsumes irreversible production of entropy and losses of classical work potential, caused by the resistances and explains restrictive applicability of classical thermodynamic bounds. Formal analogies between the entropy production expressions for work-assisted and conventional exchange operations help to formulate optimization models of the former. Optimal work potentials, which incorporate a residual minimum of the entropy production, are analyzed in terms of end states, duration and (in discrete processes) number of stages. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Carnot cycles; Second law; Heat pumps; Endoreversible engines; Exergy (available energy); Thermodynamic limits

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1. Introduction: aims and scope

The objective of this paper is the optimization of work in systems with complex fluids. We shall consider the optimization of work produced or consumed by the ideal thermal machine (Carnot engine or heat pump) in an non-equilibrium system containing a polymeric fluid and the environment. Important thermoeconomic extensions of this problem are possible, which, however are not considered in this paper. Our optimization problems belong in thermodynamic optimization, where process performance criteria are set on purely thermodynamic ground; in a related thermoeconomic problem investment costs and economic considerations are involved. Optimization of an operation requires the knowledge of a performance criterion, a process model and constraints. It is best if the model is analytical; it must be selfconsistent and describing the considered operation in a reasonably broad range of changes of the process state variables and controls. The optimal solution must extremize a performance criterion. This and next section enunciate: the underlying ideas of the theory, its main physical and mathematical ingredients, the methods involved, and the physical and mathematical structure of the theory. A synthesizing form allows to stimulate a state-of-the-art discussion. Issues written for experts are reduced, to allow a mixed, interdisciplinary audience. A special effort is made to convince the reader that the non-Newtonian nature of heat and/or mass transfer (when described in terms of Carnot intensities T' and μ') does not complicate the general thermodynamic

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Nomenclature

A, a	cumulative and local heat exchange area, respectively
A	finite time availability, generalized exergy
a_v	specific area of heat exchange (per unit volume)
B	classical exergy of controlled phase
c, c	molar and specific heat
F	cross-sectional area of the system
G	mass flux (G_0 refers to circulating flux)
g_1, g_2	partial conductances
g	overall conductance
$\mathscr{H}$	enthalpy of polymeric solution (solvent basis)
I'	enthalpy of driving phase
$\mathscr{L}$	natural scale of length
ℓ	transfer area coordinate
M	molar mass
N	total number of stages in a multistage process
n	current stage number of a multistage process
P	cumulative power output
Q	cumulative heat exchanged
q_1	driving heat in the engine mode of the stage
R	universal gas constant
$R(\mathbf{x}, t)$	optimal work function of cost type in terms of state and time
S	entropy of controlled phase
S_σ	specific entropy production
T	temperature of controlled phase
T^{e}	constant equilibrium temperature of reservoir
T'	driving temperature, temperature of controlling phase
T_1, T_2	temperatures of upper and lower reservoirs (usually $T_2 = T^{\mathrm{e}}$ and $T_1 \equiv T$)
$T_{1'}, T_{2'}$	upper and lower temperature of circulating fluid
T^n	temperature of stream leaving the stage n
t	physical time, contact time
$u = \mathrm{d}T/\mathrm{d}\tau$	rate of the temperature change as the control variable
V	volume of the physical system
$V \equiv \max W$	optimal work function of profit type
$V^n(\mathbf{x}, t)$	optimal work function for n-stage process
v	linear velocity of the fluid
$W \equiv \mathsf{P}/G$	total specific work or total power per unit mass flux
$\mathscr{W}$	solvent content in dense solution (polymer basis)
$\mathscr{X}$	polymer's concentration in controlled solution (solvent basis)
α'	heat transfer coefficient
β	relative pressure of solvent
Γ	negative Hessian matrix of entropy function
γ	coordinate of overall cumulative conductance
γ_1, γ_2	coordinates of partial conductances
$\eta = p/q_1$	first-law efficiency
θ^n	free interval of an independent variable or time interval at stage n
μ_k	chemical potential of kth component
ξ	logarithmic intensity constant
ρ	density
σ_{s}	entropy production
τ	non-dimensional time, number of the heat transfer units ($\ell/\mathscr{L}$)

Subscripts

C	Carnot point
i	ith state variable
s	saturation, equilibrium
σ	dissipative quantity
1, 2	resource fluid and reservoir fluid

Superscripts

e	environment, equilibrium
f	final state
I	initial state
k or n	number of kth or nth stage

formalism, while it influences the formal structure of exchange equations (only) beyond the linear regime. This facilitates and unifies the state-of-the-art discussion.

We explain first the underlying ideas of the theory. Consider a macroscopic process and its evolution in the corresponding thermodynamic space, i.e., in the state space (x) in which the coordinates x are the set of independent thermodynamic quantities. The general formulation of finite-time thermodynamics (FTT) states that a completely general extension of classical thermodynamic evolution between two points $A(x)$ and $B(x)$ can be achieved by adding only one constraint: the process under consideration must go to completion in a finite time (either given or undetermined). This single requirement which clearly goes beyond reversible operation opens up a wealth of new results and considerations. Some of them are extensions of well established concepts (e.g. thermodynamic potential and exergy) while others are new (e.g. thermodynamic distance and the need for distinction between objective functions which govern the finite-time evolution. In this paper, we focus on the extremum of work in a finite time.

One of possible objectives that can be chosen is work that can be released (or consumed) from a sequence of reversible thermal machines when the system which changes its states between two points $A(x)$ and $B(x)$ interacts actively with the environment. (This work also contains the environment intensities, T^e, μ^e, etc., which we shall exclude from the set of the state coordinates x as they are constant parameters.) While the work released or produced in any reversible evolution from $A(x)$ to $B(x)$ is the path independent quantity, this work becomes a path dependent function in the case of any finite-time transition occuring between $A(x)$ and $B(x)$. The reason is the finiteness of the entropy generation in a finite time process. This quantity defines both the availability losses and – after its minimizing – the finite-time availability, with a residual (minimal) entropy production. The extremum of work produced (consumed) is then associated with an evolution that minimizes the entropy production, in agreement with the well-known Gouy–Stodola law. The work extremization (or the associate entropy production minimization) is by no means the iron rule when considering a finite-time evolution. Optimization criteria other than work, such as economic profit, costs, transfer area, etc., can be considered which are not less relevant for finite-time transitions. However, we restrict here to work optimization problems.

The main physical and mathematical ingredients of the theory are dynamical equations of change which describe the time evolution of a work-producing system (called sometimes "an active system"). These may be continuous or discrete. They are derived by combining balance laws of energy and mass (written in terms of bulk state coordinates) with laws of energy and mass transfer through the boundary layers (or resistances) that are present both in the system and in the environment. As compared with traditional systems (without work), the essential system ingredient is the work flux delivered from engines (or consumed by heat pumps), located between the system and the environment. This work flux is maximized in all engine modes and minimized in all heat-pump modes of the system subject to constraints of entropy and mass conservation, characteristic of each perfect thermal machine. From the formal viewpoint, each such a machine constitutes a physical discontinuity separating the system from the environment. This discontinuity is a sort of work-producing or work-consuming jump that works due to the difference between the intense parameters of the system and the environment at their disjoint interface (i.e., due to the difference between temperatures $T_{1'}$ and $T_{2'}$ in Figs. 1 or 2). This disjoint property enuntiates the inherent non-equilibrium nature of the problem. The methods involved in the theory are those used in dynamic optimization. Thus variational calculus, maximum principle and dynamic programming can be applied; some of them are discussed in Section 5. They cause that the mathematical structure of the theory is symplectic, and the optimal evolutions are governed by Hamiltonian canonical sets (continuous or discrete).

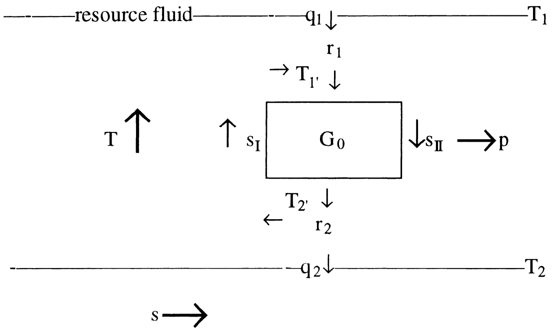

Fig. 1. Generic irreversible engine $(0 \leqslant \eta \leqslant \eta_C)$ on the temperature–entropy diagram.

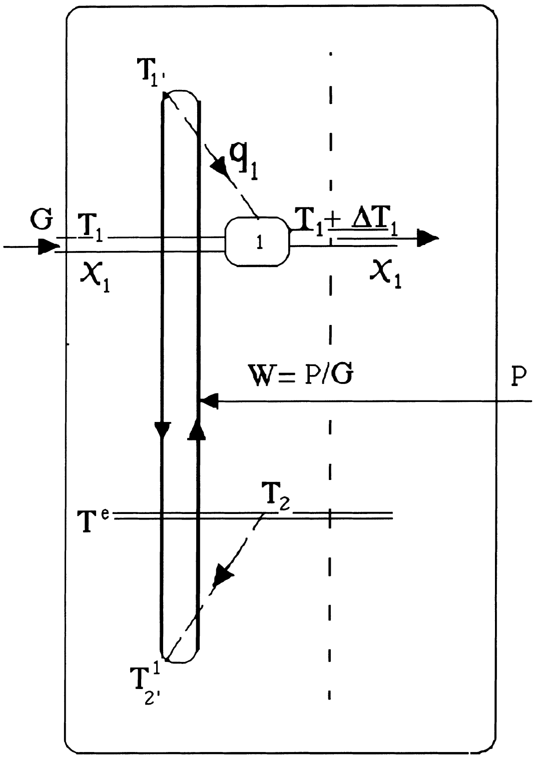

Fig. 2. A scheme of one-stage heating of a polymeric solution by a heat pump.

Knowledge of both classical and non-equilibrium thermodynamics of complex fluids helps significantly in optimization. Relevant classical topics involve thermomechanics of complex elastic materials, equilibrium thermophysics and statistical physics of polymers [1–5]. Associated non-classical topics involve thermomechanical theories of flowing polymeric fluids, often derived from non-equilibrium statistical theory of polymers [6–10]. However, at the present time, no systematic results are reported in the field of complex fluids optimization. One basic reason for an insufficient progress in this direction is the scant development in theory of non-isothermal complex fluids to date; even advanced and modern textbooks on rheology and mechanics of polymeric fluids do not treat systematically the subject of energy transformations in non-isothermal fluids. Important contemporary problems of thermodynamic optimization, such as irreversible extensions of the Carnot problem, extremize work from systems with different temperatures. For a system containing a finite resource that interacts with an infinite environment in an infinite time the extremal solutions should yield the classical exergy at the reversible limit [11]. These problems can be stated either for resting or for flowing fluids. Yet irreversible extensions of exergy to non-Newtonian fluids are unknown to date in spite of recent progress in classical and irreversible thermodynamics of complex fluids.

There is an important link between thermodynamic optimization and process economics. If the process performance criterion is set on the economic ground, the optimal solution extremizes an economic profit. When the equipment in which the process runs is fixed (constant investment cost) and all outputs are prescribed by the technology requirements, the exploitation cost or the sum of all economic inputs associated with consumption of energy and materials can be minimized. In view of the incompleteness and uncertainty of economic prices data, thermodynamic optimization is often used to replace the economic problem of minimum costs by the thermodynamic problem in which the corresponding exergy costs (usually total exergy input) are minimized. Approximately, for all participating forms of matter under assumption of a common economic value of exergy unit, e, thermodynamic and economic optimizations are equivalent. In reality, however, the values of e are different for various process participants, and the equivalence is seldom satisfied. Yet, even if the results of both optimizations diverge, those generated by thermodynamic optimization have the virtue of larger universality. For example, the minimum of work necessary to condense the unit mass of oxygen is the function of the oxygen's end states, independent of the fluctuating economic conditions. It is the state function property of the exergy which causes thermodynamic optimization to generate the universal data [11].

Fluxes of work can drive open, thermally isolated macroscopic systems off the thermodynamic equilibrium, thus increasing their exergy. The resulting exergy surplus can be stored and then exploited. A polymer or a polymeric fluid can be regarded as a storage system for the exergy; the work delivered from that system can be used for suitable benefits. Yet it is well known that (the dynamical properties of) natural transfer processes are governed by a common criterion of minimum entropy production [12]. In this work we show how the criteria of work and entropy can become reconciled in the realm of complex fluids and traditional heat and mass transfer processes. We also show the power of thermodynamic approaches when using these basic criteria in modeling and optimization of sequential thermal machines.

We shall construct exergy and entropy criteria for optimization of sequential work-assisted thermomechanical operations which run jointly with 'endoreversible' thermal machines, and compare the structures of these criteria with those describing traditional (heat and mass) transfer operations (without work). At the present time three basic approaches are available while modeling and optimizing thermomechanical systems with production or consumption of mechanical energy (work): classical second law analyses [11], finite time thermodynamics (FTT, [12]) and entropy generation minimization (EGM, [13]). Of these approaches especially FTT and EGM systematically include the various concepts of contemporary irreversible thermodynamics. Their potential for incorporating results from dissipative fluid mechanics or non-equilibrium field thermodynamics can also be shown [12,13]. The significance of FTT and EGM methods will increase in the future because of (i) their flexibility in incorporating irreversible theories through the use of the independent information contained in the entropy generation σ, (ii) the broad range of realistic power-type or cost-type criteria encompassed, and (iii) their explicit use of the concepts of the process state and state control in the generalized sense of process dynamics. The traditional second law analyses are less suitable; their globality is a dangerous feature, which may lead to errors [14,15]. Because of their own limitations, global analyses are more useful for identifying improper processes than for proving that an actual design will work. Therefore, only local approaches, such as FTT and EGM, which link the differential balances with kinetics are fully reliable. But such approaches while still under the development for thermomechanical systems [16–19] are practically absent in the realm of polymeric fluids. For optimization of systems of heat pump type which consume work or systems of engine type which produce work, the need for local approaches (which include local treatments of balance and kinetics) is explicit even in those works which contain otherwise detailed thermoeconomic accounting [18,19].

This work contributes to the theory of energy production (consumption) in all thermal systems in which effect of fluxes on efficiencies is essential. As the incorporation of non-Carnot efficiencies into optimization models requires usually rather advanced analyses [20–23], optimization of systems containing thermal machines (engines or work consumers) with complex fluids is the new subject. In view of this fact, our present work shows in Section 3, how to derive non-Carnot efficiencies and formulate suitable thermodynamic criteria for optimization of operations with non-Newtonian heat exchange. This particularly refers to sequential systems with finite and infinitesimal stages, analyzed in Section 4. In this analysis the development of analogy between the work-assisted and traditional operations should be pointed out. In an efficiency expression for a thermomechanical machine, a simple substitution applies which introduces the 'driving temperature' T', a suitable control variable. In terms of T' the first-law efficiency of the machine is simply given by the Carnot formula, $\eta = 1 - T^{\mathrm{e}}/T'$. Furthermore, by using T' we arrive at the structure of the entropy production $\boldsymbol{\sigma}_{\mathrm{s}}$ which is in agreement with the well-known expression for $\boldsymbol{\sigma}_{\mathrm{s}}$ in the conventional processes, which do not produce any work [12,23,24]. Also, in terms of T', the Gouy–Stodola law [11] holds in the form which is precisely that of the traditional processes. In fact, we observe in Sections 4–6 a number of intriguing analogies between the work-assisted and traditional operations which help optimize the former. In particular, Section 6 shows how to obtain generalized functionals of work and entropy production for the case of heat transfer coupled with transfer of mass. In Section 7 we exploit the thermodynamic data of Section 2 to obtain finite-time exergies for operations with coupled heat and mass transfer. Section 8 summarises our results and presents the most important conclusions.

For multistage thermomechanical operations, equations of the theory apply discrete models based on difference rather than differential equations. An analogy between optimal multistage processes with free time intervals θ^n (described by difference equations and optimization criteria in form of sums) and continuous processes (described by differential equations and optimization criteria in form of integrals) is essential [24–30]. Thanks to this analogy, optimization algorithms obtained in the continuous framework can easily be transformed to algorithms of discrete processes, which means that analyses made in one framework need not be repeated in the other. A discrete Hamiltonian function, which is constant along optimal trajectories, is a suitable tool that governs the discrete optimization scheme. Optimization theory for the discrete processes with free time intervals θ^n is similar to Pontryagin's continuous theory, in contrast to standard theory of discrete processes [24]. This Pontryagin's-type discrete theory was developed in the context of multistage separation operations and chemical reactors [24–30]. The parallelism between continuous and discrete models of thermomechanical operations is a new subject [31] which is worth exploiting as it helps generate the results of optimal work and thermodynamic limits in a systematic way. In this development we refer the reader to our earlier publications on extremum work generated from (or supplied to) Newtonian systems [21–23,32].

2. Finite-time generalization of classical reversible work

This section shows the link between classical and irreversible thermodynamis of maximum work in a finite time. As the finite-time work depends on both thermodynamic and flow properties, both classical and irreversible thermodynamics are applied in modeling of energy production (consumption). The suitable systems involve a polymeric fluid that interacts through an engine or a heat pump with the environment or an infinite bath, Figs. 1 and 2. To study thermodynamics and transport phenomena in polymeric fluids, some kind of mechanical model which represents the actual molecule of the polymer should be accepted first. As the motion of molecules in flowing systems is more complicated than in equilibrium systems, we cannot model rheological systems rigorously. Hence the lumped-parameter framework is often accepted; it is also accepted here. Simplifications are also made in molecular models, both in those describing dilute polymeric solutions and in those for concentrated polymers, melts and amorphous solids. Of many kinds of synthetic and biological polymers, such as: long chainlike molecules, rigid molecules, chains with side branches, etc., we may consider only the first of these: long flexible chains with repeating units. Even the elastic dumbbell, a highly oversimplified surrogate of the bead-spring chain, is quite applicable in exploratory investigations. For qualitative aims, dumbell models with finitely extensive non-linear elastic (FENE) spring forces can be used. These models can simulate well both mechanical and thermal properties of the chain: its stretchability, its orientablility and its many degrees of freedom. However, to date, these models were used to simulate mainly mechanical properties of flows (such as: steady shear flow, inception of shear flow, steady elongational flow and inception of elongational flow). Based on these models, statistical theories of polymer conformations appeared aimed to find the probability distribution for the distance d between the ends of the n-mer, for a definite model of the chain. The cell (or lattice) theory of chain molecules can also be exploited [4]. It lead to very good correlations of specific heats for hydrocarbons and it was shown to interpret well properties of non-polar polymer solutions. The phase-space molecular theory can describe thermal and transport properties for both dilute solutions and for concentrated solutions and melts. For the latter, other theories, those of network type, derivable from the kinetic theory of rubber elasticity or Doi–Edwards 'slipping network model' [5,7] can also be used. As the extremum work problem can be stated for polymers in solid, liquid or glassy states and also for polymeric solutions and suspensions, properties of polymers in diverse states are generally required.

When the polymers long-chain properties are taken into account, the thermodynamic data stemming from Flory–Huggins theory [1–6] make it possible to calculate exergy functions, which are directly related to the reversible-minimum separation work of polymers from their solutions. The so-called engine convention is used here in which the work produced during the polymer's dissolving W is positive. This corresponds with the negative work W [or the positive work $(-W)$] which is consumed during the solution separation. Assuming an s-component mixture in which the solvent is the first component, the reversible exergy per unit mass of the mixture at flow is

$$A^{\mathrm{class}} = \sum_{i=1}^{s} \left\{ H_i - H_i^{\mathrm{e}} - T^{\mathrm{e}}\left(S_i - S_i^{\mathrm{e}}\right) \right\} x_i, \tag{1}$$

where x_i are mass fractions.

With this equation, the reversible separation work for a definite system follows from the input–output analysis applied to A^{class}. A generalized expression obtained from the above formula in the finite-time thermodynamics takes into account irreversible losses of work

$$\begin{aligned}(-W) &= \Delta \sum_{i=1}^{s} \left(H_i - T^{\mathrm{e}} S_i - \mu_i^{\mathrm{e}}\right) x_i + T^{\mathrm{e}} S_\sigma \\ &= \Delta H - T^{\mathrm{e}} \Delta S - \sum_{i=1}^{s} \mu_i^{\mathrm{e}} \Delta x_i + T^{\mathrm{e}} S_\sigma \\ &= (-W)_{\min}^{\mathrm{rev}} + T^{\mathrm{e}} S_\sigma \end{aligned} \tag{2}$$

where S_σ is the entropy production per unit flow of the mixture and the operator Δ refers to two arbitrary states of the system of which the second follows the first. This equation incorporates the Gouy–Stodola law for the process in which a dissipative fluid changes its states by interacting with the environment through the perfect thermal machine. The work $(-W)$ is a functional which is expressed above as the change of the exergy (availability) potential plus the product of T^{e} and the entropy production functional. The classical exergies correspond with $S_\sigma = 0$. See [11] for classical exergies.

Similar formulae refer to work per unit amount of the solvent. For dilute solutions, it coincides with the work per unit mass of the solution. For a solvent–polymer system

$$\begin{aligned}(-W) = \Delta\big\{ & H_1 - H_1^{\mathrm{e}} - T^{\mathrm{e}}(S_1 - S_1^{\mathrm{e}}) + \mathscr{X}\big[H_2 - H_2^{\mathrm{e}} \\ & - T^{\mathrm{e}}(S_2 - S_2^{\mathrm{e}})\big]\big\} + T^{\mathrm{e}} S_\sigma \end{aligned} \tag{3}$$

or, equivalently,

$$\begin{aligned}(-W) &= \Delta\left\{ H_1 - T^{\mathrm{e}} S_1 - \mu_1^{\mathrm{e}} + \left(H_2 - T^{\mathrm{e}} S_2 - \mu_2^{\mathrm{e}}\right)\mathscr{X} \right\} + T^{\mathrm{e}} S_\sigma \\ &= \Delta H - T^{\mathrm{e}} \Delta S = \mu_2^{\mathrm{e}} \Delta \mathscr{X} + T^{\mathrm{e}} S_\sigma \\ &= (-W)_{\min}^{\mathrm{rev}} + T^{\mathrm{e}} S_\sigma. \end{aligned} \tag{4}$$

On the other hand, the polymer's dissolving can produce work. This requires considering the process with inverted thermodynamic states. As for any two thermodynamic states $\mathscr{A}$ and $\mathscr{B}$ the modules of the reversible work are equal after the end states are inverted, i.e., $W_{\max}^{\mathrm{rev}}(\mathscr{B} \to \mathscr{A}) = (-W)_{\min}^{\mathrm{rev}}(\mathscr{A} \to \mathscr{B}) = \Delta A^{\mathrm{class}}$, we find for the *inverse* process of work production during the polymer's dissolving

$$W - W_{\max}^{\mathrm{rev}} = -T^{\mathrm{e}} S_\sigma. \tag{5}$$

It is the finite rates which decrease the mechanical energy yield. Eq. (5) may be compared with the previous result for the excess of separation work caused by finite rates

$$(-W) - (-W_{\min}^{\mathrm{rev}}) = T^{\mathrm{e}} S_\sigma. \tag{6}$$

As the entropy production is always positive, the above formulae state that the finite-time separation work of the polymer from its solution, $(-W)$, is larger than the change of the classical exergy or $(-W)_{\min}^{\mathrm{rev}}$, whereas the work which could be produced during the process of polymer's dissolving, W, must be smaller that the corresponding change of the classical exergy, $W_{\max}^{\mathrm{rev}}$. In fact, for a majority of processes in which polymers are dissolved, the real work W equals zero, corresponding with a natural process and a finite rate of the entropy production, $S_\sigma = W_{\max}^{\mathrm{rev}}/T^{\mathrm{e}}$, associated with a finite rate of spontaneous dissolving.

Clearly, our expressions take into account the entropy generation in the non-equilibrium system composed of a polymeric solution and the thermal reservoir. Our formulae show how the classical results which describe the reversible work can be generalized when evalulating the extremum work delivered with a finite rate, when irreversibilities play a role. When one of the end states is that of equilibrium the extremum values of the work functionals describe the so-called finite time exergies as they refer to changes of the system between two different thermodynamic states in a finite time.

The finite-time extremum work depends on transport properties of a complex fluid under consideration (as opposed to the reversible-extremum work, which is independent on these transport properties). Hence the need for at least a residual information helping to evaluate thermal conductivities and diffusion coefficients, such as that in Eqs. (7)–(9). From these data conductances of heat and mass transfer follow which are used to calculate finite time exergies. These conductances are defined as products of respective transfer areas and heat (or mass) transfer coefficients – ratios of corresponding conductivities (diffusivities) and thicknesses of resistive layers. To evaluate data of solid conductances, the calculation of thermal conductivity of solid polymers, λ, is required; this is based on generally accepted principles of the heat transfer mechanism in solids [2]. The phonon model of heat conduction leads to expression of the type $\lambda = Kc_v ul$, where K is a constant, u average sound speed and l mean free path for phonons. For crystalline polymers the product $c_v u$ decreases with T and so does λ; approximately one can have: $\lambda = \lambda_m \equiv 0.2$ J/(mKs) at $T > T_m$ and $\lambda = \lambda_m + 0.17$ $(T_m - T)$ at $T < T_m$ [3]. For amorphous polymers at $T < T_c$ the mean free path l is temperature independent and λ increases with T; approximately: $\lambda = \lambda_c \equiv 0.19$ J/(mKs) at $T > T_c$ and $\lambda = \lambda_c - 0.02(T_c - T)$ at $T < T_c$. The adduced sources also help to estimate thermal conductivities of polymeric solutions. In solutions essential changes of λ with concentration are observed for mass fractions x less than 0.2–0.3 [3]. For larger x the thermal conductivity of a solution λ is approximately concentration independent and its temperature dependence is analogous to that for melts, which predicts the decrease of λ with T. This agrees with the additivity of the 'free volume' effect [3,4]; thus for evaluations of λ in solutions the following formula can be used

$$\lambda = \lambda_0 + (\lambda_1 - \lambda_0)x/(1 - b(1 - x)), \tag{7}$$

where λ_0 and λ_1 are respectively the thermal conductivities of the solvent and molten polymer and b is the polymer constant. The above formula was proposed in [3]; its engineering approximation is based on an average value of $b = 0.7$, where $\lambda_1 = 0.19$ J/(mKs) can be used as the simplest estimate in the absence of more exact data. Evaluations of λ for T lower than the melting or dissolving temperature are less important as solid polymers are then usually in forms of suspensions whose thermal conductivities in convective heat transfer processes are determined by the thermal conductivity of surrounding liquid. In sheared polymeric liquids experiments show the effect of polymer conformation on the anisotropy of thermal conductivity: the values of λ parallel to the molecule backbone are higher than those perpendicular to it. Theoretical analyzes of microstructure [5–7] derive a general equation for the thermal conductivity tensor applicable to amorphous polymers and polymeric solutions. The first term of this equation is related to the thermal conductivity of the solvent, the second to the mass fraction of the polymer and the other to microscopic parameters of the model. Here we shall neglect these anisotropic effects; however we refer the reader to review of these issues [9]. Amongst many specific effects, one may take into account the effect of the concentration affected heat transfer [5]. It should also be stressed that the applicability of the Fourier's law, $q = -\lambda \nabla T$, does not necessarily mean the Newtonian equation of heat exchange, $q = \alpha \Delta T$. Examples are natural convection and boiling systems, where α may be proportional to $\Delta T^{1/4}$. In fact, we consider in this paper an exchange equation of the form $q_1 = g_1 \Delta T^a$, where g_1 is a conductance-like constant.

Mass transfer conductances in polymeric solutions folllow from their diffusivity coefficients. As the rate of thermal motion of molecules can be characterized by the selfdiffusion coefficient, a polymer–solvent system can be characterized by two selfdiffusion coefficients: that of the solvent, D_1 and that of the solved substance (polymer), D_2. Frenkel's vacancy model can be used to evaluate these selfdiffusion coefficients and related mobilities. The resulting coefficient of mutual diffusion D_v (which appears in the second Fick's law) can be calculated in terms of D_1 and D_2. It refers to the crosssection satisfying the condition that on its both sides the system volume conserves the constant value. Then, in terms of the molar concentrations C_k, at constant P and T,

$$D_v = \frac{1}{RT} D_1 \bar{v}_1 \frac{\partial \mu_1}{\partial \ln C_1} = \frac{1}{RT} D_2 \bar{v}_2 \frac{\partial \mu_2}{\partial \ln C_2}, \tag{8}$$

where the coefficients D_1 and D_2 satisfy the equality $D_1/M_1 = D_2/M_2$ and the subscript 2 refers to the polymer as the solved substance [3]. For ideal systems $D_1 = D_2 = D_v = D$, where D is the selfdiffusion coefficient. If the crosssection associated with the stagnant solvent is used (the case of interest here), the coefficient $D_0 \equiv D_v/(1 - \phi_2)$ should be used, where ϕ_2 is the volume fraction of the polymer. Then the following working formula holds for the diffusion of polymer with respect to the solvent

$$D_0 = \frac{D_1}{1 - \phi_2}(\phi_2 + (\phi_1/m - 2\mathscr{X}))\phi_1\phi_2, \tag{9}$$

where $D_1 = kT/\Lambda_1$ is the selfdiffusion coefficient of the solvent based on the frictional coefficient Λ_1, and $m = \overline{V}_2/\overline{V}_1$. The interaction coefficient $\mathscr{X}$ can be evaluated from Flory's theory or red off from respective diagrams [3,4]. We assume that the above equations are sufficient to calculate the diffusion coefficients and related mass conductances.

3. Power generation or consumption in sequential operations with heat transfer

From the view point of energy transformations the complex fluid plays the role of a resource whenever its intense parameters differ from those in equilibrium with an environment. This difference causes the yield of mechanical energy in an engine-type process. During the energy yield the value of any finite resource decreases, the depreciation is associated with change of the resource's intense parameters towards its equilibrium with the environment. Yet the resource utilization is possible in the inverse process, that of heat-pump type, where work is consumed and state changes of the resource are directed outwards the equilibrium. Here we shall consider these energy- transforming processes in two cases, the first (simpler) in which the fluid's state changes are restricted to changes in fluid's temperature only, whereas the polymer's concentration in the fluid is fixed at the level of its initial value, and the second, more realistic but also more involved, in which the concentration may vary.

To begin with, let us consider the work generation or consumption in an "endoreversible" (internally reversible) thermal machine, an engine or heat pump, which interacts with a high-T fluid flowing with the mass flux G. Principles of modeling of sequential endoreversible systems composed of engines or heat pumps working at steady state are known [12]. Fig. 2 presents a scheme of a single-stage system in which a polymeric fluid is heated by an endoreversible heat pump to which work is supplied; the second fluid is an infinite reservoir. This operation can be contrasted with an endoreversible engine where a resource fluid drives the Carnot engine from which the work is taken out (the second fluid is again an infinite reservoir).

On the other hand, Fig. 3 shows a scheme of multistage power consumption. The fluids are of finite thermal conductivity, hence there are finite thermal resistances in the system, representing the dissipative effect of their thermal boundary layers. In a multistage heating the fluid's T changes at each stage; the whole process is characterized by the sequence $T^0, T^1, \dots, T^N$.

We use the common 'engine convention' in which the work generated in an engine, W, is positive, and the work generated in a heat pump is negative; this means that a positive work $(-W)$ is consumed in the heat pump. The quantity W has the dimension of work per unit mass, thus it describes a specific work produced or consumed by the fluid at flow. In thermodynamic optimization, the work generated by an engine is maximized and the work consumed by a heat pump is minimized. The optimization is made under a set of various process constraints which may include those imposed on total investment costs. When the final state of the resource fluid is the state of equilibrium with the environment $(T^N = T^e)$, the maximal specific work represents a finite-time exergy of the engine mode for the fluid at flow. When the initial state of the controlled fluid is at the state of equilibrium with the environment $(T^0 = T^e)$, the minimal specific work to achieve T^N represents a finite-time exergy of the heat-pump mode.

The considerations below are constrained for stationary or cyclic processes in which there is no entropy accumulation and the entropy production vanishes in the reversible part of the system. In a single-stage process the fluid's temperature changes between T^0 and T^1, the related heat flux is $q_1 = Gc(T^1 - T^0)$. We can evaluate the specific work produced in a single endoreversible engine or that consumed in a single endoreversible heat pump [12]. As the endoreversible machine is a lumped-parameter model for a generic class of real work-producing devices with irreversible dissipators (heat and mass conductors), the problem of finite-time optimization of work can be imbedded in (or derived from) the general economic problem of optimization of a practical device subject to the constrained investment. The constrained investment means that the device or an industrial enterprise requires the investment money to be used with limitations, hence the system size and/or the residence time of flowing entities (e.g. heat media, reacting species, etc.) must be finite. Thus, it is only a finite time possible to accomplish required changes of state in a real process.

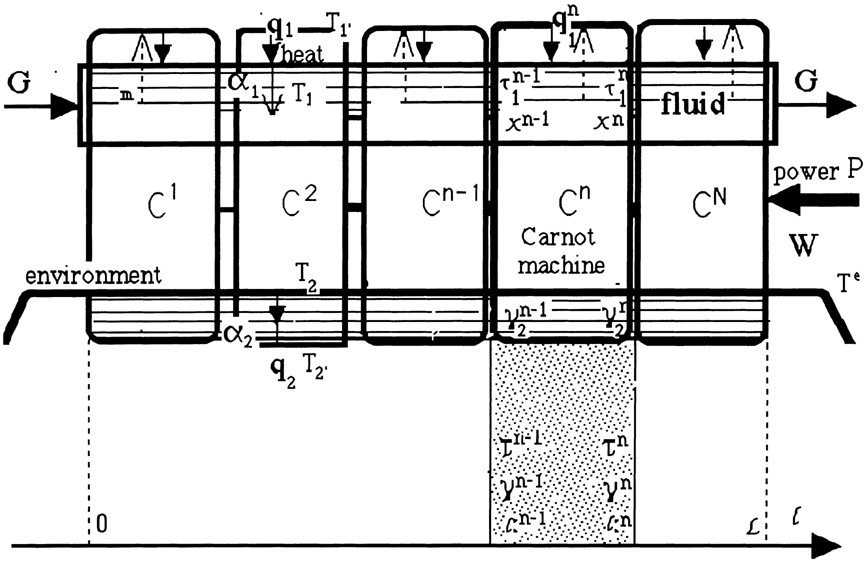

Fig. 3. A scheme of multistage work-assisted removal of solvent from a polymeric solution, driven by heat and mass transfer processes in boundary layers and thermal machines.

This property is not taken into account in classical thermostatics in which reversible changes of state (associated with vanishing rates and infinite durations) admit an infinite investment. It is for the economical reasons, associated with tradeoff between the investment and fuel costs, that the optimal times are finite. An immediate consequence of this fact is that the optimal efficiency of an endoreversible engine is smaller than the Carnot efficiency whereas the optimal efficiency of an endoreversible heat pump is larger than the Carnot efficiency. The latter is approached by an endoreversible engine either in the case of a very slow fluid flow G or for a very large transfer area A. The first case cannot be, however, an optimum as it corresponds with vanishing thermal and mechanical powers, q_1 and p (consider Eq. (15)). Otherwise, the second case could only occur at the expense of a very large investment, i.e., for an infinite transfer areas (infinite length of the system). Thus the optimal powers q_1, p and the optimal duration must be finite, and it is the optimization that decides about the most proper regime in which the system should work. These effects can be enunciated in the quantitative way [21,22].

For an endoreversible process without mass transfer, the power optimization at the process stage can be achieved by using a single control variable which affects the mechanical power through its influence on the actual efficiency. The endoreversible efficiency of the engine, $\eta = 1 - T_{2'}/T_{2'}$, is, of course, lower than that of a Carnot engine working between the temperatures T_1 and T_2 because the engine itself operates on the reduced temperature difference $T_{1'} - T_{2'}$. The temperatures $T_{1'}$ and $T_{2'}$ are unknown, but they may be expressed in terms of the temperatures T_1 and T_2 and a single control variable at the stage under consideration. The choice of the control variable is in principle arbitrary; for example, the control may be the heat flux, q_1, the related entropy flux ϑ, the efficiency, η, the temperature difference $T_{1'} - T_{2'}$, or others. By setting one of these variables, subject the continuity of the entropy flux through the engine, a finite intensity of the process is decided, and all other quantities follow along with the power p.

At first, however, we have to accept a heat exchange law between the engine or heat pump and the complex-fluid resource which drives the engine or receives the upgrated heat from the heat pump. Linear law (Newtonian heat exchange) may be too restrictive; otherwise the power-law heat exchange, heat flux proportional to the ath power of ΔT, is sufficiently general to our purposes. The non-unit exponents in the power-law heat transfer occur, for example, in natural convection heat exchange. If the heat flux q_1 is the control variable and the power law, heat flow proportional to the ΔT^a, describes the heat exchange, the first primed temperature $T_{1'}$ follows in terms of the controlling heat q_1 directly

$$T_{1'} = T_1 - (q_1/g_1)^{1/a}. \tag{10}$$

On the other hand, the entropy balance is necessary to evaluate the temperature $T_{2'}$ in terms of q_1. It has here the form of the continuity equation for the entropy flux through the reversible part of engine, $q_1/T_{1'} = q_2/T_{2'}$. With Eq. (10) and the power law for q_2 with the exponent b, the entropy balance can be written in the form

$$\frac{q_1}{T_1 - (q_1/g_1)^{1/a}} = \frac{g_2(T_2' - T_2)^b}{T_{2'}}. \tag{11}$$

After defining the entropy flux function

$$\vartheta(q_1, T_1, g_1) \equiv \frac{q_1}{T_1 - (q_1/g_1)^{1/a}} = q_1(T_1 - (q_1/g_1)^{1/a})^{-1} \tag{12}$$

we write the entropy balance (11) in the form of an equation for the temperature $T_{2'}$

$$(T_{2'} - T_2)^b - T_{2'}\vartheta(q_1, T_1, g_1)g_2^{-1} = 0. \tag{12$'$}$$

To obtain $T_{2'}$ for an arbitrary b, this equation should be solved by numerical methods. However, in some cases analytical solutions can be found. This is so in the case when $b = 1$, which refers to the Newtonian heat exchange between the engine fluid and the thermal reservoir. The solution to Eq. (12′) in terms of $T_{2'}$ is then

$$\begin{aligned} T_{2'}(q_1, T_1, T_2) &= \frac{T_2}{1 - \vartheta(q_1, T_1, g_1)/g_2} \\ &= \frac{T_2}{1 - q_1/(g_2(T_1 - (q_1/g_1)^{1/a}))} \\ &= \frac{T_2}{1 - (q_1/g_2)(T_1 - (q_1/g_1)^{1/a})^{-1}} \\ &= \frac{T_2}{1 - q_1/(g_2 T_{1'})}. \end{aligned} \tag{13}$$

Note that this equation is still quite general as the exchange of the a-heat can refer to an arbitrary a. Only the exchange of the b-heat must be Newtonian, i.e., satisfying $b = 1$. Eq. (13) will be the basis for our considerations here.

Yet, just for the sake of showing the correspondence with simpler but otherwise familiar solution, we shall occasionally digress our attention to the most special case, when both power coefficients a and b equal the unity, i.e., $a = b = 1$. This pertains to the Newtonian heat exchange between the thermal machine and both fluids (the resource fluid and the reservoir fluid). We then recover the familiar formula

$$\begin{aligned} T_{2'}(q_1, T_1, T_2) &= T_2\left(1 - \frac{q_1/g_2}{T_1 - q_1/g_1}\right)^{-1} \\ &= T_2\frac{T_1 - q_1/g_1}{T_1 - q_1/g_1 - q_1/g_2} \\ &= T_2\frac{T_1 - q_1/g_1}{T_1 - q_1/g}, \end{aligned} \tag{13$'$}$$

where the overall conductance of heat transfer is defined in the traditional way, as the harmonic mean; $g \equiv (1/g_1 + 1/g_2)^{-1}$ or $g_1 g_2/(g_1 + g_2)$.

Now we return to our basic formula, Eq. (13). The first-law efficiency of the internal engine satisfies the Carnot formula in terms of $T_{1'}$ and $T_{2'}$. With Eqs. (10) and (13) this efficiency is obtained in terms of T_1, T_2 and q_1 as

$$\begin{aligned}\eta &= 1 - \frac{T_{2'}}{T_{1'}} = 1 - \frac{T_2}{(1 - q_1/(g_2 T_{1'}))T_{1'}} = 1 - \frac{T_2}{T_{1'} - q_1/g_2} \\ &= 1 - \frac{T_2}{T_1 - (q_1/g_1)^{1/a} - q_1/g_2} \\ &\equiv 1 - \frac{T_2}{T_1 - (-u_1)^{1/a} + (g_1/g_2)u_1}, \end{aligned} \tag{14}$$

where $u_1 \equiv -q_1/g_1$ is a measure of the heat added to the fluid 1, a suitable control if g_1 is constant. It has units of ath power of temperature, and is positive for fluid heating and negative for fluid cooling. The quantity u_1 should be distinguished from a similar one, $u \equiv -q_1/g$, that was used in our earlier publications [21–23,31,32] and is suitable only for Newtonian transfer. From Eq. (14) we conclude that a quite simple equation links mechanical power p with heat flux q_1

$$\begin{aligned} p &= q_1\left(1 - \frac{T_2}{T_1 - (q_1/g_1)^{1/a} - q_1/g_2}\right) \\ &= -g_1 u_1\left(1 - \frac{T_2}{T_1 - (-u_1)^{1/a} + (g_1/g_2)u_1}\right), \end{aligned} \tag{15}$$

where the bracketed expression is the first-law efficiency. In the case of Newtonian heat transfer in both resistive layers $(a = b = 1)$ we recover the well-known formula

$$p = q_1\left(1 - \frac{T_2}{T_1 - g^{-1}q_1}\right) = -gu\left(1 - \frac{T_2}{T_1 + u}\right), \tag{15$'$}$$

where $u \equiv -q_1/g$ is based on the total conductance g [21,22,31,32].

The efficiency of an engine, Eq. (14) or the bracketed term in Eq. (15), deviates monotonically from the Carnot law with the finite q_1 or u. Also, the power p deviates from that of the Carnot model due to a finite q_1. For a quasistatic transfer, i.e for very low q_1 or u, the efficiency η is that of Carnot. Yet the efficiency is zero for a sufficiently large q_1 at the Fourier point, where the heat flux satisfies an equation

$$(q_F/g_1)^{1/a} + q_F/g_2 - T_1 + T_2 = 0. \tag{16}$$

This corresponds to pure heat conduction and no power production at all. Thus the power vanishes at both $q_1 = 0$ and $q_1 = q_F$, hence there is a maximum of power p at an intermediate point. The mechanical power may be produced only in the range of efficiencies between 0 and η_c.

The inverted forms of Eqs. (15) or (15$'$) could be used to present quantities of interest (power p, released heat ω, etc.) in terms of the efficiency control η instead of the heat flux control q_1. For the Newtonian heat transfer, it follows from Eq. (15$'$) that the mechanical power $p = \eta q_1$, equals $p = g\eta(T_1 - T_2/(1 - \eta))$. This is the formula available for mathematical analysis. However, the non-Newtonian generalization of this formula requires explicit solving of Eq. (15) with respect to q_1. This is why the heat flux representation of control is more suitable in analysis than the efficiency representation.

Using Eq. (15), the specific work produced in a single endoreversible engine (or that consumed in a single endoreversible heat pump) equals $W = p^{1/G}$ [12], where G is the fluid's mass flux. Each of the quantities: q_1, g_1 or q_2 and g_2 influence W; each is proportional to the corresponding transfer area, $\mathfrak{a}_1$ or $\mathfrak{a}_2$. Only in the Newtonian case $(a = 1)$ the overall thermal conductance of the thermal machine can be found as the product $g = \alpha'\mathfrak{a}$ where α' – an overall heat transfer coefficient, $\mathfrak{a}$ – total area (the sum of upper and lower areas) and c – fluid's specific heat. Whenever the heat exchange is non-Newtonian one has to deal with both partial conductances, g_1 and g_2. The maximum of W defines the bound for the one-stage work production. In the non-Newtonian case, the condition $\partial p/\partial q_1 = 0$ applied to Eq. (15) leads to an equation

$$\begin{aligned} &\frac{1}{T_2} - \frac{1}{T_1 - (q_1/g_1)^{1/a} - q_1/g_2} \\ &\quad = q_1 \frac{(ag_1)^{-1}(q_1/g_1)^{1/a-1} + 1/g_2}{T_1 - (q_1/g_1)^{1/a} - q_1/g_2)^2}, \end{aligned} \tag{17}$$

that can be simplified into the form

$$\begin{aligned} &(T_1 - (q_1/g_1)^{1/a} - q_1/g_2)^2 - T_2T_1 + T_2(1 - 1/a) \\ &\quad \times (q_1/g_1)^{1/a} = 0. \end{aligned} \tag{17$'$}$$

From this equation an optimal value of q_1 is obtained by a search procedure. The associated maximum power and efficiency then follow from Eq. (15). The benefit of having the analytical expression for the work production at the stage, Eq. (15), is more essential than the disadvantage caused by the numerical solving of Eq. (17$'$). In the Newtonian case, when $a = 1$ and analytical solution exists, Eq. (17$'$) yields the optimal value $(q^1)_m = g(T_1 - \sqrt{T_1T_2})$ which corresponds with the first-law efficiency $\eta_m = 1 - \sqrt{T_1T_2}$ called the Novikov–Curzon–Ahlborn efficiency or NCA efficiency [12,13,32]. Note that this NCA efficiency is not an extremum efficiency but the efficiency at the maximum power point.

To apply the power generation function, Eq. (15), to a continuous sequential system, the ratios q_1/g_1 and q_1/g_2 should be expressed in terms of the derivatives of the state variable T_1. To achieve this goal, we define for each transfer area, $\mathfrak{a}_1$ or $\mathfrak{a}_2$, the "length of the transfer unit" $\mathscr{L}$ and the non-dimensional length $\ell/\mathscr{L}$ called the "number of transfer units". Also the unit volume counterparts, $a_{v1} \equiv \mathfrak{a}_1/V_1$ or $a_{v2} \equiv \mathfrak{a}_2/V_1$, of the transfer areas involved, $\mathfrak{a}_1$ or $\mathfrak{a}_2$, are defined. They are always referred to the volume occupied by the resource fluid (fluid 1). Consequently

$$\frac{Gc_1}{\alpha_1 a_{v1} F_1} \equiv \mathscr{L}_1, \quad \tau_1 \equiv \frac{\ell}{\mathscr{L}_1} = \frac{\alpha_1 a_{v1} F_1}{Gc_1}\ell = \frac{\alpha_1 a_{v1}}{\rho_1 c_1} t_1 = \frac{t_1}{\kappa_1} \tag{18a}$$

and

$$\frac{Gc_1}{\alpha_2 a_{v2} F_1} \equiv \mathscr{L}_2, \quad \tau_2 \equiv \frac{\ell}{\mathscr{L}_2} = \frac{\alpha_2 a_{v2} F_1}{Gc_1}\ell = \frac{\alpha_2 a_{v2}}{\rho_1 c_1} t_1 \equiv \frac{t_1}{\kappa_2}, \tag{18b}$$

where $t_1 = \ell/V_1 = \rho_1 F_1 \ell/G$ is the fluid's residence time and κ_1 and κ_2 play the role of the time constants of the system. With these definitions, the heat balance over the differential length $\mathrm{d}\ell$ yields

$$\begin{aligned} u_1 &\equiv -q_1/g_1 = -\mathrm{d}Q_1/\mathrm{d}\gamma_1 = Gc(T_1)\,\mathrm{d}T_1/(\alpha_1\,\mathrm{d}A_1) \\ &= Gc(T_1)\,\mathrm{d}T_1/(\alpha_1 a_{V1} F_1\,\mathrm{d}\ell) = \mathscr{L}_1(T_1)\,\mathrm{d}T_1/\mathrm{d}\ell \end{aligned} \tag{19a}$$

and

$$\begin{aligned} -q_1/g_2 &= u_1 g_1/g_2 = -\mathrm{d}Q_1/\mathrm{d}\gamma_2 \\ &= Gc(T_1)\,\mathrm{d}T_1/(\alpha_2\,\mathrm{d}A_2) \\ &= Gc(T_1)\,\mathrm{d}T_1/(\alpha_2 a_{v2} F_1\,\mathrm{d}\ell) \\ &= \mathscr{L}_2(T_1, T_2)\,\mathrm{d}T_1/\mathrm{d}\ell, \end{aligned} \tag{19b}$$

where $u_1 \equiv -q_1/g_1$. Note that $\mathscr{L}_1/\mathscr{L}_2 = g_2/g_1$. Thus, in continuous systems, the cumulative specific work of the fluid at flow is described by the Lagrange differential

$$\begin{aligned} \mathrm{d}W \equiv \mathrm{dp}/G &= -c(T_1)\left(1 - \frac{T_2}{T_1 - (q_1/g_1)^{1/a} - q_1/g_2}\right)\mathrm{d}T_1 \\ &= -c(T_1)\left(1 - \frac{T_2}{T_1 - (-\mathscr{L}_1\,\mathrm{d}T_1/\mathrm{d}\ell)^{1/a} + \mathscr{L}_2\,\mathrm{d}T_1/\mathrm{d}\ell}\right) \\ &\quad \times (\mathrm{d}T_1/\mathrm{d}\ell)\,\mathrm{d}\ell. \end{aligned} \tag{20}$$

In this equation the temperature of the infinite reservoir, $T_2 = T^{\mathrm{e}}$, is the constant parameter. In the first approximation $\mathscr{L}_1$ and $\mathscr{L}_2$ can be assumed as the temperature independent quantities. The constancy assumption for c_1 is more risky, and should be restricted to ideal fluids. The total work W is the corresponding integral with respect to ℓ, whose Euler–Lagrange equation defines the extremal temperature profile $T(\ell)$.

Consider now multistage sequential systems. The sign of the optimal work function $V^N = \max W^N$ defines the working mode for an optimal sequential process as a whole. In agreement with our conventions, W^N and V^N are positive in work production modes. An engine process accompanies the (overall) system's relaxation to equilibrium, whereas the heat-pump process assures the system's departure from equilibrium. Therefore in engine modes, $W > 0$ and $V > 0$. In heat-pump modes, $W < 0$ and $V < 0$, thus working with a function $R^N = -V^N = \min(-W^N)$ is more convenient. However the direction of any sequential process is determined by the positivity of entropy production rather than by the sign of a work function. Of special attention are two processes: that which starts with the state $T^0 = T^{\mathrm{e}}$ and terminates at an arbitrary $T^N = T$, and that which starts at an arbitrary $T^0 = T$ and terminates at T^{e}. In these cases the functions V^N generalize the classical exergy for discrete processes with finite durations (which run in pumping or engine modes).

In multistage systems one should sum expressions corresponding with Eq. (15) over stages. All nth stage quantities are designated by the superscript n. As in the continuous case, the partial conductance g_1^n (the product of the transfer coefficient α_1^n and the change of a cumulative area A_1^n at the nth stage) is the basic transfer variable. A suitably transformed form of this equation, Eq. (21) below, is useful. It applies the previous definitions in an expression for the work delivered or consumed at the stage n per unit flow of the resource fluid (the fluid driving an engine or the fluid heated in the condenser of a heat pump)

$$\begin{aligned} p^n/G &= -c_1(T^n)\left(1 - \frac{T^{\mathrm{e}}}{T_1^n - (q_1^n/g_1^n)^{1/a} - q_1^n/g_2^n}\right)(T_1^n - T_1^n) \\ &= -c_1(T^n)\left(1 - \frac{T^{\mathrm{e}}}{T_1^n - (-u_1^n)^{1/a} + (g_1^n/g_2^n)u_1^n}\right)(T_1^n - T_1^n). \end{aligned} \tag{21}$$

It was assumed here that the reservoir temperature T_2 is equal to the constant temperature of the environment, T^{e}.

4. Discrete and continuous integrals for work and entropy production

Summing the local work expressions over stages and casting the problem in the format of the discrete maximum principle we arrive at the discrete functional of consumed work

$$\begin{aligned} (-W^N) &= \sum_{n=1}^{N} c_1(T^n)\left(1 - \frac{T^{\mathrm{e}}}{T_1^n - (-u_1^n)^{1/a} + (g_1^n/g_2^n)u_1^n}\right) \\ &\quad \times (T_1^n - T_1^{n-1}) = \sum_{n=1}^{N} c_1(T^n) \\ &\quad \times \left(1 - \frac{T^{\mathrm{e}}}{T_1^n - (-u_1^n)^{1/a} + (g_1^n/g_2^n)u_1^n}\right) u_1^n \theta_1^n. \end{aligned} \tag{22}$$

where $\theta_1^n \equiv (\ell^n - \ell^{n-1})/\mathscr{L}_1^n$. A special form of this equation which deals with the Newtonian heat transfer in a fluid with a constant c may be written as

$$(-W^N) = \sum_{n-1}^{N} c\left(1 - \frac{T^{\mathrm{e}}}{T_1^n + u^n}\right) u^n \theta^n, \tag{22$'$}$$

where $u^n \equiv -q_1^n/g^n$. In this formula the interval θ^n refers to the overall conductance g^n and to the overall non-dimensional quantity: the number of overall heat transfer units, whereas its counterpart θ_1^n in the general formula, Eq. (22), refers to the partial quantity $\mathscr{L}_1^n$ and hence to the partial number of heat transfer units, τ_1^n.

The discrete functional (22) has to be minimized subject to the difference constraints

$$\frac{T_1^n - T_1^{n-1}}{\theta_1^{n-1}} = u_1^n \tag{23a}$$

and

$$\frac{\tau_1^n - \tau_1^{n-1}}{\theta_1^n} = 1. \tag{23b}$$

Eq. (22) describes the work which must be supplied to processes in which the controlled fluid is sequentially heated in condensers of N endoreversible heat pumps. Yet, this formulation is valid for both process modes, i.e., for the heat-pump mode in which work is consumed and for the engine mode in which work is generated.

In the limiting case of an infinite number of stages a work integral follows from Eq. (22)

$$\begin{aligned} W &\equiv \mathtt{P}/G \\ &= -c_1(T_1)\left(1 - \frac{T^{\mathrm{e}}}{T_1 - (\mathrm{d}Q_1/\mathrm{d}\gamma_1)^{1/a} - (\mathrm{d}Q_1/\mathrm{d}\gamma_2}\right)\mathrm{d}T_1 \\ &= -c_1(T_1)\left(1 - \frac{T^{\mathrm{e}}}{T_1 - (-\dot{T}_1)^{1/a} + (g_1/g_2)\dot{T}_1}\right)\dot{T}_1\,\mathrm{d}\tau_1, \end{aligned} \tag{24}$$

where the derivative $\mathrm{d}Q_1/\mathrm{d}\gamma_1 = \lim(q_1/g_1) = -\mathrm{d}T_1/\mathrm{d}\tau_1$ is the limiting driving heat at an infinitesimal stage per unit thermal conductance 1. The temperature derivative $\dot{T}_1$ is with respect to the non-dimensional time τ_1 or the partial number of heat transfer units, which satisfies the second definition in Eq. (18a). The special case of Eq. (24) refers to the Newtonian heat transfer with a constant specific heat

$$\begin{aligned} W \equiv \mathtt{P}/G &= -\int_{T^{\mathrm{i}}}^{T^{\mathrm{f}}} c\left(1 - \frac{T^{\mathrm{e}}}{T_1 - \mathrm{d}Q/\mathrm{d}\gamma}\right)\mathrm{d}T_1 \\ &= -\int_{T^{\mathrm{i}}}^{T^{\mathrm{f}}} c\left(1 - \frac{T^{\mathrm{e}}}{T_1 + \dot{T}_1}\right)\dot{T}_1\,\mathrm{d}\gamma. \end{aligned} \tag{24$'$}$$

This formula involves the overall non-dimensional quantity τ and the related derivative $\dot{T} = \mathrm{d}T_1/\mathrm{d}\tau$.

Integral (24) generalizes for non-Newtonian heat exchange the recent result, Eq. (24′) of [32]. The two extrema for work (24), $(-W_{\min})$ and $(W_{\max})$, describe the work limits for fluid state changes in two continuous processes of which the first runs in an original direction and the second in the inverse direction. In an original process, the initial temperature is T^{i} and the final temperature is T^{f}, in the inverse process the direction is from T^{f} to T^{i}. The result for $(-W_{\min})$ defines the lower bound referred to fluid's heating in an infinite sequence of infinitesimal heat pumps, whereas that for $(W_{\max})$ defines the upper bound referred to fluid's cooling in an infinite sequence of inifinitesimal engines. For pure heat transfer processes, to which Eq. (11) applies, these bounds can conveniently be evaluated as differences between finite-time exergies evaluated for initial and final states of the process [21,22,31]. Further we will consider generalized exergies which describe coupled heat and mass transfer; this will make it possible to determine generalized bounds on work production or consumption for more difficult processes.

First, however, we recall the Gouy–Stodola law which allows to identify the entropy production in work functionals without direct recourse to an irreversible entropy balance. Indeed by integration of Eq. (24) a non-Newtonian generalization of the work functional (24′) is found

$$\begin{aligned} W \equiv \mathtt{P}/G = &-\int_{T^{\mathrm{i}}}^{T^{\mathrm{f}}} c_1(T_1) \\ &\times \left(1 - \frac{T^{\mathrm{e}}}{T_1} + \frac{T^{\mathrm{e}}}{T_1} - \frac{T^{\mathrm{e}}}{T_1 - (-\dot{T}_1)^{1/a} + (g_1 g_2)\dot{T}_1}\dot{T}_1\right)\mathrm{d}\tau_1 \\ = &-\int_{T^{\mathrm{i}}}^{T^{\mathrm{f}}} c_1(T_1)\left(1 - \frac{T^{\mathrm{e}}}{T_1}\right)\mathrm{d}T_1 - T^{\mathrm{e}}\int_{T^{\mathrm{i}}}^{T^{\mathrm{f}}} c_1(T_1) \\ &\times \left(\frac{\left[-(-\dot{T}_1)^{1/a} + (g_1/g_2)\dot{T}_1\right]}{T_1\left[T_1 - (-\dot{T}_1)^{1/a} + (g_1/g_2)\dot{T}_1\right]}\right)\dot{T}_1\,\mathrm{d}\tau_1. \end{aligned} \tag{25}$$

In the second line, the reversible thermodynamic work W^{rev} (the classical exergy change) was singled out as the separate integral. The second integral represents the total production of the specific entropy when fluid changes its temperature from T^{i} to T^{f}. To effectively deal with this entropy production we will use the substitution defining the "driving temperature"

$$T' \equiv T_1 - (-\dot{T}_1)^{1/a} + (g_1/g_2)\dot{T}_1. \tag{26}$$

With this substitution the classical form of the entropy production is explicit in the work functional

$$\begin{aligned} W &\equiv \mathtt{P}/G \\ &= -\int_{T^{\mathrm{i}}}^{T^{\mathrm{f}}} c_1(T_1)\left(1 - \frac{T^{\mathrm{e}}}{T_1}\right)\mathrm{d}T_1 \\ &\quad - T^{\mathrm{e}}\int_{T^{\mathrm{i}}}^{T^{\mathrm{f}}} c_1(T_1)\left(\frac{1}{T_1} - \frac{1}{T'}\right)\mathrm{d}T_1. \end{aligned} \tag{25$'$}$$

whereas the associated efficiency (24) takes the Carnot form with respect to T' and T^{e}

$$\eta = 1 - \frac{T_{2'}}{T_{1'}} = 1 - \frac{T^{\mathrm{e}}}{T_1 - (-\dot{T}_1)^{1/a} + (g_1/g_2)\dot{T}_1} = 1 - \frac{T^{\mathrm{e}}}{T'}. \tag{14$'$}$$

Note that the associated equation of the heat exchange is not of the simple form $\dot{T} = T' - T_1$; it is rather contained in the definition of T', Eq. (26). If, however, $a = 1$, i.e., the fluid is Newtonian, the linear kinetics $\dot{T}_1 = T' - T_1$ is obtained from Eq. (26) in which the overall rather than partial number of heat transfer units represents the non-dimensional time variable τ. With T' in Eq. (24′) a familiar functional for Newtonian heat exchange is recovered [32]

$$\begin{aligned} W &\equiv \mathrm{P}/G \\ &= -\int_{T^{\mathrm{i}}}^{T^{\mathrm{f}}} c\left(1 - \frac{T^{\mathrm{e}}}{T_1}\right)\mathrm{d}T_1 - T^{\mathrm{e}}\int_{T^{\mathrm{i}}}^{T^{\mathrm{f}}} c\frac{(T' - T_1)^2}{T_1 T'}\,\mathrm{d}\tau. \end{aligned} \tag{24$'$}$$

All above equations apply the 'driving temperature' T', as an alternative control. [1] Due to this special control variable we have arrived at the entropy production in Eq. (25) which is in agreement with the well-known expression for the entropy production in conventional heating processes, which do not produce any work [12,23–26]. The driving temperature T' appears as an absolute temperature of an external fluid whose thermal effect exerted on the fluid heated or cooled by a thermal machine replaces the joint effect of the Carnot machine and the reservoir. In terms of T' and T^{e} the first-law efficiency is simply given by the Carnot formula, Eq. (14′). It can also be proven that T' is a positive quantity [23].

The second integral in Eq. (25′) relates the specific entropy production to the product of the differential change of fluid's enthalpy, $\mathrm{d}I = c\,\mathrm{d}T$, and the driving force $(1/T_1 - 1/T')$. In this analysis we observe that it is the entropy production which causes the non-potential component of the work integral. In terms of T' Eqs. (25) and (25′) describe the Gouy–Stodola law in the control space. They prove that minimizing of the entropy production in a fixed-end control problem assures a minimum of the work consumption in the heat-pump mode and a maximum of work production in the engine mode. Since their first terms are path independent (potential) terms, the (non-potential) entropy production plays the role of a kernel which solely determines properties of extremal paths.

5. Optimization results for operations with pure heat transfer

For the Newtonian case an analytical result can be obtained from the Euler–Lagrange equation for integrals (24′) or (24″). The result is a common (mode independent) differential equation that holds for both fixed-end and free-end extremals of the extremum work and minimum entropy production problems [21,22]

$$T_1\ddot{T}_1 - \dot{T}_1^2 = 0. \tag{27}$$

Eq. (27) is restricted to the pure heat transfer processes and is satisfied by the function $T(\tau)$ which is a solution to a simple differential formula, $\dot{T}(\tau) = \xi T$, where the constant ξ is the rate indicator which is positive for fluid's heating and negative for fluid's cooling. Using the boundary conditions for T_1 ($T_1 = T^{\mathrm{i}}$ at τ^{i} and $T_1 = T^{\mathrm{f}}$ at τ^{f}) we conclude that an unconstrained extremal path is an exponential curve $T_1(\tau) = T_1^{\mathrm{i}}(T_1^{\mathrm{f}}/T_1^{\mathrm{i}})^{\tau/\tau^{\mathrm{f}}}$ whose accomplishment in time requires the following temperature control

$$\begin{aligned} T'(\tau) &= T_1(\tau)(1 + \xi) \\ &= \left(T_1^{\mathrm{i}}(T_1^{\mathrm{f}}/T_1^{\mathrm{i}})^{\tau/\tau^{\mathrm{f}}}\right)\left(1 + \ln\left(T_1^{f}/T_1^{\mathrm{i}}\right)/(\tau^{\mathrm{f}} - \tau^{\mathrm{i}})\right). \end{aligned} \tag{28}$$

In terms of T', the structure of the optimal control is the same for both traditional processes (without work) and processes in thermal machines. In this paper we also show other properties of this sort. They help to model the work-assisted operations which are much less known that the traditional ones. Modeling that uses T' is especially helpful for non-Newtonian transfer processes, for which analytical formulae cannot be found, and only numerical approaches can generate results generalizing Eqs. (27) and (28).

The difficulties due to non-existence of analytical solutions for non-Newtonian heat exchange stimulate considerations towards numerical evaluation of extremals of multistage processes with finite stages. The general discrete model of the non-Newtonian heat exchange is represented by Eqs. (22), (23a) and (23b). Two modern optimization methods can be applied: Bellman's dynamic programming (DP) and (a discrete version of) Pontryagin's maximum principle.

Let's first briefly describe the typical DP algorithm. As the time τ_1^n does not appear explicitly in the process model, a modified rather than original criterion is minimized to reduce the problem dimensionality and increase the results accuracy. The criterion is defined as the sum $\sum(1_0^n + h_1)\theta^n$, where $1_0^n \equiv -p^n/G$ is the intensity of specific work consumption per unit time τ_1, and h_1 is both the Lagrange multiplier of the time constraint and the numerical value of the Hamiltonian function H. A computer program serves to generate tables of the

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[1] For an additional discussion of the physical interpretation and properties of T' the reader is referred to [23], where, however, its generalization to coupled transfer processes was still unknown. Eqs. (41)–(57) of the present work show the role of T' in a coupled transfer process.

potential function $R_*^n(T^n) \equiv \min(-W_*^N)$ along with optimal controls, u_1^n and θ_1^n, and optimal states T_1^n. This is accomplished by solving Bellman's recurrence equation of the problem

$$R_*^n(T_1^n) = \min_{u_1^n,\theta_1^n}\left\{\left(c(T_1^n)\left(1-\frac{T^{\mathrm{e}}}{T_1^n-(-u_1^n)^{1/a}+(g_1^n/g_2^n)u_1^n}\right)u_1^n+h_1\right)\times\theta_1^n+R_*^{n-1}\left(T_1^n-u_1^n\theta_1^n\right)\right\}. \tag{29}$$

With h_1 used as the Lagrange multiplier of the time constraint, equations of this sort do not contain the time τ_1^n as the state variable. The end coordinates, T^0 and T^N, may be fixed, but the total duration, τ_1^N, must be free. In an optimal process this duration follows for an assumed h_1 as a function of fixed end values and total number of stages, N. A generalization of this equation which contains the polymer concentration serves to generate numerical solutions for operations in which the mass transfer is essential.

To apply the discrete maximum principle, we should first of all note that the process model is linear with respect to the unconstrained variable θ^n. In this case, a discrete algorithm with a constant Hamiltonian constitutes the suitable optimization scheme. Discrete optimization theory is then similar to the Pontryagin's continuous theory, as shown on examples of multistage separations and chemical reactors [24–30]. In [23] we have initiated application of this discrete theory to multistage energy systems with Newtonian heat exchange. For the general non-Newtonian model, Eqs. (22), (23a) and (23b), the constancy of the discrete Hamiltonian (the consequence of the optimality of θ^n) is expressed by the equality

$$H^{n-1} \equiv p_1^{n-1}u_1^n - \left(c(T_1^n)\left(1-\frac{T^{\mathrm{e}}}{T_1^n-(-u_1^n)^{1/a}+(g_1^n/g_2^n)u_1^n}\right)u_1^n\right) = h_1, \tag{30}$$

where, by definition, $p_1^n \equiv \partial R^n/\partial T_1^n$, and $h_1 = 0$ refers to the quasistatic process. We search for the maximum of the above Hamiltonian with respect to the controls u_1^n. For a stationary optimal control u_1^n, the Hamiltonian H^{n-1} satisfies the stationarity condition $\partial H^{n-1}/\partial u_1^n = 0$ which yields

$$p_1^{n-1} = c(T_1^n)\left(1-\frac{T^{\mathrm{e}}\left(T_1^n+(a^{-1}-1)(-u_1^n)^{1/a}\right)}{\left(T_1^n-(-u_1^n)^{1/a}+(g_1^n/g_2^n)u_1^n\right)^2}\right). \tag{31}$$

As $(1+g_1^n/g_2^n)u_1^n$ equals u^n, the negative of the heat flux q_1 per unit of the *overall* conductance g, we obtain for the Newtonian heat transfer $(a = 1)$

$$p_1^{n-1} = c(T_1^n)\left(1-\frac{T^{\mathrm{e}}T_1^n}{\left(T_1^n+(1+g_1^n/g_2^n)u_1^n\right)^2}\right) = c\left(1-\frac{T^{\mathrm{e}}T_1^n}{(T_1^n+u^n)^2}\right) = p^{n-1}. \tag{31'}$$

After eliminating p_1^n from Eqs. (30) and (31) an integral of the discrete motion follows

$$c(T_1^n)T^{\mathrm{e}}\frac{(g_1^n/g_2^n)(u_1^n)^2+a^{-1}(-u_1^n)^{(1+1/a)}}{\left(T_1^n-(-u_1^n)^{1/a}+(g_1^n/g_2^n)u_1^n\right)^2} = h_1. \tag{32}$$

When the conductances and specific heat are constant and $a = 1$, Eq. (32) goes over into the recent Newtonian result [31,32]

$$\frac{h_1g_1}{cT^{\mathrm{e}}g} = \frac{g_1^n(g_1^n/g_2^n+1)(u_1^n)^2}{g^n\left(T_1^n+(g_1^n/g_2^n+1)u_1^n\right)^2} = \frac{(u^n)^2}{(T_1^n+u^n)^2} = \frac{h}{cT^{\mathrm{e}}} \tag{32'}$$

which is consistent with the equalities $hg = h_1g_1$ and $\mathrm{d}R = -h\,\mathrm{d}\tau = -h_1\,\mathrm{d}\tau_1$. Accordingly, one obtains two modes of control corresponding to increasing and decreasing temperatures T^n in time, τ_1^n or τ^n. Neither Newtonian nor non-Newtonian optimal control is invariant with respect to the control's sign change. Only in the Newtonian case, the solution of Eq. (32′) with respect to u^n, is analytical. It corresponds with Eqs. (27) and (28), and has the form

$$\frac{u^n}{u^n+T_1^n} = \pm\sqrt{\frac{h}{cT^{\mathrm{e}}}}, \tag{33}$$

where the positive sign refers to the fluid's heating and the negative one to the fluid's cooling. Using the state equation (23a) we find (in terms of the time τ^n rather than τ_1^n) an equation for the optimal evolution of the process state

$$\frac{T_1^n-T_1^{n-1}}{\theta^n} = \xi T_1^n, \tag{34}$$

where $\theta^n = \Delta\tau^n, u^n = 1+(g_1^n/g_2^n)u_1^n$, and an intensity constant ξ was defined in terms of the constant h as

$$\xi = \pm\sqrt{\frac{h}{cT^{\mathrm{e}}}}\left(1-\pm\sqrt{\frac{h}{cT^{\mathrm{e}}}}\right)^{-1}. \tag{35}$$

Eq. (34) proves that the discrete rate in an extremal Newtonian process changes proportionally to the temperature, the result analogous to that obtained for an optimal intensity of temperature change in continuous systems [32–37]. For an extremal non-Newtonian process simple optimal formula (34) does not hold, thus a numerical procedure should be designed. First Eq. (32) is solved numerically for the optimal control data in the form $u_1^n(T_1^n, T^{\mathrm{e}}, g_1^n, g_2^n, a, h_1)$. Next a difference equation, or a non-Newtonian generalization of Eq. (34)

$$\frac{T_1^n - T_1^{n-1}}{\theta_1^n} = u_1^n(T_1^n, T^{\mathrm{e}}, g_1^n, g_2^n, a, h_1) \tag{36}$$

should be solved simultaneously with the second canonical equation

$$\begin{aligned}\frac{p_1^n - p_1^{n-1}}{\theta_1^n} &= -\frac{\partial H^{n-1}}{\partial T_1^n}\\ &= \frac{\partial c(T_1^n)}{\partial T_1^n}\left(1 - \frac{T^{\mathrm{e}}}{T_1^n - (-u_1^n)^{1/a} + (g_1^n/g_2^n)u_1^n}\right)u_1^n\\ &\quad + \frac{c(T_1^n)T^{\mathrm{e}}u_1^n}{\left(T_1^n - (-u_1^n)^{1/a} + (g_1^n/g_2^n)u_1^n\right)^2}\end{aligned} \tag{37}$$

which describes the stationary extremum of a stage criterion with respect to T^n. [The Newtonian limit of the derivative is $(cT^{\mathrm{e}}u^n(T^n + u^n)^{-2}$.] The procedure leads to the interstage temperatures T^n between the stages n and $n+1$. In the Newtonian case the temperatures T^n are the geometric means of the temperatures $T^{n-1}$and T^{n+1} for any two-stage subprocess. Use of the boundary conditions for T^0 and T^N yields all interstage temperatures in terms of the boundary temperatures. For the Newtonian heat exchange we find $T^n = (T^N)^{n/N} (T^0)^{n(N-1)/N-(n-1)}$ or more specifically

$$\begin{aligned}&T^1 = (T^N)^{1/N}(T^0)^{(N-1)/N},\\ &T^2 = (T^N)^{2/N}(T^0)^{2(N-1)/N-1}, \ldots\\ &T^{N-1} = (T^N)^{(N-1)/N}(T^0)^{1/N}.\end{aligned} \tag{38}$$

Along with the condition of the constant H^n, this result yields $\theta^n = \theta^{n+1} \equiv \theta = \tau^N/N$. The driving temperatures which assure the accomplishment of that optimal trajectory are

$$\begin{aligned}T'^n = T^n(1+\xi) &= (T^N)^{n/N}(T^0)^{n(N-1)/N-(n-1)}\\ &\times\left(1 + \frac{N}{\tau^N - \tau^0}\left[1 - \left(\frac{T^0}{T^N}\right)^{1/N}\right]\right).\end{aligned} \tag{39}$$

For the non-Newtonian heat exchange the solutions of this sort can only be numerical. Two important conclusions are valid: (i) in terms of T' the optimal control solutions for the traditional and work-assisted discrete processes are identical, and, (ii) since the intervals of the number of transfer units, θ^n, are measures of exchange areas at the stages, the model incorporates the constraint on the total area of heat transfer.

Eqs. (34) and (36) describe the discrete rate of state changes in an extremal process. In the simplest (Newtonian case) this rate changes proportionally to the fluid's temperature T^n. Also the driving temperature, T'^n, changes in this case proportionally to T^n, the result analogous to Eq. (38) of a continuous optimal process. In fact, Eq. (36) and associated numerical optimal solutions are non-Newtonian generalizations of the optimality conditions (28) and (39). The continuous result (28) was recently obtained for heat exchangers, simulated annealing and infinitesimal NCA sequences [32–37].

For standard boundary conditions, the optimal work obtained through numerical optimization is a discrete generalization of the continuous finite-time exergy [38,39]. [2] The heat-pump mode exergy, $A = (-W)_{\min}$, refers to the N-stage process which starts with T^{e} and terminates at T; its optimal path (Eq. (38) or its non-Newtonian generalizations) is consistent only approximately with the equipartition principle for the entropy production [40]. This exergy defines the lower bound on the work consumption. For short durations, the bound is significantly higher than the minimal work of classical thermodynamics. Otherwise, the engine mode exergy, $A = (W)_{\max}$, can be significantly lower than the classical maximal work. This explains restrictive applicability of classical thermodynamic bounds [41] when they are applied to real processes, and shows that these bounds should be replaced by stronger bounds obtained from non-equilibrium thermodynamics [42].

In terms of the driving temperature T' optimal performance criteria have simple universal forms even for the general (non-Newtonian) heat exchange. For example, the minimum work in continuous heat-pump modes is described by the optimal performance function

$$\begin{aligned}R(T^{\mathrm{i}}, T^{\mathrm{f}}, \tau^{\mathrm{f}} - \tau^{\mathrm{i}}) &\equiv \min(-\mathrm{P}/G)\\ &= \min\int_{\tau^{\mathrm{i}}}^{\tau^{\mathrm{f}}} c_1(T_1)\left(1 - \frac{T^{\mathrm{e}}}{T'}\right)\dot{T}_1\,\mathrm{d}\tau_1\\ &= H(T^{\mathrm{f}}) - H(T^{\mathrm{i}}) - T^{\mathrm{e}}(S(T^{\mathrm{f}}) - S(T^{\mathrm{i}}))\\ &\quad + T^{\mathrm{e}}_{\min}\int_{T^{\mathrm{i}}}^{T^{\mathrm{f}}} c_1(T_1)\left(\frac{1}{T_1} - \frac{1}{T'}\right)\dot{T}_1\,\mathrm{d}\tau_1,\end{aligned} \tag{40a}$$

where the state variable T_1 and the driving temperature T' are connected by the kinetic differential constraint

$$T' \equiv T_1 - (-\dot{T}_1)^{1/a} + (g_1/g_2)\dot{T}_1. \tag{26}$$

When $T' = T_2 \equiv T^{\mathrm{e}}$ in the case without any work production, this constraint represents the overall classical kinetics under the overall driving force $T_1 - T^{\mathrm{e}}$. Eq. (40a) is an optimal expression associated with the general Eqs. (25) and (25′). The complexity appears neither in the work criteria nor in the entropy production but in the kinetic constraint.

Likewise, the maximum work in the engine mode is described by the optimal function

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[2] See [21,22,32,38,39] for the finite-time exergy of continuous processes, a detailed derivation of Eq. (28) in [32] and a thermodynamic argument for the uniformity of driving forces $T' - T$ [40].

$$\begin{aligned} V(T^{\mathrm{i}}, T^{\mathrm{f}}, \tau^{\mathrm{f}} - \tau^{\mathrm{i}}) &= \max(\mathrm{P}/G) \\ &= \max \int_{\tau^{\mathrm{i}}}^{\tau^{\mathrm{f}}} -c_1(T_1)\left(1 - \frac{T^{\mathrm{e}}}{T'}\right)\dot{T}_1 \, \mathrm{d}\tau_1 \\ &= H(T^{\mathrm{i}}) - H(T^{\mathrm{f}}) - T^{\mathrm{e}}\big(S(T^{\mathrm{i}}) - S(T^{\mathrm{f}})\big) \\ &\quad - T^{\mathrm{e}}_{\min} \int_{T^{\mathrm{i}}}^{T^{\mathrm{f}}} c_1(T_1)\left(\frac{1}{T_1} - \frac{1}{T'}\right)\dot{T}_1 \, \mathrm{d}\tau_1, \end{aligned} \tag{40b}$$

where, again, T_1 and T' are linked by differential constraint (26). Simple common expressions, contained in Eqs. (40a) and (40b), describe the associated minimum of entropy. A single common function R (or V) is capable of describing the optimal work in both modes. R can be interpretted as a thermodynamic cost that is positive for the heat-pump mode and negative for the engine mode; thus $V = -R$ is the profit-type function. For cascades of heat pumps and engines an analogous picture exists with sums replacing integrals and with differential ratios instead of derivatives.

The structure of the control equations shows that the driving temperature T' can be interpretted as the quantity replacing the upper temperature $T_{1'}$ of the thermal machine in the general case when both conductances g_1 and g_2 are essential. Whenever the effect of the second resistance (g_2^{-1}) is negligible, $T' = T_{1'}$. Indeed, when g_2^{-1} tends to zero, $T_{2'} = T_2 \equiv T^{\mathrm{e}}$, thus, from Eq. (14′), $T' = T_{1'}$. In this case the control equations are valid for the temperature $T_{1'}$. However, the crucial statement which explains how to obtain T' follows from the equality $T' = T_2$ at the state in which work is not produced (the so-called "short-circuit point" of the system, where $\eta = 0$). This leads to the theorem: *the analytical expression for the driving temperature T' can be obtained from the analysis of the short-circuit point by solving the energy (mass) exchange equations in which T' replaces T_2* or T^{e}. *The solution to these equations should be found for the temperatures $T_{1'}$ and $T_{2'}$ in terms of the common heat flux q_1*; *after making the identification $T_{1'} = T_{2'}$ the temperature T' follows in the form $T' = f(T_1, q_1, g_1, g_2)$*. The reader can verify that when this theorem is applied to our thermal problem, the temperatures $T_{1'}$ and $T_{2'}$ are: $T_{1'} = T_1 - (q_1/g_1)^{1/a}$ and $T_{2'} = T' + q_1/g_2$. Their equating yields $T' = T_1 - (q_1/g_1)^{1/a} - q_1/g_2$, which is the result equivalent with Eq. (26).

The above theorem is the basis for thermodynamic analyses of heat pumps and engines in continuous processes and cascade systems with finite number of stages. With the idea of the driving state, the analytical expression for the entropy production is precisely that of purely dissipative processes (i.e., those without work production or consumption). With the chemical potentials included, the theorem also holds for more difficult processes in which the polymeric fluid changes its concentration due to the coupled heat and mass transfer.

6. Coupled transfer and analogy between work-assisted and traditional operations

To generalize the idea of the driving state in thermal machines with coupled heat and mass transfer we need to apply the idea of the driving chemical potential. For simplicity, we shall neglect from now the subscript 1 of the controlled phase (the polymeric fluid). With the help of the results of our recent analysis [31], we find a generalized relation which links work and entropy production

$$\begin{aligned} W \equiv P/G &= -\int_{T^{\mathrm{i}}}^{T^{\mathrm{f}}} \left\{\left(1 - \frac{T^{\mathrm{e}}}{T'}\right)\mathrm{d}\mathscr{H} + T^{\mathrm{e}}\left(\frac{\mu'}{T'} - \frac{\mu^{\mathrm{e}}}{T^{\mathrm{e}}}\right)\mathrm{d}\mathscr{X}\right\} \\ &= -\int_{T^{\mathrm{i}}}^{T^{\mathrm{f}}} \left\{\left(1 - \frac{T^{\mathrm{e}}}{T}\right)\mathrm{d}\mathscr{H} + T^{\mathrm{e}}\left(\frac{\mu}{T} - \frac{\mu^{\mathrm{e}}}{T^{\mathrm{e}}}\right)\mathrm{d}\mathscr{X}\right\} \\ &\quad - T^{\mathrm{e}} \int_{T^{\mathrm{i}}}^{T^{\mathrm{f}}} \left\{\left(\frac{1}{T} - \frac{1}{T'}\right)\mathrm{d}\mathscr{H} + \left(\frac{\mu'}{T'} - \frac{\mu}{T}\right)\mathrm{d}\mathscr{X}\right\}, \end{aligned} \tag{41}$$

where $\mathscr{H}$ is the enthalpy of a polymeric solution per unit mass of the solvent and $\mathscr{X}$ is the polymer's concentration. As before, the Gouy–Stodola law links the real work W (the first integral) with the reversible work W^{rev} (the second integral) and the negative product of T^{e} and the entropy production (the third integral). The driving chemical potential, μ', appears here as an extra operational variable.

Eq. (41) incorporates the result of invariancy of the entropy production in a work-assisted operation with respect to the transformation of variables. This equation exploits the fact that an original expression for the entropy production is in terms of the upper and lower thermal potentials of the fluid circulating in the thermal machine ($T_{1'}, T_{2'}, \mu_{1'}$ and $\mu_{2'}$). From this original expression the appropriate result for T' is the same as for the processes with pure heat transfer, and it can be written in the form

$$T' \equiv T^{\mathrm{e}} \frac{T_{1'}}{T_{2'}} \tag{42}$$

[23]. Note that the theorem of Section 5 which applies the equality $T' = T^{\mathrm{e}}$ or $T' = T_2$ at the short-circuit point where $T_{1'} = T_{2'}$ is consistent with this equation. Likewise, in terms of the upper and lower thermal potentials of the circulating fluid ($T_{1'}, T_{2'}, \mu_{1'}$ and $\mu_{2'}$), the driving chemical potential μ' follows as:

$$\mu' \equiv T'(\mu^{\mathrm{e}}/T^{\mathrm{e}} + T_{2'}/T^{\mathrm{e}}(\mu_{1'}/T_{1'} - \mu_{2'}/T_{2'})). \tag{43}$$

Again, at the short-circuit point, where $\mu_{1'} = \mu_{2'}$, the equality $\mu' = \mu^{\mathrm{e}}$ holds which proves that the generalized theorem (including mass transfer) is valid. Again, the most essential result obtained here is the conclusion that in terms of the driving temperature T' and driving chemical potential μ' the entropy production in a work-assisted process acquires the form of the entropy production for a traditional process without any work production. Accordingly, we shall implement below entropy production formulae which are known for traditional processes of non-isothermal mass transfer into the work formulae describing processes with thermal machines.

Now an extension of Eqs. (40a) and (40b) will be derived for simultaneous heat and mass transfer. The controlled phase is described in terms of the solution's enthalpy $\mathscr{H}$ and polymer's concentration $\mathscr{X}$.; they both are referred to the unit mass of the solvent. The space $(\mathscr{H},\mathscr{X})$ is the state space of the process. Note that the accepted pair of the state variables is suitable for dilute solutions as then $G \cong$ constant. As the possible candidates, we consider two models of control. The first is that of a conventional crosscurrent process in which an external immiscible phase with the controlling parameters (I' and $\mathscr{Y}'$) and the flow G' exchanges the energy and mass with the controlled solution of a polymer. The second control model applies the Onsagerian scheme of coupled heat and mass transfer. In the first model, our choice of the state and control variables is caused by the fact that the most appropriate form of energy balance for a fluid at flow is in terms of the enthalpy. Using the Lewis analogy linking the coefficients of energy and mass flows we can write down a linear exchange equation and the corresponding non-linear expression (following the arrow)

$$\dot{\mathscr{H}} = I' - I'_{\mathrm{s}}(\mathscr{H},\mathscr{X}) \to \dot{\mathscr{H}}(\mathscr{H},\mathscr{X},I',\mathscr{Y}'), \tag{44}$$

where the time derivatives involve the time defined such that $\mathrm{d}\tau_1 \equiv \mathrm{d}G'/G$ and the controlling enthalpy I' is that of the external or driving phase. The s-subscripted quantities refer to equilibrium of the external phase with the solution. The above energy equation should be supplemented by an equation for the exchanged mass, which is

$$\dot{\mathscr{X}} = \dot{\mathscr{Y}} - \mathscr{Y}'_{\mathrm{s}}(\mathscr{H},\mathscr{X}) \to \dot{\mathscr{X}}(\mathscr{H},\mathscr{X},I',\mathscr{Y}'). \tag{45}$$

Again, the controlling concentration $\mathscr{Y}'$ is that of the external driving phase. See Eqs. (48)–(54) below for Onsagerian scheme of control. For each control scheme we shall derive a suitable formula for the entropy production in conventional operations which will model the entropy production in operations with thermal machines.

The specific entropy produced per unit mass of the polymeric solution is the path integral over the scalar product of the differential enthalpy–mass vector $(\mathrm{d}\mathscr{H},\mathrm{d}\mathscr{X})$ and the driving force vector $(1/T - 1/T'$, $\mu/T - \mu'/T')$. With the energy and mass balances, Eqs. (44) and (45), the discussed integral can be written as follows:

$$\begin{aligned} S_\sigma &= \int_{T^{\mathrm{i}}}^{T^{\mathrm{f}}} \left(\frac{1}{T} - \frac{1}{T'}\right)\mathrm{d}\mathscr{H} - \left(\frac{\mu}{T} - \frac{\mu'}{T'}\right)\mathrm{d}\mathscr{X} \\ &= \int_{T^{\mathrm{i}}}^{T^{\mathrm{f}}} \left\{\left(\frac{1}{T} - \frac{1}{T'}\right)\dot{\mathscr{H}}(\mathscr{H},\mathscr{X},I',\mathscr{Y}) \right. \\ &\qquad \left. + \left(\frac{\mu'}{T'} - \frac{\mu}{T}\right)\dot{\mathscr{X}}(\mathscr{H},\mathscr{X},I',\mathscr{Y})\right\}\mathrm{d}\tau. \end{aligned} \tag{46}$$

The temperatures and chemical potentials are here functions of respective enthalpies and concentrations, however, for brevity, this fact is not explicit in Eq. (46). This equation can incorporate arbitrarily complex nonlinear relationships of thermodynamic and kinetic origin. By using Eq. (46) in work formula (41), changes of work potentials and finite time exergies can be evaluated through optimization of the following work criterion

$$\begin{aligned} W \equiv P/G &= -\int_{T^{\mathrm{i}}}^{T^{\mathrm{e}}} \left\{\left(1 - \frac{T^{\mathrm{e}}}{T'}\right)\mathrm{d}\mathscr{H} + T^{\mathrm{e}}\left(\frac{\mu'}{T'} - \frac{\mu^{\mathrm{e}}}{T^{\mathrm{e}}}\right)\mathrm{d}\mathscr{X}\right\} \\ &= \mathscr{H}^{\mathrm{i}} - \mathscr{H}^{\mathrm{f}} - T^{\mathrm{e}}(\mathscr{S}^{\mathrm{i}} - \mathscr{S}^{\mathrm{f}}) - \mu^{\mathrm{e}}(\mathscr{X}^{\mathrm{i}} - \mathscr{X}^{\mathrm{f}}) \\ &\quad - T^{\mathrm{e}} \int_{T^{\mathrm{i}}}^{T^{\mathrm{f}}} \left\{\left(\frac{1}{T} - \frac{1}{T'}\right)\dot{\mathscr{H}}(\mathscr{H},\mathscr{X},I',\mathscr{Y}) \right. \\ &\qquad \left. + \left(\frac{\mu'}{T'} - \frac{\mu}{T}\right)\dot{\mathscr{X}}(\mathscr{H},\mathscr{X},I',\mathscr{Y})\right\}\mathrm{d}\tau, \end{aligned} \tag{47}$$

where the kinetic constraints (which link the state coordinates of the fluid with those of the controlling phase) are implicit.

To formulate and handle these constraints we use the theorem of Section 5 in its generalized form, which tells us that in the special case without any work production (i.e., at the short-circuit point) expressions for the driving thermal parameters $(T', \mu', \mathscr{H}', \mathscr{X}'$, etc.) in terms of the state variables $(T, \mu, \mathscr{H}, \mathscr{X}$, etc.) and their time derivatives $(\dot{T}, \dot{\mu}, \dot{\mathscr{H}}, \dot{\mathscr{X}}$, etc.) describe the environment (or reservoir) parameters. Thus by exploiting a given *classical* kinetics (the one which governs the process without work production) we are able to determine intensive parameters of driving states. We thus obtain constraints which describe an overall classical kinetics under the overall driving force. In the first model these constraints are represented by Eqs. (44) and (45), in the second – by Eqs. (54) and (55).

Consider now the second model. It is based on coupled linear kinetics which satisfy Onsager's reciprocity relations. For the resource fluid as the phase 1 the following kinetics is valid

$$\begin{aligned} \frac{1}{T_1} - \frac{1}{T'_1} &= r_1^{\mathscr{H}\mathscr{H}}\,\dot{\mathscr{H}}_1 + r_1^{\mathscr{H}\mathfrak{x}}\,\dot{\mathscr{X}}_1, \quad \frac{\mu_{1'}}{T_{1'}} - \frac{\mu_1}{T_1} \\ &= r_1^{\mathscr{X}\mathscr{H}}\,\dot{\mathscr{H}}_1 + r_1^{\mathscr{X}\mathscr{X}}\,\dot{\mathscr{X}}_1 \end{aligned} \tag{48}$$

whereas for the thermal reservoir as the phase 2 or the environment

$$\frac{1}{T_{2'}}-\frac{1}{T_2}=r_2^{\mathscr{H}\mathscr{H}}\dot{\mathscr{H}}_2+r_2^{\mathscr{H}\mathscr{X}}\dot{\mathscr{X}}_2,\quad \frac{\mu_2}{T_2}-\frac{\mu_{2'}}{T_{2'}}=r_2^{\mathscr{X}\mathscr{X}}\dot{\mathscr{H}}_2+r_2^{\mathscr{X}\mathscr{X}}\dot{\mathscr{X}}_2. \tag{49}$$

These kinetic equations hold at the purely dissipative state (short circuit point) of the system where there is no work production ($T_{1'}=T_{2'}$ and $\mu_{1'}=\mu_{2'}$), the energy and mass fluxes are continuous through the interface (i.e., $\dot{\mathscr{H}}_1=\dot{\mathscr{H}}_2=\dot{\mathscr{H}}$ and $\dot{\mathscr{X}}_1=\dot{\mathscr{X}}_2=\dot{\mathscr{X}}$), and the identities $T_2=T'$ and $\mu_2=\mu'$ hold. Applying these identities in Eqs. (48) and (49) we find

$$\frac{1}{T_{1'}}=\frac{1}{T}-r_1^{\mathscr{H}\mathscr{H}}\dot{\mathscr{H}}-r_1^{\mathscr{H}\mathscr{X}}\dot{\mathscr{X}},\quad \frac{\mu_1'}{T_1'}=\frac{\mu}{T}+r_1^{\mathscr{X}\mathscr{H}}\dot{\mathscr{H}}+r_1^{\mathscr{X}\mathscr{X}}\dot{\mathscr{X}}, \tag{50}$$

and

$$\frac{1}{T_{2'}}=\frac{1}{T'}+r_2^{\mathscr{H}\mathscr{H}}\dot{\mathscr{H}}_2+r_2^{\mathscr{H}\mathscr{X}}\dot{\mathscr{X}}_2,\quad \frac{\mu_{2'}}{T_{2'}}=\frac{\mu'}{T'}-r_2^{\mathscr{X}\mathscr{H}}\dot{\mathscr{H}}_2-r_2^{\mathscr{X}\mathscr{X}}\dot{\mathscr{X}}_2. \tag{51}$$

(As in Eqs. (41), (46) and (47), the subscript 1 of the resource fluid was omitted.) After taking $T_{1'}=T_{2'}$ and $\mu_{1'}=\mu_{2'}$ we obtain the driving intensities T' and μ' in the form

$$\frac{1}{T'}=\frac{1}{T}-\left(r_1^{\mathscr{H}\mathscr{H}}+r_2^{\mathscr{H}\mathscr{H}}\right)\dot{\mathscr{H}}-\left(r_1^{\mathscr{H}\mathscr{X}}+r_2^{\mathscr{H}\mathscr{X}}\right)\dot{\mathscr{X}} \tag{52}$$

and

$$\frac{\mu'}{T'}=\frac{\mu}{T}+\left(r_1^{\mathscr{X}\mathscr{H}}+r_2^{\mathscr{X}\mathscr{X}}\right)\dot{\mathscr{H}}+\left(r_1^{\mathscr{X}\mathscr{X}}+r_2^{\mathscr{X}\mathscr{X}}\right)\dot{\mathscr{X}}. \tag{53}$$

Therefore the overall kinetics in terms of the driving and controlled intensities, i.e., in the form which applies in Eq. (41), is represented by the equations

$$\frac{1}{T}-\frac{1}{T'}=r^{\mathscr{H}\mathscr{H}}\dot{\mathscr{H}}+r^{\mathscr{H}\mathscr{X}}\dot{\mathscr{X}}, \tag{54}$$

$$\frac{\mu'}{T'}-\frac{\mu}{T}=r^{\mathscr{X}\mathscr{H}}\dot{\mathscr{H}}+r^{\mathscr{X}\mathscr{X}}\dot{\mathscr{X}}. \tag{55}$$

With the Onsager's reciprocity relations the entropy production assumes the classical form

$$S_\sigma=\int_{T^{\mathrm{i}}}^{T^{\mathrm{f}}}\left(\frac{1}{T}-\frac{1}{T'}\right)\mathrm{d}\mathscr{H}+\left(\frac{\mu'}{T'}-\frac{\mu}{T}\right)\mathrm{d}\mathscr{X}=\int_{T^{\mathrm{i}}}^{T^{\mathrm{f}}}\left\{\left(r^{\mathrm{HH}}\dot{\mathscr{H}}^2+2r^{\mathrm{HX}}\dot{\mathscr{X}}\dot{\mathscr{H}}+r^{\mathrm{XX}}\dot{\mathscr{X}}^2\right)\right\}\mathrm{d}\tau_1. \tag{56}$$

This proves that the second law of thermodynamics is satisfied identically by the (second) model based on the Onsager's theory.

Consider yet the first model in the linear case, i.e., when its thermodynamic flows are proportional to differences of enthalpies and concentrations. The entropy production (46) is then

$$S_\sigma=\int_{T^{\mathrm{i}}}^{T^{\mathrm{f}}}\left(\frac{1}{T}-\frac{1}{T'}\right)\mathrm{d}\mathscr{H}-\left(\frac{\mu}{T}-\frac{\mu'}{T'}\right)\mathrm{d}\mathscr{X}=\int_{T^{\mathrm{i}}}^{T^{\mathrm{f}}}\left\{\left(\frac{1}{T}-\frac{1}{T'}\right)\left(I'-I'_{\mathrm{s}}(\mathscr{H},\mathscr{X})\right)+\left(\frac{\mu'}{T'}-\frac{\mu}{T}\right)\times\left(\mathscr{Y}'-\mathscr{Y}'_S(\mathscr{H},\mathscr{X})\right)\right\}\mathrm{d}\tau. \tag{46$'$}$$

Now it seems that the satisfaction of the second law is not assured. Nonetheless our numerical tests showed that models of this sort can also preserve the second law in a broad range of states. To substantiate the results of these tests, we introduce the Hessian of the entropy of driving phase, $\partial^2\mathscr{S}'/\partial I'\partial\mathscr{X}'$, which is the matrix of the second order derivatives of $\mathscr{S}'$ with respect to I' and $\mathscr{Y}'$. The entropy production can then be written in the form of a positive integral

$$S_\sigma=\int_{T^{\mathrm{i}}}^{T^{\mathrm{f}}}\left\{\begin{bmatrix}\left(\frac{1}{T}-\frac{1}{T'}\right)\\ \left(\frac{\mu'}{T'}-\frac{\mu}{T}\right)\end{bmatrix}\begin{pmatrix}c^{II} & c^{I\mathscr{Y}}\\ c^{\mathscr{Y}I} & c^{\mathscr{Y}\mathscr{Y}}\end{pmatrix}\left[\left(\frac{1}{T}-\frac{1}{T'}\right)\times\left(\frac{\mu'}{T'}-\frac{\mu}{T}\right)\right]\right\}\mathrm{d}\tau, \tag{57}$$

where the positive matrix of capacities $c_{I'\mathscr{Y}'}=-(\partial^2\mathscr{S}'/\partial I'\partial\mathscr{Y})^{-1}$ is the reciprocal of the negative entropy Hessian. These equations correspond to the entropy differential in the form $\mathrm{d}(-\mathscr{S}')=-T^{-1}\,\mathrm{d}I'+(\mu T^{-1})\,\mathrm{d}\mathscr{Y}'$; they apply the entropy production and the second law in their forms known from the thermodynamic theory of stability. The entropy production in the corresponding multistage process is

$$S_\sigma^N=\sum_1^N\left\{\begin{bmatrix}\left(\frac{1}{T^n}-\frac{1}{T'^n}\right)\\ \left(\frac{\mu'^n}{T'^n}-\frac{\mu^n}{T^n}\right)\end{bmatrix}\begin{pmatrix}c^{II} & c^{I\mathscr{Y}}\\ c^{\mathscr{Y}I} & c^{\mathscr{Y}\mathscr{Y}}\end{pmatrix}\left[\left(\frac{1}{T^n}-\frac{1}{T'^n}\right)\times\left(\frac{\mu'^n}{T'^n}-\frac{\mu^n}{T^n}\right)\right]\right\}\theta^n. \tag{57$'$}$$

Optimization of typical criteria of entropy production, made under assumption of the constancy of coefficients, leads quite generally to the conclusion about the constancy of the entropy production intensity along an optimal path [33–37,40]. For quadratic approximations of these criteria, optimization implies the constancy of driving forces along an optimal path. These properties are sometimes imbeded in the so-called principle of equipartition of the entropy production or principle of equipartition of thermodynamic forces [40]. However, the 'principle' is valid only when there is no constraints imposed on parameters of the controlling phase. In the case of operative constraints, the principle is violated. Postquadratic terms in the optimization criterion and non-linearities in kinetic equations may also cause violation of the principle. For all these reasons exact work functionals, such as Eq. (41) or (47), should be preferred in optimization.

Using the idea of driving intensities, we achieved the coincidence of the entropy production expressions in conventional and work-assisted operations. Eqs. 46), (46′), (56), (57) and (57′ thus apply for thermal machines as representations of their lost work divided by T^e. This is important; up to now it was unknown whether an equation of the classical structure could serve as a sufficiently exact model for a work-assisted system. Discovery of the driving controls was the necessary fact to prove the equivalence of mathematical models for both sorts of operations.

7. Generalized exergies for dilute and dense solutions of polymers

When one of the end states is that of the equilibrium with the environment, extremizing of the total work over a finite period of time leads to finite-time exergies [21,22,31,32,38,39]. In finite time processes two distinct exergies exist: that of the engine mode and that of the heat-pump mode. Depending on the state coordinates used, dilute or dense polymeric solutions can be described. For dilute solutions we use the concentration $\mathscr{X}$ or the mass of the polymer per unit mass of the solvent and the related (solvent basis) enthalpy $\mathscr{H}$. For dense solutions the concentration $\mathscr{W}$ defined as the mass of solvent per unit mass of polymer is more suitable.

For a given state of a dilute polymeric fluid $(\mathscr{H},\mathscr{X})$ and the state of equilibrium of this fluid with the environment $(\mathscr{H}^e,\mathscr{X}^e)$, the finite-time exergy of the engine mode is the maximum work produced during the optimal passage from $(\mathscr{H},\mathscr{X})$ to $(\mathscr{H}^e,\mathscr{X}^e)$ and that of the heat-pump mode is the minimum work consumed during the optimal passage from $(\mathscr{H}^e,\mathscr{X}^e)$ to $(\mathscr{H},\mathscr{X})$. It follows from this definition that in the heat pump mode the classical exergy [11] is increased by the product of the environment temperature T^e and the *minimum* entropy production, $R_\sigma \equiv \min S_\sigma$. In the engine mode the classical exergy is decreased by the product of T^e and $R_\sigma \equiv \min S_\sigma$. For continuous changes of the fluid's state

$$A(T,\mathscr{X},T^e,\mathscr{X}^e,\tau^f-\tau^i) = A^{\mathrm{class}}(T,\mathscr{X},T^e,\mathscr{X}^e) \pm T^e R_\sigma(T,\mathscr{X},T^e,\mathscr{X}^e,\tau^f-\tau^i), \tag{58}$$

where A^{class} is the classical exergy of the fluid. The plus sign refers to processes departing from the equilibrium whereas the minus sign to those approaching the equilibrium. The classical reversible exergy

$$\mathscr{A}^{\mathrm{class}}(T,\mathscr{X},T^e,\mathscr{X}^e) = H_s - H_s^e - T^e(S_s - S_s^e) + (H_p - H_p^e - T^e(S_p - S_p^e))\mathscr{X}, \tag{59}$$

(see [11,41]) is consistent with the general Eq. (3). The subscript s designates the partial quantities of the solvent and the subscript p refers to the polymer.

Eqs. (58) and (59) are suitable for dilute polymeric solutions. For a multistage process, a discrete counterpart of Eq. (58) can be numerically generated with Eq. (57′); the computations should refer to a sufficiently large N if one wants to approximate the continuous exergy well enough. The minimum entropy production, $R_\sigma \equiv \min S_\sigma$, in the last term of Eq. (58) is a function of end thermodynamic states and non-dimensional duration (the number of mass transfer units). This last term is non-classical, duration dependent term which vanishes for infinite durations. It should be distinguished from the first or classical term that has properties independent of the direction of time. With the knowledge of the classical exergy, explicit in the above equation, the numerical procedure can generate data for both A and R_σ. From the finite-time exergy enhanced bounds follow on the work production and consumption [32,42].

Consider now exergies of dense polymeric solutions. Any classical exergy contains exclusively linear combination of differences of state functions which change only sign but not magnitude of work when end thermodynamic states are inverted. This fact facilitates the generation of work potentials for prescribed end states, from which reversible exergies are recovered. Under the assumption of constant heat capacities and with a formula for the solution exergy per unit mass of solid basis [43] we obtain the following finite-time work potential for a dense polymeric solution

$$\begin{aligned} R\left(T^i,\mathscr{W}^i,T^f,\mathscr{W}^f,T^e,\mathscr{W}^e,\tau^f-\tau^i\right) &= \left(c_s+\mathscr{W}^i c_1\right)\left[\left(T^i-T^e\right)-T^e\ln\frac{T^i}{T^e}\right] \\ &\quad -\left(c_s+\mathscr{W}^f c_1\right)\left[\left(T^f-T^e\right)-T^e\ln\frac{T^f}{T^e}\right] \\ &\quad +\frac{\mathsf{R}T^e}{M}\left\{\int_{\mathscr{W}^f}^{\mathscr{W}^i}\ln\frac{\beta(\mathscr{W},T^e)}{\beta^e(\mathscr{W}^e,T^e)}\,\mathrm{d}\mathscr{W} \right. \\ &\quad \left. +\,T^e R_\sigma\left(T^i,\mathscr{W}^i,T^f,\mathscr{W}^f,\tau^f-\tau^i\right)\right\}. \end{aligned} \tag{60}$$

It holds in the regime where the decrease of the pressure of the solvent's vapour is a measurable effect. In Eq. (60) $\mathscr{W}$ is the solvent's concentration defined as the mass of the solvent per unit mass of the polymer, and $\beta(\mathscr{W},T)$ is the relative pressure of the solvent (the ratio of the partial pressure of solvent's vapour over the solution to the pressure of the saturated vapour over the pure solvent). The superscript e refers to the equilibrium with the reference solution in the environment. The method exploits the empirical data of $\beta(\mathscr{W}, T)$ calculated from the knowledge of solvent's pressures over the polymeric solutions and the pressures of solvent's saturated vapour. This method follows that described earlier for moist solids when the moisture creates a solution with the solid [43].

Recalling that the interchange of end states is just the transformation of system's modes, a general inequality can be stated which describes cyclic processes with solvents removal and addition. If an original process is in engine mode then the inverse process is in heat pump mode. When the dissipative term is so small that it can be ignored, the equality $V^{\text{eng}} = R^{\text{pump}} = -V^{\text{pump}}$ holds, which describes the fact that the (reversible) work consumed in the heat pump mode is completely recovered in the engine mode. When the dissipation becomes essential, the inequality $R^{\text{pump}} \geqslant V^{\text{eng}} = -R^{\text{eng}}$ is valid. Thus for any changes of states which occur within the positive durations $\mathscr{D}_{AB}$ and $\mathscr{D}_{BA}$ in a cyclic operation with the solvent's removals and additions $A \to B \to A \to B \ldots$

$$R^{\text{pump}}(\mathbf{x}_A, \mathbf{x}_B, \mathbf{x}^{\text{e}}, \mathscr{D}_{AB}) + R^{\text{eng}}(\mathbf{x}_B, \mathbf{x}_A, \mathbf{x}^{\text{e}}, \mathscr{D}_{BA}) \geqslant 0. \qquad (61)$$

This inequality represents a special form of the second law of thermodynamics. For a polymer that dissolves in a solvent, Eq. (61) states that a cyclic operation composed of the separation and dissolving can only consume net work. However, the inequality sign changes whenever the states are chosen in the range in which the polymer stops to dissolve, i.e., when its precipitation from the solution is the spontaneous process. To preserve Eq. (61) the original states should be then inverted. In this case Eq. (61) will state that the magnitude of work delivered in an engine process of precipitation is less than that supplied in a heat-pump process of virtual dissolving.

8. Concluding remarks

We are now able to formulate a few basic conclusions. Separation and heat exchange operations with polymeric fluids can be conducted conventionally in mass and heat exchangers or in a work-assisted way with thermal machines. The analysis of the derived optimization models for traditional and work-assisted operations shows that a useful parallelism is operative for expressions which describe entropy sources, exergy costs and kinetic equations in both sorts of operations. This parallelism is particularly lucid in the realm of processes with pure heat transfer for which a special control variable T', called the driving temperature, is essential. The parallelism can be generalized to include processes with simultaneous heat and mass transfer if their models use the suitable controls: driving thermal potentials ($-1/T'$ and μ'/T'). Due to the parallelism, the mathematical identity does exist between expressions which link work and entropy production through the Gouy–Stodola law in traditional and work-assisted operations.

Consistently, in terms of the driving potentials ($-1/T'$ and μ'/T'), the optimal control is the same for both operations with thermal machines and for related traditional operations, those without work production or consumption. With the intensities ($-1/T'$ and μ'/T') in equations for power produced, the *thermal* efficiency is given by the Carnot formula, $\eta = 1 - T^{\text{e}}/T'$ even if there is a coupled heat and mass transfer in the machine. Yet, in the coupled transfer case, the power production or consumption is determined not only by η but also by the second component of the efficiency vector, $\beta = T^{\text{e}}(\mu'/T' - \mu^{\text{e}}/T^{\text{e}})$, Eq. (41). The benefit from the described parallelism is that expressions for exergy losses in traditional coupled processes (without work production) can model (more difficult) exergy losses in complex thermal machines with simultaneous heat and mass transfer. Both multistage processes (described by difference equations and optimization criteria in form of sums) and corresponding continuous processes (described by differential equations and optimization criteria in form of integrals) can be modeled. Cases of thermal systems where such modeling can be appropriate are considered in the review [44].

We have developed the thermodynamic theory of work limits for complex fluids in multistage systems with thermal machines which may be different at each stage of the sequence. We have shown how to apply non-Carnot efficiencies in suitable optimization criteria whose optimal values describe these work limits. We have applied the mentioned parallelism between the work-assisted and traditional operations to optimize the former and obtain the work limits for finite time sequences. We have also shown how to derive the functionals of work and entropy production and the work limits to operations in which heat transfer is coupled with transfer of mass. Our paper outlines also optimization techniques for sequential work-assisted heating and separation operations with complex fluids. We have obtained optimal functions which define bounds on work consumption or production in thermal machines. For short durations, the consumption (lower) bound is significantly higher than the minimal work of classical thermodynamics; the production (upper) bound can even vanish. Our equations for optimization potentials, e.g. Eqs. (58), (60) and (61), which apply to processes with simultaneous heat and mass transfer, explain restrictive applicability of classical thermodynamic bounds and imply that these bounds should be replaced by stronger bounds obtained from non-equilibrium thermodynamics.

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