Maximal work problem in finite-time thermodynamics

Anatoly M. Tsirlin*
Program Systems Institute, Russian Academy of Sciences, set.''Botic,'' Perejaslavl-Zalesky 152140, Russia

Vladimir Kazakov†
Key Centre of Design Computing, The University of Sydney, New South Wales 2006, Australia
(Received 7 February 2000)

In this paper three problems are considered: (a) the maximal work that can be produced in a finite time in a thermodynamic system; (b) the minimal work which must be done in order to transform an equilibrium thermodynamic system into a number of subsystems that are out of equilibrium with each other in finite time; and (c) the maximal power that can be achieved in a finite time. The mathematical features of these problems are investigated. It is shown that in many cases the limiting work processes here are processes where intensive variables are piecewise-constant functions of time, and that these functions take not more than some predefined number of values. It is demonstrated that many results obtained for a number of particular systems (heat engines, heat transfer) follow from the general conditions for limiting processes derived in this paper. Conditions for limiting work regimes in mass transfer processes are obtained.

PACS number(s): 05.70.−a, 44.90.+c, 82.60.−s

I. INTRODUCTION

The maximal work problem is one of the major problems in reversible thermodynamics. It has the following form [1].

> Given a thermodynamic system that consists of a number of subsystems with different initial values of their intensive variables (temperatures, pressures, chemical potentials etc.) and which are insulated from each other, what is the maximal work, A_d^0, that can be produced if contacts between these subsystems were allowed? During this process the subsystems' intensive variables approach each other.

Classic thermodynamics states that in order to obtain the maximal work all the exchange processes in the system must be reversible when the differences between the values of intensive variables of the subsystems are infinitely small. In order to obtain finite work here, the duration of such processes must tend to infinity.

The inverse problem seeks the minimal work A_{i}^0 required to separate an equilibrium system into a number of subsystems with given values of intensive variables. We shall call this problem the ''minimal work problem.'' It is clear that in the case of reversible processes, when there are no irreversible equilibrium processes (mixing) in the direct problem, the minimal work required is exactly the same work as the maximal work that can be obtained in the direct problem, i.e., $A_{\mathrm{i}}^0 = A_d^0$. In a more general case $A_{\mathrm{i}}^0 = A_d^0 + A_m^0$, where A_m^0 denotes the work in irreversible equilibrium processes.

In finite-time thermodynamics the maximal work problem has the same form as above, but includes an additional constraint on the process duration τ [2]. It is assumed that each subsystem is in internal equilibrium, and the only source of irreversibility are processes that occur on the boundaries between the subsystems, which are in contact. The solution of the maximal work problem in finite-time thermodynamics gives an estimate $A_d^*(\tau)$ that is significantly more realistic than the one given by reversible thermodynamics. Unlike A_d^0, it takes into account kinetic factors (mass and heat transfer laws, kinetics of chemical transformations, etc.). Here the problem of maximal power can also be stated:

$$\overline{n} = \frac{A_d^*(\tau)}{\tau} \to \max_{\tau}.$$

The question here is how to choose τ^* such that the average power is maximal. For reversible processes the value of $\overline{n}$ is infinitely close to zero. The minimal work problem for finite τ is generalized in a similar fashion.

The following inequality holds:

$$A_i^*(\tau) \geqslant A_{\mathrm{i}}^0 = A_d^0 + A_m \geqslant A_d^*(\tau). \tag{1}$$

The characteristic dependencies of the maximal work produced $A_d^*(\tau)$ and the minimal work expended $A_{\mathrm{i}}^*(\tau)$ on τ is shown in Fig. 1.

In finite-time thermodynamics the maximal work problem for thermomechanical systems with a number of conditions imposed on the contacts was formulated by Rozonoer and Tsirlin [2] as an optimal control problem. They demonstrated that this problem can be reduced to an averaged nonlinear programming problem [3], and they used a corresponding mathematical technique to investigate the general structure of its optimal processes. The particular case of this problem for a thermodynamic system that consists of an infinite capacity source (reservoir) and a subsystem with controlled temperature (working body) was considered in Ref. [4], and later in a more detailed form in Refs. [5,6]. In Ref. [6] a system with a number of reservoirs was considered.

A large number of papers concerned with the limiting possibilities of heat engines with a finite cycle have been

*Email address: tsirlin@sarc.botik.ru
†Email address: kaz@arch.usyd.edu.au

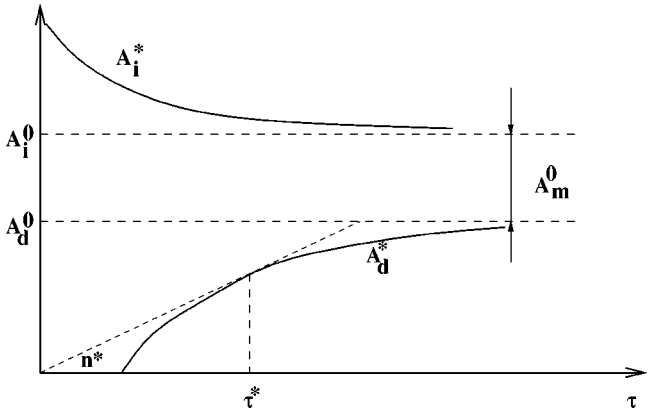

FIG. 1. The dependence of the work of separation $A_i^*(\tau)$ (that must to be spent for a separation of the uniform system into a number of subsystems) and the maximal work $A_d^*(\tau)$ (that can be produced by an equalization of the subsystems' parameters) on the duration of the process; τ^* is the duration of the process that delivers the maximal power.

published (see, for example, Refs. [7,8,11]). A heat engine is a system that consists of two or more heat reservoirs and a working body. In comparison, the minimal work problem has not been investigated as thoroughly, either for thermomechanical systems or for systems where heat exchange processes are accompanied by mass-transfer and chemical transformations [9].

In this paper we consider the problems of minimal and maximal work in a more general form than in Ref. [2], which allows us to consider not only thermomechanical systems but systems with mass transfer processes and chemical transformations. The structures of maximal and minimal work regimes, as well as those of the maximal power regimes, will be derived. We will show that for a wide class of systems in the limiting work regime the system's entropy is a piecewise-linear function of time, and that its intensive variables are piecewise-constant functions of time for any law of heat and mass transfer. The relation between the solutions of the maximal and the minimal work problems will be ascertained [10]. We will consider a number of important particular cases, and demonstrate how their solutions follow from the derived general optimality conditions.

II. FORMAL STATEMENT OF THE PROBLEM AND CHARACTERISTIC FORM OF ITS OPTIMAL SOLUTION

Let us divide all the subsystems in the thermodynamic system under consideration into three categories: (1) sources of infinite capacity (reservoirs), (2) sources of finite capacity (passive subsystems), and (3) subsystems with controlled intensive variables (working bodies). The vectors of intensive variables for each of these types of systems are denoted as z_n, z_e, and z_p correspondingly. The components of these vectors are temperatures, pressures, and chemical potentials of the corresponding subsystem. The components of the vector of extensive variables for each of these subsystems are internal energy E_i, entropy S_i, and the mass of each of the components, N_{ij} $(i=1,\ldots,n$ and $j=1,\ldots,m)$. n is the number of subsystems in the system, and m is the number of different chemical components in the system. If a contact between subsystems is established, then energy and mass flows $[q_{i\nu}(z_i,z_\nu]$ and $g_{i\nu}(z_i,z_\nu)]$ will be established between subsystems. The subscript $i\nu$ denotes the direction of the flux from the ith subsystem to the νth subsystem. $g_{i\nu}$ is the vector flux that contains m components (m is the number of different chemical components in the system). Functions $q_{i\nu}$ and $g_{i\nu}$ are equal to zero if $z_i=z_\nu$. From energy and mass conservation, it follows that

$$q_{i\nu}(z_i,z_\nu)=-q_{\nu i}(z_\nu,z_i),$$

$$g_{i\nu}(z_i,z_\nu)=-g_{i\nu}(z_\nu,z_i), \quad \forall i,\nu. \tag{2}$$

We assume that the reservoirs' intensive variables z_n are fixed and constant; the intensive variables of the working body z_p are the control variables of the problem and at each moment of time t belong to some set D_z, and the intensive variables of the passive subsystems are functions of their extensive variables:

$$z_e=f(E_e,S_e,N_e). \tag{3}$$

In addition to the vector $z_p(t)$, other control variables in this problem are the contact functions $U_{i\nu}^q(t)$ and $U_{i\nu}^g(t)$, which can be equal to 1 or zero only. If the contact function is equal to 1, then the corresponding flux can exist, and if this function is equal to zero then it cannot.

The extensive variables of each of the subsystems obey differential equations of thermodynamic balances. The energy balance has the form

$$\dot{E}_\nu=\sum_{i=1}^{n}\left[U_{i\nu}^q q_{i\nu}(z_i,z_\nu)+U_{i\nu}^g\mu_{i\nu}g_{i\nu}(z_i,z_\nu)\right]-r_\nu(t), \qquad \nu=1,\ldots,n. \tag{4}$$

The summing here is done on all i, including $i=\nu$, because $q_{\nu\nu}=g_{\nu\nu}=0$; $r_\nu(t)$ is the mechanical work produced by the νth subsystem if $r>0$ and the work expended if $r<0$; the second term in the square bracket above is the scalar product, that is, the sum on the subscript j from one to m for each combination of i and ν.

The mass balance on each component is

$$\dot{N}_\nu=\sum_{i=1}^{n}U_{i\nu}^g g_{i\nu}(z_i,z_\nu)=n_\nu(u,z). \tag{5}$$

The entropy balance is

$$\dot{S}_\nu=\frac{1}{T_\nu}\sum_{i=1}^{n}\left[U_{i\nu}^q q_{i\nu}(z_i,z_\nu)+U_{i\nu}^g\mu_{i\nu}g_{i\nu}(z_i,z_\nu)\right] =\sigma_\nu(u,z), \quad \nu=1,\ldots,n. \tag{6}$$

Because some additional constraints can be imposed on the contact functions, we will assume that $U\in D_u$, where D_u is a subset of the vertices of the unit hypercube in the positive quadrant, with one vertex at the coordinate origin.

The criteria of optimality in this problem is the work A that is produced by the system

$$A_d = \int_0^\tau \sum_{\nu=1}^{n} r_\nu(t)dt \to \max,$$

or, after taking into account Eqs. (2) and (4),

$$A_d = \sum_{\nu=1}^{n} [E_\nu(0) - E_\nu(\tau)] \to \max. \tag{7}$$

Because the initial state of the system is given, condition (7) corresponds to the condition

$$E(\tau) = \sum_{\nu=1}^{n} E_\nu(\tau) \to \min.$$

Since the internal energy of each of these subsystems depends on S_ν, V_ν, and N_ν, we obtain

$$E(\tau) = \sum_{\nu=1}^{n} E_\nu([(S_{\nu 0} + \tau\overline{\sigma_\nu(u,z)}], \times [N_{\nu 0} + \tau\overline{n_\nu(u,z)}], V_\nu(\tau)) \to \min_{u, z_p, V}. \tag{8}$$

The overbar here denotes the averaging of the corresponding function over the interval $(0,\tau)$. Thus

$$\overline{n_\nu(u,z)} = \frac{1}{\tau}\int_0^\tau n_\nu(u(t),z(t))dt.$$

The internal energy has to be minimized subject to Eqs. (5) and (6), constraints (3) for the passive subsystems, the constraints on volume of the subsystem,

$$V(t) \in D_V, \tag{9}$$

the constraints on the variables u and z_p,

$$U(t) \in D_u, \qquad z_p(t) \in D_z, \tag{10}$$

and the constraints on the final values of the entropy and chemical composition for some of the subsystems,

$$S_\nu(\tau) = S_\nu^k, \quad \nu = 1,2,\ldots,x \leqslant n, \qquad N_{\nu j}(\tau) = N_{\nu j}^k, \quad (j,\nu) \in \Omega. \tag{11}$$

Here Ω is the set of all such combinations of the subscripts j and ν, for which the amount of the jth component in the νth subsystem is fixed.

Assume that the total number of constraints [Eqs. (11)] is m. The following equations hold here:

$$\left(\frac{\partial E_\nu}{\partial S_\nu}\right)_{t=\tau} = T_\nu(\tau) > 0, \quad -\left(\frac{\partial E_\nu}{\partial V_\nu}\right)_{t=\tau} = P_\nu(\tau) > 0, \qquad \left(\frac{\partial E_\nu}{\partial N_{\nu j}}\right)_{t=\tau} = \mu_{\nu j}(\tau) > 0, \tag{12}$$

where P_ν is the pressure and the $\mu_{\nu j}$ is the chemical potential of the jth component in the νth subsystem. Let us discuss the mathematical features of this problem, which in many cases can make its solution significantly simpler.

(1) If only objective (8) and constraints (9) depend on the volumes $V_\nu(\tau)$ and neither $S(\tau)$ nor $N(\tau)$ depends on the volumes, then the optimal choice of volumes is given by the solution of the following problem:

$$E(\tau) = \sum_{\nu=1}^{n} E_\nu(S_\nu^*(\tau), N_\nu^*(\tau), V_\nu) \to \min_{V \in D_V}. \tag{13}$$

In particular, if the total volume of the system is fixed,

$$\sum_{\nu=1}^{n} V_\nu(\tau) = V_0, \tag{14}$$

and E_ν is a concave function of V_ν, then conditions (13) and (14) lead to the conditions

$$\left(\frac{\partial E_\nu}{\partial V_\nu}\right)_\tau = -P_\nu(\tau) = \text{const} \quad \forall \quad \nu. \tag{15}$$

Thus, at $t=\tau$, the volumes of the subsystems with optimal or fixed values of $S_\nu(\tau)$ and $N_\nu(\tau)$ must be chosen from the condition of equal pressures. If one of the subsystems is a reservoir whose pressure is constant, then from Eq. (15) it follows that at $t=\tau$ the pressures in each subsystem with the controlled volume must be equal to the pressure in this reservoir, P_n.

(2). If the system does not include passive subsystems, then problems (8), (5), and (6) become not optimal control problems but averaged nonlinear programming problems [3]. Indeed, in this case the right-hand sides of Eqs. (5) and (6) do not depend on the state variables N and S. Therefore, these equations can be dropped from the problem formulation, and condition (11) can be rewritten as M equations:

$$\overline{\sigma_\nu(u,z)} = \frac{1}{\tau}(S_\nu^k - S_{\nu 0}) = \overline{\sigma}_\nu, \quad \nu = 1,2,\ldots,x \leqslant n, \qquad \overline{n_{\nu j}(u,z)} = \frac{1}{\tau}(N_{\nu j}^k - N_{\nu j 0}), \quad (j,\nu) \in \Omega. \tag{16}$$

The optimal solution $W^*(t) = (U^*(t), z^*(t))$ of problems (8), and (16) (Ref. [9]) is a piecewise-constant vector function. It takes not more than $(M+1)$ values of W^l on the interval $(0,\tau)$. $W^*(t)$ takes each of these *basic* values (or *basic* solutions) W^l during the fraction γ_l of the interval $(0,\tau)(\gamma_l \geqslant 0, \Sigma_{l=0}^{M}\gamma_l = 1)$. Note that the actual sequence in which different W^l are taken does not matter. Each of the basic values obeys the condition

$$L = \left\{ \left[\sum_{\nu=x+1}^{n} T_\nu(\tau)\sigma_\nu(u,z) + \sum_{\nu,j \notin \Omega} \mu_{\nu j}(\tau) n_{\nu j}(u,z) + \sum_{\nu=1}^{x} \lambda_\nu(\sigma_\nu(u,z) - \overline{\sigma}_\nu) + \sum_{\nu,j \in \Omega} \lambda_{\nu j}(n_{\nu j}(u,z) - \overline{n}_{\nu j}) \right] \to \min_{u,z} \right\} \max_{\lambda}. \tag{17}$$

The multipliers $T_\nu(\tau)$ and $\mu_{\nu j}(\tau)$ have been used here in order to account for condition (12) of the equation of state.

In order to find the values of these variables [which in the general case differ from the optimal values $T_\nu(t)$ and $\mu_{\nu j}(t)$ on the interval $(0,\tau)$], the following equations have to be added to condition (17):

$$S_\nu(T_\nu(\tau),V_\nu^*,\mu_\nu(\tau),N_\nu(\tau))=S_\nu(0)+\tau\sigma_\nu(u,z),$$

$$\nu=x+1,\ldots,n, \tag{18}$$

$$N_{\nu,j}(\tau)=N_{\nu,j}(0)+\tau n_{\nu j}(u,z),\quad \nu,j\notin\Omega.$$

In the maximal power problems the optimal period τ^* is determined as a solution of the following problem:

$$r(\tau)=\frac{A_n^*(\tau)}{\tau}\to\max_{\tau>0}.$$

For the differentiable and convex dependence of the produced work on the duration of the process, the optimality conditions for this problem yield the following equation for τ^*:

$$\left(\frac{dA_d^*}{d\tau}\right)_{\tau^*}=\frac{A_d^*(\tau^*)}{\tau^*}. \tag{19}$$

If there are no conditions like Eq. (6) in the problem ($M=0$), then the solution $W^*(t)$ is to be found from the condition

$$\sum_{\nu=1}^{n}T_\nu(\tau)\sigma_\nu(u,z)+\sum_{\nu,j}\mu_{\nu j}(\tau)n_{\nu j}(u,z)\to\min_{u\in D_u,z\in D_z} \tag{20}$$

jointly with Eqs. (18). This solution does not depend on time for any form of process' kinetics that determine σ_ν and $n_{\nu j}$.

If the function L in Eq. (17) is concave on W for all λ, then there is only one basic solution: if the set $D_w=D_uD_z$ can be divided into M^0 subsets $[M^0<(M+1)]$, and L is a concave function on each of these subsets, then the number of basic solutions is not more than M^0. The proof of this statement follows from Eq. (17).

The fractions of the time γ_l are to be found from conditions (16), which take the following form after substitution of the basic solutions

$$\sum_l\gamma_l\sigma_\nu(W^l)=\overline{\sigma_\nu},\quad \nu=1,2,\ldots,x,$$

$$\sum_l\gamma_l n_{\nu j}(W^l)=\overline{n_{\nu j}},\quad (j,\nu)\in\Omega, \tag{21}$$

$$\gamma_l\geqslant 0,\quad \sum_l\gamma_l=1.$$

As the result of the derivations described above, we formulate the following statement (the *theorem of the maximal work*): If a thermodynamic system consists of a number of reservoirs and a number of working bodies then the maximal work that can be produced by this system during the period of time τ (if internal energy of the system decreases) or the minimal work that has to be spent (if its internal energy increases) is achieved in a process when the vector of intensive variables and contact functions are piecewise-constant functions of time on the interval $(0,\tau)$ and the number of values this vector function takes is not more than $(M+1)$. Here M is the number of fixed values of entropy and mass for the working bodies at time $t=\tau$. At the beginning and at the end of this process the intensive variables of the working bodies instantaneously change to some optimal values and the entropy of the system increases over the interval $(0,\tau)$ as a piecewise-linear function.

Conclusion: If there are no constraints on the composition and on the entropy of the working bodies at time $t=\tau$ ($M=0$) then, in a maximal work process, the system's entropy increases with a constant rate for any law of heat and mass transfer, and each one of the working bodies stays in contact with only one reservoir during a limiting work process.

The maximal work problem for a system which contains passive subsystems turns out to be an optimal control problem with discrete control variables $U(t)$. It can be solved analytically only in a very few cases.

It is clear that the problem of minimal used work A_i^*, coincides with the formulation of the maximal work, A_d^*. The only difference is the sign of the derived solution. If the work on the optimal solution A_d^* is positive, then $A_i^*=A_d^*+A_m^0$, if it is negative, then $|A_d^*|+A_m^0=A_i^*$. Here A_m^0 is the work in irreversible equilibrium processes.

III. MAXIMAL WORK PROBLEM IN THERMOMECHANICAL SYSTEMS

In a thermomechanical system temperature is an intensive variable, and extensive variables are volume, entropy, and internal energy. From the maximal work theorem, which was formulated in Sec. II, it follows that a maximal work process consists of isothermal and adiabatic branches. It includes not more than $M+1$ isothermal branches and not more than $M+2$ adiabatic temperature jumps. Two of these temperature jumps occur at the beginning and end of the process.

The rate of entropy change in a thermomechanical system is

$$\dot S_\nu=\sigma_\nu(u,T)=\frac{1}{T_\nu}\sum_{i=1}^{n}U_{i\nu}q_{i\nu}(T_i,T_\nu). \tag{22}$$

For reservoirs the entropy, volume, and internal energy are related to each other via the equation

$$E_0=T_0S_0-P_0V_0.$$

It is easy to show that if a system consists of a reservoir and $n-1$ subsystems, then the work can be rewritten as the following function of the entropy production:

$$A=\sum_{\nu=1}^{n-1}(T_0\Delta S_\nu-\Delta E_\nu)-T_0\sum_{\nu=1}^{n}\overline{\sigma_\nu(u,T)}. \tag{23}$$

The last term includes the average rate of change of the reservoir's entropy. Thus, for the given initial and final states of the subsystems, the maximal produced work (minimal spent work) corresponds to the minimal entropy production

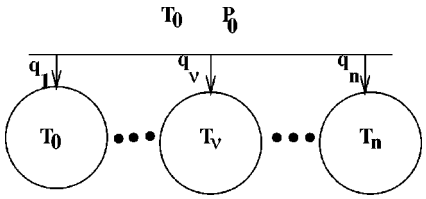

FIG. 2. The structure of a thermodynamic system which consists of insulated subsystems and reservoirs.

in the system. Therefore, in a system with reservoirs, the optimal processes turn out to be the minimal dissipation processes [9]. Let us consider what are the specific forms for these optimality conditions in some important particular cases of thermomechanical systems.

A. Independent subsystems that contact with a reservoir

Let us consider the system shown in Fig. 2. It consists of n subsystems that are insulated from each other and that contact with the reservoir. The temperature of the reservoir is T_0 and its pressure is P_0. We assume that the initial states of all subsystems and the parameters of the reservoir are given and the total volume of the system is constant.

Each one of the heat fluxes $q_\nu(T_0,T_\nu)$ and the entropy production $\sigma_\nu(T_\nu)=(1/T_\nu)q_\nu(T_0,T_\nu)$ depend on one control T_ν. Because this flux can be switched off by setting $T_\nu=T_0$, there is no need to use contact functions U_ν here.

The maximal work problem in this system can be decomposed into n subproblems about the optimal contact with a reservoir for each of the subsystems. From conditions (15) here, it follows that the pressure in each of these subsystems at $t=\tau$ is P_0. The maximal power problem requires taking into account characteristics of all subsystems.

First we consider the maximal work problem for the optimal contact between the reservoir and the working body. In this section we will now omit the subscript ν. If the entropy of the working body $S(\tau)$ at the end of the process is given and the volume V^* is determined by the condition $P=P_0$, then the internal energy of the working body $E(\tau)$ is fixed and the minimum of the system's internal energy corresponds to the minimum of E_0. Thus we arrive at the following formulation:

$$\overline{q(T_0,T)}\to\max_T \Big/ \overline{\left(\frac{q(T_0,T)}{T}\right)}=\frac{\Delta S}{\tau}. \tag{24}$$

For the linear law of heat transfer,

$$q(T_0,T)=\alpha(T_0,T), \tag{25}$$

this subproblem was investigated in Ref. [2], and for a more general law

$$q(T_0,T)=\alpha(T_0^k-T^k), \tag{26}$$

where α and k both have the same sign, it was considered in Refs. [4–6].

For the linear law of heat transfer, problem (24) is a convex one, and it has a unique solution

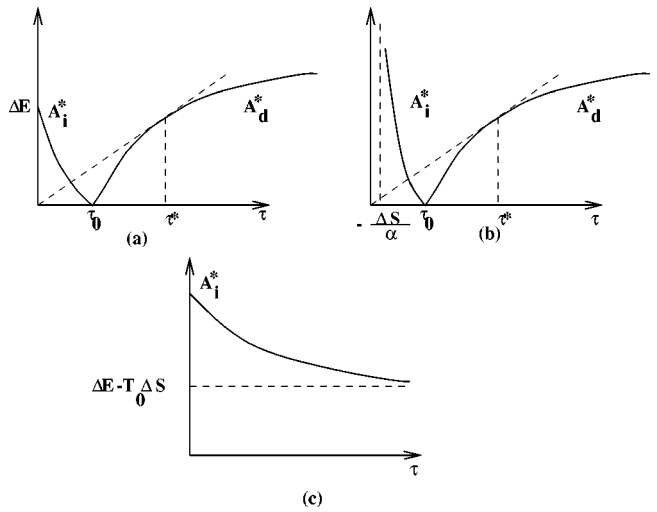

FIG. 3. The characteristic dependencies of the limiting spent work and limiting produced work on the contact duration τ. (a) corresponds to the positive increment of the system's entropy, (b) to the negative increment, and (c) to $\Delta E>T_0\Delta S$.

$$T^*=\frac{T_0}{1+\Delta S/\alpha\tau}, \quad \alpha\tau+\Delta S>0.$$

The optimal work is

$$A^*(\tau)=\frac{T_n\Delta S\alpha\tau}{\alpha\tau+\Delta S}-\Delta E. \tag{27}$$

Here $\Delta E=E(S(\tau),V^*(\tau))-E(S(0),V(0))$.

Assume that we compute $A_d^*(\tau)$ using formula (27). If it is positive then it corresponds to the maximal produced work $A_n^*(\tau)$. If it is negative then it corresponds to the minimal spent work $A_i^*(\tau)=|A^*(\tau)|$.

In order to make dependence (27) more specific, we will assume that each of the subsystems is close to the ideal gas. Then

$$\Delta S=C_p\ln\frac{T(\tau)}{T(0)}-R\ln\frac{P_0}{P(0)}. \tag{28}$$

Here we took into account the condition that at $t=\tau$ the pressures in subsystems are equal to the reservoir's pressure.

Equation (28) can be used to express $T(\tau)$ in terms of ΔS and $\Delta E=C_\nu[T(\tau)-T(0)]$:

$$\Delta E(\Delta S)=C_\nu T(0)\left[\left(\frac{P_0}{P(0)}\right)^{R/C_p}\exp\left(\frac{\Delta S}{C_p}\right)-1\right]. \tag{29}$$

The substitution of Eq. (29) into Eq. (27) yields the dependence $A^*(\tau,\Delta S)$. The characteristic forms of the dependencies of the maximal work and minimal work on τ are shown in Fig. 3.

If the value of ΔE, which is calculated using formula (29), is positive, then such a value of τ_0 exists that no work can be produced by the system in any process with a shorter duration than τ_0. If the entropy $S(\tau)$ is not fixed then, instead of problem (24), we obtain the problem of minimization of the system's internal energy. According to Eq. (20) it has the form

$$\left(\frac{T(\tau)}{T}-1\right)q(T_0,T)\rightarrow\min_{T>0} \tag{30}$$

subject to

$$\Delta S=S(\tau)-S(0)=\tau\frac{q(T_0,T^*)}{T^*}.$$

After taking Eq. (28) into account for the ideal gas and the linear law of heat transfer, the last equation can be rewritten as

$$C_p\ln\frac{T(\tau)}{T(0)}-R\ln\frac{P_0}{P(0)}=\tau\alpha\left(\frac{T_0}{T}-1\right). \tag{31}$$

According to Eq. (30), for $q=\alpha(T_0-T)$, we obtain

$$\frac{T(\tau)}{T}=\frac{T}{T_0}\Rightarrow T(\tau)=\frac{T^2}{T_0}. \tag{32}$$

Its substitution into Eq. (31) yields the following equation for T^*:

$$2C_p\ln\frac{T^*}{T_0T(0)}-R\ln\frac{P_0}{P(0)}=\tau\alpha\left(\frac{T_0}{T^*}-1\right). \tag{33}$$

Because the right-hand side of this equation is a strictly increasing function of T^*, and the left-hand side is a strictly decreasing one, this equation has a unique solution which determines the limiting work:

$$A_d^*(\tau)=-\Delta E_{\min}=C_v\left(T(0)-\frac{(T^*)^2}{T_0}\right)+\alpha\tau(T_0-T^*). \tag{34}$$

One can easily demonstrate that during a contact between a reservoir and a passive subsystem, whose temperature is a function of its internal energy, the work produced in the system is equal to 0 for any contact function $U(t)$.

In the maximal power problem

$$n(\tau)=\frac{\sum_i A_i(\tau)}{\tau}\rightarrow\max_{\tau>0},$$

the optimality condition for the convex functions $n(\tau)$, that is, for such functions $A_i(\tau)$ that obey the inequality

$$\sum_i\left(\frac{d^2A_i}{d\tau^2}\tau^2-2A_i(\tau)\right)<2\tau\sum_i\frac{dA_i(\tau)}{d\tau},$$

takes the form

$$\sum_i\left(\frac{dA_i}{d\tau}-\frac{A_i(\tau)}{\tau}\right)=0.$$

After taking into account Eqs. (29) and (30) for the above-described heat transfer laws and working body characteristics, we obtain the following equation for the duration of maximal power process, τ^*:

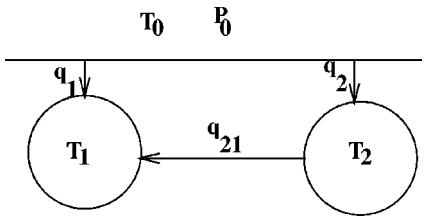

FIG. 4. Subsystems that contact with a reservoir and with each other.

$$\sum_{i=1}^n\frac{\alpha_i\Delta S_i}{\alpha_i\tau+\Delta S_i}\left(\frac{\Delta S_i}{\alpha_i\tau+\Delta S_i}-1\right)=\frac{T_0}{\tau}\sum_{i=1}^n\Delta E_i(\Delta S_i).$$

The power that can be derived in a finite-time process is limited, but the power used in it can be infinitely large.

For a heat flux that has the form of Eq. (25), for $0<k<1$ and for $\Delta S_i<0$ the regime with the minimal work $T_i^*(t)$ can be a switching regime when the temperature switches between two basic values. One of these basic values corresponds to the maximal feasible temperature of the working body [5]. But this change of the solution $T^*(t)$ does not change the dependence of $A_i^*(\tau)$ on τ.

B. Subsystems that contact with a reservoir and with each other

First we consider the system that is shown in Fig. 4. For simplicity we assume that the volumes of the subsystems at $t=\tau$ are fixed, and that $S_i(\tau)$ are also fixed. The minimization of system's internal energy at $t=\tau$ leads to conditions (17),

$$L=\left\{\sum_{i=1}^2\left[U_iq_i(T_0,T_i)+\lambda_i\left(\frac{U_iq_i(T_0,T_i)+U_{21}q_{21}(T_2,T_1)(-1)^i}{T_i}-\Delta S_i\right)\right]\rightarrow\max_{U,T}\right\}\rightarrow\min_{\lambda},$$

where $\Delta S_i=S_i(\tau)-S_i(0)$.

The limiting work in the system, which is shown in Fig. 4, is never lower than the limiting work in the system, which is shown in Fig. 2, because for $U_1=U_2=1$, and $U_{21}=0$ these systems are identical.

Since the limiting work A_d^* is a strictly decreasing function of ΔS_i and $\lambda_i=-\partial A_d^*/\partial\Delta S_i$, the multipliers λ_i are always positive. For the linear heat transfer laws

$$q_i=\alpha_i(T_0-T_i),\quad q_{21}=\alpha_{21}(T_2-T_1),$$

the function L is convex on T_1 and T_2, and the problem has only one basic value of T vector. The contact function $U_i^*=1$ if $q_i(T_0,T_i)[1+(\lambda_i/T_i)]>0$, that is, if $T_0>T_i$. Because of this, the optimal values of T_1 and T_2 are determined as

$$T_i^*=\frac{\alpha_i T_0-\tilde{q}_{21}(-1)^i}{\alpha_i+\Delta S_i},\quad i=1,2.$$

Here $\tilde{q}_{21}=U_{21}q_{21}(T_2,T_1)$. The produced work is

$$\begin{aligned}A_d&=\tau(q_1(T_0,T_1^*)+q_2(T_0,T_2^*))\\&=\tau\left\{T_0\left[\alpha_1+\alpha_2-\frac{\alpha_1}{\alpha_1+\Delta S_1}-\frac{\alpha_2}{\alpha_2+\Delta S_2}\right]\right.\\&\left.\quad+U_{21}\alpha_{21}(T_2-T_1)\left(\frac{\alpha_2}{\alpha_2+\Delta S_2}-\frac{\alpha_1}{\alpha_1+\Delta S_1}\right)\right\}.\end{aligned}\tag{35}$$

One can easily show that for any sign of q_{21} the multiplier in front of U_{21} in Eq. (35) is positive. Therefore, $U_{21}^*=1$. The temperatures T_1^* and $T_2^*$are constant over the interval $(0,\tau)$ and are to be found from the following systems:

$$\begin{aligned}\alpha_1/T_1^2(T_1^2-T_1(\tau)T_0)&=\alpha_{21}\left(\frac{T_2T_1(\tau)}{T_1^2}-\frac{T_2(\tau)}{T_2}\right),\\\alpha_2/T_2^2(T_2^2-T_2(\tau)T_0)&=\alpha_{21}\left(\frac{T_1T_2(\tau)}{T_2^2}-\frac{T_1(\tau)}{T_1}\right).\end{aligned}\tag{36}$$

For subsystems that are close to the ideal gases and for $V_i(\tau)>V_{i0}$ the following equation should be added to conditions (36):

$$\begin{aligned}\Delta S_i&=C_{vi}\ln\frac{T_i(\tau)}{T_i(0)}\\&=\frac{1}{T_i}(\alpha_i(T_n-T_i)-\alpha_{12}(-1)^i(T_2-T_1)),\quad i=1,2.\end{aligned}\tag{37}$$

This determines T_i^* and $T_i^*(\tau)$.

The maximal work A_d^* and the minimal work A_i^* are determined as the sum of the increments of the subsystems' and reservoir's internal energies:

$$A^*=\left|[E_0(0)-E_0(\tau)]+\sum_i[E_i(0)-E_i(\tau)]\right|_{T=T^*,T(\tau)=T^*(\tau)}.$$

If there is no reservoir in the system, then $U_1=U_2=0$. From Eq. (36) it follows that

$$\frac{T_1}{T_2}=\sqrt{\frac{T_1(\tau)}{T_2(\tau)}}=\omega.\tag{38}$$

Condition (37) can be rewritten as

$$C_{v1}\ln\frac{T_1(\tau)}{T_{10}}=\frac{\alpha_{21}}{T_1}(T_2-T_1)=\alpha_{21}\left(\frac{1}{\omega}-1\right),$$

$$C_{v2}\ln\frac{T_2(\tau)}{T_{20}}=-\frac{\alpha_{21}}{T_2}(T_2-T_1)=\alpha_{21}(\omega-1).\tag{39}$$

Conditions (38) and (39) determine $T_1^*(\tau)$, $T_2^*(\tau)$, and ω_*. Because the temperature T_1^* and T_2^* are not defined uniquely here, some additional condition could be imposed on the system that should define T_1^* and T_2^*. This could be, for example, the condition that the average rate of heat flux $\bar{q}$ is fixed. In this case,

$$T_1^*=\frac{\bar{q}\omega^*}{\alpha_{21}(1-\omega^*)},\quad T_2^*=\frac{\bar{q}}{\alpha_{21}(1-\omega^*)}.$$

IV. MASS TRANSFER PROCESSES

Let us consider a class of systems which are described not only by their temperatures, volumes, and pressures, but also by their chemical composition. The chemical composition for the νth subsystem is determined by the vector of concentrations $C_\nu=(C_{i1},\ldots,C_{ik})$ or by the vector of chemical potentials $\mu_\nu(T_i,P_i,C_i)=(\mu_{i1},\ldots,\mu_{ik})$.

Assume that the chemical potentials of the subsystems μ_ν and the contact functions $U_{\nu j}$ are the problem's control variables. The problem of minimal work, that must be done to transfer the system from a given initial state to a given final state, turns out to be identical to the minimal work problem for the thermomechanical system where the subsystem's temperatures are the control variables. Its solution gives a lower bound to the limiting work in the system. For any physically meaningful mass transfer law $g_{i\nu}$, this limiting work regime consists of three branches: an instantaneous jump of the chemical potentials' vector μ from $\mu(0)$ to some optimal level μ^*; a ''holding'' of this vector on this level at the interval $(0,\tau)$; and a jump at $t=\tau$ to some value $\mu^*(\tau)$. The values μ^* and $\mu^*(\tau)$ are determined by the constrained problem, and by the equations of state of the subsystems, which relay the internal energy, the entropy, and the chemical potential at $t=\tau$. Here the entropy $S(\tau)$ depends on $S(0)$ and μ^*.

But this estimate could be relatively inaccurate (although it is more accurate than a reversible estimate). This is possible because in thermomechanical systems the optimal subsystems' temperature profiles $T^*(t)$ can be easily converted into the optimal volumes' profiles $V^*(t)$ (which are the actual controls in the problem) using their equations of state. The situation is quite different for the chemical potentials. Here the changes of volume or pressure in each of the subsystems influence the chemical potentials of all the components that are present in this subsystem. Therefore, in the general case it is not possible to find such a function $V^*(t)$ which corresponds to optimal time profiles of the chemical potentials for a number of components. For systems that are close to ideal gases, the chemical potential of the ith component is [1]

$$\mu_i(T,P)=\mu_{i0}(T)+RT\ln P_i,\quad i=1,\ldots,k,$$

where P_i is the partial pressure of the ith component. Let us now denote the volume of the subsystem as V, and assume

that at any instance of time the volume and the pressure are always related to each other via the Boyle-Marriott equation

$$PV=NRT,$$

where N is the number of moles in the subsystem, and

$$P_i=PC_i=P\frac{N_i}{N},\quad i=1,\ldots,k.$$

Let us express μ_i in terms of V:

$$\mu_i(T,V)=\mu_{i1}(T)+RT\ln\frac{N_i}{V},\quad i=1,\ldots,k. \tag{40}$$

Here $\mu_{i1}(T)=\mu_{i0}(T)+RT\ln RT$.

For the νth subsystem,

$$\dot{N}_{\nu i}=\sum_j g_{ij\nu}(\mu_\nu,\mu_j)U_{j\nu},\quad \nu=1,\ldots,n,\quad i=1,\ldots,k, \tag{41}$$

$$\dot{S}_\nu=\frac{1}{T}\sum_{j=1}^{n}\sum_{i=1}^{k}U_{j\nu}\mu_{i\nu}g_{j\nu i}(\mu_\nu,\mu_j). \tag{42}$$

Since the right-hand side of Eq. (41) and μ_ν do not depend on the number of moles N_ν, Eqs. (41) are not Lyapunov equations, and the problem of finding the functions $V_\nu(t)$ that maximize the work produced (or that minimize the work expended) is a general type of optimal control problem. Here for simplicity we assume that this is an isothermal mass transfer process, that all the temperatures are equal to T, and that there is no heat exchange in the system.

A. Mass transfer with a reservoir

Assume that a system consists of a reservoir with temperature T, pressure P_0, and chemical potential μ_0, and a working body with the same temperature, volume $V>0$, and chemical potential μ. The initial states of the working body's variables E_0, S_0, N_0, and V_0 are given. For simplicity we assume that the number of components is $k=1$. The working body's variables relay to each other via an equation of state

$$E_0=E(S_0,N_0,V_0).$$

$S(\tau)$ is given. The combined volume of the reservoir and the working body is constant.

In the maximal work problem it is required to minimize the system's internal energy at $t=\tau$:

$$A=\Delta E=[E(0)-E(\tau)+E_0(0)-E_0(\tau)]\rightarrow\max. \tag{43}$$

Here E_0 and E are the internal energies of the reservoir and the working body, correspondingly. The maximization is carried out on $V(\tau)$ and on $\mu(t)$ over the interval $(0,\tau)$. The conditions of maximum on $V(\tau)$ yields that, at $t=\tau$, the pressure in the working body must be equal to the pressure in the reservoir. From the condition

$$[\Delta E_0+E(S(\tau),N(\tau),V^*(\tau))]\rightarrow\min, \tag{44}$$

where

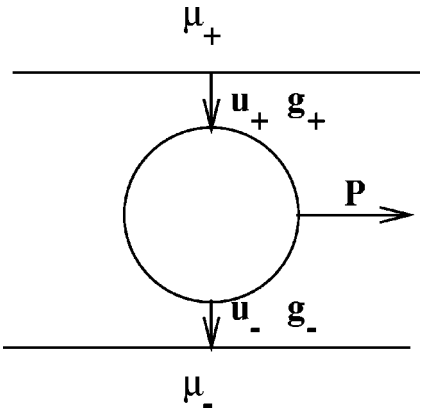

FIG. 5. The schema of a diffusion-mechanical cycle.

$$\Delta E_0=\int_0^\tau(h_0+\mu_0)g(\mu_0,\mu)dt,$$

$$\int_0^\tau\mu(t)g(\mu_0,\mu)dt=T\Delta S, \tag{45}$$

and in accordance with Eq. (17), we find for the basic values of μ by solving the auxiliary problem

$$L\left\{g(\mu_0,\mu)(\lambda_1(h_0+\mu_0)-\lambda\mu(\tau))+\lambda\frac{\Delta ST}{\tau}\right\}\rightarrow\min_{\mu}\max_{\lambda}. \tag{46}$$

After finding one or two basic values of μ^* from Eq. (46), $N^*(\tau)$ is to be calculated, and then $\mu(\tau)$ is found from the condition

$$S(\mu(\tau),N^*(\tau),V^*(\tau))=S(\tau). \tag{47}$$

If the Lagrange function L is concave on μ—that is, if

$$\frac{d^2g}{d\mu^2}>2\lambda\frac{dg}{d\mu}$$

—then the problem has a unique solution. One can show that in this problem $\lambda>0$ and $dg/d\mu<0$ always. Thus for the majority of the dependencies of $g(\mu)$, the condition of concavity of L holds, and μ^* is determined by the equations

$$\mu g(\mu_0,\mu)=\frac{[S(\tau)-S(0)]T}{\tau},$$

$$N^*(\tau)=N_0+g(\mu_0,\mu^*),$$

$$\Delta E_0=(h_0+\mu_0)g(\mu_0,\mu^*)\tau.$$

The substitution of these expressions into Eq. (43) yields A^*.

B. Cycle with two reservoirs

Consider a system with two reservoirs and a working body that can contact with each reservoir (Fig. 5). The chemical potential of the key component is μ_+ in one reservoir, and is μ_- in another (for definiteness, $\mu_+>\mu_-$).

Because this is a cyclic process, the increments of the entropy, the internal energy, and the key component's mass in the working body during the cycle are equal to zero. The temperatures of all subsystems are the same.

The change of the system's internal energy is equal to the change of the sum of reservoirs' internal energies. We denote the reservoirs' chemical potential as μ_0, and the working body's chemical potential as μ. μ_0 can take two values μ_+ and μ_-. The work

$$A=E_0(0)-E_0(\tau)=\int_0^\tau h(\mu_0)g(\mu_0,\mu)dt\rightarrow\max_{\mu_0,\mu} \quad (48)$$

is subject to constraints on the changes of the working body's entropy and mass:

$$\Delta S=\frac{1}{T}\int_0^\tau g(\mu_0,\mu)(h(\mu_0)-\mu)dt=0, \quad (49)$$

$$\Delta N=\int_0^\tau g(\mu_0,\mu)dt=0. \quad (50)$$

From Eq. (49) it follows that the maximum of the work corresponds to the maximum

$$A=\int_0^\tau g(\mu_0,\mu)dt\rightarrow\max \quad (51)$$

subject to condition (50).

In order to find the basic values μ and μ_0 in problems (50) and (51), we will write the Lagrange function and find its maximum on μ_0, and μ and its minimum on λ:

$$L=\{g(\mu_0,\mu)(\mu-\lambda)\rightarrow\max_{\mu_0,\mu}\}\rightarrow\min_{\lambda}.$$

The number of basic solutions is two; one basic solution corresponds to $\mu_0=\mu_+$, and the other one to $\mu_0=\mu_-$. For L, which is a strictly convex function of μ, the basic values μ obey the conditions

$$\frac{\partial L}{\partial\mu}=\frac{\partial g}{\partial\mu}(\mu-\lambda)+g(\mu_0,\mu)=0$$

or

$$\frac{g(\mu_0,\mu)}{\mu-\lambda}=-\frac{\partial g}{\partial\mu}.$$

Let us denote the root of this equation for $\mu_0=\mu_-$ as μ_1, and that for $\mu_0=\mu_+$ as μ_2. Because L attains its maximum in both basic solutions,

$$L(\mu_+,\mu_1,\lambda)=L(\mu_-,\mu_2,\lambda). \quad (52)$$

This equation determines the value of λ.

Let us derive the particular form of these dependencies for

$$g(\mu_0,\mu)=\alpha(\mu_0)(\mu_0-\mu). \quad (53)$$

From condition (52), we obtain

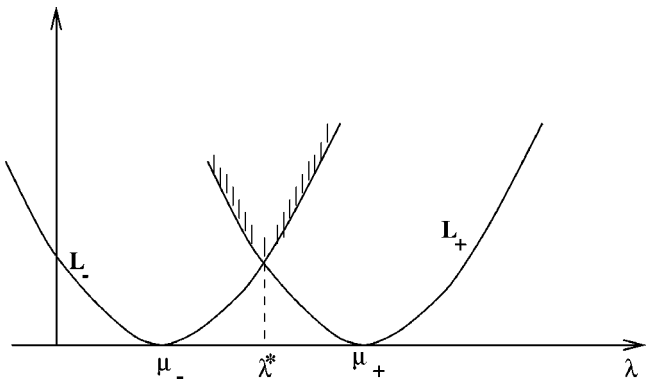

FIG. 6. The characteristic dependencies of L_+ and L_- on λ.

$$\mu=\frac{\mu_0+\lambda}{2}. \quad (54)$$

Substitutions of μ_1 and μ_2 into function L yields the dependence of L for each of the basic solutions

$$L_+=L(\mu_+,\mu_1)=\frac{\alpha_+}{4}(\mu_+-\lambda)^2,$$

$$L_-=L(\mu_-,\mu_2)=\frac{\alpha_-}{4}(\mu_--\lambda)^2.$$

The minimum on λ for the maximum of L on μ_0 and μ is attained in (see Fig. 6).

$$L_+(\lambda)=L_-(\lambda)\Rightarrow\lambda^*=\frac{\sqrt{\alpha_+}\mu_++\sqrt{\alpha_-}\mu_-}{\sqrt{\alpha_+}+\sqrt{\alpha_-}}. \quad (55)$$

The fractions of time when contacts with reservoirs are established are determined by condition (50), and are

$$\gamma_+=\frac{\alpha_-\sqrt{\alpha_+}}{\alpha_-\sqrt{\alpha_+}+\alpha_+\sqrt{\alpha_-}},$$

$$\gamma_-=\frac{\alpha_+\sqrt{\alpha_-}}{\alpha_-\sqrt{\alpha_+}+\alpha_+\sqrt{\alpha_-}}.$$

The limiting work obtained during τ is

$$A^*(\tau)=\tau[\gamma_+\mu_1\alpha_+(\mu_+-\mu_1)+\gamma_-\mu_2\alpha_-(\mu_1-\mu_2)],$$

where μ_1 and μ_2 are determined by Eq. (55), where λ is substituted from Eq. (56).

V. CONCLUSION

The solution of the problem of finding the maximal work that can be produced in a thermodynamic system without restrictions on the process duration does not depend on the equations of state and on the fluxes' kinetics in the system. This limiting work regime is achieved in a reversible process of equalization of the subsystem's intensive variables. The maximal work here is equal to the difference between the combined internal energy of the system in an initial state and in a limiting equilibrium state. In the inverse problem of minimal work that must be expended in order to transform

the system from an equilibrium state to a given final state, this minimal work exceeds the corresponding maximal work by the term that compensates for the irreversibility generated by equilibrium processes similar to mixing processes.

If these limiting work problems contain restrictions on the duration of the process, then they become optimal control problems. These optimal control problems have a number of mathematical features that make the structure of finite-time limiting work regimes independent of the equations of the subsystem's state and on the processes' kinetics in many practically important cases. Here the controlled intensive variables are piecewise-constant functions of time, and the extensive variables and the system entropy are piecewise-linear functions of time. Note that the minimal work of separation of a system in equilibrium into a number of subsystems depends uniquely on the maximal work in the direct process and on the reversible work of separation.

The limiting (maximal or minimal) work corresponds to the minimum of the combined internal energy of the system at the end of the process, subject to the constraints imposed on its initial and/or final states. For realistic equations of state the internal energy of each subsystem is a monotonically decreasing function of its entropy. Because this dependence is not linear, the minimization of the combined internal energy of the system is not equivalent to the minimization of its total entropy. However, in many particular cases the problem's constraints allow us to reduce the limiting work problem to the minimization of the internal energy of one of its subsystems, and thus to the minimization of its entropy increment. For example, this is the case if the final state of every subsystem except one is given. A similar problem was considered above [see Eq. (23)].

The maximal power problem has the same solution structure as the maximal work problem, but differs from the latter because the duration of the process τ is not fixed but is chosen to maximize the ratio $A_d^*(\tau)/\tau$.

ACKNOWLEDGMENT

This work was directly supported by a grant from the Russian Fund for Fundamental Research (Grant No. 99-01-00295).

[1] A.A. Guhman, *Foundations of Thermodynamics* (Science, Moscow, 1979) (in Russian).

[2] L.I. Rozonoer and A.M. Tsirlin, Automation Remote Control **1**, 70 (1983); **1**, 88 (1983); **1**, 49 (1983).

[3] A.M. Tsirlin, Dokl. Akad. Nauk **323**, 1 (1991) [Sov. Phys. Dokl. **37**, 3 (1992)]; **323**, 271 (1991) [**37**, 117 (1992)].

[4] P. Salamon and A. Nitzan, J. Chem. Phys. **20**, 1 (1981); **20**, 51 (1981).

[5] S.A. Amelkin, B. Andressen, P. Salamon, A.M. Tsirlin, and V.N. Umagugina, Izv. Russ. Akad. Nauk Energetics **2**, 118 (1998).

[6] S.A. Amelkin, B. Andressen, P. Salamon, A.M. Tsirlin, and V.N. Umagugina, Izv. Russ. Akad. Nauk Energetics **1**, 152 (1999).

[7] V.N. Orlov, A.V. Rudenko, Automation Remote Control **5**, 27 (1985).

[8] B. Andresen, *Finite-Time Thermodynamics* (University of Copenhagen Press, Copenhagen, 1983).

[9] R.S. Berry, V.A. Kazakov, S. Sieniutycz, Z. Szwast, and A. M. Tsirlin, *Thermodynamic Optimization of Finite-Time Processes* (Wiley, Chichester, 1999).

[10] A.M. Tsirlin, V.A. Mironova, S.A. Amelkin, and V. Kazakov, Phys. Rev. E **3**, 58 (1998); **3**, 1 (1998); **3**, 215 (1998).

[11] M.H. Rubin, Phys. Rev. **19**, 3 (1979); **19**, 1272 (1979); **19**, 1277 (1979).