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THEORY OF GENERALIZED THERMODYNAMIC SYSTEMS WITH MEMORY

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A theory of the generalized nonlinear thermodynamic systems with memory is developed. It is shown how different specific physical systems can be represented in the context of a generalized formalism. Necessary and sufficient conditions of fulfillment of the second law of thermodynamics for such nonlinear systems are found. These conditions contain, as a particular case, the previously found similar conditions for linear systems. A procedure of constructing the nonequilibrium thermodynamic potential for such systems is developed.

1. Unification of the Representation of Different Thermodynamic Systems. In this section, it will be shown how different specific thermodynamic systems can be represented in a universal way and, consequently, be embedded in some unified formal scheme. Then, on the basis of this scheme, a generalized abstract thermodynamic theory will be constructed.

The two formulations of the second law of thermodynamics (second law) most widely used in contemporary thermodynamics go back to two classical formulations of the nineteenth century:

(a) in each cyclic process the integral of reduced heat is nonpositive, i.e.,

$$\oint \frac{dQ}{\theta} \le 0 \; ; \tag{1a}$$

(b) for any process the inequality below is fulfilled

$$\int \frac{dQ}{\theta} \le S_2 - S_1 \; . \tag{1b}$$

The thermodynamic approach based on the modern variant of formulation (1a) belonging to Clausius is usually called the entropy-free one. If a thermodynamic system is a continuum, the integral of reduced heat can be represented in terms of the local field formulation, and then inequalities (1) are reduced to the following form [1–4]:

$$\oint \left[-\frac{1}{\rho} \, \text{div} \left[\frac{\mathbf{q}}{\theta} \right] + \frac{r}{\theta} \right] dt \le 0 \; , \tag{2a}$$

$$\eta \, (t_2) - \eta \, (t_1) \ge \int_{t_1}^{t_2} \left[-\frac{1}{\rho} \, \text{div} \left(\frac{\mathbf{q}}{\theta} \right) + \frac{r}{\theta} \right] dt \; . \tag{2b}$$

The last inequality can be represented in the differential form (the Clausius–Duhem inequality)

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$$\dot{\eta}(t) \geq -\frac{1}{\rho} \operatorname{div}\left[\frac{\mathbf{q}}{\theta}\right] + \frac{r}{\theta}. \tag{3}$$

Hereafter the dot above a symbol indicates a substantial derivative with respect to time.

We will consider several examples of thermodynamic systems for which the first law of thermodynamics (the law of conservation of energy) is represented as follows:

(a) a nondeformable heat-conducting body

$$\dot{e} = -\frac{1}{\rho} \operatorname{div} \mathbf{q} + r; \tag{4}$$

(b) a deformable heat-conducting body

$$\dot{e} = -\frac{1}{\rho} \operatorname{div} \mathbf{q} + \mathbf{S} \cdot \dot{\mathbf{F}} + r; \tag{5}$$

(c) a nondeformable heat-conducting dielectric body with an electromagnetic field [5]

$$\dot{e} = -\frac{1}{\rho} \operatorname{div} \mathbf{q} + \frac{1}{\rho} \dot{\mathbf{D}} \cdot \mathbf{E} + \frac{1}{\rho} \dot{\mathbf{B}} \cdot \mathbf{H} + r, \tag{6}$$

where the scalar product of the tensors $\mathbf{T}_1$ and $\mathbf{T}_2$ is determined as their convolution (a trace of the product of the tensors), i.e., $\mathbf{T}_1 \cdot \mathbf{T}_2 = \operatorname{tr}(\mathbf{T}_1 \mathbf{T}_2)$.

We express r, for instance, from (5) and substitute into (2a). As a result, introducing the inverse absolute temperature $\vartheta = 1/\theta$ and its gradient $\mathbf{g} = \operatorname{grad} \vartheta$, we arrive at

$$\oint \left(\dot{e}\,\vartheta - \vartheta\, \mathbf{S} \cdot \dot{\mathbf{F}} - \frac{1}{\rho} \mathbf{q} \cdot \mathbf{g} \right) dt \leq 0, \tag{7}$$

$$\dot{e}\,\vartheta - \vartheta\, \mathbf{S} \cdot \dot{\mathbf{F}} - \frac{1}{\rho} \mathbf{q} \cdot \mathbf{g} \leq \dot{\eta}. \tag{8}$$

Introducing a new thermodynamic potential Φ into (8)

$$\Phi = e\,\vartheta - \eta \tag{9}$$

and adding the identity

$$\oint (e\,\vartheta)^{\cdot}\, dt = 0 \tag{10}$$

to (7), we represent (7) and (8) in the form

$$\oint \left(e\,\dot{\vartheta} + \vartheta\, \mathbf{S} \cdot \dot{\mathbf{F}} + \frac{1}{\rho} \mathbf{q} \cdot \mathbf{g} \right) dt \geq 0, \tag{11}$$

$$-\dot{\Phi} + e\,\dot{\vartheta} + \vartheta\, \mathbf{S} \cdot \dot{\mathbf{F}} + \frac{1}{\rho} \mathbf{q} \cdot \mathbf{g} \geq 0. \tag{12}$$

We consider the space $\mathsf{S} = \mathcal{L}(\mathcal{E}) \times \mathcal{E} \times \mathsf{R}$ so that the elements of S are the triplets $\gamma = \{\mathbf{T}, \mathbf{a}, \lambda\}$ consisting of a tensor, a vector, and a scalar. If $\gamma_1 = \{\mathbf{T}_1, \mathbf{a}_1, \lambda_1\}$ and $\gamma_2 = \{\mathbf{T}_2, \mathbf{a}_2, \lambda_2\}$ are two elements from S, then their scalar product is determined as follows:

$$\langle \gamma_1, \gamma_2 \rangle = \mathbf{T}_1 \cdot \mathbf{T}_2 + \mathbf{a}_1 \cdot \mathbf{a}_2 + \lambda_1 \lambda_2 \,. \tag{13}$$

Then if we introduce the functions of coordinates and time

$$\sigma = \left\{ \vartheta\, \mathbf{S}, \frac{1}{\rho}\, \mathbf{q}, e \right\} \quad \text{and} \quad \varepsilon = \{ \mathbf{F}, \bar{\mathbf{g}}, \vartheta \} \,, \tag{14}$$

where

$$\bar{\mathbf{g}}\,(t) = \int_{-\infty}^{t} \mathbf{g}\,(s)\, ds \,, \tag{15}$$

then inequalities (11) and (12) can be written as

$$\oint \langle \sigma, \dot{\varepsilon} \rangle \, dt \geq 0 \,, \tag{16}$$

$$\langle \sigma, \dot{\varepsilon} \rangle \geq \dot{\Phi} \,. \tag{17}$$

Similarly, performing analogous transformations of the thermodynamic systems introduced above in items (a) and (c), we can represent both formulations of the second law in the form of (16) and (17), where

$$\text{a)}\ \ \mathsf{S} = \mathcal{E} \times \mathsf{R} \,, \quad \sigma = \left\{ \frac{1}{\rho}\, \mathbf{q}, e \right\}, \quad \varepsilon = \{ \bar{\mathbf{g}}, \vartheta \} \,; \tag{18}$$

$$\text{c)}\ \ \mathsf{S} = \mathcal{E} \times \mathcal{E} \times \mathcal{E} \times \mathsf{R} \,, \quad \sigma = \left\{ \frac{\vartheta}{\rho}\, \mathbf{B}, \frac{\vartheta}{\rho}\, \mathbf{D}, \frac{\vartheta}{\rho}\, \mathbf{q}, e \right\}, \quad \varepsilon = \{ \mathbf{H}, \mathbf{E}, \bar{\mathbf{g}}, \vartheta \} \,, \tag{19}$$

here, in the last case the thermodynamic potential is

$$\Phi = e\, \vartheta - \eta - \vartheta\, \mathbf{B} \cdot \mathbf{H} - \vartheta\, \mathbf{D} \cdot \mathbf{E} \,. \tag{20}$$

The possibility of such a unified representation of different thermodynamic systems forms the basis of the formalism used below.

Thus, the abstract notions, introduced below, of configuration space, configuration trajectory, and trajectory of generalized forces satisfy the space S determined above, the function of time $\varepsilon(t)$, and the function of time $\sigma(t)$ in each of the three considered particular cases, respectively. At the same time this formalism can describe a great number of other physical systems.

For any thermodynamic theory of complex media of the type of those considered above to be closed, it must be supplemented, in addition to the indicated relations and conservation laws, with the so-called constitutive or material equations that prescribe how the dependent variables are determined in terms of the independent ones and thus determine the properties of a medium.

In all the above cases, the independent variables are grouped into the generalized variable ε (configuration), while the dependent variables are grouped into the generalized variable σ (generalized force) with account for normalization conditioned by the form of the integral of the reduced heat.

The most universal form of the constitutive equations follows from the assumption that the values of the dependent variables at a running instant of time are determined not only by the values of the independent variables at the running instant but also by their prehistory (the causality principle). This is the so-called model of the media with memory. Moreover, the assumption called the equipresence principle is also used, according to which if some form of the dependence on the independent variables is present in one of the constitutive equations, then this dependence must be present in all the rest, provided it is not forbidden by some other general principles.

Here, since the concrete dependences on the prehistories represent functionals of the type of convolutions, then by integration by parts they can be represented through the dependence on the prehistories of their time derivatives (differential histories). For the sake of convenience and compactness of the basic relations this dependence should be represented precisely in terms of the differential histories. With regard to the aforesaid, for instance, to case (b) of the examples given above, the constitutive equations are written as

$$\mathbf{S}(t) = \hat{\mathbf{S}}(\mathbf{F}(t), \vartheta(t), \dot{\mathbf{F}}^t, \dot{\bar{\mathbf{g}}}^t, \dot{\vartheta}^t), \quad \mathbf{q}(t) = \hat{\mathbf{q}}(\mathbf{F}(t), \vartheta(t), \dot{\mathbf{F}}^t, \dot{\bar{\mathbf{g}}}^t, \dot{\vartheta}^t),$$

$$e(t) = \hat{e}(\mathbf{F}(t), \vartheta(t), \dot{\mathbf{F}}^t, \dot{\bar{\mathbf{g}}}^t, \dot{\vartheta}^t), \tag{21}$$

where $\dot{\mathbf{F}}^t(s) = \dfrac{d}{dt}\mathbf{F}(t-s)$ is the differential history of the deformation gradient; other histories are determined in the same way. In (21), $\hat{\mathbf{S}}$, $\hat{\mathbf{q}}$, and $\hat{e}$ represent the ordinary functions for the first two arguments and the functionals for the last three arguments. These relations describe a model of the viscoelastic media with thermal and deformational memory proposed by Chen and Gurtin [11]. In the generalized form with account for (14) and for the relation describing the balance of mass $\rho = \rho_0/\det \mathbf{F}$ (ρ_0 = const), the constitutive equations (21) can be written as follows*):

$$\sigma(t) = \hat{\sigma}(\varepsilon(t), \dot{\varepsilon}^t), \tag{22}$$

where according to (14)

$$\hat{\sigma} = \left\{\vartheta\,\hat{\mathbf{S}}, \frac{\det \mathbf{F}}{\rho_0}\,\hat{\mathbf{q}}, \hat{e}\right\} \quad \text{è} \quad \dot{\varepsilon}^t = \left\{\dot{\mathbf{F}}^t, \dot{\bar{\mathbf{g}}}^t, \dot{\vartheta}^t\right\}.$$

Similar relations can be provided for the remaining two examples. In the generalized theory of the thermodynamic systems with memory described below, the constitutive functional (more precisely the vector-functional) of generalized forces corresponds to constitutive equations of the type (22).

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

The function of time ε: R $\to$ S, called the *configuration trajectory of a system*, is a bounded on each interval, continuous function with its derivative bounded on finite intervals, and for which there exists t_0 such that $\varepsilon(t) = \varepsilon_0$ for all $t \le t_0$ (ε_0 is the fixed element from S). If the instant of time t_0 referred to in this definition is to be emphasized, we say the "configuration trajectory starting from the instant of time t_0."

The *configuration history of a system* before an instant of time t is a function determined as

$$\varepsilon^t(s) = \varepsilon(t-s). \tag{23}$$

The *differential configuration history* before the instant t is a function $\dot{\varepsilon}^t$: $R^+ \to$ S:

$$\dot{\varepsilon}^t(s) = \frac{d}{dt}\varepsilon^t(s) = -\frac{d}{ds}\varepsilon(t-s). \tag{24}$$

*) Relations (22) are slightly more general with respect to (21), since in (21) the dependence on one of the vector "components" of $\varepsilon(t)$, percisely, on $\bar{g}(t)$, is absent.

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

$$\|f\| = \left(\int_0^\infty \left| f(s) \right|^2 \xi(s)\, ds \right)^{1/2} \tag{25}$$

will be called the *space of histories*. In (25), ξ is the influence function. It is assumed to be positive continuous, integrable on R^+, nowhere vanishing, and possessing the property

$$\lim_{s \to \infty} \frac{\xi(s)}{\xi(s+T)} < \infty . \tag{26}$$

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

$$\|\Lambda\|_{\mathsf{G}} = (\left|\alpha\right|^2 + \|f\|^2)^{1/2} \tag{27}$$

forms the *space of states* G.

For the prescribed configuration trajectory $\varepsilon(\cdot)$ and an arbitrary instant of time t, the *state of the system at the instant t* is determined as

$$\Lambda^t = \left\{\varepsilon(t), \dot{\varepsilon}^t\right\} . \tag{28}$$

The *equilibrium state* is

$$\Lambda^+ = \left\{\alpha, 0^+\right\} , \tag{29}$$

where $\alpha \in \mathsf{S}$, $0^+ \in \mathcal{H}$, and $0^+(s) = 0$ for all $s \in \mathsf{R}$.

To the constitutive equations the notion of the *constitutive functional of generalized forces* $\hat{\sigma}$: $\mathsf{G} \to \mathsf{S}$ corresponds:

$$\hat{\sigma}(\Lambda) = \hat{\sigma}(\alpha, f) . \tag{30}$$

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

For any configuration trajectory of a system one can unambiguously determine the trajectory of generalized forces σ_ε: $\mathsf{R} \to \mathsf{S}$ with the aid of functional (30):

$$\hat{\sigma}_\varepsilon(t) = \hat{\sigma}(\Lambda^t) = \hat{\sigma}(\varepsilon(t), \dot{\varepsilon}^t) . \tag{31}$$

The *thermodynamic trajectory* is a pair $\{\varepsilon(t), \sigma_\varepsilon(t)\}$ consisting of a configuration trajectory and a trajectory of generalized forces σ_ε: $\mathsf{R} \to \mathsf{S}$ corresponding to it.

The *process* with a duration of $T (T > 0)$ is a function h: $(0, T] \to \mathsf{S}$, which is bounded and piecewise continuous and with which the transformation P_h^T: $\mathsf{G} \to \mathsf{G}$ is associated in the space of states, which is determined as follows: for any $\Lambda = \{\alpha, f\} \in \mathsf{G}$

$$P_h^T \Lambda \equiv \Lambda_{(h)} = \left\{\alpha_{(h)}, p_h^T f\right\} , \tag{32}$$

where

$$\alpha_{(h)} = \alpha + h^i(T)\,, \tag{33}$$

$$h^i(t) = \int_0^t h(s)\,ds\,, \tag{34}$$

while a transformation p_h^T in the space of histories is determined as

$$p_h^T f(s) = \begin{cases} f(s - T) & \text{for } s \in [T, \infty)\,, \\ h(T - s) & \text{for } s \in [0, T)\,, \end{cases} \tag{35}$$

P_h^T is called the transformation of states, which is induced by a process h. We say the process h transfers the system from the initial state Λ to the final state $P_h^T\Lambda$.

We denote by $\mathcal{P}$ and $\mathcal{P}_T$, respectively, the set of all processes and the set of processes with a duration of T. The process u_T such that $u_T(s) = 0$ for all $\varepsilon \in (0, T)$ is called the *fixed process* with a duration of T.

It is easy to verify that the transformation P_h^T associated with the process h takes the state of a system at the instant t $\Lambda^t = \{\varepsilon(t), \varepsilon^t\}$, corresponding to the configuration trajectory $\varepsilon(\tau)$, to the state of the system at the instant $t + T$, corresponding to the configuration trajectory $\varepsilon_{(ht)}(\tau)$, which is determined on $(-\infty, t + T)$ in the following way:

$$\varepsilon_{(ht)}(\tau) = \begin{cases} \varepsilon(\tau) & \text{for } \tau \le t\,, \\ \varepsilon(t) + h^i(\tau - t) & \text{for } \tau \in (t, T + t]\,. \end{cases} \tag{36}$$

The configuration trajectory $\varepsilon_{(ht)}(\tau)$ is called an h-extension of the trajectory $\varepsilon(\tau)$ for the instant t.

It can be shown that by the assumptions made above for any process h the transformation P_h^T associated with the latter is continuous in G.

The *composition of processes* h_1 with a duration of T_1 and of h_2 with a duration of T_2 represents a process $h_1 \circ h_2$ with a duration of $T_1 + T_2$ determined as follows:

$$h_1 \circ h_2 = \begin{cases} h_1(\tau) & \text{for } \tau \in (0, T_1]\,, \\ h_2(\tau - T_1) & \text{for } \tau \in (T_1, T_1 + T_2)\,. \end{cases} \tag{37}$$

It is easy to check that

$$P_{h_1 \circ h_2}^{T_1 + T_2}\Lambda = P_{h_2}^{T_2} P_{h_1}^{T_1}\Lambda\,. \tag{38}$$

We can also determine for any $t \le T$ the reduction of a process with a duration of T to the interval $(0, t)$ by narrowing the domain of definition of the process h on $(0, t)$. This will be the process with a duration of t. Correspondingly, the transformation P_h^t associated with it will be determined. All of the foregoing relative to the transformation P_h^t in the space of states is valid for the transformation p_h^t in the space of histories.

For formulation of the second law we introduce a generalized analog of the integral of reduced heat.

The *action* (or thermodynamic action) performed by the process h with a duration of T from state Λ is a function a: $\mathsf{G} \times \mathcal{P} \to \mathsf{R}$, which is determined in the following way:

$$a(\Lambda, h) = \int_0^T \langle \hat{\sigma}(P_h^t \Lambda), h(t) \rangle \, dt \,, \tag{39}$$

where P_h^t is the transformation associated with reduction of the process h to the interval $(0, t)$. It is obvious that the action is continuous in G at fixed h and, moreover, it is additive on the composition of two processes h_1 and h_2 with a duration of T_1 and T_2, respectively, in the sense that

$$a(\Lambda, h_1 \circ h_2) = a(\Lambda, h_1) + a(P_{h_1}^{T_1}\Lambda, h_2) = \int_0^{T_1} \langle \hat{\sigma}(P_{h_2}^{\tau}\Lambda), h_1(\tau) \rangle \, d\tau + \int_0^{T_2} \langle \hat{\sigma}(P_{h_2}^{\tau} P_{h_1}^{T_1}\Lambda), h_2(\tau) \rangle \, d\tau \,. \tag{40}$$

All the notions and definitions formulated above represent a more concrete realization of the abstract mathematical theory of thermodynamic systems developed by Coleman and Owen [6, 7], so that the basic notions and postulates of both theories show a certain distinct correspondence.

Now we pass to formulation of the thermodynamic theory.

A postulate expressing the second law in the manner of the Coleman–Owen theory [16] is formulated as follows:

P1. *At any initial state* $\Lambda \in \mathsf{G}$ *the action a possesses the following property: for any* $\zeta > 0$ *there exists* $\delta > 0$ *such that if* $h \in \mathcal{P}_T$ *and*

$$\| \Lambda - P_h^T \Lambda \|_{\mathsf{G}} < \delta \,, \tag{41}$$

then

$$a(\Lambda, h) > -\zeta \,. \tag{42}$$

Nonstrictly speaking, this postulate indicates that if some process drives a system into a sufficiently small neighborhood of the initial state, then the action performed in this process will be nonnegative with an accuracy as high as desired. This statement represents a generalization and strict mathematical formalization of the formulation of the second law used in classical thermodynamics in the form of the requirement on nonnegativeness for the integral of reduced heat in any cyclic process (1a).

The main corollary of the second law is existence of the thermodynamic potential and fulfillment of the Clausius–Duhem inequality, which is the content of the next theorem (this is an analog of Theorem 3.3 in [6] for the considered class of thermodynamic systems).

T h e o r e m 1. *The postulate* **P1** *is fulfilled if and only if the function of state* $\dot{\psi}: \mathsf{G} \to \mathsf{R}$ *(thermodynamic potential) exists that is definite and lower semicontinuous on* G *and possesses the following property: for any* $\Lambda_1, \Lambda_2 \in \mathsf{G}$ *and for any* $\zeta > 0$ *there exists* $\delta > 0$ *such that the inequality*

$$\hat{\psi}(\Lambda_2) - \hat{\psi}(\Lambda_1) < a(\Lambda_1, h) + \zeta \tag{43}$$

is fulfilled for any $h \in \mathcal{P}$ *such that* $\| P_h^T \Lambda_1 - \Lambda_2 \|_{\mathsf{G}} < \delta$.

The theorem is proved on the basis of arguments similar to those used in [6]. The lower semicontinuity of the potential $\hat{\psi}$ in state Λ implies that for any $\zeta > 0$ there exists $\delta > 0$ such that for any $\Lambda' \in \mathsf{G}$ such that

$$\| \Lambda - \Lambda' \|_{\mathsf{G}} < \delta \,, \tag{44}$$

the following inequality holds:

$$\hat{\psi}(\Lambda) - \hat{\psi}(\Lambda') < -\zeta . \qquad (45)$$

Theorem 1 is of fundamental significance since it demonstrates the interrelation between the formulations of the second law in the form of (1a) and (1b) and makes it possible to consider the nonequilibrium thermodynamic potential as a notion derived from theory.

3. Conditions of the Thermodynamic Validity of the Nonlinear Thermodynamic Systems with Memory. An important problem is to find conditions which the constitutive equations must satisfy in order to fulfill the second law.

To attain this aim, we slightly narrow the class of systems considered and confine ourselves to consideration of nonlinear constitutive equations of the form (30) possessing the following property:

$$\partial_\alpha (\hat{\sigma}(\alpha, f) - \hat{\sigma}(\alpha, 0^+)) = 0 . \qquad \cdot(46)$$

Hereafter a differential operator ∂_α is the operator of differentiation (of taking a gradient) in the space S. Introducing the equilibrium function of generalized forces σ_0: $S \to S$ as

$$\sigma_0(\alpha) = \hat{\sigma}(\alpha, 0^+) , \qquad (47)$$

it is easy to verify that condition (46) is equivalent to the statement about the possibility of representing the functional $\hat{\sigma}(\alpha, f)$ in the form

$$\hat{\sigma}(\alpha, f) = \sigma_0(\alpha) + \hat{\sigma}'(f) , \qquad (48)$$

where the functional $\hat{\sigma}'$ is determined as

$$\hat{\sigma}'(f) = \hat{\sigma}(\alpha, f) - \hat{\sigma}(\alpha, 0^+) \qquad (49)$$

and, according to (46), is independent of α, but by definition (49) it is continuous and possesses the property

$$\hat{\sigma}'(0^+) = 0 . \qquad (50)$$

Thermodynamic systems with constitutive equations possessing this property will be referred to as separable ones, and from this point on we consider only such systems.

Our main result here is the following theorem that contains the already mentioned necessary and sufficient conditions of fulfillment of the second law of thermodynamics for the separable thermodynamic systems.

T h e o r e m 2. *The postulate* **P1** *for separable thermodynamic systems is fulfilled if and only if a continuously differentiable function* ψ_0*:* $S \to R$ *exists such that*

$$\sigma_0(\alpha) = \partial_\alpha \psi_0(\alpha) , \qquad (51)$$

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

$$\int_0^T \langle \hat{\sigma}'(P_h^t 0^+), h(t) \rangle \, dt \geq 0 \qquad (52)$$

for any $h \in \mathcal{P}$.

By the formulation of the theorem, condition (52) can be represented in the more "transparent" form

$$\int_0^T \langle \hat{\sigma}' (h^t), h(t) \rangle \, dt \geq 0 \tag{53}$$

for any piecewise-continuous, locally summable functions h: $\mathcal{R} \to \mathcal{S}$ with a carrier on the positive semiaxis and for any $T > 0$; here $h^t(s) = h(t - s)$.

P r o o f. *Necessity*. We show that (51) follows from fulfillment of the postulate **P1.** We consider a process h with a duration of T such that (see (34))

$$h^i (T) = 0 \, , \tag{54}$$

and in other respects it is arbitrary. We denote by h_λ a process with duration T/λ, which for any $\lambda > 0$ is determined in terms of h as follows:

$$h_\lambda (s) = \lambda h (\lambda s) \, . \tag{55}$$

In [9] it is shown that for any $\delta > 0$ and for any equilibrium state $\Lambda_0^+ = \{\varepsilon_0, 0^+\}$ there exists $\lambda_0 > 0$ such that for all $\lambda < \lambda_0$ the following inequality is fulfilled:

$$\| \Lambda_0^+ - P_{h_\lambda}^{T/\lambda} \Lambda_0^+ \|_{\mathsf{G}} < \delta \, . \tag{56}$$

Whence, by the assumption on fulfillment of the postulate **P1** it follows that for any $\zeta > 0$ there exists $\lambda_0 > 0$ such that for any equilibrium state Λ_0^+ and the process h_λ (determined above) for all $\lambda < \lambda_0$ the following inequality holds:

$$a (\Lambda_0^+, h_\lambda) > - \zeta \, . \tag{57}$$

This inequality can be represented in the form

$$\int_0^T \langle \sigma_0 (h^i (\tau) + \varepsilon_0), h(\tau) \rangle \, d\tau + \int_0^T \langle \hat{\sigma}' (p_{h_\lambda}^{t/\lambda} 0^+), h(\tau) \rangle \, d\tau > - \zeta \, , \tag{58}$$

where h^i is determined in terms of h according to (34), while the transformation p_h^t is determined according to (35).

From statement (56) it follows that $\| p_{h_\lambda}^t 0^+ \| \to 0$ at $\lambda \to 0$; therefore, on performing this limiting transition in (56), the last integral vanishes by virtue of the continuity and property (50) of the functional $\hat{\sigma}'$ and (58) reduces to the inequality

$$\int_0^T \langle \sigma_0 (h^i (\tau) + \varepsilon_0), \dot{h}^i (\tau) \, d\tau \rangle \geq 0 \, , \tag{59}$$

which must be satisfied for any ε_0, any $T > 0$, and any h^i such that $h^i(0) = h^i(T) = 0$. After substitution of $h^i(T - s)$ for $h^i(s)$ and some transformations with replacement of the variable in the integral we arrive at the same inequality with a reciprocal sign. Whence it follows that

$$\int_0^T \langle \sigma_0 (h^i (\tau) + \varepsilon_0), h^i (\tau) \, d\tau \rangle = 0 \tag{60}$$

for any h^i which satisfy (54). As is known (the proof can be found, for instance, in [4]), this is equivalent to be requirement that σ_0 be determined as a gradient of some scalar function ψ_0, i.e., by relation (51).

Now we prove that condition (52) originates from **P1**. We consider **P1** to be realizable and for an arbitrary equilibrium state $\Lambda_0^+ = \{\varepsilon^0, 0^+\}$ consider a process h_0 with a duration of $T_0 = T + 2T_1$ which is the composition of an arbitrary process h with a duration of T_1, of a fixed process u_{T_1} with duration T_1, and of a process h_1 with a duration of T_1. Here h_1 has the specific form

$$h_1(s) = -\frac{1}{T_1} h^i(T) = \text{const}\,, \tag{61}$$

where use is made of the notation of (34). Thus

$$h_0 = h \circ u_{T_1} \circ h_1 \tag{62}$$

and it is easy to verify that

$$h_0^i(T_0) = 0\,. \tag{63}$$

Next, we consider a process h_3 with a duration of $T_3 = T_0 + T_f$ that represents the composition of the process h_0 determined above and of the fixed process u_{T_f} with a duration of T_f:

$$h_3 = h_0 \circ u_{T_f}\,. \tag{64}$$

In [8–10], the following statement is proved: for any $\delta > 0$, any process $h_0 \in \mathcal{P}$, and any arbitrary equilibrium state $\Lambda_0^+ = \{\varepsilon^0, 0^+\}$, there exists $T_f > 0$ such that for any $T_f \geq \tilde{T}_f$ in the process h_3 the following inequality is fulfilled:

$$\|\Lambda_0^+ - P_{h_3}^{T_3}\Lambda_0^+\|_{\mathsf{G}} < \delta\,. \tag{65}$$

By virtue of the assumption on the realizability of the postulate **P1**, it appears that for any $\zeta > 0$ the period T_f in h_3 can be chosen as large as to allow fulfillment of the inequality

$$a(\Lambda_0^+, h_3) > -\zeta\,. \tag{66}$$

We represent the left-hand side of this inequality in a more detailed form with due regard for the definition of action (39) and for the structure of the process under consideration:

$$\int_0^{T_0} \langle \sigma_0(h_0^i(t) + \varepsilon_0), \dot{h}_0^i(t)\rangle\, dt + \int_0^T \langle \hat{\sigma}'(h^t), h(t)\rangle\, dt - \frac{1}{T_1}\int_{T+T_1}^{T+2T_1} \langle \hat{\sigma}'(h_0^t), h^i(T)\rangle\, dt > -\zeta\,. \tag{67}$$

We transform the first integral in this inequality considering the fact that by virtue of the fulfillment of postulate **P1**, as has been proved, (51) is fulfilled and in the latter we change the variable:

$$\int_0^{T_0} \langle \partial_\alpha \psi_0(h_0^i(t) + \varepsilon_0), \dot{h}_0^i(t)\rangle\, dt + \int_0^T \langle \hat{\sigma}'(h^i), h(t)\rangle\, dt - \frac{1}{T_1}\int_0^{T_1} \langle \hat{\sigma}'(h_0^{t+T+T_1}), h^i(T)\rangle\, dt > -\zeta\,. \tag{68}$$

For the norm of the history $h_0^{t+T+T_1}$ with account for definition (25) it is easy to construct the following estimate:

$$\|h_0^{t+T+T_1}\|^2 = \int_0^t \left(\frac{h^i(T)}{T_1}\right)^2 \xi(s)\, ds + \int_{t+T_1}^{t+T+T_1} \Big(h(t+T+T_1-s)\Big)^2 \xi(s)\, ds \le \xi(0)\Big(h^i(T)\Big)^2 \frac{t}{T_1^2} +$$

$$+ \xi(t+T_1) \int_0^T (h(s))^2\, ds . \tag{69}$$

Whence we obtain that for any $t \in [0, T_1]$

$$\lim_{T_1 \to \infty} \|h_0^{t+T+T_1}\|^2 = 0 . \tag{70}$$

Then in (68) calculation of the first integral yields $\psi_0(\varepsilon_0 + h_0^i(T_0)) - \psi_0(\varepsilon_0)$ and by virtue of (63) it vanishes, but as a consequence of the limiting transition $T_1 \to \infty$, with account for (70), for the continuity, and for property (50) of the functional $\hat{\sigma}'$ we draw the conclusion that the last integral vanishes as well. As a result, (68) reduces to the proved inequality (53).

Sufficiency. Now let statements (51) and (52) (or (53)) of Theorem 2 be fulfilled. We will show that fulfillment of the postulate **P1** follows. We choose an arbitrary configuration trajectory starting from an instant of time t_0 and for the state on this trajectory at the instant $t > t_0$ we consider an arbitrary process h. On h-extension of the trajectory $\varepsilon(\tau)$ at the instant t we calculate the following integral:

$$\int_{t_0}^{t+T} \langle \hat{\sigma}'(\dot{\varepsilon}^{\tau}_{(ht)}), \dot{\varepsilon}_{(ht)}(\tau)\rangle\, d\tau \equiv \int_{-\infty}^{t} \langle \hat{\sigma}'(\dot{\varepsilon}^{\tau}), \dot{\varepsilon}(\tau)\rangle\, d\tau + \int_0^T \langle \hat{\sigma}'(p_h^{\tau}\dot{\varepsilon}^{t}), h(\tau)\rangle\, d\tau . \tag{71}$$

Here, on the right-hand side the lower limit of integration is replaced by $-\infty$ since the function $\dot{\varepsilon}(\tau) = 0$ for all $\tau < \tau_0$.

We introduce the notation

$$\tilde{h}(\tau) = \dot{\varepsilon}_{(ht)}(\tau - t_0) , \quad \tau \ge 0 ; \quad \tilde{T} = t + T - t_0 . \tag{72}$$

In terms of this notation the integral on the left-hand side of (71) acquires the form

$$\int_0^{\tilde{T}} \langle \hat{\sigma}'(\tilde{h}^{\tau}), \tilde{h}(\tau)\rangle\, d\tau \ge 0 \tag{73}$$

and is nonnegative by requirement (53), which is fulfilled according to the assumption. Then from (71) with account for (73) we have

$$\int_{-\infty}^{t} \langle \hat{\sigma}'(\dot{\varepsilon}^{\tau}), \dot{\varepsilon}(\tau)\rangle\, d\tau \ge -\int_0^T \langle \hat{\sigma}'(p_h^{\tau}\dot{\varepsilon}^{t}), h(\tau)\rangle\, d\tau . \tag{74}$$

The expression on the left-hand side of this inequality is independent of h; therefore, the integral on its right-hand side is limited from above if h runs through the set of all processes $\mathcal{P}$. Consequently, on this set its least upper bound $\hat{H}$ exists, which depends on $\dot{\varepsilon}^t$, i.e., is a functional on $\mathcal{H}$:

$$\hat{H}(\dot{\varepsilon}^t) = \sup_{\substack{h \in \mathcal{P} \\ T>0}} \left\{ -\int_0^T \langle \hat{\sigma}'(p_h^\tau \dot{\varepsilon}^t), h(\tau) \rangle \, d\tau \right\}. \tag{75}$$

Since the fixed process $u(s) \equiv 0$, in which the integral in (72) vanishes, belongs to $\mathcal{P}$, it is obvious that for any $f \in \mathcal{H}$

$$\hat{H}(f) \geq 0 . \tag{76}$$

If we assume that in (74) $\dot{\varepsilon}^t = 0^+$, then from the obtained inequality it immediately follows that $\hat{H}(0^+) \leq 0$, which together with (76) yields

$$\hat{H}(0^+) = 0 . \tag{77}$$

Since inequality (74) is fulfilled for any h in the last integral, it is also fulfilled if this integral is replaced by its smallest supremum (75):

$$\int_{-\infty}^{t} \langle \hat{\sigma}'(\dot{\varepsilon}^\tau), \dot{\varepsilon}(\tau) \rangle \, d\tau \geq \hat{H}(\dot{\varepsilon}^\tau) , \tag{78}$$

and by definition (75) we have

$$\int_0^T \langle \hat{\sigma}'(p_h^\tau \dot{\varepsilon}^t), h(\tau) \rangle \, d\tau \leq \hat{H}(\dot{\varepsilon}^t) . \tag{79}$$

Using the fact that h is arbitrary in (79), we write this inequality for a process $\hat{h} = h \circ h_1$ representing the composition of two arbitrary processes h and h_1 with a duration of T and of T_1, respectively:

$$\int_0^T \langle \hat{\sigma}'(p_h^\tau \dot{\varepsilon}^t), h(\tau) \rangle \, d\tau - \int_0^{T_1} \langle \hat{\sigma}'(p_{h_1}^\tau (p_h^T \dot{\varepsilon}^t)), h(\tau) \rangle \, d\tau \leq \hat{H}(\dot{\varepsilon}^t) . \tag{80}$$

If we vary h_1 in this inequality, then only the second integral in (80) changes; the inequality itself is retained. This means the inequality is also retained if this integral is replaced by the least upper bound determined by (75):

$$\int_0^T \langle \hat{\sigma}'(p_h^\tau \dot{\varepsilon}^t), h(\tau) \rangle \, d\tau \geq \hat{H}(p_h^T \dot{\varepsilon}^t) - \hat{H}(\dot{\varepsilon}^t) . \tag{81}$$

Since the configuration trajectory was arbitrary, this inequality is valid if an arbitrary history f is substituted for $\dot{\varepsilon}^t$. We calculate the thermodynamic action performed by an arbitrary process h with a duration of T from an arbitrary initial state $\Lambda = \{\alpha, f\}$. By definition (39) and constitutive equation (48) we have

$$a(\Lambda, h) = \int_0^T \langle \sigma_0(h^i(t) + \alpha), \dot{h}^i(t) \rangle \, dt + \int_0^T \langle \hat{\sigma}'(h^t), h(t) \rangle \, dt . \tag{82}$$

Calculating here the first integral with account for condition (51), which is fulfilled by assumption, by virtue of inequality (81) we obtain

$$a(\Lambda, h) \geq \hat{H}(p_h^T f) + \psi_0(h^i(T) + \alpha) - (\hat{H}(f) + \psi_0(\alpha)) \equiv \hat{\psi}(h^i(T) + \alpha, p_h^T f) - \hat{\psi}(\alpha, f) =$$

$$= \hat{\psi}(P_h^T \Lambda) - \hat{\psi}(\Lambda), \tag{83}$$

where the following notation is introduced:

$$\hat{\psi}(\alpha, f) = \hat{H}(f) + \psi_0(\alpha). \tag{84}$$

From relation (83) follows inequality (43) provided that the thermodynamic potential $\hat{\psi}$ determined by (84) is lower semicontinuous. To complete the proof of the theorem, we must to show that the potential $\hat{\psi}$ determined by (84) possesses this property. Then from (83) by virtue of Theorem 1 the fulfillment of the postulate **P1** follows and the proof of sufficiency is completed. Since the equilibrium part of the potential ψ_0 is continuous in structure, it is required to demonstrate only the lower semicontinuity of the functional $\hat{H}$ in the space of histories $\mathcal{H}$, i.e., in accordance with (44) and (45) to show that the functional $\hat{H}$ possesses the following property: for each history $f \in \mathcal{H}$ and any $\zeta > 0$ there exists $\delta > 0$ such that for all histories f_1 satisfying the condition

$$\| f - f_1 \| < \delta, \tag{85}$$

the inequality

$$\hat{H}(f) < \hat{H}(f_1) - \zeta \tag{86}$$

is fulfilled. In order to prove this, it should be shown, as follows from the definition of supremum (75), that for each history $f \in \mathcal{H}$ and any $\xi > 0$ there exists $\delta > 0$ such that for all histories f_1 satisfying condition (85) there exists a process h_ζ such that

$$\left| \hat{H}(f) + \int_0^{T_0} \langle \hat{\sigma}'(p_{h_\zeta}^\tau f_1), h_\zeta(\tau) \rangle \, d\tau \right| < \zeta. \tag{87}$$

Otherwise, we will prove that the integral whose least supremum is $\hat{H}(f_1)$ can approximate $\hat{H}(f)$ with an arbitrary accuracy ζ. This means that $\hat{H}(f_1)$, with an accuracy up to ζ, is no less than $\hat{H}(f)$, and this is equivalent to (86). We write the left-hand side of the inequality in (87) in the following form:

$$\left| \hat{H}(f) + \int_0^{T_0} \langle \hat{\sigma}'(p_{h_\zeta}^\tau f), h_\zeta(\tau) \rangle \, d\tau + \int_0^{T_0} \left\langle \left(\hat{\sigma}'(p_{h_\zeta}^\tau f_1) - \hat{\sigma}'(p_{h_\zeta}^\tau f) \right), \; h_\zeta(\tau) \right\rangle d\tau \right| \leq$$

$$\leq \left| \hat{H}(f) + \int_0^{T_0} \langle \hat{\sigma}'(p_{h_\zeta}^\tau f), h_\zeta(\tau) \rangle \, d\tau \right| + \int_0^{T_0} \left\| \left(\langle \hat{\sigma}'(p_{h_\zeta}^\tau f_1) - \hat{\sigma}'(p_{h_\zeta}^\tau f) \right) \right\| \; \left| h_\zeta(\tau) \right| \, d\tau. \tag{88}$$

By the definition of functional $\hat{H}$ (75), for any $\zeta > 0$ in the last expression there can be found $T_0 > 0$ and $h_\zeta \in \mathcal{P}_{T_0}$ such that the first module on the right-hand side of (88) will be smaller than $\zeta/2$ and in the last term, by virtue of the continuity of the functional $\hat{\sigma}$ and of the continuity of the transformation p_{h_ζ} induced by a process h_ζ, there exists $\delta > 0$ such that for all histories f_1 satisfying condition (85) this term will be smaller than $\zeta/2$. Whence fulfillment of (87) and, consequently, of (86) follows. The theorem is proved.

It is easy to show that the previously established necessary and sufficient conditions of fulfillment of the second law for linear thermodynamic systems [9] are a special case of this result.

It should be noted that the method of proof here is substantially easier than in [9]; at the same time it is constructive, i.e., contains a procedure of constructing the nonequilibrium thermodynamic potential. Comparing this procedure with the theory of thermodynamic potentials in the linear case [10] one can make sure of the fact that this is the potential corresponding to the so-called minimum potential. As in the linear case, here ambiguity of the nonequilibrium thermodynamic potentials might be expected, i.e., the presence of a whole family of such potentials, and, thus, here one comes across the problem of investigation of this family and the problem of the presence of an element with specific properties, which corresponds to the classical nonequilibrium potential.

Thus, in the present work necessary and sufficient conditions for fulfillment of the second law of thermodynamics (and consequently, also for existence of the nonequilibrium thermodynamic potential) for nonlinear thermodynamic systems with memory are obtained. The first of these conditions requires that the equilibrium component of generalized force be expressed as a configuration gradient of some scalar function ψ_0. The second of these conditions contains an integral similar to thermodynamic action (42), in which the expression $\sigma - \sigma_0$ in place of σ and the nonequilibrium part of the generalized force in place of generalized force are used. Such an integral is referred to as the nonequilibrium part of the thermodynamic action. Then the second of the mentioned necessary and sufficient conditions can be represented as the requirement on the property of having a fixed sign for the nonequilibrium part of the thermodynamic action in any process starting from equilibrium. This condition can be interpreted as the requirement on passivity for some accompanying dynamic system which allows one to use thereafter the formalism of the theory of dynamic systems for constructing the nonequilibrium thermodynamic potential.

There results are obtained within the framework of the theory of generalized thermodynamic systems with memory, which can represent extensive classes of specific physical systems. Several examples of such systems are given in Section 1. In particular, if the first of these examples (item a) is chosen, then the obtained necessary and sufficient conditions of thermodynamic validity represent a complete set of thermodynamic restrictions for the general theory of heat conduction with the final velocity of propagation of thermal disturbances. As a simple specific case, this theory contains a hyperbolic equation of heat conduction compatible with the thermodynamic restrictions. These results make it possible to construct nonlinear generalizations of the hyperbolic equation which are compatible with thermodynamics.

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NOTATION

Q, heat obtained by the system by the actual time; θ, absolute temperature; S_1 and S_2, entropy of the system in the initial and final state, respectively; ρ, density of the medium; $\mathbf{q}$, heat flux; r, internal heat release per unit mass; η, specific entropy; e, specific internal energy; t, t_0, t_1, t_2, and τ, time and instants of time; $\mathbf{S}$, tensor of the Piola–Kirchhoff stresses; $\mathbf{F}$, tensor of the deformation gradient; $\mathbf{E}$ and $\mathbf{H}$, intensity of the electric and magnetic field, respectively; $\mathbf{D}$ and $\mathbf{B}$, electric and magnetic induction, respectively; $\mathbf{T}$, $\mathbf{T}_1$, and $\mathbf{T}_2$, arbitrary tensors of the second rank; ϑ, inverse absolute temperature; $\mathbf{g}$, gradient of the inverse temperature; Φ, thermodynamic potential; S, configuration space; $\mathcal{E}$, three-dimensional Euclidean space; $\mathcal{L}(\mathcal{E})$, space of three-dimensional tensors of the second rank; R, set of real numbers; $\mathbf{a}$, $\mathbf{a}_1$, and $\mathbf{a}_2$, arbitrary vectors; λ, λ_1, λ_2, ζ, δ, arbitrary scalars; α, β, γ, γ_1, γ_2, ε_0, elements of the configuration space; $\langle \cdot , \cdot \rangle$, scalar product in the configuration space; σ, generalized force, the trajectory of generalized forces; ε, generalized configuration, the configuration trajectory; $\overline{\mathbf{g}}$, integral gradient of the inverse temperature; s, past, relative to present, instants of time; $\hat{\mathbf{S}}$, $\hat{\mathbf{q}}$, and $\hat{e}$, constitutive functionals of the Piola–Kirchhoff stresses, the heat flux, and the specific internal energy, respectively; $\dot{\mathbf{F}}^t$, $\dot{\overline{\mathbf{g}}}^t$, and $\dot{\vartheta}^t$, differential histories of the deformation gradient, of the integral gradient of inverse temperature, and of temperature, respectively; ρ_0, density in the reference configuration; $\hat{\sigma}$, constitutive functional of generalized forces; $\dot{\varepsilon}^t$, differential configuration history before instant t on the configuration trajectory ε; R^+, set of real nonnegative numbers; ε^t, configuration history before the instant of time on the configuration trajectory ε; $\mathcal{H}$, Hilbert space of histories; f, arbitrary element from $\mathcal{H}$ (history); $\|\cdot\|$, norm in $\mathcal{H}$; ξ, influence function; T, T_0, T_1, T_2, $\tilde{T}$, T_f, $\tilde{T}_f$, time fragments; Λ, Λ_1, Λ_2, Λ', arbitrary states; G, space of states; $\|\cdot\|_{\mathsf{G}}$, norm in the space of states; Λ^t, state of the system at instant t; Λ^+ and Λ_0^+, equilibrium states; 0^+, equilibrium history; σ_ε, trajectory of generalized forces corresponding to the configuration trajectory ε; h, h_λ, h_0, h_1, h_2, h_3, $\tilde{h}$, processes; P_h^T, transformation in the space of states associated with the process h with a duration of T; $\Lambda_{(h)}$, final state into which the process h drives the state Λ; h^i, integral process; p_h^T, transformation in space of histories associated with the process h with a duration of T; $\mathcal{P}$ and $\mathcal{P}_T$, set of all processes and set of the processes with a duration of T, respectively; u_T, fixed process with a duration of T; $\varepsilon_{(ht)}$, h-extension of the trajectory ε for the instant of time t; $h_1 \circ h_2$, composition of the processes h_1 and h_2; a, thermodynamic action; P_h^t, transformation associated with reduction of the process h to interval (0, t); $\hat{\psi}$, generalized thermodynamic potential; ∂_α, operator of differentiation (of taking a gradient) in space S; σ_0, equilibrium function of generalized forces; $\hat{\sigma}'$, nonequilibrium part of the functional of generalized forces; ψ_0, equilibrium thermodynamic potential; h^t, element of the space of histories which is determined for any process h and time $t > 0$ as $h^t(s) = h(t - s)$ in the assumption that h is supplemented with zeros for the negative arguments; $\hat{H}$, functional determined in (75) (the nonequilibrium part of the thermodynamic potential).

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