PHYSICAL REVIEW E **74**, 051401 (2006)

Generalized hydrodynamics of a dilute suspension of finite-sized particles: Dynamic viscosity

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(Received 23 May 2006; revised manuscript received 15 August 2006; published 6 November 2006)

We present a mesoscopic hydrodynamic description of the dynamics of colloidal suspensions. We consider the system as a gas of Brownian particles suspended in a Newtonian heat bath subjected to stationary nonequilibrium conditions imposed by a velocity field. By means of a generalized Fokker-Planck equation, we obtain a set of coupled differential equations for the local diffusion current and the evolution of the total stress tensor. We find that the dynamic shear viscosity of the system contains contributions arising from the finite size of the particles.

DOI: 10.1103/PhysRevE.74.051401 PACS number(s): 82.70.Dd, 47.57.J−, 47.57.E−, 47.27.eb

I. INTRODUCTION

Due to the theoretical and industrial importance of colloidal suspensions, the rheological properties of these systems have been the subject of intense investigations by using a variety of experimental and theoretical methods [1–5]. Among others, the experimental techniques used to study these systems are neutron and light scattering, and ultrasonic absorption [6–8]. From a theoretical point of view, nonequilibrium statistical mechanics and thermodynamics [1–4,9–12], mode-coupling formalism [13], and computer simulations [14–18] are current techniques used to analyze the dynamics of these systems. Particular interest has been put on the behavior of the frequency-dependent shear viscosity of semidilute suspensions of hard spheres in different situations involving direct or hydrodynamic interactions [6,7].

In this paper, we present a mesoscopic hydrodynamic description of the dynamics of colloidal suspensions subjected to stationary nonequilibrium conditions imposed by a velocity field. In particular, we analyze the behavior of the dynamic viscosity due to its importance in reflecting the microstructure details into the relaxation of the system under the conditions imposed by the applied flow. At the mesoscopic level, the contributions of the suspended phase to the dynamics of the whole system can be described by using a Fokker-Planck equation [10,19–21]. This equation has been previously obtained on the grounds of irreversible thermodynamics in the dilute regime [10,19]. However, it is important to stress that similar equations have been derived in the context of different approximations ranging from the kinetic theory of gases to the projector operator formalism [20–22]. From this Fokker-Planck equation, we calculate a set of evolution equations for the moments of the distribution function. Then, by using the fluctuating hydrodynamics approach we obtain a frequency-dependent correction to the dynamic viscosity of the system that accounts for memory effects [23,24].

The paper is organized as follows. In Sec. II, we summarize the derivation of the Fokker-Planck equation and carry out the hydrodynamic description of a gas of Brownian particles. In Sec. III, we derive the dynamic viscosity of the system and present numerical results. Finally, Sec. IV is devoted to conclusions.

II. KINETIC AND HYDRODYNAMIC DESCRIPTION OF A GAS OF BROWNIAN PARTICLES

We will analyze the dynamics of a system consisting of a "gas" of Brownian particles of mass m suspended in a Newtonian heat bath subjected to stationary nonequilibrium conditions imposed by a stationary flow $\vec{v}_0(\vec{r})$.

The usual starting point to describe the dynamics of this system is the N-particle distribution function and its corresponding multivariate Fokker-Planck equation. In this equation, microscopic expressions for the hydrodynamic and direct interactions must be introduced. In the semidilute regime, for example, one must introduce the Oseen tensor and the two-particle interaction potential. At higher concentrations, the subsequent approximations may, in general, consider the Rotne-Prager tensor and the three-particle (or higher) interaction potential. It is clear that this approach constitutes an N-body problem hard to solve by analytical methods [25,26].

Here, we will follow an alternative approach to the problem in terms of a mean-field approximation in which the difficulties of the N-body problem are avoided. This approximation, based on the one-particle distribution function, allows one to make some analytical progress when calculating the hydrodynamic equations, despite the fact that the explicit dependence of the transport coefficients on frequency and wave vector and the form of the direct interactions are *a priori* unknown. However, by assuming in first approximation that the transport coefficients appearing in the hydrodynamic equations are constants, we may use the well established formalism of fluctuating hydrodynamics to obtain the explicit expressions for the corrections to the transport coefficients as a function of the frequency and the wave vector [23,24,27].

According to this, at the mesoscopic level the dynamics of the dilute Brownian gas can be described in terms of a single-particle local probability distribution $P(\vec{r},\vec{u},t)$ depending on time t and the instantaneous position and velocity of the Brownian particle $\vec{r}$ and $\vec{u}$. This distribution function obeys the continuity equation

$$\frac{\partial}{\partial t}P+\vec{\nabla}\cdot(\vec{u}P)=-\frac{\partial}{\partial\vec{u}}\cdot(P\vec{V}_{\vec{u}}),\tag{1}$$

where $\vec{V}_{\vec{u}}$ is a streaming velocity in $\vec{u}$ space. The explicit form of $\vec{V}_{\vec{u}}$ can be obtained from the entropy production of the system, after assuming the validity of the hypothesis of local equilibrium in phase space and using the rules of mesoscopic nonequilibrium thermodynamics [19,28]. Then, entropy production can be calculated from the nonequilibrium entropy functional [27]

$$\rho s(\vec{r},t)=-k_B\int P(\vec{u},\vec{r},t)\ln\frac{z}{z_{le}}d\vec{u}+\rho s_{le}(\vec{r}),\tag{2}$$

where k_B is Boltzmann's constant and $\rho s(\vec{r},t)$ and $\rho s_{le}(\vec{r})$ are the nonequilibrium entropy per unit volume and the local equilibrium entropy per unit volume, respectively. Moreover, we have introduced the fugacities $z=P(\vec{r},\vec{u},t)A(\rho)$ and $z_{le}=\exp\{[\mu_{le}-\frac{1}{2}(\vec{u}-\vec{v}_0)^2]m/k_BT\}$ with μ_{le} the chemical potential at a local equilibrium and $\rho(\vec{r},t)=m\int P(\vec{u},\vec{r},t)d\vec{u}$ the mass density field of the Brownian gas. Finally, $A(\rho)$, related with the excess of osmotic pressure of the system, represents the activity coefficient that introduces the interactions among Brownian particles [27].

After calculating the entropy production using Eq. (2), identifying forces and currents, and using the linear-law scheme of nonequilibrium thermodynamics [29], one finds that the distribution function $P(\vec{r},\vec{u},t)$ obeys the Fokker-Planck equation

$$\begin{aligned}\frac{\partial}{\partial t}P+\vec{\nabla}\cdot(\vec{u}P)-\vec{\nabla}\left[\frac{k_BT}{m}\ln A(\rho)\right]\cdot\frac{\partial P}{\partial\vec{u}}\\=\frac{\partial}{\partial\vec{u}}\cdot\left[\vec{\vec{\beta}}\cdot(\vec{u}-\vec{v}_0)P+\frac{k_BT}{m}\vec{\vec{\xi}}\cdot\frac{\partial P}{\partial\vec{u}}\right],\end{aligned}\tag{3}$$

where k_BT is the thermal energy (assumed constant). In the general case, the friction tensor $\vec{\vec{\beta}}(\vec{r},t)$ must contain the average effect of hydrodynamic interactions. It is related to the Onsager coefficient $\vec{\vec{\xi}}(\vec{r},t)$ through $\vec{\vec{\beta}}=\vec{\vec{\xi}}+\vec{\vec{\epsilon}}\cdot\vec{\nabla}\vec{v}_0$, in which the Onsager coefficient $\vec{\vec{\epsilon}}(\vec{r},t)$ accounts for the effects of the force exerted by a fluid on a particle of finite size according to the Faxén theorem [10,28].

It is important to notice that $\vec{v}_0$ is the stationary solution of the Navier-Stokes equation $\rho_0\vec{v}_0\vec{\nabla}\vec{v}_0=-\vec{\nabla}\cdot\mathbf{P}^0$ for the heat bath, with the appropriate boundary conditions on the surface of the colloidal particle, and ρ_0 is the constant density of the bath.

Equations similar to Eq. (3) have been derived in the context of different approximations; see, for example, Refs. [10,20,21,27,28]. From Eq. (3), one may calculate a set of evolution equations for the moments of the probability distribution, giving the "hydrodynamic" description of the system [10,27]. After taking into account the usual definitions for the hydrodynamic-like fields—mass density $\rho(\vec{r},t)$, velocity $\vec{v}(\vec{r},t)$, and pressure tensor $\mathbf{P}^k(\vec{r},t)$ (see Ref. [10])—the first equation of this set corresponds to the conservation of mass,

$$\frac{\partial\rho}{\partial t}=-\vec{\nabla}\cdot\vec{J}_D,\tag{4}$$

where the diffusion current $\vec{J}_D(\vec{r},t)=\rho\vec{v}$ of the Brownian gas satisfies the evolution equation [27,28]

$$\begin{aligned}\vec{J}_D+\vec{\vec{\beta}}^{-1}\cdot\frac{D\vec{J}_D}{Dt}=\rho\vec{v}_0-\frac{k_BT}{m}\vec{\vec{\beta}}^{-1}\cdot\frac{\partial\ln A(\rho)}{\partial\ln\rho}\vec{\nabla}\rho\\-\vec{\vec{\beta}}^{-1}\cdot[\vec{\nabla}\cdot\mathbf{P}^k(\vec{r},t)],\end{aligned}\tag{5}$$

where D/Dt is the material time derivative. The matrix of relaxation times of the diffusion current is $\vec{\vec{\tau}}_1\simeq\vec{\vec{\beta}}^{-1}$. Finally, Eq. (5) contains the kinetic part of the pressure tensor $\mathbf{P}^k(\vec{r},t)$ of the suspended phase whose evolution equation is [10]

$$[\mathbf{P}^k\cdot\vec{\vec{\tau}}_2^{-1}]^s=\frac{k_BT}{m}\rho[\vec{\vec{\beta}}-\vec{\vec{\epsilon}}\cdot\vec{\nabla}\vec{v}_0]^s-\frac{1}{2}\frac{D}{Dt}\mathbf{P}^k,\tag{6}$$

where the symbol s stands for the symmetric part of a tensor and $\vec{\vec{\tau}}_2$ is a matrix of relaxation times given by

$$\vec{\vec{\tau}}_2\simeq(\vec{\vec{\beta}}+\vec{\nabla}\vec{v})^{-1},\tag{7}$$

where we have neglected inertial terms proportional to $\nabla\cdot\vec{v}$, an assumption valid for small density fluctuations $\Delta\rho/\rho\ll1$.

The explicit expression for the pressure tensor can be obtained by solving the set of differential equations (6). However, in order to make analytical progress, let us assume the approximation $\vec{\vec{\tau}}_2\simeq\vec{\vec{\beta}}^{-1}\cdot(\mathbf{1}-\vec{\vec{\beta}}^{-1}\cdot\vec{\nabla}\vec{v})$ with $\mathbf{1}$ the unit tensor, and which allows us to write Eq. (6) in the form

$$\begin{aligned}\mathbf{P}^k\simeq\frac{k_BT}{m}\rho\mathbf{1}-\{\vec{\vec{D}}_0\rho\cdot[\vec{\nabla}\vec{v}+(\vec{\vec{\epsilon}}\cdot\vec{\nabla}\vec{v}_0)^{\dagger}]\}^s\\-\frac{1}{2}\left\{(\vec{\vec{\beta}}^{-1})^{\dagger}\cdot\frac{D}{Dt}\mathbf{P}^k\right\}^s,\end{aligned}\tag{8}$$

where the $\dagger$ represents the transpose, we have defined the diffusion coefficient $\vec{\vec{D}}_0=\frac{k_BT}{m}\vec{\vec{\beta}}^{-1}$, and we assumed that the leading term in the matrix of relaxation times is $\vec{\vec{\beta}}^{-1}$. Now, the assumption of small density fluctuations implies that the diagonal terms of $\mathbf{P}^k$ relax faster than the nondiagonal ones. Therefore, Eq. (8) can be separated in the form $\mathbf{P}^k=p^{id}\mathbf{1}+\mathbf{L}$, with $\mathbf{L}(\vec{r},t)$ the traceless stress tensor. This separation leads to the equations

$$\begin{aligned}p^{id}=\frac{k_BT_B}{m}\rho\quad\text{and}\quad2\mathbf{L}+\left[(\vec{\vec{\beta}}^{-1})^{\dagger}\cdot\frac{D}{Dt}\mathbf{L}\right]^s\\=-2\{\vec{\vec{D}}_0\rho\cdot[\vec{\nabla}\vec{v}^s+(\vec{\vec{\epsilon}}\cdot\vec{\nabla}\vec{v}_0)^{\dagger}]\}^s.\end{aligned}\tag{9}$$

After substitution of Eqs. (9) into Eq. (5), we obtain

$$\vec{J}_D = \rho\vec{v}_0 - \overleftrightarrow{D}(\rho)\cdot\vec{\nabla}\rho - \overleftrightarrow{\beta}^{-1}\cdot(\vec{\nabla}\cdot\mathbf{L}) - \overleftrightarrow{\beta}^{-1}\cdot\frac{D\vec{J}_D}{Dt}, \qquad (10)$$

where we have defined the collective diffusion coefficient [8]

$$\overleftrightarrow{D}(\rho) = \overleftrightarrow{D}_0\left[1 + \frac{\partial \ln A(\rho)}{\partial \ln \rho}\right] = \overleftrightarrow{D}_0\frac{\partial\mu(\rho)}{\partial\rho} \qquad (11)$$

in accordance with Ref. [29]. Notice that in the limit of very dilute suspensions, the activity coefficient vanishes and then Eq. (10) recovers the expected form.

The evolution equations governing the behavior of the hydrodynamic fields describing the whole suspension as an effective medium can be obtained from Eqs. (9) and (10) by adding the local diffusion current $\vec{J}=\vec{J}_D-\rho\vec{v}_0$ and the traceless part of the stress tensor of the heat bath given by $\mathbf{P}^0=-2\eta_0(\vec{\nabla}\vec{v}_0)^0$ with η_0 the Newtonian viscosity of the bath [36].

Thus, multiplying Eq. (9) by $\rho_0\rho^{-1}$, adding $\mathbf{P}^0$, neglecting the convective term in the total time derivative, and using the definition of $\vec{J}$, one arrives at the evolution equation for the total traceless stress tensor of the suspension $\mathbf{Q}^0\equiv\mathbf{P}^0+2\rho_0\rho^{-1}\mathbf{L}$,

$$\mathbf{Q}^0 + \left[(\overleftrightarrow{\beta}^{-1})^{\dagger}\cdot\frac{\partial}{\partial t}\mathbf{Q}\right]^0 = -2[\overleftrightarrow{D}_0\rho_0\rho_B^{-1}\cdot(\vec{\nabla}\vec{J})]^0 - 2[\overleftrightarrow{\eta}_{fs}\cdot(\vec{\nabla}\vec{v}_0)]^0, \qquad (12)$$

where $\rho_B=mn$, with $n=N/V$ the number density of colloidal particles, and we have defined the effective viscosity coefficient $\overleftrightarrow{\eta}_{fs}$ of the whole suspension as

$$\overleftrightarrow{\eta}_{fs} = \eta_0[\mathbf{1} + \overleftrightarrow{D}_0\rho_0\eta_0^{-1}\cdot(\mathbf{1}+\overleftrightarrow{\epsilon})]. \qquad (13)$$

Equation (13) contains corrections due to the finite size of the particles through the coefficient $\overleftrightarrow{\epsilon}\simeq(m/6k_BT)a^2\overleftrightarrow{\beta}\cdot\overleftrightarrow{\beta}$ with a the radius of the particle. The expression for $\overleftrightarrow{\epsilon}$ has been obtained by taking into account the Faxén theorem [28]. In deriving Eqs. (12) and (13), we have assumed that terms of the order $\overleftrightarrow{D}_0\vec{J}\rho^{-2}\cdot\vec{\nabla}\rho$ may be neglected and that the coefficient of the first term at the right-hand side of Eq. (12) only involves the average constant value of the density of the suspended phase. This is consistent with the approximation $\Delta\rho/\rho\ll 1$ used to derive Eq. (6).

Now, by substituting $\vec{J}_D=\vec{J}+\rho\vec{v}_0$ into Eq. (10) and using the Navier-Stokes equation, one can derive the evolution equation for the local diffusion current $\vec{J}$,

$$[\overleftrightarrow{\beta} + \vec{\nabla}\vec{v}_0]\cdot\vec{J} + \frac{D\vec{J}}{Dt} = -\overleftrightarrow{\beta}\cdot(\overleftrightarrow{D}_{\text{eff}}\cdot\vec{\nabla}\rho) + \rho\rho_0^{-1}\vec{\nabla}\cdot\mathbf{Q}^0_{\text{qs}}, \qquad (14)$$

where we have introduced the effective diffusion tensor

$$\overleftrightarrow{D}_{\text{eff}} = \overleftrightarrow{D}(\rho) - \overleftrightarrow{\beta}^{-1}\cdot\overleftrightarrow{D}_0\cdot\{[(1+\overleftrightarrow{\epsilon})\cdot\vec{\nabla}\vec{v}_0]^0 + \rho^{-1}(\vec{\nabla}\vec{J})^0\}, \qquad (15)$$

and $\mathbf{Q}^0_{\text{qs}}$ is the quasistationary form of the stress tensor of the suspension whose explicit form follows from Eq. (12) for times $t\gg(\beta^{-1})_{ij}$. The dependence of $\overleftrightarrow{D}_{\text{eff}}$ on the stress tensor of the heat bath has been previously reported in Refs. [10,20,22]. Now, in accordance with the assumption of low velocity gradients, the term $\overleftrightarrow{\beta}^{-1}\cdot\vec{\nabla}\vec{v}_0$ can be neglected in Eqs. (14) and (15), and then we obtain the simplified equation

$$\vec{J} + \overleftrightarrow{\beta}^{-1}\cdot\frac{D\vec{J}}{Dt} \simeq -\overleftrightarrow{D}(\rho)\cdot\vec{\nabla}\rho + \rho_B\rho_0^{-1}\overleftrightarrow{\beta}^{-1}\cdot(\vec{\nabla}\cdot\mathbf{Q}^0), \qquad (16)$$

where we have assumed that $\mathbf{Q}^0$ can be introduced instead of $\mathbf{Q}^0_{\text{qs}}$, and that the coefficient of the last term only involves the average constant value of the density of the suspended phase ρ_B.

Equations similar to Eqs. (12) and (16) have been discussed by several authors from different macroscopic and microscopic points of view in the context of polymer solutions [31–34]. These equations incorporate viscoelastic effects into the description since they contain a term associated with the relaxation of the involved quantities $(\mathbf{Q}^0,\vec{J})$, and thus lead to more general constitutive relations than those for Newtonian fluids. Equations (12) and (16) include tensor coefficients being then suitable to describe anisotropic systems [4,35]. In the following section, we will use Eqs. (12) and (16) to analyze the rheological properties of the system when fluctuations of the suspended phase are considered.

III. THE DYNAMIC VISCOSITY

The dynamic viscosity coefficient of the suspension as a function of the frequency ω can be calculated by considering the linearized fluctuating equations for the hydrodynamic fields that follow from Eqs. (4), (12), and (16). With this purpose, we will assume that $\rho=\rho_B+\delta\rho$, $\vec{v}_0=\vec{v}_s+\delta\vec{u}$, and $\mathbf{Q}^0=\mathbf{Q}^0_0+\delta\mathbf{Q}^0$, with $\delta\rho$, $\delta\vec{u}$, and $\delta\mathbf{Q}^0$ the deviations with respect to the average values ρ_B, $\vec{v}_s$, and $\mathbf{Q}^0_0$.

Moreover, in this section we will consider the case of a dilute suspension of particles. This assumption leads to a simplification of the description in which both hydrodynamic and direct interactions can be neglected. As a consequence, the set of Onsager and transport coefficients become scalar and, in the simplest approximation, constant: $\overleftrightarrow{\beta}=\beta\mathbf{1}$, $\overleftrightarrow{\epsilon}=\epsilon\mathbf{1}$, $\overleftrightarrow{\xi}=\xi\mathbf{1}$, and $\overleftrightarrow{\eta}_{fs}=\eta_{fs}\mathbf{1}$, and the activity coefficient $A(\rho)=\mathbf{1}$, thus simplifying the expression for the diffusion coefficient to $D(\rho)=D_0$.

Then, at first order in the deviations, from Eqs. (4), (12), and (16) one obtains the following set of fluctuating hydrodynamic equations:

$$\frac{\partial(\delta\rho)}{\partial t} = -\vec{\nabla}\cdot(\delta\vec{J}) - \vec{\nabla}(\delta\rho)\cdot\vec{v}_s, \qquad (17)$$

$$\delta\vec{J} + \beta^{-1}\frac{D}{Dt}\delta\vec{J} = -D_0\vec{\nabla}\delta\rho + \beta^{-1}\rho_B\rho_0^{-1}\vec{\nabla}\cdot\delta\mathbf{Q}^0, \qquad (18)$$

$$\delta\mathbf{Q}^0 + \beta^{-1}\frac{D}{Dt}\delta\mathbf{Q}^0 = -2D_0\rho_B\rho_0^{-1}(\vec{\nabla}\delta\vec{J})^0 - 2\eta_{fs}(\vec{\nabla}\delta\vec{u})^0. \qquad (19)$$

To obtain the corrections to the dynamic viscosity of the suspension, Eq. (19) can be written in a more suitable form by taking into account the separation $\vec{v}_0=\vec{v}_s+\delta\vec{u}$, which can be interpreted as the sum of the unperturbed imposed velocity field $\vec{v}_s$, in particular a shear flow, and $\delta\vec{u}$ is the corresponding correction to the velocity field arising from the presence of the particle, which is proportional to $\vec{\nabla}\vec{v}_s$ [30]. Following Ref. [30], Eq. (19) can be written in the form

$$\delta\mathbf{Q}^0 + \beta^{-1}\frac{D}{Dt}\delta\mathbf{Q}^0 = -2D_0\rho_B\rho_0^{-1}(\vec{\nabla}\delta\vec{J})^0 - 5\phi\eta_{fs}(\vec{\nabla}\vec{v}_s)^0, \qquad (20)$$

where ϕ represents the volume fraction occupied by the Brownian particles in the whole system.

Now, by taking the Fourier transform of Eqs. (17), (18), and (20) and solving for $\delta\mathbf{Q}^0$ in terms of $i\vec{k}\delta\vec{u}$, and taking into account that the frequency-dependent correction to the viscosity $\Delta\eta(\vec{k},\omega)$ of the suspension is defined according to the relation

$$\delta\mathbf{Q}^0 = -i[\Delta\eta(\vec{k},\omega)\vec{k}\delta\vec{u}]^0, \qquad (21)$$

we find that

$$\Delta\eta(k,\omega) \simeq \frac{5}{2}\phi\frac{\eta_{fs}}{1 - i\omega\beta^{-1} - \dfrac{D_0\beta^{-1}k^2}{(1-i\omega\beta^{-1})}}, \qquad (22)$$

where, for simplicity, we have considered the case in which $\vec{k}=(k,0,0)$. Notice that the frequency dependence of the dynamic viscosity for semidiluted suspensions follows a second-order continued-fraction expansion [7]. If we now take into account the relation $\mathbf{Q}^0=\mathbf{Q}_0^0+\delta\mathbf{Q}^0$, we obtain that the total viscosity of the suspension $\eta_{fs}+\Delta\eta(k,\omega)$ can be written as

$$\eta(k,\omega) \simeq \eta_{fs}\left[1 + \frac{5}{2}\phi\frac{1}{1 - i\omega\beta^{-1} - \dfrac{D_0\beta^{-1}k^2}{(1-i\omega\beta^{-1})}}\right]. \qquad (23)$$

It is interesting to notice that by expanding Eq. (23) up to first order in ω and second order in k and taking into account Eq. (13), we obtain

$$\eta(k,\omega) \simeq \eta_0\left[1 + \frac{5}{2}\phi\left(1 + \frac{i\omega}{\beta} + k^2\frac{D_0}{\beta}\right)\right][1 + \widetilde{\mathrm{Sc}}^{-1}(1+\epsilon)], \qquad (24)$$

where $\widetilde{\mathrm{Sc}} \equiv \eta_0/(\rho_0 D_0)$ is the Schmidt number for the Brownian gas diffusing in the solvent. Equation (24) is an expression similar to that reported in Ref. [36]. Nonetheless, Eq. (24) includes corrections due to the finite size of the particles, which are not included in the theories of Refs. [8,36].

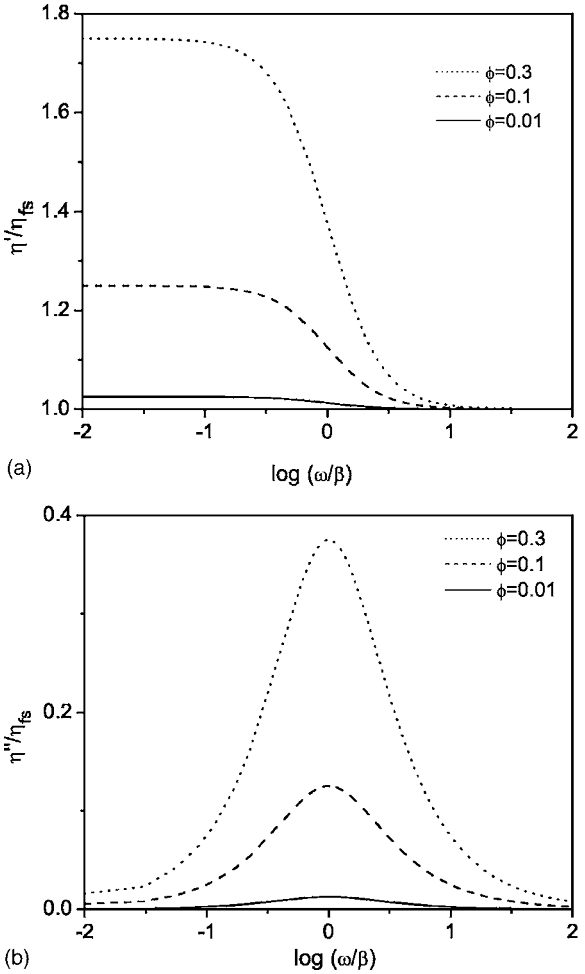

FIG. 1. (a) Real and (b) imaginary parts of the normalized dynamic viscosity as a function of $\tilde{\omega}$ for $\widetilde{\mathrm{Sc}} \gg 1$. Volume fractions as indicated in the figures.

To analyze the frequency behavior of Eq. (23), it can be recast in a more convenient form by using the dispersion relation $k^2=-i\frac{\omega\rho_0}{\eta_0}$, which can be obtained from the Navier-Stokes equations [28,30]. Substituting the last expression into Eq. (23) and using dimensionless variables defined by

$$\tilde{\omega} \equiv \frac{\omega}{\beta}, \quad \tilde{k}^2 \equiv \frac{D_0}{\beta}k^2, \quad \text{and} \quad \tilde{\eta}(\tilde{k},\tilde{\omega}) \equiv \frac{\eta(k,\omega)}{\eta_{fs}}, \qquad (25)$$

we obtain the following expression for the dynamic viscosity:

$$\tilde{\eta}(\tilde{\omega}) \simeq 1 + \frac{5}{2}\phi\frac{1}{1 - i\tilde{\omega} + i\dfrac{\tilde{\omega}}{\widetilde{\mathrm{Sc}}(1-i\tilde{\omega})}}, \qquad (26)$$

which only depends on the dimensionless frequency $\tilde{\omega}$, the volume fraction ϕ, and the Schmidt number $\widetilde{\mathrm{Sc}}$. The term containing $\widetilde{\mathrm{Sc}}$ represents a contribution arising from the coupling between diffusion and viscosity. Note that our definition of the Schmidt number is related to that used in Ref.

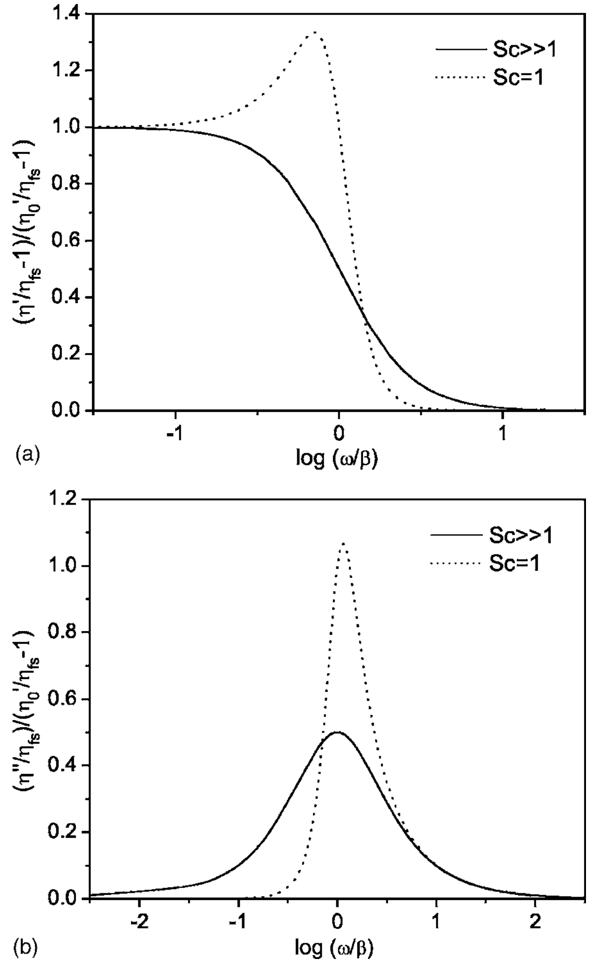

FIG. 2. (a) Real and (b) imaginary parts of the reduced dynamic viscosity as a function of $\tilde{\omega}$. The solid line corresponds to $\widetilde{\text{Sc}} \gg 1$ and the dashed line corresponds to $\widetilde{\text{Sc}} = 1$.

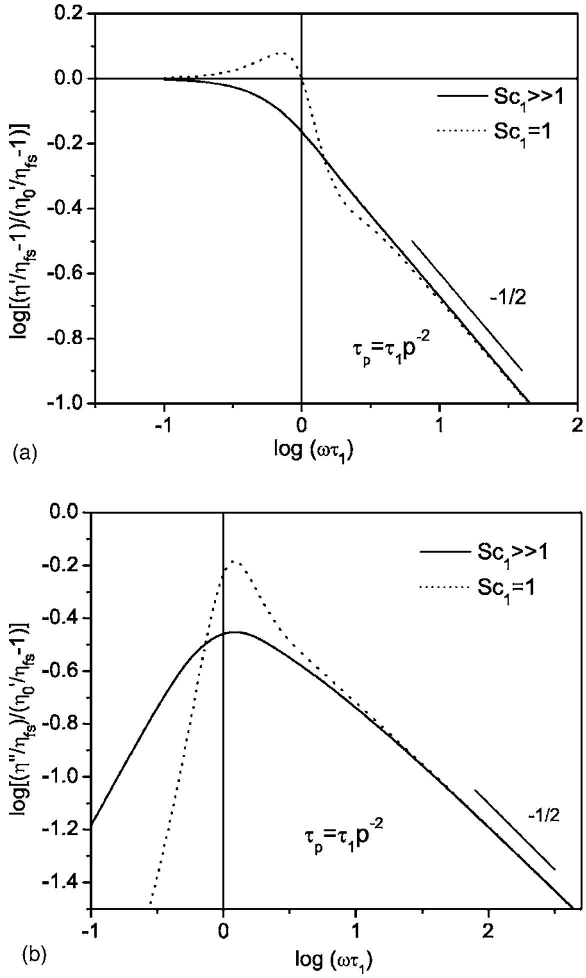

FIG. 3. (a) Real and (b) imaginary parts of the reduced dynamic viscosity as a function of $\tilde{\omega}$, for a distribution of relaxing processes. The solid line corresponds to $\widetilde{\text{Sc}}_1 \gg 1$ and the dashed line corresponds to $\widetilde{\text{Sc}}_1 = 1$. The number of relaxing processes considered was $N = 1000$.

[37] by means of the relation $\widetilde{\text{Sc}} = \text{Sc} D_f / D_0$, where D_f is the fluid self-diffusion coefficient. For a gas, $\text{Sc} \approx 1$ (this value is also used in numerical simulations of colloidal systems as, for example, the one of Ref. [15]), whereas for a liquid, $\text{Sc} \gg 1$, and since for a colloidal suspension in general $D_f \gg D_0$, then $\widetilde{\text{Sc}} \gg 1$. Therefore, the terms containing $\widetilde{\text{Sc}}^{-1}$ in Eqs. (13) and (26) can be neglected and the expression for the dynamic viscosity reduces to a form similar to that of Ref. [8], the differences being the finite-size contributions contained in η_{fs}, the explicit dependence on the volume fraction, and that the characteristic relaxation time is given by β^{-1} instead of $\tau_D = a^2 / D_0$.

In Fig. 1, we show the real $\tilde{\eta}'(\tilde{\omega})$ and imaginary $\tilde{\eta}''(\tilde{\omega})$ parts of the complex dynamic viscosity $\tilde{\eta}(\tilde{\omega})$ as a function of $\log \tilde{\omega}$ for different values of the volume fraction and considering $\widetilde{\text{Sc}} \gg 1$. Notice that $\tilde{\eta}(\tilde{\omega})$ has the usual behavior of a relaxation process with only one relaxation time [8]. From Eq. (26) it can be seen that the ratio $[\tilde{\eta}'(\tilde{\omega})-1]/[\tilde{\eta}_0'-1]$, with $\tilde{\eta}_0' \equiv \tilde{\eta}'(\tilde{\omega}=0)$, will depend only on the dimensionless parameter $\tilde{\omega}$. The imaginary term can be reduced in the same manner $\tilde{\eta}''(\tilde{\omega})/[\tilde{\eta}_0'-1]$. In Fig. 2, we plot the reduced viscosity as a function of $\tilde{\omega}$. In addition to the usual case of very large Schmidt numbers (solid line), we have also explored what would be the consequences when the Schmidt number is of the order of unity. For $\widetilde{\text{Sc}} = 1$ (dashed line), the real part of the viscosity presents a hump near $\tilde{\omega} = 1$. This characteristic appears for values of $\widetilde{\text{Sc}}$ in the range $[1, 2+\sqrt{3}]$, whereas for $\widetilde{\text{Sc}} \geq 2+\sqrt{3}$ the hump is not present [for $\widetilde{\text{Sc}} \geq 1$, the imaginary part of $\tilde{\eta}(\tilde{\omega})$ takes only positive values]. At intermediate frequencies, $\tilde{\eta}'(\tilde{\omega})$ decays following the law $\tilde{\omega}^{-2}$, independently of the value of $\widetilde{\text{Sc}}$. This is a typical behavior for processes with only one relaxation time [8]. On the other hand, the imaginary part of the viscosity has a bell-shaped form for $\widetilde{\text{Sc}} \gg 1$, whereas for $\widetilde{\text{Sc}} = 1$ it becomes asymmetric and more stretched. It is important to notice that for intermediate frequencies, $\tilde{\eta}''(\tilde{\omega})$ decays as $\tilde{\omega}^{-1}$, also a usual behavior for processes with only one relaxation time. The low-frequency region of the dynamic viscosity curves deserves also a detailed analysis. In this frequency region, $\tilde{\eta}''(\tilde{\omega})$ grows as $\tilde{\omega}$, independently of the value of the Schmidt number, except for $\widetilde{\text{Sc}} = 1$, where the curve grows as $\tilde{\omega}^3$.

Finally, it is important to point out that it has been experimentally observed that for intermediate frequencies, both the real and imaginary parts of the viscosity decay as $\omega^{-1/2}$ [8]. Such a frequency behavior can be modeled by assuming a distribution of relaxation times τ_p. In this case, the viscosity can be written as

$$\tilde{\eta}(\omega) = 1 + \sum_{p=1}^{N} \frac{G_p \tau_p}{1 - i\omega\tau_p + i\dfrac{\omega\tau_p}{\widetilde{\mathrm{Sc}}(1 - i\omega\tau_p)}}, \qquad (27)$$

where N is the number of relaxation processes involved. G_p is a constant relaxation strength of the relaxation process with relaxation time τ_p, given by a distribution of the form

$$\tau_p = \tau_1 p^{-\alpha}, \quad \alpha = 2, \qquad (28)$$

with τ_1 the longest relaxation time [8]. For a noninteracting hard-sphere system, this would correspond to a distribution on the size of the particles $a_p = a_1 p^{\alpha}$, or equivalently, $\widetilde{\mathrm{Sc}}_p = \widetilde{\mathrm{Sc}}_1 p^{\alpha}$. With this size distribution our results for the viscosity lead to the same power-law decay on frequency $\omega^{-1/2}$. In Fig. 3, we show this behavior for two different values of the Schmidt number corresponding to the longest relaxation time τ_1, $\widetilde{\mathrm{Sc}}_1 = 1$ and $\widetilde{\mathrm{Sc}}_1 \gg 1$. We notice that the intermediate frequency power-law dependency on frequency is not altered by this choice, but at low frequencies differences show up for $\tilde{\eta}''(\omega)$. A different power law for the size distribution will modify the behavior of the viscosity.

IV. CONCLUSIONS

We have proposed a model for the dynamics of colloidal suspensions based on a mesoscopic hydrodynamic description derived by applying the rules of mesoscopic nonequilibrium thermodynamics. We have derived the viscosity of a monodisperse hard-sphere system that includes effects due to the finite size of the colloidal particles. It has been shown that the normalized dynamic viscosity depends only on three dimensionless parameters: the Schmidt number $\widetilde{\mathrm{Sc}}$, the volume fraction ϕ, and the normalized frequency $\tilde{\omega}$. Also, it presents power-law exponents for different regions of the frequency space. Our results show that the mesoscopic approach leads to results that are consistent with previous theoretical descriptions derived by using the generalized hydrodynamics theory. We expect that the present model may be extended to a wider class of suspensions including particles with internal structure.

ACKNOWLEDGMENTS

This work was supported in part by Grants No. DGAPA IN-119606 (L.F.C. and S.I.H.), No. IN-110103 (C.I.M.), and No. IN-108006 (I.S.H.), and by the CONACYT under Grants No. SEP-2004-C01-47070 (L.F.C. and S.I.H.) and No. 43596-F (C.I.M.).

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