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CONSTITUTIVE HEAT-TRANSFER EQUATIONS FOR MATERIALS WITH MEMORY

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Abstract—In the paper the properties of constitutive heat-transfer equations that ensue from thermodynamic restrictions are analysed for materials with memory. In the case of the general nonlinear constitutive equation of internal energy, it is shown that the energy–temperature relaxation function must obey some integral inequality, from which it follows, in particular, that this function must have a non-negative derivative at zero. For the linear constitutive equation, the deviation of the energy–temperature relaxation function from its infinite value is nowhere greater than at the initial point. Finally, a sequence of inequalities to restrict the behaviour of the inverse energy–temperature relaxation function is suggested with somewhat different choice of independent thermodynamic variables, the linear constitutive equation being written for reverse temperature.

NOMENCLATURE

e,	internal energy;
$\mathbf{g}$,	temperature gradient;
ξ,	influence function;
t,	time;
$\mathbf{q}$,	heat flux;
x,	coordinate.

Greek symbols

α,	energy–temperature relaxation function;
γ,	inverse temperature–energy relaxation function;
ψ,	free energy;
θ,	temperature;
Λ,	thermal history.

1. INTRODUCTION

IN HIS survey of the currently central heat- and mass-transfer problems [1] Luikov has drawn attention to that of heat and mass transfer in the materials with memory. This problem is treated most completely, and from the most general standpoint, in the nonlinear thermomechanical theory developed by Truesdell [2–9] and co-workers. In these works, based on the general principles of the above theory, proofs are given for a number of rather general theorems involving thermodynamic restrictive constraints on the constitutive equations. However, due to their extreme generality these theorems stay far apart from the demands of experience. Hence, it is highly desirable to obtain such consequences of these theorems (at least for particular cases) which would be of practical use or of clear physical meaning. The present work undertakes some steps in this respect.

In Sections 3 and 4 some properties of constitutive internal energy equations that follow from thermodynamic restrictions for solid heat conductors with memory are considered with the second law of thermodynamics formulated as the Clausius–Duhem inequality. Section 3 deals with nonlinear constitutive equations governing internal energy, while in Section 4 only the properties of linear constitutive equations are concerned.

In Section 5 linear constitutive equations for reverse temperature are investigated within the same thermodynamic approach, the choice of independent variables, however, being somewhat different.

In doing this, more comprehensive information than in the previous case may be obtained on the properties of linear constitutive equations due to a specific form of the temperature functional.

2. PRELIMINARY INFORMATION

The body B is a compact domain in the three-dimensional Eucledian space $\mathscr{E}$. At each point x of the body B we consider the following time functions: density of internal energy $e(x, t)$, density of entropy $\eta(x, t)$, heat flux per unit area per unit time $q(x, t)$, absolute temperature $\theta(x, t) > 0$, temperature gradient $g(x, t) = \nabla\theta(x, t)$. The free energy density is defined as

$$\psi = e - \theta\eta. \tag{2.1}$$

A solid uniform heat conductor with memory is governed by the constitutive equations

$$\begin{aligned} \psi(t) &= \hat{\psi}[\theta^t(\cdot), \mathbf{g}^t(\cdot)] = \hat{\psi}[\Lambda(\cdot)], \\ \eta(t) &= \hat{\eta}[\theta^t(\cdot), \mathbf{g}^t(\cdot)] = \hat{\eta}[\Lambda(\cdot)], \\ \mathbf{q}(t) &= \hat{\mathbf{q}}[\theta^t(\cdot), \mathbf{g}^t(\cdot)] = \hat{\mathbf{q}}[\Lambda(\cdot)], \end{aligned} \tag{2.2}$$

where $\theta^t(s) = \theta(t-s)$ is the temperature history; $\mathbf{g}^t(s) = \mathbf{g}(t-s)$ is the temperature gradient history; and the pair $\Lambda^t(s) = [\theta^t(s), \mathbf{g}^t(s)]$ is called thermal history. The functionals $\hat{\psi}$, $\hat{\eta}$, $\hat{\mathbf{g}}$ are assumed continuous relative to the norm

$$\|\Lambda^t(s)\| = |\Lambda^t(0)| + \|\Lambda^t(s)\|_r, \tag{2.3}$$

where $|\Lambda^t(s)| = [\theta^t(s)^2 + \mathbf{g}^t(s)^2]^{1/2}$,

$$\|\Lambda^t(s)\|_r = \int_0^\infty \xi^2(s)|\Lambda^t(s)|^2\, ds,$$

$\xi(\cdot)$ is a continuous monotone-decreasing influence function, which is square-integrable over $(0, \infty)$.

The functional $\hat{\psi}$ is also assumed twice continuously differentiable in the Fréchet sense.

Norm (2.3) defines, on the set of pairs of the measurable function $[\theta^t(\cdot), \mathbf{g}^t(\cdot)]$, the Hilbert space denoted as $\mathscr{H}$. The set of pairs with the finite norm $\|\cdot\|_r$ constitutes the subspace $\mathscr{H}_r$ of the space $\mathscr{H}$.

A common domain of functionals (2.2) is the subset $\mathscr{S}$ of the space $\mathscr{H}$ consisting of the functional pairs $[\theta^t(\cdot), \mathbf{g}^t(\cdot)]$ for which $\theta^t(\cdot) > 0$. For the elements of this set the term "thermal history" is used. The subset $\bar{\mathscr{S}}$ of the set $\mathscr{S}$ consisting of continuous and piecewise-smooth thermal histories is called the set of admissible processes.

The form of norm (2.3) allows functionals (2.2) in the form

$$\begin{aligned} \psi(t) &= \hat{\psi}[\Lambda, \Lambda_r^t(\cdot)], \\ \eta(t) &= \hat{\eta}[\Lambda, \Lambda_r^t(\cdot)], \\ \mathbf{q}(t) &= \hat{\mathbf{q}}[\Lambda, \Lambda_r^t(\cdot)], \end{aligned} \tag{2.4}$$

where $\Lambda = \Lambda^t(0) = [\theta(t), \mathbf{g}(t)]$, and $\Lambda_r^t(\cdot)$ is the restriction of the function $\Lambda^t(\cdot)$ from the semi-open $[0, \infty)$ to the open $(0, \infty)$ interval. Allowing for the above assumptions, the chain rule for the time differentiation of $\hat{\psi}$ may be proved [7]

$$\dot{\psi} = \frac{\partial\psi}{\partial t} = D_\Lambda\hat{\psi}[\Lambda, \Lambda_r^t(\cdot)]\cdot\dot{\Lambda} + \delta_\Lambda\hat{\psi}[\Lambda, \Lambda_r^t(\cdot)|\dot{\Lambda}_r^t(\cdot)]. \tag{2.5}$$

Here $D_\Lambda = (D_\theta, D_g)$ and $\delta_\Lambda = (\delta_\theta, \delta_g)$ are differential operators in the first and second independent variables of functionals (2.4). Constitutive equations (2.4) will be consistent with the thermodynamics provided only they obey the Clausius–Duhem inequality of the form

$$\dot{\psi} + \dot{\theta}\eta + \frac{1}{\theta}\mathbf{g}\cdot\mathbf{q} \leq 0. \tag{2.6}$$

Theorem 2.1 [8]. Constitutive equations (2.4) obey inequality (2.6) for all admissible processes if and only if

I. $D_\theta\hat{\psi}[\Lambda^t(\cdot)] = -\hat{\eta}[\Lambda^t(\cdot)]$.
II. $D_g\hat{\psi}[\Lambda^t(\cdot)] = 0$.
III. $\hat{\mathbf{q}}[\Lambda^t(\cdot)]\cdot\mathbf{g} \leq \theta\delta_\Lambda\hat{\psi}[\Lambda^t(\cdot)|\dot{\Lambda}_r^t(\cdot)]$.

Inequality III is usually called a modified heat-conduction inequality.

Theorem 2.1 has some interesting consequences concerning the behaviour of the material at a state of equilibrium. Remind that the functional pair $(\theta^t, \mathbf{0}^t)$, where the functions $\theta^t(\cdot)$ and $\mathbf{0}^t$ are constant over $[0, \infty)$ and equal to θ and $\mathbf{0}$, respectively, is called the equilibrium history Λ^t. For equilibrium histories, functionals (2.2) reduce to equilibrium response functions being the functions of temperature

$$\hat{\eta}[\Lambda^t(\cdot)] = \eta^*(\theta), \quad \hat{\psi}[\Lambda^t(\cdot)] = \psi^*(\theta), \quad \hat{\mathbf{q}}[\Lambda^t(\cdot)] = \mathbf{q}^*(\theta). \tag{2.7$_1$}$$

Then the following consequences of Theorem 2.1 may be proved [8,10]:

Consequence 1(2.1). Of all thermal histories Λ^t ending with the temperature θ, the equilibrium history has the least free energy, i.e.

$$\hat{\psi}[\Lambda^t(\cdot)] \geq \hat{\psi}[\Lambda^t(\cdot)] = \psi^*(\theta).$$

This property of minimum free energy involves necessarily

$$\begin{aligned} &\delta_\theta\hat{\psi}(\Lambda^t|\mu_r) = 0, \quad \delta_g\hat{\psi}(\Lambda^t|\mathbf{u}_r) = 0, \\ &\delta_\theta^2\hat{\psi}(\Lambda^t|\mu_r, \mu_r) + 2\delta_\theta\delta_g\hat{\psi}(\Lambda^t|\mu_r, \mathbf{u}_r) \\ &\qquad + \delta_g^2\hat{\psi}(\Lambda^t|\mathbf{u}_r, \mathbf{u}_r) \geq 0 \end{aligned} \tag{2.7$_2$}$$

for all $(\mu_r, \mathbf{u}_r) \in \mathscr{H}_r$.

Consequence 2 (2.1). Equilibrium response functions obey the equations of classical thermostatics

$$\text{I. } \frac{\partial\psi^*(\theta)}{\partial\theta} = -\eta^*(\theta), \qquad \text{II. } \mathbf{q}^*(\theta) = 0.$$

Besides, we shall further need an integral representation of linear constitutive equations. Thus, for example, in terms of the Riesz theorem the linear functional for internal energy in the normalized space $\mathscr{S}$ with the norm $\|\cdot\|$ can be represented for isotropic materials as [10]

$$e = e_0 + \alpha(0)\theta(t) + \int_0^{\infty} \alpha'(s)\theta(t-s)\,ds \tag{2.8}$$

The continuous over $(0, \infty)$ function $\alpha(\cdot)$ having a completely integrable derivative over this interval is termed an energy–temperature relaxation function.

In Section 5 constitutive equations are considered with somewhat different choice of independent variables, namely

$$\begin{aligned} \theta^{-1} &= \hat{\theta}^{-1}[e^t(\cdot), \mathbf{g}^t(\cdot)], \\ \eta &= \hat{\eta}[e^t(\cdot), \mathbf{g}^t(\cdot)], \\ \mathbf{q} &= \hat{\mathbf{q}}[e^t(\cdot), \mathbf{g}^t(\cdot)] \end{aligned} \tag{2.9}$$

where $e^t(\cdot)$ is the internal energy history; $[e^t(\cdot), \mathbf{g}^t(\cdot)] = \Lambda(\cdot)$ is the thermal history; θ^{-1} is the reverse temperature. For such materials, the theorem similar to 2.1 holds with the above assumptions used.

Theorem 2.2. Constitutive equations (2.9) obey the Clausius–Duhem inequality for all admissible processes if and only if

I. $\hat{\theta}^{-1}[\Lambda^t(\cdot)] = D_e\hat{\eta}[\Lambda^t(\cdot)]$.
II. $D_g\hat{\eta}[\Lambda^t(\cdot)] = 0$.
III. $\delta_\Lambda\hat{\eta}[\Lambda^t(\cdot)|\dot{\Lambda}_r^t(\cdot)] \geq (1/\theta^2)\hat{\mathbf{q}}[\Lambda^t(\cdot)]\cdot\mathbf{g}$.

This theorem has a consequence of the maximum entropy for the equilibrium history which is identical to 1(2.1) and the consequence which is identical to 2(2.1).

Also, functional (2.9) in a linear case for isotropic materials may be represented in the form similar to relation (2.8)

$$\theta^{-1} = \theta_0^1 + \gamma(0)e(t) + \int_0^{\infty} \gamma'(s)e(t-s)\,ds. \tag{2.10}$$

We shall call the continuous function $\gamma(\cdot)$ an inverse temperature–energy relaxation function.

3. SOME RESTRICTIONS IMPOSED ON THE INTERNAL ENERGY FUNCTIONAL BY THE MODIFIED HEAT-CONDUCTION INEQUALITY

It is clear that the modified heat-conduction inequality places essential restrictions on the class of admissible functionals for e, ψ, η and $\mathbf{q}$. We shall further analyse in detail the properties of the internal energy functional, which is important for the study of the heat-conduction equation obtained by Nunziato [10]. To do this, the following lemma is necessary.

Lemma 3.1. From the modified heat-conduction inequality it follows that for any equilibrium thermal history $\Lambda_0^t = (\theta_0^t, \mathbf{0}^t)$ and any function h such that $(h, \mathbf{0}^t) \in \mathscr{H}$ and $(\partial h/\partial s, \mathbf{0}^t) \in \mathscr{H}$, the inequality

$$D_0\delta_0\hat{\psi}\left(\Lambda_0^t \middle| \frac{\partial h_r}{\partial s}\right)h(0) + \delta_0^2\hat{\psi}\left(\Lambda_0^t \middle| \frac{\partial h_r}{\partial s}, h_r\right) \geqslant 0 \quad (3.1)$$

holds.

Proof. Consider the subset J of the set D consisting of thermal histories of the form $[\theta^t(\cdot), \mathbf{0}^t]$. Since only thermal histories of J are considered, we shall write θ^t rather than Λ^t as an argument in constitutive functionals. From theorem 2.1(III), we have for the histories belonging to J

$$\delta_0\hat{\psi}\left(\theta^t \middle| \frac{\partial}{\partial s}\theta_r^t\right) \geqslant 0. \quad (3.2)$$

Consider the expression

$$\delta_0\hat{\psi}(\theta_0^t + u | k_r), \quad (3.3)$$

where $(k_r, \mathbf{0}_r^t) \in \mathscr{H}_r$, and u is such a function that $(\theta_0^t + u, \mathbf{0}^t) \in \mathscr{H}$. Due to the assumptions for the functional $\hat{\psi}$, the value of (3.3) at fixed k_r is continuous and Fréchet-differentiable in u and, hence, can be expanded into the following Taylor series (for the functionals)

$$\begin{aligned}\delta_0\hat{\psi}(\theta_0^t + u | k_r) &= \delta_0\hat{\psi}(\theta_0^t | k_r) + D_0\delta_0\hat{\psi}(\theta_0^t | k_r)u(0) \\ &\quad + \delta_0^2\hat{\psi}(\theta_0^t | k_r, u_r) + O(\|u\|). \quad (3.4)\end{aligned}$$

For any function h obeying the theorem condition such $\lambda_0 > 0$ can be found that $(\theta_0^t + \lambda h, \mathbf{0}^t) \in \mathscr{D}$ for all $0 < \lambda < \lambda_0$. Then, assuming $u = \lambda h$, $k = \partial(\lambda h)/\partial s$ in relation (3.4) and allowing for equation (2.7_2), we obtain

$$\begin{aligned}\delta_0\hat{\psi}\left(\theta_0^t + \lambda h \middle| \frac{\partial(\lambda h)}{\partial s}\right) &= \lambda\left[D_0\delta_0\hat{\psi}\left(\theta_0^t \middle| \frac{\partial h_r}{\partial s}\right)\lambda h(0) + \delta_0^2\hat{\psi}\left(\theta_0^t \middle| \frac{\partial h_r}{\partial s}, \lambda h_r\right) + O(\lambda)\right] \\ &= \lambda^2\left[D_0\delta_0\hat{\psi}\left(\theta_0^t \middle| \frac{\partial h_r}{\partial s}\right)h(0) + \delta_0^2\hat{\psi}\left(\theta_0^t \middle| \frac{\partial h_r}{\partial s}, h_r\right)\right] + O(\lambda^2). \quad (3.5)\end{aligned}$$

Assuming $\theta^t = \theta_0^t + h$ in inequality (3.2) and comparing it with relation (3.5) give

$$\lambda^2\left[D_0\delta_0\hat{\psi}\left(\theta_0^t \middle| \frac{\partial h_r}{\partial s}\right)h(0) + \delta_0^2\hat{\psi}\left(\theta_0^t \middle| \frac{\partial h_r}{\partial s}, h_r\right)\right] + O(\lambda^2) \geqslant 0. \quad (3.6)$$

Hence, the result to be proved. Indeed, if the reverse is supposed, i.e. that there exists such a $\tilde{h}$, obeying the conditions of the theorem, that the expression in brackets in inequality (3.6) is negative, then at λ sufficiently small the whole LHS of inequality (3.6) written for h becomes negative, which contradicts inequality (3.6). This contradiction proves that

$$D_0\delta_0\hat{\psi}\left(\theta_0^t \middle| \frac{\partial h_r}{\partial s}\right)h(0) + \delta_0^2\hat{\psi}\left(\theta_0^t \middle| \frac{\partial h_r}{\partial s}, h_r\right) \geqslant 0. \quad (3.7)$$

When written accurately, it coincides with inequality (3.1).

We shall now prove the main theorem of this section.

Theorem 3.1. For any equilibrium thermal history Λ_0^t and any $\beta > 0$ the internal energy functional obeys the inequality

$$\delta_0\hat{e}(\Lambda_0^t | \mathrm{e}^{-s/\beta}) \geqslant 0. \quad (3.8)$$

Proof. The function $\mathrm{e}^{-s/\beta}$ satisfies the conditions imposed on h by lemma 3.1, whatever the function $\xi(\cdot)$, and it can therefore be substituted into inequality (3.1) for h and into inequality (2.7_2) for μ assuming $\mathbf{u} = \mathbf{0}^t$. Thus, we arrive at

$$D_0\delta_0\hat{\psi}\left(\Lambda_0^t \middle| -\frac{1}{\beta}\mathrm{e}^{-s/\beta}\right) + \delta_0^2\hat{\psi}\left(\Lambda_0^t \middle| -\frac{1}{\beta}\mathrm{e}^{-s/\beta}, \mathrm{e}^{-s/\beta}\right) \geqslant 0, \quad (3.9)$$

$$\delta_0^2\hat{\psi}(\Lambda_0^t | \mathrm{e}^{-s/\beta}, \mathrm{e}^{-s/\beta}) \geqslant 0. \quad (3.10)$$

Using $\delta_0\eta(\Lambda_0^t | h_r) = \theta_0\delta_0\hat{e}(\Lambda_0^t | h_r)$, that ensues from equations (2.1) and (2.7_1), as well as relation (1) of the Theorem 2.1 and commutative property of the operators δ_0 and D_0, the first term in inequality (3.9) may be transformed as

$$\theta_0\delta_0\hat{e}\left(\Lambda_0^t \middle| \frac{1}{\beta}\mathrm{e}^{-s/\beta}\right). \quad (3.11)$$

Substituting relation (3.11) into inequality (3.9) for the first term, multiplying this inequality by β/θ_0 and allowing for inequality (3.10), we obtain the result to be proved

$$\delta_0\hat{e}(\Lambda_0^t | \mathrm{e}^{-s/\beta}) \geqslant \frac{1}{\theta_0}\delta_0^2\hat{\psi}(\Lambda_0^t | \mathrm{e}^{-s/\beta}, \mathrm{e}^{-s/\beta}) \geqslant 0. \quad (3.12)$$

Inequality (3.8) just proved may be presented in a more obvious form if the integral representation of the Fréchet derivative is used in terms of the energy–temperature relaxation function $\alpha(\cdot)$ introduced in Section 2 and the Riesz representation theorem for linear functionals

$$\int_0^\infty \alpha'(s)\,\mathrm{e}^{-s/\beta}\,\mathrm{d}s \geqslant 0. \quad (3.13)$$

Note that here $\alpha(\cdot)$ depends, generally speaking, on the equilibrium history Λ_0^t, at which the Fréchet derivative is taken.

It should be emphasized that inequality (3.13) as well as inequality (3.8) holds not only for the linear functional of internal energy but also for the linear portion of an arbitrary nonlinear functional.

It is obvious that inequality (3.13) considerably narrows the class of admissible energy–temperature relaxation functions $\alpha(\cdot)$ and can give some specific properties of admissible functions $\alpha(\cdot)$. Thus, assuming $\beta \to 0$ in inequality (3.13), we get

$$\alpha(\infty) \geqslant \alpha(0).$$

In the following theorem one more property of the energy–temperature relaxation function ensuing from inequality (3.13) will be proved.

Theorem 3.2. If the energy–temperature relaxation function has the limit

$$\lim_{s \to +0} \alpha'(s) = \alpha'(0) < \infty, \tag{3.14}$$

then from inequality (3.13) it follows that

$$\alpha'(0) \geqslant 0. \tag{3.15}$$

Proof. Transform the LHS of inequality (3.13), multiplying it by $1/\beta$, as follows

$$\begin{aligned} 0 &\leqslant \frac{1}{\beta}\int_0^t e^{-s/\beta}\alpha'(s)\,ds \\ &= \frac{1}{\beta}\int_0^{\varepsilon} e^{-s/\beta}\alpha'(s)\,ds + \frac{1}{\beta}\int_{\varepsilon}^{t} e^{-s/\beta}\alpha'(s)\,ds \\ &\leqslant \frac{1}{\beta}\int_0^{\varepsilon} e^{-s/\beta}\alpha'(s)\,ds + \frac{1}{\beta}\int_{\varepsilon}^{\infty} e^{-s/\beta}|\alpha'(s)|\,ds \end{aligned} \tag{3.16}$$

Adding and subtracting the quantity

$$\frac{1}{\beta}\int_0^{\varepsilon} e^{-s/\beta}\alpha'(0)\,ds$$

from the RHS of inequality (3.16) yield

$$\begin{aligned} 0 &\leqslant \frac{1}{\beta}\int_0^{\varepsilon} e^{-s/\beta}\alpha'(0)\,ds \\ &\quad + \frac{1}{\beta}\int_0^{\varepsilon} e^{-s/\beta}[\alpha'(s)-\alpha'(0)]\,ds \\ &\quad + \frac{1}{\beta}\int_{\varepsilon}^{\infty} e^{-s/\beta}|\alpha'(s)|\,ds \\ &\leqslant \frac{1}{\beta}\int_0^{\varepsilon} e^{-s/\beta}\alpha'(0)\,ds \\ &\quad + \frac{1}{\beta}\int_0^{\varepsilon} e^{-s/\beta}|\alpha'(s)-\alpha'(0)|\,ds \\ &\quad + \frac{1}{\beta}\int_{\varepsilon}^{\infty} e^{-s/\beta}|\alpha'(s)|\,ds \\ &\leqslant \alpha'(0)(1-e^{-\varepsilon/\beta}) \\ &\quad + |\alpha'(s_m^{\varepsilon})-\alpha'(0)|\cdot(1-e^{-\varepsilon/\beta}) \\ &\quad + \frac{e^{-\varepsilon/\beta}}{\beta}\int_{\varepsilon}^{\infty}|\alpha'(s)|\,ds. \end{aligned} \tag{3.17}$$

Here $s_m^{\varepsilon} \in [0, \varepsilon]$ is the point of the interval $[0, \varepsilon]$, at which the modulus $|\alpha'(s)-\alpha'(0)|$ assumes its maximum value within this interval. Now, in the RHS expression of inequality (3.17) pass to the limit at $\beta \to 0$. Since the integral

$$\int_{\varepsilon}^{\infty}|\alpha'(s)|\,ds$$

is limited by $\alpha(\cdot)$ definition, the above procedure yields

$$\alpha'(0) + |\alpha'(s_m^{\varepsilon}) - \alpha'(0)| \geqslant 0. \tag{3.18}$$

Transition to the limit at $\varepsilon \to 0$ gives $s_m^{\varepsilon} \to 0$ and, thereby, $|\alpha'(s_m^{\varepsilon}) - \alpha'(0)| \to 0$ [cf. (3.14)]. Then from inequality (3.18) it follows that

$$\alpha'(0) \geqslant 0$$

We have now proved that only those energy–temperature relaxation functions are admissible which include non-negative derivative at zero.

This finding is identical to the property of the stress relaxation function proved in [12]. The present proving is, however, different and requires less rigorous additional assumptions.

4. THERMODYNAMIC RESTRICTIONS IMPOSED ON LINEAR CONSTITUTIVE INTERNAL ENERGY EQUATIONS

Unlike Section 3 whose results hold for any constitutive equation governing internal energy, we shall be here concerned with a linearized version of this equation (2.8). The method or proving implies that through the use of theorem 2.1 and its consequences an inequality may be obtained for the internal energy functional which is similar to the dissipative inequality applied by Day [11] for viscoelasticity studies. Then, using the approach similar to the Day method, the restrictions on the behaviour of the energy–temperature relaxation function ensuing from this inequality are studied.

Consider the time-derivative of the free energy which, in line with the chain rule (2.5) and Theorem 2.1 (I, II), may be written as

$$\dot{\psi} = -\eta\dot{\theta} + \delta_{\Lambda}\psi(\Lambda^t|\Lambda_r^t). \tag{4.1}$$

By theorem 2.1 (III), we obtain from relation (4.1) the following inequality for thermal histories of the set J^*

$$\dot{\psi} \leqslant -\eta\dot{\theta}. \tag{4.2}$$

Transform this inequality as follows

$$\begin{aligned} 0 \geqslant \frac{\dot{\psi}}{\theta} + \eta\frac{\dot{\theta}}{\theta} &= \frac{\partial}{\partial t}\left(\frac{\psi}{\theta}\right) + \frac{\psi}{\theta^2}\dot{\theta} + \eta\frac{\dot{\theta}}{\theta} \\ &= \frac{\partial}{\partial t}\left(\frac{\psi}{\theta}\right) + e\frac{\dot{\theta}}{\theta^2}. \end{aligned} \tag{4.3}$$

Consider the process with the temperature being constant and equal to θ_1 for the moment t_1, somewhat changing up to the moment t_2 and then again remaining constant and being equal to θ_2 (within the whole process **g** is zero). For this process we shall integrate inequality (4.3) over the time from t_1 to t_2

$$\begin{aligned} \frac{\hat{\psi}(\theta_1^t)}{\theta_1} + \frac{\hat{\psi}[\theta^t(\cdot)]}{\theta_2} &\geqslant \int_{t_1}^{t_2} \hat{e}[\theta^t(\cdot)]\frac{\dot{\theta}(t)}{\theta(t)^2} \\ &= \int_{-\infty}^{t} \hat{e}[\theta^t(\cdot)]\frac{\dot{\theta}(t)}{\theta(t)^2}\,dt. \end{aligned} \tag{4.4}$$

*This does not restrict the generality of further considerations, for in accord with equation (2.8) $\hat{e}$ is independent of **g**.

Here the integration limits are extended to the interval $(-\infty, \infty)$, for $\dot{\theta}(t) = 0$ beyond (t_1, t_2). Taking account of the consequence I of Theorem 2.1, from inequality (4.4) we obtain

$$\int_{-\infty}^{\infty} \hat{e}[\theta^t(\cdot)] \frac{\dot{\theta}(t)}{\theta(t)^2}\,dt \leqslant \frac{\psi^*(\theta_1)}{\theta_1} - \frac{\psi^*(\theta_2)}{\theta_2} = -\int_{-\infty}^{\infty} \frac{\partial}{\partial t}\left[\frac{\psi^*[\theta(t)]}{\theta(t)}\right] dt. \quad (4.5)$$

Allowing for relation (2.1) and consequences II (2.1), this inequality is transformed as

$$\int_{-\infty}^{\infty} \{\hat{e}[\theta^t(\cdot)] - e^*[\theta(t)]\} \frac{\dot{\theta}(t)}{\theta(t)^2}\,dt \leqslant 0. \quad (4.6)$$

As is pointed out above, we shall further use linear constitutive internal energy equation (2.8) which after integration by parts and substitution of the variable in the integral may be written as

$$e = e_0 + \alpha(\infty)\theta(-\infty) + \int_{-\infty}^{t} \alpha(t-u)\dot{\theta}(u)\,du. \quad (4.7)$$

Hence, by the definition of the equilibrium response functions (2.7), we have

$$e^*(\theta) = e_0 + \alpha(\infty)\theta. \quad (4.8)$$

Regarding for equations (4.7) and (4.8), inequality (4.6) may be reduced to

$$\int_{-\infty}^{\infty}\int_{-\infty}^{t} \alpha_0(t-u)\dot{\theta}(u)\frac{\dot{\theta}(t)}{\theta(t)^2}\,du\,dt \leqslant 0, \quad (4.9)$$

where $\alpha_0 = \alpha(\cdot) - \alpha(\infty)$, and $\theta(\cdot)$ is an arbitrary function such that $\dot{\theta}(\cdot) = 0$ beyond some finite interval and $[\theta^t(\cdot), \mathbf{0}^+] \in D$. Consider the function $\theta(t)$ of the form

$$\begin{aligned}
&\theta(t) = \theta_1 && \text{for}\quad t \in [-\infty, 0],\\
&\theta(t) = \theta_1 + \frac{\lambda a}{\varepsilon} t && \text{for}\quad t \in [0, \varepsilon],\\
&\theta(t) = \theta_1 + \lambda a && \text{for}\quad t \in [\varepsilon, s],\\
&\theta(t) = \theta_1 + \lambda a + \frac{\lambda b}{\varepsilon}(t-s) && \text{for}\quad t \in [s, s+\varepsilon],\\
&\theta(t) = \theta_1 + \lambda(a+b) && \text{for}\quad t \in [s+\varepsilon, \infty].
\end{aligned}$$

Here $s \geqslant 0$, the values $a, b, \lambda > 0$ and $\varepsilon > 0$ are such that $\theta(t) > 0$ for all t. For such a process, inequality (4.9) assumes the form

$$\frac{\lambda^2 a^2}{\varepsilon^2}\int_0^{\varepsilon}\int_0^{t} \frac{\alpha_0(t-u)\,du\,dt}{(\theta_1 + \lambda a t/\varepsilon)^2} - \frac{\lambda^2 ab}{\varepsilon^2}\int_s^{s+\varepsilon}\int_0^{\varepsilon} \frac{\alpha_0(t-s)\,du\,dt}{[\theta_1 + \lambda a + \lambda b(t-s)/\varepsilon]^2} + \frac{\lambda^2 b^2}{\varepsilon^2}\int_s^{s+\varepsilon}\int_s^{t} \frac{\alpha_0(t-u)\,du\,dt}{[\theta_1 + \lambda a + \lambda b(t-s)/\varepsilon]^2}. \quad (4.10)$$

On multiplying this inequality by θ_0^2/λ^2, pass to the limit $\lambda \to 0$

$$\frac{a^2}{\varepsilon^2}\int_0^{\varepsilon}\int_0^{t} \alpha_0(t-u)\,du\,dt + \frac{ab}{\varepsilon^2}\int_s^{s+\varepsilon}\int_0^{\varepsilon} \alpha_0(t-u)\,du\,dt + \frac{b^2}{\varepsilon}\int_s^{s+\varepsilon}\int_0^{t} \alpha_0(t-u)\,du\,dt \leqslant 0. \quad (4.11)$$

Transition to the limit at $\varepsilon \to 0$ gives

$$\tfrac{1}{2}a^2\alpha_0(0) + ab\alpha_0(s) + \tfrac{1}{2}b^2\alpha_0(0) \leqslant 0, \quad (4.12)$$

at $b = -a$, we have

$$\alpha_0(0) \leqslant \alpha_0(s), \quad (4.13)$$

at $b = a$

$$\alpha_0(0) \leqslant -\alpha_0(s) \quad (4.14)$$

or, by α_0 definition,

$$\alpha(0) - \alpha(\infty) \leqslant \pm[\alpha(s) - \alpha(-\infty)]. \quad (4.15)$$

The above may be interpreted in terms of the following theorem.

Theorem 4.1. For the energy–temperature relaxation function of the linear internal-energy functional that obeys the Clausius Duhem inequality, relation (4.15) holds.

Inequality (4.15) is identical to the property of stress relaxation function which has been proved by Day for viscoelastic materials. Note that inequality (4.15) incorporates the result of Theorem 3.2 but, unlike this theorem, relation (4.15) has been proved only for the linear functional of internal energy.

5. THERMODYNAMIC RESTRICTIONS PLACED ON THE REVERSE TEMPERATURE LINEAR FUNCTIONAL

We shall further be concerned with somewhat different approach, the independent variables being chosen by relations (2.9). As has been noted in Section 2, in this case there exists a complete analogy of the theorems and their consequences with what has been considered earlier. Based on Theorem 2.2 identical to 2.1 and its consequence, for this case we may therefore repeat the calculations of Section 4 using the same arguments. For this approach, the relation similar to inequality (4.6) is of the form

$$\int_{-\infty}^{\infty} \{\hat{\theta}^{-1}[e^t(\cdot)] - \theta^{*-1}[e(t)]\}\dot{e}(t)\,dt \leqq 0 \quad (5.1)$$

for any continuous piecewise-smooth $e(\cdot)$ such that $\dot{e}(\cdot) = 0$ beyond a certain finite interval.

This inequality will be analysed together with the linear constitutive equation for reverse temperature (2.10). Similarly to equation (4.8), we have from (2.10)

$$\theta^{*-1}(e) = \theta_0^1 + \gamma(\infty)e. \quad (5.2)$$

Substituting equations (5.2) and (2.10) in the form similar to (4.7) into inequality (5.1) gives

$$\int_{-\infty}^{\infty}\int_{-\infty}^{t} \gamma_0(t-u)\dot{e}(u)\dot{e}(t)\,du\,dt \geqslant 0, \quad (5.3)$$

where

$$\gamma_0(\cdot) = \gamma(\cdot) - \gamma(\infty). \tag{5.4}$$

The structure of inequality (5.3) coincides with that of dissipative inequality of Day [11] for linear viscoelasticity. All the below results can therefore be trivially extended to the linear stress functional for viscoelastic materials.

In inequality (5.3) the region of integration can be extended to the whole plane (u, t) if the function $\gamma_0(\cdot)$ is evenly determined for negative arguments, i.e.

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \gamma_0(|t-u|)\dot{e}(u)\dot{e}(t)\,du\,dt \geq 0. \tag{5.5}$$

Consider the function $e(\cdot)$ of the form

$e(t) = a_i/\varepsilon$ for $t \in [s_i, s_i+\varepsilon]$ $i = 1, 2, \ldots n$
$e(t) = 0$ for all the remainder t

where $\varepsilon > 0$, a_i and s_i are any real numbers. For such a function, inequality (5.5) will be of the form

$$\sum_{i=1}^{n}\sum_{j=1}^{n} \frac{a_i a_j}{\varepsilon^2}\int_{s_i}^{s_i+\varepsilon}\int_{s_j}^{s_j+\varepsilon} \gamma_0(|t-u|)\,du\,dt. \tag{5.6}$$

Calculating the integrals of this inequality with regard for $\varepsilon \to 0$, we arrive at

$$\sum_{i=1}^{n}\sum_{j=1}^{n} a_i a_j \gamma_0(|s_i - s_j|) \geq 0. \tag{5.7}$$

Inequality (5.7) is the requirement for the quadratic form with the matrix $\{b_{ij}\} = \gamma_0(|s_i - s_j|)\}$ to be non-negative. For this to occur, it is necessary that

$$\det[b_{ij}] = \det[\gamma_0(|s_i - s_j|) \geq 0]. \tag{5.8}$$

Thus the following result is proved.

Theorem 5.1. That constitutive equation (2.10) be consistent with the thermodynamics, inequality (5.8) must be valid for any sequence $s_1, s_2, \ldots, s_n$.

From inequality (5.8) the conditions for the first- and second-order determinants to be non-negative give

$$\gamma_0(0) \geq 0, \tag{5.9}$$

$$\gamma_0^2(0) \geq \gamma_0^2(s). \tag{5.10}$$

Whence

$$\gamma_0(0) \geq \pm\gamma_0(s). \tag{5.11}$$

This restriction is similar to the result of Theorem 4.1. The condition for the third-order determinant to be non-negative is as follows

$$\gamma_0(0)[\gamma_0(0)^2 - \gamma_0(s)^2 - \gamma_0(s_1)^2 - \gamma_0(s_1 - s)^2] + 2\gamma_0(s)\gamma_0(s_1)\gamma_0(s_1 - s) \geq 0. \tag{5.12}$$

By writing down the conditions for the higher-order determinants to be non-negative, we shall obtain new properties of the functions $\gamma_0(\cdot)$ ensuing from inequality (5.4).

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EQUATIONS THERMIQUES CONSTITUTIVES POUR DES MATERIAUX AVEC MEMOIRE

Résumé—Les propriétés des équations thermiques constitutives conformes aux restrictions thermodynamiques sont analysées pour les matériaux avec mémoire. Dans le cas de l'équation non linéaire de l'énergie interne, on montre que la fonction de relaxation énergie—température doit obéir à une inégalité intégrale, de laquelle il résulte en particulier que cette fonction doit avoir une dérivée non négative au zéro. Pour l'équation constitutive linéaire, la déviation de la fonction de relaxation énergie—température par rapport à sa valeur infinie est partout plus grande qu'au point initial. On suggère ensuite une séquence d'inégalités pour le comportement de l'inverse de la fonction de relaxation énergie—température, avec un choix différent des variables thermodynamiques indépendantes, l'équation constitutive linéaire étant écrite en inverse de température.

DIE GRUNDGLEICHUNGEN FÜR DIE WÄRMEÜBERTRAGUNG IN MATERIALIEN MIT GEDÄCHTNIS

Zusammenfassung—Es werden die auf den thermodynamischen Grundgesetzen basierenden Grundgleichungen der Wärmeübertragung für Materialien mit Gedächtnis analysiert. Für den allgemeinen Fall der nichtlinearen Grundgleichung der inneren Energie wird gezeigt, daß die Energie-Temperatur-Relaxationsfunktion einer integralen Ungleichung gehorcht; hieraus folgt im besonderen, daß die

Ableitung dieser Funktion an der Stelle Null nicht negativ sein darf. Bei einer linearen Grundgleichung ist die Abweichung der Energie-Temperatur-Relaxationsfunktion von ihrem Endwert nirgends größer als zum Anfangszeitpunkt. Schließlich wird eine Reihe von Ungleichungen zur Eingrenzung des Verhaltens der inversen Energie-Temperatur-Relaxationsfunktion vorgeschlagen, wobei eine andere Wahl der unabhängigen thermodynamischen Variablen getroffen wird und die lineare Grundgleichung für die Kehrwerte der Temperatur angeschrieben wird.

ОБ ОПРЕДЕЛЯЮЩИХ УРАВНЕНИЯХ ТЕПЛОПЕРЕНОСА В МАТЕРИАЛАХ С ПАМЯТЬЮ

Аннотация — В работе рассматриваются свойства определяющих уравнений теплопереноса в материалах с памятью, вытекающие из термодинамических ограничений. В случае общего нелинейного определяющего уравнения внутренней энергии показано, что энерго-температурная релаксационная функция должна удовлетворять некоторому интегральному неравенству. Из этого неравенства в частности следует, что энерго-температурная функция релаксации должна иметь неотрицательную производную в нуле. Для линейного определяющего уравнения показано, что энерго-температурная функция релаксации нигде не отклоняется от своего значения на бесконечности больше, чем в начальной точке. Наконец, при несколько ином выборе независимых термодинамических переменных, когда линейное определяющее уравнение записывается для обратной температуры, указана целая последовательность неравенств, ограничивающих поведение обратной энерго-температурной релаксационной функции.