

LINEAR THERMODYNAMIC SYSTEMS WITH MEMORY. III. THEORY OF THERMODYNAMIC NONEQUILIBRIUM POTENTIALS

V. T. Borukhov, V. L. Kolpashchikov, and
A. I. Shnip

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In the last paper of this series on nonequilibrium thermodynamics of linear systems with memory, methods of the theory of linear passive dynamic systems are used to construct a complete family of thermodynamic nonequilibrium potentials for the thermodynamic systems considered. It is shown by a specific example that the property of nonuniqueness of the thermodynamic potential is inherent even in very simple thermodynamic systems, and its possible physical interpretation is discussed.

Introduction. In the previous articles of this series [1, 2] we formulated a theory of generalized linear thermodynamic systems with memory and proved the necessary and sufficient conditions for satisfaction of the second principle. In the proof we used the so-called entropy-free formulation of the second principle so that entropy (or, generally speaking, a thermodynamic potential) would be a concept constructed in the theory. The general theory gives only a definition of thermodynamic potentials as extreme constructions on a certain set of processes [1-4]; therefore, the problem of derivation of explicit expressions for them arises, and this work is concerned with this derivation for the above mentioned linear thermodynamic systems with memory. We managed to solve this problem because the theory of thermodynamic systems considered shows a far-reaching analogy with the theory of passive dynamic systems [5].

Since our main results make considerable use of concepts, methods, and results of the theory of linear passive dynamic systems and this work is mainly intended for physicists and mechanical engineers, we will start with a brief review of some necessary information from this theory [5].

1. Some Information from the Theory of Linear Passive Dynamic Systems. Let C , R , R^+ , and R^{++} be sets of complex, material, material non-negative, and material positive numbers, respectively. If $L(W_1, W_2)$ is the space of linear operators from the vector space W_1 to the vector space W_2 , the norm of the operator $L \in L(W_1, W_2)$ is defined by

$$\|L\| = \sup \{ |Lx| : x \in W_1, |x| = 1 \}, \tag{1.1}$$

and the element from $L(W_2, W_1)$ conjugated to L and denoted by L^\times is found from the relation

$${}_y^1 Lx = x^2 L^\times y, \tag{1.2}$$

where ${}_y^1$ and ${}_x^2$ represent scalar products in W_1 and W_2 , respectively.

A linear dynamic system of the input-output type is described by a relation of the type [5]

$$y(t) = W_0 u(t) + \int_{-\infty}^t W(t-\tau) u(\tau) d\tau, \tag{1.3}$$

where $u(\cdot): R \rightarrow V_I$ is the input, $y(\cdot): R \rightarrow V_O$ is the output, V_I and V_O are the finite-dimensional vector spaces of the input and output parameters, respectively, and $W_0 \delta(\cdot) + W(\cdot): R^+ \rightarrow L(V_I, V_O)$ is the pulse response.

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It is assumed that $u(\cdot)$ and $y(\cdot)$ are locally quadratically integrable with the carrier restricted from the left. Since V_I and V_O are finite-dimensional, the number of inputs and outputs is finite, and the condition that $W(\cdot)$ is a Boolean function, i.e., it is a finite sum of products of polynomials, sines, cosines, and exponents, corresponds to the condition that the system have a finite number of internal degrees of freedom. System $\Sigma_{I/O}$ is completely described by its transfer function

$$G(s) \stackrel{\text{def}}{=} W_0 + W_L(s), \quad (1.4)$$

where $W_L(\cdot): C \rightarrow L(V_I, V_O)$ is the Laplace transform of $W(\cdot)$.

It is well known that system $\Sigma_{I/O}$ can be adequately expressed by an *internal description*:

$$\Sigma_V: \quad \dot{x} = Ax + Bu, \quad y = Cx + Du, \quad (1.5)$$

where $x \in V$ is the internal state*, V is the finite-dimensional vector space of internal states with the scalar product " \cdot, \cdot ", $A \rightarrow L(V, V)$, $B \rightarrow L(V_I, V)$, $C \rightarrow L(V, V_O)$, $D \rightarrow L(V_I, V_O)$ are the operator parameters of the internal description.

It is said that Σ_V is a realization of system $\Sigma_{I/O}$ in the space of internal states if Σ_V generates the same mapping of the inputs $u(\cdot)$ to the outputs $y(\cdot)$ as $\Sigma_{I/O}$ does, and this is equivalent to the conditions

$$D = W_0, \quad Ce^{At}B = W(t), \quad t \in R^+, \quad (1.6)$$

where e^{At} is a one-parameter semigroup (occasionally called a matrix exponent, whose definition can be found, in particular, in [6]).

Relations (1.6) are equivalent to the condition

$$D + C(Is - A)^{-1}B = G(s). \quad (1.7)$$

It is known that a set of realizations of Σ_V exists for a given $\Sigma_{I/O}$. Those realizations that have the additional property that the dimension of the space of the internal states $n = \dim(V)$ is the smallest of the possible realizations are called *minimal*. This property is satisfied if and only if the realization satisfies the conditions of attainability and observability:

$$\bigoplus_{k=0}^{n-1} \mathfrak{R}(A^k B) = V \quad (\text{attainability}), \quad (1.8)$$

$$\bigcap_{k=0}^{n-1} \text{Ker}(CA^k) = 0 \quad (\text{observability}), \quad (1.9)$$

where \mathfrak{R} is the region of values, \bigoplus is the sign of the algebraic sum, and Ker is the kernel of the corresponding operator. Attainability means that any internal state can be realized by appropriate control, and observability means that in the space of internal states there are no "dead zones," i.e., regions in which a change in the internal state does not lead to a change in the output.

An important result concerning isomorphism in the space of internal states is known [7]: all possible minimal realizations can be obtained from one unique realization with parameters $\{A, B, C, D\}$ in terms of the following transformation group:

$$\{A, B, C, D\} \rightarrow \{SAS^{-1}, SB, CB^{-1}, D\}, \quad (1.10)$$

* Here we use the term "internal state" to avoid further confusion, though in the theory of dynamic systems the term "state" is ordinarily used.

where S is an arbitrary reversible operator of $L(V, V)$. Moreover, an operator S that relates one minimal realization to another is unique.

Passive dynamic systems are an important subclass of dynamic systems.

The concept of passivity is defined for dynamic systems in which the input and output spaces are one and the same space $V_I = V_O = W$ with the scalar product $\langle \cdot, \cdot \rangle$. Only such systems will be considered everywhere below.

System $\Sigma_{I/O}$ is called *passive* if

$$\int_{-\infty}^t \langle u(\tau), y(\tau) \rangle d\tau \geq 0 \quad (1.11)$$

for any inputs $u(\cdot)$ and any $t \geq 0$.

The property of passivity of a dynamic system can be expressed in terms of the transfer function: the system $\Sigma_{I/O}$ is passive if and only if

$$G(\sigma + i\omega) + G^*(\sigma - i\omega) \geq 0 \quad (1.12)$$

does not coincide with singular G for any $\sigma \geq 0$, $\omega \in R$, or $\sigma + i\omega$. This property can also be expressed in terms of realizations of dynamic systems.

If Σ_V is some minimal realization of dynamic system $\Sigma_{I/O}$ with parameters $\{A, B, C, D\}$, system $\Sigma_{I/O}$ is passive if and only if there exists a positive-definite operator solution $Q = Q^* \in L(W, W)$ of the inequality

$$[(A^*Q + QA)x + (QB - C^*u)] \cdot x + \langle [(B^*Q - C)x + Du], u \rangle \leq 0, \quad (1.13)$$

which must be satisfied for any $x \in V$ and any $u \in W$.

Moreover, the family of such solutions Q is convex, compact, and contains maximum Q^+ and minimum Q^- values (here and below, the concepts "greater," "smaller," "maximum," and "minimum" are interpreted in the sense of the positive-definiteness of the operators), so that for any solution Q the relation

$$Q^- \leq Q \leq Q^+ \quad (1.14)$$

holds.

Two Lyapunov functions defined in the space of internal states V as

$$s_a(x_0) = \sup_{T, u(\cdot)} \left\{ - \int_0^T \langle u(\tau), y(\tau) \rangle d\tau : T > 0, x(-T) = 0, x(0) = x_0 \right\}, \quad (1.15)$$

$$s_r(x_0) = \inf_{T, u(\cdot)} \left\{ - \int_{-T}^0 \langle u(\tau), y(\tau) \rangle d\tau : T > 0, x(-T) = 0, x(0) = x_0 \right\} \quad (1.16)$$

are important in analysis of the properties of passive dynamic systems. It can be demonstrated that these functions are given by the expressions

$$s_a(x) = \frac{1}{2} x \cdot Q^- x, \quad (1.17)$$

$$s_r(x) = \frac{1}{2} x \cdot Q^+ x, \quad (1.18)$$

In this case, it is clear that

$$s_r(x) \leq s_a(x) \quad (1.19)$$

for any x . It can be easily seen that with allowance for (1.5) inequality (1.13) is equivalent to

$$\frac{1}{2} \frac{d}{dt} (x(t) \cdot Qx(t)) \leq \langle u(t), y(t) \rangle. \quad (1.20)$$

Hence, with allowance for (1.17) and (1.18):

$$s_a(x(t_2)) - s_a(x(t_1)) \geq \int_{t_1}^{t_2} \langle y(\tau), u(\tau) \rangle d\tau, \quad (1.21)$$

$$s_r(x(t_2)) - s_r(x(t_1)) \geq \int_{t_1}^{t_2} \langle y(\tau), u(\tau) \rangle d\tau \quad (1.22)$$

and

$$s(x(t_2)) - s(x(t_1)) \geq \int_{t_1}^{t_2} \langle y(\tau), u(\tau) \rangle d\tau, \quad (1.23)$$

where

$$s(x) = \frac{1}{2} x \cdot Qx, \quad (1.24)$$

and Q is any of solutions (1.13).

The Lyapunov functions s , s_a , s_r will be important later in the construction of thermodynamic potentials.

2. Construction of Thermodynamic Potentials. Starting with this section, we return to the theory of linear thermodynamic systems with memory considered in this series of articles. In what follows, it is assumed everywhere that the relaxation function R (see [1]) is a Boolean function, i.e., it is a finite sum of products of exponents, polynomials, sines, and cosines. In spite of its apparent boundedness, it is a rather extensive class of functions, since any relaxation function can be approximated by a function from this class.

It should be noted that inequality (2.10a) [1], which by virtue of lemma 1 [1] and theorem 1 [2] is a necessary and sufficient condition for the relaxation function to satisfy the second principle, can be expressed in the form

$$\int_0^t \langle (\hat{\sigma}(P_h^T \Lambda) - \sigma_0 - E\varepsilon_h(\tau)), h(\tau) \rangle d\tau \geq 0. \quad (2.1)$$

This inequality must be satisfied for any equilibrium state Λ_0 and any process h . For the thermodynamic system considered we introduce a concomitant dynamic system $\Sigma_{I/O}$ for which the input u is defined as

$$u = \dot{\varepsilon}, \quad (2.2)$$

and the output y is defined as

$$y(t) = \sigma - \sigma_0 - E\varepsilon = \int_{-\infty}^t R(\tau) \dot{\varepsilon}(t-\tau) d\tau = \int_{-\infty}^t R(\tau) u(t-\tau) d\tau. \quad (2.3)$$

Thus, for this system the relaxation function R plays the role of the pulse response function W . Then, in terms of this concomitant dynamic system, inequality (2.1) is equivalent to the following:

$$\int_{-\infty}^t \langle y(\tau), u(\tau) \rangle d\tau \geq 0, \quad (2.4)$$

which is none other than the condition of passivity for this system (see (1.11)).

Since according to the assumption the function \mathbf{R} is Boolean, the dynamic system $\Sigma_{I/O}$ introduced here admits at least one finite-dimensional minimal realization Σ in terms of internal state variables. This implies that there exists a finite-dimensional vector space of internal states V , and the operators $\mathbf{A}: V \rightarrow V$, $\mathbf{B}: S \rightarrow V$, and $\mathbf{C}: V \rightarrow S$ are such that for any inputs $u(\cdot)$, the following system gives the same outputs that (2.3) does:

$$y = \mathbf{C}x, \quad \dot{x} = \mathbf{A}x + \mathbf{B}u. \quad (2.5)$$

Algorithms for construction of such realizations with preset \mathbf{R} have been developed in the theory of realization of dynamic systems and described, in particular, in [7].

As was already stated in Sect. 1, any realization is associated with the initial pulse function \mathbf{R} by the relation (see (1.6)):

$$\mathbf{R}(t) = \mathbf{C}e^{\mathbf{A}t}\mathbf{B}. \quad (2.6)$$

It should be noted that values of internal state variables $x = 0$ correspond to equilibrium (stationary) states of dynamic system Σ (2.5). Since for a thermodynamic system, any configuration trajectory is such that $\dot{\epsilon}(t) = 0$ for all t shorter than some t_0 , i.e., all trajectories start from equilibrium states, then the same property is also characteristic of processes in the concomitant dynamic system Σ , i.e., $u(t) = 0$, $x = 0$ for $t < t_0$. It is this condition that is the initial condition for differential equation (2.5), so that with this initial condition its solution has the form

$$x(t) = \int_{-\infty}^t e^{\mathbf{A}(t-s)} \mathbf{B}u(s) ds. \quad (2.7)$$

A linear functional $\hat{x}(\cdot)$ is introduced that establishes the projection of the space of differential histories \mathcal{K} (see [1]) into the space of internal state variables V as follows:

$$\hat{x}(f) = \int_0^{\infty} e^{\mathbf{A}s} \mathbf{B}f(s) ds. \quad (2.8)$$

With this definition and notation (2.2), relation (2.7) can be rewritten as

$$x(t) = \hat{x}(\dot{\epsilon}^t). \quad (2.9)$$

Since, as follows from (2.4), the dynamic system defined here is passive, the Lyapunov functions $s(x)$ defined in Sect. 1 exist for it (see (1.15) and (1.16)):

$$s(x(t_2)) - s(x(t_1)) \geq \int_{t_1}^{t_2} \langle y(\tau), u(\tau) \rangle d\tau. \quad (2.10)$$

Here s is defined as

$$s(x) = \frac{1}{2} x \cdot \mathbf{Q}x, \quad (2.11)$$

where $\mathbf{Q}: V \xrightarrow{L} V$ such that $\mathbf{Q} > 0$, $\mathbf{Q}^\times = \mathbf{Q}$ is an operator solution of the inequality

$$[(\mathbf{A}^\times \mathbf{Q} + \mathbf{Q}\mathbf{A})x + (\mathbf{Q}\mathbf{B} - \mathbf{C}^\times)u] \cdot x + \langle (\mathbf{B}^\times \mathbf{Q} - \mathbf{C})x, u \rangle \leq 0, \quad (2.12)$$

which must be satisfied for any $x \in W$, $u \in s$.

As was mentioned above, for passive dynamic systems, such a solution always exists, and the set of solutions is compact and contains minimum and maximum solutions \mathbf{Q}^+ and \mathbf{Q}^- , respectively.

The two functionals $\hat{s}: \mathcal{K} \rightarrow R$ and $\hat{\psi}: \mathcal{S} \rightarrow R$ are defined as

$$\hat{s}(f) = s(\hat{x}(f)), \quad (2.13)$$

$$\hat{\psi}_{\varepsilon_0}(\alpha, f) = \sigma_0(\alpha - \varepsilon_0) + \frac{1}{2} \langle \alpha, E\alpha \rangle - \frac{1}{2} \langle \varepsilon_0, E\varepsilon_0 \rangle + \hat{s}(f). \quad (2.14)$$

If in (2.10) the terms of the concomitant dynamic system are replaced by the terms of the thermodynamic system and definitions (2.13) and (2.14) are taken into consideration, inequality (2.10) can be rewritten as

$$\hat{\psi}_{\varepsilon_0}(\varepsilon(t_2), \dot{\varepsilon}^{t_2}) - \hat{\psi}_{\varepsilon_0}(\varepsilon(t_1), \dot{\varepsilon}^{t_1}) \leq \int_{t_1}^{t_2} \langle \sigma(\tau), \dot{\varepsilon}(\tau) \rangle d\tau. \quad (2.15)$$

If the time interval $t_2 - t_1$ is denoted by T , and the initial state at the time t_1 , by Λ , i.e.,

$$T = t_2 - t_1, \quad \Lambda = \left\{ \varepsilon(t_1), \dot{\varepsilon}^{t_1} \right\}, \quad (2.16)$$

and the process defined by

$$h(t) = \dot{\varepsilon}(t - t_1), \quad (2.17)$$

is considered, inequality (2.15) will take the form

$$\hat{\psi}_{\varepsilon_0}(P_h^T \Lambda) - \hat{\psi}_{\varepsilon_0}(\Lambda) \leq \int_0^T \langle \sigma(P_h^T \Lambda), h(\tau) \rangle d\tau, \quad (2.18)$$

which is equivalent to Clausius–Duhem inequality (2.6) [1]. Consequently, the state function $\hat{\psi}_{\varepsilon_0}$, which is defined by (2.14), (2.13), and (2.11), is a thermodynamic potential and the functions $\hat{\psi}_{\varepsilon_0}^+$ and $\hat{\psi}_{\varepsilon_0}^-$, which are defined by the same formulas but with Q^+ and Q^- substituted for Q in (2.11), are the minimum and maximum thermodynamic potentials, respectively. In this construction the fact is reflected that in its meaning any thermodynamic potential is determined within its value in a certain fixed reference state, and here the equilibrium state $\{\varepsilon_0, O^+\}$ is taken as this fixed reference state, which is denoted by the subscript. The construction given above describes the entire family of thermodynamic potentials for this system in an explicit form.

3. An Example of a Thermodynamic System with a Nontrivial Family of Thermodynamic Potentials. It appears that, contrary to possible expectations, the presence of a nontrivial family of thermodynamic potentials (i.e., the presence of noncoinciding maximum and minimum potentials) is inherent even in comparatively simple thermodynamic systems. In what follows we will give an example of such a system and a comprehensive description of the family of thermodynamic potentials for it.

We consider a one-dimensional thermodynamic system (i.e., a system with a one-dimensional configuration space $s = R$, so that E and R degenerate to scalars) for which $\sigma_0 = 0$, $E = 0$, and the relaxation function R has the special form

$$\bar{R}(s) = R_1 e^{\lambda_1 s} + R_2 e^{\lambda_2 s}, \quad (3.1)$$

where $\lambda_1 < \lambda_2 < 0$, $R_1 > 0$, and $R_2 > 0$.

An isothermal viscoelastic body with a relaxation function of the form of (3.1) can be a physical counterpart of such a system. In this case, the "mechanical" terminology introduced in this theory should be understood literally, i.e., σ is mechanical stress, ε is deformation, and R is a stress-relaxation function. For the system concomitant with this system defined by (2.6) and (2.7), we consider its following minimal realization:

$$A = A^\times = \begin{bmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{bmatrix}, \quad B = C^\times = \begin{bmatrix} \sqrt{R_1} \\ \sqrt{R_2} \end{bmatrix}. \quad (3.2)$$

For the matrix A given by (3.2), the matrix exponent has the form

$$e^{At} = \begin{bmatrix} e^{\lambda_1 t} & 0 \\ 0 & e^{\lambda_2 t} \end{bmatrix}. \quad (3.3)$$

The following parameters will be defined:

$$n = \lambda_2 \lambda_1^{-1}, \quad m = \sqrt{R_2 R_1^{-1}}, \quad \alpha = \frac{n + n^{-1}}{2}, \quad \beta = \frac{m + m^{-1}}{2}. \quad (3.4)$$

From the construction we have

$$\alpha > 1, \quad \beta \geq 1. \quad (3.5)$$

Because of peculiarities of this particular system, dissipative inequality (2.12) has the form

$$[(AQ + QA)x + 2(QB - B)u] \cdot x \leq 0. \quad (3.6)$$

The following will be proved now.

Proposition 1. All positive-definite and symmetrical inequalities (3.6) have the form

$$Q(q) = \begin{bmatrix} 1 - mq & q \\ q & 1 - m^{-1}q \end{bmatrix}, \quad q_1 \leq q \leq q_2, \quad (3.7)$$

where

$$q_1 = \frac{-2\beta - \sqrt{4\beta^2 + 2\alpha - 2}}{\alpha - 1}, \quad q_2 = \frac{-2\beta + \sqrt{4\beta^2 + 2\alpha - 2}}{\alpha - 1}; \quad (3.8)$$

and

$$Q^- = Q(q_2), \quad Q^+ = Q(q_1). \quad (3.9)$$

Proof. Since inequality (3.6) must be satisfied for any x and any u , it follows that

$$QB - B = 0, \quad (3.10)$$

since otherwise a u could always be found such that this inequality would be violated.

We will express Q in the form of the arbitrary symmetrical matrix

$$Q = \begin{bmatrix} c_1 & q \\ q & c_2 \end{bmatrix} \quad (3.11)$$

and substitute this expression into (3.10). As a result, c_1 and c_2 can be determined, and then (3.11) is reduced to

$$Q = \begin{bmatrix} 1 - mq & q \\ q & 1 - m^{-1}q \end{bmatrix}, \quad q \in R. \quad (3.12)$$

Now, (3.12) is substituted into (3.6) with allowance for (3.10) to give

$$AQ + QA = \begin{bmatrix} 2\lambda_1(1 - mq) & q(\lambda_1 + \lambda_2) \\ q(\lambda_1 + \lambda_2) & 2\lambda_2(1 - m^{-1}q) \end{bmatrix} \leq 0. \quad (3.13)$$

The conditions of non-negativity of the matrix in (3.13) are expressed as

$$2\lambda_1(1 - mq) \leq 0, \quad 2\lambda_2(1 - m^{-1}q) \leq 0, \quad (3.14)$$

$$\det (\mathbf{A}\mathbf{Q} + \mathbf{Q}\mathbf{A}) \geq 0. \quad (3.15)$$

In view of (3.1), it follows from (3.14) that

$$1 - mq \geq 0, \quad 1 - m^{-1}q \geq 0, \quad (3.16)$$

and (3.15) gives

$$4\lambda_1\lambda_2(1 - mq)(1 - m^{-1}q) - q^2(\lambda_1 + \lambda_2)^2 \geq 0. \quad (3.17)$$

Moreover, it must be that $Q > 0$, which leads to

$$1 - mq > 0 \quad (3.18)$$

and

$$1 - 2q\beta > 0. \quad (3.19)$$

It is easily seen that (3.18) together with (3.19) also ensures (3.16), and, consequently, it is necessary to solve jointly the system of inequalities (3.17), (3.18), and (3.19). The left-hand side of inequality (3.17) is expressed as a quadratic trinomial relative to q :

$$(\alpha - 1)q^2 + 4\beta q - 2 \leq 0. \quad (3.20)$$

In order that this inequality be satisfied, it is necessary that

$$q_1 \leq q \leq q_2, \quad (3.21)$$

where q_1 and q_2 are roots of the quadratic equation that is obtained from (3.20) when strict equality is fulfilled in it and are given by relations (3.8). Now, we need only verify that (3.18) and (3.19) can be satisfied. These inequalities are expressed in the form

$$q < (2\beta)^{-1}, \quad q < m^{-1}. \quad (3.22)$$

Inequalities (3.22) are corollaries of (3.21), since direct substitution easily shows that

$$q_2 < (2\beta)^{-1}, \quad q_2 < m^{-1},$$

if q_2 is defined as in (3.8). Relations (3.9) follow from the fact that the matrix $Q(q_1) - Q(q_2)$ is non-negative-definite, which is easily verified by direct substitution. The proposition is proved.

Now, the proved result allows us to construct the complete family of thermodynamic potentials for the system considered on the basis of the results from the previous section. Substitution of (3.2) and (3.3) into (2.8) and of the obtained result into (2.11) and (2.14) gives the following general expression for the thermodynamic potential (in a mechanical interpretation, it is free energy):

$$\begin{aligned} \hat{\psi}(\dot{\epsilon}^t) = & \frac{R_1}{2} \left(\int_0^\infty e^{\lambda_1 s} \dot{\epsilon}^t(s) ds \right)^2 + \frac{R_2}{2} \left(\int_0^\infty e^{\lambda_2 s} \dot{\epsilon}^t(s) ds \right)^2 - \\ & - \frac{q}{2} \sqrt{R_1 R_2} \left(\int_0^\infty (e^{\lambda_1 s} - e^{\lambda_2 s}) \dot{\epsilon}^t(s) ds \right)^2. \end{aligned} \quad (3.23)$$

Relation (3.23) covers the entire family of thermodynamic potentials for this system, when q passes through interval $[q_1, q_2]$, and also represents the minimum and maximum thermodynamic potentials, at $q = q_1$ and $q = q_2$, respectively, where q_1 and q_2 are defined in (3.8).

It is surprising that neither the minimum nor maximum potential coincides with the expression that is used sometimes in viscoelastic mechanics for free energy:

$$\hat{\psi}_{ve}(\dot{\epsilon}^t) = \frac{1}{2} \int_0^\infty \int_0^\infty \bar{R}(\tau + s) \dot{\epsilon}^t(\tau) \dot{\epsilon}^t(s) d\tau ds. \quad (3.24)$$

This expression was derived for viscoelastic bodies with relaxation functions that are superpositions of exponential functions. Such bodies can be simulated by a network of elastic and viscous elements, and in them free energy is identified with the energy of the elastic elements, and this expression is obtained on this basis.

For the present system, expression (3.24) coincides with the first two terms in (3.23), i.e., $\hat{\psi}_{ve}$ belongs to family (3.23) (at $q = 0$) but is not distinguished from other potentials in any way. For the system considered, which is understood as a viscoelastic body, as follows from (1.14) and (1.15), in its physical meaning the maximum potential in this state is the minimum work that would have to be done to transfer the body from the reference state to the present state, and the minimum potential is the maximum work that the body could do on the way from the present state to the reference state, or the maximum recoverable work, which has been studied for a rather long time in viscoelasticity theory [8]. It should be noted that at $\lambda_1 = \lambda_2$, as follows from (3.23), when the relaxation function is expressed by a single exponential function the maximum and minimum potentials coincide, i.e., the thermodynamic potential is unique.

These considerations lead to the formulation of an urgent problem: does any phenomenological principle exist that would isolate one potential from an entire nontrivial family, namely, the potential $\hat{\psi}_{ve}$, which in this particular case corresponds to mechanical potential energy, which is understood conventionally as thermodynamic free energy?

The present results allow the additional interesting conclusion that, apart from entropy production, it is likely that one more characteristic of the degree of nonequilibrium of a state (or a thermodynamic system) exists, namely, the difference between the maximum and minimum potentials. If this difference is zero for a particular nonequilibrium state, then for thermodynamic systems that are similar to the systems considered in the present example, the minimum work that must be done to transfer the system from the reference equilibrium state to a given nonequilibrium state and back (or vice versa) is equal to zero. Otherwise, this work is determined by the above-mentioned difference between the thermodynamic potentials. In other words, this difference can be considered as a measure of attainability of a particular nonequilibrium state from the reference equilibrium state.

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