A nonlinear viscoelastic model and non-equilibrium entropies

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ABSTRACT

We show that the thermodynamic conjugate of the extra stress is a more suitable independent variable than the extra stress itself for the thermodynamic description of some nonlinear models of viscoelasticity. This brings more precision to the knowledge of non-equilibrium thermodynamic potentials, and provides an illustration of a recently proposed conservation–dissipation formalism which allows bringing extended irreversible thermodynamics to the nonlinear regime.

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1. Introduction

The suitable selection of independent variables is one of the basic problems in non-equilibrium thermodynamics[1]. Rheological systems are especially challenging from this point of view, because they have a very rich and dynamic microscopic structure. For a microscopic understanding and simulation of their behavior, structural variables such as the conformation tensor $\underline{C}$, proportional to $\langle \vec{R}\vec{R} \rangle$, with $\vec{R}$ the end-to-end vector of the macromolecules and $\langle \cdots \rangle$ standing for the average over all molecules [2–5], are especially suitable and useful. The conformation tensor $\underline{C}$ is related to the stress tensor $\underline{\sigma}$ in a simple way (usually, through a linear algebraic relation). The use of this variable, and other related variables describing further structural details of the system, in combination with molecular dynamics simulations of the flowing system and with especially wide and powerful macroscopic thermodynamic formalisms as GENERIC [2–5], has been at the basis of systematic analyses of very complex rheological systems involving different time scales (see, for instance, [6–12]).

More traditional non-equilibrium and macroscopically focused thermodynamic approaches to rheological modeling [12–14] are less specific and detailed than the mentioned recent approaches. They focus on more macroscopic variables, mainly the stress tensor - or the several contributions to it -, and are mainly interested in the compatibility of rheological models with the second law of thermodynamics [12–16], without the explicit knowledge of the

microstructural variables. Whereas more microscopically-minded approaches aim to detailed descriptions of different physical systems, more macroscopically-minded theories aim to search for the features which are common to a wide diversity of systems,despite having less predictive power in the particular details.

A topic of particular interest in the macroscopic theories is the contribution of the non-equilibrium variables to the entropy and the entropy flux. Through their contribution to the entropy, these non-equilibrium variables contribute also to the equations of state and may modify the phase diagram of flowing rheological fluids. For instance, polymer solubility or miscibility is known to be influenced by the imposed shear rate or shear stress [13,15].

A phenomenological alternative to the explicit use of internal structural variables, which are not always easy to identify, measure, or control, is to directly use the extra stress, or some related macroscopic non-equilibrium quantities, as an additional independent thermodynamic variable, leading to non-equilibrium expressions for entropy[12–14]. In particular, in extended thermodynamics, $\underline{\sigma}$ is used as additional variable in the entropy s, which is of the form $s(u, \underline{\sigma})$. When $\underline{\sigma}$ and $\underline{C}$ are linearly related, one may go from the use of $\underline{\sigma}$ to the use of $\underline{C}$ by means of a Legendre transform [17]. The aim of this paper is to go to the non-linear regime in the framework of such macroscopic theories and explore the most suitable independent variables. In Section 2, we briefly review the relation between linear Maxwell viscoelastic equation and the non-equilibrium entropy of extended thermodynamics. In Section 3, we present the nonlinear version of (1) considered here, and illustrate how the entropy (2) fails to describe it. In Section 4, by using its corresponding thermodynamic conjugate instead of $\underline{\sigma}$ itself, we present a different version of non-equilibrium entropy

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which shows in a direct way the compatibility of the nonlinear viscoelastic equation with the second law of thermodynamics. In Section 5 we make some concluding comments on the new version of entropy, Legendre transforms, and GENERIC thermodynamic formalism for nonlinear constitutive equations.

2. Linear viscoelasticity and extended entropy

Here, in particular, we focus our attention on the form of macroscopic non-equilibrium entropy in connection with viscoelasticity. Though the form of entropy plays a central role in the analysis of compatibility of constitutive equations with the second law, its explicit form is rarely studied in detail, as the dynamical aspects of rheological equations, being directly observable and with relevant physical consequences, focus the attention of most researches.

The simplest model for viscoelasticity is the Maxwell model, which is characterized by the well-known equation [2,5,12,13]

$$\tau \frac{D\underline{\underline{\sigma}}}{Dt} + \underline{\underline{\sigma}} = 2\eta \underline{\underline{D}} \tag{1}$$

in which $\underline{\underline{\sigma}}$ is the extra stress tensor, τ is the viscoelastic relaxation time, η is the shear viscosity, $\underline{\underline{D}}$ is the rate of deformation tensor, which represents the symmetric part of the velocity gradient $\nabla \vec{v}$ as $\underline{\underline{D}} = \frac{1}{2}(\nabla \vec{v} + \vec{v}\nabla)$, and whose second invariant is the so-called shear rate $\dot{\gamma}$, and $D\underline{\underline{\sigma}}/Dt$ stands for frame-invariant forms of the time derivative defined as $D\underline{\underline{\sigma}}/Dt \equiv d\underline{\underline{\sigma}}/dt - a[(\nabla \vec{v})^T \cdot \underline{\underline{\sigma}} + \underline{\underline{\sigma}} \cdot (\nabla \vec{v})^T]$, with d/dt the material time derivative. In [18–21], the upper-convected time ($a = 1$) was used for the viscoelastic models to be frame-invariant, but other time derivatives like the co-rotational one, or the lower convected one ($a = -1$) could also be used [2–5,12–14]. Since the macromolecular systems usually have several relaxational degrees of freedom contributing to $\underline{\underline{\sigma}}$, model (1) is generalized by taking $\underline{\underline{\sigma}} = \sum \underline{\underline{\sigma}}_i$, with each contribution $\underline{\underline{\sigma}}_i$ being described by an equation like (1), with its own η_i and τ_i. The several relaxation times may span a wide range of time scales. Here, for the sake of simplicity, and because the corresponding extension is straightforward, we will consider a single degree of freedom.

In the linear situation that η and τ are independent of time and deformation, for compressible fluid, the corresponding Gibbs equation for the non-equilibrium thermodynamic entropy s per unit mass of the fluid in extended irreversible thermodynamics (EIT) is [13,22–24]

$$ds(u, \underline{\underline{\sigma}}) = T^{-1} du - \frac{\tau}{2\eta T \rho} \underline{\underline{\sigma}} : d\underline{\underline{\sigma}} \tag{2}$$

with u the internal energy per unit mass and T absolute temperature. In the case that $\underline{\underline{\sigma}}$ splits in several independent contributions $\underline{\underline{\sigma}}_i$, as mentioned above, the last term in (2) would be the sum of the contributions of the several $\underline{\underline{\sigma}}_i$, each of them having the same form but with the corresponding τ_i/η_i. Here, for simplicity, we will consider $\underline{\underline{\sigma}}$ as a single variable.

Note that $s(u, \underline{\underline{\sigma}})$ depends on the shear stress, a non-equilibrium variable which vanishes at equilibrium. Thus, this entropy is not the classical local-equilibrium entropy, but a typical non-equilibrium entropy. As said above, an alternative to the use of $\underline{\underline{\sigma}}$, which is a macroscopic variable, would be to consider some microscopic variable related to the microstructure of the fluid as the conformation tensor $\underline{\underline{C}}$. Whereas the use of macromolecular internal or structural variables may be especially illuminating for a microscopic understanding of the fluid, the thermodynamic description based on u and $\underline{\underline{\sigma}}$ (or on T and $\underline{\underline{\sigma}}$) may be more useful from a macroscopic point of view, because it is a directly measurable variable.

3. Non-linear viscoelastic equation

In nonlinear situations, η and τ may depend on fluid microstructure which, in its turn, depends on the shear condition. Then, η and τ may be taken to depend on some characteristic microstructure variables or, alternatively, on the shear rate $\dot{\gamma}$ as in shear-thinning fluids, or on γ and $\dot{\gamma}$ as in gel–sol transitions. An open thermodynamic question is which will be the extension of the Gibbs equation (2) for nonlinear extension, i.e. which is the form of entropy more directly related to nonlinear versions of equation (1).

For nonlinear viscoelasticity, we will consider a nonlinear extension of (1) as proposed by Marrucci et al. [18–21], and we will ask for the corresponding extension of the entropy (2), related to a recent conservation–dissipation formalism (CDF) of irreversible thermodynamics [25], and compare it to extended irreversible thermodynamics (EIT) [13,22–24] as well as the GENERIC formalism [3–5].

The simplest nonlinear extension of (1) would be to use (1) itself, but with η and τ changing with time and deformation, or depending on the microstructure. However, from an experimental point of view, this model is not satisfactory enough. Instead of (1), Marrucci et al. [18–21] have proposed for systems with structure-dependent relaxation times, to use the following generalized version

$$\eta \frac{D}{Dt}\left(\frac{\tau}{\eta}\underline{\underline{\sigma}}\right) + \underline{\underline{\sigma}} = 2\eta \underline{\underline{D}} \tag{3}$$

which becomes (1) when η and τ are constant (in particular, they take for D/Dt the upper-convected or contra-variant time derivative). The ratio η/τ is the so-called elastic modulus G, and its reciprocal is the steady-state compliance J. Eq. (3) is justified in the framework of network theories, as applied to polymer melts and concentrated solutions, where viscosity and relaxation times strongly depend on the microstructure, thus leading to a shear rate dependence $\eta(\dot{\gamma})$ and $\tau(\dot{\gamma})$. In [18–21], microscopic description of the system was proposed with emphasis on the dynamics, i. e. on the rheological aspects, and compared to experiments showing its practical suitability. Our aim, instead, will be focused on the most suitable form of non-equilibrium entropy being compatible with equation (3). Additional nonlinear effects would also be added to (3), as for instance, terms of the form $\underline{\underline{\sigma}} \cdot \underline{\underline{\sigma}}$, but the non-equilibrium entropy is known to be related to the relaxational term of the constitutive equation [13,14,22], so that we focus our attention on this term.

Note that the suitable thermodynamic potential related to (3) is not the entropy (2). Indeed, if the Gibbs equation (2) is used as a starting point for the thermodynamic analysis, one gets for the evolution equation of $\underline{\underline{\sigma}}$, equation (1) with $\eta(\dot{\gamma})$ and $\tau(\dot{\gamma})$ instead of equation (3). To see this, recall that the evolution equation for u is the energy balance equation [2,5,12,13,22,23,26]

$$\rho \dot{u} = -\nabla \cdot \vec{q} + \underline{\underline{\sigma}} : \underline{\underline{D}} \tag{4}$$

where $\vec{q}$ is the heat flux, and the last term describes viscous dissipation per unit volume and time. The evolution equation for s according to (2) is

$$\rho \dot{s} = T^{-1} \rho \dot{u} - \frac{\tau}{2\eta T} \underline{\underline{\sigma}} : \dot{\underline{\underline{\sigma}}} \tag{5}$$

In fact, in order that the several terms in (5) are frame-invariant, the $\dot{\underline{\underline{\sigma}}}$ in (5) should be interpreted as a frame-invariant time derivative as mentioned below (1) because $\underline{\underline{\sigma}}$ is a second-order tensor (in contrast, the several time derivatives reduce to the material time derivative for scalar quantities s and u).

Introducing (4) into (5) one finds

$$\rho \dot{s} = \vec{q} \cdot \nabla T^{-1} + T^{-1} \underline{\underline{\sigma}} : \underline{\underline{D}} - \frac{\tau}{2\eta T} \underline{\underline{\sigma}} : \dot{\underline{\underline{\sigma}}} - \nabla \cdot (T^{-1}\vec{q}) \tag{6}$$