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On the Constitutive Equations for Nonisothermal Bulk Relaxation

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ABSTRACT: The paper derives and discusses the constitutive equations for viscoelastic nonisothermal bulk relaxation. Methods of hidden variables and nonequilibrium thermodynamics employed enable us to establish sign definiteness of various material parameters. In the author's opinion, the results can clarify the heuristic arguments proposed in a recent publication.[6]

Introduction

In recent years, progress was achieved in understanding nonlinear viscoelastic rheology of polymers. The contribution of our group consists of a general analysis of the most popular viscoelastic constitutive equations (CEs),[1] their stability properties,[2] and the demonstration of a proper type of CE which consistently described the available data for simple flows of five polymers while satisfying all the stability constraints.[3]

These results were obtained under the assumption of incompressibility. This can be justified by the fact that the typical values of compressibility modulus K in the linear viscoelastic limit are about 1000 MPa. This is 10^3-10^4 times higher than the shear (Hookean) modulus G for polymer melts. This difference results in extremely high values of elastic shearing strains as compared with volume deformations. Also, the volume relaxation processes are much more rapid than the shearing ones. That is why the volume deformations are usually neglected in polymer rheology. However, there are examples of flows in polymer processing operations when the volume deformations are important. One example is the melt flow instability in the capillary flows of polymers (for the recent review see ref 4). In this case, the typical period of oscillations is so long that it is possible to neglect the rapid processes of volume relaxation. But the effects of compressibility are still important there. Another example is the processing of polymers by injection molding.[5] Here the operating pressures are so high and the process rates are so rapid that the time dependent effects of compressibility cannot be ignored.

The importance of the bulk relaxation was recenty discussed in ref 6 where some heuristic and controversial arguments were exposed. Although the thermodynamics of bulk relaxation was developed long ago,[7−9] there is still a need for a more rigorous and modern derivation of a CE for bulk relaxations. Below, such a CE is derived using the general approach of nonequilibrium thermodynamics.[7−11]

Thermodynamics of Bulk Relaxation. It is well-known (see, e.g., ref 12) that the knowledge of only one thermodynamic potential is quite enough to completely describe a process in thermodynamic equilibrium. When a system has “small” deviations from equilibrium, one can still assume the very possibility of such a description by using common thermodynamic potentials. But in nonequilibrium, there is generally a need to increase the amount of the state variables which serve as arguments in the thermodynamic potentials. Therefore some new hidden variables are often introduced which describe the behavior of a system in nonequilibrium.

One of the convenient thermodynamic potentials is the specific (per mass unit) free energy function F. We assume that F depends on such state variables as the temperature T, the density ρ, and a set of independent “hidden” scalar variables $\{\xi_k\}$ ($k = 1, 2, ..., n$). Thus the assumption is made that these state variables can completely describe the nonisothermal bulk relaxations. It means that a smooth function,

$$F = F(T,\rho,\xi_1,\xi_2,...,\xi_n) \tag{1}$$

is assumed to be given. The specific entropy S, and all other specific thermodynamic potentials, such as internal energy U, can then be found using common thermodynamic formulas, including the Gibbs' relation:

$$dU = dF + TdS, \qquad U = F + TS, \qquad S = -\left.\frac{\partial F}{\partial T}\right|_{\rho,\xi_k}, \qquad \text{etc.} \tag{2}$$

For various systems, the variables ξ_k may have different physical senses. In the case of polymeric systems, it is possible to treat them as the thermodynamic parameters of order[13] which may occur under the action of volume deformations.

In the following, only the weakly compressible case is analyzed, which is in accord with the above mentioned small shear to volume moduli ratio. In this case, only small variations of the system near the equilibrium with temperature T_0 and density ρ_0, are under consideration. Thus, instead of density ρ (or the specific volume $v = 1/\rho$) and temperature T, the new variables, the volume deformation ϵ_v and the temperature increment ΔT,

$$\epsilon_v = \Delta v/v_0 = -\Delta\rho/\rho_0 \qquad (\Delta v = v - v_0,\ \Delta\rho = \rho - \rho_0), \qquad \Delta T = T - T_0 \tag{3}$$

are introduced.

For small deviations from the equilibrium, the free energy function F is represented as a quadratic form with respect to variables ϵ_v, ΔT, and ξ_k:

$$\rho_0\Delta F = {}^1/_2 A(\Delta T)^2 + {}^1/_2\, K\epsilon_v{}^2 + \alpha\epsilon_v\Delta T + {}^1/_2 \sum_{k,j} \mathbf{N}_{kj}\xi_k\xi_j + \epsilon_v\sum_k M_k\xi_k + \Delta T\sum_k \beta_k\xi_k \tag{4}$$

All the parameters in eq 4, A, K, α, $\mathbf{N}_{kj}$, M_k, and β_k, are assumed to be constant. We also assume that the

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system under study is far away from phase transitions. Then, in accordance with the second law, the thermodynamic equilibrium with $\Delta T = 0$, $\epsilon_v = 0$, and $\xi_k = 0$, is related to the minimum of free energy F. This condition of thermodynamic stability of the equilibrium state means that the quadratic form in eq 4 is positive definite. It means, in turn, that the parameters A and K are positive, as well as the symmetric matrix $\mathbf{N}_{kj}$ is positive definite. All other parameters in eq 4, M_k, α, and β_k, having indefinitie signs, are subjected to more complicated constraints which follow from the positive definiteness of the form (4).

In both equilibrium and nonequilibrium cases, the thermodynamic pressure p_Y is commonly defined as

$$-\mathrm{p}_Y \equiv \left.\frac{\partial F}{\partial \epsilon_v}\right|_{T,\xi_k} = K\epsilon_v + \sum_k M_k \xi_k + \alpha\Delta T \qquad (5)$$

Let us consider first the thermodynamic relations for another state of equilibrium caused by a small increase/decrease in temperature ΔT°. In this case, generally, $\xi_k = \xi_k^\circ \neq 0$ and $\epsilon_v = \epsilon_v^\circ \neq 0$. Then the equilibrium conditions

$$\left.\frac{\partial R}{\partial \xi_k}\right|_{\Delta T,\epsilon v} = 0 \qquad (k = 1, 2, ..., n)$$

determine the equilibrium values of thermodynamic variables ξ_k°, as the solution of the linear set of equations:

$$M_k\epsilon_v^\circ + \beta_k\Delta T^\circ + \sum_j \mathbf{N}_{kj}\xi_J^\circ = 0 \qquad (k = 1, 2, ..., n) \quad (6)$$

Since the matrix $\mathbf{N}_{kj}$ is postive definite, and due to the independence of ξ_k, all M_k and β_k cannot vanish simultaneously. Therefore the set (6) has only one solution ξ_k°, expressed as

$$\xi_k^\circ = -\epsilon_v \sum_i (\boldsymbol{N}^{-1})_{ki} M_i - \Delta T \sum_i (\boldsymbol{N}^{-1})_{ki}\beta_i \qquad (7)$$

Here $\boldsymbol{N}^{-1}$ is an $n \times n$ matrix, reciprocal to the matrix $\boldsymbol{N}$. Substituting eq 7 into eq 5 yields

$$-\mathrm{p}_Y = K_e\epsilon_v^\circ + \alpha_e\Delta T^\circ \qquad (8)$$

In eq 8, the equilibrium values of bulk modulus, K_e, and the coefficient of thermal expansion, α_e, are of the form

$$K_e = K - \sum_{k,j} (\boldsymbol{N}^{-1})_{kj} M_k M_j, \qquad \alpha_e = \alpha - \sum_{k,j} (\boldsymbol{N}^{-1})_{kj} M_k \beta_j \qquad (9)$$

The positive definiteness of the quadratic form (4) yields the following chain inequality:

$$K > K_e > 0 \qquad (10)$$

Thus, K and K_e can be treated as instantaneous and equilibrium bulk moduli. Note that the signs of α and α_e are still indefinite.

Klausius−Duham Inequality and Bulk Nonisothermal Relaxation. In order to analyze the behavior of the system with the free energy function given by eq 4 in nonequilibrium, we employ the common expression for entropy production P_S in the form[7−11]

$$TP_S = -\frac{q_i}{T}\frac{\partial T}{\partial x_j} + \sigma_{ij}e_{ji} - \rho\left.\frac{\mathrm{d}F}{\mathrm{d}t}\right|_T \qquad (\geq 0) \qquad (11)$$

Here q_j are the components of thermal flux, σ_{ij} and e_{ij} are the components of stress and strain tensors, respectively. Equation 11 is commonly derived when using mass, energy, momentum, and entropy balances. Also, the Gibbs' relation shown in eq 2 and a common thermodynamic formula, $\mathrm{d}U|_S = \mathrm{d}F|_T$, were employed in the derivation. According to the second law, the entropy production P_S must be positive for all nonequilibrium processes and vanish in the equilibrium. This is denoted by the inequality sign in eq 11.

We consider below only volume relaxation phenomena, when

$$\sigma_{ij} = -p\delta_{ij} \qquad (p = -{}^1/_3\sigma_{kk}),$$
$$e_{ij} = {}^1/_3\, e_{kk}\delta_{ij} \qquad ({}^1/_3 e_{kk} \approx \mathrm{d}\epsilon_v/\mathrm{d}t) \quad (12)$$

Here σ_{kk} and e_{kk} are the traces of the respective tensors. Substituting eq 4 into eq 11 and taking into account eqs 5 and 12 yield

$$TP_S = -\frac{q_j}{T}\cdot\frac{\partial T}{\partial x_j} + (p_Y - p)\cdot\frac{\mathrm{d}\epsilon_v}{\mathrm{d}t} - \sum_k X_k\cdot\frac{\mathrm{d}\xi_k}{\mathrm{d}t} \qquad (\geq 0) \qquad (13)$$

where

$$X_k = M_k\epsilon_v + \beta_k\Delta T + \sum_k \mathbf{N}_{kj}\xi_j \qquad (14)$$

Equation 13 demonstrates three contributions of volume relaxation phenomena in entropy production: (i) nonisothermality, (ii) the deviation of pressure p from its thermodynamic value p_Y, and (iii) a time dependence of hidden variables ξ_k. The last two terms in the right-hand side of eq 13 are called the mechanical dissipation.

Equation 13 represents a typical bilinear form of a type $\sum_m Y_m\cdot Z_m$ ($m = 1, 2, 3$). Here the quantities $\partial T/\partial x_j$, $(p - p_Y)$, and X_k are treated as the "thermodynamic forces", Y_m, and the conjugated to them are quantities q_j, $\mathrm{d}\epsilon_v/\mathrm{d}t$, and $\mathrm{d}\xi_k/\mathrm{d}t$, as the "thermodynamic fluxes", Z_m. Note that the thermodynamic fluxes are represented through time derivatives which change their signs under the reverse time transformation: $t \rightarrow -t$. The thermodynamic fluxes and forces are treated above as independent.

According to the approach of linear nonequilibrium thermodynamics, the independent thermodynamic forces and fluxes are connected by some linear phenomenological relations. They give, in particular, the CEs for bulk relaxation phenomena. Although the complete case can be easily analyzed, the simplest possible scheme, when the pressure in the system is equal to the thermodynamic one, $p \equiv p_Y$, is utilized below. Then the linear phenomenological relations are of the form

$$q_j = -\lambda\partial T/\partial x_j \qquad (15)$$

$$X_k = -\sum_i \nu_{ki}\mathrm{d}\xi_i/\mathrm{d}t, \qquad \hat{\nu}_{ki} = \hat{\nu}_{ik} \qquad (k = 1, 2, ..., n) \qquad (16)$$

Here the phenomenological (kinetic) coefficients, the heat conductivity λ, and $\hat{\nu}_{ki}$, are generally assumed to be some functions of temperature T. Also, the simple considerations of tensor dimensionality ("Curie's principle"[7−11]) and the Onsager's principle of symmetry for kinetic coefficients have been taken into account in eqs 15 and 16. Using the equality $p \equiv p_{\mathrm{Y}}$ and substituting eqs 15 and 16 into eq 13, reduce the latter to the quadratic form:

$$TP_S = \frac{\lambda}{T}\cdot\frac{\partial T}{\partial x_j}\cdot\frac{\partial T}{\partial x_j} + \sum_{k,i} \hat{\nu}_{ki}\cdot\frac{\mathrm{d}\xi_k}{\mathrm{d}t}\cdot\frac{\mathrm{d}\xi_i}{\mathrm{d}t} \qquad (\geq 0) \qquad (17)$$

Here the second term in the right-hand side of eq 17 represents the contribution in the entropy production due to the mechanical dissipation. According to the second law, the entropy production must be positive in nonequilibrium. Since the two terms in eq 17 are independent, the coefficient of heat conductivity λ is positive and kinetic matrix $\hat{\nu}_{ki}$ is positive definite, separately.

With the aid of eq 14, the evolution eqs 16 for the parameters ξ_k are rewritten in the form

$$\sum_i \left(\hat{\nu}_{ki}\frac{\mathrm{d}\xi_1}{\mathrm{d}t} + \mathbf{N}_{ki}\xi_i\right) = -M_k\epsilon_v - \beta_k\Delta T \qquad (k = 1, 2, ..., n) \quad (18)$$

Equations 5 and 18 are the volume CEs searched for.

We now make an additional assumption of thermorheological simplicity:

$$\hat{\nu}_{ki}(T) = a(T)\cdot\boldsymbol{\nu}_{ki} \qquad (19)$$

where $\boldsymbol{\nu}_{ki}$ is a numerical matix and a positive function *a(T)* has the dimensionality of time. Though the assumption of thermorheological simplicity was recently criticized,[14] it usually holds in experiments above the glass transition temperature, and in some restricted frequency and time intervals.

Normal Coordinates. Both the numerical $n \times n$ matrices $\boldsymbol{\nu}_{ki}$ and $\mathbf{N}_{ki}$ are symmetric and positive definite. Therefore it is possible to introduce the "normal coordinates" $\eta_k(t)$ as follows:

$$\eta_k(t) = \sum_i \mathbf{Q}_{ki}\xi_i(t) \qquad (k = 1, 2, ..., n) \qquad (20)$$

Here $\mathbf{Q}_{ki}$ is a numerical orthogonal $n \times n$ matrix which reduces simultaneously both the matrices $\boldsymbol{\nu}_{ki}$ and $\mathbf{N}_{ki}$ to the diagonal form. In the matrix notations, eq 20 is of the form

$$\eta = \boldsymbol{Q}\cdot\xi, \qquad \boldsymbol{Q}^{\dagger}\cdot\boldsymbol{\nu}\cdot\boldsymbol{Q} = \boldsymbol{\nu}^*, \qquad \boldsymbol{Q}^{\dagger}\cdot\boldsymbol{N}\cdot\boldsymbol{Q} = \boldsymbol{N}^*, \qquad \boldsymbol{Q}^{\dagger} = \boldsymbol{Q}^{-1} \quad (21)$$

$$\boldsymbol{\nu}^* = \begin{bmatrix} \nu_1^* & 0 & & \cdots & 0 \\ \vdots & & \ddots & & \vdots \\ 0 & \cdots & & \cdots & \nu_n^* \end{bmatrix}, \qquad \boldsymbol{N}^* = \begin{bmatrix} N_1^* & 0 & & \cdots & 0 \\ \vdots & & \ddots & & \vdots \\ 0 & \cdots & & \cdots & N_n^* \end{bmatrix}$$

Here ν_k^* and N_k^* are positive eigenvalues of the matrices $\boldsymbol{\nu}$ and $\boldsymbol{N}$. Under the transformation (20), the CEs (5) and (18) are reduced to the form

$$-p(t) = K\epsilon_v(t) = \sum_k N_k^* m_k \eta_k(t) + \alpha\Delta T(t) \qquad (22)$$

$$\theta_k a(T)\mathrm{d}\eta_k/\mathrm{d}t + \eta_k = -m_k\epsilon_v - \gamma k\Delta T \qquad (k = 1, 2, ..., n) \quad (23)$$

Here the numerical parameters θ_k, m_k, and γ_k are defined as

$$\theta_k = \nu_k^*/N_k^*, \qquad m_k = \Big(\sum_j \mathbf{Q}_{kj}M_j\Big)/N_k^*, \qquad \gamma_k = \Big(\sum_j \mathbf{Q}_{kj}\beta_j\Big)/N_k^* \quad (24)$$

Equations 22 and 23 are the standard set of nonisothermal CEs for n independent linear relaxation modes.

We now represent the free energy function (4) and mechanical dissipation in eq 17 in terms of normal coordinates η_k. Using the transformation (20) in eqs 4 and 17, with the aid of eqs 21 and 24, yields

$$\rho_0\Delta F = {}^1/_2 A(\Delta T)^2 + {}^1/_2 K\epsilon_v^{\,2} + \alpha\epsilon_v\Delta T + \sum_k N_k^*[\eta_k^{\,2}/2 + (m_k\epsilon_v + \beta_k\Delta T)\eta_k] \quad (4a)$$

$$TP_S = \frac{\lambda}{T}\cdot\frac{\partial T}{\partial x_j}\cdot\frac{\partial T}{\partial x_j} + a(t)\sum_k \nu_k^*\left(\frac{\mathrm{d}\eta_k}{\mathrm{d}t}\right)^2 \qquad (\geq 0) \qquad (17a)$$

Due to eq 24, we can also rewrite eq 9 in the simplified form:

$$K_{\mathrm{e}} = K - \sum_k N_k^* m_k^{\,2}, \qquad \alpha_{\mathrm{e}} = \alpha - \sum_k N_k^* m_k\gamma_k \qquad (9a)$$

Integral Form of Nonisothermal Viscoelastic CEs. In order to represent the CEs (22) and (23) in integral form, the new timelike nondimensional variable τ is introduced:

$$\tau = \int_{-\infty}^{t}\mathrm{d}t_1/a(T) \qquad (25)$$

Utilizing eq 25 rewrites the evolution equation (23) in the integral form:

$$\eta_k(t) = -\frac{1}{\theta_k}\int_{-\infty}^{\tau}[m_k\epsilon_v(s) + \gamma_k\Delta T(s)]\exp[-(\tau - s)/\theta_k]\,\mathrm{d}s \qquad (k = 1, 2, ..., n) \quad (26)$$

Equation 26 represents the set of normal hidden variables $\eta_k(t)$ in terms of linear memory functionals of observable variables $\epsilon_v(t)$ and $\Delta T(t)$. Substituting eq 26 into eq 22 and integrating by part, finally yields

$$-p(t) = K_{\mathrm{e}}\epsilon_v(t) + \int_{-\infty}^{\tau}\dot{\epsilon}_v(s)\Psi(\tau - s)\,\mathrm{d}s + \alpha_{\mathrm{e}}\Delta T(t) + \int_{-\infty}^{\tau}\Delta\dot{T}(s)\aleph(\tau - s)\,\mathrm{d}s \quad (27)$$

Equation 27 is the constitutive equation for nonisothermal bulk relaxation searched for. It is represented in the form of a generalized Boltzmann superposition principle. In eq 27, $\Psi(\tau)$ and $\aleph(\tau)$,

$$\Psi(\tau) = \sum_i K_i\exp(-\tau/\theta_i) \qquad (K_i = N_i^* m_i^{\,2}) \qquad (28)$$

$$\aleph(\tau) = \sum_i \alpha_i\exp(-\tau/\theta_i) \qquad (\alpha_i = N_i^* m_i\gamma_i) \qquad (29)$$

are two relaxation functions form volume and temperature variations, respectively. In eq 27, the notations for the equilibrium values of bulk modulus, K_e, and thermal expansion coefficient, α_e, were used, as defined in eq 9a. There are related to the corresponding instantaneous values of K and α as

$$K = K_e + \sum_i K_i, \qquad \alpha = \alpha_e + \sum_i \alpha_i \tag{30}$$

The bulk nonisothermal relaxation constitutive equation (27) has symmetric form for both volume and temperature contributions in the pressure: (i) equilibrium ones, as described by out-of-integral terms, and (ii) the nonequilibrium contribution represented by two respective linear memory functionals. There is still one asymmetry, however. While all the components K_i of relaxation modulus are positive, it is impossible to prove it for α_i. It means that the positive definiteness of the thermal expansion coefficient cannot be thermodynamically justified. This is true even for the equilibrium coefficient α_e, whose value may be positive or negative, depending on the physical properties of the system.

Example. We consider here only one illustrative example of possible series experiments as proposed in ref 6. We assume that for $t < 0$, the material under study is in equilibrium with $\epsilon_v = 0$ and $\Delta T = 0$ ($T = T_0$). At time instant $t = +0$, an isothermal constant step variation in volume deformation, ϵ_v°, is suddenly imposed. Following that, at time $t = t_0$ ($t_0 > 0$), an isochoric constant step variation in temperature, ΔT°, is suddenly applied. Thus, mathematically,

$$\epsilon_v(t) = H(t)\,\epsilon_v^\circ, \qquad \Delta T(t) = H(t - t_0)\Delta T^\circ \tag{31}$$

Here $H(t)$ is the Heaviside step function. Then due to eqs 27−29, the time dependence of pressure is

$$-p(t) = H(t)\epsilon_v^\circ\cdot\{K_e + \sum_i K_i \exp[-t/(a_0\theta_i)]\} + H(t - t_0)\Delta T^\circ\cdot\{\alpha_e + \sum_i \alpha_i \exp[-(t - t_0)/(a_Y\theta_i)]\} \tag{32}$$

Equation 32 demonstrates how the pressure approaches equilibrium due to a sudden change in the relaxation modulus (the first figure brackets) and in relaxation thermal expansion (the second figure brackets), from their instant values K and α to the equilibrium values K_e and α_e. It is important that the discrete relaxation times in both the spectra are the same, if the temperature step variation ΔT° is small enough.

Concluding Remarks. 1. In this paper, we made rigorous thermodynamic derivations of well-known bulk nonisothermal CEs (27). For this purpose, we used the method of hidden variables and the standard approach of nonequilibrium thermodynamics.[7−10] This way of derivation not only justifies thermodynamically the CEs (27) but also allows one to know the free energy and dissipation functions for bulk nonisothermal relaxations. We also tried to estimate the sign definitiveness of equilibrium and relaxation moduli, K_e and K_i, as well as the equilibrium and relaxation thermal expansion coefficients, α_e and α_i ($i = 1, 2, ..., n$). The results that K_e and K_i are positive, and α_e and α_i are sign indefinite, are not unexpected.

2. It was recently proposed[6] to neglect the time dependence of thermal expansion, i.e. neglect the second integral term in CE (27). The physical reason for this was that an increase in temperature would result in "wiggling faster of atoms without their mean displacement" in polymer macromolecules. Though this argument does not contradict the thermodynamic scheme developed, it is, in our opinion, too simplistic. The reference to a single supporting experiment[15] is not enough to make the above general statement. The condensed polymers are quite different from gases and crystalline solids. E.g., more intense wiggling atoms in polymer chains may lead to cooperative effects, which rearrange polymer macromolecules to a new equilibrium order. Thus, in our opinion, more detailed theories or experiments should be developed to justify the importance of temperature memory effects in bulk relaxations. One such experiment to test the idea proposed in ref 6 is to make a sudden increase in temperature, ΔT°, under isochoric conditions from the rest state. This experiment will straighforwardly estimate the importance of the second relaxation function $N(t)$ in eq (27).

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