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Rheological models with microstructural constraints

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Abdellatif Ait-Kadi passed away suddenly during the course of this research. The surviving authors express their gratitude to Abdellatif for our many hours of productive work and companionship.

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Abstract Rheological models of complex fluids with a physically restricted microstructure are analyzed to obtain general classes of dynamical evolution equations for these materials. These classes insure that the appropriate mathematical constraints, associated with each type of physical restriction, are consistently incorporated into the corresponding model development. Describing the microstructure of the complex fluid with a second-rank tensor variable, a general class of dynamical evolution equations is derived for three physically meaningful constraints associated with constancy of the invariants of this microstructural tensor. The physical rationale for each of these constraints is discussed, and a corresponding set of constrained dynamical evolution equations is derived in general terms.

Keywords Constrained microstructure · Volume conservation · Polymer blends · Rigid-rod polymers

Introduction

Many complex fluids are composed of microstructural constituents that have physical restrictions associated with any conceptual model employed for their description. As an example, although a deformable polymer chain may be modeled as an elastic dumbbell, free of constraints associated with its extension, a rigid rod-like polymer must be modeled with a dumbbell of constant extension (Bird et al. 1987). These physical restrictions of some complex fluids place mathematical constraints upon the entities used to model them; in the case of the rigid rod-like polymer, the inextensibility of the dumbbell must be quantified mathematically through the use of a vector of fixed length, thus describing the dumbbell orientation only.

In many models of complex fluids, with or without physical restrictions, a second-rank conformation tensor is used to describe the distribution of the microstructural constituents within the fluid: the eigenvalues and eigenvectors of this tensor quantify the extension, volume, and surface area of the average microstructural constituent. In this article, a sample of the scalar constraints that can be imposed on a second-rank tensor through its three invariants are examined mathematically. Thus, a general class of rheological models may be determined for each case that guarantees the satisfaction of the appropriate constraint under all possible flow conditions.

Each of the three scalar constraints on a second-rank tensor associated with constancy of a specific invariant is discussed below, allowing the reader to see clearly the physical restriction on the microstructural constituents that leads to the mathematical constraint under consideration. (Recall that in virtue of the Cayley-Hamilton theorem any other scalar associated with a second-rank tensor can be written as a function of three scalar invariants, so that the procedure for dealing with any scalar constraint can be inferred from examining only these three cases.) Then, a general class of evolution equations is derived, in a mathematically rigorous fashion, for each particular constraint. This then allows for the development of rheological models for complex fluids whose microstructural constituents are guaranteed to remain faithful to the physical restriction of the material under investigation.

In this article, attention is focused on complex fluids with a microstructure that can be quantified by a single, second-rank conformation tensor. It is quite difficult, in general, to derive constrained evolution equations for a second-rank tensor directly from a molecular model of the fluid's microstructure. This problem is avoided presently by consideration of the common mathematical structure underlying the dynamics of a second-rank microstructural tensor variable (Grmela and Carreau 1987; Grmela 1988, 1989; Beris and Edwards 1990a, 1990b, 1994; Edwards and Beris 1991a, 1991b; Grmela and Öttinger 1997; Öttinger and Grmela 1997; Dressler et al. 1999). By first revealing this mathematical structure for an unconstrained fluid, the appropriate constraint can be applied to this underlying structure. Then this constrained structure can be used to determine the proper evolution equations for the constrained fluid in a mathematically rigorous fashion.

The following section reveals the common underlying mathematical structure common to complex fluids that have a microstructure free of constraints. In subsequent sections, this structure is adapted to develop the constrained evolution equations discussed above for each scalar invariant of the second-rank conformation tensor.

Complex fluids free of constraints

The underlying mathematical structure of a complex fluid, with a microstructure free of constraints, has been investigated extensively over the past 15 years (Grmela and Carreau 1987; Grmela 1988, 1989; Beris and Edwards 1990a, 1990b, 1994; Edwards and Beris 1991a, 1991b; Grmela and Öttinger 1997; Öttinger and Grmela 1997; Dressler et al. 1999). The culmination of this investigation is the starting point for the current study: a general, but succinct, equation expressing the underlying mathematical structure (Grmela and Öttinger 1997; Öttinger and Grmela 1997) common to all physically realistic dynamical processes,

$$\frac{\partial \mathbf{f}}{\partial t} = \mathbf{L}(\mathbf{f}) \cdot \frac{\delta E(\mathbf{f})}{\delta \mathbf{f}} + \mathbf{M}(\mathbf{f}) \cdot \frac{\delta S(\mathbf{f})}{\delta \mathbf{f}} \tag{1}$$

This equation, usually called *GENERIC*, expresses the dynamics of the complex fluid variables, represented collectively by the symbol $\mathbf{f}$. For the case at hand, $\mathbf{f} = (\mathbf{u}, \rho, \varepsilon, \mathbf{C})$, where $\mathbf{u}$ is the fluid momentum density ($\mathbf{u} = \rho \mathbf{v}$), ϵ the internal energy density, ρ the mass density, and $\mathbf{C}$ the "conformation density" ($\mathbf{C} = \rho \mathbf{c}$). In Eq. (1), E and S are generating functionals representing the global fluid energy and entropy, respectively, and $\mathbf{L}$ and $\mathbf{M}$ are operator matrices that dictate the fluid dynamical properties of conservative and dissipative nature, respectively. This equation has been applied to complex fluids free of internal constraints through the abovementioned variable set, $\mathbf{f}$, in the recent past (Dressler et al. 1999).

As mentioned in the introduction, deriving general equations for constrained microstructures can be quite difficult when working in terms of the evolution equations for the appropriate variable set, such as those of Eq. (1). However, this can be accomplished relatively easily by using an equivalent expression to Eq. (1) (Grmela and Öttinger 1997; Edwards 1998; Edwards et al. 1998):

$$\frac{dF}{dt} = \{F, E\} + [F, S] \tag{2}$$

where F is an arbitrary functional of the variable set $\mathbf{f}$, and the French and square brackets denote the Poisson and dissipation brackets, respectively. Equations (1) and (2) are related through the relationship

$$\frac{dF}{dt} = \int \frac{\delta F}{\delta \mathbf{f}} \cdot \frac{\partial \mathbf{f}}{\partial t} d^3 r = \int \frac{\delta F}{\delta \mathbf{f}} \cdot \mathbf{L} \cdot \frac{\delta E}{\delta \mathbf{f}} d^3 r + \int \frac{\delta F}{\delta \mathbf{f}} \cdot \mathbf{M} \cdot \frac{\delta S}{\delta \mathbf{f}} d^3 r \tag{3}$$

and thus both the Poisson and dissipation brackets are determined by defining the operator matrices $\mathbf{L}$ and $\mathbf{M}$.

In the remainder of this article, attention is restricted to isothermal fluids. This allows the more convenient bracket expression of Eq. (3) to be rewritten in terms of a single generating functional, H, called the *Hamiltonian*, that represents the free energy of the fluid (Edwards 1998; Edwards et al. 1998). Furthermore, the variables of the mathematical problem description then reduce to $\mathbf{f} = (\rho, \mathbf{u}, \mathbf{C})$. Consequently, Eq. (2) becomes

$$\frac{dF}{dt} = \{F, H\} + [F, H] \tag{4}$$

where

$$
\begin{aligned}
\{F,H\} = & -\int \left[\frac{\delta F}{\delta u_\gamma}\nabla_\beta\left(\frac{\delta H}{\delta u_\beta}u_\gamma\right) - \frac{\delta H}{\delta u_\gamma}\nabla_\beta\left(\frac{\delta F}{\delta u_\beta}u_\gamma\right)\right]d^3r \\
& -\int \left[\frac{\delta F}{\delta \rho}\nabla_\beta\left(\frac{\delta H}{\delta u_\beta}\rho\right) - \frac{\delta H}{\delta \rho}\nabla_\beta\left(\frac{\delta F}{\delta u_\beta}\rho\right)\right]d^3r \\
& -\int \left[\frac{\delta F}{\delta C_{\alpha\beta}}\nabla_\gamma\left(\frac{\delta H}{\delta u_\gamma}C_{\alpha\beta}\right) - \frac{\delta H}{\delta C_{\alpha\beta}}\nabla_\gamma\left(\frac{\delta F}{\delta u_\gamma}C_{\alpha\beta}\right)\right]d^3r \\
& -\int C_{\alpha\gamma}\left[\frac{\delta H}{\delta C_{\alpha\beta}}\nabla_\gamma\left(\frac{\delta F}{\delta u_\beta}\right) - \frac{\delta F}{\delta C_{\alpha\beta}}\nabla_\gamma\left(\frac{\delta H}{\delta u_\beta}\right)\right]d^3r \\
& -\int C_{\beta\gamma}\left[\frac{\delta H}{\delta C_{\alpha\beta}}\nabla_\gamma\left(\frac{\delta F}{\delta u_\alpha}\right) - \frac{\delta F}{\delta C_{\alpha\beta}}\nabla_\gamma\left(\frac{\delta H}{\delta u_\alpha}\right)\right]d^3r \qquad (5)
\end{aligned}
$$

and

$$
\begin{aligned}
[F,H] = & -\int \Lambda_{\alpha\beta\gamma\varepsilon}\frac{\delta F}{\delta C_{\alpha\beta}}\frac{\delta H}{\delta C_{\gamma\varepsilon}}d^3r \\
& -\int B_{\alpha\beta\gamma\varepsilon\eta\nu}\left(\nabla_\gamma\frac{\delta F}{\delta C_{\alpha\beta}}\right)\left(\nabla_\nu\frac{\delta H}{\delta C_{\varepsilon\eta}}\right)d^3r \\
& -\int Q_{\alpha\beta\gamma\varepsilon}\left(\nabla_\alpha\frac{\delta F}{\delta u_\beta}\right)\left(\nabla_\gamma\frac{\delta H}{\delta u_\varepsilon}\right)d^3r \qquad (6)
\end{aligned}
$$

with Λ, $\mathbf{B}$, and $\mathbf{Q}$ being phenomenological matrix operators that quantify the microstructural relaxational effects, microstructural diffusion, and viscous dissipation, respectively (Grmela 1988; Beris and Edwards 1990a, 1990b, 1994). The arbitrary functional, F, is associated with the global volume integral, $F[\rho,\mathbf{u},\mathbf{C}] = \int f(\rho,\mathbf{u},\mathbf{C})d^3r$,where f is the local function of variables $\mathbf{f}$. Hence, for the present article, the functional derivatives appearing in the bracket expressions, above, take on the specific forms $\frac{\delta F}{\delta \mathbf{f}} = \frac{\partial f}{\partial \mathbf{f}}$,as discussed more thoroughly below.

Note that the Poisson bracket of Eq. (5) assumes that $\mathbf{C}$ deforms as a contravariant second-rank tensor; however, the methodology presented below applies equally well to the covariant version of Eq. (5), as expressed by Beris and Edwards (1990b). This covariant version of the Poisson bracket was also derived using Hamilton's Principle of Least Action (Beris and Edwards 1994).

Under the above definitions, the evolution equations for the fluid variables can be identified as

$$\frac{\partial \rho}{\partial t} = -\nabla_\gamma(\rho v_\gamma) \qquad (7)$$

$$\rho\frac{\partial v_\alpha}{\partial t} = -\rho v_\beta \nabla_\beta v_\alpha - \nabla_\alpha p + \nabla_\beta \sigma_{\alpha\beta} \qquad (8)$$

$$
\begin{aligned}
\frac{\partial C_{\alpha\beta}}{\partial t} = & - v_\gamma \nabla_\gamma C_{\alpha\beta} + C_{\alpha\gamma}\nabla_\gamma v_\beta + C_{\beta\gamma}\nabla_\gamma v_\alpha - \Lambda_{\alpha\beta\gamma\varepsilon}\frac{\delta A}{\delta C_{\gamma\varepsilon}} \\
& + \nabla_\gamma\left(B_{\alpha\beta\gamma\varepsilon\eta\nu}\nabla_\nu\frac{\delta A}{\delta C_{\varepsilon\eta}}\right) \qquad (9)
\end{aligned}
$$

with the extra stress tensor field appearing in Eq. (8) defined as

$$\sigma_{\alpha\beta} = 2C_{\beta\gamma}\frac{\delta A}{\delta C_{\alpha\gamma}} + Q_{\beta\alpha\gamma\varepsilon}\nabla_\gamma v_\varepsilon \qquad (10)$$

and the pressure according to the standard equilibrium thermodynamical relationship, $p = -a + \rho\frac{\partial a}{\partial \rho} + C_{\alpha\beta}\frac{\partial a}{\partial C_{\alpha\beta}}$. In these expressions, the Hamiltonian is assumed to have the form

$$
\begin{aligned}
H[\rho,\mathbf{u},\mathbf{C}] & = \int \frac{1}{2\rho}u_\gamma u_\gamma d^3r + A[\rho,\mathbf{C}] \\
& = \int \frac{1}{2\rho}u_\gamma u_\gamma d^3r + \int a(\rho,\mathbf{C})d^3r \qquad (11)
\end{aligned}
$$

Once $A[\rho,\mathbf{C}]$ and the operator matrices are specified, the entire set of evolution equations for the complex fluid without microstructural constraints is completed. The functional derivatives appearing in Eqs. (9) and (10) usually take on the simple form

$$\frac{\delta A}{\delta C_{\alpha\beta}} = \frac{\partial a}{\partial C_{\alpha\beta}} \qquad (12)$$

although sometimes more complicated expressions are required (Beris and Edwards 1994). Equations (7), (8), (9), and (10) thus represent a general class of thermodynamically consistent evolution equations for this material. (Note that in the following, the operator matrices $\mathbf{Q}$ and $\mathbf{B}$ are neglected for simplicity. Also, a word on alternative formulations is offered in the Appendix.).

Complex fluids with constant extension

Examples of complex fluids possessing a microstructure with constant extension are numerous. Their microstructures span length scales from Angstroms to millimeters, from low molecular-weight liquid crystals to short fiber-filled composites. Suspensions of rigid ellipsoids, colloids, semi- and inflexible polymers, etc. all possess microstructures whose base elements are not deformable but only orientable. These materials are described by mathematical entities that incorporate this inability to deform directly into the problem formulation by imposing the constraint that the first invariant of the conformation tensor is equal to unity. Because $I_1(\mathbf{C}) = \mathrm{tr}\mathbf{C}$ represents the sum of the eigenvalues of $\mathbf{C}$, it is really a physical measure of the extension of the local material microstructure. By fixing the trace at a particular value, in this case unity, the physical restriction of inextensibility is imposed upon the mathematical description of the material's dynamical behavior.

The constant extension constraint is seemingly an easy one to implement, whether directly into the evolution equations themselves or through the underlying mathematical structure described above. Many specific cases involving this constraint have been worked out in the past by inserting the constraint directly into the evolution equations (for examples, Hand 1962; Hinch and Leal 1976; Doi 1981; Doi and Edwards 1986; Marrucci and Maffettone 1989; Leslie 1979), although many of these have thereby produced dynamically incompatible evolution equations, as demonstrated below. Edwards et al. (1990, 1991) derived a general class of equations for liquid crystalline materials using the methodology discussed below by applying the constraint on the first invariant, $I_1(\mathbf{C}) = \mathrm{tr}\mathbf{C} = 1$, to the underlying mathematical structure, embodied by the Poisson and dissipation brackets. The methodology is in fact an application of a general method of reductions of Poisson structures known as Marsden-Weinstein reduction (Marsden and Weinstein 1974). In this section this methodology is illustrated for the constraint $\mathrm{tr}\mathbf{C} = 1$ so that it may also be applied in the next two sections to the other, more complicated, invariants of **C**.

The first step in applying a microstructural constraint to the underlying mathematical structure is to define an appropriate projection mapping of the variable **C**, which is free of constraints, to a new variable, **m**, which must comply with the constraint. This projection is called, in the context of the Marsden-Weinstein reduction, a "moment mapping." In the present case, this mapping is (Edwards et al. 1990, 1991; Beris and Edwards 1994)

$$\mathbf{C} \to \mathbf{m} = \frac{\mathbf{C}}{\mathrm{tr}\mathbf{C}} \tag{13}$$

Under this relationship it is easy to see that $\mathrm{tr}\mathbf{m} = 1$ under all conditions. Given this transformation, the Volterra derivatives appearing in the Poisson bracket must be transformed according to the chain rule expression (Edwards et al. 1990, 1991; Beris and Edwards 1994)

$$\frac{\delta F}{\delta C_{\alpha\beta}} \to \frac{\delta F}{\delta m_{\gamma\varepsilon}} \frac{\partial m_{\gamma\varepsilon}}{\partial C_{\alpha\beta}} = \frac{\delta F}{\delta m_{\gamma\varepsilon}} \frac{1}{\mathrm{tr}\mathbf{C}} \left(\delta_{\alpha\gamma}\delta_{\beta\varepsilon} - m_{\gamma\varepsilon}\delta_{\alpha\beta}\right) \tag{14}$$

Under this transformation, the bracket of Eq. (5) becomes (Edwards et al. 1990, 1991; Beris and Edwards 1994)

$$\begin{aligned}
\{F,H\} = &-\int \left[\frac{\delta F}{\delta u_\gamma}\nabla_\beta\left(\frac{\delta H}{\delta u_\beta}u_\gamma\right) - \frac{\delta H}{\delta u_\gamma}\nabla_\beta\left(\frac{\delta F}{\delta u_\beta}u_\gamma\right)\right] d^3r \\
&-\int \left[\frac{\delta F}{\delta \rho}\nabla_\beta\left(\frac{\delta H}{\delta u_\beta}\rho\right) - \frac{\delta H}{\delta \rho}\nabla_\beta\left(\frac{\delta F}{\delta u_\beta}\rho\right)\right] d^3r \\
&-\int \left[\frac{\delta F}{\delta m_{\alpha\beta}}\frac{\delta H}{\delta u_\gamma}\nabla_\gamma m_{\alpha\beta} - \frac{\delta H}{\delta m_{\alpha\beta}}\frac{\delta F}{\delta u_\gamma}\nabla_\gamma m_{\alpha\beta}\right] d^3r \\
&-\int m_{\alpha\gamma}\left[\frac{\delta H}{\delta m_{\alpha\beta}}\nabla_\gamma\left(\frac{\delta F}{\delta u_\beta}\right) - \frac{\delta F}{\delta m_{\alpha\beta}}\nabla_\gamma\left(\frac{\delta H}{\delta u_\beta}\right)\right] d^3r \\
&-\int m_{\beta\gamma}\left[\frac{\delta H}{\delta m_{\alpha\beta}}\nabla_\gamma\left(\frac{\delta F}{\delta u_\alpha}\right) - \frac{\delta F}{\delta m_{\alpha\beta}}\nabla_\gamma\left(\frac{\delta H}{\delta u_\alpha}\right)\right] d^3r \\
&+2\int m_{\alpha\beta}m_{\gamma\varepsilon}\left[\frac{\delta H}{\delta m_{\gamma\varepsilon}}\nabla_\alpha\left(\frac{\delta F}{\delta u_\beta}\right) - \frac{\delta F}{\delta m_{\gamma\varepsilon}}\nabla_\alpha\left(\frac{\delta H}{\delta u_\beta}\right)\right] d^3r
\end{aligned} \tag{15}$$

The above bracket guarantees that the conservative dynamics of the system satisfy the required constraint. In order to guarantee the same for the dissipative dynamics, a similar substitution must be applied to the dissipation bracket of Eq. (6); however, only one of the two Volterra derivatives appearing in the first integral of Eq. (6) must be transformed according to Eq. (14). The Poisson bracket is linear in $\frac{\delta F}{\delta \mathbf{C}}$ and $\frac{\delta H}{\delta \mathbf{C}}$,whereas the dissipation bracket is bilinear. Consequently, the constraint can be guaranteed most simply by transforming just one of the derivatives. As an analogy, for a bilinear equation with two roots, say $xy–y–\mathbf{2}x+\mathbf{2}=0$, the expression is satisfied when either $x=1$ or $y=2$. It is not necessary for both $x=1$ and $y=2$ to be valid in order to satisfy this equation. Given the phenomenological nature of the dissipation, there is thus no point in transforming both derivatives according to Eq. (14). Transforming the Volterra derivative for the arbitrary functional F according to Eq. (14) thus gives a proper, yet general, dissipation bracket for the constrained variable **m**:

$$\begin{aligned}
[F,H] = &-\int \Lambda_{\alpha\beta\gamma\varepsilon}\frac{\delta F}{\delta m_{\alpha\beta}}\frac{\delta H}{\delta m_{\gamma\varepsilon}} d^3r \\
&+\int \Lambda_{\theta\theta\gamma\varepsilon} m_{\alpha\beta}\frac{\delta F}{\delta m_{\alpha\beta}}\frac{\delta H}{\delta m_{\gamma\varepsilon}} d^3r
\end{aligned} \tag{16}$$

where it is realized that the matrix operator and the Hamiltonian now depend on **m** rather than **C**: Λ(**m**) and H[**u**,**m**]. Thus, for arbitrary expressions for these quantities, the constraint on the microstructure is guaranteed to be imposed upon the evolution equations determined from these bracket structures. These evolution equations can be obtained from Eqs. (4), (15), and (16) as Eqs. (7), (8), and

$$\begin{aligned}
\frac{\partial m_{\alpha\beta}}{\partial t} = &- v_\gamma\nabla_\gamma m_{\alpha\beta} + m_{\gamma\alpha}\nabla_\gamma v_\beta \\
&+ m_{\beta\gamma}\nabla_\gamma v_\alpha - 2m_{\alpha\beta}m_{\gamma\varepsilon}\nabla_\gamma v_\varepsilon \\
&- \Lambda_{\alpha\beta\gamma\varepsilon}\frac{\delta A}{\delta m_{\gamma\varepsilon}} + \Lambda_{\varsigma\varsigma\gamma\varepsilon} m_{\alpha\beta}\frac{\delta A}{\delta m_{\gamma\varepsilon}}
\end{aligned} \tag{17}$$

where

$$\sigma_{\alpha\beta} = 2m_{\beta\gamma}\frac{\delta A}{\delta m_{\alpha\gamma}} - 2m_{\alpha\beta}m_{\gamma\varepsilon}\frac{\delta A}{\delta m_{\gamma\varepsilon}} \tag{18}$$

and $p = -a + \rho\frac{\partial a}{\partial \rho}$. Note that the Volterra derivatives appearing in these expressions are defined analogously to Eq. (12). Also note that the extra stress tensor for materials with inextensible microstructures, Eq. (18), possesses an additional term that arises solely on account of the mathematical nature of the imposed constraint. Thus the Poisson bracket, whence the extra stress tensor field arises, demonstrates convincingly that placing a microstructural constraint upon the evolution equations implies a similar constraint upon the extra stress tensor associated with the microstructure. This point has been neglected in many past works that dealt with mathematical descriptions of materials with inextensible microstructures.

Equations (7), (8), (17), and (18) thus provide a general class of evolution equations that describe materials with an inextensible microstructure. By defining physically proper expressions for the free energy, A, and the matrix operator, Λ, (and, if necessary, the other dissipative matrix operators as well) specialized models can be obtained for various complex fluids possessing this microstructural restriction. Particular examples of reasonable expressions for A and Λ may be found in the literature (Grmela and Carreau 1987; Beris and Edwards 1990a, 1990b, 1994).

Complex fluids with volume preservation

Another important class of complex fluids with a physical restriction is composed of those fluids that experience volume-preserving microstructural deformations. Mathematically, this volume preservation of the microstructure manifests through the constraint that the third invariant of the conformation density tensor field, $I_3(\mathbf{C}) = \det \mathbf{C}$, is a constant, herein taken as unity. This implies that the result of the multiplication of all eigenvalues of this tensor field is unity as well. It is quite reasonable to expect that incompressible polymer melts or highly concentrated polymeric solutions might exhibit volume-preserving microstructural dynamics. Even more naturally, however, one would expect a suspension of incompressible droplets within a solvent to have a volume-preserving microstructure. If the droplets are incompressible, then as they deform and orient with regard to an imposed external field, the volume of the microstructure should remain constant. Micellar and colloidal systems also evince the possibility of requiring this constraint.

Twenty-five years ago, Leonov (1976) studied the dynamics of volume preserving deformations in polymeric fluids and, more recently, Ait-Kadi et al. (1999) have extended the Leonov-like models to a general class of constitutive equations, which was guaranteed to satisfy the volume-preserving constraint, $\det\mathbf{C} = 1$. However, this class of constitutive equations was developed by pasting the mathematical constraint cited above *onto* the *GENERIC* framework, rather than by developing it *through* the framework. As a consequence, the results obtained by Ait-Kadi et al. (1999) are not as general as they could be and, therefore, place severe restrictions on the class of allowable constitutive equations. In this section the volume-preserving constraint on the complex fluid microstructure is inserted directly into the *GENERIC* framework, just as the inextensibility constraint was so treated in the previous section.

To quantify the volume-preserving constraint mathematically, a new transformation of the variable $\mathbf{C}$ must be defined to ensure that $\det\mathbf{C} = 1$. This transformation is similar to Eq. (13):

$$\mathbf{C} \to \mathbf{q} = \frac{\mathbf{C}}{\left(\det \mathbf{C}\right)^{1/3}} \tag{19}$$

Hence $\det\mathbf{q} = 1$ always. Note that this transformation implies that

$$\mathbf{q}^{-1} = \mathbf{C}^{-1}(\det \mathbf{C})^{1/3} \tag{20}$$

Also note that $\mathbf{C}$ is again assumed to be a contravariant deformation tensor. For polymer blends, as well as other multiphase materials, it might be more appropriate to use a covariant deformation measure. Again, the methodology described herein can be applied easily to a covariant deformation tensor through the appropriate modification of Eq. (5).

Under the transformation of Eq. (19), the Volterra derivatives appearing in the Poisson bracket of Eq. (5) become

$$\frac{\delta F}{\delta C_{\alpha\beta}} \to \frac{1}{(\det \mathbf{C})^{1/3}} \frac{\delta F}{\delta q_{\gamma\varepsilon}} \left(\delta_{\alpha\gamma}\delta_{\beta\varepsilon} - \frac{1}{3} q_{\gamma\varepsilon} q^{-1}_{\alpha\beta} \right) \tag{21}$$

Accordingly, the Poisson bracket of Eq. (5) becomes

$$\begin{aligned}
\{F, H\} = &- \int \left[\frac{\delta F}{\delta u_\gamma} \nabla_\beta \left(\frac{\delta H}{\delta u_\beta} u_\gamma \right) - \frac{\delta H}{\delta u_\gamma} \nabla_\beta \left(\frac{\delta F}{\delta u_\beta} u_\gamma \right) \right] d^3r \\
&- \int \left[\frac{\delta F}{\delta \rho} \nabla_\beta \left(\frac{\delta H}{\delta u_\beta} \rho \right) - \frac{\delta H}{\delta \rho} \nabla_\beta \left(\frac{\delta F}{\delta u_\beta} \rho \right) \right] d^3r \\
&- \int \left[\frac{\delta F}{\delta q_{\alpha\beta}} \frac{\delta H}{\delta u_\gamma} \nabla_\gamma q_{\alpha\beta} - \frac{\delta H}{\delta q_{\alpha\beta}} \frac{\delta F}{\delta u_\gamma} \nabla_\gamma q_{\alpha\beta} \right] d^3r \\
&- \int q_{\alpha\gamma} \left[\frac{\delta H}{\delta q_{\alpha\beta}} \nabla_\gamma \left(\frac{\delta F}{\delta u_\beta} \right) - \frac{\delta F}{\delta q_{\alpha\beta}} \nabla_\gamma \left(\frac{\delta H}{\delta u_\beta} \right) \right] d^3r \\
&- \int q_{\beta\gamma} \left[\frac{\delta H}{\delta q_{\alpha\beta}} \nabla_\gamma \left(\frac{\delta F}{\delta u_\alpha} \right) - \frac{\delta F}{\delta q_{\alpha\beta}} \nabla_\gamma \left(\frac{\delta H}{\delta u_\alpha} \right) \right] d^3r \\
&+ \frac{2}{3} \int q_{\alpha\beta} \left[\frac{\delta H}{\delta q_{\alpha\beta}} \nabla_\gamma \left(\frac{\delta F}{\delta u_\gamma} \right) - \frac{\delta F}{\delta q_{\alpha\beta}} \nabla_\gamma \left(\frac{\delta H}{\delta u_\gamma} \right) \right] d^3r
\end{aligned} \tag{22}$$

As before, the above bracket guarantees that the conservative dynamics of the volume preserving microstructure satisfy the constraint $\det\mathbf{q} = 1$. Transforming the Volterra derivative of the arbitrary functional, F, according to Eq. (21), and then substituting into the dissipation bracket of Eq. (6) subsequently leads to the dissipation bracket for the volume preserving microstructure:

$$\begin{aligned}
[F, H] = &- \int \Lambda_{\alpha\beta\gamma\varepsilon} \frac{\delta F}{\delta q_{\alpha\beta}} \frac{\delta H}{\delta q_{\gamma\varepsilon}} d^3r \\
&+ \frac{1}{3} \int \Lambda_{\alpha\beta\gamma\varepsilon} q_{\rho\eta} q^{-1}_{\alpha\beta} \frac{\delta F}{\delta q_{\rho\eta}} \frac{\delta H}{\delta q_{\gamma\varepsilon}} d^3r
\end{aligned} \tag{23}$$

where now $\Lambda(\rho,\mathbf{q})$ and $H[\rho, \mathbf{u}, \mathbf{q}]$.

Using the Poisson and dissipation brackets of Eqs. (22) and (23), the evolution equations for the volume preserving microstructural fluid are obtained as Eqs. (7), (8), and

$$\frac{\partial q_{\alpha\beta}}{\partial t} = -v_\gamma \nabla_\gamma q_{\alpha\beta} + q_{\gamma\alpha} \nabla_\gamma v_\beta + q_{\beta\gamma} \nabla_\gamma v_\alpha - \frac{2}{3} q_{\alpha\beta} \nabla_\gamma v_\gamma - \Lambda_{\alpha\beta\gamma\varepsilon} \frac{\delta A}{\delta q_{\gamma\varepsilon}} + \frac{1}{3} \Lambda_{\rho\eta\gamma\varepsilon} q_{\alpha\beta} q^{-1}_{\rho\eta} \frac{\delta A}{\delta q_{\gamma\varepsilon}} \tag{24}$$

where

$$\sigma_{\alpha\beta} = 2 q_{\beta\gamma} \frac{\delta A}{\delta q_{\alpha\gamma}} - \frac{2}{3} \delta_{\alpha\beta} q_{\gamma\varepsilon} \frac{\delta A}{\delta q_{\gamma\varepsilon}} \tag{25}$$

$$p = -a + \rho \frac{\partial a}{\partial \rho} \tag{26}$$

As in the preceding section, the Volterra derivatives appearing in Eqs. (24) and (25) are defined analogously to Eq. (12). Again, one finds that the microstructural constraint requires additional terms to be added to the extra stress tensor field expression, as required by the Poisson bracket of Eq. (22). For arbitrary Λ and A, Eqs. (7), (8), (24), (25), and (26) thus provide a system of evolution equations which are guaranteed to fulfill always this particular microstructural constraint.

A few remarks are in order regarding a comparison of Eqs. (24) and (25) with those derived by Maffettone and Minale (1998) and by Ait-Kadi et al. (1999). The Poison bracket, Eq. (22), was not identified by Ait-Kadi et al. (1999) and, as a consequence, the fourth term on the right-hand side of Eq. (24) is missing there; however, this term vanishes for incompressible fluids, which is the assumption used by Ait-Kadi et al. (1999). The dissipative part of the time evolution, i.e., the last two terms on the right-hand side of Eq. (24), becomes the same as that derived by Ait-Kadi et al. (1999) if the free energy depends only on $\frac{\mathrm{tr}\mathbf{C}}{(\det \mathbf{C})^{1/3}}$ and $\frac{\mathrm{tr}\mathbf{C}^{-1}}{(\det \mathbf{C})^{1/3}}$,and the kinetic coefficients are chosen as by Beris and Edwards (1994). Maffetone and Minale (1998) derived a volume-preserving set of time evolution equations in terms of a conformation tensor for characterizing droplets in immiscible mixtures. However, their analysis does not provide an expression for the extra stress tensor field. Grmela et al. (2001) do provide it by identifying the free energy for which the time evolution equations derived by Ait-Kadi et al. (1999) reduce to those derived by Maffettone and Minale (1998). Almusallam et al. (2000) also derived a constitutive model that at least approximately conserved volume for predicting droplet shapes and stresses in immiscible blends. Their procedure for ensuring volume preservation assumes that the droplet volume can be defined by a scalar function of the three invariants of a second-rank tensor; however, it appears that their methodology for guaranteeing this constraint is more restrictive than the methodology proposed herein.

Complex fluids with area preservation

The only remaining scalar invariant of $\mathbf{C}$ to be examined is the second, $I_2(\mathbf{C}) = \frac{1}{2}\left[(\mathrm{tr}\mathbf{C})^2 - \mathrm{tr}(\mathbf{C}\cdot\mathbf{C})\right]$. Mathematically, the constraint that $I_2 = 1$ at all times can be construed as one of area preservation from the corresponding expression for this invariant in terms of the eigenvalues of $\mathbf{C}$ (see, for example, Beris and Edwards 1994). This is also apparent by interpreting a second-rank tensor as an average of the vector product of $\langle \mathbf{R} \times \mathbf{R} \rangle^2 \propto I_2(\langle \mathbf{RR} \rangle)$. Physically, this constraint might be used to enforce a microstructural requirement of inflexible appendages on a branched polymer or copolymer. In a branched or star polymer where the branch angles must remain constant, the microstructure must be described with more than one end-to-end vector. To describe the deformation of these molecules under flow, these vectors form into multiple second-rank tensors. The tensors involving dyads of different vectors should be required to maintain the constraint that $I_2 = 1$.

In order to derive a set of dynamical evolution equations for a material with this sort of microstructural constraint, it is necessary to proceed as in the preceding sections. This constraint may be quantified mathematically using the transformation

$$z_{\alpha\beta} = \sqrt{2} \frac{C_{\alpha\beta}}{\left(C_{\gamma\gamma} C_{\varepsilon\varepsilon} - C_{\gamma\varepsilon} C_{\gamma\varepsilon}\right)^{1/2}} \tag{27}$$

Consequently, the Volterra derivatives appearing in the Poisson bracket of Eq. (5) are

$$\frac{\delta F}{\delta C_{\alpha\beta}} = \frac{\sqrt{2}}{\left(C_{\gamma\gamma} C_{\varepsilon\varepsilon} - C_{\gamma\varepsilon} C_{\gamma\varepsilon}\right)^{1/2}} \times \left[\frac{\delta F}{\delta z_{\alpha\beta}} - \frac{1}{2} \frac{\delta F}{\delta z_{\gamma\varepsilon}} z_{\gamma\varepsilon} z_{\eta\eta} \delta_{\alpha\beta} + \frac{1}{2} \frac{\delta F}{\delta z_{\gamma\varepsilon}} z_{\gamma\varepsilon} z_{\alpha\beta}\right] \tag{28}$$

so that this bracket becomes

$$\begin{aligned}
\{F,H\} = &-\int \left[\frac{\delta F}{\delta u_\gamma} \nabla_\beta \left(\frac{\delta H}{\delta u_\beta} u_\gamma\right) - \frac{deltaH}{\delta u_\gamma} \nabla_\beta \left(\frac{\delta F}{\delta u_\beta} u_\gamma\right)\right] d^3r \\
&-\int \left[\frac{\delta F}{\delta \rho} \nabla_\beta \left(\frac{\delta H}{\delta u_\beta} \rho\right) - \frac{\delta H}{\delta \rho} \nabla_\beta \left(\frac{\delta F}{\delta u_\beta} \rho\right)\right] d^3r \\
&-\int \left[\frac{\delta F}{\delta z_{\alpha\beta}} \frac{\delta H}{\delta u_\gamma} \nabla_\gamma z_{\alpha\beta} - \frac{\delta H}{\delta z_{\alpha\beta}} \frac{\delta F}{\delta u_\gamma} \nabla_\gamma z_{\alpha\beta}\right] d^3r \\
&-\int z_{\alpha\gamma} \left[\frac{\delta H}{\delta z_{\alpha\beta}} \nabla_\gamma \left(\frac{\delta F}{\delta u_\beta}\right) - \frac{\delta F}{\delta z_{\alpha\beta}} \nabla_\gamma \left(\frac{\delta H}{\delta u_\beta}\right)\right] d^3r \\
&-\int z_{\beta\gamma} \left[\frac{\delta H}{\delta z_{\alpha\beta}} \nabla_\gamma \left(\frac{\delta F}{\delta u_\alpha}\right) - \frac{\delta F}{\delta z_{\alpha\beta}} \nabla_\gamma \left(\frac{\delta H}{\delta u_\alpha}\right)\right] d^3r \\
&+\int z_{\gamma\varepsilon} z_{\rho\eta} z_{\varsigma\varsigma} \left[\frac{\delta H}{\delta z_{\rho\eta}} \nabla_\gamma \left(\frac{\delta F}{\delta u_\varepsilon}\right) - \frac{\delta F}{\delta z_{\rho\eta}} \nabla_\gamma \left(\frac{\delta H}{\delta u_\varepsilon}\right)\right] d^3r \\
&-\int z_{\gamma\varepsilon} z_{\varepsilon\varsigma} z_{\rho\eta} \left[\frac{\delta H}{\delta z_{\rho\eta}} \nabla_\gamma \left(\frac{\delta F}{\delta u_\varsigma}\right) - \frac{\delta F}{\delta z_{\rho\eta}} \nabla_\gamma \left(\frac{\delta H}{\delta u_\varsigma}\right)\right] d^3r
\end{aligned} \tag{29}$$

Similarly, the proper dissipation bracket for this system can be obtained as

$$[F,H] = -\int \Lambda_{\alpha\beta\gamma\varepsilon}\frac{\delta F}{\delta z_{\alpha\beta}}\frac{\delta H}{\delta z_{\gamma\varepsilon}}d^3r + \frac{1}{2}\int \Lambda_{\theta\theta\gamma\varepsilon}z_{\rho\eta}z_{\varsigma\varsigma}\frac{\delta F}{\delta z_{\rho\eta}}\frac{\delta H}{\delta z_{\gamma\varepsilon}}d^3r - \int \Lambda_{\alpha\beta\gamma\varepsilon}z_{\rho\eta}z_{\alpha\beta}\frac{\delta F}{\delta z_{\rho\eta}}\frac{\delta H}{\delta z_{\gamma\varepsilon}}d^3r \tag{30}$$

so that now $H[\rho,\mathbf{u},\mathbf{z}]$ and $\Lambda(\rho,\mathbf{z})$.

In light of the brackets of Eqs. (29) and (30), the evolution equations for the area preserving microstructural fluid are calculated as Eqs. (7), (8), and

$$\frac{\partial z_{\alpha\beta}}{\partial t} = -v_\gamma\nabla_\gamma z_{\alpha\beta} + z_{\gamma\alpha}\nabla_\gamma v_\beta + z_{\gamma\beta}\nabla_\gamma v_\alpha - z_{\alpha\beta}z_{\gamma\varepsilon}z_{\varsigma\varsigma}\nabla_\gamma v_\varepsilon + z_{\alpha\beta}z_{\gamma\varepsilon}z_{\varepsilon\varsigma}\nabla_\gamma v_\varsigma - \Lambda_{\alpha\beta\gamma\varepsilon}\frac{\delta A}{\delta z_{\gamma\varepsilon}} + \frac{1}{2}\Lambda_{\rho\rho\gamma\varepsilon}z_{\alpha\beta}z_{\eta\eta}\frac{\delta A}{\delta z_{\gamma\varepsilon}} - \frac{1}{2}\Lambda_{\rho\eta\gamma\varepsilon}z_{\alpha\beta}z_{\rho\eta}\frac{\delta A}{\delta z_{\gamma\varepsilon}} \tag{31}$$

where

$$\sigma_{\alpha\beta} = 2z_{\beta\gamma}\frac{\delta A}{\delta z_{\gamma\alpha}} - z_{\alpha\beta}z_{\rho\eta}z_{\varsigma\varsigma}\frac{\delta A}{\delta z_{\rho\eta}} + z_{\beta\varepsilon}z_{\varepsilon\alpha}z_{\rho\eta}\frac{\delta A}{\delta z_{\rho\eta}} \tag{32}$$

and $p = -a + \rho\frac{\partial a}{\partial \rho}$. As in the prior cases, the Volterra derivatives appearing in the expressions above are defined analogously to Eq. (12), and again the expression for the extra stress tensor field, Eq. (32), has additional terms as required by the microstructural constraint being applied through the Poisson bracket. For arbitrary $A[\rho,\mathbf{z}]$ and $\Lambda(\rho,\mathbf{z})$, Eqs. (7), (8), (31), and (32) thus provide the set of dynamical evolution equations that are compatible with the present microstructural constraint.

Conclusion

In this paper, consideration was taken of complex fluids whose internal structure can be well characterized by a symmetric second-rank conformation tensor field constrained by a mathematical restriction involving one of its three independent scalar invariants. The main results of the paper are families of governing equations (involving both the time evolution equations as well as expressions for the extra stress tensor) for rheological models whose solutions are guaranteed to satisfy the respective constraints and to agree with all known laws of thermodynamics. These families are parameterized by the fluid's free energy, as well as the kinetic coefficients entering into the dissipative part of the time evolution. It is in these two types of quantities where the individual nature of the complex fluid is expressed in the governing equations. An application of these results to a specific complex fluid consists of the following three steps: (i) specification of the proper constraint, (ii) specification of the free energy, and (iii) specification of the kinetic coefficients.

All constraints beyond those considered herein can be dealt with using the same methodology as illustrated in the body of the article. All further constraints can be represented as functions of the three independent invariants treated above. For example, if one wishes to use the constraint that $\frac{\det\mathbf{C}}{\mathrm{tr}\mathbf{C}} = 1$,then the methodology outlined above can be applied using the transformation

$$\mathbf{C} \to \mathbf{q} = \left(\frac{\mathrm{tr}\mathbf{C}}{\det\mathbf{C}}\right)^{1/2}\mathbf{C} \tag{33}$$

Furthermore, the results of this paper can also be easily extended to the case in which the constraints are not required to hold at all times, but to evolve in time in a way that is independent of the evolution of the conformation tensor itself.

An example of a complex fluid to which the results of this paper are applicable is a polymeric fluid (Bird et al. 1987). The conformation tensor represents, in this case, the deformation tensor of the macromolecules. It has been suggested (Bird et al. 1987) that the physical nature of some particular macromolecules can be well expressed by requiring that the trace of the conformation tensor is either kept constant or allowed to evolve in time in a way that is independent of the time evolution of the tensor itself. This particular situation has been worked out by Bird et al. (1987), and our results confirm their analysis. When constraints involving the other two invariants become a part of the analysis, the results of this paper represent new rheological equations of state. This is well seen, for example, in the case where the determinant of the conformation tensor is constrained. This situation arises, for instance, in immiscible blends where the conformation tensor serves to describe the shape of the droplets. The requirement of the incompressibility of the fluid inside the droplets is then expressed mathematically by constraining the determinant of the conformation tensor. Rheological models of this type have been investigated before by Leonov (1976), Maffettone and Minale (1998), Ait-Kadi et al. (1999), and Almusallam et al. (2000). The rheological equations derived there are all particular cases of the equations derived in this paper.

Appendix

Even though the formulation presented in the main body of the paper is complete, it is useful to regard it also in the light of some other types of formulations and arguments. First, note that the terms representing the dissipation in Eqs. (9) and (10), i.e., the last term on the right-hand side of Eq. (10) and the last two terms on the right-hand side of Eq. (9), can be recast in the forms of

$-\frac{\delta\Psi}{\delta\left(\frac{\delta H}{\delta \mathbf{u}}\right)}$ and $-\frac{\delta\Psi}{\delta\left(\frac{\delta H}{\delta \mathbf{C}}\right)}$,respectively, where the functional , called the *dissipation potential*, is given by

$$\begin{aligned}\Psi = &\int \frac{1}{2}\Lambda_{\alpha\beta\gamma\varepsilon}\frac{\delta H}{\delta C_{\alpha\beta}}\frac{\delta H}{\delta C_{\gamma\varepsilon}}d^3r \\ &+\int \frac{1}{2}B_{\alpha\beta\gamma\varepsilon\eta\nu}\left(\nabla_\gamma\frac{\delta H}{\delta C_{\alpha\beta}}\right)\left(\nabla_\nu\frac{\delta H}{\delta C_{\varepsilon\eta}}\right)d^3r \\ &+\int \frac{1}{2}Q_{\alpha\beta\gamma\varepsilon}\left(\nabla_\alpha\frac{\delta H}{\delta u_\beta}\right)\left(\nabla_\gamma\frac{\delta H}{\delta u_\varepsilon}\right)d^3r\end{aligned} \tag{A1}$$

The most significant aspect of the concept of the dissipation potential is that it allows one to formulate the dissipative part of the time evolution equations that depends nonlinearly on $\frac{\delta H}{\delta \mathbf{C}}$ and $\frac{\delta H}{\delta \mathbf{u}}$. The physical and geometrical significance of the dissipation potential has been recently investigated by Grmela (2002). From the historical point of view, the dissipation potential can be regarded as an appropriate generalization of the dissipation potential introduced by Rayleigh (1945). As in the main body of the paper, one can arrive at the constrained version of the dissipative part of the time evolution by a dissipation potential that depends, for the constant extension example, on $\frac{\delta H}{\delta C_{\alpha\beta}}$ only through its dependence on $\frac{\delta H}{\delta C_{\alpha\beta}} - \frac{1}{3}\frac{\delta H}{\delta C_{\gamma\gamma}}\delta_{\alpha\beta}$.

The second observation concerns the first term on the right-hand side of the Eq. (10) for the extra stress tensor field, σ. Note that one can alternatively derive it by using an argument that is weaker than the one used above. It follows from Eq. (4) that in the limit of non-dissipative time evolution, i.e., if $[F,H]=0$, then $\frac{dH}{dt}=0$ as a consequence of the antisymmetry property of the Poisson bracket. This now raises the following question: given Eqs. (7), (8), and (9) with $\Lambda=\mathbf{0}$ and $\mathbf{B}=\mathbf{0}$,what is the expression for σ appearing on the right-hand side of Eq. (8) with which the given time evolution equations imply $\frac{dH}{dt}=0$? This question has been answered by Grmela (1985), and later in a more general setting by Jongschaap (1990, 2001). The answer is the following: $\sigma_{\alpha\gamma} = -\frac{\delta H}{\delta C_{\beta\delta}}\frac{\delta \Xi_{\beta\delta}}{\delta(\nabla_\alpha v_\gamma)}$,where $\Xi_{\alpha\beta}(\mathbf{C},\nabla bfv)$ denotes the right-hand side of Eq. (9) with $\Lambda=\mathbf{0}$ and $\mathbf{B}=\mathbf{0}$. One can directly verify that this expression leads to the first term on the right-hand side of Eq. (10). Thus, this provides an alternative derivation of the first term on the right-hand side of Eq. (10), one that is based on the conservation of the free energy during the reversible time evolution. This requirement is weaker than the requirement that the reversible time evolution possesses a Hamiltonian structure.

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