Thermodynamics of viscoelastic fluids: the temperature equation

Thermodynamics of viscoelastic fluids: The temperature equation

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Synopsis

From the thermodynamics with internal variables we will derive the temperature equation for viscoelastic fluids. We consider the type of storage of mechanical energy, the dissipation of mechanical energy, the compressibility of the fluid, the nonequilibrium heat capacity and thermal expansion, and deformation induced anisotropy of the heat conduction. The well-known stress differential models that fit into the thermodynamic theory will be treated as an example. Adapting a power-law scaling of the shear moduli on temperature and density, as is usual in rubber elasticity, we will derive an approximation of the temperature equation in measurable quantities. This equation will be compared with experimental results. © *1998 The Society of Rheology.*
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I. INTRODUCTION

For viscoelastic fluids many differential and integral stress models have been proposed in the literature, see, for example, Larson (1988). As already shown by Leonov (1992) most of the differential stress models fit into the thermodynamic theory with internal variables. However, although the thermodynamics is well suited to describe nonisothermal effects and although many practical flows are highly nonisothermal, relatively little attention has been paid to nonisothermal effects. Even in the original thermodynamical derivation of the Leonov model [Leonov (1976)], the attention was focused on the stress constitutive equation. Also in later articles one has mainly focused on the stress equation. If a temperature equation was discussed, just a simple temperature equation was considered, i.e., with the heat production equal to the stress work, with isotropic heat conduction and for incompressible fluids.

Nevertheless, some nonisothermal topics received some attention in recent years. A viscoelastic fluid can both dissipate and store or release energy, so that the dissipation does not equal the stress work. The dissipation of various viscoelastic fluid models has been discussed by Leonov (1992) and Peters (1996). However, it is interesting to reconsider these expressions, because some of them are in error.

A topic that is closely related to the dissipation is the type of storage of mechanical energy, see Braun (1991), Astarita and Sarti (1976) and Sarti and Esposito (1977/1978). Mechanical energy can be stored in the form of internal energy or in the form of entropy.

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A complete storage as internal energy gives no reversible heat production, only dissipation. If it is completely stored as entropy, the calculation of the dissipation is superfluous, because then the sum of reversible heat production and dissipation equals the stress work.

Another reversible heat production source is caused by pressure changes. This effect has been discussed by Flaman and Veltman (1988) for injection moulding experiments. During compression the temperature of the fluid rises and it drops during expansion.

The deformation induced anisotropy of the heat conduction is another interesting nonisothermal effect of polymeric fluids. Experiments of Hellwege *et al.* (1963) already showed that with increasing orientation of the polymeric fluid, the thermal conductivity in the direction of orientation increases and the thermal conductivity perpendicular to the orientation decreases. More recently, the anisotropy has been derived from microrheological modeling by van den Brule (1990).

In this article we derive the temperature equation for compressible viscoelastic fluids. We start with a brief description of the thermodynamics, including the constitutive equations and their relation to well-known stress models. Next we will determine the connection between the requisite thermodynamical quantities like mechanical dissipation, free energy, pressure and entropy and show how they are related to the stress models. Based on this, we then obtain the temperature equation with the above-mentioned nonisothermal effects. By approximating the nonequilibrium coefficients (heat capacity and thermal expansion), we will derive an approximate temperature equation with measurable coefficients. Finally, we will compare this equation with experimental results.

II. THERMODYNAMICS OF VISCOELASTIC FLUIDS

A. General

In a fixed bounded space Ω the balance equations for a system without sources are [see, for example, Bird *et al.* (1960)]:

$$\dot{\rho} = -\rho\nabla\cdot\boldsymbol{v}, \tag{1}$$

$$\rho\dot{\mathbf{v}} = \nabla\cdot\boldsymbol{\sigma}, \tag{2}$$

$$\rho\dot{u} = \boldsymbol{\sigma}:\boldsymbol{d}-\nabla\cdot\boldsymbol{\phi}_q, \tag{3}$$

where ρ is the fluid density, $\boldsymbol{v}$ the velocity, $\boldsymbol{d}$ the Euler rate-of-deformation tensor defined by $\boldsymbol{d} = (\boldsymbol{L}+\boldsymbol{L}^T)/2$, with $\boldsymbol{L}^T = \nabla\boldsymbol{v}$. The constitutive equations needed for the (symmetric) total stress $\boldsymbol{\sigma}$, the heat flux $\boldsymbol{\phi}_q$ and the internal energy u can be obtained with the help of the balance of entropy from the thermodynamics.

To describe thermodynamically the relaxation phenomena of viscoelastic fluids we use a set of (internal) state variables and (external) rate variables [see, for example, Kuiken (1994) or Jongschaap *et al.* (1994)]. As the mechanical state variables we will take the density and K internal deformation tensors $\boldsymbol{b}_k$. So we will not take into account possible scalar internal variables describing the volume relaxation or internal vector variables describing the relaxation of the heat flux. The internal deformation tensor $\boldsymbol{b}_k$ has also been used by Leonov (1976, 1987) to derive the Leonov model. It is also called the conformation tensor or the configuration tensor, and in microrheology it corresponds up to a scaling factor to the second moment $\langle\boldsymbol{QQ}\rangle$. However, in this article we will use the nomenclature from the thermodynamics.

To derive the balance of entropy from the balance of internal energy, the Gibbs equation for viscoelastic fluids, including compressibility and internal processes, is needed:

$$\dot{u} = T\dot{s} + \frac{p}{\rho^2}\dot{\rho} + \sum_{k=1}^{K} \boldsymbol{P}_k : \dot{\boldsymbol{b}}_k , \tag{4}$$

where p is the thermodynamic pressure and $\boldsymbol{P}_k$ the conjugate forces of the kth internal deformation tensor $\boldsymbol{b}_k$. See Kuiken (1994) or Jongschaap *et al.* (1994) for an extensive discussion of the Gibbs equation.

Instead of the internal energy u, it is advantageous to use the Helmholtz free energy $\psi = u - Ts$, where s is the entropy per unit mass. Substitution in the Gibbs equation (4) gives

$$\dot{\psi} = -s\dot{T} + \frac{p}{\rho^2}\dot{\rho} + \sum_{k=1}^{K} \boldsymbol{P}_k : \dot{\boldsymbol{b}}_k , \tag{5}$$

with the equations of state

$$s = -\left.\frac{\partial \psi}{\partial T}\right|_{\rho,\boldsymbol{b}}, \quad p = -\left.\frac{\partial \psi}{\partial \rho^{-1}}\right|_{T,\boldsymbol{b}} = \rho^2 \left.\frac{\partial \psi}{\partial \rho}\right|_{T,\boldsymbol{b}}, \quad \boldsymbol{P}_k = \left.\frac{\partial \psi}{\partial \boldsymbol{b}_k}\right|_{T,\boldsymbol{b}'_k}, \tag{6}$$

where a $|_x$ means a quantity at constant x. A $|_{\boldsymbol{b}}$ means that all K internal deformation tensors $\boldsymbol{b}_k$ are constant. A $|_{\boldsymbol{b}'_k}$ will be used if all K internal deformation tensors $\boldsymbol{b}_k$ are constant except the kth internal deformation tensor. Combination of the balance of internal energy (3) and the Gibbs equation (4) gives the balance of entropy

$$\begin{aligned} \rho\dot{s} &= -\nabla\cdot(T^{-1}\boldsymbol{\phi}_q) + \Pi_s , \\ T\,\Pi_s &= -T^{-1}\boldsymbol{\phi}_q \cdot \nabla T + \boldsymbol{\sigma} : \boldsymbol{d} - \frac{p}{\rho}\dot{\rho} - \rho \sum_{k=1}^{K} \boldsymbol{P}_k : \dot{\boldsymbol{b}}_k , \end{aligned} \tag{7}$$

where Π_s is the entropy production. The second law of thermodynamics states that the entropy production must be nonnegative: $\Pi_s \geqslant 0$.

For the evolution equation of the internal deformation tensor, we follow Leonov (1976):

$$\overset{\triangledown}{\boldsymbol{b}}_k = -\boldsymbol{b}_k \cdot \boldsymbol{d}_{\mathrm{irr},k} - \boldsymbol{d}_{\mathrm{irr},k} \cdot \boldsymbol{b}_k , \tag{8}$$

where $\overset{\triangledown}{(\,)} = \dot{\boldsymbol{b}}_k - \boldsymbol{L}\cdot\boldsymbol{b}_k - \boldsymbol{b}_k \cdot \boldsymbol{L}^T$ is the upper-convected derivative and $\boldsymbol{d}_{\mathrm{irr},k}$ the irreversible rate-of-deformation tensor, which has to be specified by a constitutive relation. Substituting Eqs. (1) and (8) in the entropy production (7) gives

$$T\Pi_s = -T^{-1}\boldsymbol{\phi}_q \cdot \nabla T + \left(\boldsymbol{\sigma} - \sum_{k=1}^{K} 2\rho \boldsymbol{b}_k \cdot \boldsymbol{P}_k + p\boldsymbol{I} \right) : \boldsymbol{d} + 2\rho \sum_{k=1}^{K} [\boldsymbol{P}_k : (\boldsymbol{b}_k \cdot \boldsymbol{d}_{\mathrm{irr},k})], \tag{9}$$

where the antisymmetric part of $\boldsymbol{L}$ canceled out because of the isotropy of the material ($\boldsymbol{b}_k \cdot \boldsymbol{P}_k = \boldsymbol{P}_k \cdot \boldsymbol{b}_k$).

A mode of the elastic stress $\boldsymbol{\tau}_{e,k}$ is defined analogously to Jongschaap *et al.* (1994) and Grmela and Carreau (1987):

$$\boldsymbol{\tau}_{e,k} = 2\rho \boldsymbol{b}_k \cdot \boldsymbol{P}_k = 2\rho \boldsymbol{b}_k \cdot \left. \frac{\partial \psi}{\partial \boldsymbol{b}_k} \right|_{T,\rho,\boldsymbol{b}_k'} . \tag{10}$$

Note that we have not used the Leonov constraint $\det \boldsymbol{b}_k = 1$. The Brownian force is not included when this constraint is used and the constraint can be incorporated by using Lagrange multipliers, see Grmela and Carreau (1987). With Eq. (10) the entropy production (9) can be written as the sum of products of thermodynamic fluxes and forces

$$T\Pi_s = -T^{-1}\boldsymbol{\phi}_q \cdot \nabla T + \boldsymbol{\tau}_{\text{irr}} : \boldsymbol{d} + \sum_{k=1}^{K} \boldsymbol{d}_{\text{irr},k} : \boldsymbol{\tau}_{e,k}, \tag{11}$$

where the irreversible stress is defined as $\boldsymbol{\tau}_{\text{irr}} = \boldsymbol{\sigma} - \boldsymbol{\tau}_e + p\boldsymbol{I}$, with $\boldsymbol{\tau}_e = \Sigma_{k=1}^{K} \boldsymbol{\tau}_{e,k}$.

B. Constitutive equations

In thermodynamics the constitutive equations for the thermodynamic fluxes have to be specified by a linear combination of the forces. In our case the forces are $T^{-1}\nabla T$, $\boldsymbol{d}$ and $\boldsymbol{\tau}_{e,k}$. Using the Onsager–Casimir reciprocal relations and the Curie principle, see, for example, de Groot and Mazur (1984) or Kuiken (1994), we have for the thermodynamic fluxes $\boldsymbol{\phi}_q$, $\boldsymbol{\tau}_{\text{irr}}$ and $\boldsymbol{d}_{\text{irr},k}$

$$\boldsymbol{\phi}_q = T^{-1}\boldsymbol{\mathcal{L}}_{qq} \cdot \nabla T, \tag{12}$$

$$\boldsymbol{\tau}_{\text{irr}} = \boldsymbol{\mathcal{L}}_{dd} : \boldsymbol{d} + \sum_{l=1}^{K} \boldsymbol{\mathcal{L}}_{d\tau_{e,l}} : \boldsymbol{\tau}_{e,l}, \tag{13}$$

$$\boldsymbol{d}_{\text{irr},k} = -\boldsymbol{\mathcal{L}}^{T}_{d\tau_{e,k}} : \boldsymbol{d} + \sum_{l=1}^{K} \boldsymbol{\mathcal{L}}_{\tau_{e,k}\tau_{e,l}} : \boldsymbol{\tau}_{e,l}, \tag{14}$$

where the second and fourth order tensors $\boldsymbol{\mathcal{L}}$ may depend on the local state variables ρ, T and $\boldsymbol{b}_k$. We will restrict ourselves to the case where $\boldsymbol{\mathcal{L}}_{\tau_{e,k}\tau_{e,k}}$ only depends on the kth internal deformation tensor $\boldsymbol{b}_k$ and $\boldsymbol{\mathcal{L}}_{\tau_{e,k}\tau_{e,l}} = 0$ for $k \neq l$. Then Eq. (14) becomes

$$\boldsymbol{d}_{\text{irr},k} = -\boldsymbol{\mathcal{L}}^{T}_{d\tau_{e,k}} : \boldsymbol{d} + \boldsymbol{\mathcal{L}}_{\tau_{e,k}\tau_{e,k}} : \boldsymbol{\tau}_{e,k}. \tag{15}$$

This corresponds to the assumption, usually made for multimode models, that the modal stresses are decoupled. In Sec. III we will relate the fourth order tensors $\boldsymbol{\mathcal{L}}_{dd}$, $\boldsymbol{\mathcal{L}}_{d\tau_{e,k}}$ and $\boldsymbol{\mathcal{L}}_{\tau_{e,k}\tau_{e,k}}$ to the various stress differential models. Due to the dependence of $\boldsymbol{\mathcal{L}}_{qq}$ on $\boldsymbol{b}_k$, anisotropy of the heat conduction tensor $\boldsymbol{\kappa}$ can be taken into account. For experimental evidence we refer to Hellwege *et al.* (1963), Choy *et al.* (1981) and Wallace *et al.* (1985). The most general isotropic model for the heat conduction tensor is (with decoupled modes):

$$\boldsymbol{\kappa} = -T^{-1}\boldsymbol{\mathcal{L}}_{qq} = \sum_{k=1}^{K} (\kappa_{0,k}\boldsymbol{I} + \kappa_{1,k}\boldsymbol{b}_k + \kappa_{2,k}\boldsymbol{b}_k^2), \tag{16}$$

where $\kappa_{i,k}$ may depend on the invariants of $\boldsymbol{b}_k$, the pressure and temperature. For a one-mode model with constant coefficients and $\kappa_{2,k} = 0$ this model reduces to the model derived for Hookean dumbbells by van den Brule (1990). The behavior of $\boldsymbol{\kappa}$ depends on the stress model used. For a simple model for $\boldsymbol{\kappa}$ with the coefficients $\kappa_{i,k}$ independent of

$\boldsymbol{b}_k$, all stress models that we discuss in Appendix A are able to predict the increase of the thermal conductivity parallel to the direction of deformation. However, the decrease of the thermal conductivity perpendicular to the deformation in steady shear can then only be predicted by models with nonzero second normal stress difference. The equation for the heat flux will not be discussed in more detail. For the behavior of the anisotropy for various stress models see Wapperom (1996).

Substitution of Eqs. (12), (13), (15) and (16) in the entropy production (11) gives

$$T\Pi_s = \nabla T \cdot \boldsymbol{\kappa} \cdot \nabla T + \boldsymbol{d} : \boldsymbol{\mathcal{L}}_{dd} : \boldsymbol{d} + \sum_{k=1}^{K} \boldsymbol{\tau}_{e,k} : \boldsymbol{\mathcal{L}}_{\tau_{e,k}\tau_{e,k}} : \boldsymbol{\tau}_{e,k}. \tag{17}$$

Due to the restriction that the entropy production has to be nonnegative for independent ∇T, $\boldsymbol{d}$ and $\boldsymbol{\tau}_{e,k}$, the tensors $\boldsymbol{\mathcal{L}}_{dd}$ and $\boldsymbol{\mathcal{L}}_{\tau_{e,k}\tau_{e,k}}$ have to be positive definite. We will discuss these restrictions further in Sec. IV B. The cross terms with $\boldsymbol{\mathcal{L}}_{d\tau_{e,k}}$ are nondissipative, so the entropy production does not give any restriction on these tensors. Furthermore, it is easy to check that for $\kappa_{0,k} \geqslant 0$, $\kappa_{1,k} \geqslant 0$ and $\kappa_{2,k} \geqslant 0$ the heat flux contribution to the entropy production is positive, because $\boldsymbol{b}_k$ is positive definite. However, some less severe restrictions can be derived, see Wapperom (1996).

III. STRESS MODELS IN THE LITERATURE

The total stress $\boldsymbol{\sigma}$ is usually decomposed in a pressure part $-p\boldsymbol{I}$ and an extrastress tensor $\boldsymbol{\tau}$ that vanishes in equilibrium

$$\boldsymbol{\sigma} = -p\boldsymbol{I} + \boldsymbol{\tau}, \tag{18}$$

where $\boldsymbol{I}$ is the unit tensor. The pressure p is then related to the density and the temperature only. The extrastress tensor $\boldsymbol{\tau}$ consists of a Newtonian (solvent) contribution and the polymer contributions containing different modes

$$\boldsymbol{\tau} = 2\eta_s \boldsymbol{d} + \left(\eta_{s,v} - \frac{2}{3}\eta_s \right) \nabla \cdot \boldsymbol{v} \boldsymbol{I} + \sum_{k=1}^{K} \boldsymbol{\tau}_k, \tag{19}$$

in which η_s is the Newtonian shear viscosity, $\eta_{s,v}$ the Newtonian bulk viscosity and K the number of modes. The modal stress $\boldsymbol{\tau}_k$ is assumed to be a function of the internal deformation tensor (configuration tensor) which fulfills an evolution equation, see, for example, Leonov (1992).

An extensive overview of differential stress models is given by Larson (1988). For the well-known differential models that we will consider next, the modal stress is related to the internal deformation tensor with the help of the simple algebraic relation:

$$\boldsymbol{\tau}_k = \frac{G_k}{1-\xi_k}(B_k \boldsymbol{b}_k - \boldsymbol{I}), \tag{20}$$

where G_k is the shear modulus of the kth mode, and B_k may be a function of the first invariant $I_{1,k}$. We give the values of B_k for various models in Appendix A. The moduli are weak functions of the temperature and the density. For the parameter ξ_k, which will be explained shortly, we will exclude the value $\xi_k = 1$. For all well-known differential stress models it can be shown that $\boldsymbol{b}_k$ is positive definite, see Hulsen (1990) or Wapperom and Hulsen (1995).

The evolution equation for $\boldsymbol{b}_k$ has the form

$$\lambda_k \overset{\square}{\boldsymbol{b}}_k = \boldsymbol{g}_k, \tag{21}$$

where the relaxation time λ_k may depend on the temperature and pressure, and $\boldsymbol{g}_k = g_{0,k}\boldsymbol{I}+g_{1,k}\boldsymbol{b}_k+g_{2,k}\boldsymbol{b}_k^2$. The scalars $g_{i,k}$ may depend on the invariants of $\boldsymbol{b}_k$ and are given in Appendix A. The temperature dependence of the relaxation time may be described by a Williams–Landel–Ferry (WLF) or Arrhenius shift factor, see Ferry (1981) or Tanner (1985), and also its pressure dependence may be described by an exponential shift factor, see Ferry (1981) or Kadijk and van den Brule (1994). The mixed (or Gordon–Schowalter) convected derivative of $\boldsymbol{b}_k$ is defined by

$$\overset{\square}{\boldsymbol{b}}_k = \dot{\boldsymbol{b}}_k-(\boldsymbol{L}-\xi_k\boldsymbol{d})\cdot\boldsymbol{b}_k-\boldsymbol{b}_k\cdot(\boldsymbol{L}-\xi_k\boldsymbol{d})^T, \tag{22}$$

in which ξ_k is a parameter for which holds $0 \leqslant \xi_k \leqslant 2$. The values $0 < \xi_k < 2$ represent a sort of frictionless slip of the internal microstructure with respect to the macroscopic flow. In Sec. IV A we will show that the slip is indeed frictionless or nondissipative.

IV. THE RELATION BETWEEN THE STRESS MODELS AND THE THERMODYNAMIC QUANTITIES

A. The thermodynamic fluxes $\boldsymbol{d}_{\text{irr}}$ and $\boldsymbol{\tau}_{\text{irr}}$

Comparison of the model (21) with Eq. (8) gives that the irreversible rate-of-deformation tensor corresponds to

$$\boldsymbol{d}_{\text{irr},k} = \xi_k\boldsymbol{d}-\frac{1}{2\lambda_k}\boldsymbol{b}_k^{-1}\cdot\boldsymbol{g}_k. \tag{23}$$

Note that to include the slip parameter ξ_k it is not necessary to modify the left-hand side of the evolution equation (8) as done by Leonov (1992) and Jongschaap *et al.* (1994). It can be included in $\boldsymbol{d}_{\text{irr},k}$. Comparing with the equation for the irreversible rate-of-strain tensor (15), and introducing the fourth order unit tensor $\boldsymbol{\mathcal{I}}$, leads to

$$\boldsymbol{\mathcal{L}}_{d\tau_{e,k}} = -\xi_k\boldsymbol{\mathcal{I}}, \quad \boldsymbol{\mathcal{L}}_{\tau_{e,k}\tau_{e,k}}:\boldsymbol{\tau}_{e,k} = -\frac{1}{2\lambda_k}\boldsymbol{b}_k^{-1}\cdot\boldsymbol{g}_k, \tag{24}$$

which shows that the frictionless slip in the mixed convected derivative, represented by the parameter ξ_k, is indeed nondissipative [see Eq. (17)]. Comparing the constitutive equations for the irreversible stress (13) and (19), and using $\boldsymbol{\tau} = \boldsymbol{\tau}_e+\boldsymbol{\tau}_{\text{irr}}$, then gives

$$\boldsymbol{\mathcal{L}}_{dd} = 2\eta_s\boldsymbol{\mathcal{I}}+\left(\eta_{s,v}-\frac{2}{3}\eta_s\right)\boldsymbol{II}, \tag{25a}$$

$$\boldsymbol{\tau}_{e,k} = \frac{1}{1-\xi_k}\boldsymbol{\tau}_k. \tag{25b}$$

Henceforth, we will neglect the compressible Newtonian contribution, so that the irreversible stress reduces to

$$\boldsymbol{\tau}_{\text{irr}} = \boldsymbol{\tau}-\boldsymbol{\tau}_e = 2\eta_s\boldsymbol{d}-\sum_{k=1}^{K}\xi_k\boldsymbol{\tau}_{e,k}. \tag{26}$$

B. The mechanical dissipation

With the results of Sec. IV A the entropy production (17) can be written as

$$T\Pi_s = -T^{-1}\boldsymbol{\phi}_q \cdot \nabla T + D_m . \tag{27}$$

The first term represents the entropy production due to conduction of heat and D_m is the mechanical dissipation which consists of a Newtonian solvent and a viscoelastic part

$$D_m = 2\eta_s \boldsymbol{d}:\boldsymbol{d} + \sum_{k=1}^{K} D_{m,k}, \tag{28}$$

$$D_{m,k} = -\frac{1}{2\lambda_k(1-\xi_k)}(\boldsymbol{\tau}_k \cdot \boldsymbol{b}_k^{-1}):\boldsymbol{g}_k , \tag{29}$$

where $D_{m,k}$ is the modal mechanical dissipation. During deformation the mechanical dissipation D_m is smaller than the stress work and mechanical energy is stored. During relaxation it is larger and then the stored mechanical energy is dissipated.

From the restriction that the entropy production has to be nonnegative for independent ∇T, $\boldsymbol{d}$ and $\boldsymbol{\tau}_k$, it follows that $\eta_s \geqslant 0$. We examine the expression for $D_{m,k}$ for various stress models in more detail in Appendix A. Furthermore we show that for all of these models the dissipation is nonnegative, as it should be.

C. The free energy and related quantities

1. The free energy ψ and the elastic stress $\boldsymbol{\tau}_e$

For models of the form (20), it follows from Eqs. (10) and (25b) that the derivative of the free energy with respect to an internal deformation tensor $\boldsymbol{b}_k$ equals

$$\left.\frac{\partial \psi}{\partial \boldsymbol{b}_k}\right|_{T,\rho,\boldsymbol{b}_k'} = \frac{G_k}{2\rho(1-\xi_k)^2}(B_k \boldsymbol{I} - \boldsymbol{b}_k^{-1}). \tag{30}$$

With the help of $\partial I_{1,k}/\partial \boldsymbol{b}_k = \boldsymbol{I}$ and $\partial I_{3,k}/\partial \boldsymbol{b}_k = I_{3,k}\boldsymbol{b}_k^{-1}$ Eq. (30) can easily be integrated. For convenience we will split the free energy ψ in

$$\psi = \bar{\psi}(\rho,T) + \sum_{k=1}^{K} \psi_k , \tag{31}$$

where $\bar{\psi}(\rho,T)$ only depends on the density and the temperature and the modal free energy ψ_k depends on the kth internal deformation tensor $\boldsymbol{b}_k$ and possibly on the density and temperature.

For models with $B_k = 1$, see Appendix A, the elastic stresses and the corresponding modal free energies are:

$$\boldsymbol{\tau}_{e,k} = \frac{G_k}{(1-\xi_k)^2}(\boldsymbol{b}_k - \boldsymbol{I}), \quad \psi_k = \frac{G_k}{2\rho(1-\xi_k)^2}(I_{1,k} - \ln I_{3,k} - 3), \tag{32}$$

where the $\ln I_{3,k}$ term in the free energy corresponds to the isotropic term in the elastic stress and represents the free energy of noninteracting macromolecules as has been discussed by Carreau and Grmela (1991). For a large internal deformation, if the $\ln I_{3,k}$ term can be neglected, we find $2\rho\psi_k \simeq \operatorname{tr} \boldsymbol{\tau}_{e,k} = \operatorname{tr} \boldsymbol{\tau}_k$.

For the Larson elastic stress [see, for example, Leonov (1992)], where $B_k = [1 + \beta_k(I_{1,k}-3)/3]^{-1}$, we obtain

$$\boldsymbol{\tau}_{e,k} = G_k(B_k\boldsymbol{b}_k-\boldsymbol{I}), \quad \psi_k = -\frac{G_k}{2\rho}\left(\frac{3}{\beta_k}\ln B_k+\ln I_{3,k}\right), \tag{33}$$

when $\beta_k \neq 0$. For a large internal deformation, if the $\ln I_{3,k}$ term can be neglected, we find $2\rho\psi_k \simeq \text{tr}\ \boldsymbol{\tau}_k \ln[1+\beta_k(I_{1,k}-3)/3]$. This term will be assumed of $\mathcal{O}(\text{tr}\ \boldsymbol{\tau}_k)$ (for $I_{1,k} = 100$ and $\beta_k = 1$ the logarithm equals 3.5).

For the finitely extensible nonlinear elastic using the Peterlin closure approximation (FENE-P) model, see, for example, Wedgewood and Bird (1988), the elastic stress and the corresponding free energy are

$$\boldsymbol{\tau}_{e,k} = G_k(B_k\boldsymbol{b}_k-\boldsymbol{I}), \quad \psi_k = \frac{G_k}{2\rho}(b_k \ln B_k-\ln I_{3,k}), \tag{34}$$

where $B_k = b_k/(b_k+3-I_{1_k})$ and b_k a dimensionless constant. For a large internal deformation, if the $\ln I_{3,k}$ term can be neglected, we find $2\rho\psi_k \simeq \text{tr}\ \boldsymbol{\tau}_k B_k^{-1} \ln B_k$, with $B_k \gg 1$. This term is not larger than $\mathcal{O}(\text{tr}\ \boldsymbol{\tau}_k)$.

Note that in equilibrium ψ reduces to $\bar{\psi}$ for the neo-Hookean, the Larson and FENE-P models. Out of equilibrium $\psi-\bar{\psi}$ is nonnegative. This result follows after a decomposition on the principal axes. The resulting functions $x-\ln x-1$ for the neo-Hookean free energy, $1/\beta_k \ln[1+\beta_k(x-1)]-\ln x$ for the Larson free energy, are nonnegative for $x > 0$. For the FENE-P free energy it can be shown (with a decomposition on the principal axes and the fact that the minimum of $I_{1,k}$ is on the line with equal principal values) that $b_k \ln B_k-\ln I_{3,k}$ has one local minimum in equilibrium, so that $\psi-\bar{\psi} \geqslant 0$. We will examine the free energy $\bar{\psi}$ further in the remaining part of this section, because it is related to the pressure and entropy.

Theoretically, all thermodynamic quantities related to the elastic part of the free energy can now be computed. However, depending on the complexity of the free energy function, this may be rather complicated. Therefore, we make the following assumptions:

(1) The temperature and density dependence of the shear moduli are given by

$$G_k = G_{k,\text{ref}}\left(\frac{T}{T_{\text{ref}}}\right)^{\gamma_k}\left(\frac{\rho}{\rho_{\text{ref}}}\right)^{\delta_k}, \tag{35}$$

where γ_k and δ_k are constants. Temperature scaling is well known in rubber elasticity, see, for example, Treloar (1975). The values for a large number of polymers are given by Mark (1973, 1976), including a discussion on reliability of the experiments. A value of $\gamma_k = 1$ corresponds to a set of free chains, as in the kinetic theory. However, the internal rotation about bonds within the molecule is not entirely free, but is restricted by hindering potentials arising from steric interactions. This effect can be taken into account by a temperature dependence of the mean-square length of a set of free chains, which results in the temperature scaling in Eq. (35). It is claimed that because the effect is intramolecular the value of γ is characteristic for a polymer, thus valid in the rubber state, fluid state and for solutions. The value of γ is usually obtained from measurement of the force on a sample as a function of temperature. Dependent on the material, γ may be larger or smaller than 1. A value of $\gamma < 1$ indicates that a small mean-square length is energetically favored, and a value of $\gamma > 1$ that the extended conformation is energetically favored. The value of γ is often given in terms of f_e/f, the ratio of the internal energy

contribution to the force and the total force, or $d\ \ln\langle r_0^2\rangle/d\ln T$ with $\langle r_0^2\rangle$ the mean-square length of a set of free chains. These quantities are related to the temperature dependence of the modulus by $f_e/f = d\ \ln\langle r_0^2\rangle/d\ln T = 1-\gamma$. Up to moderate elongation ratios ($\epsilon \simeq 3$), indeed, an almost constant ratio f_e/f is found experimentally. A strong decrease for large extension ratios is usually ascribed to strain-induced crystallization. However, some caution does not seem superfluous, because for some polymers there is considerable scatter in the experimental results, particularly between experiments at constant density and at constant pressure. However, the range $0 < \gamma < 2$ covers the list given by Mark (1973) of tens of polymers, so that the value of $\gamma = -5$ assumed by Gupta and Metzner (1982) seems to be unrealistic. Note also that as long as G is the only temperature dependent parameter in the free energy, the ratio f_e/f is constant. However, if $\beta_k = \beta_k(T)$ in Eq. (33) or $b_k = b_k(T)$ in Eq. (34) this does not hold anymore.

The density scaling with $\delta_k = 1$ corresponds to the kinetic theory. The density scaling with $\delta_k \neq 1$ corresponds to the extra factor introduced by Tobolsky and Shen (1966) for rubber elasticity, resulting from the dependence of $\langle r^2\rangle_0$ on the density. They have supposed that this effect is caused by intermolecular forces. The parameter δ_k is then a constant that depends on the chemical structure of the chains. The value of δ_k can be obtained from volume dilatation, force-pressure or thermoelastic measurements. Although sometimes considerable scatter exists between results of various workers, the deviations from $\delta_k = 1$ do not seem to be large. Natural rubber values are found in the range $0.75 < \delta < 1.28$, and for polyvinylalcohol $\delta = 1.2$ is reported, see Shen and Croucher (1975). For the approximation of terms in the next sections we will assume $0 < \delta_k < 2$.

(2) The parameter β_k in the Larson and b_k in the FENE-P free energy are constant, for reasons of simplicity.

Due to the second assumption the free energy can be written as

$$\psi = \bar{\psi}(\rho,T) + \sum_{k=1}^{K} \psi_k = \bar{\psi}(\rho,T) + \sum_{k=1}^{K} \frac{G_k}{2\rho} f_k(\boldsymbol{b}_k), \tag{36}$$

where the functions f_k are independent of density and temperature.

2. The thermodynamic pressure p

With the assumption Eq. (35) for the moduli, the thermodynamic pressure p of Eq. (6) can easily be obtained by differentiation of Eq. (36)

$$p = \rho^2 \left.\frac{\partial\psi}{\partial\rho}\right|_{T,\boldsymbol{b}} = \bar{p}(\rho,T) + \sum_{k=1}^{K} (\delta_k - 1)\rho\psi_k, \tag{37}$$

where $\bar{p}(\rho,T) = \rho^2 \partial\bar{\psi}/\partial\rho|_{T,\boldsymbol{b}}$. This result shows that the thermodynamic pressure p is only independent of the internal deformation tensors if $\delta_k = 1$. With respect to $\bar{p}$ the pressure increases if $\delta_k > 1$ and decreases if $\delta_k < 1$ when the material is deformed. For the free energy term holds, $\rho\psi_k = \mathcal{O}(\text{tr}\ \boldsymbol{\tau}_k)$. For the assumption $0 < \delta_k < 2$, the summation may be of the same order as the trace of the stress. This may give a considerable contribution to the pressure then, because values of tr $\boldsymbol{\tau} = \mathcal{O}(10^6)$ Pa are not unusual.

For the relation between the density and the thermodynamic pressure (in equilibrium) the Tait equation, see van Krevelen and Hoftyzer (1976), is often used for polymeric fluids:

$$\rho^{-1}(\bar{p},T) = \rho_0^{-1}[1-c\ln(1+\bar{p}/B)], \tag{38}$$

where $\rho_0^{-1} = \rho^{-1}(0,T)$, c is a constant and B depends exponentially on the temperature $B = b_0 \exp[-b_1(T-273)]$. Equation (38) is equivalent to

$$\bar{p}(\rho,T) = B\left(\exp\left[\frac{1}{c}\left(1-\frac{\rho^{-1}}{\rho_0^{-1}}\right)\right]-1\right). \tag{39}$$

The order of magnitude of the various coefficients is about 2×10^8 Pa $< b_0 < 4\times10^8$ Pa, 4×10^{-3} K$^{-1} < b_1 < 7\times10^{-3}$ K^{-1} and $c \simeq 0.1$. The exponent is still between 1 and 3 for pressures lower than 0.1 GPa. Accurate values for various polymers can be found in the books by Tanner (1985) and van Krevelen and Hoftyzer (1976).

The corresponding free energy $\bar{\psi}$ can easily be obtained by integrating the equation of state for the pressure:

$$\bar{\psi}(\rho,T) = \tilde{\psi}(T)+cB\rho_0^{-1}\exp\left[\frac{1}{c}\left(1-\frac{\rho^{-1}}{\rho_0^{-1}}\right)\right]+B\rho^{-1}, \tag{40}$$

where $\tilde{\psi}(T)$ is a function of temperature only.

3. The entropy s

With the assumption Eq. (35) for the moduli, the entropy can easily be calculated by differentiation of Eq. (36)

$$s = -\left.\frac{\partial\psi}{\partial T}\right|_{\rho,\boldsymbol{b}} = \bar{s}(\rho,T)-\sum_{k=1}^{K}\gamma_k T^{-1}\psi_k, \tag{41}$$

where $\bar{s}(\rho,T) = -\partial\bar{\psi}/\partial T|_\rho$. Because ψ_k is positive, it depends on γ_k whether the entropy increases ($\gamma_k < 0$), decreases ($\gamma_k > 0$) or remains constant ($\gamma_k = 0$) with increasing internal deformation.

Differentiating $\bar{\psi}$ in Eq. (40) with respect to the temperature gives for the entropy $\bar{s}$:

$$\bar{s}(\rho,T) = Bb_1\rho^{-1}+B\left[cb_1\rho_0^{-1}-\left(c+\frac{\rho^{-1}}{\rho_0^{-1}}\right)\frac{d\rho_0^{-1}}{dT}\right]\exp\left[\frac{1}{c}\left(1-\frac{\rho^{-1}}{\rho_0^{-1}}\right)\right]+\tilde{s}(T), \tag{42}$$

where $\tilde{s} = -d\tilde{\psi}/dT$ is a function of temperature only.

V. THE TEMPERATURE EQUATION

In this section we will transform the balance of entropy into the temperature equation for viscoelastic fluids. Therefore, we have to evaluate the change of entropy. If we consider the entropy as a function of the temperature, the thermodynamic pressure and the internal deformation tensors $s = s(T,p,\boldsymbol{b}_k)$, the change of entropy can be written as

$$\dot{s} = \left.\frac{\partial s}{\partial T}\right|_{p,\boldsymbol{b}}\dot{T}+\left.\frac{\partial s}{\partial p}\right|_{T,\boldsymbol{b}}\dot{p}+\sum_{k=1}^{K}\left.\frac{\partial s}{\partial \boldsymbol{b}_k}\right|_{p,T,\boldsymbol{b}_k'}:\dot{\boldsymbol{b}}_k = \frac{c_{p,b}}{T}\dot{T}-\frac{\alpha_{T,b}}{\rho}\dot{p}+\Delta s_b, \tag{43}$$

which defines the heat capacity at constant pressure and internal deformation $c_{p,b}$, the thermal expansion coefficient $\alpha_{T,b}$ and the entropy difference Δs_b. Substitution of the

entropy change (43) in the local entropy balance (7) with the viscoelastic entropy production (27), gives the *temperature equation* for viscoelastic fluids

$$\rho c_{p,b}\dot{T} - T\alpha_{T,b}\dot{p} + \rho T\Delta s_b = T\Pi_s - T\nabla\cdot(T^{-1}\boldsymbol{\phi}_q) = D_m - \nabla\cdot\boldsymbol{\phi}_q . \tag{44}$$

In the remaining part of this section we will discuss the expressions for $c_{p,b}$, $\alpha_{T,b}$ and Δs_b. These quantities can be obtained by differentiation of the entropy, Eqs. (41) and (42). We will relate them to measured, or more easily measured, quantities.

A. The thermal expansion coefficient $\alpha_{T,b}$

The reason why we have called $\alpha_{T,b}$ the thermal expansion coefficient is that it is also related to the temperature derivative of the density:

$$-\rho^{-1}\alpha_{T,b} = \left.\frac{\partial s}{\partial p}\right|_{T,\boldsymbol{b}} = -\left.\frac{\partial \rho^{-1}}{\partial T}\right|_{p,\boldsymbol{b}}, \tag{45}$$

which follows easily from the compatibility relation for the free enthalpy $g = u - Ts - p/\rho$, see, for example, Kuiken (1994). To evaluate the thermal expansion coefficient, we note that

$$-\rho^{-1}\alpha_{T,b} = \left.\frac{\partial s}{\partial p}\right|_{T,\boldsymbol{b}} = \left.\left(\frac{\partial s}{\partial \rho^{-1}}\frac{\partial \rho^{-1}}{\partial p}\right)\right|_{T,\boldsymbol{b}} = \rho^{-1}\kappa_{T,b}\left.\frac{\partial s}{\partial \rho^{-1}}\right|_{T,\boldsymbol{b}}, \tag{46}$$

where $\kappa_{T,b}$ is the isothermal compressibility which is discussed in Appendix B. There we have shown that $\kappa_{T,b}$ is approximately independent of the internal deformation tensors and that this dependence vanishes exactly for $\delta_k = 1$. The remaining derivative of the entropy can be obtained by differentiation of the entropy (41):

$$\left.\frac{\partial s}{\partial \rho^{-1}}\right|_{T,\boldsymbol{b}} = -b_1\bar{p} + B\frac{\rho^{-1}}{c\rho_0^{-2}}\frac{d\rho_0^{-1}}{dT}\exp\left[\frac{1}{c}\left\langle 1 - \frac{\rho^{-1}}{\rho_0^{-1}}\right\rangle\right] + \rho T^{-1}\sum_{k=1}^{K}\gamma_k(\delta_k - 1)\psi_k, \tag{47}$$

so that this term, and also the thermal expansion coefficient $\alpha_{T,b}$, is only independent of the internal deformation tensors, i.e., reduces to the equilibrium value $\alpha_{T,b}^{\mathrm{eq}}$, if $\delta_k = 1$. Furthermore, we note that the derivative $\partial s/\partial \rho^{-1}|_{T,\boldsymbol{b}}$ is, for not too high values of $\bar{p}$, dominated by the second term on the right-hand side which is $\mathcal{O}(10^6)$ Pa K^{-1}. The first term plays a role for pressures of $\mathcal{O}(10^8)$ Pa. For γ_k and $(\delta_k - 1) = \mathcal{O}(1)$ the last term on the right-hand side is $\mathcal{O}(T^{-1}\ \mathrm{tr}\ \boldsymbol{\tau}) \leqslant \mathcal{O}(10^4)$ Pa K^{-1}. So $\alpha_{T,b}$ is approximately independent of the internal deformation and $\alpha_{T,b} = \alpha_{T,b}^{\mathrm{eq}}$ is a good approximation out of equilibrium. Furthermore, neglecting the lower order terms results in $\alpha_{T,b} = \alpha_{T,b}^{\mathrm{eq}} = \rho_0 d\rho_0^{-1}/dT$. Experimental data of the thermal expansion coefficient in equilibrium indicate $\alpha_{T,b}^{\mathrm{eq}} \simeq 0.16/T_g$, see van Krevelen and Hoftyzer (1976), so that the order of magnitude is about 10^{-4} K$^{-1} < \alpha_{T,b}^{\mathrm{eq}} < 10^{-3}$ K^{-1}.

B. The entropy difference Δs_b

The derivative of the entropy in Δs_b can be obtained by differentiation of the entropy (41). We will split the derivatives in two parts:

$$\left.\frac{\partial s}{\partial \boldsymbol{b}_k}\right|_{T,p,\boldsymbol{b}_k'} = \left.\frac{\partial s}{\partial \boldsymbol{b}_k}\right|_{T,\rho,\boldsymbol{b}_k'} + \boldsymbol{\Delta}_s \ , \tag{48}$$

$$\boldsymbol{\Delta}_s = \left.\frac{\partial s}{\partial \rho^{-1}}\right|_{T,\boldsymbol{b}} \left.\frac{\partial \rho^{-1}}{\partial \boldsymbol{b}_k}\right|_{p,T,\boldsymbol{b}_k'} . \tag{49}$$

For the first term we find with the help of Eqs. (41) and (10)

$$\left.\frac{\partial s}{\partial \boldsymbol{b}_k}\right|_{T,\rho,\boldsymbol{b}_k'} = -\frac{\gamma_k}{T}\left.\frac{\partial \psi_k}{\partial \boldsymbol{b}_k}\right|_{T,\rho,\boldsymbol{b}_k'} = -\frac{\gamma_k}{2\rho T}\boldsymbol{b}_k^{-1}\cdot\boldsymbol{\tau}_{e,k} . \tag{50}$$

As for rubbers, the entropy derivative at constant density is related to the temperature derivative of the stress. For viscoelastic fluids this relation becomes

$$\left.\frac{\partial s}{\partial \boldsymbol{b}_k}\right|_{T,\rho,\boldsymbol{b}_k'} = -\left.\frac{\partial}{\partial T}\left(\left.\frac{\partial \psi}{\partial \boldsymbol{b}_k}\right|_{T,\rho,\boldsymbol{b}_k'}\right)\right|_{\rho,\boldsymbol{b}_k} = -\frac{1}{2\rho}\boldsymbol{b}_k^{-1}\cdot\left.\frac{\partial \boldsymbol{\tau}_{e,k}}{\partial T}\right|_{\rho,\boldsymbol{b}_k} , \tag{51}$$

so that this term can be obtained from stress-temperature measurements.

From Appendix B we find that $\boldsymbol{\Delta}_s$ can be approximated by

$$\boldsymbol{\Delta}_s \simeq \frac{(\delta_k - 1)}{2\rho}\alpha_{T,b}\boldsymbol{b}_k^{-1}\cdot\boldsymbol{\tau}_{e,k} . \tag{52}$$

If we assume that $\gamma_k = \mathcal{O}(1)$ and $\delta_k - 1 = \mathcal{O}(1)$ the $\boldsymbol{\Delta}_s$ term is $\mathcal{O}(T\alpha_{T,b})$ times the $\partial s/\partial \boldsymbol{b}_k|_{T,\rho,\boldsymbol{b}_k'}$ term, so the $\boldsymbol{\Delta}_s$ term is in general smaller but cannot be neglected *a priori*.

Combining the two results gives that Δs_b can be approximated by

$$\begin{aligned}\Delta s_b &\simeq -\frac{1}{2\rho}\sum_{k=1}^{K}[T^{-1}\gamma_k - (\delta_k - 1)\alpha_{T,b}](\boldsymbol{b}_k^{-1}\cdot\boldsymbol{\tau}_{e,k}):\dot{\boldsymbol{b}}_k \\ &= -\frac{1}{\rho}\sum_{k=1}^{K}[T^{-1}\gamma_k - (\delta_k - 1)\alpha_{T,b}]\boldsymbol{\tau}_{e,k}:(\boldsymbol{d} - \boldsymbol{d}_{\mathrm{irr},k}),\end{aligned} \tag{53}$$

where we have used Eq. (8) for the last equality.

C. The heat capacity $c_{p,b}$

Differentiation of the entropy (41), gives for the heat capacity $c_{p,b}$:

$$c_{p,b} = T\left.\frac{\partial s}{\partial T}\right|_{p,\boldsymbol{b}} = \bar{c}_{p,b} - \frac{1}{T}\sum_{k=1}^{K}\gamma_k\psi_k[\gamma_k - 1 - T\alpha_{T,b}(\delta_k - 1)], \tag{54}$$

where $\bar{c}_{p,b}$ is given by

$$\bar{c}_{p,b} = T\left.\frac{\partial \bar{s}}{\partial T}\right|_{p,\boldsymbol{b}} . \tag{55}$$

This result shows that $c_{p,b}$ only reduces to $\bar{c}_{p,b}$ when $\gamma_k = 0$, or both $\gamma_k = 1$ and $\delta_k = 1$. Because ψ_k is positive it depends on the quantity between the brackets whether

$c_{p,b}$ is smaller or larger than $\bar{c}_{p,b}$. For $\delta_k = 1$ the heat capacity $c_{p,b}$ decreases when $\gamma_k < 0$ and $\gamma_k > 1$ and it increases when $0 < \gamma_k < 1$. Furthermore, in equilibrium $c_{p,b}$ reduces to $\bar{c}_{p,b}$ because ψ_k vanishes.

From Appendix B we find that $\bar{c}_{p,b}$ is approximately independent of $\boldsymbol{b}_k$. This means that $\bar{c}_{p,b}$ is approximately equal to $c^{\mathrm{eq}}_{p,b}$, the heat capacity at constant pressure and constant internal deformation in equilibrium. This quantity is usually measured and then denoted by c_p. However, to be consistent with the thermodynamic notation we will use $c^{\mathrm{eq}}_{p,b}$ instead of c_p. The heat capacity of a polymeric fluid is $\mathcal{O}(10^3)\mathrm{J\,kg^{-1}\,K^{-1}}$, see van Krevelen and Hoftyzer (1976), while the order of magnitude of $\psi/\rho T = \mathcal{O}(1)$–$\mathcal{O}(10)\ \mathrm{J\,kg^{-1}\,K^{-1}}$. If we assume that $\gamma_k[\,\gamma_k - 1 - T\alpha_{T,b}(\delta_k - 1)] = \mathcal{O}(1)$, we find that $c_{p,b} = \bar{c}_{p,b} = c^{\mathrm{eq}}_{p,b}$ is in general a good approximation. Because it may be difficult to perform the experiments at constant internal deformation tensor the heat capacity at constant pressure and elastic stress c_{p,τ_e} is also of importance. We will discuss this quantity in Appendix B.

D. An approximation for the temperature equation

With the results of the approximations in the Secs. V A–V C, we obtain for the temperature equation (44)

$$\rho c^{\mathrm{eq}}_{p,b}\dot{T} = T\alpha^{\mathrm{eq}}_{T,b}\dot{p} + D_m - \rho T\Delta s_b + \nabla\cdot(\boldsymbol{\kappa}\cdot\nabla T), \tag{56}$$

where $c^{\mathrm{eq}}_{p,b}$ equals the heat capacity at constant pressure and $\alpha^{\mathrm{eq}}_{T,b}$ the thermal expansion coefficient that are usually measured in equilibrium. The heat conduction tensor $\boldsymbol{\kappa}$ may be anisotropic as discussed at the end of Sec. II B. The heat production term $D_m - \rho T\Delta s_b$ can be rewritten by combining Eqs. (28) and (53). Using Eqs. (23), (25) and (29) for the irreversible rate-of-deformation tensor, the elastic stress and the modal mechanical dissipation results in

$$D_m - \rho T\Delta s_b = 2\eta_s \boldsymbol{d}:\boldsymbol{d} + \sum_{k=1}^{K}[\,\gamma_k^*\boldsymbol{\tau}_k:\boldsymbol{d} + (1-\gamma_k^*)D_{m,k}], \tag{57}$$

where $\gamma_k^* = \gamma_k - T\alpha^{\mathrm{eq}}_{T,b}(\delta_k - 1)$. Equation (57) has also been obtained by Braun (1991) for $\delta_k = 1$ and $K = 1$. This result shows that for $\gamma_k = 1$ and $\delta_k = 1$ the stress work completely contributes to the heat production (reversibly), so that the internal energy does not change when $\boldsymbol{b}_k$ changes. In this case the fluid is called entropy elastic. This elasticity would correspond to the deformation of entirely free chains, without distortion of the valent angles. For $\gamma_k = 0$ and $\delta_k = 1$ the heat production equals the dissipation, i.e., $\Delta s_b = 0$, so that the entropy does not change when $\boldsymbol{b}_k$ changes. In this case the fluid is called energy elastic. This elasticity would correspond to pure distortion in the valent angles, without a macromolecular conformation. The fact that rubbers give out heat at extension, and thus, are at least partly entropy elastic, had already been noticed in the beginning of the previous century. The effect is called the Gough–Joule effect.

VI. THE RELATION WITH EXPERIMENTAL DATA

Before we discuss two experiments for polymeric fluids, we will first mention another experiment performed for rubbers that supports the scaling (35) of the shear modulus G: anisotropic thermal expansion. This effect can be described by the equivalent of Eq. (B11) for rubbers, see, for example, Godovsky (1992). Then, however, the anisotropy is

related to the (observable) Finger tensor $\boldsymbol{b}$ instead of the internal deformation tensor. The anisotropy of rubbers is up to two orders of magnitude larger than the volume thermal expansion. In the direction of orientation, the thermal expansion is negative and perpendicular to the orientation positive. For elongated samples of natural rubber ($\epsilon < 1.6$), the value of γ agrees well with calory measurements, see Shen and Croucher (1975). However, deviations were found in Thiele and Cohen (1980) for larger elongation ratios.

Astarita and Sarti (1976) and Sarti and Esposito (1977/1978) have tried to show that some polymeric fluids are entropy elastic. Therefore, they used the integrated form of the temperature equation for entropy elastic fluids ($\gamma_k = \delta_k = 1$), where pressure effect and heat conduction have been neglected:

$$\rho \hat{c} \Delta T = \int_t \boldsymbol{\tau} : \boldsymbol{d}\, dt, \tag{58}$$

where $\hat{c}$ is a heat capacity that equals $c_{p,b}^{\text{eq}}$ for an entropy elastic fluid. To ensure that the stress work is much larger than the dissipation, the total force on the sample has been taken as a strong increasing function of time. From the obtained temperature rise and stress work, the heat capacity can be computed and compared with values from the literature. For an entropy elastic fluid the values must correspond, for an energy elastic fluid the obtained heat capacity will be too high.

Astarita and Sarti (1976) performed the experiment (at constant deformation rate) for polyisobutylene at room temperature. Both in shearing and elongational flow they obtained a good correspondence with values of the heat capacity in the literature, indicating an (almost) entropy elastic fluid (γ close to 1). This seems in agreement with the value of $\gamma = 1.03$ given by Mark (1973), obtained for rubber elasticity measurements. The small difference is probably within experimental error, because the scatter in the obtained heat capacities is about 10%.

Sarti and Esposito (1977/1978) performed adiabatic shear and elongational experiments, at various temperatures above T_g, on polyisobutylene and polyvinylacetate with different molecular weights. The materials were deformed from equilibrium at a constant rate until a maximum deformation. Then the deformation was stopped and the material relaxed adiabatically towards a stress-free state. For a purely entropy elasticity the temperature has to remain constant during the relaxation process ($\boldsymbol{d} = \boldsymbol{0}$), see Eqs. (56) and (57). For the polyisobutylene melts they found a vanishing temperature rise during the stress relaxation process, which confirms the result by Astarita and Sarti (1976) which has been discussed above. Furthermore, they obtained a constant heat capacity, equal to the equilibrium value, during deformation. However, for the polyvinylacetate at 333K, which is more than 20K above T_g, the temperature decreased during the relaxation. This can be explained by a value of $\gamma > 1$, as has also been noted by Braun (1991). For polyvinylacetate no data of γ are available in Mark (1973). However, for vinyl polymers, γ is usually positive and not close to one, for polyvinylalcohol, for example, $1.23 \pm 0.07 < \gamma < 1.68 \pm 0.12$, where the lowest value is for the syndiotactic and the highest for the isotactic form of polyvinylalcohol. The decreasing temperature does not seem to be in contradiction with the thermodynamic theory. The result that at a higher temperature the decreasing temperature is absent, might be explained by the fact that then dissipation is not negligible compared to elastic effects. The temperature dependence for polyvinylacetate can be described by a WLF shift factor with $T_g = 305$ K, $c_1 = 15.6$ and $c_2 = 46.8$ K, which gives a ratio of 100 in relaxation times. Because the elongation rate is almost equal, this results in a more viscous response for the sample at the highest temperature. And if much mechanical energy is already dissipated during elongation, the

possible temperature change during stress relaxation is much smaller or maybe almost absent. However, the increasing heat capacity $\hat{c}$ during elongation cannot be explained in this way. In view of Eq. (54) it is not expected that there will be a large change of the heat capacity $c_{p,b}$ during elastic deformation, for moderate stresses and $\gamma_k = \mathcal{O}(1)$. Furthermore, if elastic effects are dominant, the stress work is much larger than the dissipation and the heat production is larger than the stress work for $\gamma > 1$. This would result in a larger temperature rise ΔT and consequently a decreasing heat capacity $\hat{c}$. For an increase of the heat capacity $\hat{c}$ a $\gamma < 1$ would be needed. In the literature about rubber elasticity, changes of γ to negative values are observed sometimes, see Treloar (1975) and Mark (1976). The effect is ascribed to strain-induced crystallization. Whether this effect plays a role in the experiments of Sarti and Esposito (1977/1978) is not clear.

VII. CONCLUSIONS

In this article we have derived the temperature equation for compressible viscoelastic fluids, with the help of the thermodynamics. We discussed both the irreversible (dissipative) part and the reversible (elastic) part of the temperature equation. The reversible part is closely related to the free energy. From the free energy the state variables (elastic stress, pressure and entropy) can be calculated. Once these quantities are completely known, the temperature equation with all the coefficients (like the heat capacity and the thermal expansion coefficient) can be obtained.

Results have been illustrated with various stress differential models and for adapting a power-law scaling of the shear moduli on density and temperature, as is usual in rubber elasticity. We found that if the moduli depend linearly on temperature and density (as in kinetic theory) the pressure reduces to its equilibrium value. Otherwise, elastic deformation may cause a considerable pressure change. For linear scaling, the temperature equation also simplifies considerably: the nonequilibrium heat capacity and thermal expansion coefficient reduce to their equilibrium values and the heat production equals the stress work. However, rubber elasticity experiments show that linear scaling generally does not hold. We found that for the usual values of the pressure, temperature and stresses, the nonequilibrium heat capacity and thermal expansion coefficient can still be approximated by the equilibrium values, so that a much simpler approximate temperature equation for viscoelastic fluids could be derived. The heat production term, however, does not reduce to the stress work and has to be included in the approximate temperature equation.

Not many experimental results exist to test the approximate temperature equation for polymeric fluids. The results of Astarita and Sarti (1976) and Sarti and Esposito (1977/1978) for polyisobutylene seem to be in agreement with rubber elasticity experiments and thermodynamic theory. For some of the results of Sarti and Esposito (1977/1978) for polyvinylacetate, however, this is not clear.

APPENDIX A: EXPRESSIONS FOR THE MECHANICAL DISSIPATION OF VARIOUS VISCOELASTIC MODELS

The expression for the mechanical dissipation $D_{m,k}$, Eq. (29), can be obtained by substituting for a stress model Eq. (20) and the scalar $g_{i,k}$ defining $\boldsymbol{g}_k$ in Eq. (21). Because the expression is similar for all modes we will omit the subscript k for the mode number. Furthermore, we will show that the mechanical dissipation is nonnegative. One should be careful by using expressions for the dissipation of specific models presented in the literature. The incorrectness is usually caused by using the wrong expressions for the elastic stress $\boldsymbol{\tau}_{e,k}$ for models with nonconstant determinant or elastic stresses that are not of the neo-Hookean type, as, for example, in Leonov (1992) and Peters (1996). The

correctness of the dissipation can easily be checked by considering a fully developed flow, for which the dissipation equals the stress work.

1. The Johnson–Segalman model and the Phan-Thien–Tanner model

The Johnson–Segalman model and the Phan-Thien–Tanner model are defined by $g_0 = Y$, $g_1 = -Y$ and $g_2 = 0$, $B = 1$ and $0 \leqslant \xi \leqslant 2$. For the Johnson–Segalman model $Y = 1$, for the linear Phan-Thien–Tanner model $Y = 1+\epsilon(I_1-3)$, and for the exponential Phan-Thien–Tanner model $Y = \exp[\epsilon(I_1-3)]$. The parameter ϵ is positive. The mechanical dissipation (29) becomes

$$D_m = \frac{G}{2(1-\xi)^2\lambda} Y(I_1+\text{tr } \boldsymbol{b}^{-1}-6), \tag{A1}$$

for $\xi \neq 1$. Decomposition on the principal axis immediately shows that for a positive definite internal deformation tensor the term between the brackets in Eq. (A1) is nonnegative (the function $x+1/x-2$ is nonnegative for $x > 0$.) For the Johnson–Segalman model and the exponential Phan-Thien–Tanner model Y is positive and for the linear Phan-Thien–Tanner model the result of Wapperom and Hulsen (1995) that $I_1 \geqslant 3$, ensures a positive Y and thus a positive dissipation.

2. The (modified) Leonov model

The modified Leonov model is defined by $B = 1$, $\xi = 0$, $g_0 = \phi/2$, $g_1 = \phi(I_1 - I_2)/6$ and $g_2 = -\phi/2$, where $\phi^{-1} = 1+2\alpha/\pi \arctan[\beta/4(I_1+I_2-6)]$ with $\alpha \geqslant 0$ and $\beta \geqslant 0$, see Bush (1989). The modified Leonov model reduces to the Leonov model if $\phi = 1$ is taken. The mechanical dissipation (29) becomes

$$D_m = \frac{G\phi}{4\lambda}\left[\boldsymbol{b}:\boldsymbol{b}-3+\frac{I_1}{3}(I_2-I_1)\right]. \tag{A2}$$

With the help of the decomposition on the principal axis, and using $I_3 = 1$ and the results of Wapperom and Hulsen (1995) that $I_1 \geqslant 3$ and $I_2 \geqslant 3$ for the Leonov models, it can be shown that the term between the brackets in Eq. (A2) is nonnegative. Because ϕ is positive, the dissipation is nonnegative.

3. The Giesekus model

The Giesekus model is defined by $B = 1$, $\xi = 0$, $g_0 = (1-\alpha)$, $g_1 = -(1-2\alpha)$ and $g_2 = -\alpha$, where $0 \leqslant \alpha < 1$. For $\alpha = 0$ the model reduces to the upper-convected Maxwell model (the Johnson–Segalman model with $\xi = 0$). The mechanical dissipation (29) becomes

$$D_m = \frac{G}{2\lambda}[(1-\alpha)(I_1+\text{tr } \boldsymbol{b}^{-1}-6)+\alpha(\boldsymbol{b}:\boldsymbol{b}-2I_1+3)]. \tag{A3}$$

As for the Johnson–Segalman model the term $I_1+\text{tr } \boldsymbol{b}^{-1}-6$ is always nonnegative. Decomposition on the principal axis also shows that $\boldsymbol{b}:\boldsymbol{b}-2I_1+3$ is nonnegative (the function x^2-2x+1 is nonnegative for $x > 0$). Thus, for the admissible values of α the dissipation is nonnegative.

4. The Larson model

The Larson model is given by $g_0 = 1/B$, $g_1 = -1/B$ and $g_2 = 0$, $B = [1+\beta(I_1 - 3)/3]^{-1}$, where $0 \leqslant \beta \leqslant 1$, and $\xi = 0$. The mechanical dissipation (29) becomes

$$D_m = \frac{G}{2\lambda}[I_1 - 3 + B^{-1}(\text{tr } \boldsymbol{b}^{-1} - 3)]. \tag{A4}$$

After substitution of the definition of B and reordering of the terms, it follows that the term between the brackets can be written as $(1-\beta)(I_1 + \text{tr } \boldsymbol{b}^{-1} - 6) + \beta(\text{tr } \boldsymbol{b}^{-1} I_1/3 - 3)$. As for the Johnson–Segalman model the term $I_1 + \text{tr } \boldsymbol{b}^{-1} - 6$ is always nonnegative. Furthermore, by decomposition on the principle axes it can be shown that $\text{tr } \boldsymbol{b}^{-1} I_1/3 - 3$ is nonnegative. Thus, for $0 \leqslant \beta \leqslant 1$ the dissipation is nonnegative.

5. The FENE-P model

The FENE-P model is given by $g_0 = 1$, $g_1 = -B$ and $g_2 = 0$, $B = b/(b+3 - I_1)$, with $I_1 < b+3$, and $\xi = 0$, see Wedgewood and Bird (1988). The mechanical dissipation (29) becomes

$$D_m = \frac{G}{2\lambda}(B^2 I_1 - 6B + \text{tr } \boldsymbol{b}^{-1}). \tag{A5}$$

Reordering of the terms gives that the factor between the brackets equals

$$B^2 I_1 - 6B + \text{tr } \boldsymbol{b}^{-1} = I_1 + \text{tr } \boldsymbol{b}^{-1} - 6 + (B-1)[(B+1)I_1 - 6]. \tag{A6}$$

As for the Johnson–Segalman model, the first part of this expression is positive. Because $B > 1$, the second part of the expression is positive if $I_1 > 3$.

APPENDIX B: APPROXIMATIONS OF VARIOUS THERMODYNAMIC QUANTITIES

1. The isothermal compressibility $\kappa_{T,b}$

The isothermal compressibility is defined by

$$\kappa_{T,b} = \frac{1}{\rho}\frac{\partial \rho}{\partial p}\bigg|_{T,\boldsymbol{b}}, \tag{B1}$$

and can be obtained by differentiation of the thermodynamic pressure (37):

$$\kappa_{T,b}^{-1} = -\rho^{-1}\frac{\partial p}{\partial \rho^{-1}}\bigg|_{T,\boldsymbol{b}} = \frac{B\rho^{-1}}{c\rho_0^{-1}} \exp\left[\frac{1}{c}\left(1 - \frac{\rho^{-1}}{\rho_0^{-1}}\right)\right] - \rho \sum_{k=1}^{K} \delta_k(\delta_k - 1)\psi_k. \tag{B2}$$

For polymeric fluids the isothermal compressibility in equilibrium is about 10^{-10} Pa^{-1} $< \kappa_{T,b}^{\text{eq}} < 10^{-9}$ Pa^{-1}, see, for example, van Krevelen and Hoftyzer (1976). This corresponds to the order of magnitude given for B and c below Eq. (39). If $\delta_k = 0$ or if $\delta_k = 1$ (as in the kinetic theory of Gaussian networks) the last term at the right-hand side vanishes and then the isothermal compressibility only depends on density and temperature. In Sec. IV C we have shown that $\mathcal{O}(\rho\psi_k) \leqslant \mathcal{O}(\text{tr } \boldsymbol{\tau}_k)$. If δ_k is assumed to be $\mathcal{O}(1)$, the last term on the right-hand side of Eq. (B2) is negligible, because the order of magnitude is $\mathcal{O}(\text{tr } \boldsymbol{\tau})$, which is usually not larger than $\mathcal{O}(10^6)$ Pa. The order of magni-

tude of the first term on the right-hand side of Eq. (B2) is $\mathcal{O}(10^9)$ Pa. Therefore, $\kappa_{T,b} = \kappa^{\mathrm{eq}}_{T,b}$ is a good approximation out of equilibrium.

2. The entropy difference term $\boldsymbol{\Delta}_s$

The entropy difference term $\boldsymbol{\Delta}_s$ is defined by

$$\boldsymbol{\Delta}_s = \left.\frac{\partial s}{\partial \rho^{-1}}\right|_{T,\boldsymbol{b}} \left.\frac{\partial \rho^{-1}}{\partial \boldsymbol{b}_k}\right|_{p,T,\boldsymbol{b}'_k}, \tag{B3}$$

where $\partial s/\partial \rho^{-1}|_{T,\boldsymbol{b}}$ is given by Eq. (47). The other term can be obtained by differentiation of the pressure (37):

$$\left.\frac{\partial \rho^{-1}}{\partial \boldsymbol{b}_k}\right|_{p,T,\boldsymbol{b}'_k} = \frac{(\delta_k - 1)}{2}\boldsymbol{b}_k^{-1}\cdot\boldsymbol{\tau}_{e,k}\left(\frac{B}{c\rho_0^{-1}}\exp\left[\frac{1}{c}\left(1-\frac{\rho^{-1}}{\rho_0^{-1}}\right)\right]+\rho^2\sum_{l=1}^{K}(\delta_l-1)\delta_l\psi_l\right)^{-1}. \tag{B4}$$

Thus this term, and also $\boldsymbol{\Delta}_s$, only vanishes if $\delta_k = 1$. Analogously to Section B 1, it can be shown that for $\delta_k - 1 = \mathcal{O}(1)$ the sum over the free energies ψ_l can be neglected. With the estimate of Eq. (47), discussed in Sec. V A, we then find that $\boldsymbol{\Delta}_s$ can be approximated by

$$\boldsymbol{\Delta}_s \simeq \frac{(\delta_k-1)}{2}\frac{\rho^{-1}}{\rho_0^{-1}}\frac{d\rho_0^{-1}}{dT}\boldsymbol{b}_k^{-1}\cdot\boldsymbol{\tau}_{e,k} \simeq \frac{(\delta_k-1)}{2}\rho^{-1}\alpha_{T,b}\boldsymbol{b}_k^{-1}\cdot\boldsymbol{\tau}_{e,k}. \tag{B5}$$

3. The heat capacity $\bar{c}_{p,\boldsymbol{b}}$

The heat capacity $\bar{c}_{p,b}$ can be determined from the entropy $\bar{s}$ given by Eq. (42). After some calculations, it follows

$$\begin{aligned}
\left.\frac{\partial \bar{s}}{\partial T}\right|_{p,\boldsymbol{b}} &= B\left\{Z_0 + Z_1\exp\left[\frac{1}{c}\left(1-\frac{\rho^{-1}}{\rho_0^{-1}}\right)\right]\right\}+\frac{d\tilde{s}}{dT},\\
Z_0 &= -b_1^2\rho^{-1}+b_1\rho^{-1}\alpha_{T,b},\\
Z_1 &= -cb_1^2\rho_0^{-1}+b_1\left(\frac{\rho^{-1}}{\rho_0^{-1}}+c\right)\frac{d\rho_0^{-1}}{dT}+\frac{\rho^{-2}}{c\rho_0^{-2}}\alpha_{T,b}\frac{d\rho_0^{-1}}{dT}\\
&\quad -\frac{\rho^{-2}}{c\rho_0^{-3}}\left(\frac{d\rho_0^{-1}}{dT}\right)^2-b_1\rho^{-1}\alpha_{T,b}-\left(c+\frac{\rho^{-1}}{\rho_0^{-1}}\right)\frac{d^2\rho_0^{-1}}{dT^2}.
\end{aligned} \tag{B6}$$

For polymeric fluids the order of magnitude of the heat capacity is about $2\times10^3\,\mathrm{J\,kg^{-1}\,K^{-1}}$ to $3\times10^3\,\mathrm{J\,kg^{-1}\,K^{-1}}$, so that $\partial\bar{s}/\partial T|_{p,\boldsymbol{b}} = \mathcal{O}(10)\,\mathrm{J\,kg^{-1}\,K^{-2}}$. Evaluation of Eq. (B6) at atmospheric pressure, i.e., the exponential function is about 1, and neglecting nondominating terms gives

$$\left.\frac{\partial \bar{s}}{\partial T}\right|_{p=p_{\mathrm{atm}},\boldsymbol{b}} \simeq \frac{d\tilde{s}}{dT}+B\left(-b_1^2\rho^{-1}+b_1\frac{\rho^{-1}}{\rho_0^{-1}}\frac{d\rho_0^{-1}}{dT}-\frac{\rho^{-1}}{\rho_0^{-1}}\frac{d^2\rho_0^{-1}}{dT^2}\right). \tag{B7}$$

If it is assumed that the second derivative of ρ_0^{-1} has the order of magnitude of $\alpha_{T,b}/\rho T$, it follows that the derivative of $\tilde{s}$ is the dominating term, which has to be $\mathcal{O}(10)\mathrm{J\,kg^{-1}\,K^{-2}}$.

4. The heat capacity c_{p,τ_e}

The heat capacity at constant pressure and elastic stress c_{p,τ_e} is defined by

$$c_{p,\tau_e} = T\left.\frac{\partial s}{\partial T}\right|_{p,\boldsymbol{\tau}_e}. \tag{B8}$$

The difference between c_{p,τ_e} and $c_{p,b}$ equals

$$\Delta c = c_{p,\tau_e} - c_{p,b} = T\sum_{k=1}^{K}\left.\frac{\partial s}{\partial \boldsymbol{b}_k}\right|_{T,p,\boldsymbol{b}_k'} : \left.\frac{\partial \boldsymbol{b}_k}{\partial T}\right|_{p,\boldsymbol{b}_k',\boldsymbol{\tau}_{e,k}}. \tag{B9}$$

The first term on the right-hand side has already been needed for the calculation of the entropy difference in Sec. V B. For the neo-Hookean model, with the free energy (32), the second term can be computed analytically. For the other models (33) and (34) it is also possible to calculate the difference analytically. However, the $\partial \boldsymbol{b}_k/\partial T|_{p,\boldsymbol{b}_k',\boldsymbol{\tau}_{e,k}}$ is more difficult to elaborate due to the nonlinear relation between the extra stress and the internal deformation. Therefore, we will only discuss the expressions for the neo-Hookean model.

5. Example: c_{p,τ_e} for the neo-Hookean free energy.

The last term on the right-hand side of Eq. (B9) may be calculated from Eqs. (20) and (25). Differentiation of the elastic modal stress $\boldsymbol{\tau}_{e,k}$ gives

$$\mathbf{0} = \left.\frac{\partial \boldsymbol{\tau}_{e,k}}{\partial T}\right|_{p,\boldsymbol{b}_k',\boldsymbol{\tau}_{e,k}} = \frac{G_k}{(1-\xi_k)^2}\left.\frac{\partial \boldsymbol{b}_k}{\partial T}\right|_{p,\boldsymbol{b}_k',\boldsymbol{\tau}_{e,k}} + \frac{1}{(1-\xi_k)^2}(\boldsymbol{b}_k-\boldsymbol{I})\left.\frac{\partial G_k}{\partial T}\right|_{p,\boldsymbol{b}_k',\boldsymbol{\tau}_{e,k}}. \tag{B10}$$

After rearrangement of this equation we obtain

$$\left.\frac{\partial \boldsymbol{b}_k}{\partial T}\right|_{p,\boldsymbol{b}_k',\boldsymbol{\tau}_{e,k}} = -(\gamma_k T^{-1} - \delta_k \alpha_{T,b})(\boldsymbol{b}_k - \boldsymbol{I}). \tag{B11}$$

Combination of Eqs. (B9), (48) and (B11) gives the heat capacity difference Δc:

$$\Delta c = \sum_{k=1}^{K}\frac{G_k}{2\rho(1-\xi_k)^2}[\gamma_k-(\delta_k-1)T\alpha_{T,b}](\gamma_k T^{-1}-\delta_k\alpha_{T,b})(I_{1,k}+\mathrm{tr}\,\boldsymbol{b}_k^{-1}-6), \tag{B12}$$

where the last factor with the invariants is always positive out of equilibrium and vanishes in equilibrium, see Appendix A. Therefore, it depends on the signs of γ_k and δ_k whether Δc is positive or negative. If γ_k and δ_k have equal order of magnitude, Δc is positive, because $T\alpha_{T,b} \simeq 0.2$. This is analogous to the heat capacity of viscous fluids, where the heat capacity at constant pressure is larger than the heat capacity at constant volume. The heat capacity difference Δc is approximately proportional to $\gamma^2\ \mathrm{tr}\ \boldsymbol{\tau}/\rho T$

$\simeq \mathcal{O}(10\gamma^2)\mathrm{J\,kg^{-1}\,K^{-1}}$ for stresses between 10^6 and 10^7 Pa. For $\gamma_k = \mathcal{O}(1)$ the heat capacity difference Δc is relatively small, so that $c_{p,\tau_e} \simeq c_{p,b}^{\mathrm{eq}}$ is a good approximation.

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