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A Theoretical Study of an Emulsion of High Viscosity Drops Under Shear

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Abstract. *This paper shows the contribution of the deformation and orientation of high viscosity drops on the macrorheology of an emulsion. This emulsion undergoes an oscillatory shear flow and a small deformation theory is applied for studying its rheological behavior. The shape and the interfacial velocity of a stationary drop is used in order to obtain the contribution of the drop shape to the effective stress tensor of the emulsion. We have derived analytical results for slightly deformed drops in diluted emulsions at arbitrary shear-rates, which is particularly relevant for drops with viscosity ratios beyond the critical value of breakup in shear. Using our analysis we have explored the limiting high shear-rate rheology of diluted emulsions with high viscosity drops. Complex rheological features including: shear-thinning viscosities, normal stress differences, and a nonlinear frequency response are explored.*

Keywords: *emulsion, rheology, oscillatory shear, linear viscoelasticity, micro-hydrodynamics.*

1. Introduction

Emulsions arise in a wide range of applications relevant to the materials processing, food processing, cosmetics, and pharmaceutical industries (Edwards *et. al.* (1991) & Stone (1994). Emulsion rheology is difficult to predict or control because of the complex interplay between the detailed drop-level microphysical evolution and the macroscopic flow. Due to the complexity of these systems, however, there has been little progress towards a fundamental basis for understanding and predicting emulsion rheology.

Emulsions posses microscopic mechanisms for both elastic and viscous dissipation. The energy storage and dissipation per unit of volume can be represented by the frequency-dependent complex viscoelastic shear modulus $\eta^*(\omega, \phi)$, which is defined only for strain amplitude $\dot{\gamma}_o$ sufficiently small so that the shear stress is linear in strain or in the rate of strain. Here ω is the frequency and ϕ is the droplet volume fraction. The real part $\eta'(\omega, \phi)$ is the in-phase ratio of the stress with respect to an oscillatory rate of strain, and reflects viscous mechanism, whereas the imaginary part $\eta''(\omega, \phi)$, is the out-of-phase ratio of stress and reflects elastic mechanism. Linearity and causality imply that $\eta'(\omega, \phi)$ and $\eta''(\omega, \phi)$ are interrelated by the Kramers-Kronig relations (Bird *et al.*, 1987), indicating their inherent link to the dissipation of shear stress and the strain fluctuations in an emulsion. Understanding the behavior of these quantities over a wide range of ω and ϕ would provide valuable insight into the importance of the elastic and dissipative mechanisms as the emulsion become packed and deformed.

Relevant theoretical works on emulsion flows are the studies of Schowalter *et. al.* (1968), and Frankel & Acrivos (1970) on the effect of drop deformation on the rheology of a dilute emulsion, and analyzes by Barthès-Biesel & Acrivos (1973), and Rallison (1980). Progress is being made through the use of experiments and numerical simulations. Experiments are very challenging due to difficulties in characterizing these systems (Mason *et. al.*, 1997). Three-dimensional computer simulations of emulsion flows provide a potentially valuable tool for helping to understand the microstructural mechanisms of emulsions flows but they are at an early stage (Mo & Sangani , 1994; Li *et. al.*, 1995; Loewenberg & Hinch, 1996; Cunha *et al.*, 2003[a]; Cunha *et al.*, 2003[b]). In some cases, two-dimensional simulations may help in the development of the three-dimensional simulations, and the formulation of simplified models.

In this article, we present results of small deformation analysis for an emulsion in oscillatory shear. We explore the nonlinear frequency response for high strain amplitudes for a very dilute emulsion, where hydrodynamic drop interaction is a negligible effect. The results shown that the behavior of high viscosity drops depends on three rates: the shear-rate, the oscillation frequency, and the drop relaxation rate. At low shear-rates, the system exhibits a linear viscoelastic response; nonlinear behavior occurs for large shear-rates. Three asymptotic regimes are identified. The predictions give by our small deformation theory may be used to test computer simulations results in the asymptotic limits investigated.

2. Basic equations

We consider an emulsion consisting of neutrally buoyant identical viscous drops with viscosity $\mu' = \lambda\mu$ and density ρ' immersed in a incompressible Newtonian fluid of viscosity μ and density ρ. A schematic of the problem is shown in Fig.(1). In the sketch V

is the volume of the ambient fluid (external to the drops), V' is the drop volume, a is the radius of the non-deformed drop and σ_o is the uniform interfacial tension. The suspended drops are submitted to an oscillatory shearing flow $\dot{\gamma} = \dot{\gamma}_o \cos(\omega t)$, where $\dot{\gamma}_o$ is the magnitude of the oscillatory shear (i.e. the shear rate) and ω is the imposed frequency of the flow.

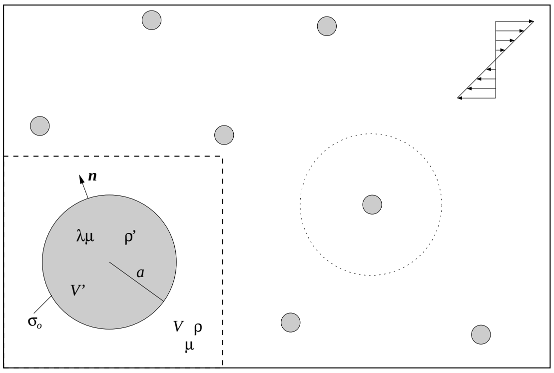

Figure 1. Sketch of deformable drops in an dilute emulsion. The insert shows details of a single drop.

2.1 Geometry

When the emulsion is caused to shear, the drop, which are spherical (with radius a) at rest, deform into a slightly elliptical shape. From continuum mechanics arguments (i.e. elasticity theory) it is straightforward to show that the shape of the drop is described by

$$S(\boldsymbol{x}, t) = r(t) - a\left(1 + \frac{\boldsymbol{x}\cdot\boldsymbol{A}\cdot\boldsymbol{x}}{r^2} + \frac{3}{2}\frac{\boldsymbol{xx}:\boldsymbol{AA}:\boldsymbol{xx}}{r^4} + \ldots\right) = 0, \tag{1}$$

where the shape tensor defined as $\boldsymbol{A} = \varepsilon\boldsymbol{\mathcal{H}}$ is a small strain tensor, ε is a small parameter of the motion and $\boldsymbol{\mathcal{H}}$ denotes a Cauchy-Green deformation tensor. Then, by definition $\boldsymbol{A}$ is positive definite symmetric tensor and traceless[1]. Here, $r = |\boldsymbol{x}|$ and the parameter ε in the case of high viscosity emulsion is defined as being $\varepsilon = 1/\lambda$. So, $|\ \boldsymbol{A}\ | \sim 1/\lambda \ll 1$ for large λ and consequently will exert only a small distortion on the drop. In the limit of $1/\lambda \ll 1$, the drop tends to rotates much faster with the ambient fluid vorticity then it may deforms in the extensional quadrant of shear. Thus, before the deformation can reach significant values, the drop commutes between the extensional and compressional quadrants of shear, and an equilibrium shape is accomplished. In other words, the characteristic time related to the rotation is small compared with the typical time of deformation. Consequently the flow can produce only a slight distortion on the initial spherical shape, even at large strain rates, (Rallison, 1980).

The unit normal vector on the drop surface S defined as $\boldsymbol{n} = \nabla S(\boldsymbol{x}, t)$ is given by

$$\boldsymbol{n} = \frac{\boldsymbol{x}}{r} - 2a\left[\frac{\boldsymbol{A}\cdot\boldsymbol{x}}{r^2} - \frac{\boldsymbol{x}(\boldsymbol{x}\cdot\boldsymbol{A}\cdot\boldsymbol{x})}{r^4} + \mathcal{O}(\varepsilon^2)\right], \tag{2}$$

and the mean curvature, expressed as the sum of the inverse principal radii of curvature, is given by

$$\kappa = \frac{1}{2}\nabla^s\cdot\boldsymbol{n} = \frac{1}{a} + \frac{2\boldsymbol{x}\cdot\boldsymbol{A}\cdot\boldsymbol{x}}{a^3} + \mathcal{O}(\varepsilon^2), \tag{3}$$

where $\nabla^s = \nabla\cdot(\boldsymbol{I} - \boldsymbol{nn})$ denotes the gradient operator tangent to the surface of the particle S.

2.2 Microhydrodynamics balance equations

Considering the involved length scales at the drop level, we see that the Reynolds numbers of the flow inside and outside of the drop are very small, *i.e.* $Re_p = a^2\dot{\gamma}_o/\lambda\nu \ll 1$ and $Re_p/\lambda \ll 1$, where ν is the kinematic viscosity of the continuous phase. This condition supports the hypothesis that the drop level flow are free of inertial effects and fluid motions are governed by the Stokes equations for incompressible flows, namely

$$\nabla\cdot\boldsymbol{u} = 0 \qquad \text{and} \qquad \nabla\cdot\boldsymbol{\sigma} = \boldsymbol{0}, \quad \forall\ \boldsymbol{x}\in V\cup V'. \tag{4}$$

Here, $\boldsymbol{u}$ is the Eulerian velocity field and $\boldsymbol{\sigma}$ the local Newtonian stress tensor. Hence

$$\boldsymbol{\sigma} = -P\boldsymbol{I} + [\nabla\boldsymbol{u} + (\nabla\boldsymbol{u})^T], \qquad \forall\ \boldsymbol{x}\in V \tag{5}$$

and

$$\boldsymbol{\sigma} = -P'\boldsymbol{I} + [\nabla\boldsymbol{u} + (\nabla\boldsymbol{u})^T], \qquad \forall\ \boldsymbol{x}\in V' \tag{6}$$

where $P = p - \rho\boldsymbol{g}\cdot\boldsymbol{x}$ and $P' = p - \rho'\boldsymbol{g}\cdot\boldsymbol{x}$ are the modified pressures of the continuous and dispersed phases respectively, $\boldsymbol{g}$ is the gravitational acceleration, $\boldsymbol{x}$ is the position vector and $p = -(\boldsymbol{\sigma}:\boldsymbol{I})/3$ denotes the mechanical pressure.

[1] $\boldsymbol{A}:\boldsymbol{I} = 0$, in order to preserve the drop volume

2.3 Scalings

In this work, lengths are non-dimensionalized by the non-deformed particle radius a, and velocities by $\sigma_o/\lambda\mu$. The principal time scales are given by: (i) surface-tension relaxation time, $\tau_\sigma \sim \lambda\mu a/\sigma_o$; (ii) imposed flow time, $\tau_e \sim 1/\dot{\gamma}_o$; (iii) deformation time, $\tau_d \sim (1+\lambda)/\dot{\gamma}_o$; and (iv) forcing time, $\tau_\omega \sim 1/\hat{\omega}$.

The physical parameters identified here are: (i) Reynolds number: for the particle, $Re_p = \rho\dot{\gamma}_o a^2/\lambda\mu$ and for the continuous phase, $Re = \rho\dot{\gamma}_o a^2/\mu$; (ii) capillary number, $Ca = \tau_\sigma/\tau_e = \lambda\mu a\dot{\gamma}_o/\sigma_o$, defined as the shear-rate normalized by the drop relaxation rate $\sigma_o/\lambda\mu a$; (iii) dispersed to continuous-phase viscosity ratio, $\lambda = \mu'/\mu$; (iv) dispersed-phase volume fraction ϕ; (v) dimensionless oscillation frequency, $\hat{\omega} = \lambda\mu a\omega/\sigma_o = \tau_\sigma/\tau_\omega$, defined as being the ratio of the imposed oscillation frequency ω to the drop relaxation rate; and (vi) Bond number $Bo = (\rho' - \rho)ga^2/\sigma_o$, that represents a typical hidrostatic pressure variations relative to interfacial tension stresses. In the absence of buoyancy-driven motions of the drop $Bo = 0$ (i.e. neutral buoyancy drops).

2.4 Boundary conditions

The boundary conditions at a drop interface S with surface tension σ_o require a continuous velocity and a balance between the net surface traction and surface forces. Mathematically, these conditions are expressed as following:

$$\boldsymbol{u} \rightarrow \boldsymbol{u}^\infty \qquad |\boldsymbol{x}| \rightarrow \infty; \qquad \boldsymbol{u}(\boldsymbol{x}) = \boldsymbol{u}'(\boldsymbol{x}), \qquad \boldsymbol{x} = \boldsymbol{x}_s \in S_i. \tag{7}$$

Furthermore, the traction jump $[\boldsymbol{\sigma} \cdot \hat{\boldsymbol{n}}]_s$ at the interface is written as being, (Pozridikis, 1992)

$$[\boldsymbol{\sigma} \cdot \boldsymbol{n}]_s = [2\kappa\sigma_o + (\rho' - \rho)\boldsymbol{g} \cdot \boldsymbol{x}]\boldsymbol{n} - (\boldsymbol{I} - \boldsymbol{nn}) \cdot \nabla\sigma. \tag{8}$$

The interface is treated here as having uniform surface tension (*i.e.* clean drops) and the gravitational effects are negligible. Under these conditions, the traction descontinuity given in (8) reduces then to a contribution from the capillary pressure

$$[\boldsymbol{\sigma} \cdot \boldsymbol{n}]_s = 2\kappa\sigma_o\boldsymbol{n}. \tag{9}$$

A kinematic condition for the drop surface S by which the drop shape changes in time t, is written as

$$\frac{DS(t)}{Dt} = 0, \qquad \forall\, \boldsymbol{x} \in S, \tag{10}$$

where D/Dt represents the material derivative operator, given by $D/Dt = \partial/\partial t + \boldsymbol{u} \cdot \nabla$.

3. Drop shape and rheology

3.1 Velocity field

The Lamb's general solution for the Stokes equations, in terms of spherical harmonic functions with order n, can be written as following (Lamb, 1932)

$$\boldsymbol{u} = \nabla\Phi + \boldsymbol{x} \times \nabla\Psi + \nabla(\boldsymbol{x} \cdot \boldsymbol{Q}) - 2\boldsymbol{Q} \qquad p = 2\mu\nabla \cdot \boldsymbol{Q}, \tag{11}$$

where Φ, Ψ, p and $\boldsymbol{Q}$ are harmonic functions and consequently determined by the solutions for the Laplace's equation, $\nabla^2\Phi = 0$, $\nabla^2\Psi = 0$, $\nabla^2\boldsymbol{Q} = 0$. In spherical coordinates (r, θ, φ), the solution for the Laplace's equation $\nabla^2\mathcal{H} = 0$ is given by $\mathcal{H} = \sum_{n=-\infty}^{\infty} h_n$, where h_n is a solid spherical harmonic of order n (Happel & Brenner, 1991)

$$h_n = r^n \sum_0^n \mathcal{P}_n^m(cos\theta)[a_{mn}cos(m\varphi) + \tilde{a}_{mn}sen(m\varphi)]. \tag{12}$$

Here, $\mathcal{P}_n^m$, $n = 0, 1, 2, \ldots$, $-n \leq m \leq n$ are Legendre polynom (Jeffreys & Jeffreys, 1946). The development of a general solution form for the fully three-dimensional velocity fields outside and inside the drop follows exactly the above Lamb's arguments for solving three-dimensional creeping flows, and the solution therefore takes the same general form obtained for a solid sphere in general linear shear. The corresponding solutions can be also constructed via the superposition of vector harmonics functions as described in (Leal, 1992), resulting for the flow inside and outside the drop, respectively

(i) outside the drop, $\boldsymbol{x} \in V$:

$$\boldsymbol{u} = \boldsymbol{\Omega} \times \boldsymbol{x} + \boldsymbol{D} \times \boldsymbol{x}\frac{a^3}{r^3} + \boldsymbol{E} \cdot \boldsymbol{x} + (\boldsymbol{x} \cdot \boldsymbol{B} \cdot \boldsymbol{x})\boldsymbol{x}\frac{a^3}{r^5} + \frac{2a^5}{r^5}\boldsymbol{C} \cdot \boldsymbol{x} - \frac{5a^5}{r^7}(\boldsymbol{x} \cdot \boldsymbol{C} \cdot \boldsymbol{x})\boldsymbol{x}, \tag{13}$$

(ii) inside the drop, $\boldsymbol{x} \in V'$:

$$\boldsymbol{u} = \boldsymbol{\omega} \times \boldsymbol{x} + \boldsymbol{G} \cdot \boldsymbol{x} + \frac{5r^2}{a^2}\boldsymbol{F} \cdot \boldsymbol{x} - \frac{2}{a^2}(\boldsymbol{x} \cdot \boldsymbol{F} \cdot \boldsymbol{x})\boldsymbol{x}, \tag{14}$$

Here, the strain rate tensor $\boldsymbol{E}$ and the angular velocity $\boldsymbol{\Omega}$ are, both, prescribed by the flow outside the drop. The symmetric tensors $\boldsymbol{B}$, $\boldsymbol{C}$, $\boldsymbol{F}$, $\boldsymbol{G}$ and the vectors $\boldsymbol{D}$, $\boldsymbol{\omega}$ can be obtained through the application of the boundary condition on the surface S of non-deformed drop. Thus, the surface velocity field at first order is given by

$$\boldsymbol{u}_s = \boldsymbol{W} \cdot \boldsymbol{x} + \frac{5}{2\lambda}\boldsymbol{E} \cdot \boldsymbol{x} - \frac{20\sigma}{19\lambda\mu a}\boldsymbol{A} \cdot \boldsymbol{x}, \tag{15}$$

where $\boldsymbol{W}$ is the vorticity tensor. From the solution of the velocity field on the surface S we shall evaluate two quantities: the evolution of the shape tensor $\boldsymbol{A}$ and the particle contribution to the bulk stress.

3.2 Shape equation

Following the general analysis given in Rallison (1980) we treat the problem of highly viscous drops ($\lambda \gg 1$) in arbitrary shear from a small deformation theory. The rate of change of $\boldsymbol{A}$ describing the drop shape evolution is determined by applying the kinematic boundary condition Eq.(10) as follows

$$\frac{D}{Dt}\left[r(t) - a(1 + \boldsymbol{n} \cdot \boldsymbol{A} \cdot \boldsymbol{n})\right] = 0, \tag{16}$$

where $\boldsymbol{n} = \boldsymbol{x}/r$ is a unit vector. Therefore,

$$\frac{Dr}{Dt} - a\left(\frac{D\boldsymbol{n}}{Dt} \cdot \boldsymbol{A} \cdot \boldsymbol{n} - \boldsymbol{n} \cdot \frac{D\boldsymbol{A}}{Dt} \cdot \boldsymbol{n} - \boldsymbol{n} \cdot \boldsymbol{A} \cdot \frac{D\boldsymbol{n}}{Dt}\right) = \boldsymbol{0}. \tag{17}$$

Since $\boldsymbol{n}$ is a unit vector, $D\boldsymbol{n}/Dt = \boldsymbol{W} \cdot \boldsymbol{n}$. Eq.(17) can be finally expressed as

$$\boldsymbol{u}_s \cdot \boldsymbol{n} - \boldsymbol{n} \cdot \left(\frac{D\boldsymbol{A}}{Dt} + \boldsymbol{A} \cdot \boldsymbol{W} - \boldsymbol{W} \cdot \boldsymbol{A}\right) \cdot \boldsymbol{n} = \boldsymbol{0} \tag{18}$$

The term inside the parenthesis in equation(18) is the Jaumman derivative

$$\frac{\mathcal{D}\boldsymbol{A}}{\mathcal{D}t} = \frac{D\boldsymbol{A}}{Dt} - \boldsymbol{W} \cdot \boldsymbol{A} + \boldsymbol{A} \cdot \boldsymbol{W}, \tag{19}$$

that is a material frame indifference derivative, and gives the temporal rate of change of $\boldsymbol{A}$ seen by an observer which translates and rotates with the drop.

Now, substituting $\boldsymbol{u}_s$ in Eq.(18) by the expression given in Eq. (15) ones obtains

$$\frac{\mathcal{D}\boldsymbol{A}}{\mathcal{D}t} = \frac{\partial \boldsymbol{A}}{\partial t} - \boldsymbol{W} \cdot \boldsymbol{A} + \boldsymbol{A} \cdot \boldsymbol{W} = \frac{5}{2\lambda}\boldsymbol{E} - \frac{20\sigma}{19\lambda\mu a}\boldsymbol{A}. \tag{20}$$

The equation (20) shows that the rate of change of $\boldsymbol{A}$ seen by an observer in a frame of reference that rotates with the particle (i.e. the Jaumann derivative), since the drop is torque-free, is due first to the effect of the ambient strain field $\boldsymbol{E}$ on a sphere, and second to the restoring effect of surface tension proportional to $\boldsymbol{A}$. The ignored terms of order $\mathcal{O}(1/\lambda^2)$ arise from the straining flow acting on the perturbed shape and from harmonics higher than the second one, associated with the disturbance flow due to the deformed drop. It should be important to note that in Eq.(20) the convective part of the Jaumann derivative is also $\mathcal{O}(1/\lambda^2)$ and, therefore, negligible.

3.3 Macroscopic Description of Emulsion Flow

The emulsion in this study is considered as a homogeneous continuous fluid in a length ℓ much large than the drop size a. Accordingly, the macroscopic flow, $\bar{\boldsymbol{u}}$ field is governed by the Cauchy and continuity equations respectively

$$\overline{\rho}\frac{D\overline{\boldsymbol{u}}}{Dt} = \nabla \cdot \overline{\boldsymbol{\Sigma}} + \overline{\rho}\boldsymbol{g} \qquad \text{and} \qquad \nabla \cdot \overline{\boldsymbol{u}} = 0. \tag{21}$$

Here, $\overline{\rho} = \phi\rho + (1 - \phi)(\rho + \Delta\rho)$ is the effective density of the emulsion and $\overline{\boldsymbol{\Sigma}}$ is the emulsion volume-averaged stress tensor. Following Batchelor (1970), if the suspending fluid is Newtonian and the flow has a low particle Reynolds number, then

$$\overline{\boldsymbol{\Sigma}} = -\overline{p}\boldsymbol{I} + 2\mu\overline{\boldsymbol{E}} + n\overline{\boldsymbol{S}}, \qquad \text{with} \qquad \overline{\boldsymbol{S}} = \frac{1}{N}\sum_{k=1}^{N}\boldsymbol{S}^k. \tag{22}$$

The first two terms on the right-hand side are the contributions from the background continuous phase with an averaged pressure $\overline{p}$ and an average rate of strain $\overline{\boldsymbol{E}}$. Here, n is the average number of drops per unit volume and N is the number of drops. According to Batchelor (1970) the stress exerted by one drop surface S^k on the fluid is given by

$$\boldsymbol{S}^k = \oint_{S_k}\left[(\boldsymbol{\sigma} \cdot \boldsymbol{n})\boldsymbol{x} - \mu(\boldsymbol{u}\boldsymbol{n} + \boldsymbol{n}\boldsymbol{u})\right]dS. \tag{23}$$

Considering that for a dilute emulsion the velocity disturbance field generated by one drop does not affect the flow near the other drops (i.e. no-interacting drops), the integral in Eq.(23) can be evaluated over a large spherical closed surface S^∞ containing the drop k. For performing the integral over S^∞ where $\boldsymbol{un} = \boldsymbol{nu}$, the terms $\boldsymbol{\sigma} \cdot \boldsymbol{nx}$ and $2\mu\boldsymbol{un}$ need to be evaluated. Again, using the Lamb's general solution for the velocity field given in §(3.1) ones obtains

$$\boldsymbol{\sigma} \cdot \boldsymbol{nx} = 2\mu \boldsymbol{B} \cdot \boldsymbol{xn} \left(\frac{a^3}{R^3}\right) - 8\mu(\boldsymbol{B} : \boldsymbol{xx})\boldsymbol{nx} \left(\frac{a^3}{R^5}\right) + \ldots \tag{24}$$

$$\begin{aligned} 2\boldsymbol{un} &= 2(\boldsymbol{B} : \boldsymbol{xx})\boldsymbol{nx} \left(\frac{a^3}{R^5}\right) + 4\boldsymbol{C} \cdot \boldsymbol{xn} \left(\frac{a^5}{R^5}\right) \\ &- 10(\boldsymbol{C} : \boldsymbol{xx})\boldsymbol{nx} \left(\frac{a^3}{R^7}\right) + \ldots . \end{aligned} \tag{25}$$

Now, using Eqs.(24) and (25) in Eq.(23) and choosing S^∞ far enough to make terms $\mathcal{O}(1/R)$ negligible, after solving the isotropic integrals on the spherical surface S^∞, the stresslet is found to be

$$\boldsymbol{S}^k = -2\mu \left(\frac{4}{3}\pi a^3\right) \boldsymbol{B}, \tag{26}$$

where $\boldsymbol{B}$ is a shape tensor adopted from Frankel & Acrivos (1970) for a $O(1/\lambda)$, namely

$$\boldsymbol{B} = -\frac{\mu_B}{\mu}\mathbf{E} - \frac{2}{\lambda}\frac{\sigma}{\mu a}\boldsymbol{A} - \frac{15}{4}\left[\boldsymbol{E} \cdot \boldsymbol{A} + \boldsymbol{E} \cdot \boldsymbol{A} - \frac{2}{3}(\boldsymbol{A} : \boldsymbol{E})\boldsymbol{I}\right]. \tag{27}$$

Here, we define $\mu_B/\mu = (5/2) - (25/4\lambda)$ as being the viscosity (due to drop contribution) of a dilute emulsion associated with a Newtonian regime of such material at high frequency.

By substituting Eq. (27) into Eq. (26), we found the mean averaged stresslet of the dispersed phase at first order approximation, $O(1/\lambda)$, given by

$$n\overline{\boldsymbol{S}} = 2\mu_B(\lambda)\phi\overline{\boldsymbol{E}} + \frac{2}{\lambda}\frac{\sigma}{\mu a}\phi\boldsymbol{A} + \frac{15}{14}\mu\phi\left[\boldsymbol{A} \cdot \overline{\boldsymbol{E}} + \overline{\boldsymbol{E}} \cdot \boldsymbol{A} - \frac{2}{3}(\boldsymbol{A} : \overline{\boldsymbol{E}})\boldsymbol{I}\right]. \tag{28}$$

The shape and the stresslet equations (20) and (28) form a pair of constitutive equation for a dilute emulsion of highly viscous drops. These equations when written in terms of non-dimensional quantities and physical parameter described in §2.3, take the form

$$\frac{d\boldsymbol{A}}{dt^*} = Ca\overline{\boldsymbol{W}}^* \cdot \boldsymbol{A} - Ca\boldsymbol{A} \cdot \overline{\boldsymbol{W}}^* + \frac{5}{2\lambda}Ca\overline{\boldsymbol{E}}^* - c\boldsymbol{A}, \tag{29}$$

$$\overline{\boldsymbol{S}}^* = 2\frac{\mu_B}{\mu}(\lambda)\overline{\boldsymbol{E}}^* + \frac{4}{Ca}\boldsymbol{A} + \frac{15}{7}\left[\boldsymbol{A} \cdot \overline{\boldsymbol{E}}^* + \overline{\boldsymbol{E}}^* \cdot \boldsymbol{A} - \frac{2}{3}(\boldsymbol{A} : \overline{\boldsymbol{E}}^*)\boldsymbol{I}\right], \tag{30}$$

where $t^* = t/\tau_\sigma$, $\overline{\boldsymbol{W}}^* = \dot{\gamma}_o\overline{\boldsymbol{W}}$, $\overline{\boldsymbol{E}}^* = \dot{\gamma}_o\overline{\boldsymbol{E}}$ and $\overline{\boldsymbol{S}}^* = n\overline{\boldsymbol{S}}/(\phi\mu\dot{\gamma}_o)$. To make the notation simpler, the volume average and the dimensionless notation will be suppressed from this point of the work.

4. Solution of drop shape for oscillatory shear

For a dilute emulsion of highly viscous drops submitted to an oscillatory shear flow with $\dot{\gamma} = Ca\cos(\omega t)$, the general drop shape equation (29) reduces to a system of coupled-differential equations, namely

$$\begin{aligned} \frac{dA_{11}}{dt} &= -cA_{11} + Ca\cos(\omega t)A_{12}; \qquad \frac{dA_{22}}{dt} = -cA_{22} - Ca\cos(\omega t)A_{12}; \\ \frac{dA_{12}}{dt} &= -cA_{12} + \frac{Ca}{2}Ca\cos(\omega t)\left(\frac{5}{4\lambda} + A_{22} - A_{11}\right), \end{aligned} \tag{31}$$

where $c = 20/19$. Considering a non-deformed drop at $t = 0$ the initial condition for the system is $\boldsymbol{A} = 0$. The other components of tensor $\boldsymbol{A}$ defines a decoupled differential system with trivial solution $A_{i3} = 0$. A strategy to solve the problem defined by Eqs.(31) and its initial condition is to apply a diagonalization process in order to recast the original system in a system of decoupled differential equations. Therefore, we write the system (31) in a matricial form $d\boldsymbol{y}/dt = \boldsymbol{T} \cdot \boldsymbol{y} + \boldsymbol{R}$, where $\boldsymbol{y} = (A_{11}, A_{12}, A_{22})$, $R = (0, Ca5/4\lambda\cos(\omega t), 0)$ and

$$\boldsymbol{T} = \begin{bmatrix} -c & Ca\cos(\omega t) & 0 \\ \frac{1}{2}Ca\cos(\omega t) & -c & \frac{1}{2}Ca\cos(\omega t) \\ 0 & -Ca\cos(\omega t) & -c \end{bmatrix}. \tag{32}$$

The appropriated uncoupling procedure consist in applying the modal transformation $d(\boldsymbol{M}^{-1}\cdot\boldsymbol{y})/dt = \boldsymbol{M}^{-1}\cdot\boldsymbol{R} + \boldsymbol{M}^{-1}\cdot\boldsymbol{T}\cdot\boldsymbol{M}\cdot\boldsymbol{M}^{-1}\cdot\boldsymbol{y}$, where $\boldsymbol{M}$ is a modal matrix, in which its columns are the eigenvectors of the matrix $\boldsymbol{T}$. Defining the vectors $\boldsymbol{v} = \boldsymbol{M}^{-1}\cdot\boldsymbol{y}$, $\boldsymbol{f} = \boldsymbol{M}^{-1}\cdot\boldsymbol{R}$ and the diagonal matrix $\boldsymbol{D} = \boldsymbol{M}^{-1}\cdot\boldsymbol{T}\cdot\boldsymbol{M}$, the system takes the simpler form $d\boldsymbol{v}/dt = \boldsymbol{D}\cdot\boldsymbol{v}+\boldsymbol{f}$ that in the explicit notation is given by

$$\frac{dv_1}{dt} + cv_1 = 0; \qquad \frac{dv_2}{dt} + [c + iCa\cos(\omega t)]v_2 = c_2 Ca\cos(\omega t);$$
$$\frac{dv_3}{dt} + [c - iCa\cos(\omega t)]v_3 = -c_2 Ca\cos(\omega t) \tag{33}$$

where $c_2 = (-5i/8\lambda)$ and $i = \sqrt{-1}$. Now, the system is uncoupled and its equations can be analitically solved. After the solution it the transformed space, we turning back to the physical one by the backward transformation $\boldsymbol{y} = \boldsymbol{M}\cdot\boldsymbol{v}$. After some algebraic calculations, it's possible to obtain a closed solution for the shape tensor in the form

$$A_{11} = \frac{5}{4\lambda}\left[1 - cI_1(Ca,t)\right], \qquad A_{12} = \frac{5}{4\lambda}cI_2(Ca,t), \tag{34}$$

$$A_{22} = -A_{11} \qquad \text{and} \qquad A_{13} = A_{23} = A_{33} = 0, \tag{35}$$

where $I_1(Ca,t)$ and $I_2(Ca,t)$ represents the following convolution integrals

$$I_1(Ca,t) = \int_0^t e^{-c\tau} cos\left[\gamma_o(sen(\hat{\omega}t) - sen(\hat{\omega}(t-\tau)))\right]d\tau \tag{36}$$

and

$$I_2(Ca,t) = \int_0^t e^{-c\tau} sen\left[\gamma_o(sen(\hat{\omega}t) - sen(\hat{\omega}(t-\tau)))\right]d\tau \tag{37}$$

being $\gamma_o = (Ca/\hat{\omega})$ the dimensionless shear strain. It should be important to note that the initial unsteady part of the above solution has being dropped since we are only interested in the steady rheological behavior of the emulsion

4.1 Asymptotic solutions for I_1 and I_2

The integrals I_1 and I_2 are the main results of the present analysis being the core for characterization of drop shape and emulsion rheology. Next, we have developed three asymptotic solutions for the integrals (36) e (37) at steady state condition (i.e. $t \to \infty$). The full details of the calculations presented below are given in Couto & Cunha (2004).

(i) *Case 1*: $\omega = 0$. This corresponds to the steady shear flow condition. This case corresponds to the limit

$$\lim_{\omega\to 0}\gamma_o[\sin(\omega t) - \sin(\omega(t-\tau))] = Ca\tau$$

Therefore,

$$I_1 \sim \int_0^\infty e^{-c\tau}\cos(Ca\tau)d\tau = \frac{c}{c^2+Ca^2} \quad \text{and} \quad I_2 \sim \int_0^\infty e^{-c\tau}\sin(Ca\tau)d\tau = \frac{Ca}{c^2+Ca^2} \tag{38}$$

(ii) *Case 2*: $\hat{\omega} \ll 1$ and $\gamma_o \gg 1$. Using Taylor expansion of the function $f(\tau) = [\sin(\hat{\omega}t) - \sin(\hat{\omega}(t-\tau))]$ for $\hat{\omega}\tau$ around zero one obtains that

$$\gamma_o f(\tau) \sim \tau Ca(1+\Theta)\cos(\hat{\omega}t) \tag{39}$$

where the capillary number is defined in terms of the dimensionless strain amplitude and the dimensionless frequency, say $Ca = \gamma_o\hat{\omega}$, and

$$\Theta = \frac{1}{2}(\hat{\omega}\tau)\tan(\hat{\omega}\tau) - \frac{(\hat{\omega}\tau)^2}{6} - \frac{1}{24}(\hat{\omega}\tau)^3\tan(\hat{\omega}\tau) + \ldots \tag{40}$$

Now, the integrals I_1 and I_2 are re-written in the following way

$$I_1 = \int_0^\infty \cos(\gamma_o f(\tau))d\tau \sim \int_0^\infty \left[\cos(\tau Ca\cos(\hat{\omega}t)) - \Theta\sin(\tau Ca\cos(\hat{\omega}t)) - \frac{1}{2}\Theta^2\cos(\tau Ca\cos(\hat{\omega}t))\right]\tau, \tag{41}$$

$$I_2 = \int_0^\infty \sin(\gamma_o f(\tau))d\tau \sim \int_0^\infty \left[\sin(\tau Ca\cos(\hat{\omega}t)) - \Theta\cos(\tau Ca\cos(\hat{\omega}t)) - \frac{1}{2}\Theta^2\sin(\tau Ca\cos(\hat{\omega}t))\right]\tau. \tag{42}$$

After performing the integral we found the following asymptotic expressions for I_1 and I_2 respectively,

$$I_1 \sim \frac{c}{c^2 + Ca^2\cos^2\hat{\omega}t}\left[1 + \frac{\hat{\omega}}{2c}Ca^2\sin\hat{\omega}t\frac{Ca^2\cos^2\hat{\omega}t - 3c^2}{(Ca^2\cos^2\hat{\omega}t + c^2)^2}\right] \tag{43}$$

$$I_2 \sim \frac{Ca}{c^2 + Ca^2\cos^2\hat{\omega}t}\left[\cos\hat{\omega}t - \hat{\omega}c^2\sin\hat{\omega}t\frac{3Ca^2\cos^2\hat{\omega}t - c^2}{(Ca^2\cos^2\hat{\omega}t + c^2)^2}\right] \tag{44}$$

It should important to note that for $\hat{\omega} = 0$ the above expressions reduce to the case 1.

(iii) *Case 3*: arbitrary $\hat{\omega}$ and $\gamma \ll 1$. This corresponds to a weakly non-linear viscoelasticity theory. Again, the solution at this limit has been obtained by expanding the kernels of the integrals $\cos(\gamma_o f(\tau))$ and $\sin(\gamma_o f(\tau))$ using a Taylor series for $O(\gamma_o^4)$ and $O(\gamma_o^3)$, respectively. The integral are then performed by using the *Mathematica* software. After several algebraic manipulations involving trigonometric functions, we found an appropriate form of the asymptotic solution for this regime in terms of Fourier series, namely

$$I_1(Ca,t) = a_o + a_2 cos(2\hat{\omega}t) + b_2 sen(2\hat{\omega}t) + a_4 cos(4\hat{\omega}t) + b_4 sen(4\hat{\omega}t) + \dots \quad (45)$$

$$I_2(Ca,t) = a_1 cos(\hat{\omega}t) + b_1 sen(\hat{\omega}t) + a_3 cos(3\hat{\omega}t) + b_3 sen(3\hat{\omega}t) + \dots \quad (46)$$

where the Fourier coefficients a_i and b_i are given by

$$a_0 = \left(\frac{1}{c}\right) - \left(\frac{1}{2c}\right)\left(1 - \frac{1}{c_1}\right)\gamma_o^2 + \left(\frac{1}{8c}\right)\left(-\frac{1}{c_1} + \frac{1}{4c_2} + \frac{3}{4}\right)\gamma_o^4;$$

$$a_2 = \left(\frac{1}{2c}\right)\left(\frac{1}{2} - \frac{1}{c_1} + \frac{1}{2c_2}\right)\gamma_o^2 + \left(\frac{1}{12c}\right)\left(\frac{7}{4c_1} - \frac{1}{c_2} + \frac{1}{4c_3} - 1\right)\gamma_o^4;$$

$$b_2 = \left(\frac{\hat{\omega}}{2c^2}\right)\left(\frac{1}{c_2} - \frac{1}{c_1}\right)\gamma_o^2 + \left(\frac{\hat{\omega}}{6c^2}\right)\left(\frac{5}{8c_1} - \frac{1}{c_2} + \frac{3}{8c_3}\right)\gamma_o^4;$$

$$a_4 = \left(\frac{1}{48c}\right)\left(\frac{1}{4} - \frac{1}{c_1} + \frac{3}{2c_2} - \frac{1}{c_3} + \frac{1}{4c_4}\right)\gamma_o^4; \quad b_4 = \left(\frac{1}{16c^2}\right)\left(-\frac{1}{3c_1} + \frac{1}{c_2} - \frac{1}{c_3} + \frac{1}{3c_4}\right)\gamma_o^4;$$

$$a_1 = \left(\frac{\hat{\omega}}{c^2}\right)\left(\frac{1}{c_1}\right)\gamma_o + \left(\frac{\hat{\omega}}{c^2}\right)\left(-\frac{1}{c_1} + \frac{1}{c_2}\right)\gamma_o^3; \quad a_3 = \left(\frac{\hat{\omega}}{4c^2}\right)\left(\frac{1}{2c_1} - \frac{1}{c_2} + \frac{1}{2c_3}\right)\gamma_o^3;$$

$$b_1 = \left(\frac{1}{c}\right)\left(1 - \frac{1}{c_1}\right)\gamma_o + \left(\frac{1}{2c}\right)\left(-\frac{3}{4} + \frac{1}{c_1} - \frac{1}{4c_2}\right)\gamma_o^3; \quad b_3 = \left(\frac{1}{8c}\right)\left(\frac{1}{3} - \frac{1}{c_1} + \frac{1}{c_2} - \frac{1}{3c_3}\right)\gamma_o^3;$$

where $c_n = 1 + (n^2\hat{\omega}^2)/c^2; \qquad (n = 1, 4)$.

5. Results and discussion

In this section we present results for the limiting high shear-rate rheology of diluted emulsions with high viscosity drops. We will show that it is a promising limit to explore since for high capillary numbers (i.e. strong flows) no large deformations are involved for high viscosity drops, corresponding then to a small drop deformation regime. As mentioned before a physical explanation of this small deformation regime is related to the fact that drop shape is spin round into the compression strain quadrant before it has extended far. When the equilibrium is such that the slightly deformed droplet has its principal extended axis in the direction of the flow, the viscous dissipation within the external fluid is decreased as a direct consequence of less distortion in the flow streamlines, and a shear thinning behavior may be observed with the presence of normal stress differences. In addition, we present theoretical results obtained for the behavior of a high viscosity emulsion undergoing steady and oscillatory shear. The results even being only applied to dilute regime and small deformation show significant contribution of the stretching and orientation of the high viscosity drops to the rheology of an emulsion. For oscillatory shear, we have developed two asymptotic limits; low strain ($\gamma_o \ll 1$) regime and high strain ($\gamma_o \gg 1$) regime. For the emulsion undergoing steady shear, complex rheological features, including shear thinning and stress differences are presented. We also will explore the nonlinear frequency response of the drop shape and emulsion rheology.

5.1 Deformation and orientation

Taylor (1934) suggested that the state of deformation may be quantified using the deformation $D_T = (\ell - b)/(\ell + b)$, where ℓ and b are the maximum and minimum dimensions of the drop in the xy plane. For a small deformation theory $O(Ca)$ this definition corresponds exactly to $D = (a_{max} - a_{min})/2$, where a_{max} and a_{min} are, respectively, the maximum and the minimum eigenvalues of the shape tensor $\mathbf{A}$. So, the expression of Taylor's deformation is simply

$$D_T = \frac{19\lambda + 16}{16\lambda(1+\lambda)}Ca, \quad (47)$$

which at the limit of high viscosity drop reduces to $D_T \sim (19/16)Ca/\lambda = (5/4)Ca/(c\lambda)$. In the present article, drop deformation is evaluated by a slightly different way in terms of the components A_{12}, A_{11} and A_{22}. We define the deformations D_1 and D_2 as being

$$D_1(Ca,\lambda) = A_{12} = \frac{5}{4\lambda}cI_2(Ca,\omega) \qquad \text{and} \qquad D_2(Ca,\lambda) = \frac{A_{11} - A_{22}}{2} = \frac{5}{4\lambda}[1 - cI_1(Ca,\omega)] \quad (48)$$

Now, using the expressions for I_1 and I_2 defined in (38) we obtain the result of D_1 and D_2 for a steady simple shear flow, namely

$$D_1 = \frac{5}{4\lambda}\frac{c\,Ca}{c^2 + Ca^2}, \qquad D_2 = \frac{5}{4\lambda}\frac{Ca^2}{c^2 + Ca^2}. \quad (49)$$

Note that at the limit $Ca \ll 1$ D_1 reduces to Taylor's deformation, i.e. $D_1 = D_T \sim (19/16)Ca/\lambda$. In particular, for $Ca \to \infty$ the expression of D_2 is able to capture the well-know limit $5/4\lambda$ of Taylor (1934), whereas D_1 goes to zero. This is an indicative that our definition of deformation in terms of the shape tensor components is quite consistent with the pure geometrical definition proposed by Taylor. In addition, drop orientation with respect to the horizontal axis x may be evaluated by the expression $\beta = \arccos(v_x^1/|\boldsymbol{v}^1|)$, where v^1 is the first quadrant eigenvector of the shape tensor $\mathbf{A}$. Note that both deformation and orientation are functions of Ca and λ.

5.2 Viscometric Quantities

In this section it is shown that the drop deformation and orientation are the key factors for emulsion characterization even at dilute regime. The drop contribution to the rheology is shown in terms of the viscometric quantities: the apparent viscosity ($\mu^* = \sigma_{12}$) and the normal stress differences, $N_1 = Ca(S_{11} - S_{22})$ and $N_2 = Ca(S_{22} - S_{33})$. These viscometric quantities μ^*, N_1 and N_2, were obtained in a non-dimensional form as being

$$\mu^*(Ca, \lambda) = \frac{\mu_B}{\mu}(\lambda)\cos(\hat{\omega}t) + \frac{5c}{\lambda Ca} I_2, \tag{50}$$

$$N_1(Ca, \lambda) = \frac{10}{\lambda}(1 - c\, I_1), \tag{51}$$

$$N_2(Ca, \lambda) = \frac{75}{28\lambda} c\, Ca \cos(\hat{\omega}t)\, I_2 - \frac{N_1}{2}, \tag{52}$$

As we have done for the drop deformation, when substituting I_1 and I_2 given by equations (38) into the above expressions, we obtain the formulae corresponding to a steady simple shearing flow, as being

$$\mu^* = \frac{\mu_B}{\mu} + \frac{5}{\lambda}\frac{c}{c^2 + Ca^2}, \qquad N_1 = \frac{10}{\lambda}\frac{Ca^2}{c^2 + Ca^2}, \qquad N_2 = \frac{75}{28\lambda}\frac{c\,Ca^2}{c^2 + Ca^2} - \frac{N_1}{2}. \tag{53}$$

The asymptotic limits of the all quantities at small and high capillary numbers are presented in table (1).

5.3 Emulsion in steady shear

The steady simple shear flow corresponds to an oscillatory shear with $\hat{\omega} = 0$. Under this condition, the small deformation theory of high viscosity drops ($\lambda \gg 1$), resulting in the integrals I_1 and I_2, reduces simply to the theoretical predictions given in Eq.(38). The theory match with the classical asymptotic calculations $O(Ca)$ of the effective viscosity by Taylor (1934) and with the $O(Ca^2)$ calculations for N_1 and N_2 developed by Schowalter *et. al.* (1968) for the limit $\lambda \to \infty$. Table (1) shows the asymptotic regimes of drop shape and rheology for a high viscosity dilute emulsion. For drops with sufficient high viscosity, the characteristic time for drop deformation $(1 + \lambda)\mu a/\sigma$ exceeds the characteristic time for drop rotation $1/\dot{\gamma}$; hence the drop rotates from the extensional to the compressional quadrant of the velocity gradient before being significantly deformed, and this prevents breakups.

Table 1. Asymptotic limits for weak ($Ca \ll 1$) and strong ($Ca \gg 1$) flows. The high viscosity emulsion ($\lambda \gg 1$) is subjected to a steady shear flow. Here, μ_T (Taylort's viscosity) and μ_B (blob viscosity) denote the two Newtonian limits of a dilute high viscosity emulsion at small Ca and high Ca, respectively.

Properties of the emulsion	$Ca \to 0$	$Ca \to \infty$
Deformation of drop, D_1 e D_2	$D_1 \sim D_T = \frac{5}{4\lambda}\frac{Ca}{c}$	$D_2 \sim \frac{5}{4\lambda}$
Orientation of drop, β	$\frac{\pi}{4}$	0
Effective viscosity, μ^*	$\mu^* \sim \mu_T = \frac{5}{2} - \frac{3}{2\lambda}$	$\mu^* \sim \mu_B = \frac{5}{2} - \frac{25}{4\lambda}$
Normal stress difference, N_1	$N_1 \sim \frac{10}{\lambda}\frac{Ca^2}{c^2}$	$N_1 \sim \frac{10}{\lambda}$
Normal stress difference, N_2	$N_2 \sim -\frac{29}{14\lambda}\frac{Ca^2}{c}$	$N_2 \sim -\frac{5}{\lambda}\left(1 - \frac{15}{28}c\right)$

The plots shown in Fig.(3) indicates that even for dilute emulsions with high viscosity drops there are shear thinning and normal stresses at high shear rate. This findings is a direct consequence of drop deformation and alignment with the flow direction shown in Fig.(2). It is seen in Fig.(3a) that the extension of drops in the direction of the flow offers less resistance for shearing the emulsion. The deformed drop orientation produces normal stress differences as shown Fig.(3b). Figure (3a) shows the asymptotic Newtonian limits at small and high dimensionless shear rates (*i.e.*, $Ca \ll 1$ and $Ca \gg 1$, respectively), and a shear thinning regime in which the emulsion apparent viscosity μ^* depends on the shear rate. At low shear rate the emulsion behaves like a Newtonian fluid with Taylor viscosity (i.e spherical drops with high surface tension). In the limit of high shear rate the emulsion is also Newtonian, but with an effective viscosity due to the presence of particles with small surface tension (*i.e.*, the time for the drops deforms is infinity). In this case of spherical blobs, the surface tension does not exert influence on the emulsion motion response. This behavior of the apparent is quite similar to one described by the shear rate dependence viscosity ad-hoc models for non-newtonian viscous fluids (no elastic effect takes place) such as the Carreau-Yasuda model (e.g. (Bird *et al.*, 1987)).

The last plot in Fig(3b) shows the elastic behavior of the emulsion and indeed a non-linear rheology in terms of the first and the second normal stress differences N_1 and N_2, respectively. We can see that for all shear rates, while N_1 is a positive function of Ca, N_2 is smaller than N_1 ($|N_2| \approx |N_1|/5$) and always negative, a typical rheological behavior of most common polymeric solutions. In addition, Fig(3b) shows that at low values of capillary numbers (low shear rates) the normal stress differences is only a second order effect, proportional to Ca^2. Again, the same behavior is observed for most elastic liquids used in industrial applications. Asymptotic formulas for N_1 and N_2 were also obtained by a small deformation theory $O(Ca^2)$ developed by (Schowalter *et. al.*, 1968). This theory however is restrict to small capillary numbers (i.e. $O(Ca^2)$) and it unfortunately fails to describe the influence of drop deformation on the emulsion shear viscosity.

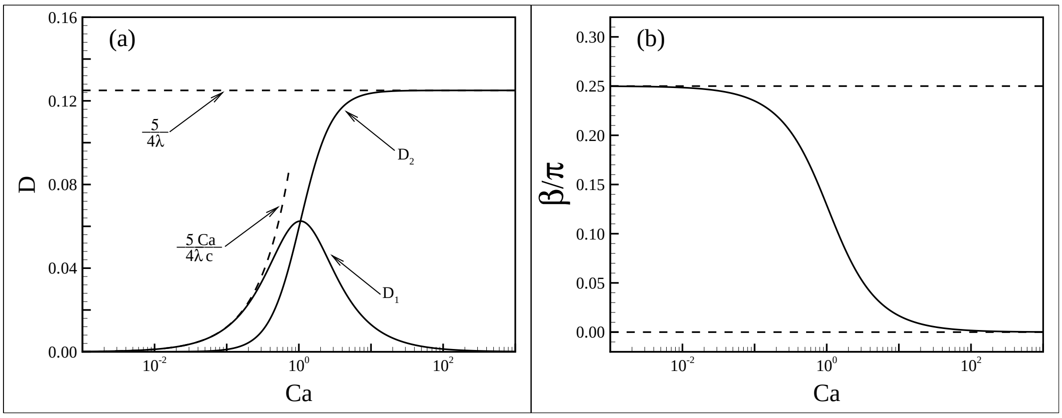

Figure 2. Microstructural behavior of a dilute emulsion for $\lambda = 10$. Deformation (a) and orientation (b) as a function of the dimensionless shear rate Ca. Dashed line presents the asymptotic results of Taylor, 1934, given in Tab.(1)

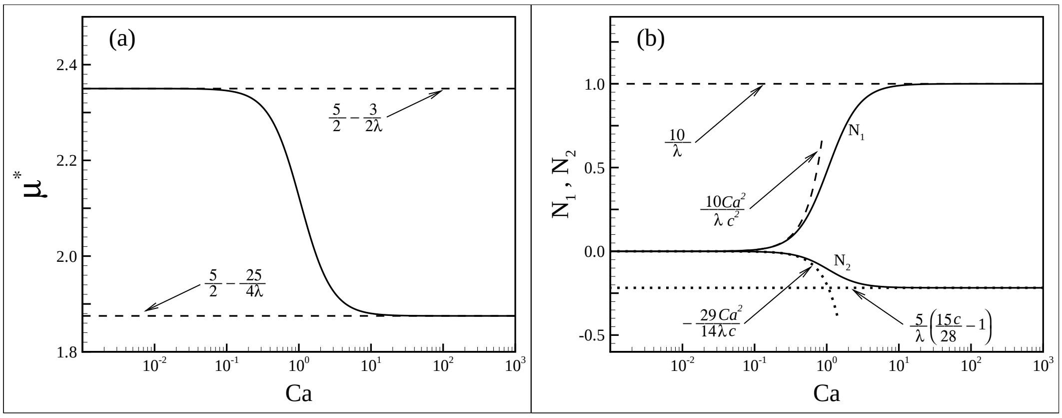

Figure 3. Rheology of an emulsion of high viscosity drops. (a) effective viscosity and (b) normal stress differences. In both plots the asymptotic regimes given in Tab.(1) are also shown.

5.4 Emulsion in oscillatory shear

Now, we explore a weakly non-linear viscoelastic response of the emulsion through the theory given by Eq.(50). To this end, the series for I_1 and I_2 given respectively by the equations (45) and (46) are substitute into equation (50) resulting in

$$\mu^* = \eta_I'(\hat{\omega},\gamma_o)cos(\hat{\omega}t) + \eta_I''(\hat{\omega},\gamma_o)sin(\hat{\omega}t) + \eta_{II}'(\hat{\omega},\gamma_o)cos(3\hat{\omega}t) + \eta_{II}''(\hat{\omega},\gamma_o)sin(3\hat{\omega}t) + \ldots, \tag{54}$$

where,

$$\begin{aligned}
\eta_I'(\hat{\omega},\gamma_o) &= \frac{\mu_b}{\mu}(\lambda) + \frac{5}{\lambda c}\left[\frac{1}{c_1} + \left(\frac{1}{c_2} - \frac{1}{c_1}\right)\gamma_o^2\right], \\
\eta_I''(\hat{\omega},\gamma_o) &= \frac{5}{\hat{\omega}\lambda}\left[\left(1 - \frac{1}{c_1}\right) + \frac{1}{2}\left(\frac{1}{c_1} - \frac{1}{4c_2} - \frac{3}{4}\right)\gamma_o^2\right], \\
\eta_{II}'(\hat{\omega},\gamma_o) &= \frac{5}{8\lambda c}\left(\frac{1}{c_1} - \frac{2}{c_2} + \frac{1}{c_3}\right)\gamma_o^2 \qquad \text{and} \\
\eta_{II}''(\hat{\omega},\gamma_o) &= \frac{5}{24\hat{\omega}\lambda}\left(1 - \frac{3}{c_1} + \frac{3}{c_2} - \frac{1}{c_3}\right)\gamma_o^2
\end{aligned} \tag{55}$$

are material functions similar to the loss and storage modulus defined in linear viscoelasticity. In the expressions Eq.(55) the term $\mathcal{O}(\gamma_o^3)$ was taken off, but the terms $\mathcal{O}(\gamma_o^2)$ were kept in order to capture at leading order a non-linear behavior due to the finiteness of γ_o. It is possible to see in Eq.(55) that the storage and loss module are functions of the dimensionless frequency and the shear strain γ_o. The emulsion rheology is a function of I_1 and I_2 such as determined in the equations (50), (51) and (52). By numerical integration of I_1 and I_2 it is possible to predict the complex emulsion behavior under several situations in the $\lambda \gg 1$ limit, including non-linear response of the flow for $\gamma_o \sim 1$, or even for the regime $\gamma_o \gg 1$.

Figure (4a) and (4b) shows, respectively, D_1 and D_2 as a function of dimensionless time $T = \omega t/\pi$, for $\lambda = 10$ and a strain harmonic forcing amplitude $\gamma_o = 15$. It is seen a non-linear frequency response of the drop shape, given by D_1 and D_2, at high strain regimes. The behavior of high viscosity drops is governed basically by the relative importance of three relative rates: the shear-rate $\dot{\gamma_o}$, the oscillatory frequency ω and the drop relaxation time $\sigma/(\lambda\mu a)$.

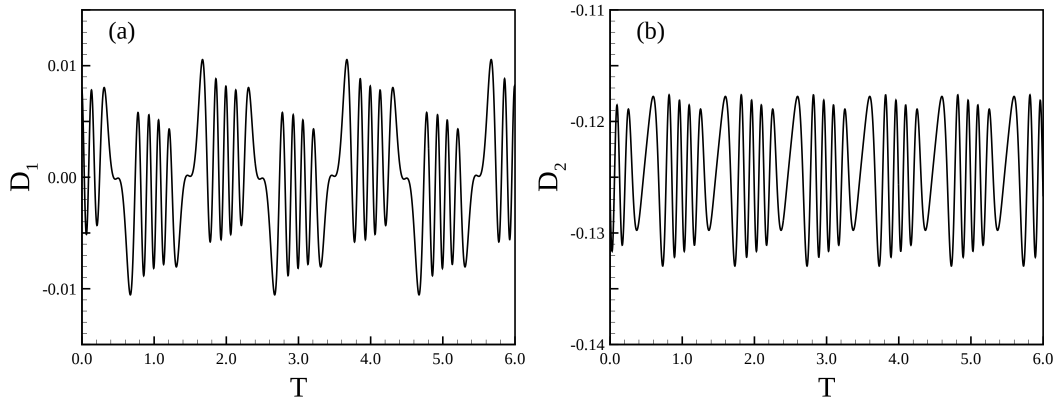

Figure 4. Drop deformation as a function of dimensionless time $T = \omega t/\pi$, for $\lambda = 10$, $\omega = 2\pi$ and $\gamma_o = 15.0$.

Next, we explore the non-linear frequency response of the emulsion using our asymptotic predictions giving in Eq.(54). We show that for low shear strain amplitudes the emulsion exhibits a linear viscoelastic response, but a non linear viscoelastic response arises at larger shear strains. Fig.(5)presents the results of the linear viscoelastic quantities η' and η'' as a function of the frequency. We see the existence of two Newtonian plateau at low and high frequency regimes. The low-frequency drop reflects the very slow relaxation of the glassy structure of the emulsion. In this viscous regime the theoretical expressions (54) reduces to the Taylor viscosity $\mu_o = 1 + (5\phi/2)(1 - 3/5\lambda)$ for the linear viscoelastic regime. On the other hand, the high-frequency limit rise reflects the fact that the emulsion is comprised solely of fluids, whose viscous behavior dominates at sufficiently high frequency. we find that the linear viscoelastic regime of our theoretical predictions reduces to the effective viscosity $\mu_\infty = 1 + (5\phi/2)(1 - 5/2\lambda)$. In this regime the surface tension relaxation time is much larger that the period of oscillations; no effect of surface tension takes part. As the origin of emulsion elasticity arises from the surface tension of the droplets or their capillary pressure, the plot of η'' against the frequency also indicates the purely viscous behavior of the emulsion at low and high frequency for which η'' is always null. Guided by our weakly nonlinear theory, we have found a way to express the linear viscoelastic formulae for η' and η'' in terms of μ_o, μ_∞ and the emulsion relation time, namely

$$\eta'(\omega, \lambda, \phi) = \frac{\mu_o + \mu_\infty \omega^2 \tau^2}{1 + \tau^2\omega^2}, \qquad \eta''(\omega, \lambda, \phi) = (\mu_o - \mu_\infty)\frac{\omega\tau}{1 + \tau^2\omega^2},$$

where τ is the emulsion relaxation time. We argue that the above expressions may be very useful to fit linear viscoelastic response of an emulsion even at moderate drop volume fraction. The results are in qualitative agreement with the linear viscoelastic behavior of η' and η'' obtained by a boundary integral numerical simulation for high drop volume fraction (up 66%) (Cunha and Loewenberg, 2003[c]) and observations on concentrated emulsion flows undergoing unsteady shear (Mason *et. al.*, 1997).

In addition, theoretical predictions obtained for the viscous and the elastic modulus for a weakly non-linear viscoelastic regime are also plotted in Fig.(5). The results indicate that a dilute emulsion of high viscosity drops may present a complex memory behavior introduced by the surface tension relaxation at high strain rate. This nonlinear viscoelastic behavior has been the subject of our current investigations. We have no experimental results with which to compare our theoretical predictions to the asymptotic limit explored in the present article.

6. Final Remarks

In this work, a constitutive model based on a microstructural study of the material behavior of dilute emulsions of high viscosity drops is presented. The model has been derived by determination of the drop stresslet from the drop shape by using a small deformation theory corresponding to high viscosity drops. The model has been applied to examine emulsion rheology under steady and oscillatory simple shear flows. The emulsion apparent viscosity and the normal stress differences were derived analytically in terms of two special integrals I_1 and I_2 given by Eq.(36) and Eq.(37), respectively. The steady shear behavior was explored in order to verify the model by comparison the present work calculation with classical results available in the literature. The previous calculations were usually developed under condition of small capillary numbers. Differently, the calculations presented here are able to explore the rheology of dilute emulsions at high capillary regimes. A weak non-linear viscoelastic theory was derived for the limit of $\gamma_o \sim 1$, which has been one of our principal results. A calculation of the loss and storage module at leading order in the shear strain was developed for $\mathcal{O}(\gamma_o^2)$.

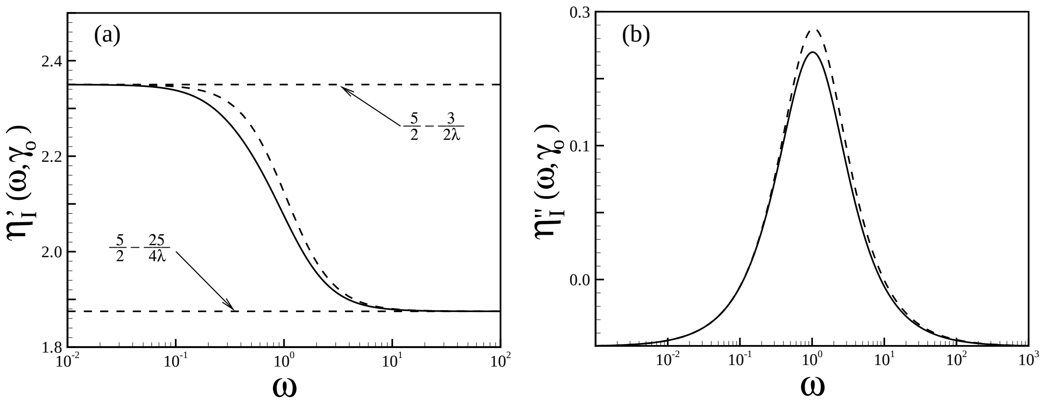

Figure 5. (a) Loss and (b) storage first harmonics modulus as functions of dimensionless frequency ω, for $\lambda = 10$ and $\gamma = 0.5$. Solid lines: $\mathcal{O}(\gamma_o^2)$ theory; dashed lines: linear viscoelasticity theory.

The small deformation theory explored in this article was able to capture a complex rheological behavior of an emulsion showing even for a dilute regime the most important features of elastic non-newtonian fluids, including shear-thinning and normal stress differences. The model still regards the dependence of this material functions with the shear rate in the same fashion of experimental observations in the regime of non-linear viscoelasticity. The non-linear viscoelastic theory for $\gamma_o \sim 1$ has shown both loss and storage module, $\eta'(\hat{\omega},\gamma)$ and $\eta''(\hat{\omega},\gamma)$, as a function of the frequency and shear strain as well.

7. Acknowledgements

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