the boundary surfaces); h, distance between LVI layers; $\Lambda$, thermal conductivity of an interval; $\overline{\lambda}_m$, mean integrated thermal conductivity; $\varepsilon_0$, reduced degree of balckness of neighboring shields; $\sigma$, Stefan–Boltzmann constant; and the subscript is the number of an interval or a cooled shield.

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# CONTRIBUTION TO THE THEORY OF THE VISCOELASTICITY OF DISPERSE SYSTEMS UNDER THE CONDITIONS OF HEAT AND MASS TRANSFER

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An open system of equations for the simultaneous description of heat and mass transfer and deformation processes in disperse materials is derived on the basis of the Boltzmann–Volterra theory and the first law of thermodynamics for open systems.

Introduction. The problem of the interplay of heat and mass transfer and deformation phenomena is of unquestionable interest from the theoretical and applied standpoints. It is important, e.g., in problems of the optimization of the technological moisture-heat treatment processes, including drying of disperse materials under loading and deformation. Modern science knows of a number of theoretical methods for taking account of the effect of heat and moisture on the deformation properties of materials. Within the framework of the hereditary Boltzmann–Volterra theory [1] the effect of heat and moisture on creep of materials and stress relaxation in them is usually taken into account by the method of factor-time analogies [2, 3] in qualitative agreement with experiment. It seems more consistent, however, not to make a one-sided allowance for only the effect of heat transfer on the rheological processes but rather to describe their effect on each other. Clearly, such a complex description requires the invocation of not only mechanical laws but also thermodynamic laws and their interaction.

In this communication we propose a variant of the complex description of the above-mentioned phenomena on the basis of the hereditary Boltzmann–Volterra relations and the first law of thermodynamics for open systems, using a number of model relations. As a result we obtain a system of equations for the concurrent description of the heat and mass transfer and deformation processes and make a preliminary analysis of a number of its general results.

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For simplicity, we consider a system with lumped parameters; we assume that a small material rod (strip, filament, band) is subjected to hydrothermal treatment under a small uniaxial load (tension).

I. Mechanical Laws. Let us consider the problem of uniaxial loading or tension of samples in the form of small rods (filaments, strips, bands, etc.) of a hydrophilic material under the conditions of heat and mass exchange with an ambient medium. We assume that the creep (cr) of the materials and the stress relaxation (r) in them can be described with the aid of the hereditary Boltzmann–Volterra relations:

$$\varepsilon(t)=\frac{\sigma(t)}{E}+\int_{t_0}^{t}K(t,\ \tau)\frac{\sigma(\tau)}{E}d\tau, \tag{1cr}$$

$$\sigma(t)=E\left[\varepsilon(t)-\int_{t_0}^{t}R(t,\ \tau)\varepsilon(\tau)d\tau\right]. \tag{1r}$$

The creep kernel $K(t, \tau)$ will be assumed to be degenerate:

$$K(t,\ \tau)=\varphi_1(t)\varphi_2(\tau),$$

where $\varphi_1(t)$ and $\varphi_2(\tau)$ are, for the present, arbitrary positive functions of time. This choice of the kernel $K(t, \tau)$ in principle narrows down the theory but, inasmuch as functions $\varphi_1$ and $\varphi_2$ are arbitrary, it may encompass a wide spectrum of variants.

It is convenient to introduce two new functions $\eta$ and L from the formulas

$$\eta(t)=\varphi_1(t)\varphi_2(t),\ L(t)=-\frac{d}{dt}\ln\left\{\frac{\varphi_1(t)}{\varphi_1(t_0)}\right\}.$$

For the creep and relaxation kernels we can easily obtain

$$K(t,\ \tau)=\eta(\tau)\exp\left(-\int_{\tau}^{t}L(\theta)d\theta\right), \tag{2cr}$$

$$R(t,\ \tau)=\eta(\tau)\exp\left(-\int_{\tau}^{t}[L(\theta)+\eta(\theta)]d\theta\right). \tag{2r}$$

We can show that the hereditary relations (1cr) and (1r) with kernels (2cr) and (2r) are equivalent to the Cauchy boundary-value problem

$$\left\{\frac{d}{dt}+L(t)\right\}\varepsilon(t)=\left\{\frac{d}{dt}+L(t)+\eta(t)\right\}\frac{\sigma(t)}{E}, \tag{3}$$

$$\varepsilon(t_0)=\frac{\sigma(t_0)}{E}. \tag{4}$$

To obtain relation (1cr) we must find $\sigma(t)$ and, after calculating the right side of (3), solve the Cauchy boundary-value problem for $\varepsilon(t)$. Then to obtain relation (1r), we must assign $\varepsilon(t)$ and, calculating the left side of (3), solve the given Cauchy boundary-value problem for $\sigma(t)$. In each case we solve an evolution boundary-value problem of the Cauchy type

$$\frac{dy}{dt}+\mathscr{L}(t)y=I(t),\ y(t_0)=y_0,$$

reflecting the causality principle. The solution of the Cauchy boundary-value problem (3) and (4) has the form

$$y(t)=y_0\exp\left(-\int_{t_0}^{t}\mathscr{L}(\theta)d\theta\right)+\int_{t_0}^{t}\exp\left(-\int_{\tau}^{t}\mathscr{L}(\theta)d\theta\right)I(\tau)d\tau. \tag{5}$$

The application of this formula to both Cauchy boundary-value problems associated with Eq. (3) and condition (4), after obvious integration by parts leads to relations (1cr) and (1r).

According to formula (5), the relation times $\tau_{cr}$ and $\tau_r$ of the processes of creep and stress relaxation processes, respectively, can be determined from the formulas

$$\tau_{cr} = \frac{1}{\overline{\mathscr{L}}_{cr}}, \quad \tau_r = \frac{1}{\overline{\mathscr{L}}_r}, \tag{6}$$

where $\overline{\mathscr{L}}_{cr}$ and $\overline{\mathscr{L}}_r$ are the mean values of the functions

$$\mathscr{L}_{cr}(t) = L(t), \quad \mathscr{L}_r(t) = L(t) + \eta(t) \tag{7}$$

in the time intervals $(t_0, \tau_{cr})$ and $(t_0, \tau_r)$, which are determined by the conditions

$$\int_{t_0}^{\tau_{cr}} \mathscr{L}_{cr}(\theta)\, d\theta = 1, \quad \int_{t_0}^{\tau_r} \mathscr{L}_r(\theta)\, d\theta = 1.$$

Analysis of Eqs. (1cr) and (1r) with kernels (2cr) and (2r) and with allowance for (6) and (7) shows that the variable creep (viscosity) coefficient $\eta(t)$ determines the magnitude of the hereditary effects and the functions $\mathscr{L}_{cr}(t)$ and $\mathscr{L}_r(t)$ (so-called evolutes) determine the rates of the respective relaxation processes. For materials whose creep increases and accelerates when moistened and heated, therefore, it is natural to set

$$\frac{\partial \mathscr{L}}{\partial m} \geqslant 0, \quad \frac{\partial \mathscr{L}}{\partial T} \geqslant 0, \tag{8}$$

taking $\mathscr{L}$ to stand for both $\mathscr{L}_{cr}$ and $\mathscr{L}_r$. It is assumed here that both evolutes depend on the time through the temperature T(t) of the "working body" and the mass m(t) of the moisture in them:

$$\mathscr{L}(t) = \mathscr{L}[T(t), m(t)]. \tag{9}$$

It is natural also to assume that

$$\frac{\partial \eta}{\partial m} \geqslant 0, \quad \frac{\partial \eta}{\partial T} \geqslant 0. \tag{10}$$

Modeling the functions $\eta(t)$ and L(t) from some considerations or others (6) we must take into account conditions (8), (9), and (10).

II. Thermodynamic Relations. As applied to the problem of drying a rod the first law of thermodynamics can be written as

$$\delta Q = dU + \delta A - \mu dm, \tag{11}$$

where the customary notation has been employed. Invoking a number of rather general model relations, we convert (11) into a "working" equation, which together with (3) and (4) can serve as a basis for the theory.

I. We express the amount of heat $\delta Q$ imprted to the rod in the time dt by using the familiar Newton-Richman law

$$\delta Q = f(t)[T_m - T(t)]\, dt. \tag{12}$$

2. During drying the specific chemical potential $\mu(t)$ coincides with the specific vaporization heat r(t) of the moisture, at first free and then bound [4], i.e., $\mu(t) = r(t)$.

The variants of modeling of the terms dU + $\delta A$ remaining in (110) will be different for different problems. For specificity, we consider the problem of stress relaxation in a moistened rod during low ($\leq$ 5%) tension under the conditions of isothermal ($T_c$ =const) and isothermal ($\ell$ = const) drying. This problem lendes itself to a simple experimental implementation [5]. The material of the rod will be assumed to swell when moistened and to shrink when dried; the material is assumed to expand when heated. Accordingly, it undergoes a latent elongation during drying as a result of the shrinkage of the material:

$$\Delta l(t) = l - l_0(t). \tag{13}$$

Here $\ell_0(t)$ the variable length of the free (not elongated) rod, corresponding to its moisture content and temperature to the time t and $\ell$ is the fixed length of the elongated rod. The extension $\varepsilon(t)$ in this case is variable because of the latent elongation (13):

$$\varepsilon(t) = \frac{l - l_0(t)}{l_0(t)} = \frac{\Delta l(t)}{l_0(t)}. \tag{14}$$

It is convenient to split the elongation $\Delta\ell$ (13) into two terms $\Delta l_0 + \Delta l_1$, where $\Delta l_0 = l - l_0(t_0)$ is the initial elongation and $\Delta l_1(t) = l_0(t_0) - l_0(t)$ is the additional elongation due to the latent shrinkage of the material. Obviously, $\Delta\ell_0$ = const and, moreover, $l_0(t) = l_0(t_0) - \Delta l_1(t)$.

From this, for $\varepsilon(t)$(14) we can easily get

$$\varepsilon(t) = \frac{\Delta l(t)}{l_0(t_0)} \left\{1 + \frac{\Delta l_1(t)}{l_0(t_0) - \Delta l_1(t)}\right\},$$

or in the linear approximation in the elongation $\Delta\ell$ and $\Delta\ell_1$ $\varepsilon(t) = \varepsilon_0 + \Delta\varepsilon(t)$, where $\varepsilon_0 = \Delta l_0 / l_0(t_0) = \text{const}$, const and $\Delta\varepsilon(t) = \Delta l(t)/l_0(t_0)$. Therefore,

$$\frac{d}{dt}\varepsilon(t) = \frac{d}{dt}(\Delta\varepsilon(t)). \tag{15}$$

Let us proceed with the interpretation of the terms in (11) as applied to the problem formulated above.

3. In the case of isometric ($\ell$ = const) drying the mechanical work is zero:

$$\delta A = 0. \tag{16}$$

4. The change dU in the internal energy here is due to three factors: a) heating (change in temperature) $C_\varepsilon(t)dT$; b) shrinkage of the material (latent extension( $V\sigma d\varepsilon$; c) energy dissipation $VD(t)\varepsilon d\sigma$ as a result of stress relaxation. Thus

$$dU = C_\varepsilon(t)\,dT + V\sigma d\varepsilon + VD(t)\,\varepsilon d\sigma. \tag{17}$$

in the last term D(t) is a dimension less dissipation coefficiente, reflecting the properties of the materials.

Substituting Eqs. (12), (16), and (17) into Eq. (11) and giving all the quantities per unit time, we obtain the equation

$$f(t)\{T_c - T(t)\} = C_\varepsilon(t)\frac{dT}{dt} + V\sigma\frac{d\varepsilon}{dt} + VD(t)\,\varepsilon\frac{d\sigma}{dt} - r(t)\frac{dm}{dt}.$$

Having changed the origin for temperature measurement, $\Delta T(t) = T(t) - T_c$, with allowance for (15) we finally arrive at the working equation

$$C_\varepsilon(t)\frac{d(\Delta T)}{dt} + f(t)\,\Delta T = r(t)\frac{dm}{dt} - V\sigma\frac{d(\Delta\varepsilon)}{dt} - VD(t)\,\varepsilon\frac{d\sigma}{dt}, \tag{18}$$

which together with (3) and condition (4) forms the initial system of equations describing the interrelated processes of stress relaxation in the material and its heat and mass exchange with the ambient medium. This system in principle makes it possible to determine any pair of the three quantities $\Delta T(t)$, $m(t)$, and $\varepsilon(t)$ when the third quantity is given. If we further take into account that the extension $\varepsilon(t)$, or to be more exact its variable part $\Delta\varepsilon(t)$, is determined by the change in the temperature T(t) and the moisture content of the rod and model the pertinent relation, then instead of the three quantities $\Delta T(t)$, $m(t)$, and $\varepsilon(t)$ in Eqs. (3) and (18) we have only two, $\Delta T(t)$ and $m(t)$, and these will be determined uniquely by the coefficient functions of Eqs. (3) and (18) and the initial conditions.

System (3), (18) in principle is also suitable for determining any two coefficients (parameters of these equations) other quantities being equal, i.e., for solving the inverse problems which indirectly determine physical quantities that are rather inaccessible to direct measurement.

Let us now consider possible variants of model relations for $\mathscr{L}(t)$, $\Delta\varepsilon(t)$, etc. and some general consequences of the main system of equations (3), (18).

III. Additional Concepts and Some Conclusions. The main system of equations (3), (18) will be completely constructional once the coefficients of the functions and other quantities appearing in it are modeled or tabulated.

As the simplest example of the realization of conditions (8) we can take a model expression of the form

$$\mathscr{L}(t)=\mathscr{L}_0+\theta(t-t_s)\{1-\exp[-\alpha(T(t)-T(t_s))-\beta(m(t)-m(t_s))]\}\tilde{\mathscr{L}}, \qquad (19)$$

where are the constants $\mathscr{L}_0$, $\tilde{\mathscr{L}}$, $\alpha$, and $\beta$ are positive. We have in mind here both evolutes $\mathscr{L}_{cr}$ and $\mathscr{L}_r$ (each with its own parameters) with allowance for the relation $\eta(t)=\mathscr{L}_r-\mathscr{L}_{cr}$ and conditions (10). Besides conditions (8), Eq. (19) reflects the relaxational nature of the change in the evolutes $\mathscr{L}(t)$, which is typical processes that lead to equilibrium.

Confining the discussion to the lineaer approximation, we have

$$\mathscr{L}(t)=\mathscr{L}_0+\theta(t-t_s)\{a[T(t)-T(t_s)]+b[m(t)-m(t_s)]\}, \qquad (20)$$

where

$$a=\frac{\partial\mathscr{L}}{\partial T}\geqslant 0;\quad b=\frac{\partial\mathscr{L}}{\partial m}\geqslant 0.$$

Obviously, comparison of the approach discussed here witeh experiment should start from the linear variant (20) and only in the event of failure should the theory be more complicated.

In the linear approximation we can also set

$$\Delta\varepsilon(t)=\theta(t-t_s)\{C_1[T(t)-T(t_s)]+C_2[m(t_s)-m(t)]\},$$

whence

$$\frac{d\varepsilon}{dt}=\frac{d(\Delta\varepsilon)}{dt}=\theta(t-t_s)\left\{C_1\frac{d(\Delta T)}{dt}+C_2\frac{dm}{dt}\right\}. \qquad (21)$$

Here $C_1$ and $C_2$ are constants (parameters of the theory). This formulation reduces the number of functions sought from three ($\Delta T$, $m$, $\varepsilon$) to two ($\Delta T$, $m$) according to the number of equations (3), (18). Without considering here the system (3), (18) as a whole which corresponds to such approximations, we confine the discussion to substitution of (21) into Eq. (18):

$$\{C_\varepsilon(t)+\theta(t-t_s)C_3V\sigma\}\frac{d(\Delta T)}{dt}+f(t)\Delta T(t)=\{r(t)-\theta(t-t_s)C_4V\sigma\}\frac{dm}{dt}+VD(t)\varepsilon(t)\frac{d\sigma}{dt}.$$

From this we see that the deformation (including shrinkage) results in an effective change in the heat capacity and the specific heat of evaporation,

$$C_\varepsilon(t)\to C_\varepsilon(t)+\theta(t-t_s)C_3V\sigma,\quad r(t)\to r(t)-\theta(t-t_s)C_4V\sigma,$$

as was observed easrlier by one of us (Lutsyk) experimentally [6]. This provides some confirmation that the discussions above are correct. It should also be noted that by slightly changing the form of the discussion concerning the terms $dU$ and $\delta A$, we can also arrive at the same system of equations (3), (18) when the extension $\varepsilon(t)$ is not latent but explicit (i.e., the length $\ell$ of the sample is not fized).

Conclusion. We have constructed a universal system of equations (3), (18) which describes the interplay of the heat and mass transfer processes and deformation processes in disperse systems (in the form fo small rods, bands, strips, etc.) under uniaxial loading as well as latent or explicit extension. A preliminary analysis of this system gives grounds for recommending it for practical applicatdions.

## NOTATION

$\varepsilon(t)$, deformation of the sample; $\sigma(t)$, stress in the sample; E, initial elastic modulus of the material; $K(t, \tau)$, kernels of the creep and relaxation, respectively; t, $t_s$, and $t_0$, running time, the time corresponding to the onset of shrinkage of the material during drying, and the initial time; f(t), integrated coefficient of heat exchange between the body being dried and the ambient medium; T(t), temperature of the body; $T_m$, temperature of the ambient medium; $C_\varepsilon(t)$, heat capacity of the rod at a fixed extension $\varepsilon$; V, volume of the body being dried; and $\theta(\tau)$, Heaviside unit function.

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