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On the rheology of immiscible blends

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Abstract We propose a family of new models making a direct link between flow and structure for immiscible mixtures of viscoelastic fluids undergoing high deformation flows. The morphology is treated both at local (Doi-Ohta-type) and more macroscopic (droplet-like) scales. The governing equations, that include expressions for the extra stress tensor, agree with the conservation laws and with the observed compatibility with thermodynamics. In the particular case in which only one of the two characterizations of the morphology is used, extended versions of the Doi-Ohta and the Maffettone and Minale models are obtained. The extension consists of involving explicitly the free energy in the governing equations and completing the expressions for the extra stress tensor.

Key words Rheology · Immiscible blend · GENERIC

Introduction

Experimental observations of interfaces separating immiscible components of polymeric mixtures subjected to imposed hydrodynamic flows reveal an astounding complexity. Viewing the interface with the aid of our instinctive ability to recognize patterns we can, in many cases, identify several scales with several different patterns. For example, on a small scale we may see a pattern in the space and orientation distribution of small pieces of the interface, on a larger scale we may see a droplet-like patterns, and on a still larger scale a pattern of various clusters of the droplets. We shall use the term morphology to denote the structure of the interface.

Modeling of immiscible blends presents the following two challenges: first, one has to choose appropriate quantities characterizing the morphology and, second, one has to formulate equations governing their time evolution in the context of the time evolution of the blend as a whole. Our aim in this paper is to contribute to the understanding of these two problems.

In the following sections we derive a new family of models with a two-level characterization of the morphology. The one level is the one used in the Doi-Ohta theory (Doi and Ohta 1991) and the other is the one used in the Maffettone and Minale theory (Maffettone and Minale 1998). We are thus introducing a setting in which the physics that is behind both of these theories is combined into one intrinsically consistent unit. However, even if we select from the family only those models in which the one-level characterization of the morphology is used, we obtain models that extend the Doi-Ohta and the Maffettone-Minale models. The extension consists of involving explicitly the free energy in the formulation of both models, providing a more complete formula for the extra stress tensor in the setting of the Doi-Ohta model, and providing a formula for the extra stress tensor in the Maffettone-Minale model (in its original derivation the extra stress tensor is absent).

As for the comparison with experimental observations, we limit ourselves in this paper to the fundamental experimental observations of the conservation of mass

and momentum and the compatibility with thermodynamics (i.e., the observation according to which externally unforced systems are seen to reach eventually states at which their behavior is seen to be well described by equilibrium thermodynamics). All models in the family are proven to agree with these fundamental experimental observations. We would like to emphasize that this type of verification of rheological models is rarely done (for example such verification is missing in the original papers in which the Doi-Ohta and the Maffettone-Minale models were introduced). A comparison of predictions of the models with experimental observations of the rheological properties and the morphology requires one first of all to select specific fluids and the quantities that represent them in the family. They are: the free energy and kinetic coefficients. The correspondence between these quantities and the fluids will be the subject of the next stage of the investigation. At this stage, only a small subfamily of the models introduced in this paper has been investigated in this detail. They are the family of the Doi-Ohta-like models (see Bousmina et al. 2001), the Maffettone-Minale model (in this model it was only the morphology that could be compared with experimental observations), and the "volume preserving" models of Ait-Kadi et al. (1999) (the Maffettone-Minale model is one of these models) whose predictions have been however investigated and compared with results of experiments only in the context of polymer solutions.

Two-stage modeling

The modeling developed in classical hydrodynamics proceeds in two stages. In the first stage one chooses a family of experimental observations and looks for a structure of the governing equations that guarantees agreement between the model predictions and the chosen observations. The selected family of experimental observations is composed by the conservation laws of the total mass, momentum, and energy, and by the compatibility with thermodynamics. In the second stage, a particular realization of the structure identified in the first stage is found. The realization (also called a constitutive relation) reflects the particular nature of the fluid under consideration.

Classical hydrodynamics considers only simple fluids whose states are completely and universally described by classical hydrodynamic fields. The structure identified in the first stage is the structure of local conservation laws (derivative with respect to time equals divergence of a flux). Immiscible mixtures are not however simple fluids. The time evolution of the morphology cannot be separated from the time evolution of the hydrodynamic fields. The classical hydrodynamic fields do not suffice to describe states of immiscible mixtures. If we want to follow the two-stage modeling developed in classical hydrodynamics in the context of immiscible mixtures, we have first to find a new structure that can also be applied for general state variables. Such a structure has been suggested and is called GENERIC (General Equation for the Non-Equilibrium Reversible-Irreversible Coupling) (Grmela and Öttinger 1997; Öttinger and Grmela 1997). The structure is based on the observation (Grmela 1984, 1988) that while the structure of local conservation laws does not extend beyond the realm of classical hydrodynamics the other structure of classical hydrodynamic equations, namely the Hamiltonian structure discovered by Clebsch (1895), does. In the rest of this section we shall recall its mathematical formulation. The second stage, consisting of a search for its realization expressing immiscible mixtures is presented later.

We assume in this paper that the system under consideration is kept under isothermal conditions. The constant temperature is denoted by T. Let x be the set of state variables. The time evolution of x, that is guaranteed to agree with the observed conservation laws of total mass, momentum, and energy, and with thermodynamics, is governed by

$$\frac{\partial x}{\partial t} = L \frac{\delta \Phi}{\delta x} - \frac{\delta \Psi}{\delta(\delta \Phi / \delta x)} \tag{1}$$

where t denotes the time, Φ is the Helmholtz free energy, $\Phi = E - TS + \mu N$, E, S, and N are respectively the global energy, the global entropy, and the global number of moles of the system, μ the chemical potential; $\delta \Phi / \delta x$ is the conjugate variable of x ($\delta / \delta x$ denotes the functional derivative). By the symbol L we denote the Poisson bivector and $\Psi(\delta \Phi / \delta x)$ is a dissipation potential. The GENERIC equation introduced in previous works (Grmela and Öttinger 1997; Öttinger and Grmela 1997) reduces to Eq. (1) since the temperature is assumed to be kept constant during the whole process of the evolution.

An operator L is a Poisson bivector if the following is satisfied. Let A and B be real valued functions of x. We construct a bracket $\{A, B\} = \left\langle \frac{\delta A}{\delta x}, L \frac{\delta B}{\delta x} \right\rangle$ where $\langle , \rangle$ is the inner product. This bracket is called a Poisson bracket if (i) $\{A,B\} = -\{B,A\}$ (this means that L is a skew symmetric matrix, i.e., $L_{ij} = -L_{ji}$), (ii) the Jacobi identity $\{\{B,C\}, A\} + \{\{A,B\}, C\} + \{\{C,A\}, B\} = 0$ holds. We require moreover that the Poisson bivector is degenerated so that $L \frac{\delta S}{\delta x} = 0$ and $L \frac{\delta N}{\delta x} = 0$. From the physical viewpoint, the Poisson bivector L expresses the Poisson kinematics of the state variables x.

The dissipation potential Ψ is a real valued function of $\delta \Phi / \delta x$ satisfying the following properties: (i) $\Psi(0) = 0$, (ii) Ψ reaches its minimum at 0, (iii) Ψ is a convex in a neighborhood of 0, and (iv) Ψ is degenerate so that $\left\langle \frac{\delta E}{\delta x}, \frac{\delta \Psi}{\delta(\delta \Phi / \delta x)} \right\rangle = \left\langle \frac{\delta N}{\delta x}, \frac{\delta \Psi}{\delta(\delta \Phi / \delta x)} \right\rangle = 0$. A particular

example of the dissipation potential that is often used in applications is the following: $\Psi\left(\frac{\delta A}{\delta x}\right) = \frac{1}{2}\left\langle\frac{\delta A}{\delta x}, M\frac{\delta A}{\delta x}\right\rangle$ where M is a nonnegative symmetric matrix satisfying $M\frac{\delta E}{\delta x} = 0$, $M\frac{\delta N}{\delta x} = 0$. It is easy to verify that Eq. (1) implies the conservation of energy $\left(\frac{dE}{dt} = 0\right)$, conservation of number of moles $\left(\frac{dN}{dt} = 0\right)$, and the dissipation inequality $\left(\frac{d\Phi}{dt} = \left\langle\frac{\delta\Phi}{\delta x}, L\frac{\delta\Phi}{\delta x}\right\rangle - \left\langle\frac{\delta\Phi}{\delta x}, \frac{\delta\Psi}{\delta(\delta\Phi/\delta x)}\right\rangle \leq 0\right)$. Equation (1) can also be written as $dA/dt = \{A, \Phi\} - \left\langle\frac{\delta A}{\delta x}, \frac{\delta\Psi}{\delta(\delta\Phi/\delta x)}\right\rangle$ that is required to hold for all sufficiently regular real valued functions A.

A particular realization of Eq. (1) consists of the following four steps: (i) specification of the state variables x, (ii) specification of their Poisson kinematics (i.e., specification of L), (iii) specification of the dissipative structure (i.e., specification of the dissipation potential Ψ), (iv) specification of the Helmholtz free energy Φ. The first step is discussed in the next section, the remaining three steps in the section following that.

State variables

In this paper we consider an isothermal immiscible mixture of two viscoelastic fluids: a fluid (A) that plays the role of the matrix in which the other fluid (B) is dispersed. The interface between the fluids (A) and (B), denoted here by the symbol (Int), is seen as a third component with its own rheological properties.

In this section we discuss the state variables that are suitable for describing the states of such a mixture. Since our desire is always to keep the model as simple as possible, we look for the smallest possible number of state variables that are able to describe the phenomena of interest. There is no universal set of state variables and no universal rule that can be used to select them. The process of selection is a trial-and-error process guided by experience and physical insight.

We begin with the state variables describing the overall behavior of the mixture. We naturally choose the classical hydrodynamic fields. Since we consider the mixture under consideration to be incompressible and kept under isothermal conditions, the only state variable that describes the overall behavior is thus the momentum field $\mathbf{u}(\mathbf{r})$, $\mathbf{r}$ being the position vector.

Interface

The interface separating the fluids (A) and (B) is a two-dimensional surface imbedded in the three dimensional space of position vectors, i.e., the image of a mapping $\mathfrak{I}$: $\mathbf{R}^2 \rightarrow \mathbf{R}^3$. Ideally, it is this mapping that we should choose to describe here the interface (Int). This is what is done in equilibrium statistical mechanics, where the equilibrium interface is found by minimizing the free energy. We may recall, for example, the Laplace relation between the curvature of the interface and the pressure difference between fluids A and B obtained in this way. At equilibrium, this detailed consideration of the interface is often feasible due to its relative simplicity. If we would however try to use the mapping $\mathfrak{I}$ as the state variable in dynamical theories, it would be essentially the same as if we were to insist on using position vectors and momenta of all atoms composing the fluids A and B to characterize their states. Due to the complexity of the interface and also in view of our interests (we do not need and do not want to know all the details of the interface), we have to replace $\mathfrak{I}$ by some incomplete (but pertinent to our purpose) characterization of the interface. Again, making analogy with the characterization of fluids, we look for appropriate distribution functions that will replace the complete microscopic characterization.

Batchelor (1970), Onuki (1987), and Doi and Ohta (1991) have suggested to describe states of the interface by one scalar field, denoted by Q($\mathbf{r}$), expressing the total interface area per unit volume, and one field of traceless symmetric tensor, $\mathbf{q}(\mathbf{r})$, having the physical meaning of a tensor expressing the orientation of a unit vector perpendicular to the interface. It has been shown in Grmela and Ait-Kadi (1994, 1998) and Grmela et al. (1998) that both these quantities can be conveniently combined into one symmetric positive definite tensor, $\mathbf{c}$. Here we call it an interfacial conformation tensor, or Batchelor-Onuki-Doi-Ohta tensor, in abbreviated form a BODO tensor. The tensor $\mathbf{c}$ is related to $\mathbf{q}$ and Q by the following one-to-one transformation:

$$c_{\alpha\beta} = \frac{1}{3}Q^2\delta_{\alpha\beta} + Qq_{\alpha\beta}; \quad \text{tr}\mathbf{c} = Q^2 \tag{2}$$

where α and β denote the coordinates, α, $\beta = 1, 2, 3$, and the summation convention over repeated indices is used, and δ is the Kronecker delta. The tensor $\mathbf{c}$ is the second moment of the distribution function of the vectors perpendicular to elements of the interface with the length measuring the surface area of the elements. The rheological models that use BODO tensor (Onuki 1987; Doi and Ohta 1991; Lee and Park 1994; Grmela and Ait-Kadi 1994, 1998; Grmela et al. 1998; Wagner et al. 1999; Wetzel and Tucker 1999; Tucker et al. 2000; Almusalam et al. 2000; Bousmina et al. 2001) have proved to be, in general, faithful to the reality (Lee and Park 1994; Takahashi et al. 1994a, b; Takahashi and Noda 1995; Okamoto et al. 1999; Yamane et al. 1998; Guenter and Baird 1996; Vinckier et al. 1996, 1997a, b, 1999; Minale et al. 1997; Kitade et al. 1997; Lacroix et al. 1997, 1998a, b, 1999; Riise et al. 1999; Iza and Bousmina 2000, Iza et al. 2001; Almusalam et al. 2000; Bousmina et al.

2001). At the same time, however, the experience with them shows their limitations. From the physical point of view, the limitation is clearly a consequence of the incompleteness of the characterization of the interface with BODO tensors. What BODO tensors express is an information about the local structure of the interface. What is completely missing is information about the larger scale morphology (a larger zoom on the structure) concerning macroscopic objects like droplets and clusters of droplets. We call here the large-scale morphology a global morphology and the morphology expressed by the BODO tensor a local morphology. It seems to be very likely that the local as well as the global morphologies influence the rheological properties of the mixture. We therefore look now for an appropriate state variable characterizing the global morphology.

To illustrate our approach, we limit ourselves in this paper to the global morphology corresponding to the droplet-like structure. A droplet is modeled as an ellipsoid. Its shape is thus described by a symmetric positive definite tensor denoted here by the symbol **b**. The new state variables are thus a scalar field n(**r**), denoting the number of droplets per unit volume and a field of conformation tensors **b**(**r**).

The local and global morphologies are clearly not completely independent; consequently the fields **c**(**r**) and (n(**r**), **b**(**r**)) characterizing them are also not completely independent. To illustrate their interdependence, let us assume that the fluid (B) is immersed in the fluid (A) in n identical and uniformly distributed droplets whose shape is described by the tensor **b**. If this is the case, then clearly the tensor **c** can be calculated from (n, **b**). In other words, the local morphology is in this case completely determined by the global morphology (see Tucker et al. 2000 and Almusallam et al. 2000). If, however, the tensor **b** expresses an average of the droplet-like features of the global morphology then the tensor **c** cannot be calculated from (n,**b**). Nevertheless, even in this case (n,**b**) and **c** are not completely independent. There are three constraints that they have to satisfy:

(i) The total volume V_B of the fluid (B) equals nV det **b**, where V is the total volume and det denotes determinant. Consequently

$$\phi = \frac{V_B}{V} = n \det b \tag{3}$$

where ϕ denotes the volume fraction of the fluid (B).

(ii) The total interface per unit volume expressed in terms of the local morphology is Q. The total interface per unit volume expressed in terms of the global morphology equals n $\wp(\mathbf{b})$, where $\wp(\mathbf{b})$ is the surface area of the ellipsoid whose shape is characterized by **b**.

$$Q = n\wp(\mathbf{b}) \tag{4}$$

The general expression for the surface area of the ellipsoid represented by $x^2/a + y^2/b + z^2/b = 1$ is given by

$$n\wp = \frac{3}{2}\phi\left(\frac{1}{a} + \frac{1}{b}\frac{\arcsin\lambda}{\lambda}\right) = \frac{3}{2}\phi\left(\frac{1}{a} + \frac{1}{2b^2 v}\log\frac{1+v}{1-v}\right)$$

$$\text{with } v = i\lambda = \sqrt{1 - (a/b)^2} \tag{3a}$$

(iii) Finally, the principal eigenvectors of **c** and **b** are required to be approximately perpendicular. This we can see as follows. The principal eigenvector of **b** is essentially the vector corresponding to the long semiaxis of the droplet. This follows from the physical interpretation assigned to **b**. The physical interpretation assigned to the BODO tensor **c** implies that its principal eigenvector is the vector perpendicular to the surface of the droplet. Since the dominant part of the surface of a droplet is parallel to the long semiaxis, the principal eigenvector of **c** is, in average, perpendicular to the principal eigenvector of **b**. This constraint will be taken into account in the kinematics of the tensors **b** and **c** (see later). We shall also see that this constraint arises naturally by requiring that in the special cases when **b** (resp. **c**) is omitted from the set of state variables, the Doi-Ohta-type (resp. Maffettone-Minale) models have to be recovered.

Fluid (A)

The fluid (A) in which the fluid (B) is dispersed is a polymeric fluid composed of macromolecules. Following Grmela (1986, 1988, 1993a, 1993b), we choose a symmetric and positive definite conformation tensor, denoted here by the symbol **a**, to describe the internal structure of the macromolecules. The tensor **a** is the second moment of the distribution function of the end-to-end vectors of the macromolecules composing the fluid (A).

Fluid (B)

The fluid (B) is also a polymeric fluid. The description of its internal structure will not be in this paper characterized by an independent state variable. The individual nature of the fluid (B) will be expressed in the quantities entering the time evolution of the droplet conformation tensor **b** (see next section).

The total set of state variables x that are chosen to describe states of the immiscible mixture of two polymeric fluids (A) and (B) is thus

$$x = (\mathbf{u}(\mathbf{r}), n(\mathbf{r}), \mathbf{a}(\mathbf{r}), \mathbf{b}(\mathbf{r}), \mathbf{c}(\mathbf{r})) \tag{5}$$

together with the constraints (i)–(iii).

The time evolution

Having specified the state variables, we proceed to discuss their time evolution. We already know the basic

architecture (Eq. 1) of the equations generating it. What remains thus is to fill out the framework (Eq. 1) by specifying: (i) the Poisson bivector L in which the kinematics of the state variables (Eq. 5) is expressed, (ii) the dissipation potential Ψ expressing the dissipation mechanisms, and (iii) the free energy Φ. In this section we shall focus our attention on (i) and (ii). This section will thus end with a family of the time evolution equations parameterized by the free energy Φ and the kinetic coefficients introduced in Ψ. In the next section we then discuss properties of solutions of these equations that are independent of the choice of Φ. The choice of the free energy will be discussed systematically in the accompanying paper.

The equations governing the time evolution of the fields included in the set of the state variables (Eq. 5) will, of course, be coupled. Their kinematics as well as dissipation can be however discussed separately (see below). The coupling among the resulting governing equations will be expressed in the constraints of Eqs. (3) and (4), in letting the kinetic coefficients (that arise in the dissipation potential) to depend on all fields included in Eq. (5), in the free energy, and in the expression for the extra stress tensor that arises as a result of the kinematics.

Fluid (A)

Since the fluid (A) is assumed to be a polymeric fluid, its internal structure is the structure of the polymer macromolecules composing it. Their internal deformations are characterized by the conformation tensor **a**. As is well known (Grmela 1986, 1988, 1993a, b; Beris and Edwards 1994; Grmela and Öttinger 1997; Öttinger and Grmela 1997), the kinematics of the state variables (**u**, **a**) is expressed by the Poisson bracket

$$\{A, B\}^{(a)} = \int d\mathbf{r}[u_\gamma(\partial_\alpha(A_{u_\gamma})B_{u_\alpha} - \partial_\alpha(B_{u_\gamma})A_{u_\alpha})$$
$$+ a_{\gamma\beta}(\partial_\alpha(A_{a_{\gamma\beta}})B_{u_\alpha} - \partial_\alpha(B_{a_{\gamma\beta}})A_{u_\alpha})$$
$$+ a_{\alpha\beta}(A_{a_{\gamma\beta}}\partial_\alpha(B_{u_\gamma}) - B_{a_{\gamma\beta}}\partial_\alpha(A_{u_\gamma}))$$
$$+ a_{\alpha\beta}(A_{a_{\gamma\alpha}}\partial_\beta(B_{u_\gamma}) - B_{a_{\gamma\alpha}}\partial_\beta(A_{u_\gamma}))] \quad (6)$$

where A, B are real valued and sufficiently regular functions of the fields (**u**,**a**), $\partial_\alpha := \frac{\partial}{\partial r_\alpha}$, $A_{u_\alpha(r)} := \frac{\delta A}{\delta u_\alpha(r)}$ is the Volterra functional derivative, $\alpha, \beta, ... = 1, 2, 3$, and the summation convention over the repeated indices is used in Eq. (6) and throughout the paper.

Following again the well-established rheological modeling of polymeric fluids, we choose the dissipation potential to be

$$\Psi^{(a)}(\Phi_\mathbf{u}, \Phi_\mathbf{a}) = \frac{1}{2}\int d\mathbf{r}\Phi_{a_{\alpha\beta}}a_{\beta\gamma}\Lambda^{(a)}\Phi_{a_{\gamma\alpha}} \quad (7)$$

By inserting Eqs. (6) and (7) into Eq. (1) we obtain

$$\frac{\partial u_\alpha}{\partial t} = -\partial_\gamma(u_\alpha\Phi_{u_\gamma}) - \partial_\alpha p - \partial_\gamma(\sigma_{\alpha\gamma}) \quad (8)$$

$$\frac{\partial a_{\alpha\beta}}{\partial t} = -\partial_\gamma(a_{\alpha\beta}\Phi_{u_\gamma}) + a_{\gamma\beta}\partial_\gamma(u_\alpha) + a_{\gamma\alpha}\partial_\gamma(u_\beta) - \Lambda^{(a)}a_{\alpha\gamma}\Phi_{a_{\gamma\beta}} \quad (9)$$

where p is the scalar hydrodynamic pressure and

$$\sigma_{\alpha\beta} = -2a_{\alpha\gamma}\Phi_{a_{\gamma\beta}} \quad (10)$$

is the extra stress tensor.

Interface : local morphology

It has been shown in (Grmela 1986, 1988, 1993a, b) that the kinematics of the state variables (**u**, **c**) is expressed in the Poisson bracket (Eq. 6) in which the last two terms on the right hand side have the sign minus (this is because in this case we are expressing the advection of a surface element, **c** is associated with the vector that is perpendicular to it). We recall the following simple observation. Let us pass in Eq. (6) from the variables (**u**, **a**) to the variables (**u**, **a**$^{-1}$), where **a**$^{-1}$ denotes the inverse of the tensor **a**. We note that this transformation is one-to-one and the Poisson bracket (Eq. 6) transforms under it into another Poisson bracket that is the same as Eq. (6) except that the signs before the last two terms are inversed. We have thus arrived in the Poisson bracket expressing the kinematics of (**u**, **c**). Consequently, the nondissipative time evolution of **c** is governed by Eq. (9) with $\Lambda^{(a)} = 0$, except that the second and the third terms have the sign minus (i.e., in other words, the upper convected time derivative in Eq. (9) is replaced by the lower convected time derivative). If we then use the one-to-one transformation (Eq. 2) relating **c** and (**q**, Q) we obtain the following time evolution equations:

$$\frac{\partial q_{\alpha\beta}}{\partial t} = -\partial_\gamma(q_{\alpha\beta})u_\gamma + q_{\alpha\beta}\partial_\gamma(Q)u_\gamma - q_{\gamma\beta}\partial_\gamma(u_\alpha)$$
$$- q_{\gamma\alpha}\partial_\gamma(u_\beta) + \frac{2}{3}\delta_{\alpha\beta}q_{\varepsilon\gamma}\partial_\gamma(u_\varepsilon) - \frac{Q}{3}(\partial_\alpha(u_\beta) + \partial_\beta(u_\alpha))$$
$$+ \frac{1}{Q}q_{\alpha\beta}q_{\gamma\varepsilon}\partial_\gamma(u_\varepsilon) - \frac{\partial\Psi^{(DO)}}{\partial\Phi_{q_{\alpha\beta}}} \quad (11)$$

$$\frac{\partial Q}{\partial t} = -\partial_\gamma(Q)u_\gamma - q_{\alpha\beta}\partial_\alpha(u_\beta) - \frac{\partial\Psi^{(DO)}}{\partial\Phi_Q} \quad (12)$$

As in Grmela and Ait-Kadi (1998) we choose the dissipation potential $\Psi^{(BODO)}$ as follows:

$$\Psi^{(\text{BODO})} = \int d\mathbf{r} \left[\Phi_{Q(\mathbf{r})} \frac{1}{2} \Lambda_1^{(\text{BODO})} \Phi_{Q(r)} \right.$$

$$+ \Phi_{q_{\alpha\beta}(\mathbf{r})} \frac{1}{2} \Lambda_2^{(\text{BODO})} \Phi_{q_{\alpha\beta}(\mathbf{r})}$$

$$\left. + \Phi_{q_{\alpha\beta}(\mathbf{r})} \Phi_{q_{\alpha\beta}(\mathbf{r})} \frac{1}{4} \Lambda_3^{(\text{BODO})} \Phi_{q_{\varepsilon\gamma}(\mathbf{r})} \Phi_{q_{\varepsilon\gamma}(\mathbf{r})} \right] \quad (13)$$

where $\Lambda_i^{(\text{BODO})}$, $i = 1,2,3$, are phenomenological parameters (they can be second order tensors and they are functions of the state variables (Eq. 5)) satisfying $\Lambda_1^{(\text{BODO})} \geq 0, \Lambda_2^{(\text{BODO})} \geq 0, \Lambda_3^{(\text{BODO})} \geq 0$, and $\Lambda_1^{(\text{BODO})} = 0$ if $\mathbf{q} = 0$. These first three inequalities are needed to satisfy the requirements on dissipation potentials listed in the text following Eq. (1), the physical meaning and consequences of the fourth requirement will be discussed later. By direct inspection (note that $\frac{\partial \Psi^{(\text{BODO})}}{\partial \Phi_{q_{\alpha\beta}}} = \Lambda_2^{(\text{BODO})} \Phi_{q_{\alpha\beta}} + \Lambda_3^{(\text{BODO})} \Phi_{q_{\varepsilon\gamma}} \Phi_{q_{\varepsilon\gamma}} \Phi_{q_{\alpha\beta}}$ and $\frac{\partial \Psi^{(\text{BODO})}}{\partial \Phi_Q} = \Lambda_1^{(\text{BODO})} \Phi_Q$) we can easily see that Eqs. (11) and (12) reduce to the Doi-Ohta equations with the modified dissipative term suggested in Lee and Park (1994) if $(\mathbf{q}, Q)$ are assumed to be independent of $\mathbf{r}$.

The equation governing the time evolution of the momentum field $\mathbf{u}$ is again Eq. (8) with

$$\sigma_{\alpha\gamma} = q_{\alpha\gamma} \Phi_Q + \frac{2}{3} Q \Phi_{q_{\alpha\gamma}} + 2 q_{\gamma\beta} \Phi_{q_{\beta\alpha}} - \frac{1}{Q} q_{\gamma\alpha} q_{\varepsilon\mu} \Phi_{q_{\varepsilon\mu}} \quad (14)$$

This expression involves terms that are absent in the expression of Onuki (1987) used in the Doi-Ohta model. We recall that in our analysis the expression at Eq. (14) appears automatically. We do not need any additional physical insight to obtain an expression for the extra stress tensor. The expression at Eq. (14) is dictated by the intrinsic consistency, expressed in Eq. (1), of the equations governing the time evolution of $(\mathbf{u}, \mathbf{c})$. The extra stress tensor at Eq. (14) has been derived in Grmela and Ait-Kadi (1994). Its consequences in predictions of rheological properties have been investigated in Bousmina et al. (2001).

Interface and fluid (B): global morphology

Now we turn our attention to the time evolution of the conformation tensor $\mathbf{b}$. From the constraint (iii) (see the text following Eq. (3a)) we conclude that $\mathbf{b}$ is advected in the same way as the conformation tensor $\mathbf{a}$. However, since we want to allow the fluids (A) and (B) to have different viscosities, we should allow for a non-affine advection (Johnson and Segalman 1977) of $\mathbf{b}$. It is not difficult to prove that the bracket at Eq. (6) is a Poisson bracket if either all the signs of all terms are as in Eq. (6) (the corresponding Poisson bivector represents then the affine upper convected time derivative)

or if the signs in front of the last two terms are changed to minus (the corresponding Poisson bivector represents then the affine lower convected time derivative). The non-affine convection is not Hamiltonian, it cannot be generated directly by a Poisson bivector. It has been shown in Grmela (1986, 1988, 1993a, 1993b) and Edwards et al. (1991) that the non-affine convection can remain Hamiltonian only in an extended setting in which the conformation tensor as well as its velocity (rate of change) are adopted as independent state variables. The non-affine convection involving only the conformation tensor can be then seen as an approximation of the Hamiltonian time evolution, an approximation in which the time evolution of the rate of change of the conformation tensor has been eliminated by assuming that it evolves faster than the conformation tensor itself (the usual way of eliminating inertia). In this paper we shall not introduce the extended setting involving the rate of change of the conformation tensor $\mathbf{b}$. We shall be content with seeing the non-affine convection as an approximation of the Hamiltonian time evolution taking place in the extended setting. There is still another important remark that has to be made in the context of the non-affine convection. The change from affine to non-affine convection implies a change in the expression for the extra stress tensor. This follows from seeing the non-affine convection as an approximation of the Hamiltonian time evolution. It follows also from the general expression (Grmela 1985) relating the type of convection to the extra stress tensor. The necessity to modify the expression for the stress tensor in case of non-affine convection has also been realized, on the basis of different types of arguments, by Larson (1988).

The constraint (i) (see Eq. (3)) represents clearly a restriction on the time evolution of $\mathbf{b}$. We introduce

$$\hat{b}_{\alpha\beta} := \frac{\phi^{\frac{1}{3}}}{n^{\frac{1}{3}}} b_{\alpha\beta} \quad (15)$$

Equation (3) implies that $\det \hat{\mathbf{b}} = 1$. We thus look for the time evolution of the conformation tensor in which its determinant is preserved. Equations governing such time evolution have been suggested in Leonov (1976, 1987) and in Maffettone and Minale (1998). The most general family of this type of the time evolution equations is given in Ait-Kadi et al. (1999):

$$\frac{\partial \hat{b}_{\alpha\beta}}{\partial t} = -\partial_\gamma \left(\hat{b}_{\alpha\beta} \Phi_{u_\gamma} \right) - \frac{1}{2} \left(\Omega_{\alpha\gamma} \hat{b}_{\gamma\beta} - \hat{b}_{\alpha\gamma} \Omega_{\gamma\beta} \right)$$

$$+ \frac{f_2}{2} \left(D_{\alpha\gamma} \hat{b}_{\gamma\beta} + \hat{b}_{\alpha\gamma} D_{\gamma\beta} \right) - B_{\alpha\beta}^{(i)}(\hat{\mathbf{b}}) \quad (16)$$

where $D_{\alpha\beta} := \partial_\beta \Phi_{u_\alpha} + \partial_\alpha \Phi_{u_\beta}, \Omega_{\alpha\beta} := \partial_\beta \Phi_{u_\alpha} - \partial_\alpha \Phi_{u_\beta}$, f_2 is the non-affine parameter (we use here the same notation as in Maffettone and Minale 1998; note that if $f_2 =$

1 – resp. $f_2 = -1$ – then the second and the third term on the right hand side of Eq. (16) represent the upper – resp. lower – convected derivative), and $B^{(i)}$, $i = 1, 2, 3, 4$ are given by

$$B_{\alpha\beta}^{(1)} = \Lambda^{(b)}\left\{\frac{4}{3}\left[-\frac{2}{3}I_1 I_2 \Phi_{\hat{b}_1} + \left(I_1 - \frac{4}{3}I_2^2\right)\Phi_{\hat{b}_{-1}}\right]\hat{b}_{\alpha\beta}\right.$$

$$+\frac{4}{3}\left[I_1^2 \Phi_{\hat{b}_1} + (2I_1 I_2 - 3)\Phi_{\hat{b}_{-1}}\right]\left(\hat{b}\hat{b}\right)_{\alpha\beta}$$

$$\left.-\frac{4}{3}\left(I_1 \Phi_{\hat{b}_1} + 2I_2 \Phi_{\hat{b}_{-1}}\right)\left(\hat{b}\hat{b}\hat{b}\right)_{\alpha\beta}\right\} \qquad (17)$$

$$B_{\alpha\beta}^{(2)} = \Lambda^{(b)}\left[-\frac{2}{3}\left(I_1 \Phi_{\hat{b}_1} + 2I_2 \Phi_{\hat{b}_{-1}}\right)\hat{b}_{\alpha\beta}\right.$$

$$\left.+2\left(\Phi_{\hat{b}_1} + I_1 \Phi_{\hat{b}_{-1}}\right)\left(\hat{b}\hat{b}\right)_{\alpha\beta} - 2\Phi_{\hat{b}_{-1}}\left(\hat{b}\hat{b}\hat{b}\right)_{\alpha\beta}\right]$$

$$(18)$$

$$B_{\alpha\beta}^{(3)} = \Lambda^{(b)}\left\{\left[-\frac{8}{3}\left(\frac{1}{3}I_1^2 - I_2\right)\Phi_{\hat{b}_1} - \frac{4}{9}I_1 I_2 \Phi_{\hat{b}_{-1}}\right]\hat{b}_{\alpha\beta}\right.$$

$$\left.-\frac{4}{3}\left(I_1 \Phi_{\hat{b}_1} - I_2 \Phi_{\hat{b}_{-1}}\right)\left(\hat{b}\hat{b}\right)_{\alpha\beta} + 4\Phi_{\hat{b}_1}\left(\hat{b}\hat{b}\hat{b}\right)_{\alpha\beta}\right\}$$

$$(19)$$

$$B_{\alpha\beta}^{(4)} = \Lambda^{(b)}\left\{\left[\frac{2}{9}\left(7I_1 I_2 - 2I_1^3\right)\Phi_{\hat{b}_1}\right.\right.$$

$$\left.+\frac{2}{3}\left(I_1 - \frac{1}{3}I_1^2 I_2 + \frac{2}{3}I_2^2\right)\Phi_{\hat{b}_{-1}}\right]\hat{b}_{\alpha\beta}$$

$$-2\left(I_2 \Phi_{\hat{b}_1} + \Phi_{\hat{b}_{-1}}\right)\left(\hat{b}\hat{b}\right)_{\alpha\beta} + \frac{2}{3}\left(2I_1 \Phi_{\hat{b}_1} + I_2 \Phi_{\hat{b}_{-1}}\right)$$

$$\left.\left(\hat{b}\hat{b}\hat{b}\right)_{\alpha\beta}\right\} \quad \text{where} \quad \hat{b}_1 := \frac{\text{tr}(\hat{b})}{(\det \hat{b})^{\frac{1}{3}}}, \hat{b}_{-1}$$

$$:= \left(\text{tr}\hat{b}^{-1}\right)(\det \hat{b})^{\frac{1}{3}}, I_1 := \text{tr}\hat{b},$$

$$I_2 := \frac{1}{2}\left(\left(\text{tr}\hat{b}\right)^2 - \text{tr}\left(\hat{b}\hat{b}\right)\right) \qquad (20)$$

The free energy Φ is assumed to depend on $\hat{b}$ only through its dependence on b_1 and b_{-1}. The family of the time evolution equations is parameterized by the free energy, by $i = 1, 2, 3, 4$ and by the kinetic coefficient $\Lambda^{(b)} > 0$, and by the non-affine parameter f_2. Note that only the case $f_2 = 1$ is considered in Ait-Kadi et al. (1999).

The time evolution of the momentum field $\mathbf{u}$ is governed by Eq. (8) with the extra stress tensor given by

$$\sigma_{\alpha\beta} = -2f_2\left[\Phi_{\hat{b}_1}\left(\hat{b}_{\alpha\beta} - \frac{1}{3}I_1\delta_{\alpha\beta}\right)\right.$$

$$\left.+\Phi_{\hat{b}_{-1}}\left(I_1\hat{b}_{\alpha\beta} - \left(\hat{b}\hat{b}\right)_{\alpha\beta} - \frac{2}{3}I_2\delta_{\alpha\beta}\right)\right] \qquad (21)$$

Finally, the equation governing the time evolution of n denoting the number of droplets per unit volume is determined by the constraint (ii) (see Eq. 4):

$$\frac{\partial Q}{\partial t} = \frac{\partial\left(n\wp\left(\left(\frac{n}{\phi}\right)^{\frac{1}{3}}\hat{b}\right)\right)}{\partial n}\frac{\partial n}{\partial t} + \frac{\partial\left(n\wp\left(\left(\frac{n}{\phi}\right)^{\frac{1}{3}}\hat{b}\right)\right)}{\partial \hat{b}_{\alpha\beta}}\frac{\partial \hat{b}_{\alpha\beta}}{\partial t} \quad (22)$$

By inserting into Eq. (22) $\frac{\partial Q}{\partial t}$ given in Eq. (12) and $\frac{\partial b_{\alpha\beta}}{\partial t}$ given in Eq. (16), we obtain the equation governing the time evolution of n.

Governing equations

Summing up, we have obtained the following equations governing the time evolution of the state variables (Eq. 5):

(i) The equation governing the time evolution of the overall momentum field is Eq. (8) with the extra stress tensor $\sigma_{\alpha\beta}$ given by Eq. (24)
(ii) The equation governing the time evolution of the conformation tensor **a** describing the polymeric structure of the fluid (A) is Eq. (9)
(ii) The equations governing the time evolution of the local morphology of the interface characterized by (**q**, Q) are Eqs. (11) and (12)
(iv) The equation governing the time evolution of the global morphology and the fluid (B) characterized by **b** is Eq. (16), ($\hat{b}$ is related to **b** by Eq. 15)
(v) The equation governing the time evolution of n denoting the number of droplets is governed by Eq. (22)

$$(23)$$

$\sigma_{\alpha\beta} =$ the expression at Eq. (10) + the expression at Eq. (14) + the expression at Eq. (21) $\qquad$ (24)

These equations constitute a family of time evolution equations parameterized by the free energy Φ, the kinetic coefficients Λ entering the dissipative part of the time evolution (see Eq. 7 where $\Lambda^{(a)}$ arises, Eq. 13 where $\Lambda_1^{(BODO)}, \Lambda_2^{(BODO)}, \Lambda_3^{(BODO)}$ arise, and Eqs. 17, 18, 19, and 20) where $\Lambda^{(b)}$ is introduced), the non-affine parameter f_2, and $i = 1,2,3,4$ in the choice of the last term

on the right hand side of Eq. (16). The parameters (Φ, Λ, f_2) are the quantities in which the individual nature of the mixture under consideration is expressed.

We now proceed to the selection of the free energy Φ. In this paper we limit ourselves to identifying Φ for which the equations at Eq. (24) become equations that have already appeared in the literature. A thorough discussion of the physics involved in the selection of Φ and Λ and a thorough analysis of solutions of Eqs. (23) and (24) will be reported in a subsequent paper.

First, we write Φ as a sum of kinetic energy and the rest that is independent of the overall momentum **u**:

$$\Phi = \int d\mathbf{r}\,\frac{\mathbf{u}^2}{2\rho} + \int d\mathbf{r}\varphi\left(\mathbf{a}, \mathbf{q}, Q, \hat{b}_1, \hat{b}_{-1}\right) \tag{25}$$

where ρ is the overall mass density. We assume that the suspensions under consideration are overall incompressible, $\rho = $ const. With Eq. (25), Φ_u appearing in the governing equations at Eq. (23) is the overall suspension velocity **v**.

As for φ, a first approximation could be a sum of three terms, each representing the contribution of one of the components:

$$\varphi\left(\mathbf{a}, \mathbf{q}, Q, \hat{b}_1, \hat{b}_{-1}\right) = \varphi^{(a)}(\mathbf{a}) + \varphi^{(BODO)}(\mathbf{q}, Q)$$
$$+ \varphi^{(b)}\left(\hat{b}_1, \hat{b}_{-1}\right) \tag{26}$$

This means that we do not consider in the free energy any interaction among the components. The governing equations will remain however coupled due to the constraints at Eqs. (3) and (4) and due to the coupling that we still can introduce in the dissipative parameters Λ. Below, we shall further specify the three terms on the right hand side of Eq. (26) and by doing so recover governing equations introduced previously on the basis of other considerations.

If $\varphi^{(BODO)} = 0$ and $\varphi^{(b)} = 0$ (i.e., if the fluid (B) is absent) then Eqs. (23) and (24) represent the standard setting of rheological modeling with conformation tensors (Grmela 1988; Beris and Edwards 1994).

If $\varphi^{(a)} = 0$, $\varphi^{(b)} = 0$, and

$$\varphi^{(BODO)}(\mathbf{q}, Q) = \varphi^{eq}(Q, T, \phi) + \frac{1}{2}A_1 q_{\alpha\beta}q_{\alpha\beta} \tag{27}$$

where φ^{eq} is the free energy arising in equilibrium thermodynamics of interfaces, A_1, a phenomenological parameter, is a nonnegative function of the temperature T and the volume fraction ϕ, then Eq. (23) reduces to the time evolution equations arising in the Doi-Ohta theory (Doi and Ohta 1991) and in the Lee and Park model (Lee and Park 1994) and Eq. (24) is an expression for the extra stress tensor that extends the formula derived by Onuki (1987) and used by Doi and Ohta (1991). An extension of the free energy (Eq. 27) needed

in the study of inhomogeneous morphologies is discussed in Grmela and Ait-Kadi (1998).

If $\varphi^{(a)} = 0$, and $\varphi^{(BODO)} = 0$,

$$\varphi^{(b)}\left(\hat{b}_1, \hat{b}_{-1}\right) = K \ln \hat{b}_{-1} \tag{28}$$

where K is a constant, $i = 2$ in Eq. (16) (i.e., we choose Eq. (18) for **B**) then Eq. (23) reduces (in the calculations we use the Cayley-Hamilton theorem) to

$$\frac{\partial \hat{b}_{\alpha\beta}}{\partial t} = -\partial_\gamma\left(\hat{b}_{\alpha\beta}v_\gamma\right) - \frac{1}{2}\left(\Omega_{\alpha\gamma}\hat{b}_{\gamma\beta} - \hat{b}_{\alpha\gamma}\Omega_{\gamma\beta}\right)$$
$$+ \frac{f_2}{2}\left(D_{\alpha\gamma}\hat{b}_{\gamma\beta} + \hat{b}_{\alpha\gamma}D_{\gamma\beta}\right) - \frac{2}{3}K\Lambda^{(b)}\left(\hat{b}_{\alpha\beta} - \frac{3}{I_2}\delta_{\alpha\beta}\right) \tag{29}$$

The extra stress tensor given by Eq. (24) becomes

$$\sigma_{\alpha\beta} = -2f_2\frac{K}{I_2}\left(I_1\hat{b}_{\alpha\beta} - \left(\hat{b}\hat{b}\right)_{\alpha\beta} - \frac{2}{3}I_2\delta_{\alpha\beta}\right) \tag{30}$$

If the tensor $\hat{\mathbf{b}}$ is independent of the position coordinate then the first term on the right hand side of Eq. (29) equals zero and Eq. (29) becomes the equation derived by Maffettone and Minale (1998) (note that $I_3 = 1$ due to Eq. (15)). Unlike Maffettone and Minale (1998) we give here also the corresponding extra stress tensor (Eq. 30). This makes a direct link between the deformation of the droplets and the involved stress.

Concluding remarks

The main result of this paper is a family of new rheological models (Eqs. (23) and (24)) of isothermal immiscible blends of viscoelastic fluids in which the morphology of the interface is characterized simultaneously on two levels of description: the microscopic level used in the Doi-Ohta theory and a more macroscopic level on which the dispersed fluid is regarded as a collection of droplets. The models in the family are parametrized by (Φ, Λ, f_2), where Φ is the free energy, Λ kinetic coefficients, and $-1 \le f_2 \le 1$ is the non-affine parameter. These are the quantities in which the individual nature of the fluids under consideration is expressed. Predictions of the models have been compared with the following experimental observations.

By virtue of the derivation of the models, solutions to the governing equations of all the models in the family agree with the experimental observation of the conservation of the total mass and momentum, and also with the experimentally observed compatibility with equilibrium thermodynamics. Two subfamilies of the models (Eqs. (23) and (24)) have then been compared with more detailed observations of the interface morphology and rheological properties.

The first such subfamily consists of the models in which the morphology of the interface is characterized only by the Batchelor-Onuki-Doi-Ohta tensor. The family (Eqs. (23) and (24)) reduces in this case to a family of extended Doi-Ohta-type models. The models are extended since they involve explicitly the free energy and a more complete formula for the extra stress tensor. The presence of the free energy in the governing equations makes it possible to express in the models more realistically the individual nature of the fluids involved. A detailed investigation of solutions to the extended Doi-Ohta-type models and their comparison with experimental measurements of rheology and the interface morphology has been made recently in Bousmina et al. (2001).

The second subfamily consists of the models which involve only the droplet-like morphology of the interface. In this case the family (Eqs. (23) and (24)) reduces to models that can be regarded as a direct extension of the Maffettone-Minale model. The models are extended since they involve explicitly the free energy and a formula for the extra stress tensor. The original Maffettone-Minale model appears in this context as a model that corresponds to one specific free energy and that is not equipped with a formula for the extra stress tensor. The new expressions for the extra stress tensor that we derive arise, as always in the type of analysis followed in this paper, as a consequence of the intrinsic consistency of the governing equations. The expression at Eq. (24) has also recently been compared with the expression derived by Batchelor (1970) in Palierne et al. (2001). Detailed rheological predictions of other models in this subfamily, that correspond to various choices of the free energy, have been investigated, but in the context of polymer solutions, in Ait-Kadi et al. (1999).

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