International Journal of Thermophysics, Vol. 9, No. 6, 1988

Extended Thermodynamic Description of Viscoelastic Materials and Dilute Polymer Solutions[1]

G. Lebon[2] and J. Casas-Vázquez[3]

It is shown that extended irreversible thermodynamics provides a simple and coherent modeling of viscoelastic bodies and dilute polymer solutions. The basic hypothesis underlying the present formalism is to raise, respectively, the inelastic stress tensor or the viscous stress tensor to the status of an independent variable in addition to the standard variables. Concerning viscoelasticity, the Poynting–Thomson, Maxwell, and Kelvin–Voigt models are recovered as particular cases of the formalism. More complicated models, such as Jeffrey's model, can also be obtained. For dilute polymer solutions, one recovers the relaxational spectrum of viscous modes. In particular, our description encompasses the Rouse model.

KEY WORDS: polymer solutions; irreversible thermodynamics; viscoelasticity.

1. INTRODUCTION

During the last three decades, several attempts have been made to describe the behavior of viscoelastic materials within the framework of a thermodynamic theory. The majority of publications is either inspired by the so-called rational thermodynamics [1] or based on the classical formulation of irreversible thermodynamics [2].

Recently, a new approach to nonequilibrium processes has received increasing attention [3] and has been called extended irreversible thermodynamics (EIT). Within this formalism, in contrast with the previously

---

[1] Invited paper presented at the Tenth Symposium on Thermophysical Properties, June 20–23, 1988, Gaithersburg, Maryland, U.S.A.

[2] Université de Liège, Institut de Physique, B5 Sart Tilman, B-4000 Liège, Belgique.

[3] División Física Estadística, Departamento de Física, Universidad Autónoma Barcelona, 08193 Bellaterra, Barcelona, Espãna.

0195-928X/88/1100-1003$06.00/0

mentioned theories, the thermodynamic fluxes (namely, the heat flux, the diffusion fluxes, the viscous stress) are not considered as dependent variables but are treated as independent variables like the usual ones (density, deformation, temperature).

Whereas the evolution equations for the usual variables are related to general conservation laws, no general criteria exist concerning the evolution equations of fluxes: their specific form depends on the class of materials to be described and on restrictions imposed by the second law of thermodynamics and the stability property of the equilibrium state.

EIT avoids the paradox of propagation of signals with an infinite velocity and its foundations have been interpreted within the kinetic theory of gases and the theory of fluctuations. It is particularly well suited for describing phenomena involving short characteristic times and wavelength. (A detailed account is given in Ref. 3.)

On the other hand, a challenge in nonequilibrium thermodynamics is to determine the theoretical tools to treat and predict the properties of polymer suspensions. A general description of the wide variety of these important systems is still lacking. The great complexity of the structure of the polymer chains in solution is the reason the theory has developed slowly. Our objective in this paper is rather limited: to show that EIT allows the interpretation of the relaxational spectrum exhibited by the stress in dilute polymer solutions. Our analysis is based heavily on the Rouse model [4], which provides a starting point for more realistic approaches.

The paper runs as follows. The thermodynamical model is presented in Section 2, and some generalizations are discussed in Section 3. Section 4 is devoted to a brief description of the Rouse model and the derivation of the evolution equations of the internal modes.

2. EIT OF VISCOELASTIC BODIES

2.1. Constitutive Equations

For the sake of simplicity, we restrict our analysis to isotropic bodies, in absence of heat flux and undergoing infinitesimally small deformations. Extensions to more general situations (anisotropic systems, heat flux, large deformations) should not raise fundamental difficulties.

In viscoelasticity, it is common to decompose the symmetric stress tensor into an elastic $\boldsymbol{\sigma}'$ and an inelastic $\boldsymbol{\sigma}''$ part,

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}' + \boldsymbol{\sigma}'' \tag{1}$$

where $\boldsymbol{\sigma}'$ obeys Hooke's law:

$$\boldsymbol{\sigma}' = 2G\boldsymbol{\varepsilon} + \lambda(\mathrm{tr}\,\boldsymbol{\varepsilon})\mathbf{u} \tag{2}$$

Here λ and G are Lamé's coefficients and $\boldsymbol{\varepsilon}$ is the symmetric strain tensor, defined in Cartesian coordinates by

$$\varepsilon_{ij} = \tfrac{1}{2}(u_{i,j} + u_{j,i}) \tag{3}$$

where $\mathbf{u}$ is the deformation vector, and a comma means a derivation with respect to the space variable; later, an over dot will denote the material time derivative, $\mathbf{U}$ is the limit tensor.

By analogy with the treatment of a viscous fluid, we choose as basic variables the rate of deformation $\dot{\mathbf{u}}$, the temperature T, and the inelastic stress $\boldsymbol{\sigma}''$. The reasons for selecting $\boldsymbol{\sigma}''$ as the supplementary variable are found in the general axioms underlying EIT. Indeed the latter demands that the set of conserved classical variables be completed by variables taking the form of dissipative fluxes, vanishing at equilibrium. Clearly, $\boldsymbol{\sigma}''$ meets these requirements; this would not be the case for the total stress $\boldsymbol{\sigma}$, as it does not vanish at equilibrium. It is also emphasized that, in contrast with earlier works [2], decomposing the strain tensor into an elastic and an inelastic part is not required.

The behavior of the classical variables $\dot{\mathbf{u}}$ and T is governed by the usual balance laws of momentum and energy:

$$\rho\ddot{u}_i = \sigma_{ij,i} + \rho f_i \tag{4}$$

$$\rho\dot{u} = -q_{i,i} + \sigma_{ij}\dot{\varepsilon}_{ij} \tag{5}$$

The summation convention on repeated indices is used throughout this paper. In Eqs. (4) and (5), ρ is the density, f_i the body force, q_i the heat flux vector, whose role is omitted in the present analysis, and u the specific internal energy to be given by the constitutive relation

$$u = u(T, \varepsilon_{ij}, \sigma''_{ij}) \tag{6}$$

That the extra variable σ''_{ij} enters in the constitutive equation besides the classical T and ε_{ij} corresponds to the line of thought of EIT.

In parallel with the classical balance laws, Eqs. (4) and (5), it is assumed that the supplementary variable σ''_{ij} or, equivalently, its isotropic and deviatoric parts σ'' and $\tilde{\sigma}''_{ij}$ satisfy balance equations of the form

$$\dot{\sigma}'' = J_{k,k} + S \tag{7}$$

$$\dot{\tilde{\sigma}}''_{ij} = J_{(ij)k,k} + S_{(i,j)} \tag{8}$$

where J_k and J_{ijk} are flux terms, while S and S_{ij} are source terms, and parentheses mean a traceless symmetrization. This formulation is also supported by the kinetic theory of gases [5]. In order for the description to be complete, it remains to express these fluxes and sources in terms of the basic set of variables by means of constitutive equations:

$$\begin{aligned} J_k &= J_k(T, \dot{u}_i, \sigma'', \tilde{\sigma}''_{ij}) \\ J_{ijk} &= J_{ijk}(T, \dot{u}_i, \sigma'', \tilde{\sigma}''_{ij}) \\ S &= S(T, \dot{u}_i, \sigma'', \tilde{\sigma}''_{ij}) \\ S_{ij} &= S_{ij}(T, \dot{u}_i, \sigma'', \tilde{\sigma}''_{ij}) \end{aligned} \tag{9}$$

The most general relations compatible with a linear analysis are

$$J_k = (\eta/\tau_\varepsilon)\, \dot{u}_k + O(2) \tag{10}$$

$$J_{ijk} = (\tilde{\eta}/\tilde{\tau}_\varepsilon)\, \dot{u}_i \delta_{jk} + O(2) \tag{11}$$

$$S = -(1/\tau_\varepsilon)\sigma + O(2) \tag{12}$$

$$S_{ij} = -(1/\tilde{\tau}_\varepsilon)\, \tilde{\sigma}''_{ij} + O(2) \tag{13}$$

τ_ε, $\tilde{\tau}_\varepsilon$, η, and $\tilde{\eta}$ are undetermined coefficients which may depend on the temperature. Substitution of Eqs. (10) and (12) in Eq. (7), and Eqs. (11) and (13) in Eq. (8), respectively, results in the following field equations for the extra variables:

$$\tilde{\tau}_\varepsilon \dot{\tilde{\sigma}}''_{ij} = -\tilde{\sigma}''_{ij} + \tilde{\eta} \dot{\tilde{\varepsilon}}_{ij} \tag{14}$$

$$\tau_\varepsilon \dot{\sigma}'' = -\sigma'' + \eta \dot{\varepsilon} \tag{15}$$

Elimination of σ and $\tilde{\sigma}''_{ij}$ between Eqs. (14) and (15) and Eqs. (1) and (2) yields

$$\tilde{\tau}_\varepsilon \dot{\tilde{\sigma}}_{ij} = 2G(\tilde{\varepsilon}_{ij} + \tilde{\tau}_\sigma \dot{\tilde{\varepsilon}}_{ij}) \tag{16}$$

$$\tau_\varepsilon \dot{\sigma} + \sigma = 3K(\varepsilon + \tau_\sigma \dot{\varepsilon}) \tag{17}$$

where K, $\tilde{\tau}_\sigma$, and τ_σ stand, respectively, for

$$K = \lambda + (\tfrac{2}{3})G \tag{18}$$

$$\tilde{\tau}_\sigma = (\tilde{\eta}/2G) + \tilde{\tau}_\varepsilon \tag{19}$$

$$\tau_\sigma = (\eta/3K) + \tau_\varepsilon \tag{20}$$

It is worth noticing that the relations (16) and (17) are the constitutive equations for a Poynting–Thomson body and that these relations arise naturally from our thermodynamical model.

The following particular cases are also of interest. By setting $\tilde{\tau}_\varepsilon = 0$ in Eq. (16), one obtains

$$\tilde{\sigma}_{ij} = 2G\tilde{\varepsilon}_{ij} + \tilde{\eta}\dot{\tilde{\varepsilon}}_{ij} \tag{21}$$

Equation (21) is representative of a Kelvin–Voigt body.

If in Eq. (16), one assumes that $G = 0$, which means that the total stress has only an inelastic contribution, one recovers the basic equation of Maxwell's model, namely,

$$\tilde{\tau}_\varepsilon \dot{\tilde{\sigma}}_{ij} + \tilde{\sigma}_{ij} = \tilde{\eta}\dot{\tilde{\varepsilon}}_{ij} \tag{22}$$

The above reasoning is also directly applicable for deriving the constitutive relations of a viscous fluid. It suffices in the previous relations to perform the identifications

$$\sigma'_{ij} = -p_{\mathrm{e}}\delta_{ij}, \qquad (\tfrac{1}{3})\sigma'' = -p^{\mathrm{v}} \tag{23}$$

where p_{e} and p^{v} are the equilibrium (or hydrostatic) and viscous pressure, respectively. Equations (14) and (15) can then be written as

$$\tilde{\tau}_\varepsilon \dot{\tilde{\sigma}}''_{ij} + \sigma''_{ij} = \tilde{\mu}\tilde{V}_{ij} \tag{24}$$

$$\tau_\varepsilon \dot{p}^{\mathrm{v}} + p^{\mathrm{v}} = -(\tfrac{1}{3})\,\mu V_{kk} \tag{25}$$

where V_{ij} is the symmetric velocity gradient tensor, $\tilde{\mu}$ the shear viscosity, and μ the bulk viscosity. By letting, in Eqs. (24) and (25), the relaxation times $\tilde{\tau}_\varepsilon$ and τ_ε go to zero, one recovers the usual Stokes–Newton relations.

Although in ordinary fluids, the relaxation times τ_ε and $\tilde{\tau}_\varepsilon$ are very short (10^{-12} to 10^{-14} s) so that it is justified to use the classical Stokes–Newton equations, this is no longer true in viscoelastic materials, for which the relaxation times are very much longer. As a matter of fact, for a high-density polyethylene at 200°C, one has calculated that $\tilde{\tau}_\varepsilon$ is 10^{-2} s, while for a polystyrene at 200°C, $\tilde{\tau}_\varepsilon$ is of the order of the unit; it may even raise up to $\tilde{\tau}_\varepsilon = 10^2$ s for a polyisobutylene solution in oil [6].

2.2. Entropy Production and Restrictions Imposed by the Second Law of Thermodynamics

It is postulated that there exists a regular and continuous function, the specific entropy, given by the constitutive equation

$$s = s(T, \varepsilon_{ij}, \sigma''_{ij}) \tag{26}$$

and obeying a balance equation of the form

$$\rho\dot{s} = -J^{s}_{i,i} + \bar{\sigma}^{s}, \qquad (\bar{\sigma}^{s} \geqslant 0) \tag{27}$$

where $\bar{\sigma}^{s}$ is the entropy production, supposed to be nonnegative, while J^{s}_{i} is the entropy flux. In the absence of heat flux, it has been shown that the entropy flux is zero [7].

For further purposes, it is useful to introduce the Helmholtz free energy f, defined by

$$f = u - Ts \tag{28}$$

with, according to Eqs. (6) and (26),

$$f = f(T, \varepsilon_{ij}, \sigma''_{ij}) \tag{29}$$

Removing $\dot{s}$ between Eq. (27) and Eq. (28) results in the following expression of the entropy production:

$$T\bar{\sigma}^{s} = -\rho\dot{f} - \rho s\dot{T} + \sigma_{ij}\dot{\varepsilon}_{ij} \geqslant 0 \tag{30}$$

where use is made of the energy balance, Eq. (5), with $q_i = 0$. Using the chain differentiation rule to calculate $\dot{f}$, one obtains

$$\begin{aligned} &-\rho\left(\frac{\partial f}{\partial T} + s\right)\dot{T} - \rho\left(\frac{\partial f}{\partial \varepsilon_{ij}} - \frac{1}{\rho}\tilde{\sigma}'_{ij}\right)\dot{\tilde{\varepsilon}}_{ij} - \rho\left(\frac{\partial f}{\partial \varepsilon} - \frac{1}{\rho}\sigma'\right)\dot{\varepsilon} \\ &\qquad -\rho\frac{\partial f}{\partial \tilde{\sigma}''_{ij}}\dot{\tilde{\sigma}}''_{ij} - \rho\frac{\partial f}{\partial \sigma''}\dot{\sigma}'' + \frac{1}{3}\sigma''\dot{\varepsilon} + \tilde{\sigma}_{ij}\dot{\tilde{\varepsilon}}_{ij} \geqslant 0 \end{aligned} \tag{31}$$

Assuming that the dependence of f with respect to the standard variables T and ε_{ij} is the same as in thermostatics, one has

$$\partial f/\partial T = -s \tag{32}$$

$$\partial f/\partial \varepsilon = (1/\rho)\,\sigma' \tag{33}$$

$$\partial f/\partial \varepsilon_{ij} = (1/\rho)\,\tilde{\sigma}'_{ij} \tag{34}$$

The entropy inequality, Eq. (31), then simplifies as

$$\frac{1}{3}\sigma''\dot{\varepsilon} + \tilde{\sigma}''_{ij}\dot{\tilde{\varepsilon}}_{ij} + \frac{\rho}{\tilde{\tau}_{\varepsilon}}(\tilde{\sigma}''_{ij} - \tilde{\eta}\dot{\tilde{\varepsilon}}_{ij})\frac{\partial f}{\partial \tilde{\sigma}''_{ij}} + \frac{\rho}{\tau_{\varepsilon}}(\sigma'' - \eta\dot{\varepsilon})\frac{\partial f}{\partial \sigma} \geqslant 0 \tag{35}$$

For isotropic systems, the most general form for f is given by

$$\begin{aligned} \rho f = {} & \frac{K}{2}\varepsilon\varepsilon + G\tilde{\varepsilon}_{ij}\tilde{\varepsilon}_{ij} + \frac{\tilde{d}}{2}\tilde{\sigma}''_{ij}\tilde{\sigma}''_{ij} + \frac{L}{2}\sigma''\sigma'' + \Lambda\tilde{\sigma}''_{ij}\tilde{\varepsilon}_{ij} \\ & + \gamma\sigma\varepsilon + O(3) \end{aligned} \tag{36}$$

where the various parameters may depend on the temperature. However, from Eqs. (33) and (34) it is inferred that the coefficients Λ and γ are zero. Substitution of Eq. (36) in Eq. (35) results in

$$\frac{\tilde{d}}{\tilde{\tau}_\varepsilon}\tilde{\sigma}''_{ij}\tilde{\sigma}''_{ij}+\tilde{\sigma}''_{ij}\dot{\tilde{\varepsilon}}_{ij}\left(1-\frac{\tilde{d}\tilde{\eta}}{\tilde{\tau}_\varepsilon}\right)+\frac{L}{\tau_\varepsilon}\sigma''\sigma''+\frac{1}{3}\sigma''\dot{\varepsilon}\left(1-\frac{3L\eta}{\tau_\varepsilon}\right)\geqslant 0 \tag{37}$$

Positiveness of Eq. (37) demands that

$$\tilde{\eta}=(\tilde{\tau}_\varepsilon/\tilde{d})\geqslant 0, \qquad \eta=(\tau_\varepsilon/3L)\geqslant 0 \tag{38}$$

Supplementary restrictions are imposed by the requirements of stability of equilibrium. Expanding f around equilibrium, for fixed values of the temperature and the strain, gives

$$\begin{aligned} f={}&f_e+\left(\frac{\partial f}{\partial\tilde{\sigma}''_{ij}}\right)_e\tilde{\sigma}''_{ij}+\frac{1}{2}\left(\frac{\partial^2 f}{\partial\tilde{\sigma}''_{ij}\,\partial\tilde{\sigma}''_{kl}}\right)_e\tilde{\sigma}''_{ij}\tilde{\sigma}''_{kl}\\ &+\left(\frac{\partial f}{\partial\sigma''}\right)_e\sigma''+\frac{1}{2}\left(\frac{\partial^2 f}{\partial\sigma''^2}\right)_e\sigma''\sigma''+O(3) \end{aligned} \tag{39}$$

Using Eq. (36), this relation takes the form

$$\rho f=\rho f_e+\tfrac{1}{2}\tilde{d}\tilde{\sigma}''_{ij}\tilde{\sigma}''_{ij}+\tfrac{1}{2}L\sigma''\sigma''+O(3) \tag{40}$$

Recalling that at equilibrium and fixed values of T and ε_{ij}, f is minimum, it is inferred from Eq. (40) that

$$\tilde{d}\geqslant 0 \quad\text{and}\quad L\geqslant 0 \tag{41}$$

Combining these inequalities with Eq. (38), it is checked that the relaxation times are positive quantities:

$$\tilde{\tau}_\varepsilon\geqslant 0 \quad\text{and}\quad \tau_\varepsilon\geqslant 0 \tag{42}$$

2.3. The Gibbs Equation

In standard irreversible thermodynamics, the cornerstone is the Gibbs equation, which is the same as that in equilibrium. In view of the previous results, the generalized Gibbs equation can be written as

$$df=-s\,dT+(1/\rho)\,\sigma'_{ij}\,d\varepsilon_{ij}+(\tilde{\tau}_\varepsilon/\rho\tilde{\eta})\,\tilde{\sigma}''_{ij}\,d\tilde{\sigma}''_{ij}+(\tau_\varepsilon/\rho\eta)\,\sigma''\,d\sigma'' \tag{43}$$

In terms of the internal energy and the time derivative, Eq. (43) reads

$$\dot{u}=T\dot{s}+(1/\rho)\,\sigma'_{ij}\dot{\varepsilon}_{ij}+(\tilde{\tau}_\varepsilon/\rho\tilde{\eta})\,\tilde{\sigma}''_{ij}\dot{\tilde{\sigma}}''_{ij}+(\tau_\varepsilon/\rho\eta)\,\sigma''\dot{\sigma}'' \tag{44}$$

It is interesting to formulate the Gibbs equation in the particular cases of a Kelvin–Voigt and a Maxwell body. A Kelvin–Voigt material being defined by $\tilde{\tau}_\varepsilon = \tau_\varepsilon = 0$, expression (44) reduces to

$$\dot{u} = T\dot{s} + (1/\rho)\,\sigma'_{ij}\dot{\varepsilon}_{ij} \tag{45}$$

In order to derive the Gibbs equation for a Maxwell body, it must be recalled that the latter is defined by $G = 0$ or, equivalently, by identifying the inelastic stress tensor with the total stress. Taking the evolution equation, Eq. (22), into account, the Gibbs relation, Eq. (44), reads

$$\dot{u} = T\dot{s} + (1/\rho)\,\tilde{\sigma}_{ij}[\dot{\tilde{\varepsilon}}_{ij} - (1/\tilde{\eta})\,\tilde{\sigma}_{ij}] + (1/\rho)\,\sigma[\dot{\varepsilon} - (1/\eta)\sigma] \tag{46}$$

At this point, we define an inelastic strain tensor ε''_{ij} through the relations

$$\dot{\tilde{\varepsilon}}''_{ij} = (1/\tilde{\eta})\,\tilde{\sigma}_{ij}, \qquad \dot{\varepsilon}'' = (1/\eta)\sigma \tag{47}$$

After substitution in Eq. (46), one obtains, finally,

$$\dot{u} = T\dot{s} + (1/\rho)\,\sigma_{ij}\dot{\varepsilon}'_{ij} \tag{48}$$

where use has been made of the decomposition

$$\varepsilon'_{ij} = \varepsilon_{ij} - \varepsilon''_{ij} \tag{49}$$

The results, Eqs. (45) and (48), are well known and were derived a few years ago [2] in a less general context than here.

3. SOME GENERALIZATIONS

Instead of writing the evolution equation of the stress tensor in the form of a differential equation, it is tantamount to formulate it in integral form. It is well known that Eq. (14) is equivalent to

$$\sigma''_{ij} = \int_{-\infty}^{t} K(t-t')\,\dot{\varepsilon}_{ij}(t')\,dt' \tag{50}$$

where the relaxation modulus $K(t-t')$ stands for

$$K(t-t') = (\eta/\tau_\varepsilon)\exp[-(t-t')/\tau_\varepsilon] \tag{51}$$

In this section, bulk effects are neglected and the various tensors may be considered as deviators; tildas are also omitted.

A natural extension of Eq. (50) is provided by

$$\sigma_{ij} = 2G\varepsilon_{ij} + \int_{-\infty}^{t} K(t-t')\,\dot{\varepsilon}_{ij}(t')\,dt' \tag{52}$$

where the memory function $K(t-t')$ is not necessarily represented by a simple exponential. Relation (52) is particularly well adapted for describing rheological materials [6].

It is worth repeating that a relation such as Eq. (52) is strictly compatible with EIT. Like any other thermodynamic theory, our formalism is not able to provide the most suitable analytical form for the function $K(t-t')$. Clearly experimental observation is the most appropriate guide in formulating an expression for the relaxation modulus. It nevertheless remains true that a thermodynamic description is very fruitful in that it eliminates various forms for $K(t-t')$ which are not compatible with the second law and because it imposes restrictions on the signs of the coefficients appearing in the constitutive and evolution equations.

Another interesting extension is provided by the following model, which is a coupling of a Navier–Stokes viscous fluid and the material described in Section 2.1. Let us write for the stress tensor a relation of the form

$$\sigma_{ij} = \sigma^{\mathrm{v}}_{ij} + \sigma^{\mathrm{s}}_{ij} \tag{53}$$

where σ^{v}_{ij} is the viscous stress tensor given by

$$\sigma^{\mathrm{v}}_{ij} = \mu\dot{\varepsilon}_{ij} \tag{54}$$

with μ the shear viscosity, while σ^{s}_{ij} is supposed to be formed of an elastic and an inelastic part,

$$\sigma^{\mathrm{s}}_{ij} = 2G\varepsilon_{ij} + \sigma''_{ij} \tag{55}$$

The above modeling is useful for describing dilute solutions of polymers [8]: σ^{v}_{ij} is the contribution of the solvent at zero dilution and σ''_{ij} is the mean stress tensor for the medium formed by the interacting polymer molecules (see Section 4). Repeating the reasoning in Section 2 with $\dot{u}_i$, and σ''_{ij} as basic variables, we are led to a relaxational equation for the stress tensor σ''_{ij} expressed by

$$\tau\dot{\sigma}''_{ij} = -\sigma''_{ij} + \eta\dot{\varepsilon}_{ij} \tag{56}$$

η represents the polymer contribution to the viscosity when relaxational effects are absent. The relaxational property of σ''_{ij} was still observed by Volkov and Vinogradov [9], who worked in a completely different context. By taking the time derivative of Eq. (53) and eliminating σ''_{ij} by means of Eq. (56), one obtains

$$\tau\dot{\sigma}_{ij} + \sigma_{ij} = 2G\varepsilon_{ij} + 2G[\tau + (\eta + \mu)/2G]\,\dot{\varepsilon}_{ij} + \tau\mu\ddot{\varepsilon}_{ij} \tag{57}$$

Setting $G = 0$ in Eq. (57) yields

$$\tau \dot{\sigma}_{ij} + \sigma_{ij} = (\eta + \mu)\, \dot{\varepsilon}_{ij} + \tau \mu \ddot{\varepsilon}_{ij} \tag{58}$$

which is nothing but Jeffrey's model, while by letting $\mu = 0$, one recovers the previous model expressed by Eq. (16).

It follows from the above considerations that EIT provides a systematic way for deriving the classical equations of viscoelasticity. In addition, it emerges in new results such as Eq. (57), which may be useful for describing solutions of polymers and which contains, as particular cases, the models of Jeffreys and Poynting–Thomson.

4. DILUTE POLYMER SOLUTIONS

4.1. The Rouse Model

One of the simplest models for dilute polymer solutions was presented by Rouse [4]. It is supposed that small quantities of macromolecules are in suspension in a Newtonian solvent; the macromolecules do not interact between them and are modeled by a chain, composed of a given number of subchains, which are themselves viewed as formed by beads and springs.

Each bead of the polymer chain suffers a drag effect from the fluid in addition to Brownian motions. The beads are linked by Hookean springs to provide the elastic forces which elongate the macromolecules. In this model, the hydrodynamic effects between individual beads are uncorrelated. The complex motions of the individual parts of the chain are described by means of normal coordinates obeying a relaxational dynamics with different times of relaxation.

Upon the action of a shear, the system undergoes a stress σ which is decomposed into two parts,

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}^{\mathrm{s}} + \boldsymbol{\sigma}^{\mathrm{p}} \tag{59}$$

where the superscripts s and p denote contributions of the solvent and the polymer, respectively. In the Rouse model, the last term is written as

$$\boldsymbol{\sigma}^{\mathrm{p}} = \sum_{\alpha=1}^{N} \boldsymbol{\sigma}_{\alpha} \tag{60}$$

where the contributions of the N normal modes are added. Moreover, in the linear regime, each individual model α satisfies a relaxational equation of the form

$$\tau_{\alpha} \dot{\boldsymbol{\sigma}}_{\alpha} + \boldsymbol{\sigma}_{\alpha} = \eta_{\alpha} \mathbf{V} \tag{61}$$

in which τ_α is the time of relaxation of the α mode, η_α the viscosity corresponding to the α mode, and $\mathbf{V}$ the symmetric velocity gradient.

As usual in fluid mechanics, we can split the total stress tensor according to

$$\boldsymbol{\sigma} = (-p + p^{\mathrm{v}})\mathbf{U} + \boldsymbol{\sigma}^{\mathrm{v}} \tag{62}$$

where p is the hydrostatic pressure, p^{v} the bulk viscous pressure, and $\boldsymbol{\sigma}^{\mathrm{v}}$ the shear stress.

4.2. EIT Description

In order to be brief, thermal effects are not considered. The basic hypothesis underlying EIT is that the specific entropy s of a system out of equilibrium depends locally not only on the natural variables u and v but also on the dissipative fluxes $\sigma_\alpha^{\mathrm{v}}$ and $\tilde{\sigma}_\alpha^{\mathrm{v}}$, i.e.,

$$s = s(u, v, \sigma_\alpha^{\mathrm{v}}, \tilde{\sigma}_\alpha^{\mathrm{v}}) \tag{63}$$

v denotes the specific volume ($v = \rho^{-1}$). This function is assumed to be analytic in the fluxes and therefore

$$ds = \frac{\partial s}{\partial u}\, du + \frac{\partial s}{\partial v}\, dv + \sum_\alpha \frac{\partial s}{\partial \sigma_\alpha^{\mathrm{v}}}\, d\sigma_\alpha^{\mathrm{v}} + \sum_\alpha \frac{\partial s}{\partial \tilde{\boldsymbol{\sigma}}_\alpha^{\mathrm{v}}} : d\tilde{\boldsymbol{\sigma}}_\alpha^{\mathrm{v}} \tag{64}$$

By analogy with classical irreversible thermodynamics, we adopt the following definitions of an (nonequilibrium) absolute temperature T and a (nonequilibrium) pressure p [3]:

$$\partial s/\partial u = T^{-1}(u, v, \sigma_\alpha^{\mathrm{v}}, \tilde{\boldsymbol{\sigma}}_\alpha^{\mathrm{v}}) \tag{65}$$

$$\partial s/\partial v = T^{-1}p(u, v, \sigma_\alpha^{\mathrm{v}}, \tilde{\boldsymbol{\sigma}}_\alpha^{\mathrm{v}}) \tag{66}$$

The remaining derivatives are denoted by

$$\partial s/\partial \sigma_\alpha^{\mathrm{v}} = T^{-1}v\gamma_\alpha(u, v, \sigma_\alpha^{\mathrm{v}}, \tilde{\boldsymbol{\sigma}}_\alpha^{\mathrm{v}}) \tag{67}$$

$$\partial s/\partial \tilde{\boldsymbol{\sigma}}_\alpha^{\mathrm{v}} = T^{-1}v\xi_\alpha(u, v, \sigma_\alpha^{\mathrm{v}}, \tilde{\boldsymbol{\sigma}}_\alpha^{\mathrm{v}}) \tag{68}$$

with α running from 0 to N, and index 0 referring to the solvent.

At the lowest linear order of approximation, the dissipative coefficients γ_α and ξ_α are written simply as

$$\gamma_\alpha = \sum_{\beta=0}^{N} \gamma_{\alpha\beta}\sigma_\beta^{\mathrm{v}}, \qquad \xi_\alpha = \sum_{\beta=0}^{N} \xi_{\alpha\beta}\tilde{\boldsymbol{\sigma}}_\beta^{\mathrm{v}} \tag{69}$$

Here the coefficients $\gamma_{\alpha\beta}$ and $\xi_{\alpha\beta}$ depend eventually on the temperature and density. It is known that in the Rouse and other hydrodynamical models of polymer suspensions, the dissipative contributions are not coupled; more precisely the solvent does not interact with the polymer chains and the normal modes are independent of each other and of the solvent. Under these simplifications, Eq. (69) reduces to

$$\gamma_\alpha = \gamma_{\alpha\alpha}\sigma^{\mathrm{v}}_\alpha, \qquad \boldsymbol{\xi}_\alpha = \xi_{\alpha\alpha}\tilde{\boldsymbol{\sigma}}^{\mathrm{v}}_\alpha \tag{70}$$

Substituting these relations in Eqs. (67) and (68), we obtain for the time derivative of entropy,

$$T\dot{s} = \dot{u} + p\dot{v} + v\sum_{\alpha=0}^{N} \gamma_{\alpha\alpha}\sigma^{\mathrm{v}}_\alpha\dot{\sigma}^{\mathrm{v}}_\alpha + v\sum_{\alpha=0}^{N} \xi_{\alpha\alpha}\tilde{\boldsymbol{\sigma}}^{\mathrm{v}}_\alpha : \dot{\tilde{\boldsymbol{\sigma}}}^{\mathrm{v}}_\alpha \tag{71}$$

Inserting now the balance equations of mass and interval energy and bearing in mind that in the absence of a heat flux vector $\mathbf{q}$, the entropy flux $\mathbf{J}^{\mathrm{s}}$ is zero, the entropy production σ^{s} is easily derived by comparison with the balance equation of entropy. Up to second order, one has

$$\bar{\sigma}^{\mathrm{s}} = \sum_{\alpha=0}^{N} T^{-1}\sigma^{\mathrm{v}}_\alpha(\nabla\cdot\mathbf{v} - \gamma_{\alpha\alpha}\dot{\sigma}^{\mathrm{v}}_\alpha) + \sum_{\alpha=0}^{N} T^{-1}\tilde{\boldsymbol{\sigma}}^{\mathrm{v}}_\alpha : (\tilde{\mathbf{V}} - \xi_{\alpha\alpha}\dot{\tilde{\boldsymbol{\sigma}}}^{\mathrm{v}}_\alpha) \tag{72}$$

which may still be written as

$$\bar{\sigma}^{\mathrm{s}} = \sum_{\alpha=0}^{N} X_\alpha\sigma^{\mathrm{v}}_\alpha + \sum_{\alpha=0}^{N} \mathbf{Y}_\alpha : \tilde{\boldsymbol{\sigma}}^{\mathrm{v}}_\alpha \tag{73}$$

where X_α and $\mathbf{Y}_\alpha$ can be identified as force conjugates to the fluxes $\sigma^{\mathrm{v}}_\alpha$ and $\tilde{\boldsymbol{\sigma}}^{\mathrm{v}}_\alpha$. Since σ^{s} is a scalar function, the representation theorems of isotropic functions impose an expression of the form

$$\bar{\sigma}^{\mathrm{s}} = \sum_{\alpha=0}^{N} l_\alpha\sigma^{\mathrm{v}}_\alpha\sigma^{\mathrm{v}}_\alpha + \sum_{\alpha=0}^{N} m_\alpha\tilde{\boldsymbol{\sigma}}^{\mathrm{v}}_\alpha : \tilde{\boldsymbol{\sigma}}^{\mathrm{v}}_\alpha \tag{74}$$

Direct comparison of these two expressions suggests that

$$\begin{aligned} l_\alpha\sigma^{\mathrm{v}}_\alpha &= T^{-1}(\nabla\cdot\mathbf{v} - \gamma_{\alpha\alpha}\dot{\sigma}^{\mathrm{v}}_\alpha) \\ m_\alpha\tilde{\boldsymbol{\sigma}}^{\mathrm{v}}_\alpha &= T^{-1}(\tilde{V} - \xi_{\alpha\alpha}\dot{\tilde{\boldsymbol{\sigma}}}^{\mathrm{v}}_\alpha) \end{aligned} \tag{75}$$

Under stationary conditions, Eqs. (75) must reduce to the results of classical irreversible thermodynamics: $\sigma^{\mathrm{v}}_\alpha = \eta_\alpha\nabla\cdot\mathbf{v}$, $\tilde{\boldsymbol{\sigma}}^{\mathrm{v}}_\alpha = 2\mu_\alpha\tilde{\mathbf{V}}$. This allows us to identify l_α and m_α as $(T\eta_\alpha)^{-1}$ and $(2T\mu_\alpha)^{-1}$, respectively. Moreover, since Eqs. (75) are of the relaxation type, it is convenient to introduce relaxation times through

$$\tau_\alpha = \gamma_{\alpha\alpha}/Tl_\alpha \tag{76}$$

$$\tau'_\alpha = \xi_{\alpha\alpha}/Tm_\alpha \tag{77}$$

Using Eqs. (76) and (77), expressions (75) take the familiar Maxwell form.

Assuming with Rouse that the solvent may be considered as a Newtonian fluid, which means that $\tau_0 \ll \tau_\alpha$ and $\tau'_0 \ll \tau'_\alpha$, one obtains the following set of equations for the various stresses:

$$\sigma_0^{\mathrm{v}} = \eta_0 \nabla \cdot \mathbf{v} \tag{78}$$

$$\tau_\alpha \dot{\sigma}_\alpha^{\mathrm{v}} + \sigma_\alpha^{\mathrm{v}} = \eta_\alpha \nabla \cdot \mathbf{v} \tag{79}$$

$$\tilde{\boldsymbol{\sigma}}_0^{\mathrm{v}} = 2\mu_0 \tilde{\mathbf{V}} \tag{80}$$

$$\tau'_\alpha \dot{\tilde{\boldsymbol{\sigma}}}_\alpha^{\mathrm{v}} + \tilde{\boldsymbol{\sigma}}_\alpha^{\mathrm{v}} = 2\mu_\alpha \tilde{\mathbf{V}} \tag{81}$$

where α runs now from 1 to N. These relations bear strong resemblances to the Rouse equations which were derived from statistical arguments. It is worth noting that Rouse results are here derived on macroscopic bases, and in addition to the Rouse approach, equations for the bulk viscosities, Eqs. (78) and (79), are also obtained.

5. CONCLUSIONS

The description of viscoelastic materials within the framework of extended irreversible thermodynamic has been the subject of recent papers [10]. These concern only Maxwell's body. A more complete description is given in Ref. 11. However, the rationale behind this work, its objectives, and the choice of the basic variables are entirely different from the line of thought of the present article.

It is also worthwhile to compare the merits of EIT with the hidden variable theory (HVT) [12], which fueled much interest during the last decade. In EIT, the physical nature of the extra variable is known from the onset, which is not necessarily true in HVT. In contrast with the latter formalism, the variables introduced in EIT take part in the mechanical work and the heat input; in HVT, the basic variables do not appear in the balance equations. Moreover, since the selection of the hidden variables is not regulated by strict rules, the same class of materials can be described by several formalisms. In EIT, the selection of the variable is unequivocal, as it consists of the dissipative part of the fluxes appearing in the usual balance laws.

It is also relevant to point out that the postulates behind EIT have been supported by the kinetic theory, generalized hydrodynamics, and the statistical theory of fluctuations [3]. To our knowledge, the foundations of HVT did not receive comparable physical support.

Another main conclusion of the present work is that the usual relaxational scheme of viscous modes in polymer solutions can be accounted for by means of EIT. This theory predicts, as a natural consequence, a relaxational spectrum for the stress tensor.

ACKNOWLEDGMENTS

This research was partially supported by NATO Grant 0353/83. One of us (J.C.-V.) is very grateful to Direccion General de Investigación Científica y Técnica for Grant PB86-0287.

REFERENCES

1. R. S. Rivlin and J. L. Ericksen, *J. Rat. Mech. Anal.* **4**:323 (1955); R. R. Huilgol and N. Phan-Tien, *Int. J. Eng. Sci.* **24**:161 (1986).
2. J. Meixner, *Z. Naturforsch.* **4a**:594 (1949); G. A. Kluitenberg, *Physica* **28**:561 (1962); J. Kestin and J. Bataille, in *Continuum Models of Discrete Systems* (University of Waterloo Press, Waterloo, 1980), p. 99.
3. J. Casas-Vázquez, D. Jou, and G. Lebon (eds.), *Recent Developments in Non-equilibrium Thermodynamics* (Springer, Berlin, 1984); D. Jou, J. Casas-Vázquez, and G. Lebon, *Rep. Prog. Phys.* **51**:1105 (1988).
4. P. E. Rouse, *J. Chem. Phys.* **21**:1271 (1953).
5. I. S. Liu and I. Müller, *Arch. Rat. Mech. Anal.* **83**:285 (1983); G. Lebon and M. S. Boukary, *Int. J. Eng. Sci.* **26**:471 (1988).
6. R. I. Tanner, *Engineering Rheology* (Oxford Science, Oxford, 1986).
7. G. Lebon, C. Pérez-García, and J. Casas-Vázquez, *Physica* **137A**:531 (1986).
8. D. D. Joseph, *J. Non-Newt. Fluid Mech.* **19**:237 (1986).
9. V. S. Volkov and G. Vinogradov, *J. Non-Newt. Fluid Mech.* **15**:29 (1984).
10. M. López de Haro, L. Castillo, and R. Rodríguez, *Rheol. Acta* **25**:207 (1986); A. Palumbo and G. Valenti, *J. Non-Equil. Thermodyn.* **10**:340 (1985).
11. B. C. Eu, *J. Chem. Phys.* **82**:4683 (1985).
12. F. Bampi and A. Morro, in *Recent Developments in Non-equilibrium Thermodynamics*, J. Casas-Vázquez, D. Jou, and G. Lebon, eds. (Springer, Berlin, 1984), p. 211.