THERMODYNAMICS AND THERMOPHYSICAL PROPERTIES OF SUBSTANCES

OPTIMUM NONEQUILIBRIUM THERMODYNAMIC FINITE-DURATION CYCLES WITH A LOCALLY NONEQUILIBRIUM WORKING SUBSTANCE

A. I. Shnip   UDC 536.7

Optimum, as to the maximum work criterion, thermodynamic cycles of finite duration and, consequently, proceeding under nonequilibrium conditions are investigated. This is a class of problems that are usually considered in finite-time thermodynamics. The specific feature of the problem considered here is the fact that the working substance of the cycle is a relaxing gas, i.e., a thermodynamic system with internal state variables. The necessary information from the thermodynamic theory of such systems is given. A system of equations for determining the parameters of the optimum cycle and relations for finding the maximum work and the efficiency have been derived. Numerical simulation has been performed.

Introduction. This paper is devoted to the modeling of the processes in the thermodynamic cycles of heat engines proceeding with a finite rate and, consequently, under nonequilibrium conditions. These studies are at the juncture of two comparatively new directions in modern nonequilibrium thermodynamics. The first direction is the nonequilibrium phenomenological thermodynamics of systems with relaxation, such as systems with memory and systems with internal state variables [1–11]. The second direction is the so-called finite-time thermodynamics in terms of which problems of optimizing the nonequilibrium processes in thermodynamic systems consisting of a set of internally nonequilibrium interacting subsystems that are not in equilibrium with one another are considered [12–17]. In the present paper, this approach has been generalized to the case where the elementary subsystems (in our case — the working substances of heat engines) are also internally nonequilibrium and their nonequilibrium states are described in terms of the theory of thermodynamic systems with internal variables. Such a generalization was possible owing to the previous studies, as a result of which expressions for nonequilibrium thermodynamic potentials of locally nonequilibrium systems [9, 10] were obtained. Knowledge of these expressions (primarily for entropy) is needed for formulating problems of such type. The problem on the finite-time thermodynamic cycle of maximum mean power with finite heat-transfer coefficients on hot and cold thermostats in which the working substance is a gas with internal relaxation has been considered. This cycle, like the classical Carnot cycle, consists of two isotherms and two adiabats, but, unlike the latter, it proceeds in a finite time and the working-substance temperature in it never reaches the temperature of the thermostats. A system of equations for determining the optimum-cycle parameters has been derived. Expressions for the maximum mean power of the optimum cycle, for the efficiency in the optimum cycle, and for the duration of the working-substance contact with both thermostats have been obtained and numerical calculations have been performed.

1. Preliminary Information. Thermodynamics of Systems with Internal Variables. The qualitative feature of media with internal relaxation, or locally nonequilibrium media, is the presence of an aftereffect and is described by the specificity of constitutive equations. Two types of constitutive equations taking into account these phenomena are known. They correspond to either thermodynamic systems with memory or thermodynamic systems with internal state variables. In the present paper, primary consideration is given to the latter.

Various systems with internal state variables (hidden variables) have been investigated by physicists for a long time. In the thermomechanics of continuous media, the introduction of such variables together with the additional

---

487

equations describing the evolution of internal variables (relaxation equations) is used to describe various phenomena, such as vibrational kinetics relaxation in nonequilibrium gases, evolution of dislocations in crystals under deformations, and many others. The systematically axiomatized thermodynamic theory of continuous media with internal state variables based on the Clausius–Duhem inequality was first developed by Coleman and Gurtin [6]. The method of giving constitutive equations taking into account the complex behavior of the system in terms of internal variables consists of taking into account the dependence of the constitutive functions on the values of independent variables only at a current instant of time, but in so doing a set of internal state variables $\{x_i\}$ is introduced and the system of constitutive equations is completed by the equations of evolution of these hidden variables.

In this case, e.g., for a deformable heat-conducting body the system of constitutive equations with internal variables can be given as

$$\mathbf{S}\,(t) = \breve{\mathbf{S}}\,(\mathbf{F}\,(t),\,\vartheta\,(t),\,\overline{\mathbf{g}}\,(t),\,x_1\,(t),\,x_2\,(t).....x_n\,(t))\,,$$

$$\mathbf{q}\,(t) = \breve{\mathbf{q}}\,(\mathbf{F}\,(t),\,\vartheta\,(t),\,\overline{\mathbf{g}}\,(t),\,x_1\,(t),\,x_2\,(t).....x_n\,(t))\,,$$

$$e\,(t) = \breve{e}\,(\mathbf{F}\,(t),\,\vartheta\,(t),\,\overline{\mathbf{g}}\,(t),\,x_1\,(t),\,x_2\,(t).....x_n\,(t))\,, \tag{1}$$

$$\dot{x}_i\,(t) = \varphi_i\,(\dot{\mathbf{F}}\,(t),\,\dot{\vartheta}\,(t),\,\mathbf{g}\,(t),\,x_1\,(t),\,x_2\,(t).....x_n\,(t))\,,\quad i = 1\,...\,n\,,$$

where $\mathbf{g}\,=\,\mathrm{grad}\,\,\vartheta$; $\overline{\mathbf{g}}(t)\,=\,\displaystyle\int_{-\infty}^{t}\mathbf{g}(s)ds.$

The last expression in (1) is a system of internal relaxation equations. The use, as an independent variable, of the inverse absolute temperature instead of the temperature permits constructing a thermodynamically consistent linear theory, and the use of the variable $\overline{\mathbf{g}}(t)$ instead of the (inverse) temperature gradient leads to a model of media with a finite velocity of propagation of thermal disturbances.

Taking into account the presence of internal variables, it is also necessary to formulate the basic thermodynamic principles. One of the most widely used in modern thermodynamics formulations of the second law of thermodynamics goes back to the classical formulation of the 19th century belonging to Clausius: *in each cyclic process the reduced heat integral is nonpositive, i.e.*,

$$\oint \frac{dQ}{T_{\mathrm{a}}} \le 0\,. \tag{2}$$

The thermodynamic approach relying on the modern variant of this formulation is usually called entropy-free. If a thermodynamic system is a continuous medium, then the reduced heat integral can be given in a local field formulation, and then inequality (2) will take on the following form [2–4]:

$$\oint \left[-\frac{1}{\rho}\,\mathrm{div}\left(\frac{\mathbf{q}}{T}\right) + \frac{r}{T} \right] dt \le 0\,. \tag{3}$$

A generalized thermodynamic theory of systems with internal state variables based on the entropy-free approach was proposed in [10]. This approach is distinguished by the fact that among the primary (undefinable) concepts of the theory there is no nonequilibrium thermodynamic potential (entropy). At the same time, one of its principal results is the fact that in the nonequilibrium state the existence of the function of state exhibiting all properties of entropy has been proved and a procedure of plotting this function has been developed. It is to be qualified that we speak of entropy in a given context only at a certain choice of independent variables. If the set of independent variables is different, then the thermodynamic potential will also be different (e.g., free energy, enthalpy, etc.). The thermodynamic theory developed in [10, 11] uses time-dependent abstract vector (with values in the vector space S) thermodynamic

variables $\sigma(t)$ and $\varepsilon(t)$ (generalized thermodynamic force and generalized configuration). For various concrete physical systems these variables represent sets of dependent and independent thermodynamic variables. Such a generalized description was possible due to the method of unified representation of various physical systems proposed in [11]. The same paper gives examples of this representation. For example, for a medium described by constitutive equations of the type of (1) the above generalized variables are written as $\sigma = \left\{ \vartheta\, \mathbf{S}, \dfrac{1}{\rho}\, \mathbf{q}, e \right\}$ and $\varepsilon = \left\{ \mathbf{F}, \overline{\mathbf{g}}, \vartheta \right\}$. Moreover, here the vector of internal variables $\overline{x}$ belonging to the vector space X is introduced so that the constitutive equations (1) in the general theory are given as

$$\sigma\,(t) = \overset{\wedge}{\sigma}\,(\varepsilon\,(t), \overline{x}\,(t))\,, \quad \dot{\overline{x}}\,(t) = \overline{\varphi}\,(\dot{\varepsilon}\,(t), \overline{x}\,(t))\,. \tag{4}$$

The formulation of the second law of thermodynamics in the Clausius form in terms of the generalized variables is represented as

$$\oint \langle \sigma, \dot{\varepsilon} \rangle\, dt \geq 0\,, \tag{5}$$

where $\langle \cdot, \cdot \rangle$ denotes the scalar product in the space S. In particular, for system (1) inequality (3) can be reduced to the form of (5) if we express in (3) the volume heat release r from the energy equation (first law):

$$\dot{e} = -\frac{1}{\rho}\,\mathrm{div}\,\mathbf{q} + \mathrm{tr}\,(\mathbf{SF}) + r\,. \tag{6}$$

In [10], Borukhov and Shnip found necessary and sufficient conditions of the feasibility of the second law for a particular case of semilinear constitutive equations of type (4), i.e., the equations of the form:

$$\overset{\wedge}{\sigma}\,(\varepsilon, x) = \sigma_0\,(\varepsilon) + \mathbf{C}x\,, \quad \varphi\,(\dot{\varepsilon}, x) = \mathbf{A}x + \mathbf{B}\dot{\varepsilon}\,, \tag{7}$$

where $\sigma_0\colon \mathsf{S} \to \mathsf{S}$; $\mathbf{A}$, $\mathbf{B}$, and $\mathbf{C}$ are the linear operators: $\mathbf{A} \in \mathcal{L}\,(\mathsf{X})$, $\mathbf{B} \in \mathcal{L}\,(\mathsf{S}, \mathsf{X})$, and $\mathbf{C} \in \mathcal{L}\,(\mathsf{X}, \mathsf{S})$. From these conditions the existence of a generalized nonequilibrium thermodynamic potential for such systems follows, and in [10] a general algorithm for constructing such potentials was found. It was shown that, as a rule, for thermodynamic systems of such a type nonuniqueness of the potential takes place so that for a particular chosen system there exists a compact family of such potentials, among which there are maximum and minimum ones. For some particular systems, explicit expressions for thermodynamic potentials were obtained. For instance, for a one-dimensional system (i.e., a system with a one-dimensional configuration space $\mathsf{S} = \mathsf{R}$ (so that σ, ε are scalars)), for which the space of internal variables is two-dimensional: $\mathsf{X} = \mathsf{R}^2$, and the operators $\mathbf{A}$, $\mathbf{B}$, and $\mathbf{C}$ are of the form

$$\mathbf{A} = \mathbf{A}^{\times} = \begin{bmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{bmatrix}, \quad \mathbf{B} = \mathbf{C}^{\times} = \begin{bmatrix} \sqrt{R_1} \\ \sqrt{R_2} \end{bmatrix},$$

with $\lambda_1 < \lambda_2 < 0$, $R_1 > 0$, $R_2 > 0$ the whole family of thermodynamic potentials will be written as [10]

$$\overset{\wedge}{\psi}\,(\alpha, x_1, x_2) = \psi_0\,(\alpha) + \frac{1}{2}\left(x_1^2 + x_2^2 - \frac{q}{\sqrt{R_1 R_2}}\left(\sqrt{R_1}\,x_2 - \sqrt{R_2}\,x_1 \right)^2 \right), \tag{8}$$

where

$$q_1 \leq q \leq q_2\,; \quad q_{1,2} = \frac{-2\beta \mp \sqrt{4\beta^2 + 2\chi - 2}}{\chi - 1}\,; \quad \chi = \frac{\lambda_1^2 + \lambda_2^2}{2\lambda_1\lambda_2}\,; \quad \beta = \frac{R_1 + R_2}{2\sqrt{R_1 R_2}}\,; \quad \sigma_0\,(\varepsilon) = \partial_\varepsilon \psi_0\,(\varepsilon)\,. \tag{9}$$

Relation (8) covers the whole family of thermodynamic potentials for a given system when q passes an interval $[q_1, q_2]$ and also represents the minimum and maximum thermodynamic potentials at $q = q_2$ and $q = q_1$, respectively.

489

2. Relaxing Gas as an Example of a System with Internal State Variables. As a specific example of a system of the above type, consider the following physical model that can be interpreted as a model of a gas with n internal degrees of freedom. Such degrees of freedom can be, for example, vibrational modes of molecules (relaxing gas). The same model can be represented more visually as a disperse system (conventionally called "dusted gas") consisting of an ideal gas with fine-disperse condensed phase particles distributed in it, and the dispersed component thereby consists of n fractions differing in properties, whose volume can be neglected. The following description is carried out in terms of such a system. If it is required to interpret this model as a relaxing gas, then the words "ith condensed fraction" should be replaced by "ith vibrational mode." We shall consider only spatially homogeneous processes in this system.

Since the general thermodynamic theory was formulated in terms of inverse temperature, we shall assume that the heat exchange between the condensed fractions and the carrier gas is described by the Newton law for inverse temperatures, and the direct heat exchange between the fractions is absent. Then the evolution of the composite system is described by the equations taking into account the subsystem interactions:

$$p = \frac{RT_a}{V} = \frac{R}{V\vartheta}, \quad E = E_r - c_0\vartheta - \sum_{i=1}^{n} c_i\vartheta_i, \quad \dot{E} = -p\dot{V} + r, \quad \dot{\vartheta}_i = -\frac{\alpha_i}{c_i}(\vartheta_i - \vartheta), \quad i = 1, 2, \dots n. \tag{10}$$

We assume that the composite system can exchange heat with the environment only through the gas phase. Then the thermodynamic (macroscopic) temperature should be identified with the gas temperature θ. By virtue of this, the second law of thermodynamics in the form of the Clausius inequality for a given system is written as follows:

$$\oint r\vartheta dt \leq 0. \tag{11}$$

This inequality should hold in all cyclic processes. The thermodynamic potential corresponding to this inequality is entropy S.

In view of the first law (the third equation in (10)), inequality (11) takes on the form

$$\oint (\dot{E}\vartheta + \vartheta p\dot{V}) \, dt = -\oint (E\dot{\vartheta} + (E\vartheta)^{\bullet} + R(\ln V)^{\bullet}) \, dt \leq 0. \tag{12}$$

Since in (12) integration with respect to the cyclic processes is implied, the integrals of total derivatives in this inequality vanish and it goes into

$$\oint E\dot{\vartheta} dt \geq 0, \tag{13}$$

and the thermodynamic potential corresponding to this inequality will be

$$\psi = S - E\vartheta - R\ln V. \tag{14}$$

Consider a particular case of the above thermodynamic system with two internal variables ϑ_1 and ϑ_2. We can see for ourselves that this system is equivalent to the generalized thermodynamic system considered at the end of Sec. 1 if we assume that $\varepsilon = \vartheta$, $\sigma = E$, $x_1 = -(\vartheta_1 - \vartheta)\sqrt{c_1}$, $x_2 = -(\vartheta_2 - \vartheta)\sqrt{c_2}$. Then, using expression (8) for the thermodynamic potential, in view of (14) we obtain the following expression for the nonequilibrium entropy of the given system:

$$S = S_0 + R\ln\frac{V}{V_0} - \frac{1}{2}\left(c_0(\vartheta^2 - \vartheta_0^2) + c_1(\vartheta_1^2 - \vartheta_0^2) + c_2(\vartheta_2^2 - \vartheta_0^2) - q\sqrt{c_1 c_2}(\vartheta_1 - \vartheta_2)^2\right), \tag{15}$$

where q has been determined according to relations (9) in which

$$\chi = \frac{(\alpha_1 c_2)^2 + (\alpha_2 c_1)^2}{2\alpha_1\alpha_2}, \quad \beta = \frac{c_1 + c_2}{2\sqrt{c_1 c_2}}. \tag{16}$$

The family of entropies (15), apart from the above-mentioned maximum (at $q = q_1$) and minimum (at $q = q_2$) elements, contains an element (corresponding to $q = 0$) that exhibits the property of absolute monotony and corresponds to the standard subsystem-additive entropy. In our case, this entropy has the form

$$S = S_0 + R \ln \frac{V}{V_0} - \frac{1}{2}\left(c_0 \, (\vartheta^2 - \vartheta_0^2) + c_1 \, (\vartheta_1^2 - \vartheta_0^2) + c_2 \, (\vartheta_2^2 - \vartheta_0^2)\right) \tag{17}$$

and corresponds to its calculation as the sum of entropies of individual subsystems.

The thermodynamic system considered is of great interest from the point of view of using its apparatus in the problems of finite-time thermodynamics.

3. Problem on the Maximum-Mean-Power Cycle for a Heat Engine with a Locally Nonequilibrium Working Substance. One of the first studies leading to the approach now called finite-time thermodynamics [12] was devoted to the problem of finding the maximum work that can be done in the Carnot cycle functioning between the hot and cold reservoirs in a finite time under the condition of finite coefficients of heat exchange between the working substance and the reservoirs. Since the duration of the cycle is fixed, this problem can be interpreted as a problem on the maximum-mean-power cycle. For the maximum efficiency of the cycle an expression has been obtained. As the known Carnot formula, this expression is only dependent on the temperature of the thermostats and depends on neither the working-substance properties nor the heat duration. Of course, this efficiency value is smaller than the value obtained by the Carnot formula. In [13], an analogous problem was solved in a more general formulation, so that the structure of the cycle is not specified in advance and the working substance can interact with a whole continuum of reservoirs whose temperatures lie in some range from the minimum temperature to the maximum one. It was shown that in this case, too, the structure of the optimum cycle follows the structure of the Carnot cycle, and for the basic parameters of this cycle we have analogous expressions. Moreover, in [15] in the general case it was shown that any problem of such a type should have a similar structure. Thus, fixing of the cycle structure similarly to the Carnot cycle, as it turns out, does not restrict the generality of the problem formulation.

Below we consider a problem that generalizes the described investigations in the sense that the working substance is no longer locally equilibrium and nonequilibrium relaxation processes with a characteristic time comparable to the cycle duration cannot proceed in it. Taking into account the foregoing, we shall consider the structure to be fixed, following the structure of the Carnot cycle. As a working substance of the heat engine, we chose a gas described by the model of a medium with internal relaxation presented in Sec. 2. Since this model is formulated in terms of inverse temperature, we shall describe the thermodynamic cycle under consideration in terms of the same quantity. In thermodynamic works, inverse temperature is referred to as "coldness." Below, for the sake of brevity, we shall also use this term.

Consider a cycle of duration T, in which the working substance executes a thermodynamic process between two thermostats: a hot one with coldness ϑ_h and a cold one with coldness $\vartheta_{low}(\vartheta_h - \vartheta_{low})$. At a thermal contact with the hot thermostat it executes isothermal expansion during the time t at a coldness ϑ^+, obtaining thereby a thermal flow

$$r_h = \alpha_h \, (\vartheta^+ - \vartheta_h) \, ; \tag{18}$$

then instantaneous adiabatic expansion of the working substance occurs so that its coldness increases to the value of ϑ^-; next, at this fixed value of the working-substance coldness it executes isothermal compression during the time $T - t$ at a thermal contact with the cold thermostat, giving up the thermal flow

$$r_{low} = \alpha_{low} \, (\vartheta^- - \vartheta_{low}) \, ; \tag{19}$$

at the final stage of the cycle instantaneous adiabatic compression of the working substance occurs so that its state returns to the initial state. The duration of the cycle T is fixed, and the parameters ϑ_h, ϑ_{low}, and t are variable and used to perform optimization aimed at finding the maximum work the working substance does in the cource of the cycle. According to the first law of thermodynamics (the third relation in (6)), this work is expressed as

$$A = \int_0^T p\dot{V}d\tau = \int_0^T rd\tau + \int_0^T \dot{E}d\tau = \int_0^T rd\tau + \Delta E . \tag{20}$$

One cyclicity condition of the process in the working substance is the return of its internal energy to its initial value at the end of the cycle, i.e., $\Delta E = 0$. This fact, with allowance for the cycle structure and representations (18) and (19) for thermal flows, permits reducing (20) to

$$A = r_h t + r_{low} (T - t) = \alpha_h (\vartheta^+ - \vartheta_h) t + \alpha_{low} (\vartheta^- - \vartheta_{low}) (T - t) . \tag{21}$$

The complete set of variables describing the working substance contains $n + 5$ quantities: p, V, ϑ, E, S, ϑ_i. Since they are related to one another by three equations of state (10) (the first two relations) and (17) (or (15)), only $n + 2$ quantities remain independent; as these, we choose E, S, and ϑ_i. The internal energy cyclicity condition has already been used to derive (21); for internal variables it can be written as

$$\int_0^T \dot{\vartheta}_i d\tau = 0 \quad \text{or} \quad \vartheta_i (T) = \vartheta_i (0) . \tag{22}$$

Solving the system of differential equations (the fourth expression in (10)) under arbitrary initial conditions $\vartheta_j(0) = \vartheta_i^0$, giving thereby $\vartheta(t)$ in accordance with the above-described structure of the cycle as being equal to ϑ^+ on the interval $[0, t)$ and ϑ^- on the interval $[t, T)$ and using then the cyclicity condition (22) to determine the arbitrary constants ϑ_i^0, we obtain the following representation for the cycles of internal variables:

$$\vartheta_i (\tau) = \begin{cases} \dfrac{(\vartheta^- - \vartheta^+) (1 - \exp (-\lambda_i (T - t)))}{1 - \exp (-\lambda_i T)} \exp (-\lambda_i \tau) + \vartheta^+ & \text{for} \quad \tau \in [0, \tau) ; \\[4mm] \dfrac{(\vartheta^- - \vartheta^+) (\exp (-\lambda_i t) - 1)}{1 - \exp (-\lambda_i T)} \exp (-\lambda_i (\tau - t)) + \vartheta^- & \text{for} \quad \tau \in [t, T) , \quad \lambda_i = \dfrac{\alpha_i}{c_i} , \quad i = 1, 2, \dots n . \end{cases} \tag{23}$$

It remains to formulate the cyclicity condition of working-substance entropy. To this end, we make use of the balance equation of entropy

$$\dot{S} = r\vartheta + \delta , \tag{24}$$

where δ is the entropy production in the working substance due to the nonequilibrium processes of internal relaxation. As was shown in [6], for thermodynamic systems with internal variables with constitutive equations of the form (4) this quantity is expressed as

$$\delta = \partial_x \psi \cdot \overline{\varphi} . \tag{25}$$

For a working substance of the type of the relaxing gas considered here, $\overline{\varphi}$ denotes the right-hand sides of the relaxation equation (the fourth expression in (10)) and ψ is the thermodynamic potential defined in (14). Thus, in our case (25) takes the form

$$\delta = \sum_{i=1}^n \left(\partial_{\vartheta_i} S - \vartheta \partial_{\vartheta_i} E \right) \frac{\alpha_i}{c_i} (\vartheta - \vartheta_i) . \tag{26}$$

Here for nonequilibrium entropy we use the standard expression (17) generalized to the case of n internal variables; it corresponds to the value of $q = 0$ in (15). Substituting (17) and the second equation of (10) into (26) and (26) into

(24) and neglecting the latter equation throughout the cycle, we require that the change in entropy in a cycle be equal to zero (cyclicity condition):

$$\Delta S = \int_0^T r\vartheta \, d\tau + \sum_{i=1}^n \int_0^T \alpha_i \, (\vartheta_i - \vartheta)^2 \, d\tau = 0 \; . \tag{27}$$

Taking into account in (27) the cycle structure given by expressions (18) and (19) as well as the variation in the temperature and internal variables of the working substance (formula (19) and the paragraph before it), upon integration we get

$$\alpha_h \, (\vartheta^+ - \vartheta_h) \, \vartheta^+ t + \alpha_{low} \, (\vartheta^- - \vartheta_{low}) \, \vartheta^- \, (T - t) + F \, (t) \, (\vartheta^- - \vartheta^+)^2 = 0 \; , \tag{28}$$

where

$$F \, (t) = \sum_{i=1}^n \frac{\alpha_i}{\lambda_i \, (1 - \exp \, (- \lambda_i T))} \, [1 + \exp \, (- \lambda_i T) - \exp \, (- \lambda_i t) - \exp \, (- \lambda_i \, (T - t))] \; . \tag{29}$$

Thus, the above-formulated problem of looking for the optimum cycle is formulated as follows: find values of the parameters ϑ^+, ϑ^-, and t at which, for expression (21), a maximum is reached under an additional constraint expressed by relations (28) and (29). We shall carry out the search for the given conditional extremum by the Lagrange multiplier method. The Lagrange function in our case is of the form

$$W_L = \alpha_h \, (\vartheta^+ - \vartheta_h) \, t + \alpha_{low} \, (\vartheta^- - \vartheta_{low}) \, (T - t) + \xi \, [\alpha_h \, (\vartheta^+ - \vartheta_h) \, \vartheta^+ t + \alpha_{low} \, (\vartheta^- - \vartheta_{low}) \, \vartheta^- \, (T - t) +$$

$$+ F \, (t) \, (\vartheta^- - \vartheta^+)^2] = 0 \; , \tag{30}$$

where ξ is the Lagrange undetermined multiplier. The above-formulated problem is equivalent to the search for the absolute extremum for the function W_L with respect to the variables ϑ^+, ϑ^-, t, and ξ. We obtain the relevant extremum condition by equating to zero the derivatives of the function W_L with respect to these variables. As a result, we have a system of four equations for these parameters, one of which coincides with (28) and the others of which are of the form

$$\alpha_h t + \xi \, [2\alpha_h \vartheta^+ t - \alpha_h \vartheta_h t - 2F \, (t) \, (\vartheta^- - \vartheta^+)] = 0 \; , \tag{31}$$

$$\alpha_{low} \, (T - t) + \xi \, [2\alpha_{low} \vartheta^- \, (T - t) - \alpha_{low} \vartheta_{low} \, (T - t) + 2F \, (t) \, (\vartheta^- - \vartheta^+)] = 0 \; , \tag{32}$$

$$\alpha_h \, (\vartheta^+ - \vartheta_h) - \alpha_{low} \, (\vartheta^- - \vartheta_{low}) + \xi \left[\alpha_h \, (\vartheta^+ - \vartheta_h) \, \vartheta^+ - \alpha_{low} \, (\vartheta^- - \vartheta_{low}) \, \vartheta^- + \frac{dF \, (t)}{dt} \, (\vartheta^- - \vartheta^+)^2 \right] = 0 \; . \tag{33}$$

If the solution of system (28), (31)–(33), $\tilde{\vartheta}^+$, $\tilde{\vartheta}^-$, $\tilde{t}$, $\tilde{\xi}$, has been found, then the parameters of the optimum cycle are thus known and we can calculate the maximum work A_m done in a cycle and the efficiency η of the optimum cycle:

$$A_m = \alpha_h \, (\tilde{\vartheta}^+ - \vartheta_h) \, t + \alpha_{low} \, (\tilde{\vartheta}^- - \vartheta_{low}) \, (T - \tilde{t}) \; , \quad \eta = \frac{A_m}{\alpha_h \, (\tilde{\vartheta}^+ - \vartheta_h) \, \tilde{t}} \; . \tag{34}$$
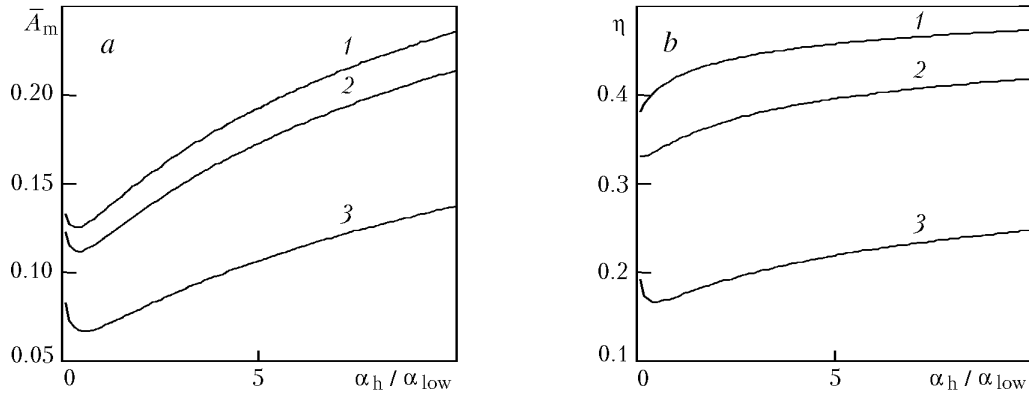
Fig. 1. Maximum relative work and efficiency of the cycle versus the ratio between the heat-transfer coefficients of the working substance and a thermostat ($\Theta = 0.3$, $\bar{\lambda}_1 = 0.1$): 1) $\bar{\lambda}_2 = 0.1$, $\bar{c}_1 = 0.1$, $\bar{c}_2 = 0.1$; 2) 10, 0.1 and 0.1; 3) 10, 0.1 and 0.7.
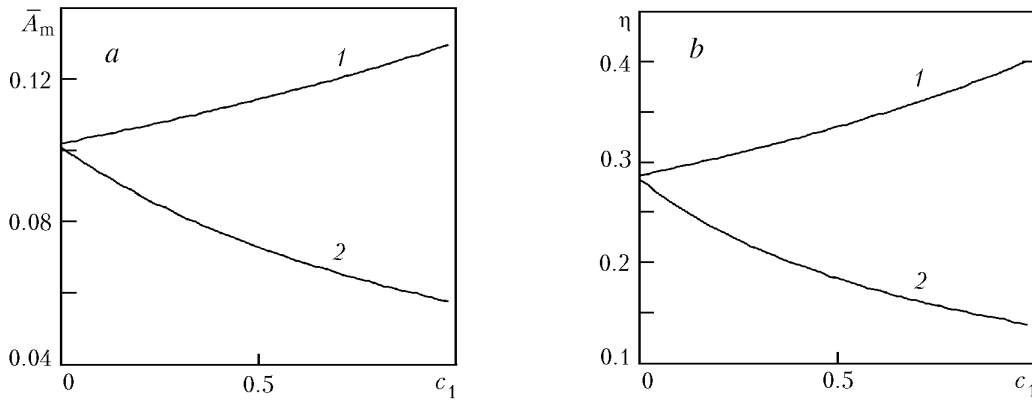

Fig. 2. Maximum relative work and efficiency of the cycle versus the heat capacities of internal modes at their constant sum ($\bar{c}_1 + \bar{c}_2 = 1$, $\Theta = 3$): 1) $\bar{\lambda}_1 = 0.1$, $\bar{\lambda}_2 = 0.1$; 2) 10 and 1.

System (28), (31)–(33) was solved numerically for the case of a working substance with two internal variables and then, with the use of these solutions, the work done and the efficiency of the optimum cycle were calculated by relations (34).

4. Results and Discussion. Figures 1–3 show the dependences of the maximum work and the efficiency of the cycle on its various parameters according to the results of the calculations. The dimensionless parameters here are determined as follows:

$$\bar{\lambda}_1 = \lambda_1 T, \quad \bar{\lambda}_2 = \lambda_2 T, \quad \bar{c}_1 = \frac{c_1}{c_0}, \quad \bar{c}_1 = \frac{c_1}{c_0}, \quad \Theta = \frac{\vartheta_h}{\vartheta_{low}}, \quad \bar{\alpha}_h = 1 + \frac{\alpha_h}{\alpha_{low}}, \quad \bar{\alpha}_{low} = 1 + \frac{\alpha_{low}}{\alpha_h}. \tag{35}$$

All calculations have been performed for the case of $\theta = 0.3$, which corresponds to the value of maximum efficiency of 0.7 according to the classical Carnot formula. As is seen from these figures, the presence of internal degrees of freedom in the working substance and the finite duration of the cycle strongly influence the characteristics of a heat engine. In general, the presence of internal modes leads to a lowering of the efficiency of the engine and a decrease in its power. It is also strongly influenced by the inequality of the heat-exchange coefficients on the hot and cold thermostats. As is seen from Fig. 1, the engine works more effectively if the heat-exchange coefficient on the hot thermostat is higher. This is easy to explain, because the quantity of heat taken out of the hot thermostat is higher than that given off on the cold thermostat. It is interesting to note the property of such an engine illustrated in Fig. 2. If the total heat capacity of internal modes is constant and in the first mode the relaxation time is comparable to the
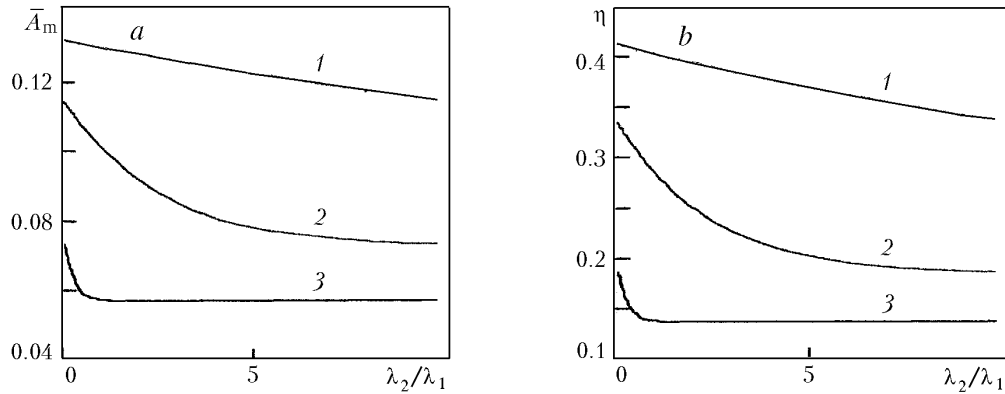
494

Fig. 3. Maximum relative work and efficiency of the cycle versus the ratio between the relaxation times of internal modes ($\Theta = 0.3$, $\bar{c}_1 = 0.5$, $\bar{c}_2 = 0.5$, $\bar{\alpha}_h = \bar{\alpha}_l = 2$): 1) $\bar{\lambda}_1 = 0.1$; 2) 1; 3) 10.

cycle duration, then in the case where the second mode is faster, when the heat capacity of internal modes is redistributed in favor of the second mode, the engine efficiency increases and, vice versa, when the second mode is slower the efficiency of the engine decreases. In so doing, the efficiency changes several times at heat capacities of the gas and internal modes of the same order. Figure 3 illustrates the influence of the relaxation times of the internal modes on the efficiency of nonequilibrium cycles. The general conclusion is as follows: the faster the internal modes, the stronger their negative effect on the heat-engine efficiency. This conclusion can also be explained physically, since at small relaxation times the passive internal reservoir, which does not participate in the accumulation of the part of the working-substance internal energy associated with the potential energy of the pressure forces and is responsible for supplying work, becomes effectively involved in the heat-exchange processes.

CONCLUSIONS

Thus, in this paper the procedure of finding thermodynamic constraints of the efficiency of nonequilibrium heat engines that permits determining the influence of the cycle and working-substance parameters on the efficiency characteristics of an engine has been developed. In its prospects, it may turn out to be useful for elucidating the role in the physical processes of other functions from the family of nonequilibrium entropies differing from the standard subsystem-additive expression for entropy.

Note that the results obtained are not only of general theoretical interest but can also prove to be useful in developing real heat engines, as well as in analyzing ways of upgrading their efficiency. For instance, in modern internal combustion engines and other heat engines the working-cycle duration measures tens of microseconds, which is comparable to the characteristic vibrational relaxation time of molecules of some gases forming combustion products. This means that the local nonequilibrium of the working medium, as was shown in this work, can markedly affect the efficiency indices of the engine. Taking account of such factors will turn out to be useful in developing promising new designs of heat engines.

NOTATION

A, work; A_m, maximum work per cycle; c_i, heat capacity (index 0 pertains to gas and i — to the ith internal mode); c_1, $\bar{c}_1$, dimensionless parameters determined in (35); E, internal energy; E_r, reference value of internal energy; e, specific internal energy; $\mathbf{F}$, deformation gradient tensor; $F(t)$, time function determined in (29); $\mathbf{g}$, coldness gradient; $\bar{\mathbf{g}}(t)$, integral coldness gradient; p, pressure; Q, quantity of heat obtained by the system by the current instant of time; $\mathbf{q}$, flow; q, parameter of the family of thermodynamic potentials; R, gas constant; R_1, R_2, parameters of the generalized thermodynamic system; r, internal heat release per mass unit; $\mathbf{B}$, Piola–Kirchhoff tensor; S, entropy; S, vector space of generalized thermodynamic variables (configuration space); T, cycle duration; T_a, absolute temperature; t, time; V, vol-

ume occupied by gas; W_L, Lagrange function; X, vector space of internal variables; x_i, ith internal variable; α_i, coefficient of heat transfer from the ith function to the gas; $\overline{\alpha}_h$, $\overline{\alpha}_{low}$, dimensionless parameters determined in (35); δ, production of entropy in the working substance; ε, generalized thermodynamic configuration; η, optimum cycle efficiency; Θ, dimensionless parameter determined in (35); $\vartheta = 1/T_a$, inverse absolute temperature (coldness); ϑ_i, coldness of the ith fraction; ϑ_h and ϑ_{low}, coldness of the hot and cold thermostats, respectively; ϑ^- and ϑ^+, coldness of the working substance at a thermal contact with the cold and hot thermostats, respectively; λ_1, λ_2, parameters of the generalized thermodynamic system; ξ, undetermined Lagrange multiplier; ρ, medium density; σ, generalized thermodynamic force; φ_i, function giving the relaxation rate of the ith internal variable; $\overline{\varphi}$, function giving the rate of change in the vector of internal variables; ψ, thermodynamic potential; $\partial\overline{x}$, gradient operator in the space of internal variables. Subscripts: a, absolute; h, hot (high-temperature); low, cold (low-temperature); m, maximum; r, reference; 0, pertaining to gas (to translational degrees of freedom).

RERERENCES

1. W. A. Day, An objection to use of entropy as a primitive concept in continuum thermodynamics, *Acta Mechanica*, **27**, 251–255 (1977).
2. W. A. Day, *Thermodynamics of Simple Media with Memory* [Russian translation], Mir, Moscow (1974).
3. J. Meixner, Processes in simple thermodynamics materials, *Arch. Rat. Mech. Anal.*, **33**, No. 1, 33–53 (1969).
4. B. D. Coleman and D. R. Owen, A mathematical foundation for thermodynamics, *Arch. Rat. Mech. Anal.*, **54**, No. 1, 1–102 (1974).
5. B. D. Coleman and D. R. Owen, Thermodynamics and elastic–plastic materials, *Arch. Rat. Mech. Anal.*, **58**, No. 1, 26–51 (1976).
6. B. D. Coleman and M. E. Gurtin, Thermodynamics with internal state variables, *J. Chem. Phys.*, **47**, No. 2, 597–613 (1967).
7. V. L. Kolpashchikov and A. I. Shnip, Linear thermodynamic systems with memory. I. Basic tenets of the thermodynamic theory, *Inzh.-Fiz. Zh.*, **68**, No. 4, 633–646 (1995).
8. V. L. Kolpashchikov and A. I. Shnip, Linear thermodynamic systems with memory. II. Necessary and sufficient conditions for applicability of the second law of thermodynamics, *Inzh.-Fiz. Zh.*, **68**, No. 5, 724–737 (1995).
9. V. T. Borukhov, V. L. Kolpashchikov, and A. I. Shnip, Linear thermodynamic systems with memory. III. Theory of nonequilibrium thermodynamic potentials, *Inzh.-Fiz. Zh.*, **69**, No. 5, 707–715 (1996).
10. V. T. Borukhov and A. I. Shnip, On the thermodynamic theory of relaxing systems, in: *Proc. IV Minsk Int. Forum "Heat and Mass Transfer–MIF-2000"* [in Russian], May 22–26, 2000, Vol. 3, Minsk (2000), pp. 151–158.
11. A. I. Shnip, Theory of generalized thermodynamic systems with memory, *Inzh.-Fiz. Zh.*, **75**, No. 1, 21–31 (2002).
12. F. L. Curzon and B. Ahlborn, Efficiency of a Carnot engine at maximum power output, *Amer. J. Phys.*, **43**, 22–24 (1975).
13. M. H. Rubin, Optimal configuration of a class of irreversible heat engines. I, *Phys. Rev. A.*, **19**, No. 3, 1272–1276 (1979).
14. M. H. Rubin, Optimal configuration of a class of irreversible heat engines. II, *Phys. Rev. A.*, **19**, No. 3, 1277–1289 (1979).
15. L. M. Rozonoér and A. M. Tsirlin, Optimal control of thermodynamic processes, *Avtomat. Telemekh.*, No. 1, 70–79; No. 2, 88–101; No. 3, 50–64 (1983).
16. V. N. Orlov and A. V. Rudenko, Optimal control in problems on limiting possibilities of thermodynamic processes, *Avtomat. Telemekh.*, **46**, 7–39 (1985).
17. A. M. Tsirlin and V. Kazakov, Maximal work problem in finite time thermodynamics, *Phys. Rev. E.*, **62**, No. 1, p. 307 (2000).