Nonequilibrium structure and rheology of concentrated colloidal suspensions: Linear response

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(Received 11 October 2000; accepted 26 February 2001)

We propose a simple theory for the pair distribution function of a sheared colloidal suspension. The starting point is an exact equation for the stationary state pair distribution. We assume that in a shear flow the higher order distributions can be expressed through the pair distribution in the same way as in an equilibrium state. To get explicit results we use a simple decoupling approximation for the higher order equilibrium correlations. For moderate volume fractions our theory predicts low-shear viscosity that agrees well with Brownian Dynamics simulations results. Low-shear distortion of the microstructure is underestimated by the theory but its shape agrees qualitatively with the simulations.

I. INTRODUCTION

It has been known since the pioneering work of Clark and Ackerson that the microstructure of concentrated colloidal suspensions can be easily influenced by flow. Their study, and a number of very interesting experimental and simulational investigations that followed it, stimulated theoretical efforts aimed at understanding and predicting the nonequilibrium structure of suspensions. It should be mentioned here that the microstructure, while itself interesting from a fundamental standpoint, is also of practical importance: it determines a host of macroscopic rheological properties such as viscosity, normal stress difference, etc.

In spite of a number of theoretical approaches the microstructure (and rheology) of flowing suspensions is still not fully understood. The most glaring gap that has been recognized as one of the major challenges in this field, is the following: essentially all theories for the microstructure of sheared colloidal suspensions predict that there is no change of the structure factor (or the pair correlation function) in the plane perpendicular to the flow. In contrast, experiments and Brownian Dynamics (BD) simulations find a nonzero distortion of the microstructure in this plane. The distortion in the plane perpendicular to the flow is negligible for small shear rates (indeed, it must vanish in the linear response regime) but it can be quite large for larger shear rates. It can be considered a precursor to a still-controversial flow-induced nonequilibrium phase transition to an ordered state in which colloidal particles form layers parallel to the flow.

It can be argued that in order to understand these complicated high-shear phenomena one should start with a simple yet reasonably accurate theory for low shear rates, i.e., the linear response regime. Such a theory could then be generalized to deal with a much more complicated problem of higher shear rates. It should be emphasized at this point that while it is possible to write down a formal expression for the distortion of the pair correlation function in the linear response regime, an explicit calculation of this expression is impossible: one has to resort to approximations. More importantly, the formal linear response expression cannot be easily generalized to include high-shear effects.

Recently a new theory for the microstructure of sheared colloidal suspensions has been proposed by Lionberger and Russel (LR). Predictions of this theory for the low-shear viscosity have been compared with available simulations. The theory has been found to be accurate up to the suspension volume fraction 0.4. Predictions of the LR theory for the microstructure have not been compared with simulations (there were no systematic studies of the microstructure in the linear response regime).

Here we propose a simpler theory for the nonequilibrium structure and rheology of shearing colloidal suspensions. The theory is compared with results of our BD simulations. Its predictions for the low-shear viscosity are accurate for moderate volume fractions, 0.43. The microstructure is reproduced qualitatively.

Our theory, as well as the LR theory, neglects hydrodynamic interactions. It can be argued that including these interactions is not crucial since the same qualitative results are observed in experiments and in BD simulations that also do not include hydrodynamic interactions. More importantly, our theory can be used to describe suspensions of charged colloidal particles. In these suspensions, hydrodynamic interactions are known to be qualitatively unimportant. Finally, our theory can serve as a basis for a comprehensive theory of colloidal systems that includes hydrodynamic interactions. For example, it can be used as a starting point for an approach that incorporates these interactions through the rescaling of the diffusion time scale.

The paper is organized as follows. In Sec. II we present the problem. In Secs. III and IV we formulate the two main approximations of our theory, a closure and a decoupling approximation, respectively. In Sec. V we present the predictions of the theory and compare them with results of the BD simulations, and with other theoretical approaches. Some de-
II. FORMULATION OF THE PROBLEM

We consider a suspension of particles interacting via a hard-sphere potential, with no hydrodynamic interactions. Such a model suspension can reasonably be used as a first approximation for a charge-stabilized colloidal system. The effective particle diameter should then be set equal to the particle separation at which the interaction energy is of the order of $k_B T$. In this work, in order to make this mapping more quantitative, we resort to matching equilibrium structure factors as described in Appendix C.

The suspension undergoes a steady shear flow of the form

$$\mathbf{v}(\mathbf{r}) = \gamma y \hat{e}_x,$$  

(1)

where $\gamma$ is the shear rate and $\hat{e}_x$ is the unit vector in the $x$-direction. The suspension is statistically uniform with mean number density $n$. The particle volume fraction is denoted by $\phi = n \pi \sigma^3/6$, where $\sigma$ is the particle diameter. In addition to the convective drift, suspended particles perform Brownian motion, with the diffusion constant of an isolated particle $D_0$. The magnitude of the influence of the shear flow on the structure of the suspension is characterized by the dimensionless shear rate $\gamma^* = \gamma \sigma^2/D_0$. Note that the Peclet number, $Pe$, is proportional to $\gamma^*$, $Pe = \gamma^* a^4/4$. Here $a$ is the colloidal particle radius.

On a time scale large compared to the relaxation time of the Brownian component of the colloidal particle velocity the state of the suspension can be described by the $N$-particle probability distribution $P_N(\mathbf{R}_1, \ldots, \mathbf{R}_N; t)$. Here $\mathbf{R}_i$ denotes the position of particle $i$. The time evolution is then given by the Smoluchowski equation which, for the present case of a sheared suspension, includes a convective term,

$$\frac{\partial}{\partial t} P_N(\mathbf{R}_1, \ldots, \mathbf{R}_N; t) = \left\{ \Omega_S - \sum_{i=1}^{N} \frac{\partial}{\partial \mathbf{R}_i} \cdot \mathbf{v}(\mathbf{R}_i) \right\} P_N(\mathbf{R}_1, \ldots, \mathbf{R}_N; t).$$  

(2)

In Eq. (2), $\Omega_S$ is the $N$-particle Smoluchowski operator,

$$\Omega_S = -D_0 \sum_{i=1}^{N} \frac{\partial}{\partial \mathbf{R}_i} \left[ - \frac{\partial}{\partial \mathbf{R}_i} + \beta \sum_{j \neq i}^{N} \mathbf{F}(\mathbf{R}_{ij}) \right].$$  

(3)

Here $\mathbf{F}(\mathbf{R}_{ij})$ is the force between particles $i$ and $j$, and $\beta = 1/k_B T$. In this work we consider hard-sphere suspensions. Thus, the interaction is singular and a no-flux boundary condition has to be imposed whenever two particles are touching.

$$\frac{\partial}{\partial \mathbf{R}_{ij}} P_N(\mathbf{R}_1, \ldots, \mathbf{R}_N; t) = 0, \quad \text{whenever } R_{ij} = \sigma^+.$$  

(4)

However, it has been shown by Cichocki$^{20}$ that the evolution equation (2) still can be used for the hard-sphere suspension if we take

$$\beta \mathbf{F}(\mathbf{R}_{ij}) = \hat{\mathbf{R}}_{ij} \delta(R_{ij} - \sigma),$$  

(5)

where $\hat{\mathbf{R}} = \mathbf{R}/R$. The boundary condition (4) is then incorporated into the evolution equation and need not be considered explicitly. To emphasize the fact that the general approach presented in this paper is in principle valid for arbitrary interactions we will keep the force $\mathbf{F}$ in all equations and only in explicit calculations will we use relation (5).

We are interested in the two-body (reduced) distribution in a stationary (time-independent) nonequilibrium state,

$$n_2(\mathbf{r}_1, \mathbf{r}_2; \gamma) = n_2^0 g_2(\mathbf{r}_{12}; \gamma)$$

$$= \left\{ \sum_{j \neq i}^{N} \delta(\mathbf{r}_1 - \mathbf{R}_j) \delta(\mathbf{r}_2 - \mathbf{R}_j) \right\}_\gamma$$

$$= N(N-1) \int d\mathbf{R}_1 \cdots d\mathbf{R}_N P_N \times (\mathbf{r}_1, \mathbf{r}_2, \mathbf{R}_3, \ldots, \mathbf{R}_N; \gamma).$$  

(6)

Here $P_N(\mathbf{R}_1, \ldots, \mathbf{R}_N; \gamma)$ denotes the stationary, flow-dependent solution of the Smoluchowski equation (2). The argument $\gamma$ in $P_N$ and $n_2$ emphasizes their dependence on the shear rate.

The reduced distribution $n_2$ satisfies the following equation that can be easily derived from Eq. (2):

$$- \frac{\partial}{\partial \mathbf{r}_1} \left\{ \mathbf{v}(\mathbf{r}_1) - D_0 \frac{\partial}{\partial \mathbf{r}_1} + D_0 \beta \mathbf{F}(\mathbf{r}_{12}) \right\} n_2(\mathbf{r}_1, \mathbf{r}_2; \gamma)$$

$$- \frac{\partial}{\partial \mathbf{r}_2} \left\{ \mathbf{v}(\mathbf{r}_2) - D_0 \frac{\partial}{\partial \mathbf{r}_2} - D_0 \beta \mathbf{F}(\mathbf{r}_{12}) \right\} n_2(\mathbf{r}_1, \mathbf{r}_2; \gamma)$$

$$- \frac{\partial}{\partial \mathbf{r}_1} D_0 \int d\mathbf{r}_3 \beta \mathbf{F}(\mathbf{r}_{13}) n_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3; \gamma)$$

$$- \frac{\partial}{\partial \mathbf{r}_2} D_0 \int d\mathbf{r}_3 \beta \mathbf{F}(\mathbf{r}_{23}) n_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3; \gamma) = 0.$$  

(7)

Equation (7) is not closed: in order to calculate the pair distribution we need to know the three-body reduced distribution $n_3$. Thus a closure approximation is needed that would allow us to express $n_3$ in terms of $n_2$.

III. CLOSURE APPROXIMATION

The closure approximation adopted in this work is similar to the one used before to describe self-diffusion and collective diffusion in colloidal suspensions.$^{21}$ That closure was inspired by the Resibois and Lebowitz approach to the linear kinetic theory of hard spheres$^{22}$ and other investigations$^{23,24}$ that followed their 1973 paper.

The basic idea of this closure is also the starting point of the LR theory. The difference between the latter theory and our approach is that LR combined the general idea of Resibois and Lebowitz with a nonequilibrium version of an integral equation theory (both HNC-type and PY-type approximations were tested). In contrast, we use the same idea but we resort to a simple decoupling approximation. The resulting theory is simpler to implement numerically.

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The idea is as follows: first let us assume that there exists a (fictitious) two-body external potential, \( V_2(\gamma) \), that, if used in an equilibrium calculation, reproduces the shear-rate-dependent pair distribution \( n_2(\gamma) \),

\[
n_2(r_1, r_2; \gamma) = n_2(r_1, r_2 | V_2).
\]  

(8)

Since the sheared suspension is macroscopically uniform, this fictitious potential should not change the one-particle distribution. It should be remembered that the fictitious potential depends on the shear rate. Note that, by definition,

\[
n_2(r_1, r_2 | V_2 = 0) = n_2^{eq}(r_{12}) = n^2 g_2^{eq}(r_{12}).
\]  

(9)

The steady state, being a nonequilibrium state, is intrinsically different from the equilibrium one. Therefore, if the fictitious potential \( V_2(\gamma) \) is used in the equilibrium calculation of the three-body distribution, it does not reproduce the exact shear-dependent distribution \( n_3(\gamma) \). There is a part of \( n_3(\gamma) \) that is missing. This part is hereafter referred to as irreducible three-body correlations \( n_{irr}^{3} \),

\[
n_3(r_1, r_2, r_3; \gamma) = n_3(r_1, r_2, r_3 | V_2) + n_{irr}^{3}(r_1, r_2, r_3; \gamma).
\]  

(10)

The closure approximation adopted in this work consists in neglecting the irreducible three-body correlations:

\[
n_3(r_1, r_2, r_3; \gamma) \approx n_3(r_1, r_2, r_3 | V_2) = n_3(r_1, r_2, r_3 | n_2(\gamma)).
\]  

(11)

The second equality above emphasizes that since the fictitious potential is determined by the two-body distribution \( n_2(\gamma) \) through Eq. (8), approximation (11) expresses implicitly \( n_3 \) in terms of \( n_2 \) and therefore closes Eq. (7). Note that this closure effectively assumes that the three-body distribution can be expressed in terms of the (nonequilibrium) two-body distribution in the same way as in an equilibrium state.

In the final step, the right-hand-side \( (r_1) \) of (11) is linearized with respect to the change of the pair distribution,

\[
n_3(r_1, r_2, r_3 | n_2(\gamma)) = n_3^{eq}(r_1, r_2, r_3) + \frac{\partial n_3}{\partial n_2} (n_2 - n_2^{eq}).
\]  

(12)

The derivative on the rhs is understood as a functional derivative taken at constant one-particle density (all necessary integrations are implied; the detailed formulas are given in Appendix A).

The linearization (12) is of course justified in the linear response (low-shear) regime considered in this work. We eventually intend to use (12) also for higher shear rates. In this case the linearization should be treated as an additional approximation.

The functional derivative in Eq. (12) can be expressed in terms of equilibrium many-body distributions. In general distributions up to \( n_5^{eq} \) will be involved. However, one should note that in Eq. (7) we will use the functional derivative multiplied by the two-particle force and integrated. It turns out that this results in a much simpler expression that involves only distributions up to \( n_5^{eq} \). The detailed calculations are presented in Appendix A. Here we give only the final, closed equation for the pair distribution \( n_2(\gamma) \):

\[
\frac{\partial}{\partial r_1} \left( \mathbf{v}(r_1) + \frac{\partial}{\partial r_2} \mathbf{v}(r_2) \right) n_2(r_{12}; \gamma) + D_0 \frac{\partial}{\partial r_1} \int dr_3 n_2^{eq}(r_{12}) \delta(r_{23}) + n_3^{eq}(r_1, r_2, r_3) - n_3^{eq}(r_1, r_2, r_3) g_2^{eq}(r_{13})
\]

\[
\cdot \frac{\partial}{\partial r_1} \int dr_4 dr_5 \left[ \frac{\delta(r_{14}) \delta(r_{35})}{n_2^{eq}(r_{13})} - C(r_1, r_3, r_4, r_5) \right] \delta n_2(r_{24} \gamma) + D_0 \frac{\partial}{\partial r_2} \int dr_3 n_2^{eq}(r_{12}) \delta(r_{13}) + n_3^{eq}(r_1, r_2, r_3)
\]

\[
-n_3^{eq}(r_{12}) g_2^{eq}(r_{23}) \cdot \frac{\partial}{\partial r_2} \int dr_4 dr_5 \left[ \frac{\delta(r_{24}) \delta(r_{35})}{n_2^{eq}(r_{23})} - C(r_2, r_3, r_4, r_5) \right] \delta n_2(r_{24} \gamma) = 0.
\]  

(13)

In Eq. (13) \( \delta n_2(r_{24} \gamma) \) denotes the distortion of the pair distribution,

\[
\delta n_2(r_{24} \gamma) = n_2(r_{24} \gamma) - n_2^{eq}(r_{24}).
\]  

(14)

Furthermore, \( C \) denotes a higher order Ornstein–Zernicke (OZ) direct correlation function that is defined in Appendix A.

**IV. DECOUPLING APPROXIMATION**

The equation (13) is closed but useless: in general we do not have simple reliable expressions for many-body equilibrium distributions. In order to proceed further approximations are needed. In this work we propose to use a simple decoupling approximation. Before formulating it we would like to emphasize that we are not interested in approximating many-body equilibrium distributions in general; what we want are simple expressions that are accurate enough to be used in Eq. (13).

We propose to use the following approximations:

\[
n_2^{eq}(r_{12}) \delta(r_{23}) + n_3^{eq}(r_1, r_2, r_3) - n_3^{eq}(r_1, r_2, r_3) g_2^{eq}(r_{13})
\]

\[
\approx n^2 \delta(r_{23}) + n(n_2^{eq}(r_{23}) - n^2),
\]  

(15)

\[
\delta(r_{13}) \delta(r_{24})
\]

\[
\approx \left( \delta(r_{13}) - nc_{eq}(r_{13}) \right) \left( \delta(r_{24}) - nc_{eq}(r_{24}) \right) / n_2^{eq}(r_{34}).
\]  

(16)
In Eq. (16) $c_{eq}$ is the equilibrium direct correlation function. The first decoupling approximation, Eq. (15), is quite simple: it amounts to decoupling variables $r_1$ and $r_2$. To get the second one, Eq. (16), we used the asymptotic form of the higher order direct correlation function $C$ (see Appendix A). It should be noted that approximation (16) is not symmetric: we keep all the correlations between variables $r_3$ and $r_4$. The reason is that expression (16) is multiplied in Eq. (13) by $\delta n_2(r_{34})$, which is nonzero only when $r_3$ and $r_4$ are correlated.

Substituting (15–16) into Eq. (13), we get:

$$\frac{\partial}{\partial r_1} \cdot \mathbf{v}(r_1) + \frac{\partial}{\partial r_2} \cdot \mathbf{v}(r_2) \cdot n_2(r_{12} ; \gamma) + \frac{\partial}{\partial r_1} \cdot D_0 \frac{\partial}{\partial r_1} \times \int dr_3 (\delta(r_{13}) - n c_{eq}(r_{13})) \frac{\delta n_2(r_{32} ; \gamma)}{g_2^{eq}(r_{32})} + \frac{\partial}{\partial r_2} \times D_0 \frac{\partial}{\partial r_2} \int dr_3 (\delta(r_{23}) - n c_{eq}(r_{23})) \frac{\delta n_2(r_{23} ; \gamma)}{g_2^{eq}(r_{13})} = 0.$$  (17)

Equation (17) leads to a violation of the nonoverlap (excluded volume) condition [i.e., $\delta n_2(r_{12})$ becomes nonzero for $r_{12} < \sigma$]. To correct for this we re-introduce a no-flux condition and arrive at the following equation:

$$\frac{\partial}{\partial r_1} \cdot \mathbf{v}(r_1) + \frac{\partial}{\partial r_2} \cdot \mathbf{v}(r_2) \cdot n_2(r_{12} ; \gamma) + \frac{\partial}{\partial r_1} \cdot D_0 \frac{\partial}{\partial r_1} - \beta \mathbf{F}(r_{12}) e^{-\beta \mathbf{V}(r_{12})} \times \int dr_3 (\delta(r_{13}) - n c_{eq}(r_{13})) \frac{\delta n_2(r_{32} ; \gamma)}{g_2^{eq}(r_{32})} + \frac{\partial}{\partial r_2} \times D_0 \frac{\partial}{\partial r_2} + \beta \mathbf{F}(r_{12}) e^{-\beta \mathbf{V}(r_{12})} \times \int dr_3 (\delta(r_{23}) - n c_{eq}(r_{23})) \frac{\delta n_2(r_{23} ; \gamma)}{g_2^{eq}(r_{13})} = 0.$$  (18)

It should be noted here that the re-introduction of the no-flux condition partially corrects the asymmetry of the decoupling approximation.

Finally, we linearize Eq. (18) w.r.t. the shear flow and obtain the following equation that is the main result of this work:

$$\frac{\partial}{\partial r_1} \cdot D_0 \left( \frac{\partial}{\partial r_1} - \beta \mathbf{F}(r_{12}) \right) e^{-\beta \mathbf{V}(r_{12})} \times \int dr_3 (\delta(r_{13}) - n c_{eq}(r_{13})) \frac{\delta g_2(r_{32})}{g_2^{eq}(r_{32})} + \frac{\partial}{\partial r_2} \cdot D_0 \left( \frac{\partial}{\partial r_2} + \beta \mathbf{F}(r_{12}) \right) e^{-\beta \mathbf{V}(r_{12})}$$

Equation (20) can be obtained from the formal result (13) using a decoupling approximation (15) and a slightly modified approximation (16) in which the equilibrium correlation function $g_2^{eq}$ is replaced by 1. It should be noted here that Ronis’ equation leads to a violation of the excluded volume condition: $\delta n_2(r_{12})$ becomes nonzero for $r_{12} < \sigma$.

The Russel and Gast equation for the nonequilibrium microstructure has the following form in our notation:

$$D_0 \left( \frac{\partial}{\partial r_1} + \beta \mathbf{F}_{mf}(r_{12}) \right) \cdot \frac{\partial}{\partial r_1} \cdot \delta g_2(r_{12}) = D_0 \left( \frac{\partial}{\partial r_1} - \beta \mathbf{F}_{mf}(r_{12}) \right) \frac{\partial}{\partial r_1} \cdot \delta g_2(r_{12})$$

Equation (21) can be obtained from the formal result (13) by neglecting all the nonlocal integral terms. It is interesting to note that essentially the same procedure (neglect of the integral terms) was used in the original derivation of the Russel and Gast theory.

Finally, one of the most successful approaches to the rheology of dense suspensions was developed by Brady and collaborators (see Ref. 15 and references therein). In Brady’s approach the nonequilibrium pair correlation function is described by the following equation:
Note that expressions $\sim c$ where $in Eq. (27) $\delta F(r_1) \cdot \frac{\partial}{\partial r_1} g_2^{eq}(r_1)$

$$ + D_0 \left[ \frac{\partial}{\partial r_2} - \beta F(r_1) \right] \cdot \frac{\partial}{\partial r_2} g_2^{eq}(r_1) $$

$$ = - \frac{\partial}{\partial r_1} \cdot \nu(r_1) \beta V(r_1) - \frac{\partial}{\partial r_2} \cdot \nu(r_2) \beta V(r_1). \quad (22) $$

Hence, Brady’s theory amounts to taking the low density limit of both the mean force $F_{md}$ and right-hand-side of the Russel and Gast equation, Eq. (21).

Theories of Wagner and Russel and Lionberger and Russel are also implicitly based on the basic closure approximation (12). However, they treat many-particle terms in a way that is completely different from the one used in this work.

V. RESULTS

The details of the solution of Eq. (19) are presented in Appendix B. Here we give the final result:

$$ \delta g_2(r) = \frac{x^r}{r^2} f(r) g_2^{eq}(r), \quad (23) $$

where

$$ f(r) = f_1(r) + 4\pi n \int_0^\infty dr' r'^2 h_{22}(r,r') f_1(r') \quad (24) $$

and

$$ f_1(r) = -\frac{\sigma^3}{6\pi} \left[ 1 - \frac{3}{\sigma^2} \int_\sigma^r dr' r'^4 (g_2^{eq}(r') - 1) \right]. \quad (25) $$

Note that expressions (23)–(24) are valid for $r \geq \sigma$. Both $\delta g_2$ and $f_1$ vanish for $r < \sigma$.

In Eq. (24), $h_{22}$ is the solution of the following integral equation:

$$ h_{22}(r,r') = c_{22}(r,r') + 4\pi n \int_\sigma^r dr'' r''^2 h_{22}(r,r'') c_{22}(r'',r), \quad (26) $$

where $c_{22}$ is a component of the equilibrium direct correlation function proportional to the second Legendre polynomial $P_2$,

$$ c_{22}(r,r') = (1/4\pi) \int d\hat{r} c^{eq}(|r-r'|) P_2(\hat{r} \cdot \hat{r'}). \quad (27) $$

In Eq. (27) $d\hat{r} \cdot \hat{r''}$ denotes angular integration over the solid angle.

If the lower limit of the integration in Eq. (26) is replaced by 0, the resulting equation is just an $l=2$ component of the standard OZ equation, and its solution is given by the following formula:

$$ h_{22}(r,r') = (1/4\pi) \int d\hat{r} h_2^{eq}(|r-r'|) P_2(\hat{r} \cdot \hat{r'}), \quad (28) $$

where $h_2^{eq} = g_2^{eq} - 1$. This approximate $h_{22}$ was used in numerical calculations. For a couple of volume fractions we also solved the original equation (26) and checked that the error introduced by using expression (28) was a small one and was restricted to small $r$.

In the end only input required to evaluate (23)–(25) is the equilibrium pair correlation function $g_2^{eq}$. In numerical calculations we used the Verlet–Weiss modification of the Percus–Yevick hard-sphere pair distribution function.

To compare the theoretical predictions to numerically exact results we performed BD simulations of a system of colloidal particles interacting via repulsive screened Coulomb interactions. A brief description of the simulations and the mapping from the screened Coulomb to the hard-sphere potential are presented in Appendix C.

In Fig. 1 we compare theoretical predictions for the low-shear viscosity with results of BD simulations. The quantity plotted is

$$ \frac{\Delta \eta}{\eta_s} = \lim_{\gamma \to 0} \frac{1}{\gamma^3} \frac{3\pi}{k_B T} \int d\hat{r} (-x F_x) \delta n_2(r; \gamma), \quad (29) $$

e.g., the contribution to the low-shear viscosity due to inter-particle interactions [$\eta_s$ is the solvent viscosity that is related to the isolated particle diffusion coefficient $D_0$ through $D_0 = k_B T/(3\pi \eta_s \sigma^3)$].

The agreement is very good at moderate volume fractions, i.e., up to $\phi \approx 0.43$. A more careful look at the data shows that at these volume fractions the theory slightly overestimates low-shear viscosity. On the other hand, at high volume fractions, $\phi \approx 0.45$, the theory loses its accuracy: it significantly underestimates low-shear viscosity. It should be recalled at this point that a theory for self-diffusion, that is based on a similar closure, suffers from the same deficiency: it slightly underestimates the self-diffusion coefficient for moderate volume fractions and significantly overestimates it for high volume fractions.

In Fig. 2 we compare our predictions for the low-shear viscosity with those resulting from other approaches (note that the LR results were obtained for a suspension interacting via a continuous repulsive potential and then mapped on the hard-sphere system; see Ref. 16 for details). Brady’s and the Lionberger and Russel theories give results comparable to

![FIG. 1. Reduced low-shear viscosity, $\Delta \eta/\eta_s$, as a function for the volume fraction $\phi$. Solid line: present theory; circles: Brownian Dynamics simulations (see Appendix C for estimates of the error bars).](Image)
where $S$ one, agreement between the theory and simulations: the shape and

\[ \frac{\Delta \eta}{\eta} = \frac{S(k; \gamma) - S(k)}{\gamma(k, k_x/k^2)}, \]

where $S(k; \gamma) = 1 + n \int \! dr \exp(-ik \cdot r)(g(r; \gamma) - 1)$.

For both volume fractions there is only a qualitative agreement between the theory and simulations: the shape and

position of the distortion are reproduced reasonably well whereas its magnitude is underestimated. It should be noted that at the high volume fraction the theory underestimates the simulations result much more than at the moderate one. Curiously, the shape of the distortion is slightly better reproduced for a higher volume fraction.

In Figs. 4 and 5 we show the distortion of the pair correlation function $\left( g_2(r; \gamma) - g_2^{eq}(r) \right) / \left( \gamma^*(xy/r^2) \right) = f(r) g_2^{eq}(r)$ for three representative volume fractions. Both the value at contact and the amplitude of the oscillations decrease with a decreasing volume fraction. It should be noticed here that the LR theory gives qualitatively similar results for $\delta g_2$. At $\phi = 0.5$ the LR theory predicts slightly less pronounced oscillations than does the present approach.

Finally, in Figs. 6 and 7 we explicitly compare our predictions to those resulting from other approaches. Just by comparing the vertical scales in Fig. 3 and in Figs. 6 and 7 we note that none of the theories are quantitatively accurate at a higher volume fraction. Qualitatively, some theories reproduce the general shape of the low-shear change of the structure factor reasonably well.

We start from theories that can be derived from the formal result (13): Ronis, Russel and Gast, and Brady (Fig. 6). It is evident that Ronis’ theory is the most accurate one. Its disadvantage is that at all shear rates it leads to vanishing distortion of the structure factor in the plane perpendicular to the flow. This is closely related to the fact that Ronis’ theory
violates the excluded volume condition. Next, in Fig. 7 we compare our predictions to those of the LR theory. While both theories are quantitatively off, the magnitude of the distortion is slightly better described by our approach whereas the shape is slightly better predicted by Lionberger and Russel.

Comparing Figs. 2 and 6–7 one notices that the accuracy of the viscosity predictions is not related to the quality of the microstructure. The viscosity is determined by the short-range behavior of the distortion of the pair correlation function, $\delta g_2$, whereas the microstructure (more precisely, the distortion of the structure factor, $\delta S$) seems to be quite sensitive to the overall shape of $\delta g_2$.

VI. CONCLUSIONS

We presented here a simple yet reasonably accurate theory for the microstructure and rheology of concentrated colloidal suspensions undergoing a steady shear flow. We believe that this theory is a good starting point for the development of a comprehensive approach to the microstructure of suspensions in high-shear flows.

An obvious point of departure for such an approach is Eq. (18). It should be noted here that while this equation contains higher order shear flow effects it is derived from the linearized closure (12). Thus Eq. (18) implicitly assumes that while the distortion of the pair structure may be substantial, the change of the three-body can be expressed in terms of the distortion in the same way as in the low-shear regime. It remains to be checked whether this assumption is correct.

We would like to emphasize that the higher order shear rate effects cannot be incorporated via a power-series expansion in the shear rate: as shown by Ronis,9 Dhont13 and Brady and Vicic15 the pair correlation function under shear flow is a nonanalytical function of the shear rate.

Finally, while the present theory is reasonably accurate at moderate volume fractions, it is quantitatively wrong for high volume fractions. To address this issue we have to investigate the closure approximation. It can be shown that the linearized closure (12) includes only the simplest mode-coupling effects. To include nontrivial irreducible memory functions one has to go beyond it. On the level of linearized closures this can be achieved by moving the closure to the next higher level. To this end one would have to introduce a three-body potential that would reproduce $n_{13}^{\text{irr}}$. To determine the three-body potential one would go to the steady-state equation for $n_{13}^{\text{irr}}$. In this equation the four-body distribution, $n_{14}$, would be divided into three parts. Next, in a new closure approximation the part not accounted for by the two- and three-body potentials would be neglected. Such a scheme is straightforward in principle but it leads to complicated expressions containing many-body equilibrium distributions. It remains for future work to investigate whether these expressions can be used as a starting point for explicit calculations.

ACKNOWLEDGMENTS

I would like to thank Scott Brown and Aaron Nelson for help with Brownian Dynamics simulations. This work was partially supported by National Science Foundation Grant No. CHE-9624596.

APPENDIX A: LINEARIZED CLOSURE APPROXIMATION

In this appendix we discuss the linearized closure (12) and its application in Eq. (7). We start by writing out the exact form of the “kernel” that we are interested in,

$$\int dr_3 \beta F(r_3) \left( \frac{\delta n_3(t_1, t_2, t_3)}{\delta n_2(t_4, t_5)} \right)_{n_1}.$$  

(A1)

This kernel has to be multiplied by the distortion of the pair distribution, $\delta n_3(t_{15}, t_5)$, and integrated over $r_4$ and $r_5$ in order to be substituted into Eq. (7). In Eq. (A1) the subscript $n_1$ denotes functional differentiation at constant one-particle density.

To evaluate this kernel we start from the second equation of the equilibrium BGY hierarchy for a system in external one- and two-body potentials, $V_1$ and $V_2$. 

![Figure 6](image-url)

**FIG. 6.** Low-shear change of the structure factor, $\delta S(k)$ for the system: present theory; dashed: Ronis’ theory (Ref. 9); dotted: approach of Brady, data taken from Fig. 12 of Ref. 16.

![Figure 7](image-url)

**FIG. 7.** Low-shear change of the structure factor, $\delta S(k)$ for the system: solid: this work; dashed: LR theory (Ref. 16) data taken from Fig. 12 of Ref. 16.
\[
\begin{align*}
\left( \frac{\partial}{\partial r_1} - \beta F(r_{12}) + \beta \frac{\partial V_1(r_1)}{\partial r_1} \right) \\
+ \beta \frac{\partial V_2(r_1, r_2)}{\partial r_1} & n_2(r_1, r_2|V_1, V_2) \\
= \int dr_3 \beta F(r_{13}) n_3(r_1, r_2, r_3|V_1, V_2) \\
- \beta \int dr_3 n_3(r_1, r_2, r_3|V_1, V_2) \frac{\partial V_2(r_1, r_2)}{\partial r_1}. \tag{A2}
\end{align*}
\]

The reason for introducing \( V_1 \) is to enforce the condition of constant (unchanged) one-body distribution.

Equation (A2) is functionally differentiated with respect to the two-body distribution with the one-body distribution kept constant. The derivative is evaluated at the external potentials set to zero. In this way we obtain the following identity:

\[
\begin{align*}
\left( \frac{\partial}{\partial r_1} - \beta F(r_{12}) \right) I(r_1, r_2|r_4, r_5) + n_2^{\text{eq}}(r_{12}) \\
\times \left\{ \beta \frac{\partial}{\partial r_1} \left( \frac{\delta V_1(r_1)}{\delta n_2(r_4, r_5)} \right) + \beta \frac{\partial}{\partial r_1} \left( \frac{\delta V_2(r_1, r_2)}{\delta n_2(r_4, r_5)} \right) \right\} \\
= \int dr_3 \beta F(r_{13}) \left( \frac{\delta n_3(r_1, r_2, r_3)}{\delta n_2(r_4, r_5)} \right) \\
- \beta \int dr_3 n_3^{\text{eq}}(r_1, r_2, r_3) \frac{\partial}{\partial r_1} \left( \frac{\delta V_2(r_1, r_3)}{\delta n_2(r_4, r_5)} \right). \tag{A3}
\end{align*}
\]

where the functional identity \( I \) is defined as

\[
I(r_1, r_2|r_4, r_5) = \frac{1}{2} \{ \delta(r_{14}) \delta(r_{25}) + \delta(r_{15}) \delta(r_{24}) \}. \tag{A4}
\]

To eliminate the term involving \( \delta V_1/\delta n_2 \) we start from the first equation of the equilibrium hierarchy for a system in external potentials,

\[
\begin{align*}
\left( \frac{\partial}{\partial r_1} + \beta \frac{\partial V_1(r_1)}{\partial r_1} \right) n_1(r_1|V_1, V_2) \\
= \int dr_3 \beta F(r_{13}) n_2(r_1, r_3|V_1, V_2) \\
= \frac{1}{2} \int dr_3 n_2(r_1, r_3|V_1, V_2) \frac{\partial V_2(r_1, r_3)}{\partial r_1}. \tag{A5}
\end{align*}
\]

Then we functionally differentiate Eq. (A5) with respect to \( n_2 \) with \( n_1 = \text{const} \) and evaluate the resulting identity at zero external potentials. In this way we obtain the following equation:

\[
\begin{align*}
n \beta \frac{\partial}{\partial r_1} \left( \frac{\delta V_1(r_1)}{\delta n_2(r_4, r_5)} \right) \\
= \int dr_3 \beta F(r_{13}) I(r_1, r_3|r_4, r_5) \\
- \beta \int dr_3 n_2^{\text{eq}}(r_1, r_3) \frac{\partial}{\partial r_1} \left( \frac{\delta V_2(r_1, r_3)}{\delta n_2(r_4, r_5)} \right). \tag{A6}
\end{align*}
\]

Combining Eqs. (A3) and (A6) we obtain the following formula for the kernel (A1):

\[
\begin{align*}
\int dr_3 \beta F(r_{13}) \left( \frac{\delta n_3(r_1, r_2, r_3)}{\delta n_2(r_4, r_5)} \right) \\
= \frac{\partial}{\partial r_1} - \beta F(r_{12}) \left( \frac{\delta i(r_1, r_2)}{\delta n_2(r_4, r_5)} \right) \\
+ (n_2^{\text{eq}}(r_{12})/n) \int dr_3 \beta F(r_{13}) I(r_1, r_3|r_4, r_5) \\
+ \beta \int dr_3 n_3^{\text{eq}}(r_1, r_2, r_3) \delta(r_{23}) + n_3^{\text{eq}}(r_1, r_2, r_3) \\
- n_3^{\text{eq}}(r_1, r_2, r_3) \delta(r_{23}) \frac{\delta V_2(r_1, r_3)}{\delta n_2(r_4, r_5)} \tag{A7}
\end{align*}
\]

The derivative \( \delta V_2/\delta n_2 \) is proportional to the inverse of the irreducible part of the pair-pair correlation function that was introduced in the context of the linear kinetic theory\(^{24}\) and later used, e.g., in the thermodynamic perturbation theory.\(^{27}\) Explicitly, following Ref. 27, we get

\[
\begin{align*}
- \beta \left( \frac{\delta V_2(r_1, r_3)}{\delta n_2(r_4, r_5)} \right) &= I(r_1, r_3|r_4, r_5) - C(r_1, r_3, r_4, r_5) \tag{A8}
\end{align*}
\]

Here the function \( C \) plays the role of the Ornstein–Zernicke direct correlation function, but on a higher (pair–pair) level. This function can be written in the following form:

\[
C(r_1, r_3, r_4, r_5) = \left[ 1 + \hat{P}(45) \right] \left[ n^{-1} c^{\text{eq}}(r_{14}) \delta(r_{35}) \right. \\
\left. + n^{-1} \delta(r_{14}) c^{\text{eq}}(r_{35}) - c^{\text{eq}}(r_{14}) c^{\text{eq}}(r_{35}) \right] \\
+ C_{22}(r_1, r_3, r_4, r_5), \tag{A9}
\]

where the operator \( \hat{P}(45) \) permutes the variables \( r_4 \) and \( r_5 \). It can be shown that the function \( C_{22} \) is the only term on the rhs of Eq. (A9) which has a group property. Note that our normalization for the higher order Ornstein–Zernicke function \( C \) is different from that used in Ref. 27.

Combining (A7) with (A8) and using the result in Eqs. (12) and, subsequently (7), we obtain Eq. (13). We should remark at this point that, in addition, the equation for the one-particle distribution of a sheared suspension has to be used.
APPENDIX B: SOLUTION OF THE DIFFUSION EQUATION

In this appendix we derive solution (23) of Eq. (19). This equation is, essentially, a two-body diffusion equation for the function $f_1$ defined as

$$f_1(r) = \int_{\text{out}} d r' \{ \delta(r-r') - ne^{\text{eq}}(r-r') \} \frac{\delta g_2(r')}{g_2^{\text{eq}}(r')},$$  

(B1)

where $\int_{\text{out}}$ denotes integration “outside the core,” i.e., over $r'$ such that $r' > 1$. In terms of $f_1$, Eq. (19) reads as

$$2D_0 \frac{\partial^2}{\partial r^2} f_1(r) = \frac{\gamma^* \sigma^3}{10 \sigma^3} \frac{g^{\text{eq}}(r) - 1}{r^2},$$

(B2)

with the boundary condition (i.e., the no-flux condition)

$$\hat{r} \cdot 2D_0 \frac{\partial}{\partial r} f_1(r) = \frac{\gamma^* \sigma^3}{10 \sigma^3} \frac{g^{\text{eq}}(r)}{r^2},$$

(B3)

where $\hat{r} = r / r$. To proceed we first solve Eq. (B2) disregarding the boundary condition. In this way we obtain

$$f_1^{\text{eq}}(r) = \frac{\gamma^* \sigma^3}{10 \sigma^3} \left[ g^{\text{eq}}(r) - 1 \right] + \frac{5}{\sigma^3} \int_{\sigma} d r' \ r' \left[ g^{\text{eq}}(r') - 1 \right].$$

(B4)

To take care of the boundary condition (B3) we add to this expression a function that satisfies a homogeneous diffusion equation for $r > 0$ and has a proper symmetry,

$$f_1^{\text{bd}}(r) = \frac{\gamma^* \sigma^3}{10 \sigma^3} \frac{\sigma^3}{r^3},$$

(B5)

where the coefficient $\alpha$ is adjusted to satisfy (B3). In this way we obtain

$$f_1(r) = \frac{\gamma^* \sigma^3}{10 \sigma^3} \left[ 1 - \frac{3}{\sigma^3} \int_{\sigma} d r' \ r' \left[ g^{\text{eq}}(r') - 1 \right] \right] = \frac{\gamma^* \sigma^3}{10 \sigma^3} f_1(r),$$

(B6)

where the second equality defines a new function $f_1$. To obtain $\delta g_2(r)$ we now have to invert relation (B1). This is facilitated by the symmetry of the kernel $\delta - ne^{\text{eq}}$ that allows us to perform angular integrations explicitly. On the other hand, the inversion is impeded by the fact that it has to be performed within the space of functions defined “outside the core,” i.e., for $r > \sigma$. It can be checked that the final result has the following form:

$$\delta g_2(r) = \gamma^* \frac{\chi y}{r^2} g_2^{\text{eq}}(r) \left[ f_1(r) + 4 \pi n \int_{\sigma} d r' \ r'^2 h_{22}(r, r') f_1(r') \right].$$

(B7)

where $h_{22}$ satisfies Eq. (26).

APPENDIX C: BROWNIAN DYNAMICS SIMULATIONS

A detailed description of the BD simulations will be published separately. Here we just give the essential information related to the comparison between our theory and the simulations.

We performed a number of BD simulations of 1372 spherical colloidal particles. We used the screened Coulomb interaction potential,

$$V(r) = A \exp \left( - \kappa (r - \sigma_{\text{BD}}) \right),$$

(C1)

with $A = 475k_B T \sigma_{\text{BD}}$ and $\kappa \sigma_{\text{BD}} = 24$. Note that the parameters were chosen in such a way that our highest volume fraction point reproduces the state point used by Rastogi et al. The cutoff distance was $2.5 \sigma_{\text{BD}}$, and the time step was $10^{-4} \tau_{\text{BD}}$, where $\tau_{\text{BD}} = \sigma_{\text{BD}}^2 / D_{\text{BD}}$.

We simulated systems at dimensionless densities, $n \sigma_{\text{BD}}^3$, equal to 0.51, 0.408, 0.306, and 0.204. At each density we first simulated an equilibrium suspension and then proceeded to investigate the influence of the flow. We used four different dimensionless shear rates, $\gamma^*$, equal to 0.1, 0.2, 0.5, and 1. Comparing results obtained at these shear rates we can show28 that even at the highest volume fraction the system approaches the low-shear regime at $\gamma^* = 0.1$ (at lower volume fractions the linear regime is considerably broader). The major problem was to obtain statistically accurate data at lower densities and shear rates. To this end we performed very long runs, up to $20 \tau_{\text{BD}}$ at the lowest density and $\gamma^* = 0.1$.

During equilibrium simulations we monitored, among other quantities, the structure factor. We compared measured structure factors with those predicted for hard-sphere suspensions by the Verlet–Weiss modification of the Percus–Yevick expression. In this way we determined that the above mentioned densities correspond to the following effective hard-sphere volume fractions: 0.50, 0.43, 0.32, and 0.23. In addition, we got a relation between $\sigma_{\text{BD}}$ and the effective hard-sphere diameter $\sigma$.

During nonequilibrium runs we monitored, among other quantities, interaction contribution to the stress and the $xy$ component of the pair distribution. To evaluate these quantities we used the procedure outlined in Ref. 8 [see Eqs. (8) and (17) therein]. From the stress we obtained shear-rate-dependent viscosity whereas from the $xy$ component of the pair distribution we got the distortion of the structure factor.

To calculate the limiting low-shear viscosity we followed Ref. 8 and extrapolated shear-dependent viscosity to zero shear rate. For dimensionless densities, $n \sigma_{\text{BD}}^3$, equal to 0.51, 0.408, 0.306, and 0.204 we obtained dimensionless
low-shear viscosities, $\Delta \eta/\eta_s$, equal to $13.2 \pm 1.2$, $1.66 \pm 0.062$, $0.468 \pm 0.028$, and $0.142 \pm 0.023$, respectively.

To calculate the distortion of the structure factor an extrapolation of the $r$-space pair distribution to larger distances is required in order to get reasonable results for smaller $k$ values. This extrapolation has little influence on the structure factor above $k_s=6$. Note that unlike the low-shear viscosity, the structure factor distortion presented in this work has not been extrapolated to the zero shear rate.