Model of clustering in the string phase of a shearing hard sphere colloidal dispersion

R. S. Farr*
Cavendish Laboratory, Madingley Road, Cambridge CB3 OHE, United Kingdom
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We consider a system where shear thickening can only be produced by clustering. A model is presented for the growth of clusters from a string phase, and the model is solved analytically in two and three dimensions for the case of nearly circular and nearly spherical clusters. The equations are homogeneous and so do not predict a preferred cluster size, but approximate results for the ratio of the first normal stress difference $N_1=\sigma_{xx}-\sigma_{yy}$ to the viscous enhancement are obtained. [S1063-651X(98)08909-0]

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I. INTRODUCTION

Continuous shear thickening, in which there is a smooth increase of viscosity, η with shear rate $\dot{\gamma}$ is observed in a wide range of colloidal systems at sufficiently high shear rate (see, e.g., [1] for a review of the field).

We are concerned here with a fairly concentrated colloid in which all interactions and hydrodynamics may be approximated to be pairwise additive in the resistance matrix. Therefore a pair of particles (i,j) at positions $\mathbf{r}_i$, $\mathbf{r}_j$ experience a conservative repulsive force, given for the first by

$$\mathbf{F}^c_{ij}=f(r)\mathbf{e}_r \tag{1}$$

for some function *f*. Here $r=|\mathbf{r}_i-\mathbf{r}_j|$ and $\mathbf{e}_r=(\mathbf{r}_j-\mathbf{r}_i)/r$ is a unit vector in the direction of the line of centers.

Furthermore, if there is no viscoelastic coupling such a pair experiences a dissipative force, given for the first by

$$\mathbf{F}^d_{ij}=-\boldsymbol{\alpha}(r)\cdot(\mathbf{v}_i-\mathbf{v}_j)-\beta\mathbf{v}_i\,. \tag{2}$$

Here $\mathbf{v}_i$ and $\mathbf{v}_j$ are the velocities of the closest surface points of the two bodies, β represents a one particle drag term through the fluid, and $\boldsymbol{\alpha}(r)$ is a positive semidefinite rank 2 tensor, whose components are the various pair drag coefficients.

We consider the colloid particles to have a central hard core of radius r_c on which the solvent satisfies stick boundary conditions. This said, we expect real systems described by Eqs. (1) and (2) to fall into two categories. The first is where the volume fraction of the cores is high; the hydrodynamics is now well approximated by lubrication theory applied to the gaps between the particles, and a form of Eq. (2) will hold in which β is relatively unimportant. The second case, which we do not consider here, will be the dilute limit where the conservative interactions become pair interactions and if we adopt a Rouse level (free draining) approximation to the hydrodynamics, Eq. (2) will hold, with $\boldsymbol{\alpha}$ negligible.

The viscous interactions of Eq. (2) will dissipate a power

$$P=\frac{1}{2}\sum_{i,j}\,[(\mathbf{v}_i-\mathbf{v}_j)\cdot\boldsymbol{\alpha}\cdot(\mathbf{v}_i-\mathbf{v}_j)+2\beta|\mathbf{v}_i|^2]. \tag{3}$$

From this we can calculate the shear stress σ which will be related to $\tilde{P}$, the power dissipated per unit volume (in three dimensions) or per unit area (in two dimensions) by $\tilde{P}=\sigma\dot{\gamma}$.

For such a system under simple shear, one can imagine two mechanisms whereby the viscosity may increase with shear rate.

First, even in the absence of shear thickening, the stress required to drive the system increases with shear rate. For a disordered system, a typical pair of particles near the compression direction of the flow must be driven together with greater force, to generate this stress. If the conservative force of Eq. (1) is soft, then the minimum separation of pairs of particles in this direction will decrease, and consequently for typical viscous interactions, we expect $|\boldsymbol{\alpha}(r)|$ to increase. In a continuous flow, the velocities in Eqs. (2) and (3) will scale with $\dot{\gamma}$ and so the bulk viscosity must increase [2].

On the other hand, if extended rigid structures form in the flow [3–5], the relative velocities between some pairs of particles are forced to increase for a given shear rate. These will produce a greater power dissipation from Eq. (3) and hence a greater bulk viscosity compared with when there is no clustering.

In this paper, I shall try to separate the effects of these two mechanisms by considering a system in which the first is inoperative. The system consists of colloidal particles with a hard repulsive potential, for example, an infinite potential step preventing particle overlap, together with possibly a weak repulsive part, or Brownian motion. The function in Eq. (1) is therefore assumed to approximate the form

$$f(r)=\begin{cases}\infty & \text{for } r<2a\\ F_0 & \text{for } r<2a\end{cases} \tag{4}$$

for some F_0 and $a>r_c$. This rigorously prevents particles approaching more closely than $r=2a$.

In order to prevent shear thickening from the first mechanism, we consider the case where either the fluid is free draining (that is, we adopt a Rouse level approximation to the hydrodynamics which will be a very poor approximation at high concentrations), or the drag coefficients are independent of separation, save for some cutoff at separations several times larger than the particle radius a. We can arrange this second case in the following way: the drag coefficients

*Electronic address: rsf10@phy.cam.ac.uk

of Eq. (2) arise from fluid flow in the gaps between particles, treated in the lubrication approximation. Some of the components of $\boldsymbol{\alpha}$ will therefore diverge as the hard cores come into contact (a particle separation of $2r_c$). The repulsive force of Eq. (4) thus serves to hold the particles at a greater separation where $\boldsymbol{\alpha}$, although not strictly constant, is a weaker function of the interparticle gap.

We must now consider what experimental systems conform to the requirements of our model; a reasonable approximation may be produced by a swollen polymer brush chemically attached to the particle surface. Here the conservative force is produced entropically as the brush is compressed, and the drag coefficients are well represented by lubrication theory for closely approaching particles.

Large computer simulations of such colloidal systems under simple shear have recently been performed [4,5]. It is observed that at low shear rates, the particles order into a ''string phase'' in which the particle centers are arranged in lines parallel to the ''flow'' direction. These lines frequently form a well ordered, triangular array in the ''gradient-vorticity'' (y-z) plane. (See [7] for a theoretical treatment.)

If the shear rate is increased, the importance of the constant repulsive term in Eq. (4) which stabilizes the string order will be reduced. It is then observed that disordered regions (as well as dislocations) appear in the flow [4,6] and this change is associated with shear thickening (although in other systems, shear thickening can occur from a disordered state). It should be noted, however, that in the simulations, the disordered regions are often comparable in size to the simulation cell and so their dynamics are affected by the periodic boundary conditions.

The sections below describe and solve a model for the dynamics of an isolated cluster in such a dispersion. If clusters are not dilute, or grow very large, as will happen if the volume fraction defined on the hard sphere radius a is high, then the isolated clusters will aggregate, and we expect some kind of logjam (as analyzed, for example, in [8]).

II. THE MODEL

Consider either a two dimensional (2D), or three dimensional simple shear flow where $\hat{\mathbf{x}},\hat{\mathbf{y}},\hat{\mathbf{z}}$ are unit vectors in the ''flow,'' ''gradient,'' and (in 3D only) ''vorticity'' directions, respectively. The bulk string phase deforms in simple shear, with a uniform strain rate $\dot{\gamma}$, and we consider an isolated cluster that has formed in this bulk flow. The cluster is a random glassy region of the colloidal particles composing the string phase, and resists the local affine deformation $\dot{\gamma}$ present in the string phase. It therefore rotates as a rigid body with some angular velocity $\boldsymbol{\omega}=\omega\hat{\mathbf{z}}$ in the bulk flow of particles. The situation is shown schematically for the 2D case in Fig. 1.

We consider the case where the dimensions of the cluster are much greater than a, the colloid radius. In this limit, the string phase may be regarded as a continuum.

Let the unit normal to the surface of the cluster at position $\mathbf{r}$ from its center be $\hat{\mathbf{n}}$, then the velocity of this point of the cluster is

$$\mathbf{v}=\boldsymbol{\omega}\times\boldsymbol{r}. \tag{5}$$

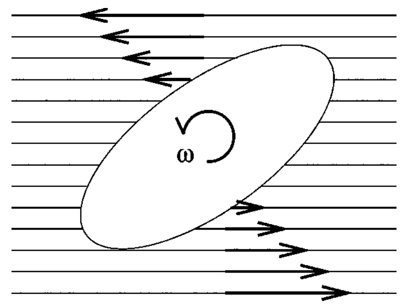

FIG. 1. Schematic picture of a cluster in a simple shear flow. ω (dimensions s^{-1}) is the angular velocity of the cluster, approximately equal to one-half the shear rate.

The local velocity of the string phase, which, in a free draining approximation to the hydrodynamics (discussed below), we assume to be approximately undisturbed by the presence of the cluster, will be

$$\mathbf{u}=-\dot{\gamma}(\mathbf{r}\cdot\hat{\mathbf{y}})\hat{\mathbf{x}}. \tag{6}$$

There will therefore be a flux of particles onto the cluster surface, given by

$$J=\hat{\mathbf{n}}\cdot(\mathbf{v}-\mathbf{u})\rho_0, \tag{7}$$

where ρ_0 is the number of particles per unit area (2D) or per unit volume (3D) in this phase.

The flux J according to this formula may have either sign. It is a simple matter to write down an equation embodying the assumption that particles may be accreted with greater ease than they are lost by the cluster [as an extreme example, one might set $J=0$ if $\hat{\mathbf{n}}\cdot(\mathbf{v}-\mathbf{u})<0$]. However, this nonlinear constraint leads to a difficult mathematical problem as the flux J would no longer be a linear function of $\hat{\mathbf{n}}\cdot(\mathbf{v}-\mathbf{u})$ and Eqs. (8) and (9) would be fully nonlinear partial differential equations. A numerical solution would then be necessary.

For our system, where the hydrodynamic forces are independent of separation for small separations, I shall make the simpler assumption that the particles are torn from the cluster in the same manner in which they are added. We thus interpret negative J as removal of particles from the cluster, and the growth equation for the cluster may readily be constructed. In 2D, we adopt plane polar coordinates $\{r,\theta\}$ with the $\theta=0$ axis being parallel to $\hat{\mathbf{x}}$, while in 3D we use spherical polars $\{r,\theta,\phi\}$ with $\theta=0$ being in the $\hat{\mathbf{z}}$ direction, and $\theta=\pi/2$, $\phi=0$ in the $\hat{\mathbf{x}}$ direction. In these coordinates, the growth equation in two dimensions becomes

$$\frac{\partial r}{\partial t}+\omega\frac{\partial r}{\partial\theta}=Ja^2\left(\frac{a}{h}\right), \tag{8}$$

while in three dimensions we find

$$\frac{\partial r}{\partial t}+\omega\frac{\partial r}{\partial\phi}=Ja^3\left(\frac{a}{h}\right), \tag{9}$$

where h is the gap between the hard spheres (of radius a) in the string phase. These equations are homogeneous in r and therefore do not single out a preferred size for the clusters in the flow.

The factor of (a/h) in Eqs. (8) and (9) represents the effect of the volume excluded to the particles, reflecting the fact that the surface of the cluster is a density wave in the concentrated system, and so its velocity may be high, even when the individual particles are moving slowly. This is the same physics that governs the growth of traffic jams on urban streets; the individual vehicles may be moving slowly, while the boundary between moving and stationary vehicles can have a much larger velocity (in the opposite direction). See, for example, [9].

Given that the system may be concentrated, it is important to consider the applicability of the free draining approximation in the growth equation. For a strictly 2D system, it is clearly inappropriate, as the particle contacts will percolate at a low area fraction; however, if the 2D system consists of disks at a fluid-fluid interface, then free draining may be a good approximation up to high area fraction.

In 3D, we define a ''hydrodynamic volume fraction'' $\phi_{\rm hydr}$ for the string phase, in the following manner: if the suspension is diluted with solvent to increase its volume by a large factor L, then the volume fraction $\phi_{\rm dlt}$ of this new dilute suspension may be measured from its bulk viscosity $\eta_{\rm dlt}$, using the Einstein relation

$$\eta_{\rm dlt}=\eta_0[1+(5/2)\phi_{\rm dlt}]. \tag{10}$$

We then define the hydrodynamic volume fraction by

$$\phi_{\rm hydr}=L\phi_{\rm dlt}. \tag{11}$$

Let the string phase be at a volume fraction $\phi_{\rm hard}$, defined on the radius of hard sphere repulsion; we therefore expect $\phi_{\rm hydr}\leqslant\phi_{\rm hard}\leqslant\phi_{\rm max}$ for some maximum packing fraction $\phi_{\rm max}$. Furthermore, let $\phi_{\rm clus}$ be the hydrodynamic volume fraction in the cluster. Then (a/h) will diverge as

$$\frac{a}{h}\sim\frac{1}{1-\phi_{\rm hard}/\phi_{\rm max}} \tag{12}$$

close to $\phi_{\rm max}$. Let the physical rate of approach of particles to the cluster surface be $v_p=\hat{\mathbf{n}}\cdot(\mathbf{v}-\mathbf{u})$, then the speed of the cluster surface will be [Eq. (9)]

$$v_{\rm surf}=a^3\rho_0\left(\frac{a}{h}\right)v_p\sim\frac{a^3\rho_0 v_p}{1-\phi_{\rm hard}/\phi_{\rm max}}, \tag{13}$$

and the average back flow velocity will be

$$v_{\rm back}\approx\frac{\phi_{\rm clus}-\phi_{\rm hydr}}{1-\phi_{\rm hydr}}v_p. \tag{14}$$

In particular, the ratio $v_{\rm back}/v_{\rm surf}\to 0$ as the maximum packing fraction $\phi_{\rm max}$ is approached. Thus back flow becomes negligible and it is a reasonable approximation that the velocity of particles in the string phase is not disturbed by the presence of the cluster in this limit.

III. THE EQUATION FOR NEARLY CIRCULAR CLUSTERS IN 2D

For a nearly circular cluster, $\epsilon=(1/r)(\partial r/\partial\theta)$ is a small number and consequently I truncate Eq. (5), retaining only terms of $O(\epsilon)$. For $\epsilon<0.4$, this corresponds to an axial ratio for a cluster, of less than 2. Furthermore, for such a cluster,

$$\omega=\frac{\dot{\gamma}}{2}+O(\epsilon), \tag{15}$$

therefore in the basis $\{\hat{\mathbf{x}},\hat{\mathbf{y}}\}$

$$\hat{\mathbf{n}}\approx\begin{pmatrix}\cos\theta+\dfrac{1}{r}\dfrac{\partial r}{\partial\theta}\sin\theta\\[2ex] \sin\theta-\dfrac{1}{r}\dfrac{\partial r}{\partial\theta}\cos\theta\end{pmatrix}, \tag{16}$$

and the flux of particles onto the surface is, from Eq. (7),

$$J=\rho_0\left(\frac{a}{h}\right)\frac{\dot{\gamma}}{2}\left[r\sin(2\theta)-\frac{\partial r}{\partial\theta}\cos(2\theta)\right]. \tag{17}$$

The equation of motion after the change of variables

$$t=\tilde{t}\dot{\gamma}/2, \tag{18}$$

$$\frac{\rho_0 a^3}{h}=\rho, \tag{19}$$

and dropping the tilde on the new time variable, is

$$\frac{\partial r}{\partial t}+\frac{\partial r}{\partial\theta}=\rho\left[r\sin(2\theta)-\frac{\partial r}{\partial\theta}\cos(2\theta)\right]. \tag{20}$$

Equation (20) may readily be transformed into a conservation law:

$$\frac{\partial r^2}{\partial t}+\frac{\partial}{\partial\theta}\{r^2[1+\rho\cos(2\theta)]\}=0, \tag{21}$$

from which we see that

$$\frac{d}{dt}\int_0^{2\pi}\frac{1}{2}r^2d\theta=-\frac{r^2}{2}[1+\rho\cos(2\theta)]\Big|_0^{2\pi}=0, \tag{22}$$

or in other words, the total area of the cluster is conserved.

The cluster does not therefore increase the number of particles it contains, but it will increase the viscosity of the suspension as it becomes more elongated in the compression or extensional directions [i.e., $(\hat{\mathbf{x}}\pm\hat{\mathbf{y}})/\sqrt{2}$].

Equation (21) possesses the obvious stationary solution

$$r^2\propto\frac{1}{1+\rho\cos(2\theta)}, \tag{23}$$

which is an ellipse with major axis parallel to the ''gradient'' direction. This solution has the unphysical limit that the ratio of major to minor axes diverges as $\rho\to 1$. The solution is of course not valid in this limit, but the origin of the divergence may readily be seen; for, suppose the cluster becomes extended in the compression direction from accreting particles, and then rotates a little beyond this direction. Accretion will then occur preferentially on the side nearest the flow direction, and the effective angular velocity of the boundary of the cluster will be reduced from $\dot{\gamma}/2$. The $\rho\to 1$ limit corresponds to this effective angular velocity tending to zero, as will be seen quantitatively in the next section. In practice, what will actually happen is that as the axial ratio of the ellipse increases, the approximation that the material angular velocity ω of the cluster stays equal to $\dot{\gamma}/2$ will break down. The cluster will rotate more nearly as a one dimensional rod, i.e.,

$$\omega_{\rm rod}=\dot{\gamma}\,\sin^2\,\theta_{\rm maj}, \tag{24}$$

where $\theta_{\rm maj}$ is the angle the major axis of the ellipse makes with $\hat{\mathbf{x}}$, and will be greater than $\pi/4$ so that $\omega_{\rm rod}>\dot{\gamma}/2$. This will alleviate the problem, sweeping the growing cluster more rapidly past the compression direction.

IV. ANALYTIC SOLUTION FOR NEARLY CIRCULAR CLUSTERS

To solve Eq. (21), which is a quasilinear partial differential equation (QLPDE), we introduce a characteristic coordinate s, so that

$$r^2=r^2(s),\quad \theta=\theta(s),\quad t=t(s). \tag{25}$$

Therefore

$$\frac{dr^2}{ds}=\frac{\partial r^2}{\partial\theta}\frac{d\theta}{ds}+\frac{\partial r^2}{\partial t}\frac{dt}{ds}, \tag{26}$$

and by comparison with Eq. (21) we find

$$\frac{dt}{ds}=1, \tag{27}$$

$$\frac{dr^2}{ds}=2r^2\rho\,\sin(2\theta), \tag{28}$$

$$\frac{d\theta}{ds}=1+\rho\,\cos(2\theta). \tag{29}$$

From Eqs. (28) and (29) we see that

$$r^2\propto\left(\frac{ds}{d\theta}\right), \tag{30}$$

which allows an easy analytic solution, for let us introduce a new variable θ_0 which is an integration constant of Eq. (29), and allows us to specify the initial conditions

$$r^2(\theta,t=0)=r_0^2(\theta_0), \tag{31}$$

then the solution is

$$r^2(\theta,t)=\frac{r_0^2(\theta_0)[1+\rho\,\cos(2\theta_0)]}{1+\rho\,\cos(2\theta)}, \tag{32}$$

where

$$\theta=\tan^{-1}\left[\left(\frac{1+\rho}{1-\rho}\right)^{1/2}\tan\{\sqrt{1-\rho^2}(t+c)\}\right] \tag{33}$$

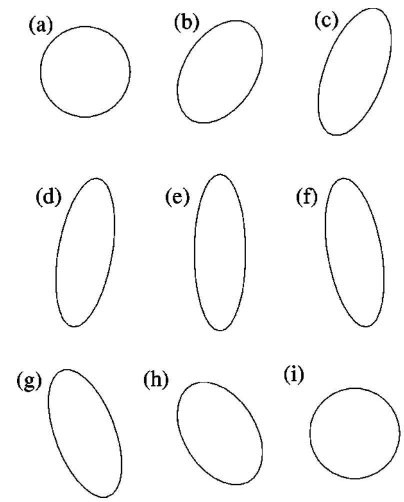

FIG. 2. Solution for a two dimensional cluster, with $\rho=0.5$. Nine configurations (shapes of the cluster) (a)–(i) are shown for equally spaced times covering a whole period of the evolution, and such that in (i) the cluster has returned to its initial state. The flow direction is left-right, and the initial shape of the cluster, shown in (a), is a circle.

$$c=\frac{1}{\sqrt{1-\rho^2}}\tan^{-1}\left[\left(\frac{1-\rho}{1+\rho}\right)^{1/2}\tan\,\theta_0\right]. \tag{34}$$

A solution in the form $r(\theta,t)$ may then be obtained by eliminating θ_0 between Eqs. (32), (33), and (34).

For circular initial conditions this leads to

$$r(\theta,t)=\frac{1}{\sqrt{1+\rho\,\cos(2\theta)}}\times\left\{1+\rho\left(\frac{1-\left(\frac{1+\rho}{1-\rho}\right)\tan^2\Delta}{1+\left(\frac{1+\rho}{1-\rho}\right)\tan^2\Delta}\right)\right\}^{1/2}, \tag{35}$$

where

$$\Delta=\tan^{-1}\left\{\left(\frac{1-\rho}{1+\rho}\right)^{1/2}\tan\theta\right\}-\sqrt{1-\rho^2}t. \tag{36}$$

The curve describing the cluster outline is therefore periodic in time, with period $\pi/(\dot{\gamma}\sqrt{1-\rho^2})$.

A plot of this solution at nine equally spaced times covering a complete period of the motion and $\rho=0.5$ is shown in Fig. 2.

V. THE EQUATION FOR NEARLY SPHERICAL CLUSTERS IN 3D

In analogy to two dimensions, we assume that both $(1/r)\partial r/\partial\phi$ and $(1/r)\partial r/\partial\theta\ll 1$. Neglecting the squares of small quantities, we find that since

$$\hat{\mathbf{n}}\propto\frac{\partial\mathbf{r}}{\partial\phi}\times\frac{\partial\mathbf{r}}{\partial\theta}, \tag{37}$$

then in the basis $\{\hat{\mathbf{x}},\hat{\mathbf{y}},\hat{\mathbf{z}}\}$,

$$\hat{\mathbf{n}} \approx \begin{pmatrix} \sin\theta\cos\phi + \dfrac{\sin\phi}{r\sin\theta}\dfrac{\partial r}{\partial\phi} - \dfrac{\cos\theta\cos\phi}{r}\dfrac{\partial r}{\partial\theta} \\ \sin\theta\sin\phi - \dfrac{\cos\phi}{r\sin\theta}\dfrac{\partial r}{\partial\phi} - \dfrac{\cos\theta\sin\phi}{r}\dfrac{\partial r}{\partial\theta} \\ \cos\theta + \dfrac{\sin\theta}{r}\dfrac{\partial r}{\partial\theta} \end{pmatrix}. \tag{38}$$

Thus

$$J = \rho_0\left(\frac{a}{h}\right)\frac{\dot{\gamma}}{2}\left[r\ \sin(2\phi)\sin^2\theta - \cos(2\phi)\frac{\partial r}{\partial\phi} - \frac{1}{2}\sin(2\phi)\sin(2\theta)\frac{\partial r}{\partial\theta}\right], \tag{39}$$

and with a change of variables

$$\tilde{t} = \frac{t\dot{\gamma}}{2}, \tag{40}$$

$$\rho = \frac{\rho_0 a^4}{h}, \tag{41}$$

and dropping the tilde on the new time coordinate, the equation of motion becomes

$$\frac{\partial r}{\partial t} + \frac{\partial r}{\partial\phi} = \rho r\ \sin(2\phi)\sin^2\theta - \rho\ \cos(2\phi)\frac{\partial r}{\partial\phi} - \frac{\rho}{2}\sin(2\phi)\sin(2\theta)\frac{\partial r}{\partial\theta}. \tag{42}$$

This may readily be transformed into the conservation law

$$\frac{\partial r^3}{\partial t} + \frac{\partial}{\partial\phi}\{r^3[1+\rho\ \cos(2\phi)]\} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\{r^3[\sin(2\phi)\cos\theta\ \sin^2\theta]\rho\} = 0, \tag{43}$$

from which we see that

$$\frac{d}{dt}\int_0^{2\pi}\int_0^{\pi}\frac{1}{3}r^3\sin\theta d\theta d\phi = -\int_{\theta=0}^{\pi}\sin\theta\frac{r^3}{3}[1+\rho\ \cos(2\phi)]\Big|_{\phi=0}^{2\pi}d\theta - \int_{\phi=0}^{2\pi}\rho\frac{r^3}{3}[\sin(2\phi)\cos\theta\ \sin^2\theta]\Big|_{\theta=0}^{\pi}d\phi = 0+0. \tag{44}$$

In other words, the volume and hence total number of particles in the cluster is conserved.

The stationary solutions to Eq. (43) are given by separation of variables: let

$$r^3(\theta,\phi,t) = A(\theta)B(\phi), \tag{45}$$

then from Eq. (43)

$$\frac{1}{\rho B\ \sin(2\phi)}\frac{d}{d\phi}[B(1+\rho\ \cos(2\phi))] = -\lambda, \tag{46}$$

$$\frac{1}{A\ \sin\theta}\frac{d}{d\theta}[A\ \cos\theta\ \sin^2\theta] = +\lambda, \tag{47}$$

where λ is an arbitrary real separation constant. Equation (46) solves immediately to give

$$B(\phi) \propto \exp\left[(\lambda-2)\frac{\rho}{2}\cos(2\phi)\right], \tag{48}$$

while Eq. (47) in the range $\theta\in(0,\pi/2)$ gives

$$A(\theta) = \frac{\sqrt{1-\cos\theta}}{\sin^2\theta}\int_{\theta_*}^{\theta}\frac{2\lambda\ \sin^2\theta'}{\sqrt{1-\cos\theta'}}d\theta', \tag{49}$$

where θ_* is arbitrary. The same qualifications apply to this solution as to the two dimensional case [Eq. (23)].

VI. ANALYTIC SOLUTION FOR NEARLY SPHERICAL CLUSTERS

Equation (43) is once more a QLPDE, which we tackle by introducing a characteristic coordinate s: Let

$$t = t(s), \quad \theta = \theta(s),$$
$$\phi = \phi(s), \quad r^3 = r^3(s). \tag{50}$$

Then Eq. (42) leads to

$$\frac{dt}{ds} = 1, \tag{51}$$

$$\frac{d\phi}{ds} = 1+\rho\ \cos(2\phi), \tag{52}$$

$$\frac{d\theta}{ds} = \rho\ \sin(2\phi)\cos\theta\ \sin\theta, \tag{53}$$

$$\frac{dr^3}{ds} = \rho r^3(2+\sin^2\theta - 2\cos^2\theta)\sin(2\phi), \tag{54}$$

and from the conservation law,

$$\frac{1}{r^3}\frac{dr^3}{ds} = -\frac{d^2\phi}{ds^2}\frac{ds}{d\phi} - \left[\frac{\sin\theta}{\sin(2\phi)}\frac{d\theta}{ds}\right]^{-1}\frac{d}{ds}\left[\frac{\sin\theta}{\sin(2\phi)}\frac{d\theta}{ds}\right]. \tag{55}$$

Equation (55) integrates to

$$r^3 \propto \frac{1}{[\sin\theta/\sin(2\phi)](d\phi/ds)(d\theta/ds)}. \tag{56}$$

Upon integrating Eqs. (52) and (53), we will introduce two constants, which we choose so that $\phi=\phi_0$, $\theta=\theta_0$ when $s=t=0$. The initial shape of the cluster is described by

$$r^3(\theta,\phi,t=0)=r_0^3(\theta_0,\phi_0). \quad (57)$$

From Eq. (56) the solution for all subsequent times will be

$$r^3(\theta,\phi,t)=\frac{r_0^3(\theta_0,\phi_0)[1+\rho\ \cos(2\phi_0)]\cos\ \theta_0\ \sin^2\ \theta_0}{[1+\rho\ \cos(2\phi)]\cos\ \theta\ \sin^2\ \theta}. \quad (58)$$

Equations (51) and (52) readily integrate as in the 2D case to

$$\tan^{-1}\left[\left(\frac{1-\rho}{1+\rho}\right)^{1/2}\tan\ \phi\right]-\tan^{-1}\left[\left(\frac{1-\rho}{1+\rho}\right)^{1/2}\tan\ \phi_0\right]$$
$$=t\sqrt{1-\rho^2}, \quad (59)$$

while for Eq. (53) we have

$$\int_{\theta'=\theta_0}^{\theta}\frac{d\theta'}{\cos\ \theta'\ \sin\ \theta'}=\int_{t'=0}^{t}\rho\ \sin[2\phi(t')]\frac{dt'}{d\phi}d\phi$$
$$=\int_{\phi'=\phi_0}^{\phi}\rho\frac{\sin(2\phi')}{1+\rho\ \cos(2\phi')}d\phi', \quad (60)$$

which leads to

$$\left(\frac{\cos(2\theta)-\sin(2\theta)}{\sin(2\theta)}\right)[1+\rho\ \cos(2\phi)]^{1/2}$$
$$=\left(\frac{\cos(2\theta_0)-\sin(2\theta_0)}{\sin(2\theta_0)}\right)[1+\rho\ \cos(2\phi_0)]^{1/2}. \quad (61)$$

Eliminating θ_0 and ϕ_0 between Eqs. (58), (59), and (61) leads to an equation for $r(\theta,\phi,t)$. Again the solution is periodic in time, with period $\pi/(\dot{\gamma}\sqrt{1-\rho^2})$.

Figure 3 shows the solution for an initially spherical cluster with $\rho=0.5$. The way the figures are shown is to choose 750 random directions in space, and for each, the corresponding point on the surface of the cluster is shown projected onto the ''flow-gradient'' (i.e., $\hat{\mathbf{x}}-\hat{\mathbf{y}}$) plane. This gives some indication of the three dimensional form of the cluster. The images are for nine equally spaced times covering a complete period of the motion.

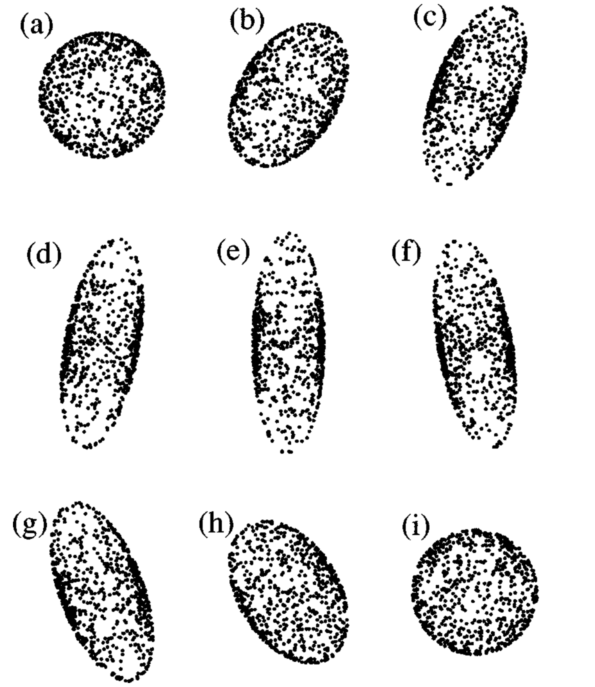

FIG. 3. Solution for a three dimensional cluster, with $\rho=0.5$. Nine configurations (shapes of the cluster) (a)–(i) are shown for equally spaced times covering a whole period of the evolution. The flow direction is left-right. The cluster is initially spherical in (a), and returns to this shape in (i). To give some impression of the three dimensional form of the cluster, what is plotted is the projection of random points on the cluster surface, onto the $\hat{\mathbf{x}}$-$\hat{\mathbf{y}}$ plane.

VII. ESTIMATES OF THE FIRST NORMAL STRESS DIFFERENCE

We now turn to the possible rheological consequences of the model, and in particular try to estimate the first normal stress difference $N_1=\sigma_{xx}-\sigma_{yy}$. In Sec. II it was shown that the solvent back flow from particles aggregating onto the cluster surface may be neglected at high volume fraction, thus justifying the assumption that the surrounding string phase is undistorted by the presence of the cluster. This said, the hydrodynamic interactions of a collection of particles are not well modeled by a purely free draining (Rouse level) approximation. Furthermore, the absence of a significant back flow, which was necessary to derive the growth dynamics of the clusters, does not rule out the possibility of a pair drag contribution to the hydrodynamic interactions, which will turn out to be the factor controlling the value of N_1.

From the growth equations derived in Secs. IV and VI, we see that in two dimensions the clusters which are circular at time $t=0$ are unchanged by the transformation $\{t\to -t,\ \theta\to\pi-\theta\}$, while in three dimensions they are invariant under $\{t\to -t,\ \phi\to\pi-\phi,\ \theta\to\theta\}$. Therefore if the stress tensor is calculated in a free draining (Stokes drag) approximation, we will find that $N_1=0$.

The pair drag part of the hydrodynamics thus provides the only contribution to the first normal stress difference, and in order to crudely estimate the effect of the cluster upon the stress tensor $\boldsymbol{\sigma}$, consider the radial component of the velocity of particles relative to the cluster surface, i.e.,

$$v_{\hat{\mathbf{r}}}=(\mathbf{v}-\mathbf{u})\cdot\hat{\mathbf{r}}, \quad (62)$$

where positive $v_{\hat{\mathbf{r}}}$ corresponds to particles leaving the surface of the cluster. We now consider another important effect of the hard sphere conservative interaction, for it introduces a physical distinction between the directions where $v_{\hat{\mathbf{r}}}$ has different signs. When $v_{\hat{\mathbf{r}}}$ is negative, the bonds in the cluster cannot deform, because the particles press against their hard sphere potentials. Consequently, the compressive force in the bonds along a radius may be estimated as

$$f_{\mathrm{comp}}\approx\alpha v_{\hat{\mathbf{r}}}, \quad (63)$$

where α is the relevant pair drag coefficient. On the other hand, when a particle is leaving the surface, all the bonds deep inside the cluster can deform a little, in order to bring the surface velocity up to $v_{\hat{\mathbf{r}}}$. An estimate of the tensional force in the bonds along a radius is therefore

$$f_{\text{ext}} \approx \alpha \frac{a}{r} v_{\hat{\mathbf{r}}}. \tag{64}$$

Let $H(x)$ be the Heaviside step function,

$$H(x) = \begin{cases} 0 & \text{if } x < 0 \\ 1 & \text{if } x \geqslant 0, \end{cases} \tag{65}$$

then we may estimate the contribution to the stress in the dispersion from the cluster by, in 2D,

$$\boldsymbol{\sigma}_{2\text{D}} \approx -\frac{1}{A_{\text{clus}}} \int_0^{2\pi} \frac{r^2 d\theta}{2a^2} \alpha a v_{\hat{\mathbf{r}}} \hat{\mathbf{r}}\hat{\mathbf{r}} \left[H(v_{\hat{\mathbf{r}}}) + H(-v_{\hat{\mathbf{r}}}) \frac{a}{r} \right], \tag{66}$$

while in 3D

$$\boldsymbol{\sigma}_{3\text{D}} \approx -\frac{1}{V_{\text{clus}}} \int_0^{2\pi} \int_0^{\pi} \frac{r^3 \sin\theta d\theta d\phi}{3a^3} \alpha a v_{\hat{\mathbf{r}}} \times \hat{\mathbf{r}}\hat{\mathbf{r}} \left[H(v_{\hat{\mathbf{r}}}) + H(-v_{\hat{\mathbf{r}}}) \frac{a}{r} \right], \tag{67}$$

where A_{clus} is the cluster area in 2D, and V_{clus} its volume in 3D.

In both of Eqs. (66) and (67), the first term, from the compressive load, will dominate for large clusters.

Just retaining this term, we can use it to find a value for the ratio of the first normal stress difference N_1 to the viscosity enhancement due to the large cluster, $\eta = |\sigma_{xy}|/\dot{\gamma}$. This ratio is significant, because, provided the clusters are large, it does not depend upon either the size of the clusters, or their concentration in the suspension. The normal stress difference N_1 is also an easily measurable characteristic of the flow in experiments and simulations.

Figure 4 shows an estimate of the ratio $N_1/|\sigma_{xy}|$ from Eqs. (66) and (67) computed as an average over a whole period of the motion [that is, a time of $\pi/(\dot{\gamma}\sqrt{1-\rho^2})$], for two and three dimensions at different values of ρ, with circular and spherical initial conditions, respectively. The figures also contain data for the maximal axial ratio of the ellipsoids in the flow, to give an indication of the range of ρ for which the results are valid.

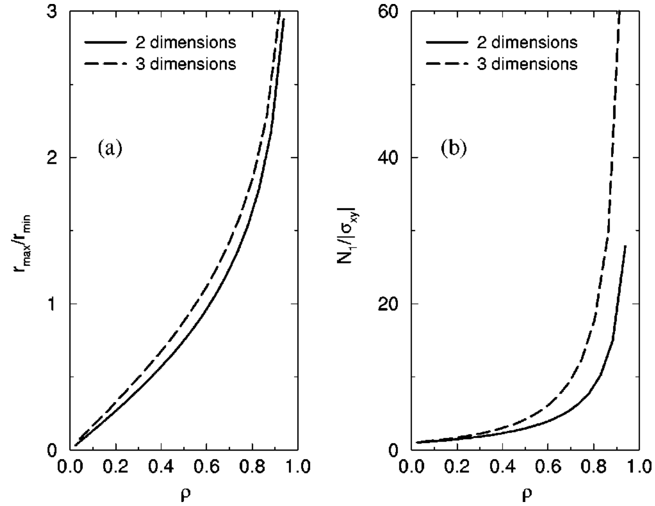

FIG. 4. (a) Plot of the maximal axial ratio $r_{\max}/r_{\min}$ (no units) encountered in one period of the motion of an initially circular and an initially spherical cluster, as a function of ρ (no units). The periodic nature of the motion is illustrated for $\rho = 0.5$ in Figs. 2 and 3. (b) Plot of the time average ratio $N_1/|\sigma_{xy}|$ (no units) using the first term in Eqs. (66) and (67). The average is performed over one period of the motion of an initially circular and an initially spherical cluster and plotted as a function of ρ (no units).

In both cases, we see that extended clusters are evidenced by a positive N_1, and both $N_1/|\sigma_{xy}|$ and the maximal axial ratio are proportional to ρ for small ρ. The divergence in $N_1/|\sigma_{xy}|$ at $\rho = 1$ is due to the divergence in the axial ratio, which, as discussed in Sec. III, is unphysical.

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