Rheology of viscoelastic suspensions of spheres under small and large amplitude oscillatory shear by numerical simulations

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Synopsis

The dynamic response of a viscoelastic suspension of spheres under small and large amplitude oscillatory shear is investigated by three-dimensional direct numerical simulations. A sliding triperiodic domain is implemented whereby the computational domain is regarded as the bulk of an infinite suspension. A fictitious domain method is used to manage the particle motion. After the stress field is computed, the bulk properties are recovered by an averaging procedure. The numerical method is validated by comparing the computed linear viscoelastic response of Newtonian and non-Newtonian suspensions with previous theories and simulations. The numerical predictions are in very good quantitative agreement with experimental data for the Newtonian case, whereas deviations are found with respect to some sets of experiments for semidilute and concentrated viscoelastic suspensions. To investigate on such discrepancies, the effect of aggregates in the bulk of the suspension is examined. The simulations show that the presence of structures significantly alters the loss modulus. Such an effect is more pronounced as the volume fraction increases. In this light, the above mentioned disagreement between simulations and data (and among experimental

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data themselves) can be rationalized, as its origin can be attributed to inhomogeneous particle configurations. For increasing strain amplitudes, both loss and storage moduli depart from the linear viscoelastic values. Although the deviations are qualitatively similar to the large amplitude response of the unfilled suspending matrix, our results for dilute and semidilute suspensions show that the decrease of the moduli is more and more pronounced as the volume fraction is higher. Furthermore, a higher concentration of solid particles reduces the value of strain amplitude such that the nonlinear behavior is observed. Simulations at higher frequencies also correctly capture the overshoot in the loss modulus for intermediate strain amplitudes. Finally, the effect of fluid elasticity on the particle motion is analyzed. The particles are found to move away from their starting positions and the average distance, computed at the beginning of each cycle with respect to the initial configuration, linearly increases with the number of cycles. The change in the microstructure is attributed to the long-range hydrodynamic interactions mediated by fluid viscoelasticity.

I. INTRODUCTION

Solid particles suspended in liquids have been extensively studied in the last decades. Due to the great importance of this issue in several application areas, many theoretical, experimental and numerical works, mainly focused on the suspension bulk rheology, appeared in the literature. As it is well-known, the volume particle concentration \( \phi \) is an important property of the suspension, and its variation can lead to very different phenomena [e.g., Laun (1984)]. Commonly, a suspension is defined “dilute” when \( \phi \leq 0.05 \), “semidilute” for \( 0.05 \leq \phi \leq 0.10 \), and “concentrated” for solid volume concentrations larger than 0.10. Due to the interest in technological applications, the most part of the works in the research literature has been devoted to concentrated suspensions [Barnes (2003)].

In several application fields (filled polymers, paints, foods, coatings, etc.), viscoelastic fluids are used as the suspending medium. In spite of their great relevance, however, viscoelastic suspensions received much less attention than particles in Newtonian liquids. Furthermore, whereas an extensive part of theoretical [Einstein (1911); Oldroyd (1953); Batchelor and Green (1972a, 1972b); Choi and Schowalter (1975); Batchelor (1977)] and numerical contributions can be found on Newtonian suspensions [Bossis and Brady (1989); Brady (1993); Ladd (1994); Phung et al. (1996); Rexha and Minale (2011)], for the viscoelastic case the study has been mainly approached through experiments, although some relevant theoretical work exists.

In this regard, it is worth to mention the so-called “correspondence principle” which states that, in linear response, the boundary value problem for a viscous and a linear viscoelastic fluid has a similar solution [see, e.g., Zwanzig and Bixon (1970), Christensen (1979) and the recent review from Xu et al. (2007)]. Indeed, by time-transforming the equations of motion for a viscoelastic fluid, the Stokes equations are obtained with the time-transformed complex viscosity in place of the Newtonian solvent viscosity. By similarly transforming the boundary conditions, the flow solution for a Newtonian and a viscoelastic liquid is identical.

From the experimental side, in a recent paper by Pasquino et al. (2008), the bulk rheology of a Newtonian and two viscoelastic noncolloidal suspensions is studied in the dilute and semidilute regime. In both continuous shear and linear oscillatory flows (the latter limited to frequencies in the terminal region), the viscoelasticity of the suspending liquid is found to enhance the bulk viscosity as well as the loss modulus \( G'' \) when comparing with the Newtonian suspension. It is remarkable that the experimental results from Pasquino et al. (2008) for linear oscillatory flows disagree with the correspondence principle mentioned above.
Similar discrepancies between theory and experiments are also found for concentrated viscoelastic suspensions. Limiting to linear viscoelasticity, Haleem and Nott (2009) have recently performed measurements of storage $G'$ and loss moduli $G''$ up to $\phi = 0.40$. In their paper, a comparison with previous works [Chan and Powell (1984); Polinski et al. (1988); Aral and Kaylon (1997)] is also performed. Although all investigators conclude that both moduli increase by adding particles, the amount of such increases as reported in those papers is drastically different (deviations of 2 orders of magnitude for the most concentrated suspensions). A further difference concerns the comparison between the relative loss and the storage moduli, $G''_n$ and $G'_n$ (defined as the suspension moduli divided by the moduli measured for the unfilled fluid, $G'_0$ and $G''_0$): At a fixed solid volume fraction, Chan and Powell (1984) report similar values, Haleem and Nott (2009) and Polinski et al. (1988) found different values but in the same order of magnitude, whereas in Aral and Kaylon (1997) the storage modulus is 1 order of magnitude greater than the loss modulus.

We remark that all the cited works refer to noncolloidal suspensions where inertia can be neglected. We would like, however, to also mention here the work of Le Meins et al. (2002). Although mainly focused on colloidal suspensions, one set of measurements is reported for particles with dimensions larger than 1 $\mu$m (Brownian forces can then be neglected). The authors found (within experimental error) identical relative loss and storage moduli up to $\phi = 0.30$.

From a theoretical point of view, Palierne (1990) exactly calculated the first order coefficients $a'$ and $a''$ in the following expansions for viscoelastic suspending liquids

$$G'_n = G'/G'_0 = 1 + a'\phi + b'\phi^2 + \cdots,$$

(1)

$$G''_n = G''/G''_0 = 1 + a''\phi + b''\phi^2 + \cdots,$$

(2)

He found that $a' = a'' = 2.5$ (i.e., as for the Newtonian prediction for $a''$). However, no exact analytic calculations have ever been performed for the coefficients $b'$ and $b''$, and only empirical models have been proposed [Graebling et al. (1993); Pal (2002)].

Numerical predictions of $G'$ and $G''$ are presented in Schaink et al. (2000). Starting from the correspondence principle, the authors extend the Stokesian dynamics simulation method [Brady and Bossis (1988)] to take into account the viscoelasticity of the suspending fluid. Their method is only valid for small Deborah numbers (i.e., slow flows). The analysis is carried out for an oscillating linear viscoelastic regime. Neglecting the Brownian contribution, the relative viscoelastic moduli are found to be the same and equal to the Newtonian loss modulus, at any frequency and volume fraction.

Several works on the rheological characterization of complex fluids deal with large amplitude oscillatory shear (LAOS) in order to generate and to describe the nonlinear behavior of the material [see Hyun et al. (2011) for a comprehensive review], as well as a tool to classify complex fluids [Hyun et al. (2002)] and obtain constitutive equation model parameters [Gurnon and Wagner (2012)]. Regarding solid viscoelastic suspensions subjected to LAOS regime, a number of experimental works have been carried out, mainly focused on colloidal particles [e.g., Kallus et al. (2001); Cracium et al. (2003); Osman and Atallah (2006)]. Noncolloidal suspensions with spherical particles have been studied by Aral and Kaylon (1997). Large strain amplitudes reduce the viscoelastic moduli as compared to the linear viscoelastic values. Furthermore, the addition of solid particles limits the linear region to smaller strain amplitudes and the moduli reduction is more pronounced as compared to the matrix. We are unaware of any numerical prediction on this problem.
In this work, we study by three-dimensional (3D) direct numerical simulations the linear and nonlinear response of a noncolloidal hard-sphere viscoelastic suspension in oscillatory shear. The Giesekus model is chosen as constitutive equation as it has been proven to realistically describe the behavior of non-Newtonian fluids under LAOS [Nam et al. (2008); Hyun et al. (2011); Gurnon and Wagner (2012)]. To deal with a many-particle system, the sliding triperiodic domain method is implemented [Hwang et al. (2004c)]: The computational domain is periodically replicated along the flow and vorticity directions whereas Lees–Edwards boundary conditions are imposed along the gradient direction. This allows to use a sufficiently small computational domain that is representative of the whole suspension. A fictitious domain is implemented in order to manage the particle motion and the governing equations are solved by the finite element method. As a consequence, the hydrodynamic interactions are not modeled but computed. Thus, the fluid–particle interactions are exact (i.e., they do not come from any multibody theory as the resistance matrices in the Stokesian dynamics). Furthermore, in our formulation, the flow fields are part of the solution and are known in the whole fluid domain. The bulk properties are, then, recovered from local stresses by an averaging procedure [Batchelor (1970)].

The response of the suspension to a small amplitude oscillatory shear (SAOS) is first addressed. The code is validated by comparing our results with the available theories and simulations for noncolloidal Newtonian and non-Newtonian suspensions. Furthermore, we investigate the effect of the microstructure on the suspension bulk rheology to elucidate and rationalize the conflicting results between experiments and theory/simulations concerning the independence of the relative moduli from the rheology of the suspending medium.

The analysis is then extended to the LAOS. The bulk shear stress and the resulting viscoelastic moduli are computed for increasing values of the strain amplitude and for different volume fractions and forcing frequencies. The nonlinear response of the suspension is evidenced by Fourier-transform analysis [Neidhöfer and Wilhelm (2003); Kallus et al. (2001); Klein et al. (2007); Hyun et al. (2011)]. Finally, the influence of the suspending fluid viscoelasticity on the particle microstructure is discussed and the potentialities and limitations of the proposed numerical method are summarized.

II. GOVERNING EQUATIONS

We consider $N$ solid spherical particles with diameter $D_0$ suspended in a Newtonian or a viscoelastic fluid. We denote the particle domain by $P(t)$ and the whole domain (fluid + solid) by $\Omega$. Under the assumptions of negligible particle and fluid inertia, buoyancy-free and isothermal conditions, the fluid domain is governed by the following continuity (mass balance) and momentum balance equations:

\begin{align}
\nabla \cdot \mathbf{u} & = 0 \quad \text{in } \Omega \setminus P(t), \\
\nabla \cdot \sigma & = 0 \quad \text{in } \Omega \setminus P(t),
\end{align}

where $\mathbf{u}$ and $\sigma$ are the velocity and the stress tensor, respectively. The latter is given by

\begin{equation}
\sigma = -p\mathbf{I} + 2\eta_s\mathbf{D} + \tau \quad \text{in } \Omega \setminus P(t),
\end{equation}

where $p$, $\mathbf{I}$, $\mathbf{D}$, $\eta_s$, and $\tau$ are the pressure, the $3 \times 3$ unity tensor, the rate-of-deformation tensor, a Newtonian contribution to the viscosity, and the non-Newtonian stress, respectively.
For a Newtonian fluid, $\tau = 0$ and the Eqs. (3)-(5) completely describe the fluid behavior. When a viscoelastic fluid is considered, we need a constitutive equation for $\tau$. Here, we consider the Giesekus model [Larson (1988)]

$$\lambda \nabla \cdot \tau + \frac{\lambda}{\eta_p} \tau \cdot \tau + \tau = 2\eta_p \dot{D} \quad \text{in } \Omega \setminus P(t),$$

$$\nabla \cdot \tau \equiv \frac{\partial \tau}{\partial t} + \mathbf{u} \cdot \nabla \tau - (\nabla \mathbf{u})^T \cdot \tau - \tau \cdot \nabla \mathbf{u}.$$  

(6)

In Eq. (6), $\eta_p$ is the non-Newtonian viscosity, $\lambda$ is the relaxation time, and $\alpha$ is the so-called “mobility” parameter.

The fluid boundary conditions on the particle surfaces, denoted by $\partial P(t) = \sum_i \partial P_i(t)$, are the rigid-body motion

$$\mathbf{u} = \mathbf{U}_i + \omega_i \times (\mathbf{x} - \mathbf{X}_i) \quad \text{on } \partial P_i(t) \quad (i = 1, \ldots, N),$$

(8)

where $\mathbf{U}_i$ and $\omega_i$ are the translational and the angular velocity, respectively, of the $i$th particle with its center at $\mathbf{X}_i$.

In this work, we investigate the bulk response of the suspension undergoing an external oscillatory shear. Assuming a Cartesian reference frame with origin at the center of the suspension, this regime is achieved by enclosing the suspension between two walls at $\pm L_w/2$ and moving them with the following time-dependent, sinusoidal velocity:

$$u_{xy}(t) = \pm \frac{L_w}{2} \gamma_0 \sin(\omega t) = \pm \frac{L_w}{2} \dot{\gamma}_0 \sin(\omega t)$$

(9)

with $x$ the flow direction, $y$ the gradient direction, and $z$ the vorticity direction. In Eq. (9), $\dot{\gamma}_0$ is the strain amplitude, $\omega$ is the frequency, and $\gamma_0$ is the amplitude of the imposed shear rate.

The boundary condition in Eq. (9) should be applied on the boundaries of the computational domain: This will be discussed in Sec. III. As initial condition for $\tau$, we consider a stress-free state, i.e., $\tau|_{t=0} = 0$, over the whole domain.

Finally, due to the assumptions of absence of inertia, and that there are no external forces and torques (force- and torque-free particles), the particle dynamics is ruled by

$$\int_{\partial P_i(t)} \mathbf{n} \cdot \mathbf{dA} = 0,$$

(10)

$$\int_{\partial P_i(t)} (\mathbf{x} - \mathbf{X}_i) \times (\mathbf{d} \cdot \mathbf{n}) \mathbf{dA} = 0,$$

(11)

where $\mathbf{n}$ is the outwardly directed unit normal vector on $\partial P_i$.

Following Hwang et al. (2004a, 2004b) and D’Avino et al. (2007, 2008), we use the “rigid-ring” description (actually, “rigid-shell,” in 3D) for the particle domain. The particle is described as a rigid-shell filled with the same fluid as in the fluid domain, and the rigid-body motion is imposed on the particle boundary. Equations (3)-(7) hold in the particle domain as well, always with boundary conditions in Eq. (8).

After the velocity, the pressure and the stress fields are calculated, together with the translational and angular velocities for each particle, the particle motion is updated through the following kinematic equations:
\[
\frac{dX_i}{dt} = U_i, \quad X_i|_{t=0} = X_{i,0}, \quad (12)
\]

\[
\frac{d\Theta_i}{dt} = \omega_i, \quad \Theta_i|_{t=0} = \Theta_{i,0}. \quad (13)
\]

In Eq. (13), \( \Theta \) is the angular rotation of the particle \( i \).

Finally, for the bulk stress calculation, we use the Batchelor’s formula [Batchelor (1970)]

\[
\langle \sigma \rangle = \frac{1}{V} \int_{V_i} \sigma \, dV + \frac{1}{V} \int_{\partial P} \sigma \cdot n \, dA, \quad (14)
\]

where \( \langle \cdot \rangle \) indicates an average quantity in a dimensionless volume \( V \), and \( V_i \) is the dimensionless volume occupied by the fluid among the particles.

Once the bulk stress tensor is calculated, we can derive the storage and loss moduli, \( G' \) and \( G'' \) from the \( xy \)-component of \( \sigma \)

\[
\sigma_{xy}(t) = -\gamma_0 G' \cos(\omega t) + \gamma_0 G'' \sin(\omega t). \quad (15)
\]

As also remarked in Franck and Novak (2008) and Hyun et al. (2011), such a definition of the moduli is unique only in small amplitude oscillatory regime, whereas different methods (giving different results) can be used to derive the moduli in LAOS. Details about the procedure adopted in this work will be given in Sec. IV B.

III. NUMERICAL METHOD

In this work, we use the sliding triperiodic scheme introduced by Hwang et al. (2004c). The details of the method in two dimensions (2D) (sliding biperiodic) can be found in Hwang et al. (2004a, 2004b) for the Newtonian and viscoelastic cases, respectively. In this section, we only give a brief outline of the method highlighting the main differences.

When dealing with solid concentrated systems, particle–particle interactions play a crucial role. In order to predict realistic bulk properties, one should take into account a large number of particles. On the other hand, the simulation domain is desired as small as possible to reduce the computational effort, especially in 3D.

A method to achieve this has been developed for a shear flow by Hwang et al. (2004a) where Lees–Edwards boundary conditions are implemented in a finite element code. The main concept is to consider a domain that is periodic in all the directions. To take into account the shear flow conditions, the periodic images of the computational frame along the gradient direction slide along the flow direction. The frame sliding velocity is, of course, dependent on the shear rate.

A scheme of the triperiodic domain is reported in Fig. 1(a). For sake of clarity, the particles in the frames adjacent with the reference one are removed and only the periodic frames along the \( x \)- and \( y \)-direction are reported (along the vorticity, the nine frames depicted in the figure are just periodically repeated). Notice that the upper row slides along the flow direction with a distance, at time \( t \), related to the shear rate and the domain height. The lower row covers the same distance but in the opposite direction. The reference frame is, then, a part of an infinite suspension.

In Fig. 1(b), the computational domain (corresponding to the reference frame) is depicted. We denote with \( L, H, \) and \( W \) the length of the domain along the \( x \)-, \( y \)-, and \( z \)-axis,
respectively. The origin of a Cartesian reference frame is selected as in the figure. Notice that the particles crossing the boundaries are split along the domain boundaries and the parts outside the domain are relocated according to the periodicity. For particles crossing the sliding boundaries $\Gamma_1$ and $\Gamma_6$, the relative motion of upper and lower rows of frames is taken into account in calculating the effective particle position on opposite sides.

In such a scheme, the fluid boundary conditions over the periodic domain surfaces $\Gamma_2 - \Gamma_4$ and $\Gamma_3 - \Gamma_5$ can be written as

$$u(0, y, z) = u(L, y, z), \quad y \in [0, H], \quad z \in [0, W], \quad (16)$$

$$\sigma(0, y, z) = \sigma(L, y, z), \quad y \in [0, H], \quad z \in [0, W], \quad (17)$$

$$u(x, y, 0) = u(x, y, W), \quad x \in [0, L], \quad y \in [0, H], \quad (18)$$

**FIG. 1.** Schematization of the sliding tri-periodic method (a) and the computational domain used in the simulations (b). For sake of clarity, in (a), only the periodic frames along the x- and y-direction are represented and the particles within these frames are removed.
\[
\sigma(x, y, 0) = \sigma(x, y, W), \quad x \in [0, L], \ y \in [0, H].
\] (19)

For the sliding periodic boundaries \( \Gamma_1 \) and \( \Gamma_6 \), we need to take into account the time-dependent coupling

\[
\mathbf{u}(x, 0, z; t) = \mathbf{u}(\{x - \Delta x\}^c, 0, z; t) + (\nabla u_{xy}^H, 0, 0), \quad x \in [0, L], \ z \in [0, W],
\] (20)

\[
\sigma(x, 0, z; t) = \sigma(\{x - \Delta x\}^c, 0, z; t), \quad x \in [0, L], \ z \in [0, W],
\] (21)

where \( \nabla u_{xy} \) is the gradient of the imposed velocity field, Eq. (9), \( \Delta x \) is the shift of the sliding frames [see Fig. 1(a)], and \( \{\cdot\}^c \) is the modular function of \( L \). The shift \( \Delta x \) can be calculated by integrating the frame velocity \( \nabla u_{xy}^H \) between \( t = 0 \) and a generic instant \( t \) and is given by \( \Delta x = \gamma_0 H (1 - \cos(\omega t)) \). Notice that, the velocities on the sliding boundaries take into account the relative motion of the upper and lower frame through the quantity \( \nabla u_{xy}^H \) (i.e., the relative velocity between the two frames). Equations (16)--(21) assure the continuity of the velocity and stress fields across the opposite boundaries [see Hwang et al. (2004b)] for further details.

A way to impose the periodic conditions above is to link the velocities on the opposite sides through constraints implemented by Lagrange multipliers [Hwang et al. (2004a)]. In the original work of Hwang et al. (2004a), the coupling of the sliding periodicity is implemented by splitting the boundary integral term into two subintegrals based on the lower (nonconforming and time-dependent) facing elements. A linear, exact integration is then performed. In our formulation, constraints are still used to couple the vertical velocities but the sliding periodicity is imposed by moving the integration points in the boundary elements. To perform an accurate integration, a sufficient number of subintervals in the sliding boundary elements should be chosen [see D’Avino and Hulsen (2010)] for further details on the implementation of the integral constraints.

In the implementation, the stress tensor is transformed in the conformation tensor that, for the Giesekus model, is linearly related: \( \tau = \eta_p / \lambda (\mathbf{c} - I) \). A further difference from the original formulation for a viscoelastic fluid is the coupling of the conformation tensor. Hwang et al. (2004b, 2004c) used a discontinuous Galerkin (DG) discretization of the constitutive equation: The periodicity of the conformation tensor is automatically satisfied. In this work, we introduce Lagrange multipliers to perform the coupling for \( \mathbf{c} \) as done for the velocity field. This allows us to use the streamline-upwind-Petrov–Galerkin (SUPG) technique for discretizing the constitutive equation (that is easier to implement in 3D).

The governing equations are solved by the finite element method. A fictitious domain method [Glowinski et al. (1999)] is used where the fluid and solid domains are embedded into a single weak form. The balance of forces and torques at fluid–particle boundaries is satisfied, but the forces and torques do not explicitly end up in the variational form. To release the constraint on the variational space, the rigid-body motion on the particle surfaces is imposed through Lagrange multipliers. In this regard, a weak implementation is used instead of collocation as in Hwang et al. (2004a, 2004b, 2004c), that is shown to give higher accuracies and better conditioned linear systems [D’Avino and Hulsen (2010)]. In conclusion, such a scheme allows to use a fixed, time-independent, regular mesh for both fluid and solid. The particle motion is easily handled by moving the particle surfaces.

Concerning the viscoelastic case, a DEVSS-G/SUPG [Brooks and Hughes (1982); Guenette and Fortin (1995); Bogaers et al. (2002)] formulation is implemented with a log-conformation representation [Fattal and Kupferman (2004); Hulsen et al. (2005)] to...
improve the numerical stability. A weak formulation of the problem can be found in D’Avino et al. (2007, 2008) for the 2D Newtonian and viscoelastic case, respectively. The extension in 3D is straightforward.

For the discretization of the weak form, we use regular hexahedral elements with continuous biquadratic interpolation ($Q_2$) for the velocity, bilinear continuous interpolation ($Q_1$) for the pressure, bilinear continuous interpolation ($Q_1$) for the velocity gradient (coming from the DEVSS-G scheme), and bilinear continuous interpolation ($Q_1$) for the log-conformation tensor.

The momentum and continuity equations are decoupled from the constitutive equation. For the latter, a second-order time Adams–Bashforth integration scheme is used. Finally, a GMRES iterative solver with an ILUT preconditioner [Saad (2001)] is used to solve the linear system coming from the spatial discretization of the momentum and continuity equations. A direct method based on a sparse multifrontal variant of Gaussian elimination (HSL/MA41) is adopted for the unsymmetric system derived from the constitutive equation discretization.

A final note concerns the bulk stress calculations. As discussed in Sec. II, the Batchelor’s formula is adopted, consisting in a fluid and solid contribution. Following D’Avino et al. (2007, 2008), the total bulk stress is calculated as

$$\langle \sigma \rangle = \frac{1}{V} \int_V \hat{\sigma} \, dV + \frac{1}{V} \sum_{i=1}^{N_p} \int_{\partial V_i} \lambda(x) \, x \, dS,$$

(22)

where $\hat{\sigma}$ is the stress tensor over the domain (including the interior of the particles) and $\lambda(x)$ are the Lagrange multipliers on the particle surface. It should be remarked that the two terms in the RHS of Eq. (22) do not correspond to the fluid and solid contributions in Eq. (14). The two contributions can be recovered by subtracting and adding the stress inside the particles to the two terms in Eq. (22), respectively [D’Avino et al. (2007, 2008)].

Equation (22) holds for no boundary-crossing particles. For particles crossing the boundaries, the second term of the RHS should be modified by accounting for the particle split [Hwang et al. (2004a, 2004b)], i.e., by replacing the particle contribution of the relocated coordinate $x'$ by that of the original coordinate $x$

$$\langle \sigma \rangle = \frac{1}{V} \int_V \hat{\sigma} \, dV + \frac{1}{V} \sum_{i=1}^{N_p} \int_{\partial V_i} \lambda(x') \, (x - x') \, dS.$$

(23)

The code is validated through a comparison with the results of Hwang et al. (2004a, 2004b) for both Newtonian and viscoelastic systems. To make a quantitative comparison, we used a 2D version of our code in simple shear flow. The same mesh resolution and time step size is considered. Our calculations for single-particle, two-particle, and six-particle systems coincide with those in Hwang et al. (2004a, 2004b), in terms of particle rotation, particle trajectories, and bulk stresses. In the six-particle systems, a slight deviation is found in the long-time behavior, likely due to the different way to discretize the particle boundaries and the use of an alternative stabilization technique for the constitutive equation (SUPG versus DG). This leads to small differences in the hydrodynamic interactions and, consequently, in the motion of the particles.

Care must be taken in choosing the proper geometrical parameters $L$, $H$, and $W$ of the simulation cell. The domain size should be chosen small enough in order to make the computation feasible but, at the same time, any artificial periodicity through the opposite
boundaries should be avoided. To properly choose the domain size, we perform preliminary tests by comparing the results for several values of the geometrical parameters of the simulation cell. We found that, for \( W \geq 2D_p \), the bulk response is independent on further enlargement of the box width \( W \). Therefore, unless differently specified, we set \( W = 2D_p \). Regarding the domain length and height, we similarly verified that \( L = H = 6D_p \) is sufficient to avoid any significant interaction among a particle and its images. Therefore, at least for the kind of flow considered in this work, it seems that the interparticle interactions along the vorticity direction have less influence as compared to the flow and gradient directions. The domain length \( L \) is chosen as characteristic length and we set \( H/L = 1, W/L = 0.334, \) and \( D_p/L = 0.167 \).

A final note concerns the initial particle configuration. Of course, the stresses are dependent on the relative positions of the particles. To reduce the influence of the particle positions, each simulation is repeated by varying the initial particle distribution that is chosen in a random way (unless differently specified). The particle centers are first generated by randomly locating the spheres in the box. If particle overlapping occurs, the positions of the particle centers are discarded and new random positions are generated. For each set of parameters, we perform 15 realizations for SAOS regime and five realizations for LAOS regime (the latter is limited by the computational effort, as discussed later). As confirmed by the error bars reported in the figures below, such numbers of realizations give a sufficiently accurate description of the average bulk response of the suspension.

IV. RESULTS

A. Small amplitude oscillatory shear

In this section, the bulk response of a hard-sphere (Newtonian and viscoelastic) suspension under SAOS regime is presented. The purpose of this section is twofold. As discussed in the Introduction, the correspondence principle provides a theoretical basis to compare the bulk response of Newtonian and viscoelastic suspensions. Furthermore, the linear viscoelasticity of viscoelastic suspensions has also been studied by simulations through a different numerical method [Schaink et al. (2000)]. Therefore, we exploit those results to test and validate our numerical method. In addition, we use our code to propose an explanation for the conflicting experimental results discussed above.

All the simulations are carried out by setting \( k = 1 \), \( g_s = g_p = 0 \), and \( a = 0.2 \). The condition of small amplitude oscillatory regime implies the linearity between the strain amplitude \( \gamma_0 \) and the stress response. This is achieved by selecting a sufficiently small \( \gamma_0 \). We verified that, for \( \gamma_0 = 5 \cdot 10^{-3} \), the system is in the small amplitude oscillatory regime (i.e., the moduli do not change by further decreasing \( \gamma_0 \)). Concerning the mobility parameter \( a \), we point out that, in linear viscoelastic regime, its value does not affect the system response. Indeed, it can be shown that, in such a regime, any viscoelastic differential constitutive equation (with a Newtonian solvent) reduces to the Jeffreys model \((a = 0)\).

The presence of a “Newtonian solvent” \((\eta_s \neq 0)\) affects the loss and storage moduli in the high-frequency region. In Fig. 2(a), we report \( G' \) and \( G'' \) of the unfilled fluid as function of \( \omega \) for different ratio \( \eta_s/\eta_p \). Notice that, without Newtonian solvent (the constitutive equations reduce to the upper convected Maxwell model), \( G'' \) increases for low frequencies and decreases for high frequencies, achieving a maximum at \( \omega = \lambda = 1 \) where the crossover with \( G' \) occurs. On the other hand, the Newtonian solvent alters the trend in the high-frequency range, with \( G'' \) continuing to increase with the frequency.
In this section, we refer to normalized viscoelastic moduli defined as

\[ G_n^0 = \frac{G_0}{G_0^0}, \quad G_n'' = \frac{G''}{G_0^0}, \]  

(24)

where \( G_0^0 \) and \( G_0'' \) are the moduli of the unfilled fluid. Notice that, even for the viscoelastic case, in \( G_0'' \) is included a Newtonian contribution [see Eq. (5)] given by \( \eta_0 \omega_0 \).

We first perform simulations by considering a Newtonian suspending liquid. In Fig. 3, the relative loss modulus \( G_n'' \) calculated by simulations (black circles) is reported for volume fractions in the dilute and semidilute regimes (\( \phi \leq 0.1 \)). The experimental data from Pasquino et al. (2008) are reported as black squares. The Einstein’s prediction [Einstein (1911)] (valid for \( \phi < 0.05 \)) and the equation \( G_n'' = 1 + 2.5\phi + 6.99\phi^2 \) calculated in Pasquino et al. (2008) by fitting the experimental data are reported as well.

**FIG. 2.** (a) Storage (dashed line) and loss (solid lines) moduli as a function of the frequency in small amplitude oscillatory regime for the Oldroyd-B model (\( \lambda = 1 \)) with different viscosity ratios. (b1) and (b2) Dimensionless shear stress as a function of the dimensionless time for a Giesekus model with different strain amplitudes: \( \gamma_0 = 0.005 \) (white circles), \( \gamma_0 = 1 \) (dashed line), \( \gamma_0 = 3 \) (dotted line), \( \gamma_0 = 5 \) (solid line). The fluid parameters are: \( \lambda = 1, \ \alpha = 0.2, \ \eta_i/\eta_0 = 0.1 \). The frequency is set to \( \omega = 0.2 \) (b1) and \( \omega = 2 \) (b2).
Notice that the latter equation is expected to be valid up to the semidilute regime ($\phi < 0.1$). For same volume fraction values, the error bars for both experimental and numerical data are also reported. Our simulations and the experiments quantitatively agree quite well. In particular, by fitting the simulation data with the quadratic function $G''_g = 1 + 2.5\phi + 6.99\phi^2$ we found $b = 7.45$ that is close to the coefficient $b = 6.99$. The small discrepancy between the two coefficients is likely due to a finite number of initial random particle configurations and numerical error related to the particle surface discretization [see D’Avino and Hulsen (2010)]. Nevertheless, the agreement can be considered satisfactory.

In Fig. 4, the normalized loss modulus $G''_n$ is reported for different volume fractions when a viscoelastic suspending fluid is considered. The frequency is chosen as $\omega = 0.2$ that is the upper limit for the terminal regime (higher frequencies will be explored below). The black circles are the simulation results for a Newtonian fluid (i.e., the black circles in Fig. 3) whereas the white circles refer to the viscoelastic case. The white squares in the inset are experimental data from Pasquino et al. (2008) for a polydimethylsiloxane (PDMS) as suspending fluid. The solid line is the quadratic equation $G''_n = 1 + 2.5\phi + 6.99\phi^2$ and the dashed line is the second-order fluid analytical prediction (valid in the dilute regime) that coincides with the Einstein’s result [Greco et al. (2005)]. Finally, the dashed-dotted line is the polynomial function calculated in Schaink et al. (2000) by a completely different numerical approach (i.e., an extension of the Stokesian dynamics). Concerning the comparison between the Newtonian and the viscoelastic simulation data, in order to remove any influence due to the initial particle configuration, for the viscoelastic case we choose the same random positions as for the Newtonian fluid (i.e., the same 15 random initial conditions).

From Fig. 4 it is evident that, for any volume fraction, the simulations predict a viscoelastic $G''_n$ coinciding with the Newtonian one. This result agrees with the above mentioned correspondence principle. In addition, the trend of $G''_n$ is also in excellent quantitative agreement with the results of Schaink et al. (2000) (within the numerical error). Concerning the storage modulus, our simulation results (not reported) show that
$G'_0$ is essentially the same as $G''_0$ (in terms of relative values). The latter again agrees with the prediction of Schaink et al. (2000). However, it has to be remarked that, for the frequency considered in Fig. 4, the storage modulus is quite lower than the loss modulus and, as a consequence, the numerical error, of course, affects the results. Nevertheless, the maximum deviation is found to be lower than 4% that confirms the good accuracy of the proposed method. In conclusion, the fair comparison with previous results validates our numerical method.

Moving now to the comparison with the experimental data of Pasquino et al. (2008) reported in the inset of Fig. 4, a discrepancy is found (the experimental estimated quadratic coefficient is $b \approx 14$). We remark that the difference between simulations and experiments observed in the inset of Fig. 4 is well beyond the numerical and experimental error as clearly visible by looking at the error bars.

A possible explanation for the larger loss modulus measured in Pasquino et al. (2008) could be the formation of solid-like, ordered structures in the preparation of the sample before linear viscoelasticity experiments actually take place. This possibility was, in fact, already pointed out by Hallem and Nott (2009). If some ordering of particles were present in the samples, it might influence the loss modulus, and alter it with respect to the “isotropic” loss modulus calculated above.

To check numerically the influence of possible structures on the loss modulus, we locate nine particles ($\phi = 0.066$) to form specific spatial initial configurations, as reported in the panels in Fig. 5. For each configuration, the particle centers are aligned on the $xy$-midplane of the cell (i.e., the parallel plane to the $xy$-plane at $z = W/2$). In the first structure, the particles are positioned on the vertices, the midside nodes and the center of a square at a center-to-center distance $1.7D_p/L$ [Fig. 5(a)]. In the second configuration, the particles are regularly located along the two diagonals of the cell at a center-to-center distance $1.7D_p/L$ [Fig. 5(b)]. The latter two configurations are similar to the second one but the particle–particle distance along the diagonals is progressively reduced to $1.27D_p/L$ and $1.18D_p/L$ [Figs. 5(c) and 5(d)]. In the four panels, the grey scale represent the intensity of the local $xy$-component of the total stress on the $xy$-midplane at the instant
FIG. 5. Plot—Relative loss modulus as a function of the volume fraction: Linear Einstein’s solution [Einstein (1911)] (dashed line), quadratic function $G''_0 = 1 + 2.5\phi + 6.99\phi^2$ calculated in Pasquino et al. (2008) by fitting the Newtonian experimental data (solid line), viscoelastic experiments from Pasquino et al. (2008) (white squares), our viscoelastic simulations (white circles), our simulation results for a nine-particle problem positioned as reported in the panels (white diamonds), our simulation results for a five-particle problem positioned along the diagonal of the box at different interparticle distances (grey triangles), our simulation results for a system consisting of three clusters of particles, as indicated in panels (e2) and (e3). Panels—Shear stresses on the xy-midplane for four different nine-particle configurations: (a) Particles located on the vertices and the midside points of a square, (b) particles equidistantly located along the diagonals of the xy-midplane, (c) and (d) as in the configuration (b) with closer particle–particle distance; (e1) random configuration of 27 particles in a cubic domain; (e2) and (e3) two configurations of three clusters of nine particles in a cubic domain.
corresponding to the maximum overall shear stress value (around \( t = 8.5 \)). The same scale is used in all figures (black and white are the highest and lowest stress, respectively). When the particles are aligned horizontally and vertically [Fig. 5(a)], the interparticle \( xy \)-stresses are weak. (Stresses stay weak even when interparticle distances are reduced, not reported here.) Therefore, a low overall loss modulus is expected, as confirmed in the plot in Fig. 5, where the corresponding point is the white diamond labeled with \( a \). On the other hand, rather large local shear stresses develop for the configurations depicted in Figs. 5(b)–5(d): In particular, the highest stresses (black zones) develop along the diagonal directions. The corresponding \( G''_n \) points are the white diamonds labeled as \( b \), \( c \), and \( d \) in the main figure. Notice that the on-diagonal stresses (and, consequently, the overall \( G''_n \)) are clearly higher as the particles are closer. The configuration \( d \) gives a loss modulus well above the “random configuration” value (white circles), and even larger than in the measurements of Pasquino et al. (2008).

Finally, we checked the effect of particle volume fraction. The grey triangles in Fig. 5 refer to five particles positioned along the diagonals (\( \phi = 0.0365 \)). As before, we changed the interparticle distance. The lower triangle is obtained for the largest distance that is progressively reduced giving a slight increase in \( G''_n \). It is noted, however, that the effect of the structure is much less significant, and the data only slightly deviate from the random configuration curve.

Although the configurations investigated above are useful to understand the directions of minimum and maximum shear stress (that is strictly related to the bulk moduli), they are idealizations of the real microstructure that one can expect in the bulk of the suspension. Real structures do not likely have preferred orientations and they have an interparticle spacing of zero (agglomerates of particles). To clarify the role of possible aggregates in the experimental measurements, we extended our analysis to clusters of particles. In order to make a direct comparison with the ordered structures discussed above, we consider the same volume fraction \( \phi = 0.066 \). Since our purpose is to investigate the effect of isolated clusters of particles on the bulk loss modulus, we need to increase the simulation box along the \( z \)-direction \( W \) (that has been previously set to \( W = L/3 = H/3 \)). Indeed, we have to avoid that a cluster is influenced by its image across the boundaries orthogonal to the \( z \)-axis. To this aim, only for the present simulations, we consider a cubic box \( W = L = H \). The volume fraction \( \phi = 0.066 \) is, then, obtained by simulating 27 particles. First, we perform simulations by considering initial random distributions, as the one depicted in the panel (e1) of Fig. 5. As expected, the average value of \( G''_n \) over 15 realizations (not shown) collapses on the solid line of Fig. 5 (the deviation is lower than 0.5%). (The latter also confirms that the use of a shorter domain along the \( z \)-direction gives the correct bulk rheology.) Configurations consisting of clusters of particles are, then, analyzed. We generate the agglomerates as follows: (i) Each cluster is formed by nine particles and it is generated by randomly positioning eight particles around one sphere at a very close distance (the interparticle distance computed from the spherical surfaces is set to \( D_p/20 \)); and (ii) the resulting three clusters are randomly positioned in the cubic box. Two examples of the configurations obtained by adopting such a procedure are shown in the panels (e2) and (e3) of Fig. 5. The computed average value of \( G''_n \) over 15 realizations is reported as a black circle in Fig. 5. It is clearly observed that a higher loss modulus is again found with respect to the random configurations.

In conclusion, our results show that ordered structures/agglomerates of particles strongly alter the isotropic loss modulus. The deviation direction from the values calculated from averages over random distributions depends on the specific configuration, since different interparticle shear stresses are generated by different configurations. It is worth emphasizing that particle structures affect both a Newtonian and a viscoelastic
suspension in the same quantitative way. However, whereas fluid viscoelasticity may readily induce the formation of structures [Michele et al. (1977); Scirocco et al. (2004); Pasquino et al. (2010)], this is not the case for an inertialess Newtonian fluid. Therefore, unless a structure is somehow forced (e.g., by using particles with attractive forces, by applying external fields, etc.), measurements in the linear viscoelastic regime of Newtonian suspensions reasonably refer to isotropic configurations. On the contrary, this could not hold for viscoelastic fluids, and one should carefully check that, in the initial configuration, structures are absent.

The effect of particle structures has also been recently investigated by Rexha and Minale (2011) for a continuous shear flow of Newtonian suspensions. Their simulations pointed out that a nonrandom initial configuration affects the start-up, although the bulk overall viscosity is unaffected, due to the laminar mixing process occurring during the shear flow. We remark that, in the linear viscoelastic regime, no mixing is possible, and the structures (if any) remain basically unaltered during the simulation/experiment (only small oscillatory motion occurs). Thus, if ordered structures are formed before the oscillatory flow begins, their presence will unavoidably alter the calculated/measured moduli.

All the results presented above refer to a fixed forcing frequency $\omega = 0.2$. We repeated the calculations at higher $\omega$-values. For any volume fraction investigated (up to $\phi = 0.30$), and for $\omega = 0.5$ and $\omega = 1.0$, the predicted relative loss modulus is basically unchanged from the corresponding low-frequency value (the discrepancies are within the 2% for the highest volume fraction). The frequency-independence of the relative loss modulus was also reported in Schaink et al. (2000), and was clearly evidenced in the experiments of Le Meins et al. (2002) where, for a noncolloidal suspension, $G''_n$ is constant over four decades of frequency. Although not explicitly reported, in Aral and Kaylon (1997) the trends $G''(\omega)$ for different volume fractions are approximately parallel, hence giving again a frequency-independence in terms of relative loss modulus. It should be signaled, however, that such frequency-independence of the relative loss modulus is not observed in Chan and Powell (1984) and Poslinski et al. (1988), where a decreasing relative loss modulus is instead found as the frequency is increased (in the latter paper, this is true up to a limit frequency above which $G''_n$ becomes constant). An opposite trend is reported in Hallem and Nott (2009) where the measured relative loss modulus increases at high frequencies, up to $\phi = 0.30$.

A comparison between our simulation results and the experimental data available in the literature is reported in Fig. 6. The experimental data are taken from Hallem and Nott (2009) except for the black squares that are taken from the original paper of Le Meins et al. (2002). All data refer to a frequency $\omega = 1\text{s}^{-1}$. The simulation results are shown as a solid line which is the interpolation of the simulation data shown in Fig. 4. The numerical predictions are in good quantitative agreement with the experiments of Le Meins et al. (2002) and Poslinski et al. (1988) in the whole volume fraction range considered whereas with measurements of Aral and Kaylon (1997) up to $\phi = 0.20$. On the contrary, data from Chan and Powell (1984) are slightly below the simulation curve (although within the same order of magnitude) whereas Hallem and Nott (2009) report an increase of 1–2 orders of magnitudes, especially for concentrated systems. To comment on the much larger measured modulus, Hallem and Nott (2009) point out the crucial role played by the rheology of the matrix fluid in determining the particle microstructure, that is in line with our discussion on the effect of particle aggregation. In this regard, it has to be pointed out that Le Meins et al. (2002) explicitly underline in their paper the adoption of a preliminary procedure to obtain homogenous suspensions of spheres. Therefore, the fair quantitative agreement between their data and our numerical predictions is not surprising. All of this further corroborates our hypothesis that nonhomogeneous initial
particle distributions (e.g., due to the loading stage, interparticle forces, etc.) can perhaps be at the origin of the conflicting results in the experimental literature.

B. Large amplitude oscillatory shear

In this section, we extend the study to an LAOS. In this regime, nonlinear effects due to the suspending fluid elasticity arise and deviations from the Newtonian-like behavior stated in the correspondence principle are expected. The arising of a nonlinear stress response also makes the choice of the viscoelastic constitutive equation now relevant. The panels (b1) and (b2) of Fig. 2 show the dimensionless shear stress as function of time (normalized by the forcing period \( T = 2\pi/\omega \)) for the Giesekus model with \( \lambda = 1.0 \), \( \alpha = 0.2 \) and viscosity ratio \( \eta_s/\eta_p = 0.1 \), for different strain amplitudes. In the upper plot the frequency is \( \omega = 0.2 \) whereas, in the lower plot we set \( \omega = 2 \). It is readily observed that, beyond a critical strain amplitude depending on the forcing frequency, deviations from the sinusoidal trend occur. In what follows, we investigate the effect of spherical fillers on the suspension response under LAOS. The suspending matrix is modeled with the Giesekus equation by choosing the same constitutive parameters as above.

Figure 7 reports the dimensionless shear stress as a function of the dimensionless time \( t/T \) for a volume fraction of \( \phi = 0.12 \). The frequency is chosen as \( \omega = 0.2 \) and different forcing amplitudes \( \gamma_0 \) are considered. The lowest \( \gamma_0 \)-value \( (\gamma_0 = 0.005, \text{open circles}) \) corresponds to the linear viscoelastic regime discussed in Sec. IV A, as confirmed by the sinusoidal trend of the curve. As \( \gamma_0 \) increases, deviations from the linear viscoelasticity are observed and the shear stress shows the typical nonsinusoidal stress response of the LAOS regime. More specifically, the maxima and minima are (in absolute value) lower than the small amplitude case and the stress is tilted forward with respect to the sinusoidal waveform. Those trends qualitatively reflect the LAOS response of the matrix [see panel (b1) of Fig. 2].

From the shear stresses, the moduli \( G' \) and \( G'' \) can be computed. As already pointed out at the end of Sec. II, whereas for the linear viscoelasticity the definition of (and the relative procedure to calculate) the moduli is univocal and is given by Eq. (15), this is not the case for an LAOS regime [Franck and Novak (2008); Hyun et al. (2011)]. In this
work, we compute $G'$ and $G''$ by fitting the oscillatory stress curve through a single-harmonic sine wave regression. The resulting moduli, normalized by the corresponding values from the linear viscoelastic regime at the same volume fraction $G'_L$ and $G''_L$, are plotted in Fig. 8 as a function of the amplitude. The black circles are the data for the same volume fraction of Fig. 7 ($\phi = 0.12$), whereas the white circles correspond to

FIG. 7. Dimensionless shear stress as a function of the dimensionless time for different strain amplitudes. The volume fraction is $\phi = 0.12$ and the frequency is $\omega = 0.2$. The inset shows a closer view around the maximum shear stress.

FIG. 8. Relative storage (top) and loss moduli (bottom) as a function of the strain amplitude for different solid volume fractions. The frequency is $\omega = 0.2$. 
The moduli for the suspending liquid without particles are also reported (white-crossed circles). For $\gamma_0 < 0.05$, the linear viscoelastic behavior is obtained and the $G''$-values correspond to the data shown in Fig. 4. As the amplitude increases, the trends deviate from the linear viscoelastic values and both moduli decrease. It is interesting to note that, although the decreasing trend is observed for both moduli at any volume fraction considered, the amount of reduction is higher for more concentrated systems. For instance, from the linear viscoelastic value to $\gamma_0 = 2$, the normalized $G''$ decreases by 10% for the matrix whereas the reduction is about 17% for the suspension with $\phi = 0.12$. In addition, the deviation from the linear viscoelastic horizontal asymptote occurs for smaller amplitudes as the volume fraction is higher. Therefore, the presence of solid particles triggers the LAOS regime to lower amplitudes as compared to the unfilled fluid, and also leads to a more pronounced reduction of both moduli. Those trends qualitatively agree with the experimental observations of Aral and Kaylon (1997).

To highlight the appearance of higher-order harmonics in the LAOS response of a hard-sphere suspension, we calculate the power spectrum by performing a Fourier-transform analysis. In Fig. 9(a), the complex modulus $|G^*|$ times the strain amplitude is plotted as function of the frequency for different strain amplitudes. Nonlinearities in the response are signaled by the appearance of a nonzero third harmonic, as shown in the inset of the figure. As expected, such a harmonic is more pronounced for higher strain amplitudes. Figure 9(b) shows the trend of the amplitude of the fundamental and of the third harmonics as a function of the strain. The limiting slope of the fundamental harmonic for vanishing strain indicates, of course, the linear viscoelastic limit, and is correctly captured by the simulations.

The data shown above refer to a frequency 1 order of magnitude lower than the fluid relaxation time. Calculations have been repeated by increasing the frequency to $\omega = 2$ that is well beyond the terminal regime. We directly report in Fig. 10 the normalized moduli as functions of the forcing amplitude, for the volume fractions considered in Fig. 8. For sake of the clarity, we do not report error bars that are of the same order of magnitude as in Fig. 8. From the upper plot, it is readily observed a trend qualitatively similar to the one found for $\omega = 0.2$, i.e., the addition of particles enhances the reduction of the normalized storage modulus. In contrast, a different behavior is found for the loss modulus (lower plot). By looking first at the trend for the unfilled matrix (crossed circles), the loss modulus shows an overshoot just beyond the linear viscoelastic limit and before the decreasing trend. As pointed out in Hyun et al. (2002) and Hyun et al. (2011), the presence of the overshoot is a typical scenario in complex fluids. Our simulations for $\phi = 0.06$ (white circles) correctly capture the overshoot. The global trend is, in agreement with the results for a lower frequency, the reduction of the normalized $G''$ as compared to the unfilled case. It is interesting to note that, by increasing the volume fraction (black circles), the loss modulus further decreases and the overshoot disappears, i.e., the addition of solid particles leads to a monotonically decreasing trend for increasing values of the strain amplitude.

A general remark on the results shown in this section is in order. The moduli as well as the higher-order frequencies have been derived from one cycle of the stress response (for instance, those given in Fig. 7). First of all, we note that the initial few cycles (the number depending on the forcing frequency) are affected by the initial transient stress development and, as such, need to be discarded for the computation of the moduli. However, it has to be pointed out that, even beyond the initial start-up, the stress response is not periodic but changes as the accumulated strain grows. Indeed, the large amplitudes combined with the viscoelasticity of the medium induce the formation of microstructures, as well documented for simple shear flows [Michele et al. (1977); Scirocco et al. (2004); Pasquino et al. (2010)], that, in turn, alter the bulk stress response.
To evaluate the influence of the structure formation, we report in Fig. 11 the projection on the shear plane of the trajectory of one particle \([\mathbf{x}_p, \mathbf{y}_p, \mathbf{z}_p] = (0.213, 0.834, 0.07)\) for 10 cycles and for four different amplitudes. It is readily observed that, for the smallest amplitude \(\gamma_0 = 0.005\) (that is the black spot near the white circle visible in the inset of the figure), the particle just weakly oscillates and, after 10 cycles, its position can be reasonably considered unchanged from the initial one. As discussed in Sec. IV A, in linear viscoelasticity the particles are “frozen” and the initial configuration (in absence of thermal motion or other external forces) remains unchanged during the whole experiment. On the other hand, as

**FIG. 9.** Complex modulus (times the strain amplitude) versus frequency for different strain amplitudes (a) and versus the strain amplitude for the first and third harmonic contributions (b). The volume fraction is \(\phi = 0.12\) and the forcing frequency is \(\omega = 0.2\).
the amplitude increases, more and more pronounced displacements from the starting position are observed. It is worthwhile to note that the origin of those displacements is fundamentally different from the diffusion-like behavior observed in concentrated Newtonian suspensions under oscillatory flows [Pine et al. (2005)]. In the latter case, as recently proven by Metzger and Butler (2010), the sources of such a phenomenon (leading to chaotic behavior and irreversibility) are the short-range repulsive forces that can arise, for instance, from particle rugosity [Ingber et al. (2006)]. In contrast, in our simulations, as we intentionally do not include short-range repulsive forces, the long-range hydrodynamic interactions mediated by the fluid elasticity induce the change of the microstructure. Irreversibility, in this case, is not surprising as, in contrast with the Stokes equation, viscoelastic constitutive models introduce nonlinearity. [Even for a two-particle shear flow problem, irreversibility of particle trajectories is found [Yoon et al. (2012)].]

To strengthen the argument above, we evaluate the mean-square displacement of the particles at the beginning of each cycle

\[
\text{MSD} = \frac{1}{N} \sum_{i=1}^{N} \Delta r_i \Delta r_i,
\]

where \(\Delta r_i = ||r_i - r_{i,0}||\) is the displacement of the \(i\)th particle computed at the beginning of each cycle with respect to the initial position. We report in Fig. 12 the MSD as a function of the number of cycles for different forcing amplitudes. It is found that the trends

![Relative storage (top) and loss moduli (bottom) as a function of the strain amplitude for different solid volume fractions. The frequency is \(\omega = 2\).](image)
can be fairly described by a quadratic function and, as such, a ballistic-like instead of a diffusion behavior is found. The nonlinear effects associated with hydrodynamic interactions mediated by viscoelasticity, in breaking reversibility, lead to a net drift, implying an $O(t^2)$ change in the mean-square displacement. We note that a superlinear MSD behavior

**FIG. 11.** Projection of the shear plane of the trajectory of the particle starting at $(x_p,0,y_p,0,z_p,0) = (0.213, 0.834, 0.07)$ (white circle) for 10 cycles and for different strain amplitudes: $\gamma_0 = 0.05$ (light grey solid line), $\gamma_0 = 0.3$ (dark grey solid line), $\gamma_0 = 1$ (black solid line). In the inset, a closer view around the starting point is shown. The black spot near the starting point visible in the inset is the trajectory corresponding to the linear viscoelastic case ($\gamma_0 = 0.005$).

**FIG. 12.** Mean-square displacement as a function of the number of cycles for different strain amplitudes.
was previously reported in the start-up of a nonlinear oscillatory shear flow of a suspension of spheres in a Newtonian fluid, and it was attributed to the “equilibration of the microstructure” [Corte et al. (2008); Metzger and Butler (2010)]. A loosely analogous orientational drift effect, hence irreversibility, also arises in nonlinear oscillatory shear for fibers in a non-Newtonian liquid [Harlen and Koch (1997)].

We can speculate that, during the formation of a well-defined microstructure triggered by fluid viscoelasticity and/or for sufficiently concentrated systems and large amplitudes, the particles come closer and short-range forces become relevant. Consequently, a diffusion-like behavior may appear and superimpose the observed one. Unfortunately, our numerical code cannot currently be utilized to explore the evolution from a random configuration to structure formation because of the huge computational times that drastically increase for large amplitudes and high volume fractions. For instance, for $\gamma_0 = 1$ and $\phi = 0.12$, the calculation of 10 cycles requires about 2 weeks of CPU time. Notice also that the absence of short-range repulsive forces limits the highest volume fraction and amplitude as well, as particle overlapping, resulting in simulation breaking down, would frequently occur. An artificial interparticle force can be, however, included in a quite straightforward way [Glowinski et al. (1999)]. Thus, the real limitation is the computational time that requires code optimization (e.g., parallelization).

In this perspective, the results presented above have to be interpreted as the rheological response that characterizes a hard-sphere viscoelastic suspension under LAOS regime for $N_{\text{bulk}}$ cycles where $N_{\text{bulk}}$ is the number of cycles such that changes in the microstructure weakly affect the bulk rheology. In this regard, it should be noted that, at least for the parameters considered in this work, the microstructure formation is a very slow process, as also reported in shear flow [Pasquino et al. (2010)]. This is clearly evidenced by evaluating the mean particle displacement at the beginning of each cycle $\sum_{i=1}^{N} \Delta r_i / N$: After 10 cycles, for $\gamma_0 = 1$, the particles have moved, on the average, by less than 15% of their radius. The slow effect of the particle motion on the bulk rheology is also proven by comparing the moduli evaluated from the shear stress at different cycles. We found that, for $\gamma_0 = 1$, both moduli show deviations lower than 0.2% over 10 cycles.

In conclusion, the data shown in this section are representative of the bulk rheology for a relatively large time window, as compared to the relaxation time of the matrix. The investigation on the evolution of the microstructure, the effect on the bulk rheology, and the extension to concentrated systems require code optimization. This aspect will be addressed in the future.

V. CONCLUSIONS

In this work, we investigated the rheological response of a viscoelastic suspension of spheres subjected to SAOS and LAOS by 3D direct numerical simulations. To account for a large number of particles and, at the same time, to reach a manageable computational effort, a sliding triperiodic domain is implemented. The particle motions are handled by a fictitious domain method where the particles are, in fact, treated as rigid-shells. Bulk properties of the overall suspension are recovered by averaging the computed local stress field.

In order to validate the numerical method, the study is first focused on the linear viscoelastic regime. The results for the Newtonian suspending liquid quantitatively agree with recent experimental data. Furthermore, the relative loss modulus calculated for a viscoelastic suspension is indistinguishable from the results for the Newtonian one as it should as a consequence of the correspondence principle. This is at variance with the recent measurements by Pasquino et al. (2008), where data with a viscoelastic liquid stay higher.
than in the Newtonian suspension. Such a discrepancy with experiments can be justified by assuming that structures/aggregates had somehow formed before the oscillatory measurements took place. Therefore, the effect of an ordered initial particle configuration and agglomerates on the loss modulus is explored. Our simulations show significant variations with respect to the isotropic value when specific structures are considered. More specifically, when particles are closer along the principal shear directions, the tangential stress in between them is higher, thus increasing the loss modulus as well. Notice that such an effect is observed for a Newtonian suspension too. However, it has to be remarked that particles in a Newtonian liquid do not tend to form structures in flow. On the other hand, fluid elasticity could be responsible for structure formation during sample preparation, and this would affect the ensuing linear viscoelastic measurements.

The numerical code is, then, used to extend the study to the large amplitude oscillatory regime of dilute and semidilute viscoelastic suspensions. For large amplitudes, the expected deviations from the linear viscoelastic behavior are found. Our simulation results show that the typical decrease of the moduli observed in LAOS regime for a viscoelastic fluid without particles is more and more pronounced as the volume fraction is higher. The latter also leads to a reduction to the value of strain amplitude such that deviations from the linear viscoelastic limit occur. Finally, our simulations correctly capture the overshoot in the loss modulus observed just beyond the linear viscoelastic limit that is hindered by the addition of solid particles.

The effect of fluid elasticity on the particle motion is also analyzed. Our simulations show that the particles move away from their starting positions and the average distance, computed at the beginning of each cycle with respect to the initial configuration, linearly increases with the number of cycles. The change in the microstructure is attributed to the long-range hydrodynamic interactions mediated by fluid viscoelasticity that give rise to particle migration and, presumably, to the formation of ordered structures, as experimentally observed in continuous shear flow. Because of the large computational time, our simulations are currently limited to few numbers of cycles that are not sufficient to follow the evolution of structure formation (that is a very slow process). Large CPU times also limit the maximum volume fraction that can be handled. Code optimization (e.g., parallelization) and the implementation of particle–particle artificial repulsive forces, needed to prevent particle overlapping, are required to apply the proposed numerical method to concentrated systems. This will be part of future work.

References


