Journal of Engineering Physics and Thermophysics, Vol. 78, No. 6, 2005

THERMODYNAMICS AND KINETIC THEORY OF TRANSFER PROCESSES

MAXIMUM WORK OF RELAXING SYSTEMS RECOVERABLE IN A FINITE TIME

A. I. Shnip

UDC 536.7

The problem on minimization of the thermodynamic action performed by a linear relaxing thermodynamic system from an arbitrary nonequilibrium state on a finite time interval has been solved. In specific applications, this problem solves that on the maximum mechanical or electric energy (work) which can be recovered in a finite time interval from such systems as a viscoelastic body, electric RC and LC circuits, an ideal gas with relaxation, and others in an arbitrary nonequilibrium initial state.

A new trend in nonequilibrium thermodynamics (called "thermodynamics at a finite time") has begun to intensely develop since the mid-1970s [1–3]. This trend, which appeared at the interface of the thermodynamics of irreversible processes and the theory of optimum control, considers thermodynamic systems consisting of individual subsystems which can be assumed to be equilibrium but out of equilibrium with each other. This approach can be interpreted as that based on a certain discrete principle of local equilibrium, which is similar to the continuum principle used in the thermodynamics of equilibrium processes. Such systems can be described in the language of standard thermodynamics and one can formulate classical thermodynamic problems on the maximum efficiency of heat engines in cycles occurring in a finite time in a rigorous statement for them. Such problems are reduced to the typical problems of optimum control; their solution has led to interesting results providing a more realistic evaluation of the efficiency of the existing heat engines. Composite systems possess relaxation properties, since the system of equations that describes their interaction is relaxation-type.

Such systems are similar in many properties to the relaxing thermodynamic systems considered in [4, 5]. The latter can equivalently be presented as systems with internal state variables for which the constitutive equation of generalized forces is dependent on the running value of the configuration of the system and the vector of internal state variables whose evolution is described by supplementary relaxation equations [4, 11]. The equivalence conditions and the procedure of mutual identification of the parameters of two corresponding systems of both types are constructed based on the well-known theory of realization of dynamic systems [6, 7]. There can be an analogy with systems considered in the thermodynamics with a finite time, since each internal degree of freedom (associated with an individual internal variable) for thermodynamic systems with internal state variables can be interpreted as an individual subsystem whose interaction with the remaining subsystems and the "thermostat" is described by relaxation equations. Thermodynamic action for the systems in question in specific applications is the integral of work or reduced heat; therefore, an analog of finite-time thermodynamic problems in our case will be those of optimization (minimization) of the thermodynamic action performed from a certain nonequilibrium state on a finite time interval. Below, we consider such a problem in terms of generalized variables (configuration, generalized force, and thermodynamic action). Examples of how this formalism can describe physical systems have been given in [5].

Preliminary Data from the Theory of Generalized Thermodynamic Systems with a Memory. Let S be a finite-dimensional Euclidean space of the elements α, β, and γ with a scalar product $\langle .,. \rangle$ and a norm $|\cdot| = \langle .,. \rangle^{1/2}$ (this space will be called a configuration space) and R and R^+ be the sets of real and real nonnegative numbers.

A. V. Luikov Heat and Mass Transfer Institute, National Academy of Sciences of Belarus, 15 P. Brovka Str., Minsk, 220072, Belarus. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 78, No. 6, pp. 3–13, November–December, 2005. Original article submitted September 28, 2004.

1062-0125/05/7806-1047

The time function ε: $\mathsf{R} \to \mathsf{S}$, called the configuration trajectory of a system, is a continuous function bounded on each interval and with a derivative bounded on finite intervals; for this function there exists t_0 such that $\varepsilon(t) = \varepsilon_0$ for all $t \le t_0$ (ε_0 is a fixed element from S).

The configuration history of the system to the instant of time t is a function determined as follows:

$$\varepsilon^t(s) = \varepsilon(t - s) . \tag{1}$$

A differential configuration history to the instant of time t will be called the function $\dot{\varepsilon}^t$: $\mathsf{R}^+ \to \mathsf{S}$

$$\dot{\varepsilon}^t(s) = \frac{d}{dt}\varepsilon^t(s) = -\frac{d}{ds}\varepsilon(t - s) . \tag{2}$$

The Hilbert space $\mathcal{H}$ of specific piecewise-continuous functions f: $\mathsf{R}^+ \to \mathsf{S}$ with a compact support and a finite norm

$$\|f\| = \left(\int_0^\infty |f(s)|^2 \gamma(s)\, ds \right)^{1/2} \tag{3}$$

will be called the *space history*, where $\gamma(s)$ is the positive monotonically decreasing influence function integrable on R^+.

The state Λ is a pair $\Lambda = \{\alpha, f\}$, where $\alpha \in \mathsf{S}$ and $f \in \mathcal{H}$, and the set of all these pairs with a norm $\|\cdot\|_{\mathsf{G}}$,

$$\|\Lambda\|_{\mathsf{G}} = (|\alpha|^2 + \|f\|^2)^{1/2} , \tag{4}$$

forms the state space G.

For a prescribed configuration trajectory $\varepsilon(\cdot)$ and an arbitrary instant of time t, the system's state at the instant t is determined as

$$\Lambda^t = \{\varepsilon(t), \dot{\varepsilon}^t\} . \tag{5}$$

The constitutive equations correspond to the notion of a constitutive functional of generalized forces $\hat{\sigma}$: $\mathsf{G} \to \mathsf{S}$:

$$\hat{\sigma}(\Lambda) = \hat{\sigma}(\alpha, f) . \tag{6}$$

The functional $\hat{\sigma}$ is assumed to be continuous on G and bounded for any bounded values of the arguments.

For each configuration trajectory of the system we can uniquely determine, using the functional (6), the trajectory of generalized forces σ_ε: $\mathsf{R} \to \mathsf{S}$:

$$\sigma_\varepsilon(t) = \hat{\sigma}(\Lambda^t) = \hat{\sigma}(\varepsilon(t), \dot{\varepsilon}^t) . \tag{7}$$

A process of duration $T (T > 0)$ is the bounded and piecewise-continuous function h: $(0, T] \to \mathsf{S}$ with which the transformation P_h^T: $\mathsf{G} \to \mathsf{G}$ in the state space is associated; this transformation is determined as follows: for each $\Lambda = \{\alpha, f\} \in \mathsf{G}$, we have

$$P_h^T \Lambda \equiv \Lambda_{(h)} = \{\alpha_{(h)}, p_h^T f\} , \tag{8}$$

where

$$\alpha_{(h)} = \alpha + h^i(T) ; \quad h^i(t) = \int_0^t h(s)\, ds , \tag{9}$$

the transformation p_h^T in the history space is determined as

$$p_h^T f(s) = \begin{cases} f(s-T), & s \in [T, \infty); \\ h(T-s), & s \in [0, T), \end{cases} \tag{10}$$

and P_h^T is called the transformation of states associated with the process h. The process h is said to transfer the system from the initial state Λ to the final state $P_h^T\Lambda$.

The action (or thermodynamic action) performed by the process h of duration T from the state Λ is determined as the function a: $\mathsf{G} \times \mathcal{P} \to \mathsf{R}$ prescribed as follows:

$$\mathsf{a}(\Lambda, h) \equiv \mathsf{a}(\alpha, f, h) = \int_0^T \langle \hat{\sigma}(P_h^t\Lambda), h(t) \rangle \, dt, \tag{11}$$

where P_h^t is the transformation associated with the reduction of the process h by the interval $(0, t)$.

The postulate expressing the second law of thermodynamics in the sense of Coleman and Owen [13] is formulated as follows:

In any initial state $\Lambda \in \mathsf{G}$, *the action* a *possesses the following property: for any* $\xi > 0$ *there exists* $\delta > 0$ *such that, if* $h \in \mathcal{P}$ *and*

$$\|\Lambda - P_h^T\Lambda\|_s < \delta, \tag{12}$$

we have

$$\mathsf{a}(\Lambda, h) > -\xi. \tag{13}$$

In other words, this postulate means that if a certain process transfers the system to a fairly small vicinity of the initial state, the action performed in this process will be nonnegative with a degree of accuracy as high as is wished. This statement is a generalization and a rigorous mathematical formalization of the formulation (used in classical thermodynamics) of the second law in the form of the requirement that the integral of the reduced heat be nonnegative in any cyclic process.

In [5], for the functionals (6) of the partial form

$$\hat{\sigma}(\alpha, f) = \sigma_0(\alpha) + \hat{\sigma}'(f) \tag{14}$$

it has been proved that for the postulate formulated above to hold true it is necessary and sufficient that a continuously differentiable state function Ψ_0: $\mathsf{S} \to \mathsf{R}$ exists such that

$$\sigma_0(\alpha) = \partial_\alpha \psi_0(\alpha), \tag{15}$$

and the functional $\hat{\sigma}'$ satisfies the following inequality:

$$\int_0^T \langle \hat{\sigma}'(P_h^t 0^+), h(t) \rangle \, dt \geq 0, \quad \forall h \in \mathsf{P} \quad \text{and} \quad T > 0. \tag{16}$$

Formulation of the Problem. Let the thermodynamic system be described by a constitutive equation of the form (6), which is linear in both arguments. It can be shown that in the state space determined above the general solution of such an equation can be represented as

$$\hat{\sigma}(\alpha, f) = \mathbf{E}\alpha + \int_0^\infty \mathbf{R}(s) f(s)\, ds\,, \tag{17}$$

where $\mathbf{E}$: $\mathsf{S} \to \mathsf{S}$ is a linear operator, which must be symmetric ($\mathbf{E} = \mathbf{E}^\times$) in accordance with thermodynamic condition (15), and $\mathbf{R}$: $\mathsf{R}^+ \to \mathcal{L}(\mathsf{S})$ is the relaxation function, for which, according to (16), the condition

$$\int_0^T \int_0^t \langle (\mathbf{R}(t-s)\, h(s)), h(t)\rangle\, dsdt \geq 0\,, \quad \forall h \in \mathsf{P} \quad \text{and} \quad T > 0 \tag{18}$$

must be fulfilled. Furthermore, for the condition of stability of equilibrium states to be fulfilled we set $\mathbf{E} \geq 0$ (here and below, the sign of inequality in relation to the operator must be understood as $\langle \alpha, \mathbf{E}\alpha\rangle \geq 0$, and $\forall \alpha \in \mathsf{S}$).

The action performed by such a system in the process h of duration T from the state $\Lambda = \{\alpha, f\}$, with account for (11) and (17) and the symmetry of $\mathbf{E}$, is represented as

$$\mathsf{a}(\alpha, f, h) = \int_0^T \langle \hat{\sigma}(P_h^t \Lambda), h(t)\rangle\, dt =$$

$$= -\frac{1}{2}\langle \alpha, \mathbf{E}\alpha\rangle + \frac{1}{2}\langle \alpha + h^i(T), \mathbf{E}(\alpha + h^i(T))\rangle + \int_0^T \int_0^t \langle (\mathbf{R}(s)\, p_h^t f(s)), h(t)\rangle\, dsdt\,. \tag{19}$$

We symmetrically complete the definition of the relaxation function $\mathbf{R}$ prescribed on the positive semiaxis on the negative semiaxis, i.e., we introduce the function $\tilde{\mathbf{R}}$ as follows:

$$\tilde{\mathbf{R}}(s) = \begin{cases} \mathbf{R}(s)\,, & s \in [0, \infty)\,; \\ \mathbf{R}^\times(-s)\,, & s \in (-\infty, 0)\,. \end{cases} \tag{20}$$

It has been allowed for in relation (20) that (18) yields the symmetry of $\mathbf{R}(0)$, i.e., $\mathbf{R}(0) = \mathbf{R}^\times(0)$, as has been shown in [14]. Using this definition and relations (8) and (10), we can transform expression (19) to the form

$$\mathsf{a}(\alpha, f, h) = \langle \alpha, \mathbf{E}h^i(s)\rangle + \frac{1}{2}\langle h^i(T), \mathbf{E}h^i(T)\rangle +$$

$$+ \int_0^T \int_0^\infty \langle h(t), \mathbf{R}(s+t) f(s)\rangle\, dsdt + \frac{1}{2}\int_0^T \int_0^T \langle h(t), \tilde{\mathbf{R}}(t-s)\, h(s)\rangle\, dsdt\,. \tag{21}$$

Then the problem on minimization of the thermodynamic action performed from a certain nonequilibrium state on a finite time interval T is reduced to the classical problem of finding the minimum of the functional (21) on the set of all processes of duration T. Computing the functional derivative with respect to h (at a fixed T) for this functional and equating it to zero, we arrive at the necessary condition of its minimum

$$\mathbf{E}\alpha + \int_0^\infty \mathbf{R}(t+s) f(s)\, ds + \int_0^T (\tilde{\mathbf{R}}(t-s) + \mathbf{E})\, h(s)\, ds = 0\,, \quad \forall t \in [0, T]\,. \tag{22}$$

Solving Eq. (22) for h, we can find the optimum process and subsequently calculate the minimum action from it.

We consider the formulated problem for a particular case of a relaxation system [4, 7] (this case is of practical importance). For these systems the relaxation function is represented as follows:

$$\mathbf{R}(t) = \sum_{i=1}^{N} \mathbf{R}_i \exp(-\lambda_i t), \tag{23}$$

where $\mathbf{R}_i = \mathbf{R}_i^{\times} \geq 0$, $\forall i \in \{1, 2, \ldots N\}$, and $\lambda_N > \lambda_{N-1} > \ldots > \lambda_1 > 0$. The overwhelming majority of continuum models with a memory or with internal state variables and electric *RC* or *LC* circuits, mechanical elasto-damped systems, and others are described by such systems. The thermodynamic constraint (18) for them holds true even in a stronger formulation of the strict inequality (see [7]). Also, these systems differ in that the family of nonequilibrium thermodynamic potentials for them contains the central potential [4] distinguished by its special properties and corresponding to the standard potential in the cases where it can be constructed. Thermodynamic systems with a memory and relaxation functions of the form (23) can be represented as systems with internal state variables [4], where the number of exponents N in this case corresponds to the number of internal state variables. We consider a one-dimensional case (one-dimensional configuration space S) for which σ and ε as well as R_i and E in (22) are scalars. For an infinite time interval and $E = 0$, such a problem has been solved in [8] in terms of the maximum work which can be done by a viscoelastic body from an arbitrary nonequilibrium state (maximum recoverable work). For such a mechanical system the work done by the system in an arbitrary process is expressed as the integral (21) with a minus sign; therefore, the problem on the minimum action corresponds to the problem on the maximum work. Since the latter is attained in this case in the process performed in an infinite time interval, the average power will be equal to zero; therefore, the formulation and solution of an analogous problem for a finite time interval would make it possible to provide a more realistic evaluation of the limiting power characteristics of such systems.

Finding the Optimum Process. We will seek the solution of Eq. (22) with the relaxation function (17) for the one-dimensional system in the following form:

$$h_0(t) = C + A_0\delta^+(t) + B_0\delta^-(t-T) + \sum_{j=1}^{N-1} A_j \exp(-\mu_j t) + \sum_{j=1}^{N-1} B_j \exp(\mu_j t), \tag{24}$$

where C, A_0, B_0, A_j, B_j, and μ_j ($j = 1, 2, \ldots, N-1$) are the undetermined constants and δ^+ and δ^- are the Dirac delta functions determined here so that $\delta^+(s) = 0$ and $\delta^-(s) = 0$ for $t \neq 0$ and $\int_{-0}^{\infty} \delta^+(s)ds = 1$ and $\int_{-\infty}^{+0} \delta^-(s)ds = 1$. Introducing the notation

$$K_i = \int_0^{\infty} \exp(-\lambda_i s) f(s)\, ds, \quad i = 1, 2, \ldots, N; \quad K_0 = -\alpha \tag{25}$$

and substituting the selected form of the solution (24) and the scalar relaxation function (23) into (22), after certain transformations we obtain

$$EK_0 - \sum_{i=1}^{N} R_i K_i \exp(-\lambda_i) = E\left(CT + A_0 + B_0 + \sum_{j=1}^{N-1}\left(\frac{A_j}{\mu_j}(1 - \exp(-\mu T)) + \frac{B_j}{\mu_j}(\exp(\mu T) - 1)\right)\right) +$$

$$+ 2C\sum_{i=1}^{N}\frac{R_i}{\lambda_i} + \sum_{i=1}^{N} R_i \exp(-\lambda_i t)\left[-\frac{C}{\lambda_i} + A_0 - \sum_{j=1}^{N-1}\left(\frac{A_j}{\lambda_i - \mu_j} + \frac{B_j}{\lambda_i + \mu_j}\right)\right] +$$

$$+ \sum_{i=1}^{N} R_i \exp(\lambda_i t)\exp(-\lambda_i T)\left[-\frac{C}{\lambda_i} + B_0 - \sum_{j=1}^{N-1}\left(\frac{A_j \exp(-\mu T)}{\lambda_i + \mu_j} + \frac{B_j \exp(\mu T)}{\lambda_i - \mu_j}\right)\right] +$$

$$+ 2\sum_{j=1}^{N-1} A_j \exp(-\mu_j t) \sum_{i=1}^{N} \frac{R_i \lambda_i}{\lambda_i^2 - \mu_j^2} + 2\sum_{j=1}^{N-1} B_j \exp(\mu_j t) \sum_{i=1}^{N} \frac{R_i \lambda_i}{\lambda_i^2 - \mu_j^2}. \tag{26}$$

We note that the variables K_i (i = 1, 2, ..., N) introduced in (25) correspond to the internal state variables [4, 11]. Taking into account that the parameters μ_i are arbitrary, let us assume that the condition

$$\sum_{i=1}^{N} \frac{R_i \lambda_i}{\lambda_i^2 - \mu_j^2} = 0 \quad \text{for} \quad j = 1, 2, ..., N-1 \tag{27}$$

is fulfilled in (26), i.e., that μ_j^2 are $N-1$ roots of the equation

$$F(x) \equiv \sum_{i=1}^{N} \frac{R_i \lambda_i}{\lambda_i^2 - x} = 0. \tag{28}$$

We easily assure ourselves that Eq. (28) has $N-1$ real roots x_f, since the function F is continuous on each time interval $\lambda_f^2 \le x \le \lambda_{j+1}^2$ (j = 1, 2, ..., $N-1$) and varies from $+\infty$ to $-\infty$ and consequently must have a root within the interval. Hence it is clear that

$$\lambda_j^2 < x_j < \lambda_{j+1}^2, \quad j = 1, 2, ..., N-1. \tag{29}$$

Thus, (27) will be fulfilled if we set

$$\mu_i = +\sqrt{x_j}, \quad j = 1, 2, ..., N-1 \tag{30}$$

in (24). Then the last two terms in (26) disappear, and for this relation to hold true it only remains for us to assume that the coefficients of the linearly independent functions 1, exp ($-\lambda_1 t$), exp ($-\lambda_2 t$), ..., exp ($-\lambda_N t$), exp ($\lambda_1 t$), exp ($\lambda_2 t$), ..., exp ($\lambda_N t$) are equal to zero. As a result, we arrive at the following linear system of $2N+1$ equations for $2N+1$ unknown constants C, A_j, and B_j, (j = 0, 1, 2, ..., $N-1$):

$$C\left(T + \frac{2}{E}\sum_{i=1}^{N} \frac{R_i}{\lambda_i}\right) + A_0 + B_0 + \sum_{j=1}^{N-1} \frac{A_j}{\mu_j}(1 - \exp(-\mu_j T)) + \sum_{j=1}^{N-1} \frac{B_j}{\mu_j}(\exp(\mu_j T) - 1) = K_0,$$

$$\frac{C}{\lambda_i} - A_0 + \sum_{j=1}^{N-1} \frac{A_j}{\lambda_i - \mu_j} + \sum_{j=1}^{N-1} \frac{B_j}{\lambda_i + \mu_j} = K_i, \quad j = 1, 2, ..., N; \tag{31}$$

$$\frac{C}{\lambda_i} - B_0 + \sum_{j=1}^{N-1} \frac{A_j \exp(-\mu_j T)}{\lambda_i + \mu_j} + \sum_{j=1}^{N-1} \frac{B_j \exp(\mu_j T)}{\lambda_i - \mu_j} = 0, \quad j = 1, 2, ..., N.$$

It is easily shown that system (31) has a unique solution. Indeed, if the assumed optimum process (24) is substituted into the expression for the thermodynamic action (21), this will result in a polynomial of second order in parameters C, A_j, and B_j. The quadratic terms of this polynomial are obtained from the second and fourth terms on the right-hand side of (21). However the last of these terms is always strictly positive by virtue of the thermodynamic requirements (18) fulfilled for relaxing systems in the strong form of a strict inequality, and the first term is either strictly positive (for $E > 0$) or disappears (for E = 0; in this case one also sets C = 0). Thus, the leading terms of this polynomial always form a positive-definite quadratic form whose coefficients matrix can be reduced, using (27), to a form coinci-

dent with the matrix of system (31). A necessary condition of the positive-definiteness of the quadratic form is the strict positiveness of the determinant of its matrix; hence the matrix of system (31) is not degenerate and, consequently, the system has a unique solution.

Thus, determining the constants μ_i from (28) and (30) and the constants C, A_j, and B_j from (31), we find the minimum thermodynamic action by substitution of the solution (24) together with (23) into (21). To simplify computations we can use Eq. (22). Next we interpret the results in terms of the maximum recoverable work for viscoelastic systems (for example, continua). If σ and ε mean the mechanical stress (force) and the relative deformation, then the work done by the system, as has been indicated above, will be expressed as the action (21) taken with an opposite sign; therefore, the above-formulated problem on the minimum thermal action corresponds to the problem on the maximum recoverable work. Carrying out the substitutions indicated above, we obtain the following expression for the maximum work recoverable during the time T for the relaxing system with the relaxation function (23):

$$W_{\mathrm{m}T}(T) = \frac{1}{2} EK_0^2 - K_0 C \sum_{i=1}^{N} \frac{R_i}{\lambda_i} -$$

$$- \frac{1}{2} \sum_{i=1}^{N} R_i K_i \left[A_0 + B_0 \exp(-\lambda_i T) + \sum_{j=1}^{N-1} \left(A_j \frac{1 - \exp(-(\lambda_i + \mu_j) T)}{\lambda_i + \mu_j} + B_j \frac{1 - \exp(-(\lambda_i - \mu_j) T)}{\lambda_i - \mu_j} \right) \right]. \tag{32}$$

The optimum process in which this maximum work is attained is described by relation (24) with the constants determined from (27) and (31). Passing to the limit $T \to \infty$ in (31) and (32), we arrive at relations generalizing the results of [8], where the case $E = 0$ has been considered, and expressing the maximum recoverable work for this system without constraints on the duration of the process in which it is recovered:

$$W_{\mathrm{m}} = \frac{1}{2} EK_0^2 - \frac{1}{2} \sum_{i=1}^{N} R_i K_i \left[\tilde{A}_0 + \sum_{j=1}^{N-1} \frac{\tilde{A}_j}{\lambda_i + \mu_j} \right], \quad j = 0, 1, 2, ..., N-1, \tag{33}$$

where $\tilde{A}_j$ is the solution of the system

$$- A_0 + \sum_{j=1}^{N-1} \frac{A_j}{\lambda_i - \mu_j} = K_i, \quad i = 1, 2, ..., N. \tag{34}$$

The optimum process in which the maximum work (33) is recovered is a composition (successive implementation) of two processes of infinite duration:

$$h(t) = \tilde{A}_0 \delta^+(t) + \sum_{j=1}^{N-1} \tilde{A}_j \exp(-\mu_j t) \tag{35}$$

and

$$h_1(t) = \left(K_0 - \tilde{A}_0 - \sum_{j=1}^{N-1} \frac{\tilde{A}_j}{\mu_i} \right) \frac{1}{T_1}, \quad t \in [0, T_1], \quad T_1 \to \infty. \tag{36}$$

The analytical expression obtained in [8] for the constants $\tilde{A}_j$ disregards the component (36) of the optimum process, since the case $E = 0$ has been considered there.

Discussion of the Results. We note that the quantities presented in (32) and (33) are the state functions for the thermodynamic system (22) and (23), since the parameters K_i in (32) and (33) and (31) and (34) are related to the

state parameters $\{\alpha, f\}$ by relations (25). The state function (33) is equivalent by definition to the so-called minimum nonequilibrium thermodynamic potential defined in [9, 10]. It is of interest to compare them to another state function that is interpreted as free energy for viscoelastic systems and is the central thermodynamic potential for generalized thermodynamic systems [9, 10]. It is calculated as the elastic energy of a viscoelastic system subjected to deformation, which has failed to relax. For example, for a viscoelastic mechanical system of springs and viscous dampers, this is the total potential energy of the springs, for an electric *RC* circuit, this is the energy of the capacitors, etc. For the case considered, this function is expressed as [12]

$$W = \frac{1}{2} E K_0^2 + \frac{1}{2} \sum_{i=1}^{N} R_i K_i^2 . \tag{37}$$

In numerical analysis of the results obtained, it is also of interest to compare the work W_{mT} recovered over the period T in the process optimum for this time interval and the work W_T done over the same period in the process optimum in the absence of constraints on its duration. To calculate the latter we must substitute the reduction by the interval [0, T] of the composition of the processes (35) and (36) into (21) with account for (23) and for the opposite signs of the work and the action. Since the component (36) is "cut out" in reduction, we use only (35) in the computations to give

$$W_T(T) = \frac{1}{2} E K_0^2 - \frac{1}{2} E \left(K_0 - \tilde{A}_0 - \sum_{j=1}^{N-1} \frac{\tilde{A}_j}{\mu_i} \right)^2 +$$

$$+ \frac{1}{2} \tilde{A}_0^{\,2} \sum_{i=1}^{N} R_i - \sum_{i=1}^{N} R_i K_i \sum_{j=1}^{N-1} \frac{\tilde{A}_j \left(1 - \exp\left(-(\lambda_i + \mu_j) T\right)\right)}{\lambda_i + \mu_j} + \tilde{A}_0 \sum_{i=1}^{N} \sum_{j=1}^{N-1} \frac{R_i \tilde{A}_j}{\lambda_i + \mu_j} \exp\left(-(\lambda_i + \mu_j)\right) -$$

$$- \sum_{i=1}^{N} \sum_{j=1}^{N-1} \sum_{k=1}^{N-1} \frac{R_i \tilde{A}_j \tilde{A}_k}{(\lambda_i + \mu_j)(\mu_j + \mu_k)} \left(1 - \frac{(\lambda_i + \mu_j) \exp\left(-(\mu_j + \mu_k) T\right) (\mu_j + \mu_k) \exp\left(-(\lambda_i + \mu_j) T\right)}{\lambda_i - \mu_k} \right). \tag{38}$$

A numerical analysis of the results obtained will be carried out for a system with a three-dimensional space of internal variables, i.e., for $N = 3$. We consider the system with the following parameters (the parameters are prescribed in dimensionless form; if we are dealing with a specific physical system, it is assumed that all the variables are appropriately made dimensionless): $\lambda_1 = 0.5$, $\lambda_2 = 2$, $\lambda_3 = 8$, $R_1 = 1.5$, $R_2 = 3$, $R_3 = 9$, and $E = 0$. The state parameters in the space of internal variables are the variables K_i ($i = 1$, 2, and 3) determined in (25). Since the system is linear, multiplying the three-dimensional vector K_i by an arbitrary scalar leads just to a scaling change in the result. Therefore, to eliminate these trivial variations of state from consideration we set

$$K_1^2 + K_2^2 + K_3^2 = 1 \tag{39}$$

and will prescribe the state as a function of two parameters ω and φ as follows:

$$K_1 = \cos\omega , \quad K_2 = \sin\omega \sin\varphi , \quad K_3 = \sin\omega \cos\varphi . \tag{40}$$

It is clear that relation (39) holds true, and the parameters ω and φ are the azimuth and meridian angles for the end of the vector K_i on a unit sphere. Figure 1 shows, for different states, the free energy W (relation (37), curve 1), the maximum recoverable work W_m (relation (33), curve 2), and the instantaneous initial work in the optimum process recovering the maximum work $W_T(0)$ (relation (38) at $T = 0$, curve 3). The latter quantity describes the contribution of the work done in instantaneous initial deformation of the system to W_m (delta function in (35)). In constructing all the dependences, the coefficients C, A_j, B_j, and $\tilde{A}_j$ were determined numerically as the solutions of the corresponding systems (31) and (34). The system's parameter E (having the meaning of the elastic modulus in our case)

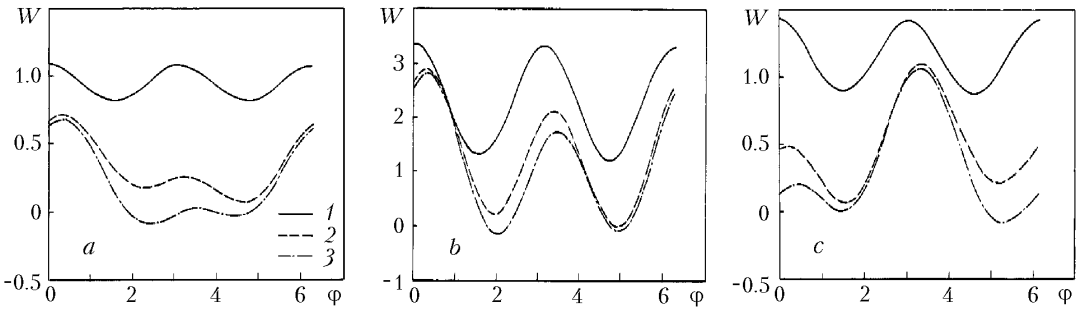

Fig. 1. Force energy (1), maximum recoverable work (2), and instantaneous initial work in the optimum process (3) for different states for $E = 0$: a) $\omega = 0.3$; b) 0.99; c) 2.7.

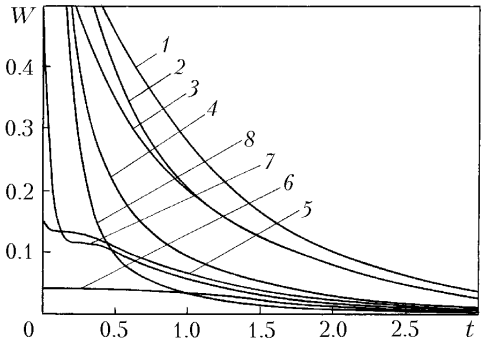

Fig. 2. Relaxation of the free energy (1–4) and the maximum recoverable work (5–8) from different nonequilibrium states: 1 and 5) $\varphi = 3$ and $\omega = 0.15$; 2 and 6) 4.8 and 0.55; 3 and 7) 2.7 and 0.55; 4 and 8) 0.75 and 0.99.

was set to be equal to zero and was not varied, since the terms determined by it introduce a trivial addition of the potential energy into W.

The calculation results show that for most states, the maximum recoverable work is much smaller than the free energy (see Fig. 1), i.e., most of the stored free energy cannot, in principle, be recovered from the system and will inevitably be scattered as heat when the work is done by the system.

In most cases, a considerable part of the work recovered (and sometimes the entire work) is done by initial instantaneous deformation in the optimum process (Fig. 1, curve 3). Of interest is the fact that, in many states, the instantaneous initial work in the optimum process is negative, i.e., to recover the maximum work from the system it is necessary at first to do work over the system in the optimum process (see, for example, Fig. 1a (φ = 2–3), Fig. 1b (φ = 1.8–2.3), and Fig. 1c (φ = 5–5.9)). For a single found state in which the entire free energy can be recovered from the system (Fig. 1b, $\varphi = 0.78$ and $\omega = 0.99$), the entire work is done in instantaneous initial deformation much as in systems with a one-dimensional space of internal states [8]. The values of the parameters ω and φ for this state correspond to the vector of the internal variables K_i; with three identical components and in instantaneous deformation from it the system acts as a one-dimensional one. We note that the curve of the maximum work recoverable in a finite time interval W_{mT} is always located between curves 2 and 3 or curve 2 and the abscissa in Fig. 1. This follows from the definition of this work; at $T \to 0$, it is either smaller than the zero one (absence of deformation) or no smaller than $W_T(0)$, if the latter is positive, but when $T \to \infty$ the indicated work tends to W_m by definition.

If the system which is initially in a nonequilibrium state is left at rest, its internal state will relax to an equilibrium one; the free energy and the maximum recoverable work will accordingly decrease. Figure 2 shows the relaxation of these quantities with time from different nonequilibrium states. These data have been calculated according to relations (33), (34), and (37) with allowance for the fact that the state variables determined by relation (25) evolve for the system at rest with time as follows:

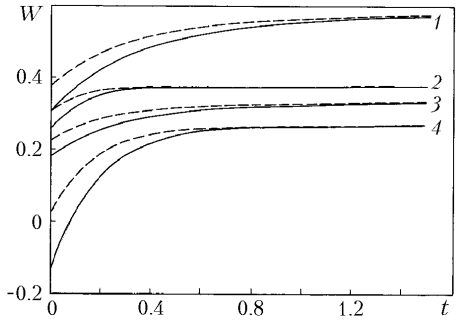

Fig. 3. Time dependence of the work done during the time t in the process optimum for an infinite time (solid curve) and in the process optimum for the time interval t (dashed curve) for different initial states: 1) $\varphi = 3$ and $\omega = 0.5$; 2) 5.3 and 0.99; 3) 1.5 and 0.3; 4) 5.2 and 2.

$$K_i(t) = K_i^0 \exp(-\lambda_i t), \tag{41}$$

where K_i^0 are the state parameters at the initial instant of time. This follows from (25) with allowance for the fact that the initial history $f(s)$ in relaxation is transformed to a one-parameter (parameter t) family of the histories $p_u^t f(s)$, determined by relation (10), where $u(s) \equiv 0$ is a stationary process. As is clear from Fig. 2, the free energy mainly relaxes accordingly to an exponent-like profile, whereas the relaxation profiles of the maximum recoverable work are much more diverse and show an interesting feature in some cases: they have a "shelf," i.e., a time interval during which this quantity is virtually constant (Fig. 2, curves 5 and 8). Such a feature can manifest itself, for example, in the gasdynamics of a relaxing gas; therefore, the use of the concept of a minimum thermodynamic potential (corresponding to the maximum recoverable work in this case) would make it possible to more purposefully optimize nonequilibrium gasdynamic processes.

The maximum recoverable work is done by the system in the optimum process whose duration is unlimited. If we consider the work done in this process in a finite time, it will certainly be smaller and even negative in most cases. Conversely, the work done in the process, which is optimized for recovery of the maximum work in a finite time, is always positive and exceeds that mentioned above. The time dependences of these two works calculated respectively from formulas (38) and (32) are presented in Fig. 3 whose data confirm the foregoing. Thus, curves 4 show that, in the process optimized for an infinite time interval, work significantly differing from that for the process optimized for a finite time is done at short times. To the instant of time $t = 0.08$, they differ in sign; therefore, by the instant $t = 0.08$, the zero work is done in the first process, whereas the positive work equal to approximately half the maximum recoverable work is done in the second process. For the initial states in which a considerable part of the maximum recoverable work is done in instantaneous initial deformation, this difference is not so significant.

Figure 4 shows the optimum processes in which the maximum recoverable work is produced for finite and infinite time intervals. These plots represent the time behavior of deformation in such processes. Since the process h has been determined as the deformation rate, the above data have been plotted as the time integrals of the functions (24) and (35). The duration of the time interval for which this process is optimum is determined on the plot by the instants of time from which the deformation becomes constant. The curve for which there is no portion with a fixed deformation corresponds to the optimum process on an infinite time interval. As follows from the results presented, the main difference in the optimum processes for the finite and infinite intervals is the presence of the second instantaneous deformation at the end of the process. Although the smooth parts of the processes do not coincide, they differ only slightly. In certain initial states (Fig. 4c), the direction of the instantaneous deformation closing the process changes with growth in the duration of the time interval. In this case, we have such a duration of the interval for which there is no instantaneous final deformation (process optimum for the interval $T = 0.5$ in Fig. 4c). In the case of the initial states the optimum processes for which are presented in Fig. 4a and c, there are data on the dynamics of recovery of work in processes finite and infinite with time; these data are presented in Fig. 3 (curves 2 and 4). Their analysis shows that even for very short finite intervals the work done in the processes is nearly the same, although the form

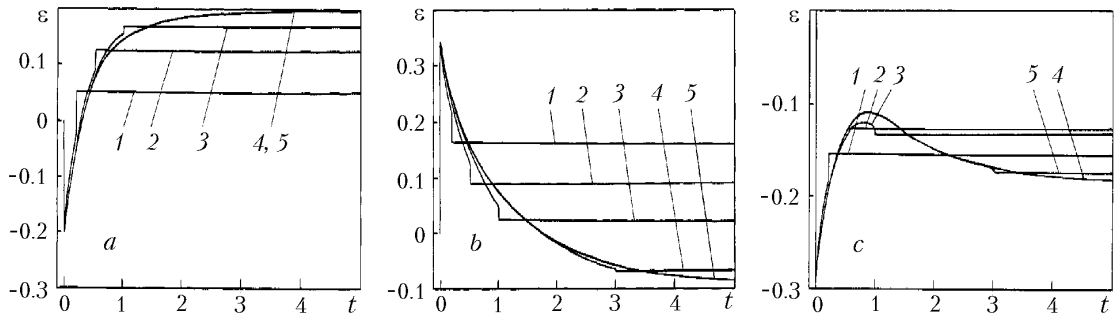

Fig. 4. Optimum processes realizing the maximum recoverable work for finite time intervals (1–4) or an infinite (5) interval (the duration of the interval is determined by the instant of time from which deformation becomes constant): a) $\varphi = 5.2$ and $\omega = 2$; b) 3.5 and 0.5; c) 5.3 and 0.99.

of them differs quite significantly for the finite and infinite time intervals. Thus, according to the data presented in Fig. 4c and Fig. 3 (curves 2), even for the duration of the interval $T = 0.2$, the works done over this period in the process optimized on the finite interval mentioned and in the process optimized on an infinite interval differ by no more than 3%, whereas for $T = 0.5$ they virtually coincide, although the curves of the corresponding processes differ quite significantly.

In closing, we note that the given results are also the solution of an analogous problem for a system where, instead of the constitutive equation with a memory (17) (with the relaxation function (23)), one prescribes equations for thermodynamic systems with internal state variables [4] of the form

$$\hat{\sigma}(\alpha, x) = \mathbf{E}\alpha + \mathbf{C}x , \tag{42}$$

$$\dot{x}(t) = \mathbf{A}x(t) + \mathbf{B}\dot{\varepsilon}(t) , \tag{43}$$

where x is the vector of internal state variables (this is the set K_i in the case considered above), which belongs to the vector space of internal variables X, and $\mathbf{A}$, $\mathbf{B}$, and $\mathbf{C}$ are the linear operators: $\mathbf{A} \in \mathcal{L}(\mathsf{X})$, $\mathbf{B} \in \mathcal{L}(\mathsf{S}, \mathsf{X})$, and $\mathbf{C} \in \mathcal{L}(\mathsf{X}, \mathsf{S})$; they are such that the relaxation function (17) can be represented by these operators as

$$\mathbf{R}(\tau) = \mathbf{C} \exp(\mathbf{A}\tau)\, \mathbf{B} . \tag{44}$$

In such a representation, this problem can find application to a wider class of physical systems.

This work was carried out with financial support from the Belarusian Foundation for Basic Research, project F99-R153.

NOTATION

a, thermodynamic action; $\tilde{A}_j$, solution of system (34) ($j = 0, 1, 2, ..., N-1$); A_0, B_0, A_j, B_j, μ_j, and C, undetermined constants in the representation (24) for the solution of Eq. (22) ($j = 1, 2, ..., N-1$); $\mathbf{A}$, $\mathbf{B}$, and $\mathbf{C}$, linear operators in the representation (42) and (43) of the system with internal variables; $\mathbf{E}$, operator prescribing the linear equilibrium part of a generalized force; G, state space; h, process of duration T; $\mathcal{H}$, Hilbert history space; K_i, parameters determined in (25); P_h^T, transformation in the state space associated with the process h; p_h^T, transformation in the history space associated with the process h; $\mathcal{P}$, set of processes; $\mathbf{R}$, relaxation function; $\mathbf{R}_j$, operator coefficients prescribing the relaxation function (23); R and R^+, sets of real and real nonnegative numbers respectively; S, finite-dimensional Euclidean space of the elements α, β, γ, ...; t and t_0, time and instant of time; W, free energy for the relaxing system; $W_{\mathrm{m}T}$, maximum work recoverable over the period T for the relaxing system; W_{m}, maximum work recoverable over an arbitrary period for the relaxing system; W_T, work done during the time T in the process optimum for the case of the absence of constraints on its duration; x_j, roots of Eq. (28); x, vector of internal state variables;

$\gamma(s)$, influence function; δ^+ and δ^-, Dirac delta functions; ε, configuration trajectory of the system; ε^t, configuration history of the system to the instant of time t; $\dot{\varepsilon}^t$, differential configuration history of the system to the instant of time t; Λ, state; Λ^t, state of the system at the instant t; $\hat{\sigma}$, constitutive functional of generalized forces; σ_ε, trajectory of generalized forces; ξ and δ, positive parameters; σ_0, equilibrium generalized force; $\hat{\sigma}'$, nonequilibrium part of a generalized force; ψ_0, equilibrium thermodynamic potential; λ_i, inverse times of relaxation in (23); ω and φ, parameters in the representation (40) for states. Subscripts: m, maximum; 0, equilibrium.

REFERENCES

1. F. L. Curzon and B. Ahlborn, Efficiency of a Carnot engine at maximum power output, *Amer. J. Phys.*, **43**, 22–24 (1975).
2. L. M. Rozonoér and A. M. Tsirlin, Optimum control over thermodynamic processes, *Avtomat. Telemekh.*, No. 1, 70–79; No. 2, 88–101; No. 3, 50–64 (1983).
3. V. N. Orlov and A. V. Rudenko, Optimum control in the problems of limited possibilities of thermodynamic processes, *Avtomat. Telemekh.*, **46**, 7–39 (1985).
4. V. T. Borukhov and A. I. Shnip, Thermodynamic theory of relaxing systems, in: *Proc. IV Minsk Int. Forum "Heat and Mass Transfer–MIF-2000"* [in Russian], 22–26 May 2000, Vol. 3, Minsk (2000), pp. 151–158.
5. A. I. Shnip, Theory of generalized thermodynamic systems with memory, *Inzh.-Fiz. Zh.*, **75**, No. 1, 21–31 (2002).
6. R. E. Kalman, P. L. Falb, and M. A. Arbib, *Topics in Mathematical System Theory*, McGraw-Hill, New York (1969).
7. J. Willems, Realization of systems with internal passivity and symmetry constraints, *J. Franklin Inst.*, **301**, No. 6, 605–621 (1978).
8. S. Breuer and E. T. Onat, On recoverable work in linear viscoelasticity, *ZAMP*, **15**, No. 2, 12–21 (1964).
9. V. T. Borukhov, V. L. Kolpashchikov, and A. I. Shnip, Linear thermodynamic systems with memory. III. Theory of thermodynamic nonequilibrium potentials, *Inzh.-Fiz. Zh.*, **69**, No. 5, 707–715 (1996).
10. V. L. Borukhov and A. I. Shnip, Subordinated systems and dissipative inequality for linear finite-dimensional passive systems, *System Sci.*, **25**, No. 4, 15–24 (1999).
11. B. D. Coleman and M. E. Gurtin, Thermodynamics with internal state variables, *J. Chem. Phys.*, **47**, No. 2, 597–613 (1967).
12. D. Bland, *Theory of Linear Viscoelasticity*, Pergamon Press, London (1960).
13. B. D. Coleman and D. R. Owen, A mathematical foundation for thermodynamics, *Arch. Rat. Mech. Anal.*, **54**, No. 1, 1–102 (1974).
14. V. L. Kolpashchikov and A. I. Shnip, Thermodynamic constraints of constitutive equations in thermoviscoelasticity: New interrelations of cross effects, *Prikl. Mat. Mekh.*, **59**, No. 1, 280–289 (1995).