CONSTITUTIVE EQUATIONS FOR VOLUME RECOVERY IN AMORPHOUS POLYMERS

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Abstract. *Constitutive relations are derived for the kinetics of volume recovery in amorphous polymers. The model is based on the theory of temporary networks in the version of a concept of adaptive links. A glassy polymer is treated as a network of permanent chains and temporary chains, whose breakage and reformation are caused by micro-Brownian motion. The relative rates of reformation for temporary chains, as well as the equilibrium concentration of permanent chains are determined by the current temperature. Simple kinetic equations are proposed for the evolution of these parameters.*

A polymer is modeled as a compressible viscoelastic medium whose specific mechanical energy equals the sum of the energies of individual links and the energy of their interaction. In nonisothermal processes these energies are changed due to thermal expansion (contraction) of the network. Volume recovery of polymeric glasses (slow changes in the specific volume after quenching or rapid heating) is explained by some misfit between the coefficients of thermal expansion for individual links and for the network as a whole. A difference between the coefficients of thermal expansion leads to internal stresses in a temporary network. Relaxation of these stresses caused by reformation of temporary links is revealed in tests as structural relaxation.

Constitutive relations for a temporary network at finite strains are derived using the laws of thermodynamics. Nonlinear ordinary differential equations are developed for the kinetics of volume recovery. To verify these equations, experimental data are fitted for polystyrene and poly(vinyl acetate). Fair agreement is demonstrated between observations and the model's predictions.

1. INTRODUCTION

The paper deals with volume recovery during physical aging (structural relaxation) of glassy polymers. Physical aging is treated as changes in mechanical and physical

properties (specific volume, specific enthalpy, relaxation spectrum) over an extended period of time (up to several years). Structural relaxation in polymeric and metal glasses has attracted essential attention in the past four decades because of its effects on strength and residual stresses [26,28,29,40].

Volume relaxation is observed in a simple test, where a specimen (equilibrated at some reference temperature Θ_r is quenched or rapidly heated to another temperature Θ below the glass transition temperature Θ_g and isothermally loaded at the temperature Θ:

$$\Theta(t) = \begin{cases} \Theta_r, & t < 0, \\ \Theta, & t \geq 0. \end{cases} \tag{1}$$

Experimental data show that the specific volume υ slowly changes with time approaching its limiting value $\upsilon(\infty)$. This phenomenon is conventionally explained by the nonequilibrium character of the glassy state [44]. The parameter

$$\delta(t) = \frac{\upsilon(t) - \upsilon(\infty)}{\upsilon(\infty)} \tag{2}$$

serves as a measure of departure from the equilibrium state of a glass. The evolution of the specific volume demonstrates the following characteristic features [26]:

1. asymmetry of the function $\delta(t)$ after positive and negative temperature jumps, which implies the nonlinearity of this function with respect to the initial departure from equilibrium;
2. memory effects observed after several temperature jumps, which imply the nonexponentiality of the function $\delta(t)$.

We confine ourselves to one-step thermal tests (1) and concentrate on the nonexponentiality, nonlinearity, and asymmetry of the dependence $\delta(t)$.

To model volume recovery, several authors use phenomenological differential equations for the function $\delta(t)$. The simplest relationship reads [24]

$$\frac{d\delta}{dt} = -\frac{\delta}{T}, \tag{3}$$

where T is the characteristic time of volume relaxation. According to more sophisticated theories, the free volume δ is partitioned into free volumes δ_m corresponding to different kinds of polymeric chains [1, 18, 26, 35]

$$\delta = \sum_{m=1}^{M} \delta_m,$$

and kinetic equations similar to Eq. (3) (but with different relaxation times T_m are written for each parameter δ_m. In the present study, we restrict ourselves to the case $M = 1$.

To describe the nonlinearity of the volume relaxation, the relaxation time T should depend on some measure of departure from equilibrium. According to the free volume theory [12], the time T is a function of the free volume fraction f, that is the ratio of the free volume per chain to the volume occupied by this chain:

$$T = T_0 \exp\left[B\left(\frac{1}{f} - \frac{1}{f_0}\right)\right], \tag{4}$$

where B is an analog of the activation energy, and f_0, T_0 are the reference values of the free volume fraction and the relaxation time.

Gardon and Narayanaswamy [19] proposed to use fictive temperature θ [45] to characterize departure of a glass from its equilibrium state. The fictive temperature is defined as a temperature at which a glass (with the current specific volume) would be in thermodynamic equilibrium. Accepting the Arrhenius equation for the relaxation time, we write

$$T = T_0 \exp\left[B_0\left(\frac{1}{\theta} - \frac{1}{\theta_0} \right) \right],\tag{5}$$

where B_0 is a material parameter, θ_0 is the initial fictive temperature [which coincides with θ_r for the program (1)]. More sophisticated expressions for the characteristic time T have been discussed in [23].

Formula (5) requires an additional equation for the fictive temperature. The KAHR model [26] implies that

$$\delta = \Delta\beta(\theta - \Theta)$$

where $\Delta\beta$ is the difference between the coefficients of (volume) thermal expansion in the rubbery and glassy states. Evolution of the fictive temperature is described by nonlinear differential equations in [8, 36] and linear integral equations in [31, 37, 42]. This issue has been discussed in detail in [17].

Another approach to the description of volume recovery treats evolution of free volume as diffusion of hypothetical elements of free volume (vacancies, holes) to some surfaces [3, 4, 5, 9, 39]. The effect of holes on the viscoelastic properties of polymers has been discussed in [11, 22, 38]. Based on the Cohen–Turnbull model [5], Curro *et al*. [9] proposed to employ the Doolittle equation (4) for the diffusivity D of a glassy polymer as a function of the free volume fraction f. To describe the kinetics of volume recovery, a nonlinear diffusion equation was integrated in a spherical domain with an unspecified radius under the assumption that the free volume fraction on the boundary coincided with the equilibrium free volume fraction at the current temperature Θ. Changes in the specific volume of a domain were estimated by an integral of the free volume fraction over the domain. Chow [3] used a similar technique to develop a set of diffusion equations based on a statistical model. No correlations have been previously established between phenomenological relationships and constitutive models based on diffusion of holes.

The objective of this paper is to derive a new model for volume recovery in amorphous polymers based on the theory of temporary networks [20, 27, 43, 47] in the version of a model of adaptive links [13, 14, 15, 16]. We analyze a polymeric network consisting of two types of chains: temporary and permanent. Breakage and reformation of chains are thought of as thermally activated processes, which implies that the equilibrium concentrations of chains in a network are functions of temperature. After rapid heating (cooling), the equilibrium concentration of permanent chains changes and the number of these chains decreases (increases) approaching a new equilibrium value. The evolution of the concentration of permanent chains with time is described by a linear kinetic equation.

A polymer is modeled as a compressible transient network whose mechanical energy equals the sum of the mechanical energies of individual chains and the energy of their interaction. Thermal treatment of the medium causes changes in the natural (stress-free)

configurations of chains and in the natural (stress-free) configuration of the network. These changes are characterized by the coefficients of linear thermal expansion α for a chain and of volume thermal expansion β for a network. Our main hypothesis is that some misfit exists between these parameters:

$$\beta \neq 3\alpha \qquad\qquad\qquad (6)$$

which causes internal stresses in the network. Relaxation of these stresses due to reformation of temporary chains and annihilation (creation) of permanent chains determine changes in the specific volume observed in experiments. Inequality (6) is valid when links form a fractal network, in particular, this is expected to be true for amorphous polymers.

Unlike previous studies, where nonlinear phenomenological relations for the relaxation time T are introduced *a priori*, our governing equations for the reformation kinetics remain linear, see Eq. (13). The nonlinearity in structural relaxation emerges *a posteriori* because of interaction between individual temporary chains and entire network (bulk material) which have different coefficients of thermal expansion.

From the engineering standpoint, evolution of specific volume is important not because it causes large displacements in a viscoelastic material (volume deformation driven by physical aging after heating or cooling by scores of degrees is of the order of 0.1 %), but because it produces (or, at least, is accompanied by) drastic changes in relaxation spectra [7, 41], yield stress [2], and the incubation energy for crazing [34].

The exposition is organized as follows. Section 2 deals with governing equations for the breakage and reformation of chains. The specific mechanical energy of a transient network is calculated in Section 3 for nonisothermal processes with finite strains. In Section 4 thermodynamic potentials are introduced for a network, and constitutive relations are derived using the laws of thermodynamics. Section 5 deals with volume recovery of a polymer after a temperature jump. A nonlinear integral equation is derived for the evolution of specific volume at finite strains. This equation is simplified for small strains and reduced to a set of nonlinear ordinary differential equations. Adjustable parameters in these equations are determined by fitting experimental data for polystyrene and polyvinyl acetate). Fair agreement is demonstrated between observations and the predictions. Some concluding remarks are formulated in Section 6.

2. A MODEL OF TEMPORARY NETWORKS

A polymeric material is treated as a network of long chains connected to junctions [43]. Two types of chains are distinguished: active and dangling. An active chain is a chain whose ends are connected to separate junctions. When an end of an active chain snaps from a junction, the chain is transformed into a dangling chain. A dangling chain becomes active when its free end captures a junction in its neighborhood.

Breakage and reformation of long chains are driven by micro-Brownian motion of junctions. Since the intensity of thermal oscillations grows with the absolute temperature θ, the rates of loss and creation increase with temperature.

At elevated temperatures, the amplitude of thermal oscillations is large and all active chains annihilate in time. With a decrease in temperature, the amplitude decreases, which implies that some chains arise that always remain active. The equilibrium number of

permanent chains (per unit mass) at temperature Θ is denoted as $N^o = N^o(\Theta)$. Permanent chains are chemical crosslinks or physical crosslinks whose lifetime exceed the duration of experiments.

For simplicity, we suppose that a network consists of one kind of chain. However, the results of this study can be easily extended to the case when M different kinds of chain form a network.

Conventional theories of transient networks deal with polymeric melts and rubbery polymers, which are characterized by a relatively large number of segments in a chain. This implies that the mechanical energy of a chain is small compared to its configurational entropy. Neglecting the contribution of strain energy into the free energy of a network, we arrive at the standard relationships in the theory of rubber elasticity.

When the temperature Θ decreases and passes through the glass transition temperature Θ_g, the number of entanglements drastically increases. This leads to an essential decrease in the average number of segments in a chain. As a result, the configurational entropy of a chain decreases, whereas its mechanical energy increases [25]. We assume that below the glass transition temperature Θ_g, the configurational entropy is small compared to the strain energy of a chain, which implies that a chain may be treated as an elastic spring (link).

The reformation process is determined by the function $\Xi(t,\tau)$, which equals the number (per unit mass) of active temporary chains that have been created before time τ and exist at time t. In particular, $\Xi(t,0)$ is the number of initial temporary chains existing at the current instant t, $\Xi_0(t) = \Xi(t,t)$ is the total number of active temporary chains at time t, and

$$\frac{\partial \Xi}{\partial \tau}(t,\tau)d\tau$$

is the number of temporary chains created within the interval $[\tau, \tau + d\tau]$ and existing at time t. The relative rates of breakage for temporary chains are given by

$$\Gamma_0(t) = -\frac{1}{\Xi(t,0)}\frac{\partial \Xi}{\partial t}(t,0), \quad \Gamma(t,\tau) = -\left[\frac{\partial \Xi}{\partial \tau}(t,\tau)\right]^{-1}\frac{\partial^2 \Xi}{\partial t\partial \tau}(t,\tau) . \tag{7}$$

The relative rate of reformation is calculated as

$$\gamma(\tau) = \frac{1}{\Xi(0,0)}\frac{\partial \Xi}{\partial t}(t,\tau)\bigg|_{t=\tau} . \tag{8}$$

Integration of Eqs. (7) with the initial condition (8) results in

$$\Xi(t,0) = \Xi_0(0)\exp\left[-\int_0^t \Gamma_0(s)ds\right],$$

$$\frac{\partial \Xi}{\partial \tau}(t,\tau) = \Xi_0(0)\gamma(\tau)\exp\left[-\int_\tau^t \Gamma(s,\tau)ds\right]. \tag{9}$$

Substitution of expressions (9) into this equality

$$\Xi_0(t) = \Xi(t,0) \int_0^t \frac{\partial \Xi}{\partial \tau}(t,\tau) d\tau$$

implies the balance equation

$$\Xi_0(t) = \Xi_0(0) \left\{ \exp\left[-\int_0^t \Gamma_0(s) ds \right] + \int_0^t \gamma(\tau) \exp\left[-\int_\tau^t \Gamma(s,\tau) ds \right] d\tau \right\}. \qquad (10)$$

At finite strains, the parameters γ, Γ_0, and Γ are functions of the current temperature and the current intensity of stresses. At small strains, they depend on the current temperature Θ only:

$$\gamma(t) = \Gamma_0(t) = \Gamma(t,\tau) = \Gamma^o(\Theta(t)). \qquad (11)$$

In particular, at isothermal loading with small strains, the parameters (11) are constants, and Eq. (10) turns into the conservation law for the number of temporary links

$$\Xi_0(t) = \Xi_0(0). \qquad (12)$$

Analogs of Eqs. (7) and (8) have been proposed in [32, 33]. The balance law (10) is similar to that discussed in [43, 47]. The novelty of the present approach is that together with temporary chains, we introduce permanent chains, whose equilibrium concentration is determined by the current temperature Θ. We assume that permanent chains exist in the glassy state only, and their concentration vanishes when temperature Θ reaches the glass transition temperature Θ_g. This hypothesis is in good agreement with experimental data demonstrating the time-dependent nature of the glass transition point. According to the Eyring concept of thermally activated processes, the rate of changes in the number of permanent chains at nonisothermal loading is determined by the factor

$$\exp\left(-\frac{E}{k_B \Theta} \right),$$

where E is the energy of a permanent chain, and k_B is Boltzmann's constant. This implies that the temperature for total destruction of permanent chains in a glassy polymer heated with a constant rate increases monotonically with the rate of heating (since the current temperature increases linearly with time, whereas the time for destruction weakly depends on the rate of heating). This conclusion is confirmed by experimental data which show that Θ_g increases with the growth of the heating rate [21, 30].

We suppose that breakage and reformation of temporary chains are relatively fast processes which can be observed at isothermal, as well as in nonisothermal loading. The number of permanent chains changes in nonisothermal processes only. An increase or decrease in the concentration of permanent chains are treated as relatively slow processes of approaching thermodynamic equilibria. The number $N(t)$ of permanent chains (per unit mass) at time t obeys the linear kinetic equation:

$$\frac{DN}{Dt}(t) = -\frac{N(t) - N^o(\Theta(t))}{T(\Theta(t))} \qquad (13)$$

where $N^o(\Theta(t))$ is the equilibrium number of permanent chains, and $T(\Theta(t))$ is the relaxation time at the current temperature $\Theta(t)$. Equation (13) is similar to Eq. (3) for the free volume fraction and to the Grest–Cohen equation [21] for the probability of liquid-like cells. However, there is a significant difference between our approach and conventional techniques: the relaxation time T in Eq. (13) is thought of as a function of temperature only, whereas other models treat the parameter T as a function of some measure of departure from thermodynamic equilibrium (for instance, the increment of the free volume fraction, the Tool temperature, or the difference between the current and equilibrium specific volumes), which implies that the constitutive equation becomes *a priori* nonlinear. Since volume recovery in amorphous polymers is a nonlinear process, Eq. (13) should also lead to nonlinear governing equations for the specific volume. However, the nonlinearity of these equations is established as a consequence of interaction between individual chains and the bulk medium, which allows us to avoid introducing phenomenological hypotheses regarding the dependence of characteristic time T on a measure of departure from equilibrium.

3. THERMAL DEFORMATION OF A NETWORK

The specific mechanical energy W of a network (per unit mass) equals the sum of the specific energy of interaction between individual chains W_1 and the mechanical energy of active chains W_2:

$$W(t) = W_1(t) + W_2(t) . \tag{14}$$

Neglecting changes in the number of active chains, we treat the energy of their interaction W_1 as a function of the current density ρ. We assume that at an arbitrary temperature Θ, some natural (stress-free) configuration exists with the mass density $\rho^o(\Theta)$, and set

$$W_1 = \tilde{\omega}\left(\frac{\rho}{\rho^o}\right), \tag{15}$$

where $\tilde{\omega}(x)$ is a given function. The specific volume in the equilibrium state at temperature Θ reads

$$\upsilon^o(\Theta) = \frac{1}{\rho^o(\Theta)} .$$

The coefficient of (volume) thermal expansion for a network β is defined as

$$\beta = \frac{1}{\upsilon^o}\frac{d\upsilon^o}{d\Theta} . \tag{16}$$

Assuming β to be constant (this hypothesis is quite acceptable when changes in temperature do not exceed several tens of degrees), we integrate Eq. (16) and find that

$$\upsilon^o(\Theta) = \upsilon^o(\Theta_r)\exp[\beta(\Theta - \Theta_r)], \quad \rho^o(\Theta) = \rho^o(\Theta_r)\exp[-\beta(\Theta - \Theta_r)] . \tag{17}$$

We accept the model of affine networks, where junctions are frozen in the bulk material

[46]. Denote by $\hat{F}_0(t)$ the Finger tensor for transition from the natural configuration of the bulk medium at the reference temperature Θ_r to its actual configuration at temperature $\Theta(t)$. Let $I_{k0}(t) = I_k(\hat{F}_0(t))$ be the k-th principal invariant of $\hat{F}_0(t)$. Combining Eqs. (15) and (17) and bearing in mind that

$$\frac{\rho}{\rho^o(\Theta_r)} = \frac{1}{\sqrt{I_{30}}} ,$$

we arrive at the formula

$$W_1(t) = \omega\left(\frac{I_{30}(t)}{\exp[2\beta(\Theta - \Theta_r)]}\right), \tag{18}$$

where $\omega(x) = \tilde{\omega}(x^{-1/2})$. For definiteness, we suppose that the energy of interaction between active chains vanishes in the stress-free state at the reference temperature, which implies that

$$\omega(1) = 0 . \tag{19}$$

The mechanical energy of active chains $W_2(t)$ equals the sum of the mechanical energy of initial chains existing at time t and the mechanical energy of chains arising within the interval $(0,t]$ and existing at time t:

$$W_2(t) = [N(0) + \Xi(t,0)]U_0(t) + \int_0^t \left[\frac{dN}{dt}(\tau) + \frac{\partial\Xi}{\partial\tau}(t,\tau)\right]U(t,\tau)d\tau , \tag{20}$$

where $U_0(t)$ is the average mechanical energy of an initial chain at the current instant t, and $U(t,\tau)$ is the average mechanical energy of a chain that was created at time τ and exists at time t.

We confine ourselves to relatively slow reformation processes, where stress in a dangling chain totally relaxes before this chain captures a new junction. This means that the natural (stress-free) configuration of a chain created at time τ coincides with the actual configuration of a network at that instant.

To determine the quantities U_0 and U, we consider a chain merging with the network at time τ and directed along some unit vector $\bar{e}$ at the instant of its creation. Denote by $l_0(\tau)$ the length of this chain at the instant of its creation, and by $l^o(t,\tau)$ its length in the natural configuration at time t. Since all chains are created free of stresses, the quantity $l^o(\tau)$ coincides with the chain's length in the natural configuration at temperature $\Theta(\tau)$:

$$l_0(\tau) = l^0(\tau,\tau) . \tag{21}$$

The coefficient of (linear) thermal expansion for individual chains α is introduced by the formula similar to Eq. (16):

$$\frac{1}{l^o}\frac{dl^o}{d\Theta} = \alpha . \tag{22}$$

Assuming α to be constant, we integrate Eq. (22) with the initial condition (21) and find that

$$l^o(t,\tau) = l_o(\tau)\exp[\alpha(\Theta(t) - \Theta(\tau))] . \tag{23}$$

Denote by $l(t,\tau,\overline{e})$ the length of the chain at time t and by $\lambda(t,\tau,\overline{e})$ its extension ratio,

$$\lambda(t,\tau,\overline{e}) = \frac{l(t,\tau,\overline{e})}{l^o(t,\tau)} .$$

Substitution of expression (23) into this equality yields

$$\lambda(t,\tau,\overline{e}) = \frac{l(t,\tau,\overline{e})}{l_o(\tau)\exp[\alpha(\Theta(t) - \Theta(\tau))]} . \tag{24}$$

Let us consider a chain that connects junctions A and B with radius vectors $\overline{r}_A$ and $\overline{r}_B$. The radius vectors at times t and τ satisfy the equalities

$$\overline{r}_A(t) = \overline{r}_A(\tau) + \overline{u}_A(t,\tau,\overline{r}_A(\tau)) , \quad \overline{r}_B(t) = \overline{r}_B(\tau) + \overline{u}_B(t,\tau,\overline{r}_A(\tau)) , \tag{25}$$

where $\overline{u}(t,\tau,\overline{r})$ is the displacement vector at point $\overline{r}$ for transition from the actual configuration of the network at time τ to its actual configuration at time t. The end-to-end vector for the link at time t is

$$\begin{aligned}
\Delta\overline{r}(t,\tau,\overline{e}) &= \overline{r}_B(t) - \overline{r}_A(t) \\
&= [\overline{r}_B(\tau) - \overline{r}_A(\tau)] + [\overline{u}(t,\tau,\overline{r}_B(\tau)) - \overline{u}(t,\tau,\overline{r}_A(\tau))] \\
&= l_0(\tau)\overline{e} + [\overline{u}(t,\tau,\overline{r}_A(\tau) + l_0(\tau)\overline{e}) - \overline{u}(t,\tau,\overline{r}_A(\tau))].
\end{aligned}$$

Neglecting terms beyond the first order compared to $l_0(\tau)$, we find that

$$\Delta\overline{r}(t,\tau,\overline{e}) = l_0(\tau)\overline{e} \cdot [\hat{I} + \overline{\nabla}(\tau)\overline{u}(t,\tau)] , \tag{26}$$

where $\overline{\nabla}(t)$ is the gradient operator in the actual configuration at instant t, $\hat{I}$ is the unit tensor, the dot denotes inner product, and the argument $\overline{r}_A$ is omitted. It follows from Eqs. (25) and (26) that

$$\Delta\overline{r}(t,\tau,\overline{e}) = l_0(\tau)\overline{e} \cdot \overline{\nabla}(\tau)\overline{r}(t) = [\overline{\nabla}(\tau)\overline{r}(t)]^{\mathsf{T}} \cdot l_0(\tau)\overline{e} ,$$

where T stands for transpose. The length $l(t,\tau,\overline{e})$ is calculated as

$$l^2(t,\tau,\overline{e}) = \Delta\overline{r}(t,\tau,\overline{e}) \cdot \Delta\overline{r}(t,\tau,\overline{e}) = l_0^2(\tau)\overline{e} \cdot \hat{G}(t,\tau) \cdot \overline{e} , \tag{27}$$

where

$$\hat{G}(t,\tau) = \overline{\nabla}(r)\overline{r}(t) \cdot [\overline{\nabla}(r)\overline{r}(t)]^{\mathsf{T}}$$

is the relative Cauchy deformation tensor.

The mechanical energy of an adaptive link $\varpi(t,\tau,\overline{e})$ created at time τ with the guiding vector $\overline{e}$ is a given function of the extension ratio $\lambda(t,\tau,\overline{e})$:

$$\varpi(t,\tau,\overline{e}) = \Omega(\lambda(t,\tau,\overline{e})) , \tag{28}$$

where the function $\Omega(\lambda)$ satisfies condition (19)

$$\Omega(1) = 0. \tag{29}$$

Combining Eqs. (24), (27), and (28), we obtain

$$\varpi(t,\tau,\overline{e}) = \Omega\left(\frac{[\overline{e}\cdot\hat{G}(t,\tau)\cdot\overline{e}]^{1/2}}{\exp[\alpha(\Theta(t)-\Theta(\tau)]}\right). \tag{30}$$

The average mechanical energy reads

$$U(t,\tau) = \int_S \varpi(t,\tau,\overline{e})\phi(\overline{e})dA(\overline{e}) , \tag{31}$$

where S is the surface of a unit sphere in the space of guiding vectors $\overline{e}$, dA is the area element on S, and $\phi(\overline{e})$ is the probability density for a chain to have a guiding vector $\overline{e}$. This study focuses on isotropic networks with

$$\phi(\overline{e}) = \frac{1}{4\pi} . \tag{32}$$

Substitution of expressions (30) and (32) into Eq. (31) results in

$$U(t,\tau) = \frac{1}{4\pi}\int_0^\pi \sin\vartheta d\vartheta \int_0^{2\pi} \Omega\left(\frac{[\overline{e}\cdot\hat{G}(t,\tau)\cdot\overline{e}]^{1/2}}{\exp[\alpha(\Theta(t)-\Theta(\tau)]}\right)d\varphi , \tag{33}$$

where ϑ and φ are spherical angles, which determine the position of the unit vector $\overline{e}$ with respect to the unit vectors $\overline{e}_i$ of a Cartesian coordinate frame:

$$\overline{e} = \overline{e}_1 \cos\vartheta + \sin\vartheta(\overline{e}_2 \cos\varphi + \overline{e}_3 \sin\varphi) .$$

The average mechanical energy of an initial chain is determined by the formula analogous to Eq. (33),

$$U_0(t) = \frac{1}{4\pi}\int_0^\pi \sin\vartheta d\vartheta \int_0^{2\pi} \Omega\left(\frac{[\overline{e}\cdot\hat{G}_0(t)\cdot\overline{e}]^{1/2}}{\exp[\alpha(\Theta(t)-\Theta_r)]}\right)d\varphi , \tag{34}$$

where

$$\hat{G}_0(t) = \overline{\nabla}_0\overline{r}(t)\cdot[\overline{\nabla}_0\overline{r}(t)]^\mathsf{T}$$

is the Cauchy deformation tensor, and $\overline{\nabla}_0$ is the gradient operator in the initial configuration at the reference temperature Θ_r.

We combine Eqs. (14), (18), (20), (33), and (34) and arrive at the formula for the specific energy of a temporary network

$$\begin{aligned}W(t) = \omega&\left(\frac{I_{30}(t)}{\exp[2\beta(\Theta(t)-\Theta_r)]}\right)+ \\ &+\left\{\frac{1}{4\pi}[N(0)+\Xi(t,0)]\int_0^\pi \sin\vartheta d\vartheta \int_0^{2\pi}\Omega\left(\frac{[\overline{e}\cdot\hat{G}_0(t)\cdot\overline{e}]^{1/2}}{\exp[\alpha(\Theta(t)-\Theta_r)]}\right)d\varphi+\right. \\ &+\left.\int_0^t\left[\frac{dN}{dt}(\tau)+\frac{\partial\Xi}{\partial\tau}(t,\tau)\right]d\tau\int_0^\pi \sin\vartheta d\vartheta\int_0^{2\pi}\Omega\left(\frac{[\overline{e}\cdot\hat{G}_0(t,\tau)\cdot\overline{e}]^{1/2}}{\exp[\alpha(\Theta(t)-\Theta(\tau))]}\right)d\varphi\right\}.\end{aligned} \tag{35}$$

Our purpose now is to calculate the derivative of the function $W(t)$ with respect to time. It follows from Eqs. (7), (29), and (35) that

$$\frac{dW}{dt}(t) = J_1(t) - J_2(t) + J_3(t),\qquad (36)$$

where

$$J_1(t) = \frac{d\omega}{dt}\left(\frac{I_{30}(t)}{\exp[2\beta(\Theta(t)-\Theta_r)]}\right),$$

$$J_2(t) = \frac{1}{4\pi}\left\{\Gamma_0(t)\Xi(t,0)\int_0^\pi \sin\vartheta d\vartheta \int_0^{2\pi}\Omega\left(\frac{[\bar{e}\cdot\hat{G}_0(t)\cdot\bar{e}]^{1/2}}{\exp[\alpha(\Theta(t)-\Theta_r)]}\right)d\varphi + \right.$$

$$\left. + \int_0^t \Gamma(t,\tau)\frac{\partial\Xi}{\partial\tau}(t,\tau)d\tau\int_0^\pi \sin\vartheta d\vartheta \int_0^{2\pi}\Omega\left(\frac{[\bar{e}\cdot\hat{G}(t,\tau)\cdot\bar{e}]^{1/2}}{\exp[\alpha(\Theta(t)-\Theta(\tau))]}\right)d\varphi\right\},$$

$$J_3(t) = \frac{1}{4\pi}\left\{[N(0)+\Xi(t,0)]\int_0^\pi \sin\vartheta d\vartheta \int_0^{2\pi}\frac{d\Omega}{dt}\left(\frac{[\bar{e}\cdot\hat{G}_0(t)\cdot\bar{e}]^{1/2}}{\exp[\alpha(\Theta(t)-\Theta_r)]}\right)d\varphi + \right.$$

$$\left. + \int_0^t\left[\frac{dN}{dt}(\tau)+\frac{\partial\Xi}{\partial\tau}(t,\tau)\right]d\tau\int_0^\pi \sin\vartheta d\vartheta \times \int_0^{2\pi}\frac{\partial\Omega}{\partial t}\left(\frac{[\bar{e}\cdot\hat{G}(t,\tau)\cdot\bar{e}]^{1/2}}{\exp[\alpha(\Theta(t)-\Theta(\tau))]}\right)d\varphi\right\}.\qquad (37)$$

The first equality in Eqs. (37) reads

$$J_1(t) = \frac{1}{\exp[2\beta(\Theta(t)-\Theta_r)]}\omega'\left(\frac{I_{30}(t)}{\exp[2\beta(\Theta(t)-\Theta_r)]}\right)\left[\frac{I_{30}}{dt}(t)-2\beta I_{30}(t)\frac{d\Theta}{dt}(t)\right],\quad (38)$$

where the prime denotes derivative. Bearing in mind that [17]

$$\frac{dI_{30}}{dt}=\left(\frac{\partial I_{30}}{\partial\hat{F}_0}\right)^{\mathsf{T}}:\frac{d\hat{F}_0}{dt},\quad \frac{\partial I_{30}}{\partial\hat{F}_0}=I_{30}(\hat{F}_0^{\mathsf{T}})^{-1},\quad \frac{d\hat{F}_0}{dt}=(\overline{\nabla}\upsilon)^{\mathsf{T}}\cdot\hat{F}_0+\hat{F}_0\cdot\overline{\nabla}\upsilon,$$

where $\overline{\upsilon}(t)$ is the velocity vector, we obtain

$$\frac{dI_{30}}{dt}(t) = 2I_{30}(t)\hat{I}:\hat{D}(t),\qquad (39)$$

where

$$\hat{D}(t) = \frac{1}{2}[\overline{\nabla}(t)\overline{\upsilon}(t)+(\overline{\nabla}(t)\overline{\upsilon}(t))^{\mathsf{T}}],$$

is the rate-of-strain tensor. Equations (38) and (39) result in

$$J_1(t) = \frac{2I_{30}(t)}{\exp[2\beta(\Theta(t)-\Theta_r)]}\omega'\left(\frac{I_{30}(t)}{\exp[2\beta(\Theta(t)-\Theta_r)]}\right)\left[\hat{I}:\hat{D}(t)-\beta\frac{d\Theta}{dt}(t)\right].\qquad (40)$$

By analogy with Eq. (38), one can write

$$\frac{\partial \Omega}{\partial t}\left(\frac{[\overline{e}\cdot\hat{G}(t,\tau)\cdot\overline{e}]^{1/2}}{\exp[\alpha(\Theta(t)-\Theta(\tau))]}\right) = \frac{[\overline{e}\cdot\hat{G}(t,\tau)\cdot\overline{e}]^{-1/2}}{2\exp[\alpha(\Theta(t)-\Theta(\tau))]}\Omega'\left(\frac{[\overline{e}\cdot\hat{G}(t,\tau)\cdot\overline{e}]^{1/2}}{\exp[\alpha(\Theta(t)-\Theta(\tau))]}\right)\times$$

$$\times\left\{\left[\overline{e}\cdot\frac{\partial\hat{G}}{\partial t}(t,\tau)\cdot\overline{e}\right] - 2\alpha[\overline{e}\cdot\hat{G}(t,\tau)\cdot\overline{e}]\frac{d\Theta}{dt}(t)\right\}. \tag{41}$$

Bearing in mind that [17]

$$\frac{\partial\hat{G}}{\partial t}(t,\tau) = 2\overline{\nabla}(\tau)\overline{r}(t)\cdot\hat{D}(t)\cdot[\overline{\nabla}(\tau)\overline{r}(t)]^{\mathsf{T}},$$

we obtain

$$\overline{e}\cdot\frac{\partial\hat{G}}{\partial t}(t,\tau)\cdot\overline{e} = \mathrm{F}^{\wedge}(t,\tau,\overline{e}):\hat{D}(t), \tag{42}$$

where

$$\mathrm{F}^{\wedge}(t,\tau,\overline{e}) = [\overline{\nabla}(\tau)\overline{r}(t)]^{\mathsf{T}}\cdot\overline{e}\overline{e}\cdot\overline{\nabla}(\tau)\overline{r}(t) \tag{43}$$

is the generalized relative Finger tensor. Replacing the tensor product $\overline{e}\overline{e}$ in expression (43) by the unit tensor $\hat{I}$, we arrive at the relative Finger tensor

$$\hat{F}(t,\tau) = [\overline{\nabla}(\tau)\overline{r}(t)]^{\mathsf{T}}\cdot\overline{\nabla}(\tau)\overline{r}(t) \tag{44}$$

When the operator $\overline{\nabla}(\tau)$ coincides with the gradient operator in the initial configuration $\overline{\nabla}_0$, Eq. (44) provides the conventional Finger tensor

$$\hat{F}_0(t) = [\overline{\nabla}_0\overline{r}(t)]^{\mathsf{T}}\cdot\overline{\nabla}_0\overline{r}(t)$$

It follows from Eqs. (41) and (42) that

$$\frac{\partial\Omega}{\partial t}\left(\frac{[\overline{e}\cdot\hat{G}(t,\tau)\cdot\overline{e}]^{1/2}}{\exp[\alpha(\Theta(t)-\Theta(\tau))]}\right) = \frac{[\overline{e}\cdot\hat{G}(t,\tau)\cdot\overline{e}]^{-1/2}}{2\exp[\alpha(\Theta(t)-\Theta(\tau))]}\Omega'\left(\frac{[\overline{e}\cdot\hat{G}(t,\tau)\cdot\overline{e}]^{1/2}}{\exp[\alpha(\Theta(t)-\Theta(\tau))]}\right)\times$$

$$\times\left\{\mathrm{F}^{\wedge}(t,\tau,\overline{e}) - 2\alpha[\overline{e}\cdot\hat{G}(t,\tau)\cdot\overline{e}]\frac{d\Theta}{dt}(t)\right\}. \tag{45}$$

Similarly,

$$\frac{\partial\Omega}{\partial t}\left(\frac{[\overline{e}\cdot\hat{G}_0(t)\cdot\overline{e}]^{1/2}}{\exp[\alpha(\Theta(t)-\Theta_r)]}\right) = \frac{[\overline{e}\cdot\hat{G}_0(t)\cdot\overline{e}]^{-1/2}}{2\exp[\alpha(\Theta(t)-\Theta_r)]}\Omega'\left(\frac{[\overline{e}\cdot\hat{G}_0(t)\cdot\overline{e}]^{1/2}}{\exp[\alpha(\Theta(t)-\Theta_r)]}\right)\times$$

$$\times\left\{\mathrm{F}^{\wedge}_0(t,\overline{e}) - 2\alpha[\overline{e}\cdot\hat{G}_0(t)\cdot\overline{e}]\frac{d\Theta}{dt}(t)\right\}, \tag{46}$$

where

$$\mathrm{F}^{\wedge}_0(t,\overline{e}) = [\overline{\nabla}_0\overline{r}(t)]^{\mathsf{T}}\cdot\overline{e}\overline{e}\cdot\overline{\nabla}_0\overline{r}(t).$$

Substitution of expressions (45) and (46) into the third equality in Eqs. (37) implies that

$$J_3(t) = \hat{M}(t):\hat{D}(t) - \alpha\mathrm{M}(t)\frac{d\Theta}{dt}(t) \tag{47}$$

where

$$\hat{M}(t) = \frac{1}{8\pi} \int_0^\pi \sin\vartheta d\vartheta \int_0^{2\pi} \left\{ [N(0) + \Xi(t,0)] \left(\frac{[\bar{e} \cdot \hat{G}_0(t) \cdot \bar{e}]^{-1/2}}{\exp[\alpha(\Theta(t) - \Theta_r)]} \right) \times \right.$$

$$\times \Omega' \left(\frac{[\bar{e} \cdot \hat{G}_0(t) \cdot \bar{e}]^{1/2}}{\exp[\alpha(\Theta(t) - \Theta_r)]} \right) \hat{F}_0(t,\bar{e}) + \int_0^t \left[\frac{dN}{dt}(\tau) + \frac{\partial\Xi}{\partial\tau}(t,\tau) \right] \frac{[\bar{e} \cdot \hat{G}(t,\tau) \cdot \bar{e}]^{-1/2}}{\exp[\alpha(\Theta(t) - \Theta(\tau))]} \times$$

$$\times \Omega' \left(\frac{[\bar{e} \cdot \hat{G}(t,\tau) \cdot \bar{e}]^{1/2}}{\exp[\alpha(\Theta(t) - \Theta(\tau))]} \right) \hat{F}(t,\tau,\bar{e}) d\tau \right\} d\varphi,$$

$$M(t) = \frac{1}{4\pi} \int_0^\pi \sin\vartheta d\vartheta \int_0^{2\pi} \left\{ [N(0) + \Xi(t,0)] \left(\frac{[\bar{e} \cdot \hat{G}_0(t) \cdot \bar{e}]^{1/2}}{\exp[\alpha(\Theta(t) - \Theta_r)]} \right) \times \right.$$

$$\times \Omega' \left(\frac{[\bar{e} \cdot \hat{G}_0(t) \cdot \bar{e}]^{1/2}}{\exp[\alpha(\Theta(t) - \Theta_r)]} \right) + \int_0^t \left[\frac{dN}{dt}(\tau) + \frac{\partial\Xi}{\partial\tau}(t,\tau) \right] \frac{[\bar{e} \cdot \hat{G}(t,\tau) \cdot \bar{e}]^{1/2}}{\exp[\alpha(\Theta(t) - \Theta(\tau))]} \times \qquad (48)$$

$$\times \Omega' \left(\frac{[\bar{e} \cdot \hat{G}(t,\tau) \cdot \bar{e}]^{1/2}}{\exp[\alpha(\Theta(t) - \Theta(\tau))]} \right) d\tau \right\} d\varphi.$$

Equations (36), (37), (40), and (47) determine the derivative of the specific mechanical energy for a temporary network. These formulas will be used in Section 4 to derive constitutive equations for a viscoelastic medium at finite strains.

4. THERMODYNAMIC POTENTIALS AND CONSTITUTIVE RELATIONS

The first law of thermodynamics reads [6]

$$\rho \frac{d\Phi}{dt} = \hat{\sigma} : \hat{D} - \overline{\nabla} \cdot \bar{q} + \rho r, \qquad (49)$$

where Φ is the specific internal energy per unit mass, $\bar{q}$ is the heat flux vector, r is the supply per unit mass, and $\hat{\sigma}$ is the Cauchy stress tensor.

The Clausius–Duhem inequality [6] implies that

$$\rho \frac{dQ}{dt} = \rho \frac{dS}{dt} + \overline{\nabla} \cdot \left(\frac{\bar{q}}{\Theta} \right) - \frac{\rho r}{\Theta} \geq 0, \qquad (50)$$

where S is the specific entropy per unit mass, and Q is the specific entropy production. Excluding the term $\overline{\nabla} \cdot \bar{q}$ from Eqs. (49) and (50) and taking into account that $\Phi = \Psi + S\Theta$, where Ψ is the specific free energy, we arrive at the formula

$$\Theta \frac{dQ}{dt} = -S \frac{d\Theta}{dt} - \frac{d\psi}{dt} + \frac{1}{\rho} \left(\hat{\sigma} : \hat{D} - \frac{1}{\Theta} \bar{q} \cdot \overline{\nabla}\Theta \right) \geq 0. \qquad (51)$$

We accept the following expression for the specific free (Helmholtz) energy ψ per unit

mass [17]:

$$\psi = \psi_0 + (c - S_0)(\Theta - \Theta_r) - c\Theta \ln \frac{\Theta}{\Theta_r} + W \; . \tag{52}$$

Here c is the specific heat, and ψ_0 and S_0 are the specific free energy and the specific entropy in the initial configuration at the temperature Θ_r. It follows from Eqs. (36) and (52) that

$$\frac{d\psi}{dt} = -\left(S_0 + c\ln\frac{\Theta}{\Theta_r}\right)\frac{d\Theta}{dt} + J_1 - J_2 + J_3 . \tag{53}$$

Substitution of expressions (40), (47), and (53) into Eq. (51) results in

$$\Theta\frac{dQ}{dt} = -\left\{S - S_0 - c\ln\frac{\Theta}{\Theta_r} - \frac{2\beta I_{30}}{\exp[2\beta(\Theta - \Theta_r)]}\omega'\left(\frac{I_{30}}{\exp[2\beta(\Theta - \Theta_r)]}\right) - \alpha M \right\}\frac{d\Theta}{dt} +$$

$$+ \left\{\frac{\hat\sigma}{\rho} - \frac{2I_{30}}{\exp[2\beta(\Theta - \Theta_r)]}\omega'\left(\frac{I_{30}}{\exp[2\beta(\Theta - \Theta_r)]}\right)\hat I - \hat M\right\} : \hat D + J_2 - \frac{1}{\rho\Theta}\overline q \cdot \overline\nabla\Theta \geq 0 . \tag{54}$$

Equating the expressions in curly braces to zero, we arrive at the constitutive equation

$$\hat\sigma(t) = \frac{2\rho(t)I_{30}(t)}{\exp[2\beta(\Theta(t) - \Theta_r)]}\omega'\left(\frac{I_{30}(t)}{\exp[2\beta(\Theta(t) - \Theta_r)]}\right)\hat I + \rho(t)\hat M(t) \tag{55}$$

and the expression for the specific entropy

$$S(t) = S_0 + c\ln\frac{\Theta(t)}{\Theta_r} + \frac{2\beta I_{30}(t)}{\exp[2\beta(\Theta(t) - \Theta_r)]}\omega'\left(\frac{I_{30}(t)}{\exp[2\beta(\Theta(t) - \Theta_r)]}\right)\hat I + \alpha M \quad (t) .$$

It follows from these formulas and Eq. (54) that

$$\Theta\frac{dQ}{dt} = J_2 - \frac{1}{\rho\Theta}\overline q \cdot \overline\nabla\Theta \geq 0 . \tag{56}$$

According to Eq. (37), the Clausius–Duhem inequality (56) is satisfied for an arbitrary loading program provided that the heat flux vector $\overline q$ obeys the Fourier law $\overline q = -\kappa\overline\nabla\Theta$ with a positive thermal diffusivity κ.

5. GOVERNING EQUATIONS FOR VOLUME RECOVERY

Time-dependent dilatation of a medium is described by the formula

$$\overline r(t) = k(t)\overline r_0 , \tag{57}$$

where $\overline r_0$ and $\overline r$ are radius vectors of a point in the initial and actual configurations, respectively, and $k(t)$ is a function of time to be found. We substitute expression (57) into Eq. (48),calculate the integrals, and find that

$$\hat{M}(t) = \frac{1}{6}\left\{[N(0) + \Xi(t,0)]\frac{k(t)}{\exp[\alpha(\Theta - \Theta_r)]}\Omega'\left(\frac{k(t)}{\exp[\alpha(\Theta - \Theta_r]}\right) + \right.$$
$$\left. + \int_0^t \left[\frac{dN}{dt}(\tau) + \frac{\partial\Xi}{\partial\tau}(t,\tau)\right]\frac{k(t)}{k(\tau)}\Omega'\left(\frac{k(t)}{k(\tau)}\right)d\tau\right\}\hat{I}. \tag{58}$$

Combining Eqs. (55) and (58) and bearing in mind that $I_{30}(t) = k^6(t)$, we obtain

$$\hat{\sigma}(t) = \rho(t)\left\langle\frac{2k^6(t)}{\exp[2\beta(\Theta - \Theta_r)]}\omega'\left(\frac{k^6(t)}{\exp[2\beta(\Theta - \Theta_r)]}\right) + \right.$$
$$+ \frac{1}{6}\left\{[N(0) + \Xi(t,0)]\frac{k(t)}{\exp[\alpha(\Theta - \Theta_r)]}\Omega'\left(\frac{k(t)}{\exp[\alpha(\Theta - \Theta_r)]}\right) + \right. \tag{59}$$
$$\left.\left. + \int_0^t\left[\frac{dN}{dt}(\tau) + \frac{\partial\Xi}{\partial\tau}(t,\tau)\right]\frac{k(t)}{k(\tau)}\Omega'\left(\frac{k(t)}{k(\tau)}\right)d\tau\right\}\right\rangle\hat{I}.$$

Since the stress tensor vanishes in the initial configuration, Eq. (59) implies that

$$\omega'(1) = 0, \quad \Omega'(1) = 0. \tag{60}$$

Volume recovery after a thermal jump satisfies the condition $\hat{\sigma}(t) = 0$. Combining this equality with Eq. (59), we arrive at the nonlinear integral equation for the function $k(t)$

$$\frac{12k^6(t)}{\exp[2\beta(\Theta - \Theta_r)]}\omega'\left(\frac{k^6(t)}{\exp[2\beta(\Theta - \Theta_r)]}\right) + $$
$$+ [N(0) + \Xi(t,0)]\frac{k(t)}{\exp[\alpha(\Theta - \Theta_r)]}\Omega'\left(\frac{k(t)}{\exp[\alpha(\Theta - \Theta_r)]}\right) + \tag{61}$$
$$+ \int_0^t\left[\frac{dN}{dt}(\tau) + \frac{\partial\Xi}{\partial\tau}(t,\tau)\right]\frac{k(t)}{k(\tau)}\Omega'\left(\frac{k(t)}{k(\tau)}\right)d\tau = 0.$$

We expand the functions $\omega'(x)$ and $\Omega'(x)$ into Taylor series in the vicinity of the point $x = 1$, use Eq. (60), neglect terms beyond the first order compared to x, and obtain

$$\omega'(x) \approx \omega''(x - 1), \quad \Omega'(x) \approx \Omega''(x - 1). \tag{62}$$

At small strains and small changes in temperature,

$$k(t) = 1 + \frac{1}{3}\varepsilon(t), \tag{63}$$

where $\varepsilon(t)$ is the volume strain. Substitution of expressions (62) and (63) into Eq. (61) results in the linear integral equation for the function $\varepsilon(t)$

$$A[\varepsilon(t) - \beta(\Theta - \Theta_r)] + [N(0) + \Xi(t,0)][\varepsilon(t) - 3\alpha(\Theta - \Theta_r)] +$$

$$+ \int_0^t \left[\frac{dN}{dt}(\tau) + \frac{\partial\Xi}{\partial\tau}(t,\tau)\right][\varepsilon(t) - \varepsilon(\tau)] = 0 \tag{64}$$

with $A = 72\omega''(1)/\Omega''(1)$. Equation (64) has a time-independent solution

$$\varepsilon = \beta(\Theta - \Theta_r)$$

if and only if

$$\alpha = \frac{1}{3}\beta, \tag{65}$$

which means that the coefficients of thermal expansion for the network and for individual links are interrelated. When condition (65) is violated [see Eq. (6)], the volume strain changes in time (volume recovery).

Equation (64) reads

$$[A + N(t) + \Xi_0(t)]\varepsilon(t) = [A + N(0) + \Xi_0(0)]\varepsilon(0) + 3\alpha(\Theta - \Theta_r)[\Xi_0(t,0) - \Xi_0(0)] +$$

$$+ \int_0^t \left[\frac{dN}{dt}(\tau) + \frac{\partial\Xi}{\partial\tau}(t,\tau)\right]\varepsilon(\tau)d\tau. \tag{66}$$

Differentiation of Eq. (66) with respect to time with account for Eqs. (7) and (8) results in

$$[A + N(t) + \Xi_0(t)]\frac{d\varepsilon}{dt}(t) + \left[\frac{d\Xi_0}{dt}(t) - \gamma(t)\Xi_0(t)\right]\varepsilon(t) =$$

$$= -3\alpha(\Theta - \Theta_r)\Gamma_0(t)\Xi_0(t,0) - \int_0^t \Gamma(t,\tau)\frac{\partial\Xi}{\partial\tau}(t,\tau)\varepsilon(\tau)d\tau. \tag{67}$$

Excluding the integral term from Eqs. (66) and (67), using Eqs. (11) and (12), and bearing in mind that [see Eq. (64)]

$$\varepsilon(0) = \frac{3\alpha[N(0) + \Xi_0(0)] + A\beta}{N(0) + \Xi_0(0) + A}(\Theta - \Theta_r), \tag{68}$$

we arrive at the formula

$$[A + N(t) + \Xi_0(0)]\frac{d\varepsilon}{dt}(t) + \Gamma^o[A + N(t)]\varepsilon(t) - \Gamma^o\int_0^t \frac{\partial N}{\partial\tau}(\tau)\varepsilon(\tau)d\tau$$

$$= \Gamma^o[A\beta + 3N(0)\alpha](\Theta - \Theta_r). \tag{69}$$

Differentiation of Eq. (69) implies the ordinary differential equation

$$\frac{dz}{dt}(t) = -[A + N(t) + \Xi_0(0)]^{-1}\left\{\frac{\partial N}{\partial t}(t) + \Gamma^o[A + N(t)]\right\}z(t) \tag{70}$$

for the function

$$z(t) = \frac{d\varepsilon}{dt}(t). \tag{71}$$

To derive an initial condition for Eq. (70), we set $t = 0$ in Eq. (69), use Eq. (68), and obtain

$$z(0) = \frac{a(\beta - 3\alpha)(\Theta - \Theta_r)}{A + N(0) + \Xi_0(0)} .$$

At small strains and small changes in temperature, the specific volume υ is given by

$$\upsilon(t, \Theta) = \upsilon^o(\Theta_r)[1 + \varepsilon(t)] .$$

It follows from this equality and Eq. (2) that

$$\delta(t) = \frac{\varepsilon(t) - \varepsilon(\infty)}{\varepsilon(\infty)} \tag{72}$$

Equalities (71) and (72) result in the differential equation

$$\frac{d\delta}{dt}(t) = \frac{z(t)}{\varepsilon(\infty)} . \tag{73}$$

Equations (13), (70), and (73) describe evolution of the specific volume at physical aging. In the dimensionless variables

$$\tau = \frac{t}{T(\Theta)} , \quad n = \frac{N}{N^o(\Theta)} - 1 , \quad Z = \frac{T(\Theta)z}{\varepsilon(\infty)} ,$$

$$\Gamma_* = \Gamma^o T(\Theta) , \quad A_* = \frac{A}{N^o(\Theta)} + 1 , \quad \Xi_* = \frac{\Xi_0(0)}{N^o(\Theta)} ,$$

these equations read

$$\frac{dn}{d\tau} = -n , \quad \frac{d\delta}{d\tau} = z , \quad \frac{dz}{d\tau} = \left(\frac{\text{A}}{n + a} - \text{B} \right) Z , \tag{74}$$

where

$$a = A_* + \Xi_* , \quad \text{A} = (A_* + \Xi_*)(\Gamma_* - 1) - A_* \Gamma_* , \quad \text{B} = \Gamma_* - 1 .$$

The boundary conditions for Eqs. (74) are given by

$$n(0) = \frac{N^o(\Theta_r) - N^o(\Theta)}{N^o(\Theta)} , \quad \delta(\infty) = 0 ,$$

$$Z(0) = \frac{\varepsilon(\infty)}{T(\Theta)} \frac{A_* - 1}{n(0) + a} (\beta - 3\alpha)(\Theta - \Theta_r) . \tag{75}$$

Formulas (74) and (75) provide new constitutive relations for the kinetics of volume recovery. These equations are determined by five adjustable parameters a, $\mathscr{A}$, $\mathscr{B}$, $n(0)$, and $Z(0)$, which are found by fitting experimental data.

To demonstrate that Eqs. (74) adequately predict volume recovery at heating and cooling, we plot experimental data for poly(vinyl acetate) and polystyrene obtained in dilatometric tests together with their predictions by the model. Figures 1 to 3 show fair agreement between observations and the results of numerical simulation.
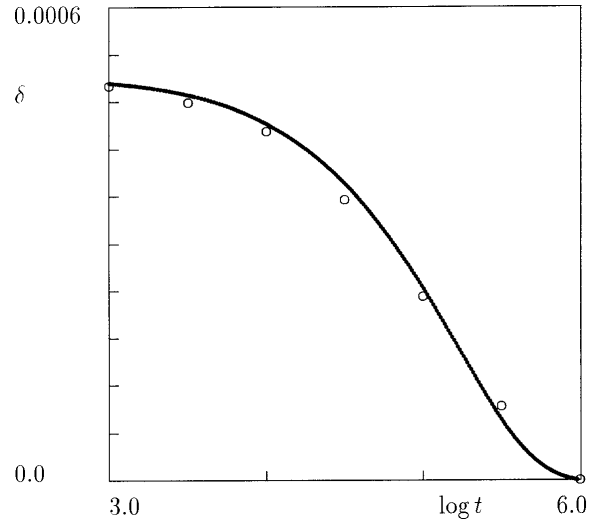
Fig. 1. The excess volume fraction δ versus time $t(s)$ for poly(vinyl acetate) quenched
from $\Theta_r = 32.5$ to $\Theta = 30.0$ $^{\circ}$C. Circles: treatment of experimental data adapted
from [39]. Solid lines: prediction of the model with $A_* = 0.5$, $\Gamma_* = 1.0$, $\Xi_* = 0.55$,
$n(0) = -1.0$, $\delta(0) = 0.00851$, $Z(0) = -0.0013$, and $\log t = \log \tau + 3.0$.
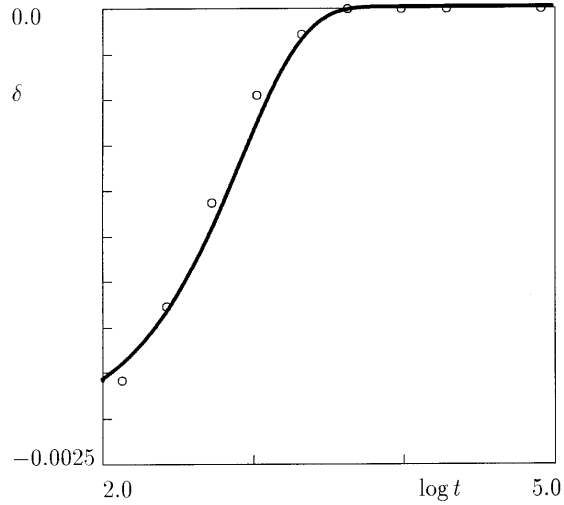

Fig. 2. The excess volume fraction δ versus time $t(s)$ for polystyrene heated from
$\Theta_r = 93.5$ to $\Theta = 100.0$ $^{\circ}$C. Circles: treatment of experimental data obtained in
[18]. Solid lines: prediction of the model with $A_* = 3.0$, $\Gamma_* = 1.4$, $\Xi_* = 5.0$,
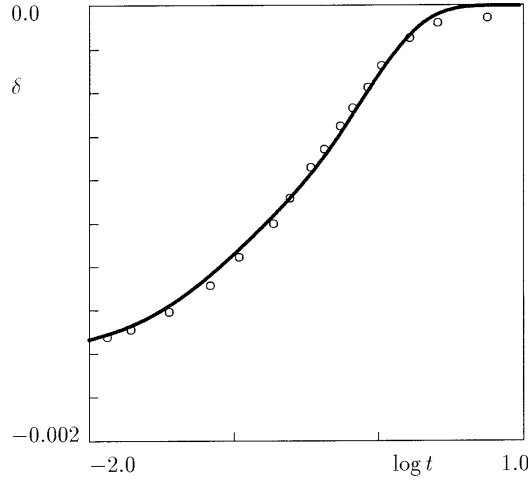$n(0) = 1.0\$$, $\delta(0) = -0.0023$, $Z(0) = 0.0012$, and $\log t = \log \tau + 5.35$.

Fig. 3. The excess volume fraction δ versus time $t(h)$ for poly(vinyl acetate) heated from $\Theta_r = 32.5$ to $\Theta_r = 36.20$ °C. Circles: experimental data obtained in [10]. Solid line: prediction of the model with $A_* = 0.09\$$, $\Gamma_* = 2.0\$$, $\Xi_* = 2.0\$$, $n(0) = 10.0$, $\delta(0) = -0.0016\$$, $Z(0) = 0.00052$, and $\log t = \log \tau + 1.17$.

The number of adjustable parameters can be significantly reduced, provided that the rate of reformation Γ^o for temporary links coincides with the rate of changes in the number of permanent links T^{-1}, which implies that $\Gamma_* = 1$, $\mathscr{A} = -A_*$, and $\mathscr{B} = 0$. To solve Eqs. (74), we divide the third equality by the first equality, integrate the resulting equation, and find that

$$Z = Z(0)\left[\frac{n(0)+a}{n(0)}\frac{n}{n+a}\right]^{\nu},\tag{76}$$

where

$$\nu = \frac{A_*}{a} = \frac{A_*}{A_* + \Xi_*}.$$

Integration of the first equality in Eqs. (74) yields

$$n(\tau) = n(0)\exp(-\tau).\tag{77}$$

We substitute expressions (76) and (77) into the second equation in Eqs. (74), integrate the resulting equality, use the boundary conditions (75), and find that

$$\delta(t) = -Z(0)\int_{\tau}^{\infty}\left[\frac{1+\mu}{\exp(s)+\mu}\right]^{\nu}ds,\tag{78}$$

where

$$\mu = \frac{n(0)}{a} = \frac{n(0)}{A_* + \Xi_*}.$$

Two limiting cases are considered: when the dimensionless initial number of permanent links is small compared to the sum $A_* + \Xi_*$, and when the dimensionless parameter A_* essentially exceeds the dimensionless parameter Ξ_*.

In the first case, $\mu \ll 1$. Neglecting terms of the first order compared to μ in Eq. (78) and calculating the integral, we arrive at the exponential law of volume recovery

$$\delta(\tau) = -\frac{Z(0)}{\nu}\exp(-\nu\tau).$$

In the other case, $\nu \approx 1$. Setting $\nu = 1$ in Eq. (78) and calculating the integral, we obtain

$$\delta(\tau) = \frac{Z_0}{\mu}\ln\frac{\exp(\tau)}{\mu + \exp(\tau)}$$

with

$$Z_0 = \frac{(A_* - 1)\varepsilon(\infty)}{aT}(\beta - 3\alpha)(\Theta - \Theta_r).$$

Figures 4 and 5 demonstrate fair agreement between observations and the predictions of Eq. (79). Curves depicted in these figures reflect the characteristic features of volume relaxation discussed in the Introduction, that is the nonlinearity, the nonexponentiality, and the asymmetry of changes in the specific volume after up and down temperature jumps. Formula (79) ensures good matching of experimental data by using only two adjustable parameters, μ and Z_0, compared to conventional models for structural relaxation, which contain at least four parameters to be found by approximation experimental data.
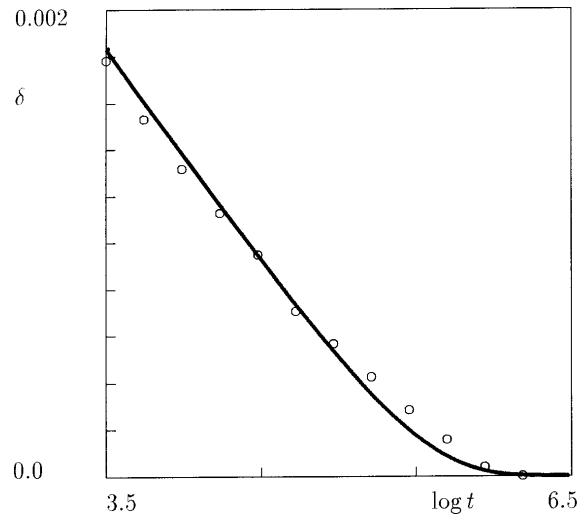

Fig. 4. The excess volume fraction δ versus time $t(s)$ for poly(vinyl acetate) quenched from 37.5 to 30 °C. Circles: experimental data adopted from [35]. Solid line: prediction of the model with $\log t = \log \tau + 3.5$, $Z_0 = -0.0004$ and $\mu = -1.0$.
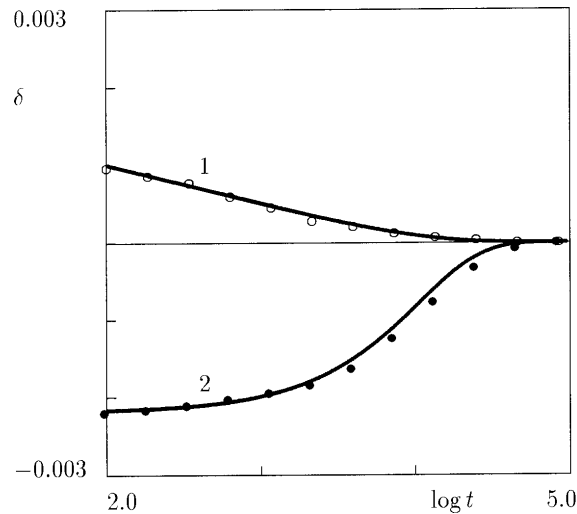
Fig. 5. The excess volume fraction δ versus time $t(s)$ for poly(vinyl acetate) quenched from 40 to 35 °C (curve 1) and heated from 30 to 35 °C (curve 2). Circles: experimental data adopted from [35]. Solid lines: predictions of the model with $t = \log \tau + 3.0\$$. Curve 1: $Z_0 = -0.00022$, $\mu = -1.0$; curve 2: $Z_0 = 0.0025$, $\mu = 0.3$.

6. CONCLUDING REMARKS

New constitutive relations have been derived for the kinetics of volume recovery after rapid heating and cooling. Governing equations are based on the concept of transient networks in the version of a model of adaptive links. It is assumed that a network consists of permanent and temporary chains, and the equilibrium concentration of permanent chains is a function of temperature. The reason for nonlinearities in the governing equations (74) is a misfit (6) between the coefficients of (linear) thermal expansion for long chains and (volume) thermal expansion for a network. The distortion caused by thermal treatment of a polymer slowly relaxes because of reformation of active chains in a network with a time-varying concentration of permanent chains. This relaxation is revealed in dilatometric tests as volume recovery after temperature jumps. Equations (74) are determined by five parameters found by fitting experimental data. Solutions of these equations fairly well approximate data for polystyrene and poly(vinyl acetate) after rapid cooling and heating. To reduce the number of adjustable parameters, Eqs. (74) are simplified in two limiting cases. A new explicit expression (79) has been derived for the function $\delta(\tau)$. Formula (79) contains only two constants to be found, provides good agreement with experimental data for poly(vinyl acetate), and adequately reflects the characteristic features of volume relaxation.

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KONSTITUTIVNE JEDNAČINE ZAPREMINSKOG OPORAVKA (OBNAVLJANJA) U AMORFNIM POLIMERIMA

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Rad sadrži model vremenskih mreža, termičkih deformacija mreža, termodinamičke potencijale i konstitutivne relacije.

Nove konstitutivne relacije su izvedene za kinetiku zapreminskog oporavka (obnavljanja) nakon naglog grejanja i hlađenja. Konstitutivne jednačine su bazirane na konceptu promenljivih mreža u obliku modela sa adaptivnim vezama.