

**A thermodynamic theory of solid viscoelasticity.  
Part III: Nonlinear glassy viscoelasticity,  
stability constraints, specifications**

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**Abstract**

This paper, the last in the series, continues developing the nonlinear constitutive relations for non-isothermal, compressible, solid viscoelasticity. We initially discuss a single integral approach, more suitable for the glassy state of rubber-like materials, with basic functionals involved in the thermodynamic description for this type of viscoelasticity. Then we switch our attention to analyzing stability constraints, imposed on the general formulation of the nonlinear theory of solid viscoelasticity. Finally, we discuss specific (known from the literature or new) expressions for material functions that are involved in the constitutive formulations of both the rubber-like and glassy-like, complementary parts of the theory.

**Keywords:** Non-equilibrium thermodynamics, Viscoelasticity, Free energy, Dissipation, Strain, Stress

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## 1. Introduction

A thermodynamic theory for linear viscoelastic phenomena that accounts for thermo-rheological complexity has been developed in the first paper of this series (Freed and Leonov, 2002<sub>1</sub>). There, different temperature dependences for various parts of the relaxation spectra were modeled differently for the rubbery and glassy types of mechanical behavior for solid polymers. It has been demonstrated experimentally and discussed in various papers that matching of both time-temperature scales is quite possible.

In the second paper of the series (Freed and Leonov 2002<sub>2</sub>), a theory of solid viscoelasticity for large strain analysis has been developed. This nonlinear theory, originated from linear viscoelasticity with a discrete relaxation spectrum, is suitable for analyzing the non-isothermal and (generally) compressible behavior of rubber-like materials with large strains.

For the sake of convenience, we now briefly present the main results from our previous paper (Freed and Leonov 2002<sub>2</sub>) for nonlinear viscoelasticity with a single (bulk and shearing) nonlinear relaxation mode. The thermodynamic state variables in this case are: the temperature  $T$ , the density  $\rho$ , the “relaxing density”,  $\rho^i$ , the “incompressible” part of the total Finger tensor,  $\hat{\underline{\underline{B}}}$ , and the incompressible part of the relaxing Finger elastic strain,  $\hat{\underline{\underline{b}}}$ . Completely bulk/shear decoupled, nonlinear, non-isothermal CE’s for solid rubbery viscoelasticity with a single relaxation mode, derived previously (Freed and Leonov, 2002<sub>2</sub>) consist of:

- (i) A completely decoupled free-energy function,

$$F = F_b^0(T, \rho) + F_b^1(T, \rho^i) + F_{sh}^0(T, \hat{I}_1^B, \hat{I}_2^B) + F_{sh}^1(T, \hat{I}_1, \hat{I}_2); \quad (1)$$

- (ii) A corresponding, additive presentation of the stress,

$$\begin{aligned} \underline{\underline{\sigma}} &= -(p_0 + p_1)\underline{\underline{\delta}} + \hat{\underline{\underline{\sigma}}}_0 + \hat{\underline{\underline{\sigma}}}_1, \quad p_0 = \rho^2 \partial \hat{F} / \partial \rho, \quad p_1 = \rho \rho^i \partial \hat{F} / \partial \rho^i, \\ \hat{\underline{\underline{\sigma}}}_0 &= 2\rho [\hat{F}_1^0(\hat{\underline{\underline{B}}} - 1/3\hat{I}_1^B \underline{\underline{\delta}}) - \hat{F}_2^0(\hat{\underline{\underline{B}}}^{-1} - 1/3\hat{I}_2^B \underline{\underline{\delta}})], \\ \hat{\underline{\underline{\sigma}}}_1 &= 2\rho [\hat{F}_1^1(\hat{\underline{\underline{b}}} - 1/3\hat{I}_1 \underline{\underline{\delta}}) - \hat{F}_2^1(\hat{\underline{\underline{b}}}^{-1} - 1/3\hat{I}_2 \underline{\underline{\delta}})]; \end{aligned} \quad (2)$$

- (iii) Continuity and (shear) kinematical relations,

$$d \ln \rho / dt = -tr \underline{\underline{e}}, \quad \hat{\underline{\underline{B}}} \equiv \hat{\underline{\underline{B}}} - \hat{\underline{\underline{B}}} \cdot \hat{\underline{\underline{e}}} - \hat{\underline{\underline{e}}} \cdot \hat{\underline{\underline{B}}} = \underline{\underline{0}} \quad (\hat{\underline{\underline{e}}} \equiv \underline{\underline{e}} - 1/3 \delta tr \underline{\underline{e}}); \quad (3)$$

- (iv) Bulk and shear evolution (relaxation) equations,

$$d \ln \rho^i / dt + [\alpha(\rho^i) / \theta_b^1(T)] \rho \rho^i \partial \hat{F}_b^1 / \partial \rho^i(T, \rho^i) = d \ln \rho / dt, \quad (4a)$$

$$\underline{\hat{b}} - \underline{\hat{b}} \cdot \underline{\hat{e}} - \underline{\hat{e}} \cdot \underline{\hat{b}} + 1/2[\beta(\hat{I}_1, \hat{I}_2)/\theta_1(T)] \cdot [\underline{\hat{b}}^2 - 1/3(\hat{I}_1 - \hat{I}_2)\underline{\hat{b}} - \underline{\hat{\delta}}] = \underline{0}. \quad (4b)$$

These equations have been shown (Freed and Leonov, 2002<sub>2</sub>) to easily extended to the multimode case with an arbitrary number of nonlinear relaxation modes. Additionally, there is a strain-induced anisotropy in the thermal conductivity, which in the simplified version depends on temperature  $T$  and the actual component  $\underline{B}$  of Finger strain.

In the rubbery region, the well-known, WLF time-temperature superposition principle, originated from entropy elasticity and uniform temperature scaling for relaxation modes, is applicable for scaling of the linear viscoelastic spectrum. It is also applicable in the nonlinear region of deformations, too. However, in the glassy state there is another temperature scaling related to the possible fractal properties of polymers in the glassy region. Therefore, viscoelastic effects in the glassy region are well described by the stretched exponential and/or the fractional derivative approaches. Using a discrete relaxation spectrum approach in this region is awkward, as it usually includes a lot of relaxation modes. In order to expand this type of formalism into the nonlinear region of deformation, a slightly modified single integral approach to constitutive modeling of the K-BKZ type (Kaye, 1962; Berstain, Kersley, Zapas, 1963) is introduced in the next Section of this paper. This approach has a long history of use for describing nonlinear viscoelastic properties of solid polymers. Some new approaches have also been recently attempted. They combine continuum mechanics with more physical insight in the behavior of materials in the glassy region. For instance, Drozdov (2000<sub>1</sub>) recently proposed CE's for nonlinear viscoelasticity of glassy polymers based on the concept of traps. He also developed a model of cooperative relaxation in finite viscoelasticity for amorphous polymers (Drozdov, 2000<sub>2</sub>). Huang (1999) recently extended Drozdov's approach to the non-isothermal case. Another approach that has also been developed recently, is based on non-equilibrium thermodynamics and the concept of the soliton-like propagations of the specific structures in glassy polymers (Cho and Kim, 2000). However, these approaches contain a lot of fitting parameters, many assumptions, and have been tested only for the one deformation (1D) case, as uniaxial extension.

Another issue addressed in this paper deals with stability constraints, which secure fundamental properties of CE's, such as obeying the second law of thermodynamics, and well-posedness. We will also discuss some recent results in this area in the third Section of this paper.

At the end of this paper we discuss formulae proposed by various authors for the purpose of specifying material functions and parameters that appear in our viscoelastic theory.

## 2. Single integral constitutive equations for viscoelastic solids

The general CE for viscoelastic materials, presented in a form of hereditary functionals with fading memory, mostly applicable to viscoelastic liquids, has been established in the field of rational mechanics and thermodynamics (Truesdell and Noll, 1992). In order to apply to a viscoelastic solids the fading memory concept using a single integral CE, it is reasonable represent the Helmholtz' free energy as a sum of the equilibrium free energy

depending on temperature and actual strain,  $F^0(T, \underline{B})$ , and the liquid-like free energy in a form of a single integral hereditary functional with the integrand depending on temperature and a relative total strain,  $F^1\{T, \underline{B}_\tau\}$ . We assume further that both components of the free energy vanish in the unloaded state, where  $\underline{B} = \underline{B}_\tau = \underline{\delta}$ . For isotropic materials, the free energy can then be expressed as:

$$F = F^0(T; I_1^B, I_2^B, I_3^B) + \int_{-\infty}^t F^1(T; I_{1\tau}^B, I_{2\tau}^B, I_{3\tau}^B; t - \tau) d\tau. \quad (5)$$

Here the integrand in (5) depends on the "relative" Finger strain  $\underline{B}_\tau(t, \tau)$  which acts in the past time region  $\{\tau\}$  and degenerates into the unity tensor at the actual time  $\tau = t$ . Consequently, the kinematical equation for the evolution of the relative Finger strain  $\underline{B}_\tau$  holds here too, but with a specific initial condition:

$$\overset{\nabla}{\underline{B}}_\tau \equiv \overset{0}{\underline{B}}_\tau - \underline{B}_\tau \cdot \underline{e} - \underline{e} \cdot \underline{B}_\tau = \underline{0}; \quad \underline{B}_\tau|_{t=\tau} = \underline{\delta}. \quad (6)$$

The initial condition in (6) means that the strain, initiated at the current time  $t$ , "propagates" into the past. The stress tensor is defined now by the Finger formula but with a functional (Frechet) derivative:

$$\underline{\sigma} = \frac{\delta F}{\delta \underline{B}} \equiv 2\rho \underline{B} \cdot \partial F^0 / \partial \underline{B} + 2\rho \int_{-\infty}^t \underline{B}_\tau \cdot \partial F^1 / \partial \underline{B}_\tau d\tau. \quad (7)$$

Substituting into (7) the isotropic expressions for  $F^0$  and  $F^1$  yields a BKZ type of formula, with an additional out-of-integral, equilibrium term:

$$\underline{\sigma} = 2\rho [F_1^0 \underline{B} + F_2^0 (I_1^B \underline{B} - \underline{B}^2) + F_3^0 I_3^B \underline{\delta}] + 2\rho \int_{-\infty}^t d\tau [F_1^1 \underline{B}_\tau + F_2^1 (I_{1\tau}^B \underline{B}_\tau - \underline{B}_\tau^2) + F_3^1 I_{3\tau}^B \underline{\delta}] \quad (8)$$

$$F_j^0 = \partial F^0 / \partial I_j^B; \quad F_j^1 = F_j^1(T; I_{k\tau}^B; t - \tau) = \partial F^1 / \partial I_{j\tau}^B; \quad \rho(t) = \rho_0 (I_3^B)^{-1/2}; \quad \rho = \rho_\tau (I_{3\tau}^B)^{-1/2}.$$

Here  $\rho_\tau$  is the density at a past time  $\tau$ . To find the expression for the dissipation  $D$  we employ the expression for the entropy production under isothermal condition:

$$D \equiv TP_s|_T = \text{tr}(\underline{\sigma} \cdot \underline{e}) - \rho dF / dt|_T (\geq 0)$$

Substituting here relation (5), taking into account the kinematical relation of (6) yields:

$$D = -\rho \int_{-\infty}^t \mathcal{F}_j^{\hat{\sigma}}(T; I_{1\tau}^B, I_{2\tau}^B, I_{3\tau}^B; t-\tau) d\tau \quad (9)$$

Here  $\mathcal{F}_j^{\hat{\sigma}}$  means a differentiation of the function  $F^1$  taken with respect to the third (“pure time”) argument. Note that the positive definiteness of the multipliers in the integrand of (9) necessitates the inequality  $\mathcal{F}_j^{\hat{\sigma}} < 0$ . This is the nonlinear extension of the decaying exponential factors in the Prony series, well known in linear viscoelasticity.

Instead of invariants  $I_3^B$  and  $I_{3\tau}^B$ , we now introduce density variables into the equilibrium and non-equilibrium components of the free energy as was done in the previous paper (Freed and Leonov, 2002<sub>2</sub>):

$$F = \hat{F}^0(T; \rho / \rho_0, \hat{I}_1^B, \hat{I}_2^B) + \int_{-\infty}^t \hat{F}^1(T; \rho / \rho_\tau, \hat{I}_{1\tau}^B, \hat{I}_{2\tau}^B; t-\tau) d\tau \quad (10)$$

Here the invariants  $\hat{I}_j^B$  and  $\hat{I}_{j\tau}^B$  are defined as in the incompressible case. Then the constitutive equation in (8) is presented as:

$$\begin{aligned} \underline{\underline{\sigma}} &= -p\underline{\underline{\delta}} + \hat{\underline{\underline{\sigma}}} \quad (\text{tr} \hat{\underline{\underline{\sigma}}} = 0); \quad p = \rho^2 \left[ \partial \hat{F}^0 / \partial \rho + \int_{-\infty}^t d\tau \partial \hat{F}^1 / \partial \rho \right]; \\ \hat{\underline{\underline{\sigma}}} &= 2\rho [\hat{F}_1^0(\underline{\underline{\hat{B}}} - 1/3 \hat{I}_1^B \underline{\underline{\delta}}) - \hat{F}_2^0(\underline{\underline{\hat{B}}}^{-1} - 1/3 \hat{I}_2^B \underline{\underline{\delta}})] \\ &\quad + 2\rho \int_{-\infty}^t d\tau [\hat{F}_1^1(\underline{\underline{\hat{B}}}_\tau - 1/3 \hat{I}_{1\tau}^B \underline{\underline{\delta}}) - \hat{F}_2^1(\underline{\underline{\hat{B}}}_\tau^{-1} - 1/3 \hat{I}_{2\tau}^B \underline{\underline{\delta}})]. \end{aligned} \quad (11)$$

Here  $\hat{F}_j^0$  and  $\hat{F}_j^1$  are defined similarly to that shown in the previous paper (Freed and Leonov, 2002<sub>2</sub>). The relations in (11) can be simplified, if there is an additivity (or uncoupling) assumption between the bulk and shearing responses of elasticity and viscoelasticity:

$$\hat{F}^0 = \hat{F}_b^0(T; \rho / \rho_0) + \hat{F}_{sh}^0(T; \hat{I}_1^B, \hat{I}_2^B); \quad \hat{F}^1 = \hat{F}_b^1(T; \rho / \rho_\tau; t-\tau) + \hat{F}_{sh}^1(T; \hat{I}_{1\tau}^B, \hat{I}_{2\tau}^B; t-\tau). \quad (12)$$

Note that the time dependencies of functions  $\hat{F}_b^1$  and  $\hat{F}_{sh}^1$  in (12) for the compressible (scalar) and “incompressible” (tensor) terms are in general different.

The constitutive equation in (11) with assumption (12) can be further simplified when it is possible to employ a factorization called time-strain separability:

$$\hat{F}_b^1 = m_b(t-\tau) \phi(T; \rho / \rho_\tau); \quad \hat{F}_{sh}^1 = m_{sh}(t-\tau) f(T; \hat{I}_{1\tau}^B, \hat{I}_{2\tau}^B) \quad (13)$$

Here  $m_b(t-\tau)$  and  $m_{sh}(t-\tau)$  are respectively related to the bulk,  $K(t)$ , and shearing,  $G(t)$ , relaxation moduli defined in the linear theory of viscoelasticity as follows:

$$m_b(t-\tau) = \partial K(t-\tau) / \partial \tau (>0), \quad m_{sh}(t-\tau) = \partial G(t-\tau) / \partial \tau (>0). \quad (14)$$

Thus the most simplified version of a single integral CE for viscoelastic solids has the form:

$$\hat{F}^0 = \hat{F}_b^0 \left( T; \frac{\rho}{\rho_0} \right) + \hat{F}_{sh}^0(T; \hat{I}_1^B, \hat{I}_2^B) + \int_{-\infty}^t m_b(t-\tau) \phi \left( T; \frac{\rho}{\rho_\tau} \right) d\tau + \int_{-\infty}^t m_{sh}(t-\tau) f(T; \hat{I}_{1\tau}^B, \hat{I}_{2\tau}^B) d\tau \quad (15)$$

$$D = -\rho \int_{-\infty}^t \partial m_b(t-\tau) / \partial t \phi \left( T; \frac{\rho}{\rho_\tau} \right) d\tau - \rho \int_{-\infty}^t \partial m_{sh}(t-\tau) / \partial t f(T; \hat{I}_{1\tau}^B, \hat{I}_{2\tau}^B) d\tau (>0) \quad (16)$$

$$\begin{aligned} \underline{\underline{\sigma}} &= -p \underline{\underline{\delta}} + \underline{\underline{\hat{\sigma}}} \quad (\text{tr} \underline{\underline{\hat{\sigma}}} = 0); \quad p = \rho^2 \left[ \partial \hat{F}_b^0 / \partial \rho + \int_{-\infty}^t m_b(t-\tau) \partial \phi / \partial \rho d\tau \right] \\ \underline{\underline{\hat{\sigma}}} &= 2\rho [\hat{F}_1^0(\underline{\underline{\hat{B}}} - 1/3 \hat{I}_1^B \underline{\underline{\delta}}) - \hat{F}_2^0(\underline{\underline{\hat{B}}}^{-1} - 1/3 \hat{I}_2^B \underline{\underline{\delta}})] \\ &+ 2\rho \int_{-\infty}^t m_{sh}(t-\tau) [f_1(\underline{\underline{\hat{B}}}_\tau - 1/3 \hat{I}_{1\tau}^B \underline{\underline{\delta}}) - f_2(\underline{\underline{\hat{B}}}_\tau^{-1} - 1/3 \hat{I}_{2\tau}^B \underline{\underline{\delta}})] d\tau \quad (f_j = \partial f / \partial \hat{I}_{j\tau}^B). \end{aligned} \quad (17)$$

Due to the definitions given in (14), the dissipation in (16) is positive, because

$$\partial m_b(t-\tau) / \partial t = \partial^2 K(t-\tau) / \partial t \partial \tau (<0), \quad \partial m_{sh}(t-\tau) / \partial t = \partial^2 G(t-\tau) / \partial t \partial \tau (<0).$$

Comparing the single integral (SI) approach considered here with the differential approach analyzed in the previous paper (Freed and Leonov, 2002<sub>2</sub>), we can conclude:

(i) The SI CE's are more rigid when compared to the CE's of the differential type. As seen from equations (15) and (16), the dissipative function  $D$  is almost proportional to the integral part of the free energy. For the CE's of differential type, these two fundamental functions are completely separated. This happens in part because of the use of relative strain measures in SI CE, instead of the hidden tensor variables in the differential CE's.

(ii) The viscoelastic SI CE's are considerably "less nonlinear" than CE's of the differential type. The latter can be, in principle, represented by a multiple integral approach. More nonlinearity, as e.g. a "strain clock", could be introduced into the non-time separable versions of SI CE's, however, at an expense of tractability.

(iii) For viscoelastic liquids, SI CE's with time-strain separability were proved to be unstable (Kwon and Leonov, 1995; Kwon and Co, 2001); however, for viscoelastic solids, stable SI CE's with time-strain separability can be constructed. Therefore, unlike the CE's of differential type, it is impossible to use the SI CE's in the continuous modeling of rubber viscoelastic properties, from liquid-like to solid-like via cure reaction, using the chemo-rheological approach (Mitra, 2000).

(iv) There are also some advantages of the SI CE's: 1) relative simplicity since it is necessary to specify only one integrand (and out-of-integral, equilibrium term in the solid case); 2) the possibility to involve in the formulation a continuous viscoelastic spectrum with such features as fractional derivatives and "stretched exponents" (e.g. see Kolrausch, 1847, 1854), valuable for glasses; and 3) the use of a rigorous approach to viscoelastic kinematics.

Finally, it seems that a combination of the differential approach with a few modes and the SI CE's for fast deformations may create a good opportunity for a unified description of nonlinear thermo-rheologically complex viscoelastic solids and liquids. In this unified scheme, the differential approach can take care of the rubbery region, with relatively slow deformations and potentially high strains, and with the WLF temperature scaling. The SI constitutive approach, with relatively small strains and another temperature scaling, is capable of describing the glassy region.

### 3. Stability constraints for constitutive equations for viscoelastic solids

Formulation of field equations for viscoelastic solids should obey some stability constraints. These constraints reflect the most fundamental properties of CE's, related to the second law of thermodynamics, propagating various fast waves, and continuity along the time axis for any solution for a viscoelastic solid problem. We will show below that the stability constraints in the case of viscoelastic solids are exactly the same as in the pure elastic case, i.e. they are related only to Hadamard stability (or well posedness, or strong ellipticity, or strong hyperbolicity in case of wave propagation).

In the theory of finite elasticity, the necessary and sufficient condition for strong ellipticity is the positive definiteness of the bi-quadratic fourth order form,

$$\mathbf{A} = A_{ijmn}(\underline{B})x_i y_j x_m y_n > 0, \quad (18)$$

where the tensor  $A_{ijmn}$  is related to the elastic properties of the continuum.

The rank of four tensor  $A_{ijmn}$  is symmetric in its first and second pairs of indices, and also by a transposition between these. For isotropic solids it has the form:

$$A_{ijmn}(\underline{B}) = \frac{\partial \sigma_{ij}}{\partial H_{mn}} = \frac{\partial}{\partial H_{mn}} \left( \rho \frac{\partial F}{\partial H_{ij}} \right) = 4B_{mk} \frac{\partial}{\partial B_{kn}} \left( \rho B_{il} \frac{\partial F}{\partial B_{ij}} \right) \quad (19)$$

Here  $\underline{H}$  is the Hencky strain measure. The condition (18) of strong ellipticity means the positive definiteness of the tensor  $A_{ijmn}$  considered in terms of a bi-quadratic form. In the isotropic case, when  $F = F(T, I_1, I_2, I_3)$ , the stability constraint (18) was reduced in both incompressible (Zee and Sternberg, 1983) and compressible (Knowles and Sternberg, 1977; Simpson and S.J. Spector, 1983) cases to corresponding sets of algebraic inequalities imposed on the first and second free energy derivatives with respect to the three basic invariants  $I_k$ . In the case of the linear stability analysis of disturbances imposed on an arbitrary, nonlinear, and generally time dependent stress-strain

deformation field, condition (18) of strong ellipticity is changed to the condition of strong hyperbolicity:

$$\rho\Omega^2\bar{v}_i\bar{v}_i = A_{ijmn}(\underline{B})\bar{v}_i k_j \bar{v}_m k_n > 0. \quad (20)$$

Here  $\Omega = \omega - \underline{k} \cdot \underline{v}$  is the frequency oscillations in the disturbance wave with a Doppler's shift of the basic velocity field  $\underline{v} = \underline{v}(\underline{x}, t)$  taken into account,  $k_i$  and  $\bar{v}_j$  are respectively the components of the wave vector and the vector of amplitude in the velocity disturbances. In the limit  $\omega \rightarrow \infty, k \rightarrow \infty$ , one can consider disturbances as presented by monochromatic plane waves, being restricted to a local analysis of stability. It is also worth mentioning that the condition of stability (20) is exactly the same as that shown in (18).

When a system is described by the quasi-linear set of PDE, the analysis of small disturbances has been shown to coincide with the more general method of characteristics (e.g., see Joseph, 1990). Positive definiteness of the fourth order form in (20) means the possibility to continue at any time instant, any solution of the equations for finite elasticity in the positive direction of time axis. If this is impossible, the characteristics are turned back, and near a turning point, their derivatives go to infinity. Thus the Hadamard instability is a typical ill posedness accompanied by a blow-up instability. In the general case of compressibility, all possible types of waves of disturbances are allowed, including the longitudinal waves. However, when an elastic material is treated as incompressible, i.e.  $\rho = const$ , then the longitudinal waves of disturbances are forbidden because in this case the wave and the velocity amplitude vectors are orthogonal:  $k_j \bar{v}_j = 0$ .

When analyzing static stability, with infinitesimal (symmetric) strain disturbances  $\underline{\varepsilon}$  imposed on a given finite elastic strain  $\underline{B}_0$  as  $\underline{B} = \underline{B}_0 + \underline{\varepsilon}$ , one can obtain instead of the strong ellipticity condition (18), a condition of thermodynamic stability:

$$\mathbf{A}_T = A_{ijmn}(\underline{B})\varepsilon_{ij}\varepsilon_{mn} > 0. \quad (21)$$

Although the tensor  $A_{ijmn}$  is still defined by (19), the condition of stability is different from that which is shown in (18). It is easy to see that the thermodynamic condition of stability (21) is only a necessary condition for the full condition of strong ellipticity (18). This is because the condition of strong ellipticity degenerates into the condition of thermodynamic stability for a particular case when the diadic matrix  $x, y_j$  in (18) is symmetric. In this case, instead of positive definiteness of the bi-quadratic form (18) for 3D vectors, the thermodynamic stability condition reduces to the positive definiteness of the quadratic form (21) for 3D matrices.

In the case of CE's for viscoelastic liquids with instantaneous elasticity, the general stability constraints have also been revealed and analyzed (Kwon and Leonov, 1995; Kwon, 1996; Kwon and Co, 2001). It was found that the Hadamard stability constraints for CE's of viscoelastic liquids coincide with those found for the elastic solids. However, another source of instability, caused by dissipative terms in liquid-like viscoelastic CE's, can generate dissipative instability even in the Hadamard stable case. Therefore the combined constraints have been imposed on liquid-like viscoelastic CE's.

For CE's of differential type the degree of freedom was high enough to allow a completely stable class of viscoelastic CE's to exist. This class described well the various rheological properties for five polymers {Simhambhatla and Leonov, 1995; Leonov, 1999} while obeying all the stability constraints. However, the combined stability constraints imposed on the single integral CE's with strain-time separability are so stiff that a stable version of these does not exist (Kwon and Leonov, 1995).

It is a great relief that the dissipative instability does not exist in solid-like viscoelastic CE's. Therefore, only the Hadamard stability conditions of (18) or (20) must be satisfied to guarantee a stable constitutive behavior for viscoelastic solids, whenever the dissipative terms there subordinate to the second law. It should be mentioned that the same necessary and sufficient stability criterion of (18) or (20) for elastic terms in each mode of the multi-modal differential CE's or in a single integral CE (with the strain-time separability admissible here) can be proven for the CE's of viscoelastic solids. Strictly speaking, this means that the above Hadamard stability criterion is only sufficient. However, since the various viscoelastic modes and the equilibrium elastic term are almost independent, the sufficient stability criteria of (18) or (20) should be considered as close to the necessary one.

The strong ellipticity (Hadamard stability) conditions are too awkward to apply them for newly proposed CE's. Therefore several attempts have been undertaken to find non-trivial and simple enough sufficient conditions for strong ellipticity. We discuss below only two literature approaches to this problem.

- (i) Renardy (1985) derived the following sufficient condition of strong ellipticity for the incompressible viscoelastic Kaye-BKZ equation:

The CE's for incompressible elastic and viscoelastic solids are strong elliptic, if the strain energy function  $F = F(T, I_1, I_2)$ , depending on two basic invariants,  $I_1$  and  $I_2$ , can be presented as a monotonically increasing and convex function of  $\sqrt{I_1}$  and  $\sqrt{I_2}$ . The condition for this convexity,

$$\frac{\partial^2 F}{\partial \sqrt{I_1} \partial \sqrt{I_1}} \cdot \frac{\partial^2 F}{\partial \sqrt{I_2} \partial \sqrt{I_2}} \geq \left( \frac{\partial^2 F}{\partial \sqrt{I_1} \partial \sqrt{I_2}} \right)^2, \quad (22)$$

is reduced to the following:

$$(F_{11}F_{22} - F_{12}^2)I_1I_2 + 1/2(F_{11}F_2I_1 + F_{22}F_1I_2) + 1/4F_1F_2 > 0 \quad (23)$$

$$(F_k \equiv \partial F / \partial I_k; F_{ik} \equiv \partial^2 F / \partial I_i \partial I_k)$$

Evidently, inequality (23) is less strong than the convexity condition,  $F_{11}F_{22} > F_{12}^2$ , imposed on  $F$  in terms of the basic strain invariants,  $I_1, I_2$ .

- (ii) Kwon (1996) derived a sufficient condition of strong ellipticity for compressible viscoelastic liquids, which can also be used for both elastic and viscoelastic solids. Since

these conditions are considerably more sophisticated than Renardy's, we refer the reader to the original Kwon paper (1996).

#### 4. Specification of material functions and parameters

This Section discusses many formulae derived, or proposed *at hoc*, by various authors for material functions, which are involved in the general theory.

##### 4.1. Equilibrium (elastic) properties

These properties in our simplified approach are described by two independent parts of the free energy function, the bulk part,  $\hat{F}^b$  depending on temperature  $T$  and density  $\rho$ , and the "shearing" part,  $\hat{F}^{sh}$  depending on  $T$  and two "incompressible" invariants,  $\hat{I}_1 = tr \hat{\underline{\underline{B}}}$  and  $\hat{I}_2 = tr \hat{\underline{\underline{B}}}^{-1}$  ( $\det \hat{\underline{\underline{B}}} = 1$ ).

(i). Spenser and. Bauer (1946), and Spenser and Gilmore (1960) have established that the *bulk properties* of cross-linked rubbers can be well described by a van der Waals-like equation:

$$\hat{F}^b(T, \rho) = \frac{RT}{M} \ln \left[ \frac{\rho(M/b - \rho_0)}{\rho_0(M/b - \rho)} \right] - \frac{a(\rho - \rho_0)}{M^2}. \quad (24)$$

Here  $\rho$  is the density,  $T$  is the Kelvin temperature,  $M$  is the molecular weight,  $R$  is the universal gas constant,  $\rho_0$  is the density at a reference state under temperature  $T_0$ . The parameters  $a$  and  $b$  in (24), treated as empirical constants, describe the effects of internal pressure and the self-volume of molecules, respectively. In accordance with relation (24), the dependence of pressure  $p$  on  $\rho$  and  $T$  is:

$$p = \rho^2 \partial \hat{F}^b / \partial \rho = \rho RT / (M - b\rho) - a\rho^2 / M^2 \quad (0 < \rho < M/b). \quad (25)$$

The global (Hadamard) stability condition,  $\hat{F}_\rho^b + \rho \hat{F}_{\rho\rho}^b / 2 > 0$ , well known from thermodynamics of gases, reduces to the inequalities:

$$\rho < \rho_c = M/(3b), \quad T > T_c = (8a)/(27bR), \quad (26)$$

Here  $\rho_c$  and  $T_c$  are the critical density and the temperature at the point of phase separation for gases.

(ii) Consider now the specifications of potential  $\hat{F}^{sh} = \hat{F}^{sh}(T, \hat{I}_1, \hat{I}_2)$  for *shearing equilibrium properties*. To simplify the notations, we consider the incompressible case

below, where  $\hat{F}^{sh}$  is changed to  $F$ , and the modified invariants  $\hat{I}_1$  and  $\hat{I}_2$  are changed to  $I_1$  and  $I_2$ , i.e.  $F = F(T, I_1, I_2)$ . Additionally we will use the notation:  $\rho F = W$ .

The most popular mode is the Mooney-Rivlin potential:

$$W = G/2[(1 - \alpha)(I_1 - 3) + \alpha(I_2 - 3)], \quad (27)$$

where  $G$  and  $\alpha$  are respectively the Hookean modulus and a numerical constant. The stability constraint provided by the incompressible stability theory (Kwon and Leonov, 1995) is:  $0 \leq \alpha \leq 1$ . However, when the Mooney potential is combined with an additional compressible part, the constraint on the parameter  $\alpha$  is tougher:  $1/3 < \alpha \leq 1$  (Kwon, 1996). The descriptive ability of this potential in the incompressible case has been widely discussed (e.g., see Treloar, 1975).

To the authors' knowledge, the widest range in descriptive capability of various experimental data for cross-linked rubbers has been achieved using the BST potential (Blats, Sharda, Tschoegl, 1974):

$$W = (G_0/2n)I_n + GI_n^m, \quad I_n = n^{-1}tr(\underline{\underline{B}}^n - \underline{\underline{\delta}}). \quad (28)$$

Here  $G_0$  and  $G$  are effective moduli, and  $n$  and  $m$  are numerical constants. It should be noted that using the generalized strain measure  $\underline{\underline{B}}^n$  introduces an additional computational expense, because the stress-strain relation with potential (28) can be effectively treated only in the principal axes of tensor  $\underline{\underline{B}}$ . This creates a computational burden when using FEM to solve a complex problem. The stability constraints for the potential (28) are unknown, mostly because of the generalized strain measure involved in its formulation.

Simhambhatla and Leonov (1995) recently proposed another expression for elastic potential involved in their constitutive theory for viscoelastic liquids:

$$W = \frac{3G}{2n}[(1 - \alpha)[(I_1/3)^n - 1] + \alpha[(I_2/3)^n - 1]]. \quad (29)$$

The corresponding stress-strain relation is:

$$\underline{\underline{\sigma}} = -p\underline{\underline{\delta}} + G[(1 - \alpha)(I_1/3)^{n-1}\underline{\underline{B}} - \alpha(I_2/3)^{n-1}\underline{\underline{B}}^{-1}]. \quad (30)$$

Here  $G$  is the Hookean modulus, while  $\alpha$  and  $n$  are numerical constants. Expression (29) is a combination of the formulae used for Mooney-Rivlin and Knowles' (1979) potentials, widely used for calculations of large deformations of elastic solids. Using the combined Hadamard and dissipative stability criteria, it has been established that the sufficient conditions for Hadamard stability of viscoelastic liquids using potential (29) are:  $n \geq 1$ ,  $0 \leq \alpha \leq 1$ . However, using the Renardy sufficient condition of strong ellipticity, results in softer stability criteria:  $n > 1/2$ ,  $0 \leq \alpha \leq 1$ , suitable for elastic solids.

Several expressions for an elastic potential were recently proposed for very large deformations of elastic solids (e.g., see Arruda and Boyce, 1993; Bergstrom and Boyce, 1998; Boyce and Arruda, 2000). These formulae were derived using an extension of the finite extensibility approach for polymeric chains (e.g. see Treloar, 1975). These formulae employ the inverse Langevin function, which is too complicated for solving complex problems. An easy semi-empirical way to involve these effects into consideration was recently proposed by Gent (1996). Gent was unaware that Warner (1972) had earlier proposed the same approach for approximating the inverse Langevin function. The Warner approximation is widely used for viscoelastic liquids as the “Warner spring” (e.g., see Larson, 1988). This type of potential and its corresponding stress-strain relation are:

$$W = -(G/2)(I_* - 3) \ln \left( \frac{1 - I_1/I_*}{1 - 3/I_*} \right), \quad (31)$$

$$\underline{\underline{\sigma}} = -p \underline{\underline{\delta}} + G \frac{1 - 3/I_*}{1 - I_1/I_*} \underline{\underline{B}}. \quad (32)$$

Here  $I_*$  ( $\sim 100$ ) is a limiting value for the first invariant  $I_1$  related to the finite extensibility of polymer chains. The potential in (31) is stable in the entire domain of admissible strains:  $3 < I_1 < I_*$ . It should be noted that when  $I_1$  approaches  $I_*$ , the concept of entropic elasticity is becoming invalid. Here the “solid-like” elasticity, related to the distortion of valence angles between monomeric units, needs to be brought into consideration.

The potential of (31) might describe large elastic deformations very well. These usually occur in uniaxial extension or in situations close to that, which can be met in complex deformations with high-level concentrations of stresses. However, at relatively low strains, predictions of potential (31) contradict experimental data (Treloar, 1975). These data clearly indicate that elastic stress also depends on the second invariant  $I_2$ . This means that in low and intermediate regions of elastic strain, the potential (29) might be more preferable. To combine both potentials, (29) and (31), we suggest an interpolation formula for the elastic potential and a corresponding expression for the stress-strain relation of the type:

$$W = \frac{3G}{2n} \left[ -(1 - \alpha) [(I_*/3)^n - 1] \ln \left( \frac{1 - (I_1/I_*)^n}{1 - (3/I_*)^n} \right) + \alpha [(I_2/3)^n - 1] \right], \quad (33)$$

$$\underline{\underline{\sigma}} = -p \underline{\underline{\delta}} + \frac{3G(1 - \alpha)}{I_*} \cdot \frac{[(I_*/3)^n - 1] \cdot (I_1/I_*)^{n-1}}{1 - (I_1/I_*)^n} \cdot \underline{\underline{B}} - G\alpha (I_2/3)^{n-1} \underline{\underline{B}}^{-1}. \quad (34)$$

Here  $G$  is the Hookean modulus, and  $I_*$  ( $\sim 100$ ),  $n$  and  $\alpha$  are three numerical parameters. It is seen that the formulae (33) and (34) practically coincide with (29) and (30) at relatively small strains, but at large value of  $I_1$ , only the first, singular terms, in (33) and (34) are dominant. When  $n = 1$ , formulae (33) and (34) reduce to a combination of Warren-Gent and Mooney-Rivlin potential. Using the Renardy stability constraints, it is easy to establish that in the whole admissible wedge-like domain of invariants,

$3 < I_1 < I_*, I_2 > 3$ , when  $I_* \gg 3$ , these sufficient stability constraints are almost the same as for the potential in (29), i.e.  $0 \leq \alpha \leq 1$ ,  $n > 1/2$ .

#### 4.2. Non-equilibrium (viscoelastic) properties

These properties include the linear viscoelastic spectrum, and the stress-elastic strain (potential) relations for both the differential and single integral parts of the combined CE.

(i) *The linear viscoelastic spectra*, for bulk and shearing infinitesimal deformations can be established from a series of isothermal experiments (either dynamic, or creep, or relaxation) by using the Pade-Laplace technique (e.g. Simhambhatla and Leonov, 1993), after extracting the equilibrium (static) term. This method of treatment of experimental data can also reveal the thermo-rheological complexity, when present. Although some molecular models also exist, they usually do not describe well the relaxation spectra.

(ii) For the *large deformation and slow relaxing differential modes*, both the nonlinear bulk and shearing viscoelastic properties are described by a quasi-equilibrium elastic potential and non-equilibrium relaxation functions in the respective evolution equations. A great deal of simplification has been achieved for incompressible CE's for viscoelastic liquids, using "uniform modeling" (Simhambhatla and Leonov, 1995; Leonov, 1999). Uniformity means that the same specifications apply to all nonlinear relaxation modes, with the same nonlinear numerical parameters, while keeping the linear viscoelastic parameters established in the linear viscoelastic region. In addition, uniformity provides nonlinear viscoelastic CE's with easily formulated stability constraints. This uniform and stable modeling has been successfully tested with various modes of deformation for five common polymeric melts (Simhambhatla and Leonov, 1995; Leonov, 1999). Moreover, in this type of modeling, a scaling approach introduced by Leonov and Padovan (1999) can also be used, that provides a great computational economy when solving problems with complex deformations.

In the incompressible case (or the shearing part of CE's), two material functions have to be specified in the  $k$ -th nonlinear relaxation mode: the mode's free-energy function  $F^k$ , scaled by the Hookean elastic modulus  $G_k \sim \rho RTg_k$ , and a determining scalar  $\beta_k$ ; both functions depend on the basic invariants  $I_1^{(k)}$  and  $I_2^{(k)}$ . A good descriptive capability is achieved here when  $F^k$  is used in the form of (29), where  $G_k$  is used instead of  $G$ , and  $I_1^{(k)}$  and  $I_2^{(k)}$  instead of  $I_1$  and  $I_2$ . Uniformity here means that the values of the nonlinear numerical parameters  $\alpha$  and  $n$  are mode independent. Uniformity in modeling functions  $\beta_k$  means that  $\beta_k = \beta(I_1^k, I_2^k)$ , with the same, mode independent numerical parameters characterizing this function. The existence of a linear viscoelastic limit imposes the additional condition:  $\beta_k \rightarrow 1$  as  $I_1 \rightarrow 3$  and  $I_2 \rightarrow 3$ . In many cases, the simplest "power law" specification,  $\beta_k = (I_2^k / 3)^m$ , where  $m$  is a mode independent numerical parameter, serves very well for modeling.

(iii) As mentioned, *relatively low strain and fast-relaxing* processes could be formally described by the CE of single-integral type (15)-(17). Here, different approaches to the linear viscoelastic response can be used, including fractional derivatives and fractal arguments (see the book edited by Hilfer, 2000). It is also possible to use here a more compact description of the linear relaxation spectrum, such as the Kolrausch (1847,1854) relaxation function:

$$G(t) = G_0 \exp[-(t/t_0)^s], \quad (35)$$

with a positive numerical parameter  $s$ .

#### 4.3. Strain induced anisotropy in thermal conductivity

As shown by Freed and Leonov (2002<sub>2</sub>), our thermodynamic arguments resulted in a prediction of strain-induced anisotropy in the heat conductivity at large total deformations, i.e. in the occurrence of isotropic tensor dependence  $\underline{\underline{\kappa}}(\underline{\underline{B}})$ . Some additional physical arguments (Hellwege, Henning and Knappe, 1963; Novichionok and Shulman, 1971) resulted in the simple expression for components of heat conductivity in the uniaxial extension:

$$1/\kappa_p + 2/\kappa_{\perp} = \text{const} = 3/\kappa_0. \quad (36)$$

Here  $\kappa_0$  is the heat conductivity coefficient in isotropic (unloaded) state,  $\kappa_p$  and  $\kappa_{\perp}$  being respectively the heat conductivities in the longitudinal and cross-sectional directions. Formula (36) has been experimentally confirmed for various elastomers.

To describe (36) with the use of a general isotropic tensor function  $\underline{\underline{\kappa}} = \underline{\underline{\kappa}}(\underline{\underline{B}})$  we neglect compressibility effects at large deformations, and assume a quasi-linear dependence of the form:

$$\underline{\underline{\kappa}} = \kappa_0 \varphi \underline{\underline{B}}. \quad (37)$$

Here the unknown scalar factor  $\varphi$  can depend on temperature and the basic invariants  $I_1$  and  $I_2$  of tensor  $\underline{\underline{B}}$ . In uniaxial extension, the left-hand side in (36) is represented as  $\text{tr} \underline{\underline{\kappa}}^{-1}$ . Then the relations (36) and (37) yield:

$$1/\kappa_p + 2/\kappa_{\perp} = \text{tr} \underline{\underline{\kappa}}^{-1} = \frac{\text{tr} \underline{\underline{B}}^{-1}}{\kappa_0 \varphi} = \frac{I_2}{\kappa_0 \varphi} = \frac{3}{\kappa_0}.$$

This means that  $\varphi = I_2/3$ , and the final expression for the heat conductivity tensor is:

$$\underline{\underline{\kappa}}(\underline{\underline{B}}) = 1/3 \kappa_0 I_2 \underline{\underline{B}}. \quad (38)$$

This remarkable simple result needs to be tested experimentally for other deformations.

## 6. Conclusion to the series

1. Based on the quasi-linear approach of non-equilibrium thermodynamics, a general nonlinear theory has been developed for arbitrary non-isothermal deformations of a viscoelastic solid with one relaxation mechanism.
2. The theory has then been simplified using several modeling arguments:
  - (i) Decoupling of the free energy into a sum of equilibrium and quasi-equilibrium parts;
  - (ii) Decoupling each component into a sum of compressible and incompressible parts;
  - (iii) Decoupling of the evolution equation for the hidden tensor variable (elastic strain in the viscoelastic mode) into two, almost independent evolution (relaxation) equations for bulk and “shear” components;
  - (iv) Modeling of anisotropic heat conductivity as induced by the equilibrium (total) strain.

It should be mentioned that the decoupling of bulk and shear phenomena is usually treated as evidence that the bulk (compressibility) effects are small. This is definitely true for large elastic deformations of rubber-like materials, but incorrect for small deformations, when the shear and bulk effects happen to be of the same order. Nevertheless, at small deformations, where the linear theory is approximately valid, additivity of the bulk and shear deformations remains correct. Therefore the proposed decoupling of bulk and shear effects seems to be approximately valid over the total range of deformations.

3. The models in 2 have been extended for a nonlinear decoupled multi-mode CE's.
4. Some thermodynamic arguments have been used for a solid-like Kaye-BKZ type of single integral equation with out-of-integral equilibrium term, when decoupling equilibrium and non-equilibrium properties. The time-strain separable version of the single integral approach has also been discussed.
5. It was suggested to combine the model in 3 with the single-integral approach for the description of fast, weakly nonlinear relaxation processes in the glassy polymer region.
6. Stability constraints have also been discussed for the proposed CE's. It has been shown that unlike the CE's for viscoelastic liquids where the strong ellipticity (Hadamard) stability constraints should be complemented by some criteria for dissipative stability, only strong ellipticity criteria should be used for stability of CE's for viscoelastic solids. Special attention was attached to the sufficient stability criterion.
7. Several formulae, some of them being new, have been proposed and discussed to specify the equilibrium and non-equilibrium terms in the solid viscoelastic CE's, including the derivation of a simple formula for strain induced anisotropy in heat conductivity.

Finally, predictions of this theory for nonlinear solid viscoelasticity, developed in this series of papers, need to be tested experimentally for several well defined and easily

checked problems. The work on this is in progress, and results will be published elsewhere.

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