Generalized Doi–Ohta Model for Multiphase Flow Developed via GENERIC

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The model of Doi and Ohta for multiphase flow is developed and analyzed from a thermodynamic perspective using the general equation for the nonequilibrium reversible irreversible coupling (GENERIC) formalism. A procedure for obtaining a set of "thermodynamically consistent" transport equations is illustrated. The results demonstrate that the Doi−Ohta model is thermodynamically consistent and is thus a valid set of transport equations for multiphase flow. A modification of the original model is proposed to enable comparison with exact theories and validation with published simulation results, for which reasonable agreement is achieved. Extensions for more complex cases are derived within the GENERIC framework. The derivation demonstrates the ability of the GENERIC formalism to improve the theoretical basis of models for transport in complex fluids.

Introduction and Problem Statement

The flow of fluids composed of multiple, immiscible phases is of interest in many fields, such as biology and food science, but especially concerning the technological importance of the rheology of immiscible polymer blends in the polymer processing industry (NMAB, 1994; Utracki, 1991). Attempts to develop rheological constitutive equations include microscopic analysis of single droplets as well as more mesoscopic, average fluid approaches. As an initial step toward developing a full constitutive equation valid for immiscible blends of viscoelastic polymers, the simplified problem of the transport of a fluid composed of two immiscible Newtonian fluids of equal viscosity is considered. The interesting, non-Newtonian rheology arises from the presence of the interface between the phases, which is itself of technological importance, as the dispersion of one fluid in another ultimately governs the final engineering material properties.

Detailed, micromechanical calculations for single drops in viscometric flows by Taylor (1932, 1934), Oldroyd (1953), and Batchelor (1970), and extensions to multiple drops by Choi and Schowalter (1972), Palierne (1990) and others (Delaby et al., 1995), as well as simulation methods (Rallison and Acrivos, 1978; Rallison, 1984; Loewenberg and Hinch, 1996), exist. However, for modeling a complex flow of immiscible fluids, these calculations are not tractable and their validity for concentrated systems remains to be proven. For engineering calculations of multiphase flow, we consider the "coarse-grained" approach put forth by Doi and Ohta (Doi and Ohta, 1991; Doi, 1992, 1993), which has received significant attention by others (Krall et al., 1993; Grmela, 1994; Lee and Park, 1994; Takahashi et al., 1994; Grmela and Ait-Kadi, 1998; Grmela et al., 1998; Guenther and Baird, 1996; Lacroix et al., 1998; Vinckier et al., 1997a,b; Vermant et al., 1998). In particular, derivations have been put forward to show that the "Doi−Ohta" model is thermodynamically inconsistent (Grmela, 1994), or consistent (Grmela and Ait-Kadi, 1998; Grmela et al., 1998), and attempts toward improvement, both rigorous (Grmela and Ait-Kadi, 1998; Grmela et al., 1998; Lacroix et al., 1998) and ad hoc (Lee and Park, 1994) are evident. Further, the model or its variants have been used to

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analyze the multiphase flow of immiscible fluids (Takahashi et al., 1994) and polymers (Lee and Park, 1994; Lacroix et al., 1998; Vinckier et al., 1997a,b; Vermant et al., 1998), polymer blends containing liquid crystalline polymers (Guenther and Baird, 1996; Kernick and Wagner, 1999), defect textured liquid crystalline polymers (Doi, 1993), and simple fluids undergoing spinodal decomposition (Krall et al., 1992, 1993).

Given this expanded interest, it is important to establish (a) the thermodynamic validity of the Doi–Ohta transport equations, and (b) the accuracy of the transport equations as gauged against ''exact'' numerical and asymptotic solutions for viscometric flows of simple fluids that satisfy the constraints imposed in the original derivation. In the following, the model and its phenomenological derivation are reviewed, with attention to the limiting assumptions. Then, a new method known as GENERIC (general equation for the nonequilibrium reversible irreversible coupling) (Grmela and Öttinger, 1997; Öttinger and Grmela, 1997; Öttinger, 1997, 1998; Edwards et al., 1997, 1998) is used to derive more general transport equations from a thermodynamic viewpoint, which also ensures their thermodynamic validity and rigorously identifies the full set of transport equations necessary for a complete simulation or calculation. A modification to the original equations is derived that enables direct comparison with rigorous asymptotic theories and numerical comparison with recent simulations, enabling a rigorous validation of the accuracy. Finally, additional modifications are presented that extend the model to other systems, and comments are made concerning future theoretical work needed to relax key restrictions in the model.

Review: Phenomenological Derivation of the Doi–Ohta Model of Multiphase Flow

In this mesoscopic approach at the continuum mechanical level, the presence of the interface in a multiphase fluid is represented through two parameters that correspond to the amount of interface per unit volume (Q) and the shape of this interface (q) as given by a second-rank tensor. The properties of these variables derive from their definition, which is in terms of the interface orientational distribution density function $f(n)$, with n the unit normal to the interface. This function is the probability density of finding a region of interface with the orientation n; the normalization is such that the integral over all orientations gives the total interface per unit volume. The relevant averages are:

$$\overline{nn} = \int f(n)\, nn\, d^2 n = q + \frac{1}{3} Q I$$

$$Q = \int f(n)\, d^2 n = Tr\left(\overline{nn}\right)$$

$$q = \int f(n)\left(nn - \frac{1}{3} I\right) d^2 n. \qquad (1)$$

In the preceding equations, Tr denotes a trace; $d^2 n$ denotes a differential solid angle such that $\int d^2 n$ is an integration over the unit sphere; and I is the unit tensor.

The physical picture is that of a fluid that has embedded in it an interface as characterized by the new variables Q and q. The coarse-graining sacrifices details of the interfacial shape (dispersed phase morphology) by introducing a distribution and then by averaging to further reduce the level of information. The details of the dispersed phase morphology (that is, particle shape, size, orientation, and distributions) are not explicitly known; rather, the model proposed by Doi and Ohta retains only the *average* amount of interfacial area per unit volume and the second moment of the surface distribution, which gives some measure of the net, or average, interfacial distortion.

The coupling of the fluid to the interface proposed by Doi and Ohta takes the following form for the dynamics of these interfacial quantities:

$$\left.\frac{\partial Q}{\partial t}\right|_{\text{total}} = \left.\frac{\partial Q}{\partial t}\right|_{\text{convection}} + \left.\frac{\partial Q}{\partial t}\right|_{\text{relaxation}}$$

$$\left.\frac{\partial q}{\partial t}\right|_{\text{total}} = \left.\frac{\partial q}{\partial t}\right|_{\text{convection}} + \left.\frac{\partial q}{\partial t}\right|_{\text{relaxation}}. \qquad (2)$$

The convected part is derived by considering the convection of the interface with the flow, but under the constraint of conserving the volume of the dispersed phase. The result is (with $\kappa = [\nabla \boldsymbol{v}(r)]^T$ and $\dot{\gamma} = \kappa + \kappa^T$):

$$\left.\frac{\partial Q}{\partial t}\right|_{\text{convection}} = -\kappa : q$$

$$\left.\frac{\partial q}{\partial t}\right|_{\text{convection}} = -\kappa^T \cdot q - q \cdot \kappa + \frac{2}{3} I \kappa : q - \frac{Q}{3}\dot{\gamma} + \frac{q:\kappa}{Q} q. \qquad (3)$$

The relaxation processes are postulated to occur by two separate mechanisms, each having a rate scaling with a dimensionless, phenomenological constant c_i multiplied by a characteristic frequency given by $(\Gamma Q/\eta_0)$, where Γ is the interfacial tension and η_0 is the fluid viscosity. The derivation by Doi and Ohta leads to:

$$\left.\frac{\partial Q}{\partial t}\right|_{\text{relaxation}} = -c_1 \frac{\Gamma}{\eta_0} Q^2$$

$$\left.\frac{\partial q}{\partial t}\right|_{\text{relaxation}} = -(c_1 + c_2)\frac{\Gamma}{\eta_0} Q q. \qquad (4)$$

These equations constitute the dynamical model for the evolution of the interface for a given flow field and initial condition.

The stress tensor is

$$\Sigma = \eta_0 \dot{\gamma} - \Gamma q - pI. \qquad (5)$$

The first term is the Newtonian fluid's contribution to the stress (the viscosities and densities of both phases are taken to be equal and the fluid mixture is treated as a pseudo-one-component fluid). The second term was derived by Batchelor (1970) as the contribution to the stress due to the interfacial tension obtained by calculating the hydrodynamic stress on the surface of a droplet. Notice that, due to the presence of an elastic interface, it is possible to generate normal stresses. In particular, the first and second normal stress differences are given explicitly in terms of the deformation of the interface as (for simple shear flow with x the flow direction and y the gradient direction):

$$N_1 = -\Gamma(q_{xx} - q_{yy})$$
$$N_2 = -\Gamma(q_{yy} - q_{zz}). \tag{6}$$

The viscosity is also modified by the presence of the interface, and again for simple shear flow one obtains

$$\eta = \eta_0 - \Gamma \frac{q_{xy}}{\dot{\gamma}} \tag{7}$$

Therefore, as $q_{xy} \propto \dot{\gamma}$, this model predicts a Newtonian viscosity for the flow of an immiscible mixture of two Newtonian fluids, but with normal stresses arising from deformation of the interface.

Especially noteworthy are the scaling properties of these equations. The presence of non-Brownian microstructures that have no inherent molecular relaxation time leads to the scaling of their contributions to the stress with *strain*, and not time. This result is significant in modeling the contribution of mesoscopic microstructures to the rheology of complex fluids [such as the texture in liquid crystalline polymers (Doi, 1992, 1993) or the fluid–fluid interface (Takahashi et al., 1994; Vinckier et al., 1997a,b; Lacroix et al., 1998) studied here].

This model is also attractive because it links the rheology and microstructure of these complex fluids together in the rheological constitutive equation. Further, it explains certain non-Newtonian behaviors of such fluids directly in terms of the interface dynamics. These equations have been the subject of discussion in the literature (Doi and Ohta, 1991; Doi, 1992; Grmela, 1994; Lee and Park, 1994; Grmela and Ait-Kadi, 1998; Grmela et al., 1998; Lacroix et al., 1998), and have already been applied by others to analyze multiphase flow problems (Takahashi et al., 1994; Lee and Park, 1994; Guenther and Baird, 1996; Vinckier et al., 1997a,b; Lacroix et al., 1998). Therefore, as the model is being applied, it is important to determine its thermodynamic origin and the *thermodynamic validity* of the transport equations. In the following, the method known as GENERIC is outlined and applied to derive this model from a thermodynamic basis. The results of this derivation are a complete set of thermodynamically consistent transport equations, including a rheological constitutive equation, for the multiphase flow of two equidensity, equiviscosity Newtonian fluids with a constant interfacial tension.

GENERIC Method for Formulating Transport Equations

The GENERIC form of the equations of motion for the vector of independent variables (X) is (Grmela and Öttinger, 1997; Öttinger and Grmela, 1997)

$$\frac{\partial X}{\partial t} = L\frac{\delta E}{\delta X} + M\frac{\delta S}{\delta X}, \tag{8}$$

where $\delta/\delta X$ denotes a functional derivative (Beris and Edwards, 1994). This postulated form has separated the reversible operator (L) from the dissipative operator (M), and relates the equation of motion for the independent variables to the total system energy (E) and entropy (S). The operators must satisfy the following criteria ("null space" criteria):

$$L\frac{\delta S}{\delta X} = 0; \qquad M\frac{\delta E}{\delta X} = 0. \tag{9}$$

Further, as defined and detailed in the Appendix, the operators have symmetry requirements. The L operator must be antisymmetric and must satisfy the Jacobi identity, while the M operator must be symmetric and positive semidefinite. The former ensures "mechanical validity" in that the L operator can be traced to a Poisson bracket, while the latter ensures that the Onsager reciprocity relations and the second law of thermodynamics are respected.

The procedure for constructing Eq. 8 for the problem considered here is given in the following. To formulate a new model, one has first to choose the independent variables X, and determine the forms of E, S, and parts of M. The dynamical equations are then dictated mechanistically by the GENERIC framework. The resultant model is guaranteed to be "mechanically" as well as "thermodynamically" consistent. Further, by identifying the GENERIC structure, increasingly complex models can be built upon the "building blocks" of simplier ones by extending the set of independent variables, as demonstrated in the following.

One important consequence of thermodynamic consistency is that we expect these equations to yield physically meaningful (but not *necessarily* accurate) results for all types of flows. (Accuracy is not at all guaranteed, as that depends on the skill of the modeler in formulating the problem. For example, in classic equilibrium thermodynamics the accuracy of predictions for thermodynamic properties is only as good as the assumed thermodynamic potential function. Choosing a poor potential yet respecting the basic thermodynamic structure will still lead to poor predictions.) The contrary statement is perhaps more elucidating: namely, that equations *not* satisfying thermodynamic consistency *could* yield physically untenable results in an unpredictable manner. Thus, we can confidently apply a thermodynamically consistent set of equations to new problems or flow types without fear of generating physically meaningless results due to violations of thermodynamics, whereas inconsistent or unproven equations must be treated with the requisite skepticism when applied to previously untried situations.

Choice of variables

To start, it is convenient to take as the basic variable set those that yield the hydrodynamics of the fluid, namely the mass, momentum, and internal energy densities [$\rho(r)$, $u(r)$, and $\epsilon(r)$, respectively]. In Öttinger and Grmela (1997) it is shown how to obtain the Navier–Stokes, continuity, and energy equations for a homogeneous, single-component Newtonian fluid with the first three variables. The resulting GENERIC equations presented therein are "building blocks" for the new operators derived here. The interfacial variables defined by Doi and Ohta are included to complete the set:

$$X = [\rho(r), u(r), \epsilon(r), Q(r), q(r)]. \tag{10}$$

Energy

The total system energy is composed of the sum of the fluid's internal and kinetic energy, plus the energy contained in the interface (as given by the interfacial energy density, that is, the interfacial tension (Γ) times the area per unit volume). It has the following form:

$$E = \int \left[\epsilon(r) + \frac{1}{2}\frac{|u(r)|^2}{\rho(r)} + \Gamma Q(r) \right] d^3r, \tag{11}$$

where the integration is over the system volume. Notice that the energy depends on the interfacial surface area, which will lead to possible exchanges between the fluid's internal energy density (ϵ) and the relaxation processes of the interfacial area (Q).

Entropy

The total system entropy is composed of the entropy of the two Newtonian fluids (s), plus any contributions from the interface. As the interface is taken to be a non-Brownian structure of mesoscopic (that is, greater than one micron) extent, the entropy of dispersion of one immiscible fluid in another is negligible. Under the assumption of local equilibrium in the fluid phase, the entropy density is a thermodynamic function of the two intrinsic variables of mass and internal energy densities. Therefore,

$$S = \int s(\epsilon, \rho)\, d^3r. \tag{12}$$

Reversible dynamics

To calculate the reversible or conservative dynamics as contained in the operator L, the convective behavior of the independent variables must be specified. The following are well established as convective transport for the fluid phase variables (Bird et al., 1960; Schowalter, 1978):

$$\left.\frac{\partial \rho(r)}{\partial t}\right|_{\text{convection}} = -\nabla\cdot[\boldsymbol{v}(r)\rho(r)]$$
$$\left.\frac{\partial u(r)}{\partial t}\right|_{\text{convection}} = -\nabla\cdot[\boldsymbol{v}(r)u(r)] - [\nabla \boldsymbol{v}(r)]\cdot u(r). \tag{13}$$

Note that the mass density and entropy density both transform as scalars and the momentum vector transforms as a covariant vector density field. The convection of the internal energy density is

$$\left.\frac{\partial \epsilon(r)}{\partial t}\right|_{\text{convection}} = -\{\nabla\cdot[\boldsymbol{v}(r)\epsilon(r)] + (pI + \boldsymbol{\Pi}):\nabla \boldsymbol{v}(r)\}. \tag{14}$$

Remember that the energy density does *not* convect as a simple scalar density. The fluid's internal energy density has the additional work of expansion against the pressure (p) and osmotic pressure ($\boldsymbol{\Pi}$) that must be included. This is related to the use of enthalpy in deriving energy balances for flowing systems (Bird et al., 1960; Sandler, 1999).

The convective behavior of the interface variables Q and q follow the derivation outlined by Doi and Ohta. Basically, the procedure considers the transformation properties of the normal vector to the interface n, which transforms as a covariant vector field with the added constraint that the volume enclosed by the surface defined by this normal must be conserved (for an incompressible flow). The derivation is given in Doi and Ohta (1991). The results are as follows:

$$\begin{aligned}
\left.\frac{\partial Q(r)}{\partial t}\right|_{\text{convection}} &= -\left\{\kappa : q(r) - \frac{2}{3}Q(r)I:\kappa + \nabla\cdot \boldsymbol{v}(r)Q(r)\right\}\\
\left.\frac{\partial q(r)}{\partial t}\right|_{\text{convection}} &= -\Big\{\kappa^T\cdot q(r) + q(r)\cdot\kappa\\
&\quad + \frac{1}{3}Q(r)\dot{\gamma} + \nabla\cdot \boldsymbol{v}(r)q(r) - \frac{1}{3}I\kappa : q(r)\\
&\quad - \left[q(r) + \frac{1}{9}Q(r)I\right]Tr(\kappa) - \overline{nnnn}:\kappa^T\Big\}.
\end{aligned} \tag{15}$$

Note that in these equations, the term $\overline{nnnn}$ arises due to the constraint of volume conservation of the dispersed phase. This must be expressed in terms of the variable set X, requiring a *closure*, such as that proposed by Doi and Ohta. We have considered $\overline{nnnn}$ as a function of the independent variables, the allowed forms of which will be considered later. This is necessary to render the L operator, and hence the time evolution equations, as only a function of the variables X.

The procedure for developing the L operator is detailed in Öttinger and Grmela (1997). Given the preceding spatial transformation behavior, the second column of the L operator can be readily identified. The application of the null-space requirement (Eq. 9) and the symmetry requirements (Appendix) then develop the coupling between these variables due to reversible dynamics. Note that the final evolution equations for the independent variables will include additional terms than those given by the convective behavior due to these couplings generated from the null space criterion and the antisymmetry requirement:

$$L(r) = (-)\begin{bmatrix} 0 & \nabla\cdot\rho & 0 & 0 & 0\\ \rho\nabla & [\nabla u + u\nabla]^T & L_{23} & L_{24} & L_{25}\\ 0 & L_{32} & 0 & 0 & 0\\ 0 & L_{42} & 0 & 0 & 0\\ 0 & L_{52} & 0 & 0 & 0 \end{bmatrix}. \tag{16}$$

The elements are as follows:

$$L_{32} = \nabla \cdot \epsilon + (pI + \mathbf{\Pi}):\nabla \tag{17}$$

$$L_{42} = \left[\left(q - \frac{2}{3}QI\right) \cdot \nabla\right]^T + [\nabla Q]^T \tag{18}$$

$$L_{52\alpha\beta\nu} = \left(q + \frac{1}{3}QI\right)_{\nu\beta} \nabla_\alpha + \left(q + \frac{1}{3}QI\right)_{\alpha\nu} \nabla_\beta - \frac{1}{3} I_{\alpha\beta} \times \left(q + \frac{1}{3}QI\right)_{\nu\eta} \nabla_\eta - \overline{n_\alpha n_\beta n_\nu n_\eta} \nabla_\eta + \nabla_\nu q_{\alpha\beta} - q_{\alpha\beta} \nabla_\nu \tag{19}$$

In the preceding equations, the dependence on r has been suppressed for clarity, as will be the custom in the following. For this problem, since the entropy does not depend explicitly on the interface variables, the osmotic pressure is zero.

The rest of the elements in the second row of L are determined from the antisymmetry of the Poisson bracket:

$$L_{23} = \epsilon \nabla + \nabla p \tag{20}$$

$$L_{24} = \nabla \cdot \left(q - \frac{2}{3}QI\right) + Q\nabla \tag{21}$$

$$L_{25\alpha\beta\nu} = \nabla_\beta \left(q + \frac{1}{3}QI\right)_{\alpha\nu} + \nabla_\nu \left(q + \frac{1}{3}QI\right)_{\beta\alpha} - \frac{1}{3} \nabla_\eta I_{\beta\nu} \times \left(q + \frac{1}{3}QI\right)_{\alpha\eta} - \nabla_\eta \overline{n_\beta n_\nu n_\alpha n_\eta} + q_{\alpha\beta} \nabla_\nu - \nabla_\nu q_{\alpha\beta}. \tag{22}$$

Metric matrix

The metric matrix gives the dissipative contributions to the equations of time evolution. The basic starting point is the formulation of the energy dissipation. Following the usual developments in linear, irreversible thermodynamics, the entropy generation is written as the product of fluxes and driving forces. Linear irreversible thermodynamics (Beris and Edwards, 1994; deGroot and Mazur, 1984; Evans and Morriss, 1990; Callen, 1985) assumes a linear relationship between the fluxes and the driving forces, such that the entropy generation will be quadratic in the driving forces. This plus the fact that the material properties that appear as coefficients are positive guarantees that the entropy generation will also be nonnegative, regardless of the sign of the driving forces. In the following development, this basic structure is assumed. For notational convenience, the metric matrix is broken into two parts $M = M^{(1)} + M^{(2)}$, where the first is the classic hydrodynamics part, whereas the second part contains the components for the relaxation of the interface variables.

Energy can be dissipated by the conduction of heat and by viscous heating. For the problem at hand, considering the standard hydrodynamic variables yields the following expressions:

$$\left.\frac{\partial \epsilon}{\partial t}\right|_{\text{dissipation}} = \Sigma'_f:\nabla \boldsymbol{v} - \nabla \cdot j,$$

where

$$\Sigma'_f = \eta\dot{\gamma} + \left(\eta_d - \frac{2}{3}\eta\right)(\nabla \cdot \boldsymbol{v}) I$$

$$j = -K\nabla T. \tag{23}$$

The dissipative stress (Σ'_f) and heat flux vector (j) contain the fluid's material properties. This leads to the form for the matrix element $M^{(1)}_{33} = (1/2)T\mathbf{\Sigma}'_f:\dot{\gamma} - \nabla \cdot KT^2\mathbf{\nabla}$. The null-space requirement for M, Eq. 9, and the symmetry requirements of the dissipative operator then fix all the other elements of the M matrix.

The result of these constructions is

$$M^{(1)}(r) = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & -(\nabla\eta T\nabla + I\nabla \cdot \eta T \nabla)^T - 2\nabla\eta_d T\nabla & \nabla \cdot T\Sigma'_f & 0 & 0 \\ 0 & -T\Sigma'_f \cdot \nabla & \frac{1}{2}T\Sigma'_f:\dot{\gamma} - \nabla \cdot KT^2\nabla & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix}. \tag{24}$$

Notice that these mathematical manipulations generate the contribution to the fluid's momentum from dissipative processes in the equation for the internal energy density. Thus, the coupling of energy dissipation and momentum evolution is evident, which enables identifying the macroscopic stress tensor.

To generate relaxation processes for the interface variables terms must be postulated. The simplest processes are characterized by a rate coefficient, λ_Q, which is taken to be positive. The nature of this coefficient will be determined by dimensional analysis. The element $M^{(2)}_{44} = -\lambda_Q$ is introduced. A similar relaxation process can be postulated for the variable q by introducing an element $M^{(2)}_{53} = -\lambda_Q \tilde{\psi} \Gamma \hat{q}$, with $\tilde{\psi}$ a dimensionless, positive constant and $\hat{q} = q/Q$ a dimensionless shape factor. Physically, this element provides for a mechanism by which shape relaxations can occur. The simplest example would be the relaxation of a single, distorted droplet back to an equilibrium spherical shape under the constraint of constant volume. Here, the driving force depends not only on the relaxation rate coefficient, but also on the degree of distortion as measured by $\hat{q}$ (similar to the stretching of a Hookean spring). Again, applying the null space criterion and the symmetry requirements generates additional terms and coupling in the equations of motion.

This completes the formulation of $M^{(2)}$, leaving a nicely symmetric form, which is clearly positive semidefinite:

$$M^{(2)}(r) = \lambda_Q \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \Gamma^2 & -\Gamma & -\tilde{\psi}\Gamma\hat{q} \\ 0 & 0 & -\Gamma & 1 & \hat{\psi}\hat{q} \\ 0 & 0 & -\tilde{\psi}\Gamma\hat{q} & \tilde{\psi}\hat{q} & \tilde{\psi}^2\hat{q}\hat{q} \end{bmatrix}. \quad (25)$$

Resultant Transport Equations

The equations of motion for the independent variables are as follows:

mass

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot [\rho \boldsymbol{v}] \quad (26)$$

momentum

$$\frac{\partial u(r)}{\partial t} = -\nabla \cdot [\boldsymbol{v} u] + \nabla \cdot \Sigma'_f - \nabla \cdot pI - \nabla \cdot \Gamma \left(q + \frac{4}{3} QI \right) \quad (27)$$

energy

$$\frac{\partial \epsilon(r)}{\partial t} = -\nabla \cdot [\epsilon \boldsymbol{v}] - \nabla \cdot j_q - pI:\nabla \boldsymbol{v} + \Sigma'_f:\nabla \boldsymbol{v} + \lambda_Q \frac{\Gamma^2}{T} \quad (28)$$

interfacial area

$$\frac{\partial Q(r)}{\partial t} = -\kappa:q + \frac{2}{3} QI:\kappa - \nabla \cdot Q\boldsymbol{v} - \lambda_Q \frac{\Gamma}{T} \quad (29)$$

interfacial shape

$$\frac{\partial q(r)}{\partial t} = -\kappa^T \cdot q - q \cdot \kappa - \frac{1}{3} Q\dot{\gamma} - \nabla \cdot \boldsymbol{v} q + q \nabla \cdot \boldsymbol{v} + \frac{1}{3} I\kappa:q + \frac{1}{9} QI\kappa:I + \overline{nnnn}:\kappa^T - \lambda_Q \tilde{\psi} \frac{\Gamma}{T} \hat{q}. \quad (30)$$

The stress tensor can be identified by inspection of the momentum equation,

$$\Sigma = \Sigma'_f - pI - \Gamma \left(q + \frac{4}{3} QI \right), \quad (31)$$

which is the total, measurable stress.

Note that the fourth moment of the interface normal appears in the interfacial shape equation (Eq. 30). As in the original Doi and Ohta article, a closure is required to yield a self-contained set of transport equations. The requirements of the GENERIC form put constraints on the form of this closure. Doi and Ohta postulated the following closure approximation:

$$\overline{nnnn}:\kappa \approx \frac{1}{Q} \overline{nn}\,\overline{nn}:\kappa. \quad (32)$$

They verified this closure in the limiting cases of complete alignment and complete randomness in orientation. For simple shear and elongation, Doi and Ohta provide calculational evidence for the accuracy of this approximation.

The GENERIC formalism puts additional constraints on the closure, because it appears in the reversible dynamics of the L operator. Therefore, the closure must result in an L operator that satisfies the Jacobi identity (Edwards and Öttinger, 1997). In general, satisfaction of the Jacobi identity is a general axiom of the reversible dynamics, which can be traced back to the fundamental principles of classic mechanics. Detailed analysis of all possible closures was presented in a separate article (Edwards and Öttinger, 1997), where it is shown that the Jacobi identity is satisfied for this closure. Thus, the preceding closure is "mechanically valid." It has also been shown by Grmela and coworkers (Grmela, 1994; Grmela and Ait-Kadi, 1998; Grmela et al., 1998) and verified by us that the tensor $Q\overline{nn}$ satisfies the bracket formalism (Beris and Edwards, 1994) as a conserved, covariant tensor, thus also satisfying the Jacobi identity. This is equivalent to the L operator presented here for an incompressible fluid using the closure proposed by Doi and Ohta.

The positive semidefinite character of the metric matrix guarantees that the resultant transport equations respect the second law of thermodynamics. This can be readily illustrated, as the thermodynamic approach of the GENERIC formulation enables construction of the equation of motion for the system entropy. The equation for the total system entropy in terms of the set of independent variables is

$$\frac{ds^{\text{tot}}}{dt} = \frac{\delta S}{\delta X} \frac{dX}{dt} = \frac{\delta S}{\delta \rho} \frac{d\rho}{dt} + \frac{\delta S}{\delta \epsilon} \frac{d\epsilon}{dt} + \frac{\delta S}{\delta u} \frac{du}{dt} + \frac{\delta S}{\delta Q} \frac{dQ}{dt} + \frac{\delta S}{\delta q} \frac{dq}{dt}. \quad (33)$$

Evaluation of the entropy generation is straightforward, yielding the final result for the conservation equation for the total entropy density:

$$\frac{\partial s^{\text{tot}}}{\partial t} = -\nabla \cdot s^{\text{tot}} \boldsymbol{v} + \frac{1}{T} \left[\nabla \cdot K \nabla T + \frac{1}{2} \eta \dot{\gamma}:\dot{\gamma} + \left(\eta_d - \frac{2}{3} \eta \right) (\nabla \cdot \boldsymbol{v})^2 \right] + \lambda_Q \left(\frac{\Gamma}{T} \right)^2. \quad (34)$$

The form of this equation is of the usual entropy balance: the first term is just the convected fluid's entropy density; the second term is the change in entropy due to heat flux in the system; the rest of the terms define the entropy generation due to internal dissipation from the fluid's viscosities as well as relaxation of the interfacial area generated during flow.

Analysis of the relaxation parameter

The parameter λ_Q in Eq. 25 can be partially obtained by dimensional analysis. The inverse time scale is $(k_B T Q^3/\eta)\,[=]$ time^{-1}. The scaling for the entropy is k_B, and Q has units of length^{-1}. Therefore, we can write, with total generality:

$$\lambda_Q = \tilde{\lambda}_Q \left(\frac{k_B T Q^3}{\eta} \right) \left(\frac{Q^2}{k_B Q^3} \right) = \tilde{\lambda}_Q \frac{TQ^2}{\eta}. \tag{35}$$

It is important to recognize that, as the system has no natural length scale due to coalescence and droplet breakup, there is no natural system relaxation time, that is, the relaxation parameter depends on the state of the system, which in turn depends on the relaxation parameter. It is this lack of a permanent, characteristic length that removes any linear-viscoelastic character from this model. We also note, as suggested by Doi and Ohta, that the term $(q{:}q)^{1/2}$ could be substituted in place of Q if the physics of the problem were such that the rate of relaxation is to go to zero for a net isotropic surface.

This choice of the relaxation parameter is approximate if the system has no "natural" relaxation time, as in the model originally treated by Doi and Ohta. However, if droplet coalescence and breakup are nonexistent or suppressed, then the system has a natural length scale. For consideration here, a system of droplets at rest is sheared and no breakup or coalescence is permitted. The system has a natural lengthscale defined as the original droplet radius $l = 3\phi/Q_0$. This enables defining a fixed time scale as $\eta l/\Gamma$, with the capillary number then defined as $Ca = \eta_0 \dot{\gamma}/(\Gamma/l)$. Experimentally, specifying the volume fraction, initial number density, and polydispersity of the spherical droplets then specifies Q_0 the initial rest value of Q.

The suppression of droplet breakup also demands that the driving force for further coarsening cease when the system returns to its original state. Thus, the relaxation parameter and the relaxation equations become

$$\lambda_Q = \tilde{\lambda}_Q \frac{TQ}{\eta} (Q - Q_0). \tag{36}$$

Original Doi–Ohta equations of motion

The original equations proposed by Doi and Ohta are recovered by restricting the flow to be incompressible ($\nabla \cdot \boldsymbol{v} = 0$) and spatially homogeneous (i.e., $\nabla Q = 0$, etc.), and using the first form (Eq. 35) of the relaxation parameters. As for notation, $\tilde{\lambda}_Q = c_1$ and $\tilde{\psi} = (c_1 + c_2)/c_1$ recovers the Doi–Ohta equations. With these constraints, the same deviatoric stress tensor is recovered:

$$\Sigma'_{DO} = \eta \dot{\gamma} - \Gamma q \tag{37}$$

The following evolution equations result for the interfacial variables:

$$\frac{\partial Q}{\partial t} = -\kappa{:}q - c_1 \left(\frac{\Gamma Q}{\eta} \right) Q$$

$$\frac{\partial q}{\partial t} = -\kappa^T \cdot q - q \cdot \kappa - \frac{1}{3} Q \dot{\gamma} + \frac{2}{3} I \kappa{:}q + \frac{1}{Q} q \kappa{:}q - (c_1 + c_2) \left(\frac{\Gamma Q}{\eta} \right) q, \tag{38}$$

which are identical to those proposed by Doi and Ohta.

Generalized Doi–Ohta equations of motion

To capture flow startups as well as deformation of noncoalescing droplets, the second, generalized form of the relaxation parameters is used, along with the assumptions of spatial homogeneity and incompressibility, to yield the following equations of motion:

$$\Sigma'_{DO} = \eta \dot{\gamma} - \Gamma q \tag{39}$$

$$\frac{\partial Q}{\partial t} = -\kappa{:}q - c_1 \left(\frac{\Gamma Q}{\eta} \right) (Q - Q_0)$$

$$\frac{\partial q}{\partial t} = -\kappa^T \cdot q - q \cdot \kappa - \frac{1}{3} Q \dot{\gamma} + \frac{2}{3} I \kappa{:}q + \frac{1}{Q} q \kappa{:}q - (c_1 + c_2) \left(\frac{\Gamma Q}{\eta} \right) q. \tag{40}$$

Results for Simple Shear Flow

The microstructural equations (Eq. 38) can be solved analytically for steady-state shearing (defined by $\boldsymbol{v} = \dot{\gamma} y \hat{x}$). For reference, the solution for the original model (using the relaxation parameter given by Eq. 35) yields the rheological functions:

$$(\eta - \eta_0) \dot{\gamma} = \frac{1}{3} \eta_0 \dot{\gamma} \frac{1}{\lambda \mu} \left[\frac{(\mu^{-1} - 1)}{(1 + \mu^{-1})^2} \right]$$

$$N_1 = \frac{\eta_0 \dot{\gamma}}{\lambda \mu} \left[\frac{\sqrt{\frac{1}{3}(\mu^{-1} - 1)}}{(1 + \mu^{-1})^2} \right]$$

$$N_2 = -N_1 \tag{41}$$

where $\mu = c_1/(c_1 + c_2)$ and $\lambda = (c_1 + c_2)$. Notice that the interface produces a constant (independent of shear rate) viscosity contribution, as well as normal stress differences that are linear in the applied shear rate. This lack of a linear viscoelastic regime is a consequence of the lack of natural lengthscale. This lack leads to strain scaling, as the characteristic lengthscale given by Q^{-1} evolves with the applied flow, that is, any flow induces an order (1) distortion of the interface, with the system's rest state being fully phase separated ($Q \rightarrow 0$). Of course, this model cannot be compared with the exact solutions known for single droplets in simple shear, as coalescence occurs.

Because the simulations suppress any droplet breakup or aggregation, their rest state is spherical droplets of a given size (giving a finite Q_0). This is captured in the modified Doi–Ohta equations. Although no analytic solution of the microstructure equations is available, numerical results are readily available, as are asymptotic solutions.

Given a numerical solution for q_{xy}, the rheological functions are given for all Ca by

$$(\eta-\eta_0)\dot{\gamma} = -\Gamma Q_0 \hat{q}_{xy}\left(1-\hat{q}_{xy}\frac{Ca}{3\phi\mu\lambda}\right)$$

$$N_1 = 2\Gamma Q_0\left(1-\hat{q}_{xy}\frac{Ca}{3\phi\mu\lambda}\right)\left(\frac{1}{\hat{q}_{xy}(1+\mu^{-1})-\dfrac{3\phi\mu\lambda}{Ca}}\right)$$

$$N_2 = -N_1. \tag{42}$$

Note that this model has a linear viscoelastic regime precisely because of the introduction of a characteristic lengthscale, Q_0^{-1}. This is consistent with single- and multiple-droplet models that suppress coalescence (Taylor, 1934; Oldroyd, 1953; Batchelor, 1970; Choi and Schowalter, 1972; Palierne, 1990; Delaby et al., 1995).

The behavior of these equations is qualitatively different from that of the original Doi–Ohta model at low *Ca* number and for finite values of Q_0. For reference, an asymptotic analysis is possible, which is valid for small *Ca*:

$$q_{xy}/Q = \hat{q}_{xy} = \left[-\frac{1}{3}\left(\frac{Ca}{3\phi\lambda}\right)-\left(\frac{\mu^{-1}-1}{9}\right)\left(\frac{Ca}{3\phi\lambda}\right)^3 + \left(\frac{\left((\mu^{-1}-1)^2-4\right)}{27}\right)\left(\frac{Ca}{3\phi\lambda}\right)^5+\cdots\right]. \tag{43}$$

The expansion is valid for $(Ca/3\phi\lambda)<1$. This results in the limiting behaviors for $Ca \ll 1$:

$$(\eta-\eta_0)\dot{\gamma} \approx Ca\left(\frac{\Gamma/l}{3\lambda}\right)$$

$$N_1 = -N_2 \approx \Gamma/l\left(\frac{2}{3\lambda^2}\right)Ca^2+\cdots. \tag{44}$$

Thus, for asymptotically low shear rates, the orientation angle is 45° and the viscosity is constant, indicative of linear viscoelastic behavior. Further, the normal stress differences are proportional to shear rate squared, which is expected terminal behavior. Note that the stresses can be rearranged to yield:

$$\frac{\eta-\eta_0}{\eta_0} \approx \frac{1}{3\lambda}$$

$$N_1 = -N_2 \approx \frac{\eta_0^2 a}{9\Gamma\phi\lambda^2}\dot{\gamma}^2. \tag{45}$$

Examining the preceding equations shows that the shear viscosity and normal stress differences in the low shear limit are not sufficient to yield both unknown relaxation coefficients, as only the combination of parameters embodied in λ appears to linear order.

The viscosity expansion is consistent with the rigorous limit for asymptotic deformation of spherical inclusions obtained by Einstein and Taylor for the case of infinite interfacial tension (solid particles) if $\lambda = 2/15\phi$, and for equiviscosity, Newtonian fluids dispersed as droplets if $\lambda = 4/21\phi$. To linear order in concentration and *Ca*, the interfacial tension does not affect the viscosity directly for a given drop size. Deformation of the interface introduces normal stresses and elasticity. Choi and Schowalter's (1972) expression for the first normal stress difference in the linear viscoelastic limit is recovered if $\lambda = 0.12/\phi$. Note already that, despite the two adjustable parameters in the Doi and Ohta model, it is not possible to satisfy both rigorous (viscosity and first normal stress difference) limits exactly. Choi and Showalter also derive that, in the linear viscoelastic limit, $N_2 = -(2/7)N_1$, showing that the Doi–Ohta model overestimates the relative magnitude of the second normal stress difference. Although the modified model does not reduce to rigorous continuum models that fully account for the complex kinematics of shear flow with droplet inclusions, the comparison can provide ready estimates of the values of the phenomenological relaxation coefficient λ, as will be shown.

For high shear rates, $Ca \gg 1$, the limiting behavior is analytic. The equations reduce to the original equations of Doi and Ohta when $Q \gg Q_0$ at high shear rates, as expected. The interface grows linearly in extent with the applied flow rate, resulting in a constant viscosity and orientation angle with respect to the flow direction. The normal stress differences now scale linearly with the applied shear rate.

Comparison with Simulation Data

As noted, the simulations of Loewenberg and Hinch (1996) provide "exact" data for comparison with the modified model. The simulations start with $N = 13$ spherical droplets of fixed radius (l) and a given volume fraction (ϕ). A boundary integral method is used to numerically integrate the equations of motion for the discretized interface for the startup of steady shear flow. The steady state results of Loewenberg and Hinch for equiviscosity mixtures of Newtonian fluids at a volume fraction of 30% are explicitly illustrated for comparison.

The steady-state model was solved numerically using a *Mathematica* routine. Numerical results for the shear stress at low capillary number are fit to determine the parameters $c_1 + c_2$ in the Doi and Ohta model. For the modified model the results are insensitive to the value of c_2 for the range of parameters of interest, so it was taken to be zero. The best-fit value of $c_1 = 0.42$ is close to the value of $\lambda \approx 0.12/\phi = 0.4$ that would be obtained from the match to the rigorous results of Choi and Schowalter for N_1, but smaller than that estimated from the low shear viscosity. This is not surprising, as N_1 is entirely due to interface distortion, whereas the first term in the viscosity expansion is entirely due to circulation patterns in the droplet morphology. Further calculations were carried out for comparison to the rest of the equiviscosity simulation data of Loewenberg and Hinch at lower blend compositions using the modified model. The results for equiviscosity fluids at lower compositions are qualitatively similar to those presented for $\phi = 0.3$, and so they will not be explicitly shown here. The fit values are, to within uncertainty, equal to those expected from Choi and Schowalter's prediction that $\lambda \approx 0.12/\phi$.

As a comparison, the original model was also fit to the simulation data, using the shear stress and the initial values of N_1 and N_2 to determine c_1 and c_2, but this is somewhat

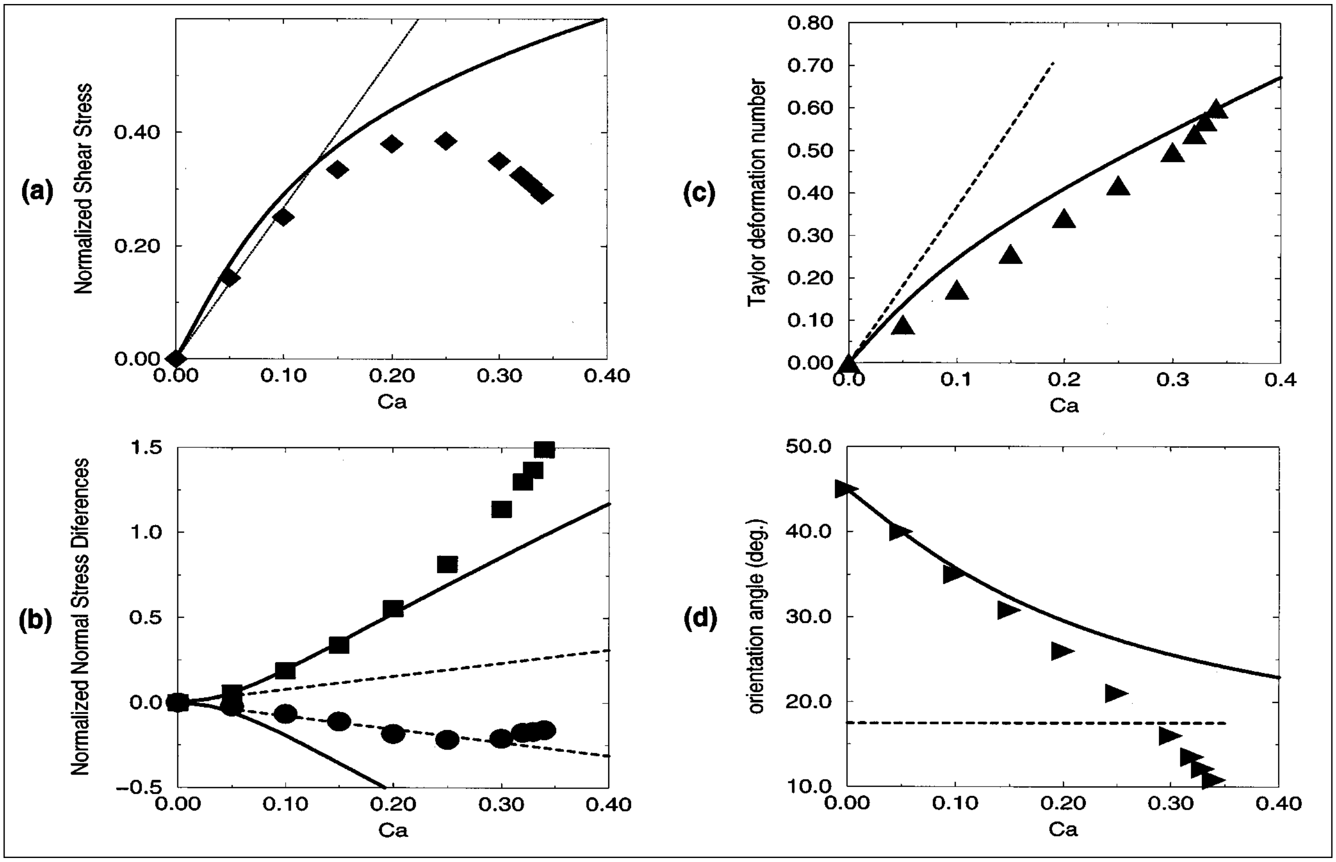

Figure 1. Comparison of the results of Loewenberg and Hinch (symbol) for $\phi = 0.3$ with the modified model (solid line) and original Doi and Ohta equations (dashed line) vs. capillary number *Ca*.

(a) Dimensionless shear stress; (b) first (positive values) and second (negative values) normal stress differences; (c) Taylor deformation parameter; and (d) orientation angle.

arbitrary, as the model does not predict the observed terminal viscoelastic behavior. A comparison of the simulation data and the predictions of the original and modified Doi–Ohta equations are shown in Figure 1. As seen, the rise in shear stress with *Ca* (increasing shear rate) is captured qualitatively, but the turnover observed in the simulations at higher capillary number is not captured. The first normal stress difference (which has no adjustable parameters once the viscosity is fixed) is reasonably well represented by the modified model (Loewenberg and Hinch estimate their simulations to have a numerical accuracy of around 5%). The second normal stress difference is much lower in magnitude than predicted by the modified model. Thus, the modified model captures the linear viscoelastic behavior at small deformations that are not represented in the original model.

For comparison to the detailed microstructural simulations of Hinch and Loewenberg (1996) a shape of monodisperse spherocylinders is assumed, as the authors reported their simulations results mapped onto this particular geometry. The deformed droplets are analyzed as spherocylinders, with spherical caps of radius b and cylinder of length $2a$, both lengths being dimensionless with the original sphere radius (l). The orientation is assumed to lie in the shear plane, with angle α relative to the shear direction. The coarse-grained interface variables are calculated from their definitions for this shape assumption. This results in the following rheological predictions:

$$\eta - \eta_0 = \frac{\Gamma}{l}\frac{3\phi}{4} ab \sin 2\alpha$$

$$N_1 = \frac{\Gamma}{l}\frac{3\phi}{2} ab \cos 2\alpha. \tag{46}$$

Shown in Figure 1 are also the orientation angle α and Taylor deformation parameter $D = a/(a+2b)$, which are obtained from matching the shear stress and normal stress predicted from the Doi–Ohta equations to the spherocylinder model. Note that the geometric symmetry of the spherocylinder precludes any second normal stress difference. Specifically, the angle and the Taylor deformation parameter are obtained as:

$$\alpha = \frac{1}{2}\tan^{-1}\left[\frac{2(\eta - \eta_0)\dot{\gamma}}{N_1}\right]$$

$$ab = \frac{2D}{(1+3D-4D^3)^{1/3}}, \tag{47}$$

where the product ab is obtained from the shear viscosity (Eq. 46). The modified model provides a reasonable, quantitative prediction of the Taylor deformation parameter over the entire range, and qualitatively predicts the alignment of the orientation angle toward the flow direction. Again, the lack of a maximum in the shear stress leads to the discrepancy in the predicted angle at higher *Ca* numbers. For the original model, the higher shear stress predicted by the model necessitates a greater deformation than observed in the simulations. Also, because the original Doi–Ohta equations predict that both the shear stress and normal stress differences are linear in applied shear rate, the predicted orientation angle is independent of applied shear rate.

Modifications and Comparison with Other Models in the Literature

For completeness, we note that Grmela and coworkers have analyzed the same problem within the framework of the dissipative bracket formalism (Grmela and Öttinger, 1997; Grmela and Ait-Kadi, 1998; Grmela et al., 1998). They postulated the existence of a tensor $Q\overline{nn}$ that transforms as a conserved, covariant tensor. They are unable to fully reproduce the equations derived herein, specifically obtaining new derivative terms in the stress tensor (Grmela and Ait-Kadi, 1998) that *must* be included if the time evolution equation for the shape tensor q is to have a relaxation term. This would, however, violate the strain scaling behavior of the original model. Thus, they conclude that the original model of Doi and Ohta is inconsistent with the thermodynamic derivation they provide. By our treatment of the variables Q and q as *independent* (rather than in combination), however, we are able to capture the full range of the model as proposed by Doi and Ohta, still maintaining the strain scaling, and without adding additional physical processes or additional contributions to the stress tensor. Although Grmela et al. have "guessed" that the quantity $Q\overline{nn}$ is conserved and that it transforms as a covariant tensor, it is difficult to envision adopting this form *a priori* given the lack of physical meaning of this tensor. In this sense, the problem addressed here nicely illustrates the complementary power of unifying both theoretical approaches. The definition of the spatial transformation behavior and the system energy and entropy are much more intuitive and physically appealing to all but perhaps those well versed in the bracket formalism.

A natural extension of the model is to consider entropic effects, whereby entropy will favor creation of interface in opposition to the tendency of interfacial tension to ripen the dispersion. As an illustration of the rich behavior of the model, the simpliest entropic contribution will be considered as follows. An entropy functional can be constructed by considering the entropy per unit area of surface to be quadratic in the interface variable Q. Dimension analysis then introduces a factor of Q to convert from entropy per unit area to entropy density. Thus, the following is postulated for the total system entropy:

$$\begin{aligned} S &= \int s^{\text{tot}}(r)\, d^3r \\ &= \int \left\{ s[\epsilon(r), \rho(r)] + k_B Q(r) \left[\frac{1}{3} \alpha_Q Q^2(r) \right] \right\} d^3r. \end{aligned} \tag{48}$$

In this equation, α_Q is an undetermined, dimensionless *positive* coefficient that has to be determined experimentally, as it has no direct microphysical definition at this course-grained level. The state variable Q appears inside the brackets in quadratic form (deGroot and Mazur, 1984; Beris and Edwards, 1994; Callen, 1985), with overall cubic dependence resulting from dimensional analysis. A more sophisticated functional form could be invoked, but as will become apparent, this simple form contains a rich and fruitful physics for this problem.

Following the GENERIC procedure, the following contribution to the osmotic pressure tensor is derived

$$\frac{\mathbf{\Pi}}{T} = -\frac{\partial S}{\partial Q}\left(q - \frac{2}{3} Q I \right). \tag{49}$$

Notice that, because the entropy contains the interface variable Q explicitly, it now enters directly into the osmotic pressure. This is a consequence of the null-space condition.

With this analysis, the specific form for the relaxation part of the interface evolution equations becomes:

$$\begin{aligned} \left.\frac{\partial Q}{dt}\right|_{\text{relaxation}} &= -\tilde{\lambda}_Q \left(\frac{\Gamma Q}{\eta} \right) Q \left(1 - \alpha_Q \frac{k_B T}{\Gamma} Q^2 \right) \\ \left.\frac{\partial q}{\partial t}\right|_{\text{relaxation}} &= -\tilde{\lambda}_Q \tilde{\psi} \left(\frac{\Gamma Q}{\eta} \right) q \left(1 - \alpha_Q \frac{k_B T}{\Gamma} Q^2 \right). \end{aligned} \tag{50}$$

In comparison to Eq. 36, the extra term at the end of each of the preceding equations is a direct consequence of the *entropy* depending on Q, and acts to increase the value of Q to maximize the entropy of the system. The original term is a consequence of the dependence of the *energy* on Q, and it drives the system toward macroscopic phase separation ($Q \to 0$). (It is important to note that because of its physical significance, Q is constrained to be positive.) Notice that the competing effects of the two terms can be equated to yield a characteristic droplet size given by $Q = \sqrt{\Gamma / \alpha_Q k_B T}$. The significance of the entropic term depends on the relative strength of the interfacial energy (per unit volume) relative to the thermal energy per volume (as defined by the coarse-grained length scale Q^{-1}). This balance is inherently *unstable*, however. If the lengthscale is larger (that is, Q small, a few large droplets), the interfacial energy is significant relative to the thermal energy and the system is driven toward phase separation. However, if the length scale is very small (that is, Q large, many smaller droplets) then the thermal energy of the droplets is significant and the dispersed phase continues to disperse with increasing Q. This behavior is characteristic of nucleation and growth models, where a critical nucleate size is required to initiate stable ripening. Microemulsion-like stability could be achieved by the addition of a bending energy into the energy functional, which is the subject of ongoing work.

The introduction of a thermal energy scale into the problem defines a new relaxation time for the system. Introduction of the additional source of entropy also results in new entropic contributions to the stress tensor that enter via the osmotic pressure that must be accounted for if the preceding evolution equations are used. The stress tensor that is thermodynamically consistent with this model (for incompressible flow) is extracted from the GENERIC analysis as:

$$\Sigma = \eta\dot{\gamma} - pI - \Gamma\left(q + \frac{4}{3}I\right) - \frac{2}{3}\alpha_Q k_B T Q^3 I + \alpha_Q k_B T Q^3 q. \tag{51}$$

These additional terms are also found in the overall momentum and energy balances. This result is comparable in qualitative structure to that derived by Grmela and Ait-Kadi (1998), differences arise due to differences in the free energy function postulated. This model may be useful for examining multiphase systems close to a nucleation threshold, such as are seen in off-critical spinodal decomposition.

Discussion, Conclusions, and Outlook

The mesoscopic, phenomenological model of Doi and Ohta is thermodynamically consistent and has been derived successfully from a thermodynamic basis, including a consistent expression for the stress tensor. Note that the model sacrifices accuracy by coarse graining the detailed and complex flow patterns in multiphase flow to robustly capture the evolution of the interface and the resultant extra stress due to distortion of the interface by the applied flow. Indeed, the model completely decouples the kinematics of the flow from the presence of the interface, thus enabling analytic solutions, or for the modified model, at least in asymptotic limits. Comparison with the exact simulation results for equiviscosity fluids and noncoalescing droplets demonstrates the accuracy of the model.

The GENERIC derivation also provides the full set of transport equations that can be used to simulate multiphase flow in a more complex flow field, relaxing the need to assume the flow kinematics *a priori*. The asymptotic analysis and comparison to rigorous models for viscometric flows demonstrate that bounds can be put on the phenomenological coefficients, and *a priori* estimates even can be made. The original model has the qualitative features of strain scaling evident in immiscible blend rheology. A modification of the model for the case of suppressed coalescence and breakup that enables recovery of a terminal and linear viscoelastic behavior is presented. Comparison with numerical results from previous simulations show both quantitative as well as qualitative agreement for the steady-state rheology and microstructure.

Just as important, the derivation illustrated here is a paradigm for the robust development of thermodynamically consistent transport equations. Compared to the more phenomenological method taken by Doi and Ohta, and others who have built on their model, the derivation presented here requires specification of the convection of the fundamental variables taken to describe the system. Unlike the phenomenological approach, the method described here places the ‘‘burden’’ of the effort on defining the system energy and entropy in terms of the chosen set of variables. Indeed, this then leads automatically to the specification of a stress tensor, which was the starting point in the derivation by Doi and Ohta. As with Doi and Ohta’s work, additional relaxation processes can be postulated; however, unlike their work, the consequences of these processes on the equations of motion and stress tensor result from the GENERIC structure of the equations of motion, that is, they are not independently formulated.

It is our *belief*, that just as with equilibrium thermodynamics, where equations of state, mixing, and combining rules that do not violate the first and second laws and are shown to satisfy known ‘‘boundary’’ conditions, are given preference in engineering practice, the formulation of thermodynamically consistent transport equations is a worthwhile and valid activity. More precisely, the failure to do so leaves open the possibility of aphysical and meaningless results from such flawed equations when applied to new, unproven problems. Of equal value is the thermodynamic insight extracted from the GENERIC derivation. Construction of the energy and entropy functions enables identifications of the source of the driving and relaxation terms in the transport equations, which has conceptual value in understanding what terms can be neglected for particular applications, and in identifying the source of the couplings that arise between processes.

There has been a significant experimental effort to measure microstructure and rheology in model polymer blends, including the use of the Doi and Ohta model to analyze the results, or try and interpret microstructural information from bulk rheological data (Lee and Park, 1994; Guenther and Baird, 1996; Lacroix et al., 1998; Vinckier et al., 1997b; Kernick and Wagner, 1999). Indeed, experimental programs are being directed to provide data analogous to the simulation results quoted here, but on these more complex blends. Application of the interface equations presented here to these complex systems requires extending the model to the case of unequal viscosities and non-Newtonian fluids. This requires an additional assumption of a ‘‘mixing rule’’ to describe the stress coming from the bulk fluids, with the extra stress arising from the interface in the same manner as for Newtonian fluids. Proposals of continuity of shear rate, continuity of stress, log-additivity, and so on [see Utracki (1991), Lee and Park (1994), and Lacroix et al. (1998) for discussions], for the ‘‘mixing rule’’ abound, but essentially no rigorous justification is evident. Indeed, little is known theoretically about the influence of non-Newtonian effects on multiphase flow (Palierne, 1990; Delaby et al., 1995) for guidance, although for Newtonian fluids solutions exist for unequal viscosities and higher concentrations (Choi and Schowalter, 1972). Thus, extending this model to unequal viscosities and, ultimately non-Newtonian effects, is imperative, but the procedure is far from evident. The GENERIC derivation presented here demonstrates that the stress tensor, and hence the mixing rule for stress, and the interface kinematics can, in principle, be derived self-consistently, providing one path toward developing a successful model for these more complicated, but relevant, blends.

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Notation

Note that our system is divided into two phases, "fluid" and "interface," each with their associated variables. Here, "fluid" refers to the average properties of the two equiviscous, equidensity Newtonian fluids that compose the system, while "interface" denotes properties inherent to the existence of an interface.

I = unit tensor
K = thermal conductivity
N_1 = primary normal stress difference
N_2 = secondary normal stress difference
T = temperature
V = volume
k_B = Boltzmann's constant
$\boldsymbol{r}$ = spatial position
s^{tot} = total entropy density
t = time
$\boldsymbol{v} = \boldsymbol{u}/\rho$ = fluid velocity
z = Cartesian coordinate, vorticity direction
η_d = dilational viscosity
$\boldsymbol{\kappa} = (\nabla \boldsymbol{v})^T$ = velocity gradient tensor
$\nabla = \dfrac{\partial}{\partial \boldsymbol{r}}$ = gradient operator
$\dfrac{dY}{dt} = \dfrac{\partial Y}{\partial t} + \boldsymbol{v} \cdot \nabla Y$ = substantial derivative of Y
$\dot{\boldsymbol{\gamma}} = (\boldsymbol{\kappa} + \boldsymbol{\kappa}^T)$ = symmetric part of velocity gradient
$\tilde{\lambda}_Q$ = dimensionless λ_Q
$\boldsymbol{\Sigma}'$ = deviatoric stress tensor

Literature Cited

Batchelor, G. K., "The Stress System in a Suspension of Force-Free Particles," *J. Fluid Mech.*, **41**, 545 (1970).

Beris, A. N., and B. J. Edwards, *Thermodynamics of Flowing Systems*, Oxford Univ. Press, Oxford (1994).

Bird, R. B., W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, Wiley, New York (1960).

Callen, H. B., *Thermodynamics and an Introduction to Thermostatics*, 2nd ed., Wiley, New York (1985).

Choi, S. J., and W. R. Schowalter, "Rheological Properties of Nondilute Suspensions of Deformable Particles," *Phys. Fluids*, **18**, 420 (1972).

deGroot, S. R., and P. Mazur, *Non-Equilibrium Thermodynamics*, Dover, New York (1984).

Delaby, I., B. Ernst, and R. Muller, "Drop Deformation During Elongational Flow in Blends of Viscoelastic Fluids. Small Deformation Theory and Comparison with Experimental Results," *Rheol. Acta.*, **34**, 525 (1995).

Doi, M., and T. Ohta, "Dynamics and Rheology of Complex Interfaces," *J. Chem. Phys.*, **95**, 1242 (1991).

Doi, M., "Rheology of a System with Mesoscopic Domain Structure," *Proc. Int. Cong. on Rheology*, P. Moldenaers and R. Keunings, eds., Elsevier, Amsterdam (1992).

Doi, M., "Rheology of Textured Materials," *Complex Fluids*, L. Garrido, ed., Springer-Verlag, Berlin (1993).

Edwards, B. J., A. N. Beris, and H. C. Öttinger, "An Analysis of Single and Double Generator Thermodynamic Formalisms for Complex Fluids: II. The Microscopic Description," *J. Non-Equilib. Thermodyn.*, in press (1999).

Edwards, B. J., and H. C. Öttinger, "Time-Structure Invariance Criteria for Closure Approximations," *Phys. Rev. E*, **56**, 4097 (1997).

Edwards, B. J., H. C. Öttinger, and R. J. J. Jongschaap, "On the Relationships Between Thermodynamic Formalisms for Complex Fluids," *J. Non-Equilib. Thermodyn.*, **22**, 356 (1997).

Evans, D. J., and G. P. Morriss, *Statistical Mechanics of Nonequilibrium Liquids*, Academic Press, London (1990).

Grmela, M., and A. Ait-Kadi, "Rheology of Inhomogeneous Immiscible Blends," *J. Non-Newt. Fluid Mech.*, **77**, 191 (1998).

Grmela, M., A. Ait-Kadi, and L. A. Utracki, "Blends of Two Immiscible and Rheologically Different Fluids," *J. Non-Newt. Fluid Mech.*, **77**, 253 (1998).

Grmela, M., "Comments on the Doi−Ohta Theory of Blends," *J. Non-Newt. Fluid Mech.*, **55**, 191 (1994).

Grmela, M., and H. C. Öttinger, "Dynamics and Thermodynamics of Complex Fluids. I. Development of a Generic Formalism," *Phys. Rev. E*, **56**, 6620 (1997).

Guenther, G. K., and D. G. Baird, "An Evaluation of the Doi-Ohta Theory for an Immiscible Polymer Blend," *J. Rheol.*, **40**, 1 (1996).

Kernick, W. A., III, and N. J. Wagner, "The Role of Liquid-Crystalline Polymer Rheology on the Evolving Microstructure of Immiscible Blends Containing Liquid-Crystalline Polymers," *J. Rheol.*, in press (1999).

Krall, A. H., J. V. Sengers, and K. Hamano, "Viscoelasticity of a Simple Liquid Mixture During Spinodal Decomposition," *Phys. Rev. Lett.*, **69**, 1963 (1992).

Krall, A. H., J. V. Sengers, and K. Hamano, "Experimental Studies of the Rheology of a Simple Liquid Mixture During Phase Separation," *Phys. Rev. E*, **48**, 357 (1993).

Lacroix, C., M. Grmela, and P. J. Carreau, "Relationship Between Rheology and Morphology for Immiscible Molten Blends of Polypropylene and Ethylene Copolymers Under Shear Flow," *J. Rheol.*, **42**, 41 (1998).

Lee, H. M., and O. O. Park, "Rheology and Dynamics of Immiscible Polymer Bends," *J. Rheol.*, **38**, 1405 (1994).

Loewenberg, M., and E. J. Hinch, "Numerical Simulation of a Concentrated Emulsion in Shear Flow," *J. Fluid Mech.*, **321**, 395 (1996).

National Materials Advisory Board, Committee on Polymer Sci., Eng. and Nat. Res. Council, *Polymer Science and Engineering*, National Academy Press, Washington, DC (1994).

Öttinger, H. C., "Generic Formulation of Boltzmann's Kinetic Equation," *J. Non-Equilib. Thermodyn.*, **22**, 1997 (1997).

Öttinger, H. C., "On the Structural Compatibility of a General Formulation for Nonequilibrium Dynamics with Special Relativity," *Physica A*, **259**, 24 (1998).

Öttinger, H. C., and M. Grmela, "Dynamics and Thermodynamics of Complex Fluids: II. Illustrations of the Generic Formalism," *Phys. Rev. E*, **56**, 6633 (1997).

Oldroyd, J. G., "The Elastic and Viscous Properties of Emulsions and Suspensions," *Proc. Roy. Soc. A*, **218**, 122 (1953).

Palierne, J. F., "Linear Rheology of Viscoelastic Emulsions with Interfacial Tension," *Rheol. Acta*, **29**, 204 (1990).

Rallison, J. M., and A. Acrivos, "A Numerical Study of the Deformation and Burst of a Viscous Drop in an Extensional Flow," *J. Fluid Mech.*, **89**, 191 (1978).

Rallison, J. M., "The Deformation of Small Viscous Drops and Bubbles in Shear Flows," *Annu. Rev. Fluid. Mech.*, **16**, 45 (1984).

Sandler, S. I., *Chemical Engineering Thermodynamics*, 3rd ed., Wiley, New York (1999).

Schowalter, W. R., *Mechanics of Non-Newtonian Fluids*, Pergamon Press, Oxford (1978).

Takahashi, Y., N. Kurashima, I. Noda, and M. Doi, "Experimental Tests of the Scaling Relation for Textured Materials in Mixtures of Two Immiscible Fluids," *J. Rheol.*, **38**, 699 (1994).

Taylor, G. I., "The Viscosity of a Fluid Containing Small Drops of Another Fluid," *Proc. Roy. Soc. A*, **138**, 41 (1932).

Taylor, G. I., "The Formation of Emulsions in Definable Fields of Flow," *Proc. Roy. Soc. A*, **146**, 501 (1934).

Utracki, L. A., "On the Viscosity-Concentration Dependence of Immiscible Polymer Blends," *J. Rheol.*, **35**, 1615 (1991).

Vermant, J., P. Van Puyvelde, P. Moldenaers, and J. Mewis, "Anisotropy and Orientation of the Microstructure in Viscous Emulsions During Shear Flow," *Langmuir*, **14**, 1612 (1998).

Vinckier, I., J. Mewis, and P. Moldenaers, "Stress Relaxation as a Microstructural Probe for Immiscible Polymer Blends," *Rheol. Acta*, **36**, 513 (1997a).

Vinckier, I., P. Moldenaers, and J. Mewis, "Transient Rheological Response and Morphology Evolution of Immiscible Polymer Blends," *J. Rheol.*, **41**, 705 (1997b).

Appendix: Symmetry of the Operators

Conservation of energy and time-reversal symmetry imposes a requirement on the Poisson bracket [denoted by {,} (Beris and Edwards, 1994)] of:

$$\{A, B\} = -\{B, A\} = \left\langle \frac{\delta A}{\delta X}, L\frac{\delta B}{\delta X} \right\rangle, \tag{A1}$$

where $\langle\,\rangle$ denotes an inner product. Consider the term, $L_{12} = -\boldsymbol{\nabla}\rho$. This requirement becomes:

$$-\frac{\delta A}{\delta \rho}\cdot\boldsymbol{\nabla}\cdot\left(\rho\frac{\delta B}{\delta u}\right) = -\frac{\delta B}{\delta u}\cdot L_{21}\frac{\delta A}{\delta \rho}. \tag{A2}$$

The former term can be written as

$$-\frac{\delta A}{\delta \rho} * \nabla\cdot\left(\rho\frac{\delta B}{\delta u}\right) = -\nabla\cdot\left(\frac{\delta A}{\delta \rho}\rho\frac{\delta B}{\delta u}\right) + \rho\frac{\delta B}{\delta u}\cdot\nabla\frac{\delta A}{\delta \rho}, \tag{A3}$$

where, when integrated over the volume (remember, $\langle,\rangle$ denotes a scalar product, which involves integration over the variable r), the divergence of the total quantity is zero. Therefore, it is determined that $L_{21} = -\rho\nabla$.

Nonnegative entropy generation imposes a constraint on the symmetry of the metric matrix [denoted by the bracket [,] (Öttinger and Grmela, 1997)]:

$$[A, B] = [B, A] = \left\langle \frac{\delta A}{\delta X}, M\frac{\delta B}{\delta X} \right\rangle. \tag{A4}$$

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