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Constitutive modeling of dispersive mixtures

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Synopsis

A rheological model for the stress in liquid–liquid systems is developed based on unifying the theory of the present phenomenological models and by applying a description of the dispersed phase microstructure to remove most of the adjustable parameters present in the rheological models. However, this introduces new parameters in the model for the microstructure. The main features of the model are: (a) the stress related to the viscosity difference is not purely viscous, (b) a closure approximation is used for the stress contribution due to the interfacial stress, and (c) the stress relaxation time depends on the droplet deformation. Especially the latter is of importance to get the description of some characteristic rheological behavior of dispersive mixtures right. The interfacial area, the droplet stretch ratio, and the rate of change of the interfacial area show up explicitly in the equation for the stress evolution. The description of the spatial evolution of the dispersed phase microstructure is accomplished by coupling preexisting models of coalescence and breakup yielding a description of the evolution of the microstructure. Model predictions are compared with experimental results from literature [Vinckier *et al.* (1997); Vinckier (1998)]. It is shown that, by incorporating a structure dependent relaxation time, remarkably good agreement between the model and experiment is obtained, even for very different experimental conditions. Moreover, the complex rheological phenomena observed can now be understood in terms of the evolution of the microstructure. © 2001 The Society of Rheology. [DOI: 10.1122/1.1366714]

I. INTRODUCTION

A first step toward understanding the interplay between mixing, breakup, and coalescence processes is the two-zone mixing model of Janssen (1993); Janssen and Meijer (1993, 1995, 1997). They envision mixing processes as consisting of alternating strong and weak zones. In a principally dynamic process, in the strong zones droplets extend into filaments, while in the weak zones filaments break up and the resulting droplets may coalesce. The model gives a good approximation of the morphology developing in a liquid–liquid system and, compared to the frequently cited but basically quasistatic results of the classical approach of dispersive mixing [Grace (1971, 1982)], yields rather interesting results, emphasizing the dynamics of mixing processes as they usually occur in practice. In particular, the influence of the “optimum” viscosity ratio between dispersed and continuous phase, to obtain the smallest dispersion, is strikingly different in dynamic processes. Consequently, the model of Janssen provides a framework for analyzing breakup/coalescence processes. More work is, however, necessary to tie this

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model with the dynamics of mixing processes which are frequently chaotic and oversimplified by the two-zone mixing model.

The goal of this work is the development of a model for the macroscopic rheology of liquid–liquid systems. Although a system of two Newtonian fluids is considered, non-Newtonian effects are predicted as a result of the presence of the dispersed phase. We improve upon the Lee–Park model [Lee and Park (1994)] for the rheology of a blend. The new model incorporates a contribution to the stress caused by the viscosity difference that is *not purely viscous* [see Eq. (17)] as often assumed by others. For the stress contribution due to the interfacial stress a new closure approximation is used [see Eq. (29)]. Moreover, an important extension of the model is the *deformation dependent relaxation time* for extended droplets [see Eqs. (39) and (74)] which is based on the results and insights from the work of Vinckier (1998), van Puyvelde (1999), and Stegeman *et al.* (1999).

The Lee–Park model requires prediction of the interfacial area between the two phases with a rather *ad hoc* kinetic equation. In order to improve upon that we use a liquid–liquid mixing model to determine the interfacial area of the dispersed phase and thus reduce the number of unknowns appearing in the Lee–Park model (see Sec. III). This model for the spatial evolution of dispersed phase microstructure is accomplished by revisiting much of the earlier work of Janssen from a slightly different perspective. We focus on systems composed of viscous fluids which can be described by the Stokes equations. (In many applications, the dispersion is rheologically complex, and also further complicated by interfacial phenomena resulting from surfactants or compatibilizers. Some of the influences of viscoelasticity and surfactants are discussed in Janssen (1993); Ottino *et al.* (1999); Stone (1994). Idealizations are however necessary as the problem becomes intractable when all complexities are included. We neglect non-Newtonian effects and interfacial phenomena, thus highlighting the physics central to coalescence and breakup.)

The (coarse) modeling of the structure development together with the constitutive equation for the stress provides, in principle, a means for a complete analysis of the evolution of complex dispersive mixing flows. This requires the implementation of these models in, for example, a finite element method (FEM) package. When the full coupling between the rheological behavior and the structure development can be, or is partly, neglected, methods are available (as, for example, so-called Mapping methods) that allow for studying even geometrically complex flows over (realistic) long mixing times [Kruijt (2000); Kruijt *et al.* (2001); Galaktionov *et al.* (2001a, 2001b, 1997); Anderson (1999); Anderson *et al.* (1999, 2000)] and this paves the way to optimization of mixing processes. When both approaches meet, real mixing processes can be studied both spatially and temporally in full detail.

This paper is organized as follows: After developing the rheological model (Sec. II), a short description of the model for the microstructure evolution is given (Sec. III), next the combined parts are tested by investigating different models aspects and comparing with the experimental results from literature Vinckier *et al.* (1997), Vinckier (1998) (Sec. IV). Finally, the main conclusions are summarized (Sec. V).

II. MACROSCOPIC RHEOLOGY

The study of the rheology of a dispersion dates back to the work of Einstein (1906), (1911) yielding the effective viscosity of a dilute suspension of solid spheres

$$\mu_e = \mu_c(1+2.5\phi), \quad (1)$$

in which ϕ is the volume fraction of the dispersed phase. Later, Taylor (1932) found the effective viscosity for a dispersion containing spherical droplets. The effective viscosity—like Einstein's relation—has the form

$$\mu_e = \mu_c \left[1 + 2.5\phi \left(\frac{p+0.4}{p+1} \right) \right], \quad (2)$$

where $p = \mu_d/\mu_c$ is termed the viscosity ratio. As Taylor notes, the term inside the parentheses is similar to a term that corrects the Stokes drag to calculate the drag on a spherical droplet of *fluid*.

Schowalter *et al.* (1968) considered the influence of the first-order deformation of the droplets on the rheology of the dispersion. The analysis assumes a dilute emulsion of two highly viscous Newtonian fluids and droplets with $\text{Ca} \ll \text{Ca}_{\text{crit}}$ [see Eqs. (54), (72), and (73) for definitions of Ca and Ca_{crit} , respectively]. The macroscopic rheology of this type of emulsion exhibits elastic properties with normal stress differences resulting from the deformation of the droplets. A more advanced work by Choi and Schowalter (1975) determines the rheology of a nondilute dispersion of Newtonian fluids with slightly deformed droplets. The results show that the macroscopic rheology can be described by a special case of the Oldroyd 8-constant model [Bird *et al.* (1987)], and that by dropping nonlinear terms in the rate-of-deformation tensor the convected Jeffreys model results.

Palierne (1990) derived an expression for the linear viscoelastic modulus of a dispersion. The analysis allows for linear non-Newtonian behavior of the two fluids and for dynamic interfacial tension. Still, the model does not allow for deformation of the droplets. The Palierne model is equivalent to the Jeffreys model when the droplet size distribution is monodisperse.

An alternative method of determining the rheology of a liquid–liquid system focuses on the evolution of the interface between the two fluids. An early study from this perspective by Doi and Ohta (1991) considers a system of two Newtonian liquids with the same viscosities and densities, mixed in nearly equal ratio. The Reynolds number is also low. Only three parameters characterize the system: viscosity, volume fraction, and interfacial tension.

Lee and Park (1994) extended this model to allow for a wider range of blend properties. Here, we derive the Lee and Park model with a slightly different approach, yielding a more exact constitutive equation, containing the dispersed phase interfacial area and the droplet stretch ratio as dependent parameters. Both parameters can be approximated by our model for a dispersed phase microstructure (see Sec. III).

According to Mellema and Willemse (1983), who adopted Batchelor's approach [Batchelor (1998)], the bulk stress in a dispersion $\langle \mathbf{T} \rangle$ can be written for Stokes flow as

$$\langle \mathbf{T} \rangle = -P\mathbf{I} + 2\mu_c \langle \mathbf{D} \rangle + \mathbf{T}_s + \mathbf{T}_\mu, \quad (3)$$

where the angular brackets $\langle \rangle$ denote a quantity averaged over the local volume V , having the limitations that it contains many droplets and that its statistical properties vary negligible [Batchelor (1998)], $\mathbf{T}_s$ is a structure dependent stress resulting from interfacial tension, and $\mathbf{T}_\mu$ is referred to as the “viscosity ratio term” [Lee and Park (1994)], but it too is structure dependent.

The viscosity ratio term can be written in terms of a series of surface integrals as

$$\mathbf{T}_\mu = (\mu_d - \mu_c) \frac{1}{V} \sum \int_{A_i} (\mathbf{u}\mathbf{n} + \mathbf{n}\mathbf{u}) ds, \quad (4)$$

in which A_i is the interfacial area of an individual droplet in V , ds is a differential element of the droplet interface, $\mathbf{n}$ is the unit normal to the interface directed into the continuous phase, and $\mathbf{u}$ is the local fluid velocity—including disturbance terms due to the dispersed phase—of the flow. The summation indicates that the quantity is taken over all the droplets, indexed by i , within V .

The structure dependent stress $\mathbf{T}_s$, reflecting the anisotropy of the disperse phase microstructure, can be expressed as [Mellema and Willemse (1983); Batchelor (1998)]

$$\mathbf{T}_s = \frac{\sigma}{V} \sum \int_{A_i} \left(\frac{1}{3} \mathbf{I} - \mathbf{n}\mathbf{n} \right) ds, \quad (5)$$

in which σ is the interfacial tension. This form appears in Mellema and Willemse (1983), but differs slightly from that of Batchelor (1998). Equation (5) is the deviatoric part of the expression used by Batchelor (1998); the isotropic terms are incorporated into the pressure. This structure dependent stress is zero for “perfectly” spherical droplets [Landau and Lifshitz (1959)].

The structure dependent terms, $\mathbf{T}_\mu$ and $\mathbf{T}_s$, can be determined analytically for a handful of simple cases. For instance, considering a single droplet in the dispersion, we can write [Mellema and Willemse (1983)]

$$(\mu_d - \mu_c) \int_{A_i} (\mathbf{u}\mathbf{n} + \mathbf{n}\mathbf{u}) ds + \sigma \int_{A_i} \left(\frac{1}{3} \mathbf{I} - \mathbf{n}\mathbf{n} \right) ds = \int_{A_i} [(\mathbf{T}_c \cdot \mathbf{n})\mathbf{y} - \mu_c(\mathbf{u}\mathbf{n} + \mathbf{n}\mathbf{u})] ds, \quad (6)$$

where $\mathbf{T}_c$ is the local stress in the continuous phase, and $\mathbf{y}$ is the position on the droplet interface. The right-hand side of this equation can be evaluated for a nearly spherical droplet. Schowalter *et al.* (1968) used this approach to determine a rheological equation for a dilute dispersion of droplets slightly deformed by the flow.

Based on this work, Mellema and Willemse (1983) show that for nearly spherical droplets

$$\mathbf{T}_\mu = \frac{6(p-1)}{5(p+1)} \mu_c \phi \mathbf{D}_0 + \text{second-order terms in } \mathbf{D}_0, \quad (7)$$

and

$$\mathbf{T}_s = \frac{19p+16}{5(p+1)} \mu_c \phi \mathbf{D}_0 + \text{second-order terms in } \mathbf{D}_0, \quad (8)$$

with the subscript “0” denoting the corresponding tensor of the flow undisturbed by the dispersed phase. Note that the undisturbed rate-of-deformation tensor is not necessarily equal to the average rate-of-deformation tensor in Eq. (3). In fact, Mellema and Willemse (1983) and Schowalter *et al.* (1968) disagree on this point. Nevertheless, $\langle \mathbf{D} \rangle$ is generally approximated with $\mathbf{D}_0$. Substituting the two relations above for the structure dependent terms into Eq. (3) yields Taylor’s result for the effective viscosity [Eq. (2)]. At first glance, this seems inconsistent, because $\mathbf{T}_s$ is identically zero for perfectly spherical

droplets, and Taylor (1932) calculated the effective viscosity with the right-hand side of Eq. (6) assuming spherical droplets. However, the left-hand side and right-hand side of Eq. (6) are indeed equal. Taylor's assumption of spherical droplets implies that $\sigma \rightarrow \infty$, and not that droplets are "perfect" spheres. The droplets are actually infinitesimally deformed.

Mellema and Willemse (1983) also find for a dilute dispersion of initially spherical droplets with $\sigma \rightarrow 0$ that

$$\mathbf{T}_\mu = \frac{10(p-1)}{2p+3} \mu_c \phi \mathbf{D}_0, \quad (9)$$

during the first moments of shear when the droplets are nearly spherical. Likewise, Palierne (1990) obtains

$$\mathbf{T}_\mu = \frac{10(p-1)}{2(1-\phi)p + (3+2\phi)} \mu_c \phi \mathbf{D}_0 \quad (10)$$

for a concentrated dispersion without interfacial tension in oscillatory shear flow. Equation (10) approaches Eq. (9) as $\phi \rightarrow 0$.

The first-order results for the structure dependent terms Eqs. (7)–(10) have led others to assume that $\mathbf{T}_\mu$ is purely viscous. We demonstrate that this assumption is incorrect. By Green's divergence theorem, the viscosity ratio stress can also be expressed as

$$\mathbf{T}_\mu = 2 \frac{(\mu_d - \mu_c)}{V} \sum \int_{V_i} \mathbf{D} dv, \quad (11)$$

where V_i is the volume of the i th droplet in the volume V , and dv is a differential volume element. We rewrite this as

$$\mathbf{T}_\mu = 2(\mu_d - \mu_c) \phi \mathbf{D}_0 + 2 \frac{(\mu_d - \mu_c)}{V} \sum \int_{V_i} (\mathbf{D} - \mathbf{D}_0) dv. \quad (12)$$

Assuming that inertia forces due to fluctuations about the average flow are negligible, and manipulating a result from Mellema and Willemse (1983), we express the disturbance in the rate-of-deformation tensor as a summation of surface integrals

$$\begin{aligned} \mathbf{D}(\mathbf{x}) - \mathbf{D}_0 &= \frac{1}{8\pi\mu_c} \sum \int_{A_i} \left[3 \frac{(\mathbf{x} - \mathbf{y})(\mathbf{x} - \mathbf{y})}{|\mathbf{x} - \mathbf{y}|^5} - \frac{\mathbf{I}}{|\mathbf{x} - \mathbf{y}|^3} \right] \\ &\quad \times (\mathbf{x} - \mathbf{y}) \cdot [\sigma \mathbf{n}(\mathbf{y}) \nabla_s \cdot \mathbf{n}(\mathbf{y}) - 2(\mu_d - \mu_c) \mathbf{D}(\mathbf{y}) \cdot \mathbf{n}(\mathbf{y})] ds(\mathbf{y}). \end{aligned} \quad (13)$$

This equation for part of the viscosity ratio term [Eq. (12)] contains two contributions. One due to the interfacial tension at every point on the interface between the two fluids, and another containing the rate-of-deformation tensor. Based on this result, we assume that the last term in Eq. (12) can be expressed in the form of a constitutive equation dependent upon $\mathbf{T}_s$ and $\mathbf{D}_0$. The simplest possibility is the linear form

$$\frac{2}{V} \sum \int_{V_i} (\mathbf{D} - \mathbf{D}_0) dV = \alpha \mathbf{D}_0 + \beta \mathbf{T}_s. \quad (14)$$

According to Mellema and Willemse (1983), in the limiting case of a dilute dispersion of nearly spherical droplets,

$$\frac{2}{V} \sum \int_{V_i} (\mathbf{D} - \mathbf{D}_0) dV = -\frac{2}{5\mu_c} (\mathbf{T}_\mu + \mathbf{T}_s). \quad (15)$$

For this case, we can analytically determine α and β , and show that

$$\mathbf{T}_\mu = \frac{10(\mu_d - \mu_c)}{2\mu_d + 3\mu_c} \mu_c \phi \mathbf{D}_0 - \frac{2(\mu_d - \mu_c)}{2\mu_d + 3\mu_c} \mathbf{T}_s. \quad (16)$$

Clearly, the viscosity ratio terms possesses an elastic component due to interfacial tension. Also, by setting $\mathbf{T}_s = 0$, it is possible to verify that the rheology of spherical droplets with $\sigma \rightarrow 0$ is accurately described by Eq. (16), i.e., Eq. (9) is recovered. For morphologies differing from slightly deformed drops, the linear approximation in Eq. (14) may not be exact, and/or α and β may be different. An interesting area of further research is the development of a constitutive equation for fluid filaments. One possible approach to this problem is to follow the methodology of Schowalter *et al.* (1968), using the velocity field for long slender droplets provided by Khakhar and Ottino (1986). However, without a more accurate approximation, we assume that Eq. (14) is valid for all structures.

We use the results of Palierne (1990), see Eq. (10), to determine that

$$\mathbf{T}_\mu = \frac{10(\mu_d - \mu_c)}{2(1 - \phi)\mu_d + (3 + 2\phi)\mu_c} \mu_c \phi \mathbf{D}_0 - \frac{2(1 - \phi)(\mu_d - \mu_c)}{2(1 - \phi)\mu_d + (3 + 2\phi)\mu_c} \mathbf{T}_s \quad (17)$$

for high volume fractions of the dispersed phase.

Consider the contribution to $\mathbf{T}_s$ by one droplet denoted $\mathbf{T}_i$. According to, e.g., Ottino (1990), the rate of stretching of an element on the interface of the droplet can be expressed as

$$\frac{1}{ds} \frac{D ds}{Dt} = \nabla \cdot \mathbf{v} - \mathbf{D} : \mathbf{nn}, \quad (18)$$

where $\mathbf{n}$, the vector normal to the interface, changes as

$$\frac{D\mathbf{n}}{Dt} = (\mathbf{D} : \mathbf{nn})\mathbf{n} - \mathbf{n} \cdot \mathbf{L}, \quad (19)$$

in which $\mathbf{L}$ is defined by $\mathbf{L} \equiv (\nabla \mathbf{v})^T$. Assuming incompressible fluids, the first term on the right-hand side of Eq. (18) is zero. Thus, using Eqs. (5) and (18), we can write

$$\begin{aligned} \frac{D\mathbf{T}_i}{Dt} &= \frac{\sigma}{V} \frac{D}{Dt} \int_{A_i} \left(\frac{1}{3} \mathbf{I} - \mathbf{nn} \right) ds \\ &= \frac{\sigma}{V} \int_{A_i} \left[-\frac{D}{Dt} (\mathbf{nn}) - \left(\frac{1}{3} \mathbf{I} - \mathbf{nn} \right) (\mathbf{D} : \mathbf{nn}) \right] ds. \end{aligned} \quad (20)$$

This assumes that the averaging volume V remains constant. (In some circumstances, the dispersed phase volume fraction will change during mixing and V will effectively increase. It is possible to show that the final constitutive equation does not change if this effect is considered.) Substituting Eq. (19) into this equation yields

$$\frac{D\mathbf{T}_i}{Dt} = \frac{\sigma}{V} \int_{A_i} \left[\mathbf{L}^T \cdot \mathbf{nn} + \mathbf{nn} \cdot \mathbf{L} - \left(\frac{1}{3} \mathbf{I} + \mathbf{nn} \right) (\mathbf{D} : \mathbf{nn}) \right] ds. \quad (21)$$

An important, simplifying assumption [Doi and Ohta (1991)] is that $\mathbf{T}_s$ can be split into a term dependent upon the flow and another accounting for interfacial tension. That is,

$$\frac{D\mathbf{T}_i}{Dt} = \frac{D\mathbf{T}_i}{Dt} \Big|_{\text{flow}} + \frac{D\mathbf{T}_i}{Dt} \Big|_{\sigma}. \quad (22)$$

A similar assumption will be made about the interfacial area [see Eq. (36)]. The flow dependent part of $\mathbf{T}_i$ is evaluated by assuming that the interface is passive [Doi and Ohta (1991)]. Therefore, we replace $\mathbf{D}$ and $\mathbf{L}$ with their undisturbed tensors, $\mathbf{D}_0$ and $\mathbf{L}_0$, to determine from Eq. (21), also using Eq. (5)

$$\frac{D\mathbf{T}_i}{Dt} \Big|_{\text{flow}} = -[\mathbf{L}_0^T \cdot \mathbf{T}_i + \mathbf{T}_i \cdot \mathbf{L}_0] + \frac{2Q_i\sigma}{3} \mathbf{D}_0 + \frac{1}{3} (\mathbf{D}_0 : \mathbf{T}_i) \mathbf{I} - \frac{\sigma}{V} \int_{A_i} \mathbf{D}_0 : \mathbf{nnnn} ds, \quad (23)$$

where Q_i is the interfacial area of the i th droplet divided by V . Following Doi and Ohta (1991), the last term on the right-hand side is approximated by assuming that

$$\int_{A_i} \mathbf{D}_0 : \mathbf{nnnn} ds \approx \frac{1}{VQ_i} \int_{A_i} \mathbf{D}_0 : \mathbf{nn} ds \int_{A_i} \mathbf{nn} ds, \quad (24)$$

in which the factor $1/VQ_i$ accounts for the presence of the extra surface integral on the right-hand side. This closure approximation obeys the condition that

$$\text{tr} \left(\int_{A_i} \mathbf{nnnn} ds \right) = \int_{A_i} \mathbf{nn} ds. \quad (25)$$

Equation (24) is however incorrect for nearly spherical droplets. As noted by Frankel and Acrivos (1970), for a spherical droplet with the surface area A_i the surface integral

$$\int_{A_i} n_j n_k n_l n_p \mathbf{e}_j \mathbf{e}_k \mathbf{e}_l \mathbf{e}_p ds = \frac{VQ_i}{15} (\delta_{jk} \delta_{lp} + \delta_{jl} \delta_{kp} + \delta_{jp} \delta_{kl}) \mathbf{e}_j \mathbf{e}_k \mathbf{e}_l \mathbf{e}_p, \quad (26)$$

in which n_j is the j th component of $\mathbf{n}$, and $\mathbf{e}_i$ is the unit vector of the j th coordinate. The fourth-order tensor resulting from this surface integral demonstrates that cross terms appear in the last term of Eq. (23). Examining Eq. (26) and recalling that

$$\int_{A_i} \mathbf{nn} ds = \frac{VQ_i}{3} \mathbf{I}, \quad (27)$$

for a sphere, suggests another possible closure approximation of the form

$$\int_{A_i} \mathbf{D}_0 : \mathbf{nnnn} ds \approx \frac{3}{5VQ_i} \left[\mathbf{D}_0 : \int_{A_i} \mathbf{nn} ds \int_{A_i} \mathbf{nn} ds + 2 \int_{A_i} \mathbf{nn} ds \cdot \mathbf{D}_0 \cdot \int_{A_i} \mathbf{nn} ds \right]. \quad (28)$$

This closure approximation does not satisfy Eq. (25).

Other possible corrections to allow for spherical droplets could be formed by adding a linear combination of the traceless tensors $\mathbf{D}_0$ and $(\mathbf{T} \cdot \mathbf{D} + \mathbf{D} \cdot \mathbf{T}) - 2(\mathbf{T} : \mathbf{D})\mathbf{I}/3$ to Eq. (24). Here, we use the closure

$$\int_{A_i} \mathbf{D}_0 : \mathbf{n} \mathbf{n} \mathbf{n} \mathbf{n} ds \approx \frac{1}{VQ_i} \int_{A_i} \mathbf{D}_0 : \mathbf{n} \mathbf{n} ds \int_{A_i} \mathbf{n} \mathbf{n} ds + \frac{2VQ_i}{15} \mathbf{D}_0, \quad (29)$$

giving the correct result for spherical droplets and satisfying condition (25). Inclusion of other traceless terms might be necessary to accurately describe more deformed droplets. A possible starting point for determining a more accurate closure is provided by Larson (1997), who shows

$$\mathbf{T}^* \propto \mathbf{C}^{1/2}, \quad (30)$$

where $\mathbf{C}$ is the Cauchy strain tensor, and $\mathbf{T}^*$ is the stress tensor for a foam or a dispersion of droplets which deform passively. [The constitutive equation for a foam under shear is shown by Reinelt (1993) to be very similar to the predictions of the Doi–Ohta model. Reinelt's analysis is based on a discrete version of Eq. (5). It assumes that the foam structure consists of tetrakaidekahedras and, thus, the surface integral in Eq. (5) can be written in terms of a summation over the 14 surfaces of a tetrakaidekahedra.] Larson's constitutive equation is maybe too complicated, in its present form, to incorporate into a model which allows for viscous dissipation and droplet shape relaxation due to interfacial tension. Further improvement of the closure approximation used could be based on the work of Wetzel and Tucker (1999).

Substituting Eq. (29) into Eq. (23) and expressing the surface integrals in terms of $\mathbf{T}_i$ yields

$$\left. \frac{D\mathbf{T}_i}{Dt} \right|_{\text{flow}} = -[\mathbf{L}_0^T \cdot \mathbf{T}_i + \mathbf{T}_i \cdot \mathbf{L}_0] + \frac{8Q_i\sigma}{15} \mathbf{D}_0 + \frac{2}{3}(\mathbf{D}_0 : \mathbf{T}_i)\mathbf{I} - \frac{\mathbf{D}_0 : \mathbf{T}_i}{Q_i\sigma} \mathbf{T}_i. \quad (31)$$

Summing this equation over all the droplets in the local volume V and assuming that these droplets possess a similar structure allows, as a first-order approximation, substitution of $\mathbf{T}_s$ and Q , where Q is the total interfacial area per volume V , for $\mathbf{T}_i$ and Q_i .

In order to complete the constitutive equation, we determine the interfacial tension contribution to $\mathbf{T}_s$. As noted by Doi and Ohta (1991), the degree of anisotropy of the dispersed phase can be represented in terms of the ratio of $\mathbf{T}_s/Q$. Elastic forces tend to restore droplets to spheres. We assume that both elastic forces resulting from interfacial tension $\mathbf{T}_s$ and from unequal viscosities [second term on the right hand side of Eq. (17)] contribute to this

$$\left. \frac{D}{Dt} \left(\frac{\mathbf{T}_s}{Q} \right) \right|_{\sigma} = -c_1 E \mathbf{T}_s, \quad (32)$$

in which

$$E = \left(\frac{5\mu_c}{2(1-\phi)\mu_d + (3+2\phi)\mu_c} \right). \quad (33)$$

We note that the Lee–Park model assumes that this rate of structure relaxation is proportional to $\mathbf{T}_s$. This is not an issue in the Doi–Ohta model because $\mathbf{T}_s$ is equal to the elastic part of $\mathbf{T}_\mu + \mathbf{T}_s$ when the viscosity ratio is one and thus $E = 1$. Our correction to the Lee–Park model allows for the fact that higher viscosity ratio droplets relax slower than low viscosity ratio droplets. Dimensional analysis shows that

$$c_1 = \frac{1}{\lambda} \frac{\sigma}{\phi \mu_c}, \quad (34)$$

with λ a dimensionless factor. The volume fraction is included in this relation to make the resulting constitutive equation consistent with Taylor's effective viscosity, but λ may be a function of ϕ and structure.

The factor λ is likely to depend upon the viscosities and the microstructure. When λ is structure dependent, the constitutive equation can become significantly more complex, containing time scales for different structures. However, it will be shown that with a relatively simple relation the model can already be considerably successful in the prediction of very different rheological phenomena. We will postpone a suggestion for this expression until results are presented. For the moment the factor λ is written as

$$\lambda = \lambda_0 f_{\text{struct}}, \quad (35)$$

in which the structure part f_{struct} should be chosen such that for the linear case, i.e., only slightly deformed droplets, its value approaches one. Applying Eq. (34) and assuming that the change in interfacial area can be expressed in terms of a flow contribution and an interfacial tension contribution, like Eq. (22) for the structure related stress, we rewrite Eq. (32) as

$$\left. \frac{D\mathbf{T}_s}{Dt} \right|_{\sigma} = -\frac{E}{\lambda} \frac{\sigma Q}{\phi \mu_c} \mathbf{T}_s + \frac{1}{Q} \left(\left. \frac{DQ}{Dt} \right|_{\text{flow}} - \left. \frac{DQ}{Dt} \right|_{\text{flow}} \right) \mathbf{T}_s. \quad (36)$$

Analysis of the interfacial area similar to that for the flow dependent terms in $\mathbf{T}_s$ shows that

$$\left. \frac{DQ}{Dt} \right|_{\text{flow}} = \frac{1}{\sigma} \mathbf{D}_0 : \mathbf{T}_s. \quad (37)$$

Using Eqs. (22), (31), (36), and (37) we determine that

$$\mathbf{T}_s^{(1)} = -\left(\frac{1}{\tau} - \frac{1}{Q} \frac{DQ}{Dt} \right) \mathbf{T}_s + \frac{8\sigma Q}{15} \mathbf{D}_0 + \frac{2}{3} (\mathbf{D}_0 : \mathbf{T}_s) \mathbf{I} - \frac{2(\mathbf{D}_0 : \mathbf{T}_s)}{\sigma Q} \mathbf{T}_s, \quad (38)$$

where $\mathbf{T}_s^{(1)}$ is the covariant (or lower) convected derivative of $\mathbf{T}_s$ and the relaxation time τ is given by [with E defined by Eq. (33)]

$$\tau = \frac{\lambda \phi \mu_c}{E \sigma Q}. \quad (39)$$

In order to determine λ for nondilute concentrations, we approximate the relaxation time τ for the linear case, i.e., $\lambda \rightarrow \lambda_0$, with that for a nondilute dispersion of spherical droplets, shown by Graebling *et al.* (1993), to be

$$\tau_0 = \frac{3\phi}{4\sigma Q_0} F(p, \phi); \quad F(p, \phi) = \frac{(19\mu_d + 16\mu_c)[2(1-\phi)\mu_d + (3+2\phi)\mu_c]}{10(1-\phi)\mu_d + (10-4\phi)\mu_c}. \quad (40)$$

This relaxation time is not constant, since the equilibrium interfacial area Q_0 in our model changes after every drop/filament breakup. Since the interfacial area is related to the averaged drop radius and volume fraction by $Q_0 = 3\phi/R_a$, the relaxation time τ_0 can also be written as

$$\tau_0 = \frac{R_a \mu_c}{4\sigma} F(P, \phi), \quad (41)$$

a well know form, also named the Palierne relaxation time [Vinckier (1998)], and originally obtained by Oldroyd (1953).

The relaxation time τ for deformed droplets is now given by

$$\tau = \frac{Q_0}{Q} \tau_0 f_{\text{struct}}. \quad (42)$$

We determine that [using Eqs. (39) and (40)]

$$\lambda_0 = \frac{15}{8} \left(\frac{19\mu_d + 16\mu_c}{5(1-\phi)\mu_d + (5-2\phi)\mu_c} \right). \quad (43)$$

The final constitutive equation is written in terms of the sum of elastic forces resulting from interfacial tension and from unequal viscosities $\mathbf{T}_\sigma \equiv E\mathbf{T}_s$ as

$$\langle \mathbf{T} \rangle = -P\mathbf{I} + \left[2 + \frac{10(\mu_d - \mu_c)}{2(1-\phi)\mu_d + (3+2\phi)\mu_c} \phi \right] \mu_c \mathbf{D}_0 + \mathbf{T}_\sigma, \quad (44)$$

with

$$\mathbf{T}_\sigma^{(1)} + \left[\frac{1}{\tau} - \frac{D \ln(Q)}{Dt} \right] \mathbf{T}_\sigma = {}^4\mathbf{L} : \mathbf{D}_0, \quad (45)$$

in which ${}^4\mathbf{L}$ is a fourth order tensor given by

$${}^4\mathbf{L} = \frac{8\sigma QE}{15} {}^4\mathbf{I} + \frac{2}{3} \mathbf{I} \mathbf{T}_\sigma - \frac{2}{E\sigma Q} \mathbf{T}_\sigma \mathbf{T}_\sigma. \quad (46)$$

Equation (44) was suggested by Lacroix *et al.* (1997) for describing the rheology of a blend in oscillatory shear. However, they determined different coefficients in relation (45) for $\mathbf{T}_\sigma$. In the case of small deformations, the differences for $\mathbf{T}_\sigma$ are, however, negligible.

The fourth order tensor ${}^4\mathbf{L}$ can be rewritten as

$${}^4\mathbf{L} = \frac{19\mu_d + 16\mu_c}{[5(1-\phi)\mu_d + (5-2\phi)\mu_c]} \frac{Q}{Q_0} \phi \frac{\mu_c}{\tau_0} {}^4\mathbf{I} + \frac{2}{3} \mathbf{I} \mathbf{T}_\sigma - \frac{2}{E\sigma Q} \mathbf{T}_\sigma \mathbf{T}_\sigma, \quad (47)$$

which helps for comparison with the results of Schowalter *et al.* (1968); Choi and Schowalter (1975), and Frankel and Acrivos (1970) for slightly deformed droplets. Equation (45) is therefore rewritten in terms of the Jaumann derivative $\mathcal{D}/\mathcal{D}t$ as

$$\begin{aligned} \frac{\mathcal{D}\mathbf{T}_\sigma}{\mathcal{D}t} + \left[\frac{1}{\tau} - \frac{D \ln(Q)}{Dt} \right] \mathbf{T}_\sigma &= \frac{19\mu_d + 16\mu_c}{E[5(1-\phi)\mu_d + (5-2\phi)\mu_c]} \frac{Q}{Q_0} \phi \frac{\mu_c}{\tau_0} \mathbf{D}_0 - \left[\mathbf{T}_\sigma \cdot \mathbf{D}_0 + \mathbf{D}_0 \right. \\ &\quad \left. \cdot \mathbf{T}_\sigma - \nu \frac{2}{3} (\mathbf{D}_0 : \mathbf{T}_\sigma) \mathbf{I} \right] - \frac{2}{E\sigma Q} (\mathbf{D}_0 : \mathbf{T}_\sigma) \mathbf{T}_\sigma. \end{aligned} \quad (48)$$

The constitutive equations for nearly spherical droplets are in terms of droplet radius, while Eq. (48) allows for more deformed structures as the droplet stretch is included. This difference aside, Eq. (48) is very similar to constitutive equations for slightly deformed

droplets when the linear limit is considered, i.e., $f_{\text{struct}} = 1$ and $Q \rightarrow Q_0$. Then the relaxation times and effective zero-shear viscosities are the same. We forced the linear relaxation time by approximating it with the relaxation time from one of these models, but the viscosity is not forced. This similarity in the effective zero-shear viscosities supports our result. The second term on the right-hand side of our constitutive equation is not present in constitutive equations for slightly deformed droplets; however, if our constitutive Eq. (48) is expressed in terms of $\langle \mathbf{T} \rangle$, then another second-order term in $\mathbf{D}$ appears due to this second term. This term also appears in the constitutive equation for nearly spherical droplets, but the coefficient is different. For this reason, the dimensionless constant ν is included to allow for more flexibility, as these terms may be influenced by the closure. However, the present analysis yields $\nu = 1$. The last terms on the left and right sides of Eq. (48) do not appear in the equation for slightly deformed droplets, because Q is approximately constant in this case, and third-order terms do not appear in the equation for slightly deformed droplets.

In order to apply Eq. (44), one must determine the interfacial area. To this effect, Lee and Park (1994) use the rather *ad hoc* relationship

$$\frac{DQ}{Dt} = \frac{1}{\sigma} \mathbf{D}_0 : \mathbf{T} - \lambda c_2 \frac{\sigma}{\mu_c} Q^2 - \frac{\lambda c_3}{\sigma \mu_c} \mathbf{T} : \mathbf{T}, \quad (49)$$

in which c_2 and c_3 are dimensionless constants, which are essentially adjustable parameters. On the right-hand side, the first term is the change in interfacial area due to the passive stretching of the interface, the second term accounts for coalescence, and the last term accounts for the relaxation of the surface due to interfacial tension, including breakup.

In some cases, this approach gives reasonable results [Lee and Park (1994); Lacroix *et al.* (1997); Vinckier *et al.* (1996)], but there are limitations. According to Eq. (49), Q approaches zero when the flow is stopped and $t \rightarrow \infty$. Therefore, the approximation is only valid for cocontinuous phases, or $\phi \sim 0.5$. This limitation is generally corrected by assuming that $c_2 \propto \sqrt{\mathbf{T} : \mathbf{T}}$, i.e., interfacial area stops decaying when the droplets are spherical. Furthermore, as discussed in two recent notes [Vinckier *et al.* (1998); Lacroix *et al.* (1998)], Eq. (49) cannot predict phenomena resulting from hysteresis.

We will determine the interfacial area by applying a model for the dispersed phase morphology which is described in Sec. III. Most parts of this model for the dynamics of liquid–liquid mixing are experimentally validated.

III. BASICS OF LIQUID–LIQUID MIXING

A. Kinematics

The motion of a passive particle in a flow is described by

$$\frac{d\mathbf{x}}{dt} = \mathbf{v}(\mathbf{x}, t), \quad (50)$$

in which $\mathbf{v}(\mathbf{x}, t)$ is the Eulerian velocity field, at the position $\mathbf{x}$ and time t . The evolution equations describing the (affine) stretching β and (approximately) the affine orientation $\mathbf{m}$ of a material filament are obtained with the rate-of-deformation tensor $\mathbf{D}$

$$\dot{\epsilon}_{\mathbf{m}} = \frac{d \ln(\beta)}{dt} = \mathbf{D} : \mathbf{m} \mathbf{m}, \quad (51)$$

and

$$\frac{d\mathbf{m}}{dt} = \mathbf{m} \cdot [\nabla \mathbf{v} - \mathbf{I}(\mathbf{D}:\mathbf{m}\mathbf{m})], \quad (52)$$

respectively. The affine orientation can be obtained exactly from the maximum eigenvalue and corresponding eigenvector of the Finger tensor

$$\mathbf{B} = \mathbf{F} \cdot \mathbf{F}^T = \sum_{i=1}^3 \beta_i^2 \mathbf{m}_i \mathbf{m}_i. \quad (53)$$

B. Capillary number

The deformation and breakup of an initially spherical drop with radius R in a flow is characterized by the capillary number defined as

$$\text{Ca} \equiv \frac{\mu_c \dot{\gamma} R}{\sigma}, \quad (54)$$

in which $\dot{\gamma}$, referred to as the shear rate, is defined by $\sqrt{2\mathbf{D}:\mathbf{D}}$. When Ca is less than some critical value Ca_{crit} in a stationary, homogeneous flow field, the droplet reaches a stable ellipsoidal shape.

C. Drop deformation

When $\text{Ca} > \kappa \text{Ca}_{\text{crit}}$, where κ is a flow dependent constant (approximately two in shear and about five in planar elongational flows [Janssen (1993)]), the droplet stretches while the cross section tends to stay circular due to interfacial tension. Initially, affine stretching occurs and the droplets deform into filaments. However, depending on the ratio $\text{Ca}/\text{Ca}_{\text{crit}}$, after the initial affine stretching, the stretching becomes nonaffine and next, after the droplet is deformed substantially, the deformation becomes affine again (see for example [Janssen (1993); Meijer and Janssen (1994); Janssen and Meijer (1997)]). For elongational flow Stegeman *et al.* (1999) give an expression for this behavior in terms of the nonaffine filament stretch rate $d \ln(\beta)/dt$ as a function of the bulk stretch rate $\dot{\epsilon}$. If we assume that for shear flow, to a good approximation, the relation for elongational flow holds in the orientation direction of the filament $\mathbf{m}$ with the bulk stretch rate $\dot{\epsilon}_{\mathbf{m}}$ given by Eq. (51), then

$$\frac{d \ln(\beta)}{dt} = \frac{\beta^3 + \frac{2}{3p} + \frac{5}{12} - \frac{g}{f\text{Ca}} - \frac{g}{4p\text{Ca}}}{\beta^3 + \frac{3}{4} + \frac{1}{2p} + \frac{4p}{3f} - \frac{2}{3f}} \dot{\epsilon}_{\mathbf{m}}, \quad (55)$$

in which p the viscosity ratio and the functions g and f are defined by

$$g = \frac{\sqrt{\beta}(\beta^6 + 2\beta^3 - 3)}{2\beta^6}; \quad f = \frac{1}{\ln(2\sqrt{\beta^3})} + \frac{3}{2} \frac{1}{(\ln(2\sqrt{\beta^3}))^2}. \quad (56)$$

An exact (but rather complex) solution for the deformation of an ellipsoidal Newtonian droplet suspended in another Newtonian fluid with different viscosity and zero interfacial tension is given by Wetzel and Tucker (2001) and was experimentally verified by

Comas-Cardona and Tucker (2001). This model could be useful for further validation and/or improvement, but will not be used any further here.

From Eqs. (55) and (56) the instantaneous filament stretching, and thus the characteristic radius R can be determined by

$$\frac{R(t_{i+1})}{R(t_i)} = \sqrt{\frac{\beta(t_i)}{\beta(t_{i+1})}}. \quad (57)$$

The interfacial area of filaments is computed assuming a cylindrical shape with spherical ends. For $\text{Ca}_{\text{crit}} < \text{Ca} < \kappa \text{Ca}_{\text{crit}}$ no real filaments will grow and a different approach will be taken (see next section).

D. Modes of filament breakup

Filaments are divided into two categories: those being stretched, and those not being stretched in a relatively stagnant part of the flow. If $\dot{\beta} > 0$ and

$$\text{Ca} > 0.001/\sqrt{p}, \quad (58)$$

the filament is stretching—newly formed filaments are in this category—otherwise the filament is considered relatively static. The breakup of a static filament of fluid is driven primarily by capillary instabilities. The initial growth of the disturbance on the surface of a filament can be described by linear stability analysis [Tomotika (1935)], however, its predictions have been shown to be more general [Janssen (1993); Janssen and Meijer (1993, 1995); Meijer and Janssen (1994); Janssen and Meijer (1997)]. Static breakup is modeled by assuming that the fastest growing disturbance—termed the dominant growth rate Ω_m , with a dimensionless wavelength λ_m —, finally causes breakup. Both are unique functions of the viscosity ratio. The amplitude of the disturbance is given by

$$\alpha \approx \alpha_0 \exp\left(\frac{\sigma \Omega_m}{\mu_c R} t\right), \quad (59)$$

where α_0 is the initial amplitude of the disturbance, which depending upon the conditions may vary from 10^{-7} to 10^{-9} m—the lower value obtained by assuming thermal fluctuations of the interface, and the higher observed in experiments. A mathematical description of Ω_m can be found in Tomotika (1935); Janssen (1993); Janssen and Meijer (1993, 1995); Meijer and Janssen (1994); Janssen and Meijer (1997).

If $\alpha > \sqrt{2/3}R$, the filament breaks up in droplets with the average radius R_{ave}

$$R_{\text{ave}} = \left(\frac{3}{4} \frac{\lambda_m(p)}{R_f}\right)^{1/3} R. \quad (60)$$

This equation is based on conservation of mass.

The breakup of a fluid filament in a linear flow, also dominated by capillary breakup, can be described by linear stability theory [Tomotika (1936); Khakhar and Ottino (1987)]. A detailed analysis of this problem can be found in Janssen (1993); Janssen and Meijer (1993); Tjahjadi and Ottino (1991). The critical radius of a filament in an elongational flow can be approximated by the correlation

$$R_{\text{crit}} \approx 0.02 \alpha_0^{0.1} \left(\frac{\mu_c \dot{\epsilon}_m}{\sigma}\right)^{-0.9} p^{-0.45}, \quad (61)$$

provided that the stretching is relatively constant and positive [Tjahjadi and Ottino (1991)], and $\mu_c \dot{\epsilon}_m \alpha_0 / \sigma$ is less than some value dependent upon the viscosity ratio [Janssen (1993); Janssen and Meijer (1993)]. The average drop radius resulting from breakup is

$$R_{\text{ave}} \approx \left(\frac{3\pi}{2} \right)^{1/3} R_{\text{crit}}. \quad (62)$$

Long extended filaments also break up by a mechanism referred to as “end-pinching” [Stone (1994)]. For $Ca < \kappa Ca_{\text{crit}}$ modestly extended droplets ($L/R_0 < 15$) will occur and their behavior differs from that of a filament. When L/R_0 is very small, the droplet will retract into a sphere if the flow is stopped; otherwise, the droplet extends until breakup by one of three mechanisms: “end pinching,” “tip streaming” [Stone (1994)], or “necking” [Grace (1971)], none of which are completely understood. (Other mechanisms may also play a role in complex flows or in highly concentrated dispersion. For instance, in complex flows, “fold pinching” may occur at the bend in a filament created by stretching and folding [Tjahjadi and Ottino (1991)]. And, an interaction between a filament and a droplet, sometimes seen in concentrated dispersions, may result in breakup of the filament [Janssen and Meijer (1997)].)

Our first-order approximation assumes that for $Ca_{\text{crit}} < Ca < \kappa Ca_{\text{crit}}$ breakup is dominated by necking. Experimental data from Grace (1971) suggest that the time for breakup by necking for an initially spherical droplet in a steady two-dimensional flow where $Ca = Ca_{\text{crit}}$ can be approximated by the empirical form

$$t_{\text{neck}} \approx 85.3 \left(\frac{R_0 \mu_c}{\sigma} \right) p^{0.45}. \quad (63)$$

Assuming that the rate of necking for Ca between Ca_{crit} and κCa_{crit} increases linearly with shear rate, the evolution of the characteristic radius can be approximated by

$$\frac{dR}{dt} = -3.91 \times 10^{-3} p^{-0.45} Ca_{\text{crit}}^{-1} \dot{\gamma}_k R + r_{\text{coalesce}}, \quad (64)$$

in which r_{coalesce} is the right-hand side of Eq. (66) (see next part). The coalescence term is unimportant unless $R/(H/\sigma)^{1/2} < 10p^{-9/8}$. We neglect r_{coalesce} because it is small and probably overestimates the rate of coalescence of deforming drops. The linear dependence of the rate of necking on shear rate is consistent with another model based on a different theory [Patlazhan and Lindt (1996)]. In order to simplify the computations, we make a further, crude (but not so important) approximation: for $Ca_{\text{crit}} < Ca < \kappa Ca_{\text{crit}}$ droplets have a constant average stretch ratio $\beta = 4$.

E. Coalescence

A large capillary number implies that breakup is important, for a low capillary number ($Ca < Ca_{\text{crit}}$), droplets may come into contact and coalesce. Here, coalescence is modeled (relatively simple) according to Chesters (1991) [see also Janseen (1993); Janssen and Meijer (1993, 1995)]. The analysis is simplified by characterizing the droplet size distribution with an average size. (More complete descriptions require using cumbersome population balances.) The frequency of coalescence can be written as

$$J \approx \exp \left(- \frac{\sqrt{3}R}{4h_{\text{crit}}} p Ca^{3/2} \right) \frac{4}{\pi} \dot{\gamma} \phi n. \quad (65)$$

Here, h_{crit} is the distance at which attractive van der Waals forces begin to dominate [Chesters (1991)], ϕ is the volume fraction of droplets, and R and Ca are the characteristic droplet radius and the capillary number, respectively.

From Eq. (65), the rate of change in the characteristic radius of the subpopulation is described by

$$\frac{dR}{dt} = \exp\left(-\frac{\sqrt{3}R}{4h_{\text{crit}}} p C a_k^{3/2}\right) \frac{4}{3\pi} \dot{\gamma} \phi_k R. \quad (66)$$

When a stationary state is obtained for the case of coalescence, the stretch β of the droplets can be determined using a relation for the deformation derived by Cox

$$\frac{L-B}{L+B} = g(p, Ca) = \frac{5(19p+16)}{4(p+1) \sqrt{(19p)^2 + \left(\frac{20}{Ca}\right)^2}}, \quad (67)$$

in which L and B the long and short axis of the extend droplet. Using volume conservation, assuming the shape of the extended droplet to be ellipsoidal and defining $\beta = L/(2R_0)$ one gets

$$\beta = \left(\frac{1+g(p, Ca)}{1-g(p, Ca)} \right)^{2/3}, \quad (68)$$

where R_0 is the radius of the initial undeformed droplet.

F. Microstructure evolution

The spatial evolution of the morphology of a dispersion may be predicted by the following approach. The system is discretized in time by taking time intervals of Δt and, in general, the population of droplets/filaments may be divided in a number of subpopulations. Every subpopulation consists of either droplets *or* filaments, but not both. Subpopulations are characterized by the average droplet/filament radius R_k and volume fraction ϕ_k with the subscript k denoting the subpopulation between 1 and N . Filament subpopulations are also characterized by the orientation vector $\mathbf{m}_k$ parallel to the axes of the filaments and the disturbance amplitude α_k , which grows from α_0 . We do not allow for exchange of dispersed material between subpopulations.

The algorithm used is illustrated in Fig. 1. Starting at t_i , the flow deforms each subpopulation (for $Ca > \kappa Ca_{\text{crit}}$) until t_{i+1} . This approximation has been shown to be reasonable [Tjahjadi and Ottino (1991)] for a system with conditions similar to those of interest here.

To incorporate the influence of other droplets in the model, individual drops and threads are assumed to experience an effective matrix viscosity $\mu_{c,\text{eff}}$. Throughout the entire model for the microstructure evaluation, the matrix viscosity μ_c is replaced by this effective viscosity $\mu_{c,\text{eff}}$ which is determined by the relation given by Choi and Schowalter (1975)

$$\mu_{c,\text{eff}} = \mu_c \left[1 + \phi \frac{5p+2}{2(p+1)} \left(1 + \phi \frac{5(5p+2)}{4(p+10)} \right) \right]. \quad (69)$$

The critical radius of a stretching subpopulation is found using Eq. (61). If $R < R_{\text{crit}}$, then a filament subpopulation disperses into a droplet subpopulation with R calculated

from Eq. (62). This assumes that the time necessary to stretch a droplet to R_{crit} is much greater than the time for the disturbance to grow from α_0 to R_k . Furthermore, this approximation becomes more accurate as Δt approaches the disturbance growth time.

Although this model is rather coarse, it should provide the correct time scales for the changes in morphology and the correct order of the magnitude of the interfacial area and, therefore, provide the opportunity to investigate the influence of such changes on the rheological behavior of a liquid-liquid system. For example, using Eqs. (44) and (45) with the interfacial area determined by our model allows prediction of phenomena resulting from hysteresis.

G. Effective measures

We note that the coupling of the model for the microstructure development with the rheological model for the stress seems a difficult computational problem, because the interfacial area approximated by our model is not continuous when breakup occurs. When rheological parameters are a function of the state of the microstructure, or when the interfacial area occurs explicitly in the rheological model, step-like changes in (parts of) the rheological model will occur which are not very physical.

This problem is due to the one-droplet-models (ODMs) for droplet deformation and breakup leading to one breakup time for a population of deformed droplets at which properties change stepwise. In reality the deformation and breakup are statistical processes which will smooth the different droplet transitions. We would like to capture these smooth transitions in the rheological modeling. Smooth transitions could possibly be described by taking a (broad) distribution of droplets, i.e., a large number of subpopulations. However, this is not in line with our approach to keep the model as simple as possible and computationally tractable, i.e., restrict to one or a few droplet populations.

Therefore, so-called *effective measures* are introduced that will be applied in the rheological model instead of the measures obtained directly from the ODM. Measures from the ODM are considered to give the equilibrium values that, after step-like changes, will be approached in time by the effective measures. The difference between the ODM measure and the effective measure is the driving force for the effective measure. The rate of change is characterized by a time constant which is specific for each type of transition. This idea leads to simple first order differential equations for the two measures involved in the rheological model, namely the interfacial area Q and the droplet stretch ratio β

$$\tau_{Q,i} \dot{Q}_{\text{eff}} + Q_{\text{eff}} = Q_+, \quad (70)$$

$$\tau_{\beta,i} \dot{\beta}_{\text{eff}} + \beta_{\text{eff}} = \beta_+, \quad (71)$$

in which Q_+ and β_+ are the values obtained from the ODMs after step-like changes. When the coalescence case is reached, the β_+ is calculated using Eq. (68).

The index “ i ” indicates the type of transition being modeled in this way: $i = 1$: static breakup of a filament, $i = 2$: dynamic breakup of a filament, $i = 3$: transition from necking/end pinching to coalescence.

For all the other transitions $Q_{\text{eff}} = Q$ holds. When a few droplet subpopulations are used, and interaction between these populations is not taken into account, they can be treated separately and in the same way as one population, i.e., by applying Eq. (70) and (71) for every subpopulation and using the same parameter values for the characteristic times $\tau_{Q,i}$ and $\tau_{\beta,i}$.

Notice that with this approach not only transitions between different stages are smoothed, but also the experimentally observed phenomenon of a hampered breakup of filaments, due to the presence of other filaments [Elemans *et al.* (1997)], can be captured.

IV. RESULTS

The model is validated by comparing with experimental results from Vinckier (1998). The role of different model aspects, such as the structural function f_{struct} , introduced in Eq. (35), will be clarified. For that purpose we will use the experimental results for a 10% poly-isobutene (PIB) in poly-dimethylsiloxane (PDMS) blend and focus on the excess [excess: due to the interfacial tension, i.e., described by Eq. (45)] shear stress and the first normal stress difference for startup and cessation of shear flow.

A. Parameter settings

The important material properties (at 23.7 °C) are from Vinckier (1998):

Fraction dispersed fluid:	$\phi = 0.1$
Matrix fluid (PDMS) zero shear rate viscosity and relaxation time:	196 (Pa s), 2.710^{-4} (s)
Effective matrix fluid zero shear viscosity:	235 (Pa s)
Dispersed fluid zero shear rate viscosity and relaxation time:	86 (Pa s), 2.710^{-2} (s).
Viscosity ratio:	$p = 0.44$
Effective viscosity ratio [see Sec. III, Eq. (69)]:	$p_{\text{eff}} = 0.37$
Interfacial tension:	$\sigma = 0.0023$ (N/m)
Initial average drop diameter at initial shear rate of 0.3 (s^{-1}):	$19 \cdot 10^{-6}$ (m)
Initial amplitude of filament disturbance:	$\alpha_0 = 4.66 \cdot 10^{-9}$ m
Hamaker constant:	1×10^{-20}

With these values, the factor that combines the viscoelastic stresses due to unequal

viscosity and interfacial stress [Eq. (33)] becomes $E = 1.25$. Droplet breakup in a Newtonian system is governed by the viscosity ratio and the Capillary number as defined in Eq. (54). For a given viscosity ratio, under quasistatic conditions, there is a critical capillary number at which a droplet will continuously deform and finally break. For shear flow, the critical capillary number Ca_{crit} used in the morphology model is based on Grace's experimental data [Grace (1971)] and given by the empirical relation de Bruijn (1989)

$$\log(Ca_{\text{crit}}) = -0.506 - 0.0994 \log(p) + 0.124(\log(p))^2 - \frac{0.115}{\log(p) - 0.6107}. \quad (72)$$

For planar elongational flow the empirical relation used is given by

$$\log(Ca_{\text{crit}}) = 0.0331(\log(p) - 0.5)^2 - 0.699. \quad (73)$$

The rheology of the blend components is such that a clear contribution to the shear and normal stress is observed. For the system studied here, these contributions can be dealt with separately using a linear mixing rule as was done by Vinckier (1998). Here, we subtract the contribution of the components from the experimental results before we compare them with the extra stresses as predicted by our model.

The choice of the function f_{struct} is based on the experimental findings of Vinckier. For the blend considered the rheological relaxation time τ was found to correlate with the aspect ratio r_p , for moderate aspect ratios up to 20, (i.e., for values of β up to eight) as $\tau = \tau_0 r_p^{2/3}$. Because the relaxation time expressed in terms of the structure parameter [see Eq. (42)] depends also on the interfacial area, and for large stretch ratios the interfacial area scales with the stretch ratio as $\sqrt{\beta}$, f_{struct} correlates with the stretch ratio as $\beta^{1.5}$. Based on these findings we use a simple power-law relation for f_{struct}

$$f_{\text{struct}} = (\beta - 1)^{1.5} + 1. \quad (74)$$

To define this relation in a more precise way, indications can be found in, for example, van Puyvelde (1999) who presents detailed experimental results.

The characteristic times for the effective measures [Eqs. (70) and (71)] are chosen to fit one of the measurements [step-up strain rate $0.3\text{--}3 \text{ (s}^{-1}\text{)}$, see Fig. 5 for the dynamic breakup transitions and Fig. 9 for the static breakup transition]. The effect of varying these parameters is demonstrated in the next paragraph. The static breakup transition of a filament is described using one value for the characteristic times $\tau_{Q,1} = \tau_{\beta,1} = 5 \text{ (s)}$. For the transitions of a filament to droplets by dynamic breakup and from necking to coalescence one characteristic value was sufficient for both the effective interfacial area and the stretch ratio: $\tau_{Q,i} = \tau_{\beta,i} = 10 \text{ [s]}$, $i = (2,3)$. The function f_{struct} is taken according to Eq. (74). This is used as the standard set. The effect of using the ODM measures instead of the effective measures is shown in the paragraph on polydispersity.

Numerical integration of Eq. (45) was performed using an implicit Euler scheme using a constant time step [typically $\Delta t = 0.1 \text{ (s)}$].

The predictions for the excess first normal stress difference $N_{1,\text{excess}}$ and excess shear stress T_{12} will be used to finalize the parameter setting. We consider (again) the case of step up from a shear rate of $\dot{\gamma} = 0.3 \text{ (s}^{-1}\text{)}$ to a shear rate of $\dot{\gamma} = 3 \text{ (s}^{-1}\text{)}$. The initial shear rate was used by Vinckier for all experiments to create the same initial morphology. In the model, this situation can also be obtained by starting with an initial stretch ratio $\beta_{\text{init}} = 2$. Results are given in Figs. 2(a) and 2(b) [the experimental results correspond to Fig. 5.3 in Vinckier (1998)]. When the parameter ν , introduced in Eq. (48), is chosen so that $\nu = 1$, excess stresses are typically overpredicted by a factor 2 [Figs. 2(a) and 2(b),

FIG. 2. Excess first normal stress difference (a) and shear stress (b) after step up from 0.3 to 3 (s^{-1}). Asterisk denotes measurements according to Vinckier (1998). Lines indicate model predictions for (1) parameter $\nu = 1$; (2) reduction of the interfacial area by a factor 2; and (3) parameter $\nu = 2$.

curve 1]. Although effective measures are used that smooth the stress response, small wiggles are still visible when the stress reaches final levels. In this range, coalescence dominates (see e.g., Fig. 5). However, due to small changes in the variables, the model frequently switches from the coalescence to the necking mode. This is illustrated in Figs. 3(a) and 3(b) where the development of the values of the normal and effective measures is shown. This switching between coalescence and necking causes the wiggles.

The order of magnitude of the difference between model predictions and the experimental results could be reduced by lowering the amount of interfacial area by the same

FIG. 3. Development of the normal and effective interfacial area Q (a) and the stretch ratio β (b). Flow conditions and measurements as in the caption of Fig. 1.

order [see Figs. 2(a) and 2(b), curve 3]. However, there is no reason for such a dramatic adoption of a quantity which is quite well determined experimentally. Adopting the relaxation times in the modeling of the effective measure only changes the transient behavior, not the final stress levels (this will be discussed in the sequel). The only flexibility left, offered by the model, is the parameter ν . With $\nu = 2$, predicted and experimental results agree well with respect to the excess first normal stress difference $N_{1,\text{excess}}$ [see Fig. 2(a), curve 2]. Considering the excess shear stress T_{12} , the final level and time scales are predicted quite well [Fig. 2(b), curve 2]. Even the initial peak is

FIG. 4. Excess first normal stress difference for (1) approximate droplet orientation [Eq. (52)] and (2) using the eigenvector corresponding to the maximum eigenvalue of the Finger tensor.

shown by the model, but the height of the maximum of this peak is not captured. It is not known how much of this experimentally observed peak is due to the viscoelastic behavior of the components. For the rest of the results presented, the parameter $\nu = 2$.

As discussed in Sec. III, droplet orientation can be determined using Eq. (52) or, more precisely, using the eigenvector of the Finger tensor which corresponds with the maximum eigenvalue. The difference in $N_{1,\text{excess}}$ is shown in Fig. 4. Using the approximate method underpredicts $N_{1,\text{excess}}$ (curve 1) in the transient part of the stress response, and the maximum stress peak is also shifted too far to the right. Therefore, in the following, only the method based on the Finger tensor is used.

Notice that the characteristic times τ_Q and τ_β for the effective measures [Eqs. (70) and (71)], and the parameter ν [Eq. (48)] are the only parameters that were chosen to fit the experimental data. All other parameters are obtained from other sources [Vinckier (1998)].

B. Model features

The role of the structure function f_{struct} is demonstrated in Figs. 5(a) and 5(b) by setting $f_{\text{struct}} = 1$. In this figure it is also indicated, with vertical lines, which mode is active, i.e., when stretching, necking or coalescence occurs (we do not distinguish between coalescence and the sporadic necking in the final stage). It is observed that the model gives rather poor results when $f_{\text{struct}} = 1$. The first part of the transient curve of $N_{1,\text{excess}}$, i.e., the upswing of the stress during filament stretching, is absent. Also the end value is far too low. Correct prediction of the end value depends on the use of an effective matrix viscosity [Eq. (69)] instead of the matrix viscosity as determined for the pure component and the use of Eq. (68) to predict the deformed state of the droplets in the stationary state.

FIG. 5. Excess first normal stress difference (a) and shear stress (b). Flow conditions and measurements as in the caption of Fig. 1. Lines indicate model predictions for (1) $f_{\text{struct}} = 1$, (2) f_{struct} according to Eq. (74).

Similar conclusions can be drawn for the shear stress [Fig. 5(b)]. Only the full model predicts the particular behavior that is observed in the experimental results, i.e., a sharp initial local maximum followed by a valley and, finally, a stationary maximum.

In Figs. 6(a) and 6(b) the effect of varying the characteristic times $\tau_{Q,i} = \tau_{\beta,i}$, $i = (2,3)$ is demonstrated. It is seen that the major effect is found in the stage of coalescence. From this the value of 10(s) for these characteristic times was chosen.

Next, using the fixed set of parameter values, the first normal stress differences were determined for a range of shear rates (Fig. 7). The experimental results were scaled by

FIG. 6. First normal stress difference (a) and shear stress (b). Flow conditions and measurements as in caption Fig. 1. Lines are for different characteristic times $\tau_{Q,i} = \tau_{\beta,i}$ $i = (2,3)$, Numbers 1–3 correspond to 4, 7, and 10 (s).

Vinckier with the initial value of the first normal stress difference $N_{1,0,\text{excess}}$ and plotted versus the strain. The scaling used here is by a factor of 16(Pa). First of all, it is seen that the end levels are predicted quite well. Furthermore, the maxima in the normal stress are mostly overpredicted, especially for the higher shear rates, and are shifted. However, considering the the rather coarse modeling of the microstructure evolution, the agreement is satisfactory. When the shear data are considered, the zero shear viscosity of the blend

FIG. 7. First normal stress difference after step up from 0.3 to different levels of shear rates: 1, 2, 3, 4, and 5 (s^{-1}). Asterisk denotes measurements according to Vinckier (1998).

is predicted quite well [220(Pa) versus 225(Pa) experimentally found], but the experimentally observed (slight) shear thinning behavior of the blend viscosity is not seen using the model.

From the excess stress tensor, the orientation development of the structure can be monitored by determining the eigenvectors. Typical results are shown in Fig. 8 where the orientation angle, the angle between the flow direction, and the main axis of the deformed droplet/filament, is given as a function of the logarithmic strain. This way of presentation is the same as used by Vermant *et al.* (1998); van Puyvelde (1999) [for example Figs. 7(b) and 4.4 in the paper and thesis, respectively]. Although the results presented by van Puyvelde are related to a different fluid–fluid combination [3% poly-butadiene (PB) in poly-isobutylene (PIB)], the characteristic behavior of the orientation angle as a function of strain and shear rate is the same. A minimum is observed only if the shear rate is strong enough. In that case, the final orientation angle is not much different for different shear rates. Moreover, for high enough shear rates the curves nearly coincide. All these phenomena are also predicted by the model.

Finally, cessation of flow is studied. Results are shown in Fig. 9 [experimental results correspond with Fig. 6.5 in Vinckier (1998)]. The characteristic times for static filament breakup were determined by fitting the result for $t_{\text{cessation}} = 10(\text{s})$; $\tau_{Q,1} = \tau_{\beta,1} = 5(\text{s})$. The effect of varying these characteristic times is demonstrated in Fig. 10 for an interrupted flow at 10(s).

It is remarkable that the complex relaxation behavior for different cessation times is reproduced quite well. The typical shoulder that is observed experimentally for intermediate cessation times is clearly present in the predicted relaxation curves.

All observed phenomena can be interpreted in terms of the structure development and the modeling thereof. For the steady state shear flow, the dispersed phase will consist of relatively small, slightly deformed, droplets and the relaxation time will be close to the

FIG. 8. Development of the orientation angle as a function of the strain for different shear rates: $\dot{\gamma} = 0.3, 0.5, 3, 5$ (s). The increase of the orientation angle after some time is due to breakup; small droplets rotate backwards somewhat since they orient less than filaments.

small (due to the large interfacial area Q_0) linear relaxation time defined by expression (40). This determines the fast exponential relaxation that is observed for cessation from the stationary state.

In the intermediate region, filaments are present causing the relaxation time to be rather large (due to the structure factor f_{struct}); this is the part of the stress relaxation curve before the shoulder. Before any substantial relaxation due to retraction will take place, static filament breakup occurs. As droplets are formed, the relaxation time will drop dramatically and further relaxation is similar to that of the higher cessation times. This is the part of the stress relaxation curve after the shoulder. However, the application of the effective measures takes care of the presence of filaments and droplets during some time, which slows down the relaxation after (theoretical) filament breakup. This process is controlled by the characteristic times $\tau_{Q,1}$ and $\tau_{\beta,1}$.

The calculated relaxation curve for $t_{\text{cessation}} = 3$ (s) (curve 1 in Fig. 8), also shows a shoulder which is not present in the experimental curve. When the flow is interrupted at an early stage, the deformation of the relatively large droplets (and thus having a relatively high linear relaxation time) is limited and the relaxation time will not have increased that much. This leads to a slower relaxation than that of the high cessation times (small droplets) but faster than that of the intermediate stages (filaments). After cessation, the model will (erroneously) handle the deformed droplet ($\beta \neq 1$) as a filament which will eventually break up into a few droplets causing no large changes in the relaxation time. In reality, this is a stage where droplets retract and/or end pinching occurs (which is not included in our model). A detailed experimental study of the deformation and retraction of one droplet, while shearing the matrix fluid, in this early stage of deformation is, for example, done by Yamane *et al.* (1998). [Using the expression for the relaxation time Eq. (42), including the function f_{struct} given by Eq. (74), in a simple differ-

FIG. 9. First normal stress difference for interrupted flow after step-up from 0.3 to 3 (s^{-1}). Time of interruption for curves 1–5: $t_{\text{cessation}} = 3, 10, 23, 43$, and 81.5 (s). Asterisk denotes measurements according to Vinckier (1998).

ential equation $\dot{\Gamma} = -(1/\tau)\Gamma$, $\Gamma = \ln(\beta)$, describing the shape relaxation, can reproduce the results of Yamane *et al.* (1998) quite well, especially for the lower droplet deformations. However, even in this simple case (one droplet, moderate deformations) the retraction of the droplet is rather complicated as the intermediate shape depends on the magnitude of the applied strain.] Using their results, further improvements could be implemented in the model. Nevertheless, for the coarse modeling used here, the results are still very reasonable.

C. Polydispersity

Extension by taking a polydisperse system is straightforward if different populations of droplets are handled in time in a decoupled way. However, to keep the system computationally tractable, the number of populations should be limited and, to get rid of step-like changes, the effective measures should still be used. We defined a blend with a normally distributed “number of droplets.” With the standard deviation equal to $0.2R_a$, five classes of droplets with five different radii were determined: $R/R_a = 1, (1 \pm 0.2), (1 \pm 0.4)$. This gives a distribution of the fractions as $[13, 114, 354, 386, 166]10^{-4}$. Since every class of droplets will evolve according to its own time scales, it has a corresponding stress mode, i.e., polydispersity leads to a multimode rheological model.

Results are shown in Figs. 11(a) and 11(b) for $N_{1,\text{excess}}$ and $T_{12,\text{excess}}$, respectively. The separate contributions of the five modes, the sum of these five modes, and the corresponding experimental results are depicted. Notice that every mode has a maximum at different times. It is observed that the results become, as was expected, more smooth. The stress maximum in $N_{1,\text{excess}}$ does not show the sharp kink as observed with the monodisperse modeling.

FIG. 10. First normal stress difference for interrupted flow at 10 (s) after step up from 0.3 to 3 (s^{-1}). Lines are for different characteristic times $\tau_{Q,1} = \tau_{\beta,1}$, Numbers 1–3 correspond to 2, 5, and 7 (s).

One could wonder whether the modeling of polydisperse systems, although described with only a few (five) droplet populations, makes the use of effective measures superfluous. A clear indication to the answer to this question is given in Fig. 12 where the first normal stress is depicted using the above described five-populations system in combination with ODM measures. Of course, when the smoothing due to the effective measures is not active, sharp peaks and step-like changes occur. Adding up the contributions of the different modes leads to a result that becomes somewhat smoother and tends toward the experimental results but certainly still not enough, and peaks and step-like changes are still present. This indicates that, to get reasonable results using a polydisperse system and no effective measures, the number of droplet populations should be rather high, which is, from a computational point of view, not very favorable.

V. CONCLUSIONS

We developed a model that couples the evolution of the microstructure of a disperse liquid–liquid system directly to the rheological behavior of the dispersion.

The rheological model is a rederivation of the Lee–Park model using a new approach and making several adaptations to the existing model. A new closure approximation has been proposed for the fourth-order moment in Eq. (23).

The part describing the microstructure evolution is largely based on known (approximate) theory and experimental observations [Meijer and Janssen (1994); Janssen and Meijer (1997)]. Nonaffine deformation is modeled using an expression as proposed in Stegeman *et al.* (1999). Effective measures that capture the state of the dispersed structure in a smooth way were introduced, inspired by the usual experimental findings. These measures have a major influence on the predicted rheological behavior. Without applying them, but using ODM measures instead, nonphysical, step-like changes in the stress are observed. Moreover, with the effective structure measures, typical experimentally ob-

FIG. 11. First normal stress difference (a) and shear stress (b) for a five mode model. Separate contributions of five modes (line 1–5), the sum of the five modes, and the corresponding experimental results.

served phenomena, such as the hampering of the dynamic filament breakup due to the presence of other filaments and droplets, can be captured.

In line with our objectives, the interfacial area and stretch ratio are parameters in our rheological constitutive equation. In existing models, generally, the interfacial area is determined with approximate kinetic equations in terms of the stress and they contain several adjustable parameters. It is questionable whether the rich and complex behavior of liquid–liquid dispersions, as so clearly demonstrated in the work of Vinckier, can ever be fully captured using such an approach. However, we have demonstrated that this approach can be avoided.

FIG. 12. First normal stress difference for a five mode model not using effective measures. Separate contributions of five modes (line 1–5), the sum of the five modes, and the corresponding experimental results.

From the results we obtained thus far we conclude that a reasonably good description of the microstructure development is of decisive importance for quantitative stress predictions.

Of course, the results presented are based on some coarse assumptions and strong simplifications and should therefore be treated with some caution. Introducing the parameter ν in the constitutive Eq. (48) to get more flexibility is, in our opinion, a weak point and it is worthwhile to investigate whether the rheological part could be improved such that this parameter is no longer needed. Considering the microstructure, it is rather straightforward to implement more advanced models for different parts of the structure development. In order to improve the model, end pinching and a more refined relation between the relaxation time and the stretch ratio could be implemented. The first would lead to a more refined description of the breakup of relatively short filaments and improve the coupling between structure and relaxation times. With respect to the latter, the experimental findings of van Puyvelde (1999) can, for example, help to find a better description of f_{struct} in terms of the droplet deformation.

Furthermore, the use of effective measures needs further investigation and the model should be validated for a broader range of shear rates and for other types of flow (extensional and mixed, complex flows). Also, the model should be validated for a range of liquid–liquid systems including polymer melt blends which are more important from a practical point of view.

Finally, for complex flows an implementation of the model in a finite element computer code is required which is, however, not a demanding task. Extending such a code with a model for the evolution of the dispersed phase will not increase the computational efforts tremendously even if the model is formulated in terms of a polydisperse liquid–liquid system with a limited set of subpopulations. Most of the degrees of freedom are

related to the viscoelastic stresses, and these types of computer codes already work for the most part with multimode viscoelastic models.

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