NON NEWTONIAN PROPERTIES OF EMULSIONS

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Abstract. *In this paper, three-dimensional boundary integral computer simulations of emulsions in oscillatory shear flow will be described. We obtain results for ordered BCC emulsions with dispersed-phase volume fractions below the critical concentration $\phi_c = 68\%$ (maximum packing for BCC). Complex rheological features including: shear-thinning viscosities, normal stress differences, and a nonlinear frequency response are explored. We have derived analytical results for slightly deformed drops in diluted emulsions at arbitrary shear-rates, which is particularly relevant to drops with viscosity ratios beyond the critical value for breakup in shear. Using our analysis and numerical simulations, we also explore the limiting high shear-rate rheology of diluted emulsions with high viscosity drops.*

1. INTRODUCTION

An emulsion is an immiscible mixture of two fluids , one of which is dispersed in the continuous phase, typically made by rupturing droplets down to colloidal sizes through mixing. To inhibit coalescence a surfactant which concentrates at the interfaces must be added to create a short-ranged interfacial repulsion between droplets. Emulsions arise in a wide range of applications relevant to the materials processing, food processing, cosmetics, and pharmaceutical industries (Edwards, Brenner & Wason 1991, and 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. Currently, there is an active interest emulsions for a diverse range of applications. Due to the complexity of these systems, however, there has been little progress towards a fundamental basis for understanding and predicting the rheology of such comples systems.

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 γ_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 ration 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 el 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 mechanism as the emulsion become packed and deformed.

Relevant to the theoretical part of the present work are the studies of Schowalter, Chafey & Brenner (1968) and Frankel & Acrivos (1970) of 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 (e.g. Mason et al. 1997). Computer simulations 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, Zhou & Pozrikidis 1995; Loewenberg & Hinch 1996). Numerical simulations of more concentrated emulsion flow is needed to help with the interpretation of experimental observations and to predict the rheology and microstructure of disordered emulsion flows. In this article, we present results of small deformation analysis and numerical simulations of emulsion dynamics in oscillatory shear.

2. THEORY

Consider the creeping flow motion of an emulsion of freely suspended droplets, with radius a, undergoing oscillatory shearing flow field $\dot{\gamma}_o \cos(\omega t)$. Let $\dot{\gamma}_o$ be the magnitude of the oscillatory shear, μ_o is the continuous-phase viscosity and Γ the interfacial tension. We non-dimensionalize all velocity by Γ/μ_o and all lengths by a. The relevant parameters for the problems here include the dispersed-phase volume fraction ϕ, the dispersed- to continuous-phase viscosity ratio λ, the capillary number and Strouhal number. The capillary number is defined as the shear-rate normalized by the drop relaxation rate $\Gamma/\mu_o a$

$$Ca_o = \frac{\mu_o \dot{\gamma}_o a}{\Gamma}, \tag{1}$$

The Strouhal number is relevant to problems involving oscillatory shear flow. It is the ratio of the imposed oscillation frequency ω to the drop relaxation rate:

$$Sh = \frac{\mu_o \omega a}{\Gamma}. \tag{2}$$

2.1. Governing equations

In the regime of low Reynolds number, incompressible fluid motions are governed by the Stokes and continuity equations

$$-\nabla P + \mu_o \nabla^2 \mathbf{u} = \mathbf{0} \quad \text{and} \quad \nabla \cdot \mathbf{u} = 0, \tag{3}$$

Here, $\mathbf{u}$ is the Eulerian velocity field, P is the modified pressure $P = p - \rho \mathbf{g} \cdot \mathbf{x}$, μ_o and ρ are the fluid viscosity and density,respectively, $\mathbf{g}$ is the gravitational acceleration, $\mathbf{x}$ is the position vector and p is the mechanical pressure.

2.2. Boundary Conditions.

The boundary conditions at a drop interface S_i with surface tension Γ require a continuous velocity and a balance between the net surface traction and surface tension forces (Pozrikidis 1992). Mathematically, these conditions are expressed as

$$\mathbf{u} \to \mathbf{u}^{\infty} \qquad |\mathbf{x}| \to \infty; \qquad \mathbf{u}(\mathbf{x}) = \mathbf{u}'(\mathbf{x}), \qquad \mathbf{x} = \mathbf{x}_i \in S_i \tag{4}$$

and the traction jump (discontinuity in the interface surface tension) at the interface $[\mathbf{n} \cdot \boldsymbol{\sigma}]$, is written as (Pozrikidis 1992)

$$\Delta \mathbf{t} = [\mathbf{n} \cdot \boldsymbol{\sigma}] = \kappa \Gamma \mathbf{n} - (\mathbf{I} - \mathbf{nn}) \cdot \boldsymbol{\nabla} \Gamma. \tag{5}$$

Here $(\mathbf{I} - \mathbf{nn}) \cdot \boldsymbol{\nabla}$ denotes the gradient operator $\boldsymbol{\nabla}^s$ tangent to the interface, $\mathbf{I}$ is the identity tensor and $\mathbf{n}$ is the unit normal vector to S_i. $\boldsymbol{\nabla}^s \cdot \mathbf{n}$ defines the mean curvature of the interface κ. In general, it can be expressed as the sum of the inverse principal radii of curvature $\kappa = R_1^{-1} + R_2^{-1}$. This article considers the case of clean interface deformable drops (no Marangoni stress) and the drops are neutrally buoyancy. Under these conditions the interface is treated with uniform surface tension and the traction discontinuity given in (5) reduces to

$$\Delta \mathbf{t} = \kappa \Gamma \mathbf{n}. \tag{6}$$

The interface evolution may be described with a Lagrangian representation $D\mathbf{x}_i/Dt = \mathbf{u}(\mathbf{x}_i)$.

2.3. Stress and linear viscoelastic response

The average stress Σ of an emulsion is described as follows (Landau & Lifshitz 1987),

$$\boldsymbol{\Sigma} = -\overline{P}\mathbf{I} + 2\mu_o \overline{\mathbf{E}} + \phi \boldsymbol{\Sigma}'. \tag{7}$$

The first two terms on the RHS are the contributions from the background continuous phase (i.e. a newtonian effect) with an average pressure $\overline{P}$ and an average rate of strain $\overline{\mathbf{E}}$. Here $\phi \boldsymbol{\Sigma}'$ is the average stress contribution of the dispersed phase (i.e. a non-newtonian effect) due to drop deformation and orientation, and interactions between them. The average shear-rate of the flow can be defined as $\dot{\gamma} = \sqrt{(1/2) Tr(\overline{\mathbf{E}} \cdot \overline{\mathbf{E}})}$. For the case of oscillatory simple shear considered here $\dot{\gamma}(t) = E_{12} = \dot{\gamma}_o e^{i\omega t}$, where t denotes time, ω and $\dot{\gamma}_o$ are the frequency and the amplitude of the oscillations, respectively.

When the strain or the rate of strain in a system is small its response is linear. Then, whether an emulsion is subject to small amplitude simple shear the flow is $\mathbf{u} = (\dot{\gamma}_o x_2 e^{i\omega t}, 0, 0)$. The stress of the system oscillate with the same frequency but not necessarilly in phase. Based on a linear viscoelastic formulation for dilute limit of an emulsion (Cunha, Toledo and Loewenberg, 1999), we have developed a Maxwell model with a single relaxation time. According to this model, the in-phase part of the response (viscous dissipation) is found to be $\eta'(\omega) = \frac{\eta_o + \eta_\infty \tau_o^2 \omega^2}{1 + \tau_o^2 \omega^2}$, whereas the out-of-phase ration of stress reflecting elastic effect is given by $\eta''(\omega) = (\eta_o - \eta_\infty) \frac{\omega \tau_o}{1 + \tau_o^2 \omega^2}$. Here $\eta_o = \frac{1 + 5\lambda/2}{1 + \lambda}$ (Taylor's viscosity 1932) is the viscosity in the limit of low frequency, whereas $\eta_\infty = \frac{5(\lambda - 1)}{2\lambda + 3}$ is the viscosity in the limit of high frequency corresponding to the viscosity of an emulsion composed of spherical blobs (surface tension is an unimportant effect). Here $\tau_o = 40(2\lambda + 3)(19\lambda + 16)(\lambda + 1)^{-1}$ is a single drop relaxation time.

Following the model above, the drop stress contribution, for any concentration, can be expressed in an appropriate form as a purely viscous contribution plus a complex stress contribution from the surface tension, Σ^*. $\Sigma' = \eta_\infty(\omega, \phi)\dot{\gamma} + \Sigma^*$. Now, a complex viscosity η^* can be defined from $\Sigma^* = \eta^*(\omega,\phi)\dot{\gamma}(t)$, and Σ^* is obtained from the stress relation function spectrum $\Phi(t,\phi)$ by using the convolution integral (Bird et al. 1987),

$$\Sigma^* = \int_{-\infty}^{t} \Phi(t-t',\phi)\dot{\gamma}(t')dt'. \tag{8}$$

Aternatively we may define the complex viscosity in terms of the stress relaxation function, directly. By Fourier transformation we can show that

$$\eta^*(\omega,\phi) = \eta'(\omega,\phi) - i\eta''(\omega,\phi) = \int_0^{\infty} \Phi(\tau,\phi)e^{-i\omega\tau}d\tau \tag{9}$$

The stress relaxation function is defined, for example, as the response of the system to step strain $\dot{\gamma}(t) = \gamma_o\delta(t)$. Here we define the average relaxation time $\overline{\tau}(\phi) = \eta'(0)/\Phi(0)$ by the integral

$$\overline{\tau}(\phi) = \frac{1}{\Phi(0)}\int_0^t \Phi(t',\phi)dt'. \tag{10}$$

It is instructive to note that for dilute limit of emulsions $\overline{\tau} = \tau_o$ and $\Phi(0) = \Phi_o = \eta_o/\tau_o$. The simplest model for the system studied here is one relaxation time Maxwell model

$$\Phi(t) = \Phi_o e^{-t/\tau_o}, \quad \text{with} \quad \eta^*(\omega) = \frac{\Phi_o}{\tau_o^{-1} + i\omega}. \tag{11}$$

Dilute emulsion are well described by such a model. On the other hand, it will be shown in §4 that a multiple relaxation time Maxwell model, as defined bellow, is needed to describe the behaviour of concentred emulsions undergoing oscillatory shear with small amplitudes and arbitrary frequencies, $\Phi(t) = \sum_k \Phi_k e^{-t/\tau_k}$.

3. NUMERICAL SIMULATIONS

All simulations rely on the boundary integral method. Periodic boundary conditions are enforced through the use of periodic Green's functions. These are obtained by Ewald summation using accurate computationally-efficient tabulation of the nonsingular background contribution (Loewenberg & Hinch 1996).

We develop two and three-dimensional boundary integral simulations that are capable for describing the dynamics of concentrated random emulsions in oscillatory shear. Accordingly, the evolution of M deformable drops is described by time-integrating the fluid velocity $\mathbf{u}(\mathbf{x}_o)$ on a set of interfacial marker points $\mathbf{x}_o$ on each drop surface. The fluid velocity is governed by the second-kind integral equation on the interfaces S_m $(m = 1, \cdots, M)$ of all drops in the simulation (Rallison & Acrivos 1978) :

$$u_j(\mathbf{x}_o) - \frac{\lambda-1}{\lambda+1}\frac{3}{2\pi}\sum_{m=1}\int_{S_m} u_i T_{ijk} n_k dS = F_j(\mathbf{x}), \tag{12}$$

where $\mathbf{T}$ is the periodic stresslet (Loewenberg & Hinch 1996), and $\mathbf{F}(\mathbf{x}_o)$ is defined as below

$$F_j(\mathbf{x}_o) = \frac{2}{\lambda+1}x_o^j\delta_{2j}Ca\ (t) - \frac{1}{\lambda+1}\frac{1}{4\pi}\sum_{m=1}\int_{S_m} \Delta t_i G_{ij} dS. \tag{13}$$

$\mathbf{G}$ is the periodic stokeslet (Beenaker 1986, Cunha 1995) $O(1/r)$ for the 3D case and $Ca(t) = Ca_o\cos(Sh\ t)$ for oscillatory shear e $Ca(t) = Ca_o$ for stationary shear. In the absence of Marangoni stresses the traction jump across the drop interfaces is given simply by $\Delta t_j = \kappa\Gamma n_j$, where κ is the mean curvature and $\mathbf{n}$ is the normal vector.

The boundary integral simulations here uses an adaptive discretization of the drop interface that depends only on the instantaneous drop shapes. It is independent of the fluid velocity and the history of drop deformation. In particular, the algorithm incorporates a prescribed marker-point density function (interface area per marker point) that is used to define an equilibrium edge length between marker points. This density function resolves the minimum local length scale everywhere on the drop interface. Equilibration velocities for marker points are determined by the resultant of local spring-like tensions projected onto the drop interface. The resulting dynamical system of damped massless springs has a well-defined minimum energy equilibrium state that is attained in several iterations after every fluid dynamic displacement of the marker points. Marker point equilibration is an inexpensive $O(N)$ calculation compared to the time-controlling $O(N^2)$ fluid velocity calculation. The interface discretization algorithm maintains optimal marker-point connectivity using a local reconnection rule. Accordingly, the edge between adjacent triangles is switched to connect opposite vertices if the resulting edge is shorter. By maintaining a nearly equilateral triangulation, this procedure maximizes the time step for the time-controlling fluid dynamical calculations (Cristini et al. 1998). The normal vector and curvature were calculated by the local surface-fitting algorithm of Zinchenko et al. (1997).

The fluid velocity on the drop interfaces is obtained by an iterative solution of (12) using the GMRES algorithm (a generalization of the conjugate gradient method to non-symmetric matrices) to achieve convergence for the closely-spaced interface configurations that characterize dense emulsions.

In Fig. (1) two drop shapes are depicted for steady and oscilattory shear flows, respectively. An inspection of the drops in Fig. (1) illustrates that the adaptative discretization resolves regions of high curvatures where a high density of marker points is needed. In particular, Fig. 1 a shows that drops with sufficiently high viscosity (in this result $\lambda = 3.8$) the characteristic time for drop deformation $(1+\lambda)\mu a/\Gamma$, 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 signicantly deformed, and this prevents breakup. Cunha, Toledo & Loewenberg (1999) have shown theoretically that dilute emulsions with high viscosity drops are shear thinning and have normal stresses at high shear rate. This behavior is a direct consequence of drop deformation and alignment with the flow such as it is shown in this figure. The result depicted in Fig. 1b shows that drops with small viscosity can break in oscillatory shear with large strain amplitudes.

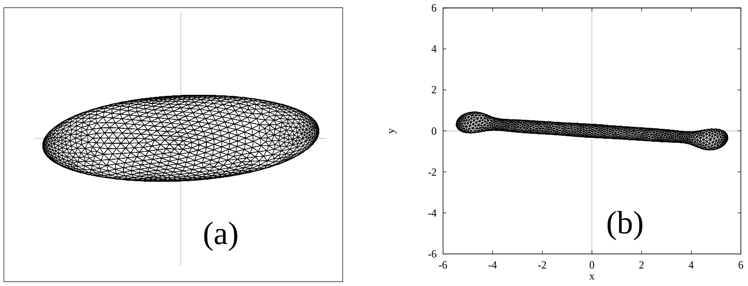

Figure 1: Adaptative surface discretization. (a) Stationary drop shape of a viscous drop in a steady simple shear; $\lambda = 3.8$ $Ca_o = 1.8$ and initial number of marker points N_o over drop surface equal to 1000. (b) Drop in oscillatory shear; $\lambda = 1$, $Ca_o = 0.8$, $Sh = 0.08$, and $N_o = 252$.

The volume-averaged stress tensor $\mathbf{\Sigma}$ is evaluated numerically from an integral of the traction jump and fluid velocity over the drop interfaces. Following Batchelor (1970) ones obtain

$$\langle \mathbf{\Sigma} \rangle = \frac{1}{V} \sum_{i=1}^{N} \int_{S_i} \{(\kappa \Gamma \mathbf{x}\mathbf{n} + \mu(\lambda - 1)(\mathbf{u}\mathbf{n} + \mathbf{n}\mathbf{u})\} \, dS(\mathbf{x}). \tag{14}$$

Equation (14) is the contribution of the dispersed phase to the macroscopic stress of the emulsion due to the dipole stresslet that each drop torque free generates in the flow.

4. RESULTS

Fig.2 shows a typical numerical result of an isolated high viscosity drop ($\lambda = 5$) deforming in oscillatory shear with a dimensionless shear rate (capillary number) $Ca_o = 3$ and $Sh = 0.5$. The motion is periodic and the drop deforms, rotates, but it does not break under the conditons of this simulation.

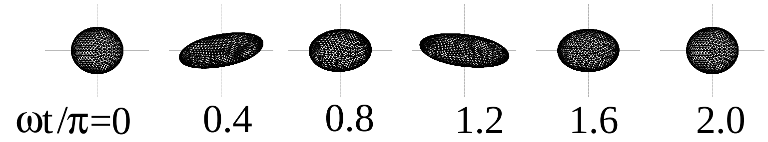

Figure 2: Simulation of high viscosity drops in oscillatory shear ($\lambda = 5$) with $Ca = 3$ and $Sh = 0.5$. Three-dimensional mesh is shown for $N_o = 1000$ nodes.

The results depicted in Fig.3 shows the comparison between the drop shear stress contribution predicted theoretically and the boundary integral simulations for the following set of the physical parameters: $Ca = 3.0$, and $Sh = 0.5$. We have explored the limiting high shear-rate rheology of diluted emulsions with high viscosity drops. Even at high capillary number (i.e. strong flow) no large deformation results for high viscosity drop because the extended part of the shape is spun round into the compression 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 difference. We find that the behavior of high viscosity drops depends on three rates: the shear-rate $\dot{\gamma}_o$, the oscillation frequency ω, and the drop relaxation rate $\Gamma/\lambda\mu_o a$. At low shear-rates, the system exhibits a linear viscoelastic response and a nonlinear behavior occurs for large shear-rates. In these plots the analytical expressions for the drop shear stress contribution and the first normal stress difference were developed by Cunha & Loewenberg, 1999.

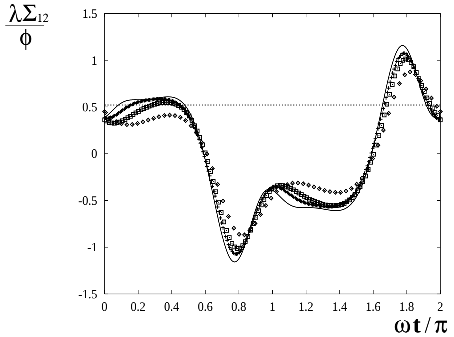

Figure 3: Drop shear stress contribution as a function of the phase for oscillatory shear with $Ca = 3.0$ and $Sh = 0.5$. Comparison between a first order high λ theory (solid curve) and the boundary integral simulations $\diamond$ $\lambda = 5$, $\square$ $\lambda = 10$ and $+$ $\lambda = 20$. The dashed curve corresponds to the solution for stationary shear with $\lambda\frac{\Sigma_{12}}{\phi\mu_o\dot{\gamma}} = \frac{5c}{c^2+Ca^2}$.

In Figs. 4 and 5 it is shown the linear viscoelastic quantities η' and η'' as a function of the frequency for different concentrations based on boundary integral simulations of a monodisperse

BCC emulsion with viscosity ratio $\lambda = 1$. At all ϕ, we observe a low-frequency regime in which η' is independent of the frequency and the elastic contribution is null. It is seen that the low-frequency plateau for $\phi = 60\%$ is about four times bigger than its value for dilute emulsion. The high-frequency rise reflects the fact that the system is composed solely of fluid (i.e. an emulsion of blobs, no effect of surface tension takes part), whose viscous behavior dominates at sufficiently high frequencies.

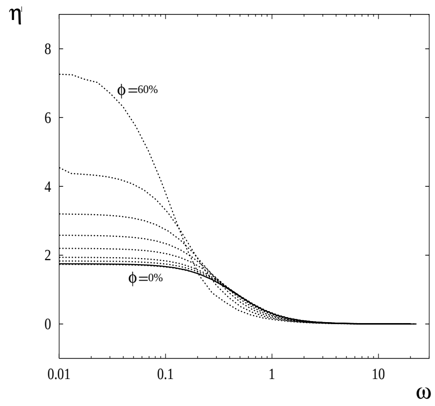

Figure 4: The frequency dependence of the viscous modulus η' of a monodisperse BCC emulsion with $\lambda = 1.0$ for volume fractions ϕ, ranging from 0 to 0.6. Dashed curves are numerical results from boundary integral simulation whereas the solid curve is predicted by linear viscoelasticity theory for dilute emulsion.

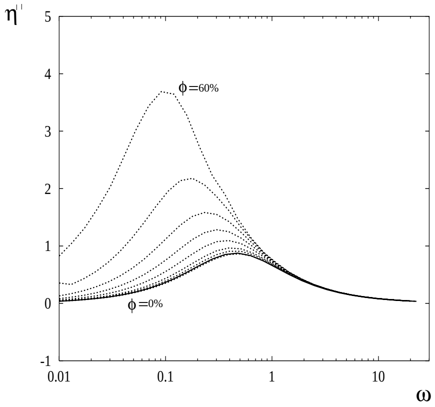

Figure 5: The frequency dependence of the elastic moduli η'' of a monodisperse BCC emulsion with $\lambda = 1.0$ for volume fractions ϕ, ranging from 0 to 0.6. Dashed curves are numerical results from boundary integral simulation whereas the solid curve is predicted by linear viscoelasticity theory for dilute emulsion.

Next we present preliminary results of 3D step strain simulations for drop concentration below the maximum packing of spherical drops ($\phi < \phi_c = \pi\sqrt{3}/8$) and viscosity ratio $\lambda = 1$. The emulsion was subject to a step strain and allowed to relax and we measure the response. Fig.6 shows the dimensionless stress relaxation function as a function of the time normalized by the average relaxation time for three different concentrations: dilute ($\phi < 0.3$), 0.5 and 0.66. It is seen that the dilute system has a simple exponential decay and one relation time Maxwell model describes well the response of the system. For all volume fraction simulated it is observed a long time exponential decay, but short time scales show some multiple time scales , specially at highest volume fraction shown ($\phi = 0.66$).

Relaxation times can be extract directly from our numerical simulations. The spectrum

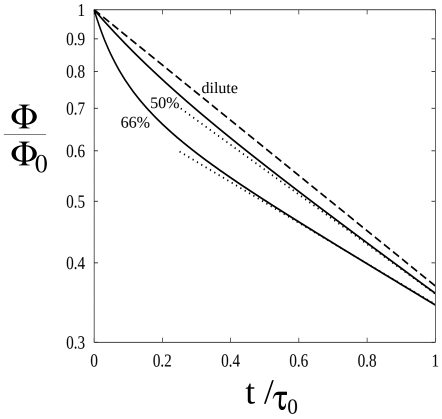

Figure 6: Normalized stress relaxation function from 3D step strain simulations as a function of time for several concentrations. Ordered BBC lattice with $\lambda = 1$. Dot lines are the exponential decay.

of these relaxation times is shown in Fig. 7. It is seen that the long time mode diverges and dominates the average relaxation time. At higher concentrations it is clear the presence of multiple modes (i.e. multiple time scales) that should be attributed to the higher order multipole interactions between the drops and the lubrication resistence between them. In particular, from Fig.7, it can be seen that the frequency response of a dilute emulsion can be described by one relaxation time, whereas four relaxation times is needed to describe the response of the system at 66%. The results obtained for the real (i.e. viscous contribution) and imaginary (i.e. elastic contribution) parts of the complex viscosity are presented in Fig.7. As it can be seen a multiple relaxation time Maxwell model using the spectra shown in Fig.7 describes well the viscoelastic reponse of an BCC emulsion at 66% drop volume fraction.

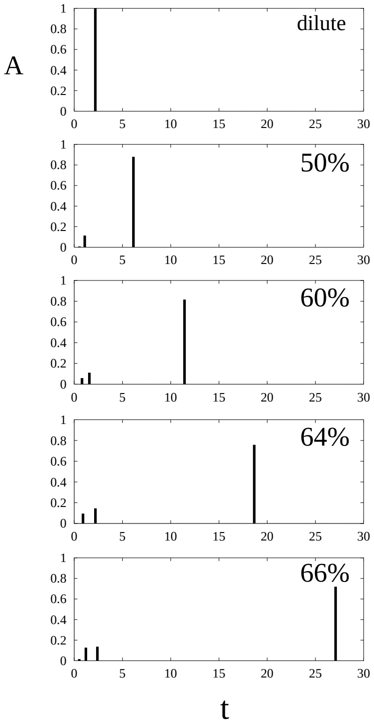

Figure 7: Relaxation time distribution for several concentrations. Boundary integral simulation of a BBC emulsion for $\lambda = 1$ that was subject to a step strain.

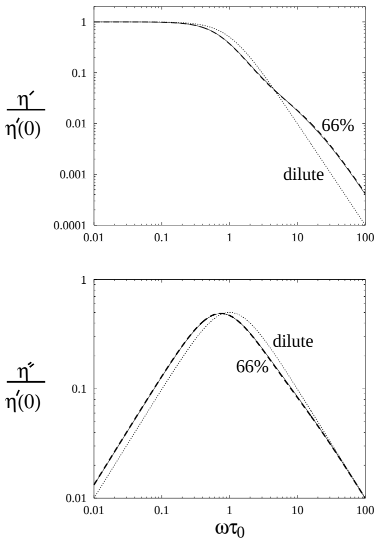

Figure 8: The frequency dependence of the viscoelastic quantities for dilute regime and $\phi = 0.66$. Ordered B.C.C. emulsion with $\lambda = 1$. The dashed solid curve corresponds to the numerical results and coinciding line is a four relaxation time Maxwell model.

5. CONCLUSIONS

In this work we have presented results for the frequecy response of an emulsion in oscilattory shear. The results reveal a complex rheology of emulsions at dilute and moderated regime of drop volume fraction below critical. The main conclusions of this work are: i) The stress relaxation function decay exponentially at long time for all concentrations tested; ii) The spectra relaxation time was found to be discrete for ordered BBC emulsion; iii) The average relaxation time diverges and this divergence was related to the lubrication resistense between the drops when $\phi \to \phi_c$; iv) Dilute emulsion ($\phi < 30\%$) are well described with one relaxation time Maxwell model, whereas a superpositon of four relaxation time Maxwell model is needed for describing sucessfully the viscoelastic response of an emulsion with drop volume fraction 66%. We plan in a future work explore, in more details, the behaviour of emulsions for concentrations above the critical volume fraction when it is expected this complex system exihibiting yields stress. In addition we intend to investigate the effect of finite strains on the rheology of disordered dense emulsions in oscillatory shear.

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