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.

Keywords: Entropy; Nonlinear viscoelasticity; Extended irreversible thermodynamics; Conservation-dissipation formalism

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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
5 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

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the average over all molecules [2, 3, 4, 5], are especially suitable and useful. The conformation tensor $\underline{\underline{C}}$ is related to the stress tensor $\underline{\underline{\sigma}}$ 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, 3, 4, 5], has been at the basis of systematic analyses of very complex rheological systems involving different time scales (see, for instance, [6, 7, 8, 9, 10, 11, 12]).

More traditional non-equilibrium and macroscopically focused thermodynamic approaches to rheological modelling [12, 13, 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, 13, 14, 15, 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, 13, 14]. In particular, in extended thermodynamics, $\underline{\underline{\sigma}}$ is used as additional variable in the entropy s , which is of the form $s(u, \underline{\underline{\sigma}})$.

When $\underline{\underline{\sigma}}$ and $\underline{\underline{C}}$ are linearly related, one may go from the use of $\underline{\underline{\sigma}}$ to the use of
40 $\underline{\underline{C}}$ 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)
45 considered here, and illustrate how the entropy (2) fails to describe it. In section
4, by using its corresponding thermodynamic conjugate instead of σ itself, we
present a different version of non-equilibrium entropy 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
50 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
55 entropy plays a central role in the analysis of compatibility of constitutive e-
quations 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 char-
60 acterized by the well-known equation[5, 12, 13, 2]

$$\tau \frac{\mathbf{D}\underline{\underline{\sigma}}}{\mathbf{D}t} + \underline{\underline{\sigma}} = 2\eta \underline{\underline{D}} \quad (1)$$

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 $\mathbf{D}\underline{\underline{\sigma}}/\mathbf{D}t$ stands for frame-
65 invariant forms of the time derivative defined as $\mathbf{D}\underline{\underline{\sigma}}/\mathbf{D}t \equiv \mathbf{d}\underline{\underline{\sigma}}/\mathbf{d}t - a[(\nabla \vec{v}) \cdot$

$\underline{\underline{\sigma}} + \underline{\underline{\sigma}} \cdot (\nabla \vec{v})^T$], with d/dt the material time derivative. In [18, 19, 20, 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, 3, 4, 5, 12, 13, 14]. Since the
70 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,
75 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, 23, 24]

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

80 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 σ as a single variable.

85 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
90 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.

95 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.
 100 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, 19, 20, 21], and we will ask for the correspond-
 105 ing 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, 23, 24] as well as the GENERIC formalism [5, 3, 4].

The simplest nonlinear extension of (1) would be to use (1) itself, but with η
 110 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, 19, 20, 21] have proposed for systems with structure-dependent relaxation times, to use the following generalized version

$$\eta \frac{\mathbf{D}}{\mathbf{D}t} \left(\frac{\tau}{\eta} \underline{\underline{\sigma}} \right) + \underline{\underline{\sigma}} = 2\eta \underline{\underline{D}} \quad (3)$$

115 which becomes (1) when η and τ are constant (in particular, they take for $\mathbf{D}/\mathbf{D}t$ 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 . Equation (3) is justified in the framework of network theories, as applied to polymer melts and concentrated solutions, where viscosity and relaxation times
 120 strongly depend on the microstructure, thus leading to a shear rate dependence $\eta(\dot{\gamma})$ and $\tau(\dot{\gamma})$. In [18, 19, 20, 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
125 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
130 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 [5, 12, 13, 2, 22, 23, 26]

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

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

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

In fact, in order that the several terms in (5) are frame-invariant, the $\underline{\underline{\dot{\sigma}}}$ 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 .)

140 Introducing (4) into (5) one finds

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

The first and last terms on the right-hand side come from the term $-T^{-1} \nabla \cdot \vec{q}$
obtained when (4) is introduced into the first term of the right-hand side of (5).

If one compares (6) to the general evolution equation for the entropy, namely
[5, 12, 13, 22, 23, 26],

$$\rho \dot{s} + \nabla \cdot \vec{J}^s = \sigma^s \quad (7)$$

145 with $\vec{J}^s$ entropy flux and σ^s entropy production per unit volume and time, one
finds $\vec{J}^s = \vec{q}/T$, which is the usual expression for the entropy flux, and

$$\sigma^s = \vec{q} \cdot \nabla T^{-1} + T^{-1} \underline{\underline{\sigma}} : \left(\underline{\underline{D}} - \frac{\tau}{2\eta} \underline{\underline{\dot{\sigma}}} \right) \geq 0 \quad (8)$$

In (8), we impose $\sigma^s \geq 0$, which is the usual requirement of the second law of thermodynamics [5, 12, 13, 22, 23, 26].

The simplest way of satisfying requirement (8) is to assume constitutive
 150 equations for the flux $\vec{q}$ and the **extra stress** tensor $\underline{\underline{\sigma}}$ in terms of their respective
 conjugate forces, i.e. the terms multiplying them in the bilinear expression (8),
 according to the usual procedure of non-equilibrium thermodynamics [5, 13, 26].
 One gets in this way

$$\vec{q} = L_1 \nabla T^{-1} \quad (9)$$

for the vectorial part related to $\vec{q}$, and

$$T^{-1} \underline{\underline{\sigma}} = L_2 (\underline{\underline{D}} - \frac{\tau}{2\eta} \dot{\underline{\underline{\sigma}}}) \quad (10)$$

155 for the tensorial part related to $\underline{\underline{\sigma}}$, where L_1 and L_2 are positive coefficients which
 may be interpreted as $L_1 = \lambda T^2$, with λ thermal conductivity, and $L_2 = 2\eta/T$,
 with η shear viscosity. In this way, (10) becomes (1), irrespectively of whether
 η and τ depend or not on time and deformation, or on the microstructure, and
 (9) becomes Fourier's law of heat transfer $\vec{q} = -\lambda \nabla T$. Thus, the usual strategy
 160 of extended thermodynamics is not leading to (3) but to (1). This suggests that
 some modification is necessary to analyze the thermodynamic consistency of the
 nonlinear expression (3). In particular, we will explore a change in the form of
 entropy, as proposed by Zhu et al. [25], which is aimed to the description of
 nonlinear situations.

165 4. Conservation-dissipation formalism and nonlinear viscoelasticity

Zhu et al. [25] have proposed the conservation-dissipation formalism (CD-
 F), which reduces to Extended Thermodynamics in the linear case but which
 differs from it in some crucial aspects in the nonlinear domain. We will show
 here that this formalism provides indeed a suitable framework for the nonlinear
 170 viscoelastic equation (3), and we will pay special attention to the corresponding
 form of non-equilibrium entropy, as compared to the extended entropy (2).

In CDF model the non-equilibrium entropy is not dependent on u and $\underline{\sigma}$, as in EIT, but on u and $\underline{w}$, with $\underline{w}$ being the thermodynamic conjugate of $\underline{\sigma}$, which is discussed below.

175 4.1. Entropy representation

Here, we will separately consider two options for $\underline{w}$, namely, the conjugate in entropy representation and the conjugate in internal energy representation. To find the relation between $\underline{w}$ and $\underline{\sigma}$, let us rewrite (2) as

$$ds = T^{-1}du + \underline{w} : d\underline{\sigma} \quad (11)$$

Here, $\underline{w}$ is the thermodynamic conjugate of $\underline{\sigma}$ with respect to s , defined by

$$\underline{w} = \left(\frac{\partial s}{\partial \underline{\sigma}} \right) \quad (12)$$

180 By comparing (11) with (2) one sees that $\underline{w}$ is related to $\underline{\sigma}$ as

$$\underline{w} = -\frac{\tau}{2\eta T \rho} \underline{\sigma} \quad (13)$$

In the steady state, where $\underline{\sigma} = 2\eta \underline{D}$, $\underline{w}$ may be identified as $\underline{w} = -(\tau/\rho) \underline{D}$. Using $\underline{w}$ instead of $\underline{\sigma}$ as a variable, Zhu et al. [25] write a generalized entropy $\tilde{s}(u, \underline{w})$, whose corresponding differential form (Gibbs equation) is

$$d\tilde{s} = T^{-1}du + \underline{s}_w : d\underline{w} \quad (14)$$

where $\underline{s}_w \equiv (\partial \tilde{s} / \partial \underline{w})$. If one combines the time derivative of (14) with the
185 energy balance equation (4) one obtains

$$\rho \dot{\tilde{s}} = \vec{q} \cdot \nabla T^{-1} + T^{-1} \underline{\sigma} : \underline{D} + \rho \underline{s}_w : \underline{\dot{w}} - \nabla \cdot (T^{-1} \vec{q}) \quad (15)$$

Here, as in (5), $\underline{\dot{w}}$ stands not for the material time derivative, but for the frame-invariant derivative $D\underline{w}/Dt$, but we keep $\underline{\dot{w}}$ for notational simplicity. By following the method leading from (6) to (8), we obtain in this case for the entropy production

$$\sigma^{\tilde{s}} = \vec{q} \cdot \nabla T^{-1} + T^{-1} \underline{\sigma} : [\underline{D} + \rho \underline{s}_w : \underline{\dot{w}}] \geq 0 \quad (16)$$

190 Here, $\underline{s}_w$ is not known a priori. Since $\tilde{s}(u, \underline{w})$ is a function of u and $\underline{w}$, and in principle it could be written according to representation theories of isotropic functions, as

$$\tilde{s}_w(s, \underline{w}) = \alpha'_1 \underline{U} + \alpha'_2 \underline{w} + \alpha'_3 \underline{w} \cdot \underline{w} \quad (17)$$

where the scalar coefficients α_i may be functions of u , $I_{\underline{w}}$ and $II_{\underline{w}}$, being $I_{\underline{w}} = \text{tr}(\underline{w})$, $II_{\underline{w}} = \text{tr}(\underline{w} \cdot \underline{w})$ the scalar invariants of the tensor $\underline{w}$. However, to be
 195 able to encompass (3) it will be sufficient to take $\alpha'_2 = \alpha'(u)$ and $\alpha'_1 = \alpha'_3 = 0$, as seen below. To rewrite the second term in (16) in a more compact form, it is convenient to reexpress $\underline{s}_w$ as a function of $\underline{\sigma}$. By using (13) and the simplified form of (17) with $\alpha'_1 = \alpha'_3 = 0$, we have $\tilde{\underline{s}}_w = (\alpha/T)\underline{\sigma}$ with $\alpha = -(\tau/2\eta\rho)\alpha'$. In terms of this representation, (16) is rewritten as (18)

$$\sigma^{\tilde{s}} = \vec{q} \cdot \nabla T^{-1} + T^{-1} \underline{\sigma} : (\underline{D} + \rho \alpha \underline{\dot{w}}) \geq 0 \quad (18)$$

200 An analogous argument to that leading from (8) to (10) leads now for the tensorial part of (18) to

$$T^{-1} \underline{\sigma} = \tilde{L}_2 (\underline{D} + \rho \alpha \underline{\dot{w}}) \quad (19)$$

with $\tilde{L}_2$ positive. By taking $\alpha = T$, $\tilde{L}_2 = 2\eta/T$ and using (13), we get

$$\underline{\sigma} = [2\eta \underline{D} - T \frac{D}{Dt} (\frac{\tau \underline{\sigma}}{\eta T})] \quad (20)$$

which may be rewritten as

$$\underline{\sigma} + T\eta \frac{D}{Dt} (\frac{\tau \underline{\sigma}}{\eta T}) = 2\eta \underline{D} \quad (21)$$

When T is constant, (21) reduces to (3). The situation of T changing with time is
 205 also of interest, especially in systems with sol-gel transitions due to the dissolved particles which may precipitate and aggregate at low enough temperatures, in such a way that their physical properties may strongly depend on temperature [27, 28].

4.2. Internal energy representation

210 An ambiguity in the definition of the thermodynamic conjugate of $\underline{\sigma}$ arises if instead of using the entropy representation, as in Section 3.1, one uses the

energy representation. In this case, (2) could be rewritten as

$$du = Tds + \underline{\underline{w}}' : d\underline{\underline{\sigma}} \quad (22)$$

with

$$\underline{\underline{w}}' = \left(\frac{\tau}{\eta\rho}\right)\underline{\underline{\sigma}} \quad (23)$$

being the conjugate of $\underline{\underline{\sigma}}$ in this representation. If one uses $\underline{\underline{w}}'$ instead of $\underline{\underline{w}}$ defined in (13), as an independent variable of entropy $s^*(u, \underline{\underline{w}}')$, a thermodynamic analysis analogous to that of Section 3.1 would be

$$ds^* = T^{-1}du - \underline{\underline{s}}_{w'} : d\underline{\underline{w}}' \quad (24)$$

where $\rho \underline{\underline{s}}_{w'} = \alpha' \underline{\underline{\sigma}}/T$. This leads to an entropy production

$$\sigma^{s^*} = q \cdot \nabla T^{-1} + T^{-1} \underline{\underline{\sigma}} : (\underline{\underline{D}} + \rho \alpha' \underline{\underline{w}}') \geq 0 \quad (25)$$

and the corresponding stress equation

$$T^{-1} \underline{\underline{\sigma}} = L'_2 (\underline{\underline{D}} + \rho \alpha' \underline{\underline{w}}) \quad (26)$$

with L'_2 positive. For $\alpha' = -1$ and $L'_2 = \eta/T$, equation (3) is obtained.

Thus the entropy $\tilde{s}(u, \underline{\underline{w}})$ leads to (21) and the entropy $s^*(u, \underline{\underline{w}}')$ leads to (3). For constant T both equations coincide, but they differ when T changes with time. A comparison of the predictions of (3) and of (11) with experimental observations in situations with time-dependent temperature would clarify whether $\underline{\underline{w}}$ in (12) or $\underline{\underline{w}}'$ in (23) is more useful as independent variable of the entropy.

5. Concluding remarks

As final remarks related to the non-equilibrium entropies, we comment on Legendre transforms, and on GENERIC formalism in connection with the analysis about non-equilibrium entropy, in order to get a wider perspective on it.

5.1. Legendre transforms

Legendre transform is a powerful tool in classical thermodynamics [29] to set a relation between equivalent thermodynamic formalisms in terms of different variables, namely, by replacing a variable (like u) by its thermodynamic conjugate (T^{-1} in the entropy representation), or replacing s by T , in the energy representation. Since in (14) the thermodynamic conjugate of σ is used, it is natural to explore whether $s(u, \underline{\sigma})$ of EIT and $\tilde{s}(u, \underline{w})$ of CDF are mutually related by means of a Legendre transform.

The main difference between EIT and CDF is that the former one uses $\underline{\sigma}$ as independent variable, whereas the second one uses its thermodynamic conjugate $\underline{w}$. Both theories coincide in the linear case. Now, we focus our attention on the relation between $s(u, \underline{\sigma})$ and $\tilde{s}(u, \underline{w})$. According to our interpretation $\alpha = T$ in (19), it follows in (14) $\underline{s}_w = \underline{\sigma}$, in such a way that (14) becomes

$$d\tilde{s} = T^{-1}du + \underline{\sigma} : d\underline{w} \quad (27)$$

Note, then, that the entropy used in CDF [25] is not a Legendre transform of the entropy used in extended irreversible thermodynamics [13, 22, 23, 24]. Indeed, such a Legendre transform, let us say $s^{**}(u, \underline{w})$, would be defined, according to the usual formulation of Legendre transforms [29]

$$s^{**}(u, \underline{w}) \equiv s(u, \underline{\sigma}) - \underline{\sigma} : \frac{\partial s}{\partial \underline{\sigma}} = s(u, \underline{\sigma}) - \underline{\sigma} : \underline{w} \quad (28)$$

where $\underline{\sigma}$ should be expressed in terms of $\underline{w}$. Thus using (2), (28) leads to the differential form

$$ds^{**}(u, \underline{w}) = T^{-1}du - \underline{\sigma} : d\underline{w} \quad (29)$$

which differs from the differential form (27). It is known that thermodynamic potentials related by Legendre transforms are thermodynamically equivalent. The fact that the respective thermodynamic potentials $s(u, \underline{\sigma})$, used in EIT, and $s^{**}(u, \underline{w})$ used in CDF are not related by a Legendre transform means that they are not thermodynamically equivalent, except in the case where η/τ does not depend on the structure or on the shear rate. In contrast, a Legendre-transform

relation between the internal-variable entropy $s(u, \underline{\underline{C}})$, having as variable the
 255 conformation tensor $\underline{\underline{C}}$ of a dilute polymer solution, and the EIT entropy $s(u, \underline{\underline{\sigma}})$
 was shown in [30], in the linear regime.

5.2. GENERIC formalism

GENERIC formalism is a powerful and elegant tool for the analysis of highly
 nonlinear situations, expressing the evolution of any variable A_i as

$$\frac{dA_i}{dt} = \{A, E\} + [A, S] \quad (30)$$

260 with E the energy, S the entropy, $\{\dots\}$ the Poisson (antisymmetric) brackets
 and $[\dots]$ a dissipative (symmetric) brackets. Given a set of dynamical variables
 A_i and the form of E and S , (30) sets a number of physical basic requirements
 on the evolution equations. Nonlinearities in GENERIC are more diverse than
 in (3), because nonlinear terms, for instance, like $\underline{\underline{\sigma}} \cdot \underline{\underline{\sigma}}$ may be also present. Here,
 265 we consider the particular situation where the nonlinear viscoelastic equation
 (3) is used. Several years ago, in the framework of the GENERIC formalism
 [5, 3, 4], it was already pointed out by Ottinger and Grmela [4] that the use of
 the **extra stress** $\underline{\underline{\sigma}}$ as independent variable of the non-equilibrium entropy in
 EIT was not satisfactory beyond the linear regime. In fact, they found equation
 270 (3) for dilute polymer solution as a particular result of the GENERIC approach.
 For that particular case, they proposed to use as independent variable $\underline{\underline{\sigma}}/nk_{\text{B}}T$,
 n being the macromolecular number density (per unit volume of solution) and
 k_{B} Boltzmann constant, instead of $\underline{\underline{\sigma}}$. Since for polymer dilute solutions one
 has $\eta = nk_{\text{B}}T\tau$, this suggestion was leading to the use of $\tau\underline{\underline{\sigma}}/\eta$ as independent
 275 thermodynamic variable. In the conservation-dissipation formalism it seems
 $\tau\underline{\underline{\sigma}}/\eta T$ that (i. e. $\underline{\underline{w}}$) would be a more suited variable than $\underline{\underline{\sigma}}$ itself. Both
 proposals lead to result (3) in the isothermal situation. In fact, in the nonlinear
 domain, GENERIC is wider and more systematic than EIT or CDF, but much
 more demanding and richer in some aspects especially because the Hamiltonian
 280 requirement on the evolution equations leads to a deep structure in the non-
 dissipative terms (which is lacking in usual thermodynamic theories) and other

nonlinearities than those included in (3) may arise [5, 3, 4, 31].

In particular, Grmela and Ottinger [4] obtain the non-equilibrium entropy for the polymer contribution

$$s_p = \frac{1}{2}nk_B \int [\text{tr}(\frac{\underline{\underline{\Pi}}}{nk_BT}) + \ln \det(\underline{\underline{U}} - \frac{\underline{\underline{\Pi}}}{nk_BT})] d^3\vec{r} \quad (31)$$

285 with $\underline{\underline{U}}$ the unit tensor, and $\underline{\underline{\Pi}}$ the polymer pressure tensor, whose non-equilibrium part is $\underline{\underline{\sigma}}$, for which they find

$$\underline{\underline{\Pi}} = nk_BT(C\underline{\underline{C}}) \cdot (\underline{\underline{U}} - C\underline{\underline{C}}) \quad (32)$$

where $\underline{\underline{C}}$ is the macromolecular conformation tensor, and C a scalar quantity properly chosen so that at equilibrium $C\underline{\underline{C}} = \underline{\underline{U}}$. Note that (32) is more general than the usual microscopic expression [5, 13]

$$\underline{\underline{\Pi}} = nk_BT(\underline{\underline{U}} - C\underline{\underline{C}}) \quad (33)$$

290 Expression (32) reduces to (33) for situations not too far from equilibrium, i.e. when $C\underline{\underline{C}}$ is close to $\underline{\underline{U}}$. This formalism may be generalized to more complex systems (concentrated polymer solutions, polymer melts, etc.). Here we have mentioned it to illustrate from an independent perspective that: a) the use of $\underline{\underline{\Pi}}$ or $\underline{\underline{\sigma}}$ as independent variables is suited in linear situation but in nonlinear
295 situations, the thermodynamic conjugate of the stress tensor, either the given by $\underline{\underline{\Pi}}$ or $\underline{\underline{\sigma}}$, is a more suitable variable; b) it is also seen that the use of $\underline{\underline{\Pi}}$ directly related to a macroscopically measurable quantity, may encompass in a simple formalism several different microscopic situations in which $\underline{\underline{\Pi}}$ is related to more microscopic, structural quantities (as the conformation tensor $\underline{\underline{C}}$) in
300 different ways (as for instance, (32) and (33), to mention only two particular illustrations). Thus, writing the entropy in terms of a macroscopic variable like $\underline{\underline{\Pi}}$ or $\underline{\underline{\sigma}}$ may be especially useful from a practical macroscopic perspective when its expression in terms of internal variables related to the microstructure of the particular fluid is not directly controllable or not explicitly known.

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