Viscosities of concentrated dispersions

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A theory is presented to describe the effects of particle shape, orientation, and volume fraction on the anisotopic viscosities of concentrated colloidal dispersions. We start with Stokesian dynamics; a particle-shape tensor is derived from the analysis, which is then included in a fluid lattice model for the determination of the anisotopic viscosities. The theory considers not only the interaction between the particles but also the local interaction within the equilibrium microstructure. For spherical particles, our theory compares well with experimental data from dilute, semidilute, or concentrated dispersions. For nonspherical particles at high concentrations, our calculation reveals that the system undergoes a transition which is identified as the percolation threshold. At this critical concentration (ϕ_c), the fluidity of concentrated dispersions slows down drastically. Our calculation reveals that this threshold is a strong function of particle shape and orientation.

I. INTRODUCTION

There has been a great deal of interest in the structure-property relationships of colloidal dispersions lately, as evidenced by the abundance of literature [1–13]. Additional references can be found in a recent review [14]. Colloidal dynamics is a strong function of particle size, shape, orientation and concentration, the interactions of dispersed particles and of the microstructure of liquid, and shear flow. The viscosity of dilute [1] and semidilute [2,3] solutions of hard spheres increases gradually with the volume fraction (ϕ) of particles. On the other hand, Krieger [4] and de Kruif and co-workers [5,6] have observed a drastic increase in the effective viscosity at high concentrations. Therefore the interaction mechanism in high concentrations must be different from that in low ones. It is reasonable to expect that the short-range local interaction within the equilibrium microstructure may play a far more important role in understanding such a sharp increase in viscosity. Recent publications [7,8] have pointed out that (1) the modern microscopic theories [7–11] are restricted to low volume fractions since they only include pair interactions, and (2) concentrated dispersions are bound to be studied in a different way. Furthermore, the effective viscosities of colloidal dispersions have to be strongly influenced by the particle shape and flow orientation, but there is very little work being done in this area. The focus of the above-mentioned modern theories has been on hard or adhesive hard spheres. It is not clear how they can be extended to describe nonspherical particles—the main interest of this work.

The purpose of this paper is therefore to find an alternative approach that will lead to a solution of an unsolved problem— *the effects of particle shape and flow orientation on the anisotropic shear viscosities at high particle concentrations.* Our theory consists of coupling hydrodynamics and statistical mechanics, expressed in terms of a liquid lattice model. In addition to the well-

studied long-range particle-particle interactions, we shall analyze the short-range intermolecular interaction within the equilibrium microstructure, which may be the dominant interaction mechanism at high ϕ. We start with Stokesian dynamics; the shear flow is solved in terms of Green's function and bulk stresses. For simplicity, the particle-particle interaction at finite concentrations under the influence of an applied shear field will be treated by a mean-field theory. The microstructure of liquids will be analyzed by using a lattice model. For spherical particles, the present theory will be compared with the viscosity data taken from the literature and the predictions of recent theories. For nonspherical particles, the effects of particle shape and orientation will be calculated.

II. EFFECTIVE VISCOSITIES

Stable colloidal dispersions of nonspherical particles often display clear particle orientation. To calculate the anisotropic viscosities of the two-phase system requires a determination of its flow field. Consider a uniform strain rate, e_{ij}^o, applied on the system. The total strain rate tensor in the particle or in the liquid can be written as

$$e_{kl}(\mathbf{r})=e_{kl}^0+e_{kl}^C(\mathbf{r}) . \tag{1}$$

The dispersed particles add an extra contribution: the local strain rate $\mathbf{e}_{ij}^C$, which is function of coordinates ($\mathbf{r}$). The corresponding stress tensor in a particle is

$$\sigma_{ij}^{(1)}(\mathbf{r})=C_{ijkl}^{(1)}[e_{kl}^0+e_{kl}^C(\mathbf{r})] , \tag{2}$$

where $C_{ijkl}^{(1)}$ are the viscosities of particle. The usual summation convention is followed for repeated suffixes over values 1, 2, and 3. A similar expression for the stress tensor in a liquid medium can also be written simply by replacing $C_{ijkl}^{(1)}$ in Eq. (2) with $C_{ijkl}^{(2)}$, the viscosities of liquid. Therefore the bulk stress tensor is defined as

$$\sigma_{ij}^B(\mathbf{r})=(C_{ijkl}^{(2)}-C_{ijkl}^{(1)})[e_{kl}^0+e_{kl}^C(\mathbf{r})] , \tag{3}$$

which contributes to a body force needed in seeking the solution of the steady-state shear flow in Sec. III. When $C_{ijkl}^{(1)} = C_{ijkl}^{(2)}$, we expect the trivial solution $\sigma_{ij}^B = e_{ij}^C = 0$. For simplicity, both the particle and liquid phases are assumed to be isotropic. That is,

$$C_{ijkl}^{(\alpha)} = \eta_\alpha(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk} - \tfrac{2}{3}\delta_{ij}\delta_{kl}) , \quad \alpha = 1,2 , \tag{4}$$

where δ_{ik} is the Kronecker delta and η_1 and η_2 are the shear viscosities of particle and liquid, respectively.

The effective anisotropic viscosities of a suspension dispersed with nonspherical particles are determined from

$$\eta_{ij} = \frac{\langle \sigma_{ij} \rangle}{2\langle e_{ij}^0 \rangle} , \quad i \neq j , \tag{5}$$

where the angular brackets denote the volume average. There is no summation over repeated suffixes in the above equation and in the rest of the paper unless specified otherwise. When a constant strain rate e_{ij}^0 is applied to a system at infinity, the perturbed local field is not uniform throughout the composite. The average shear stresses in Eq. (5) are given by

$$\langle \sigma_{ij} \rangle = \frac{1}{V} \int_V \sigma_{ij}(\mathbf{r}) dV$$

$$= \frac{1}{V} \left[\int_{V_2} \sigma_{ij} dV + \sum \int_{V_1} \sigma_{ij} dV \right]$$

$$= \frac{2\eta_2}{V} \int_V e_{ij} dV + \frac{1}{V} \sum \int_{V_1} (\sigma_{ij} - 2\eta_2 e_{ij}) dV , \tag{6}$$

where V is the total volume and V_1 and V_2 are the volumes of particle and liquid, respectively. The summation is taken over all particles. The stress field inside a particle is related to the bulk stresses by the volume average over a particle:

$$\langle \sigma_{ij}^B \rangle_1 = 2\eta_2 \langle e_{ij}^B \rangle_1 = -\frac{1}{V_1} \int_{V_1} (\sigma_{ij} - 2\eta_2 e_{ij}) dV . \tag{7}$$

Thus Eq. (6) becomes

$$\langle \sigma_{ij} \rangle = 2\eta_2 (e_{ij}^0 - \langle e_{ij}^B \rangle_1 \phi) , \tag{8}$$

where $\phi = \sum (\text{volume of particle}, V_1)/V$ is the volume fraction. Following Eqs. (5) and (8), the effective viscosities are related to the volume average of bulk stresses at dilute dispersions by

$$\eta_{ij} = \eta_2 \left[1 - \frac{\langle e_{ij}^B \rangle_1}{e_{ij}^0} \phi \right] , \quad i \neq j . \tag{9}$$

In the next two sections, our goal is to determine the volume average of the bulk strain rates of nonspherical particles at finite concentrations.

III. PARTICLE-SHAPE TENSOR

We start with Stokesian dynamics for shear flow in a dilute solution. The total stress tensor and velocity $(\mathbf{v})$ satisfy the linearized Stokes equations where the inertia and convection terms are neglected. In accordance with Eqs. (1) and (3), we seek the solution in the form

$$\mathbf{v} = \mathbf{v}^0 + \mathbf{v}^C \tag{10}$$

and

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}^0 + \boldsymbol{\sigma}^C - \boldsymbol{\sigma}^B . \tag{11}$$

Using Eqs. (10) and (11) and noting that the applied stress field $2\eta_2 \mathbf{e}^0$ is uniform, we obtain the equations of motion and continuity, respectively:

$$\eta_2 \nabla^2 \mathbf{v}^C - \text{grad} p = \nabla \cdot \boldsymbol{\sigma}^B , \quad \text{div} \mathbf{v}^C = 0 , \tag{12}$$

where p is the pressure. The right-hand side of the first equation in Eq. (12) represents a body force. The velocity $\mathbf{v}^C$ can best be solved by using Green's function $\mathbf{G}(\mathbf{r} - \mathbf{r}')$ governed by

$$\eta_2 \nabla^2 \mathbf{G} - \text{grad} p = -\mathbf{I}\delta(\mathbf{r} - \mathbf{r}') , \quad \text{div} \mathbf{G} = 0 , \tag{13}$$

where $\mathbf{I}$ is the unit tensor and δ is Dirac's delta function. Requiring that $\mathbf{G}$ approach zero as $|\mathbf{r} - \mathbf{r}'| \to \infty$, we get [15,16]

$$\mathbf{G}(\mathbf{r} - \mathbf{r}') = \frac{1}{4\pi\eta_2} \left[\frac{\mathbf{I}}{|\mathbf{r} - \mathbf{r}'|} - \frac{1}{2} \nabla\nabla |\mathbf{r} - \mathbf{r}'| \right] . \tag{14}$$

Equation (14) can be written more conveniently as

$$F_{ij}(r) = -8\pi\eta_2 G_{ij}(r) = -\frac{1}{r}(\delta_{ij} + l_i l_j) , \tag{15}$$

with

$$r = |\mathbf{r} - \mathbf{r}'| \quad \text{and} \quad l_i = (x_i - x_i')/r .$$

Therefore the solution of Eq. (12) is

$$v_i^C(r) = -\int_{V_1} \sigma_{jk}^B G_{ij,k}(r - r') d^3 r'$$

$$\simeq \frac{\sigma_{jk}^B}{8\pi\eta_2} \int_{V_1} F_{ij,k}(r - r') d^3 r' , \tag{16}$$

where the bulk stress tensor inside a particle is uniform for dilute dispersions. The strain rates follow directly from Eq. (16) as

$$e_{il}^C = \tfrac{1}{2}(v_{i,l}^C + v_{l,i}^C)$$

$$= \frac{\sigma_{jk}^B}{16\pi\eta_2} \int_{V_1} (F_{ij,kl} + F_{lj,ki}) dV . \tag{17}$$

The shear components of bulk stresses and strain rates are related by

$$\sigma_{jk}^B = 2\eta_2 e_{jk}^B , \quad j \neq k . \tag{18}$$

Equations (17) and (18) lead us to introduce a particle-shape tensor $\mathbf{S}$ defined by the equations

$$e_{il}^C = S_{iljk} e_{jk}^B \tag{19}$$

and

$$S_{iljk} = \frac{1}{8\pi} \int_{V_1} (F_{ij,kl} + F_{lj,ki}) d^3 r' , \tag{20}$$

where the reduced Green's function $\mathbf{F}$ is given by Eq. (15) and the integration is performed in the volume of particle, V_1. Equation (20) clearly reveals that $\mathbf{S}$ depends only

on the shape of the particle. Equations similar to Eq. (20), but with a different Green's function $\mathbf{F}$, for particulate composites in the solid state have been studied previously [17,18]. We are using the same method here to get explicit expressions of the shear components of S_{iljk} with $i \neq l$ and $j \neq k$. For simplicity, the particles are treated as identical spheroids,

$$\frac{x_1^2}{a^2} + \frac{x_2^2}{a^2} + \frac{x_3^2}{c^2} = 1 , \tag{21}$$

with corresponding axes aligned. The medium now becomes anisotropic. The coefficients coupling one shear to another ($S_{1223}, \dots$) are zero. We have two independent shear components of the particle-shape tensor. Using Eqs. (15), (20), and (21), we get

$$S_{1212} = \frac{1}{4}\left[1 - \frac{1-J}{1-\rho^2}\right] \tag{22}$$

and

$$S_{1313} = \frac{1+\rho^2}{2}\frac{1-J}{1-\rho^2} , \tag{23}$$

where $\rho = c/a$ is the aspect ratio and

$$J = \begin{cases} \dfrac{3\rho}{2(1-\rho^2)^{3/2}}[\cos^{-1}\rho - \rho(1-\rho^2)^{1/2}] \text{ for } \rho < 1 & (24a) \\[4mm] \dfrac{3\rho}{2(\rho^2-1)^{3/2}}[\rho(\rho^2-1)^{1/2} - \cosh^{-1}\rho] \text{ for } \rho > 1 . & (24b) \end{cases}$$

For spherical particles, Eqs. (22)–(24) become

$$\frac{1-J}{1-\rho^2} = S_{1212} = S_{1313} = \tfrac{1}{5} \text{ for } \rho = 1 . \tag{25}$$

Figure 1 shows the shear components of the particle-shape tensor as a function of the aspect ratio and shear orientation.
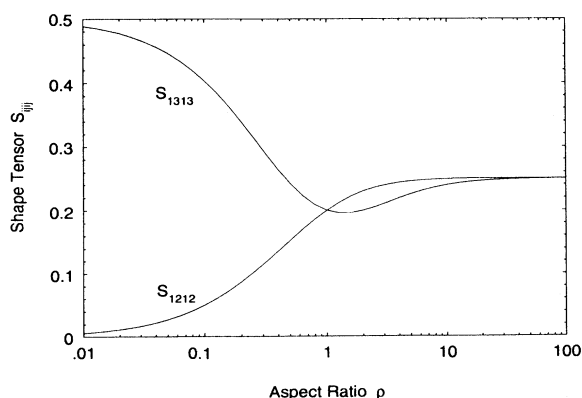

FIG. 1. Shear components of the particle-shape tensor of a spheroid as a function of the aspect ratio and shear orientation.

IV. INTERACTION OF PARTICLES

As the volume fraction increases, the interaction between particles becomes important. For simplicity, this particle-particle interaction is treated by a mean-field theory. When the spatial distribution of aligned particles is assumed to be random and homogeneous, the dispersed system as a whole has to be macroscopic homogeneous, i.e.,

$$\frac{1}{V}\int_v e_{ij}(\mathbf{r})dV - e_{ij}^0 = 0 , \tag{26a}$$

where e_{ij} is given by Eq. (1) due to a uniform shear field e_{ij}^0 acting on the system of volume V. Equation (26a) can be written more explicitly as

$$\begin{aligned}\frac{1}{V}\left[\int_{V_2} e_{ij}^C(\mathbf{r})dV + N\int_{V_1} e_{ij}^C(\mathbf{r})dV\right] \\ = \phi\langle e_{ij}^C\rangle_1 + (1-\phi)\langle e_{ij}^C\rangle_2 \\ = 0 , \end{aligned} \tag{26b}$$

where N is the number of dispersed particles in the total volume V, $\phi = NV_1/V$ is the volume fraction, and

$$\langle e_{ij}^C\rangle_2 = \frac{1}{V}\int_{V_2} e_{ij}^C(\mathbf{r})dV .$$

The average strain rate $\langle e_{ij}^C\rangle_2$ set up in the liquid is a result of the interaction of a particle with its surrounding particles in the case of finite dispersions. When $\phi \to 0$, $\langle e_{ij}^C\rangle_2$ should approach zero. Therefore, in the generalization of Eq. (19) beyond the dilute limit, it is reasonable to assume that

$$\langle e_{il}^C\rangle_1 = S_{iljk}\langle e_{jk}^B\rangle_1 + \langle e_{il}^C\rangle_2 . \tag{27}$$

Eliminating $\langle e_{ij}^C\rangle_2$ between Eqs. (26b) and (27), we obtain

$$\langle e_{il}^C\rangle_1 = (1-\phi)S_{iljk}\langle e_{jk}^B\rangle_1 . \tag{28}$$

In accordance with Eqs. (1)–(3) and (18), the average stresses in a dispersed particle have to satisfy the condition

$$C_{ijkl}^{(1)}[e_{kl}^0 + \langle e_{kl}^C\rangle_1] = C_{ijkl}^{(2)}[e_{kl}^0 + \langle e_{kl}^C\rangle_1 - \langle e_{kl}^B\rangle_1] . \tag{29}$$

The summation over the repeated subscripts applies to the left- and right-hand sides of the above equation. The volume average of the bulk strain rates can be determined from Eqs. (28) and (29), and the effective shear viscosities can then be calculated from Eq. (9):

$$\frac{\eta_{ij}}{\eta_2} = 1 + \frac{(\eta_1/\eta_2 - 1)\phi}{1 + 2(\eta_1/\eta_2 - 1)(1-\phi)S_{ijij}} , \quad i \neq j , \tag{30}$$

where S_{ijij} are given by Eqs. (22)–(24). By using Eqs. (9) and (30), the dependence of intrinsic viscosities on the viscosity ratio η_1/η_2 is calculated in Fig. 2. It clearly reveals that the hard-sphere assumption is valid for $\eta_1/\eta_2 > 100$. However, for nonspherical particles, it may require that $\eta_1/\eta_2 > 1000$. In the rest of the paper, we shall focus our attention on the case of rigid particles and Eq. (30) approximates to
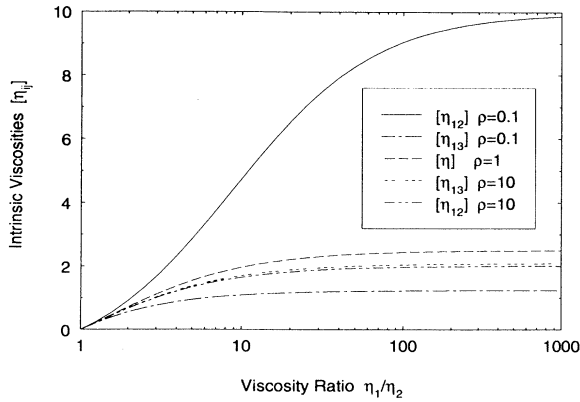
FIG. 2. Dependence of the intrinsic viscosities, $[\eta_{ij}]=(\eta_{ij}-\eta_2)/\eta_2\phi$ as $\phi\to0$, on the viscosity ratio between the particle and liquid. It illustrates the range of validity for the rigid particle assumption in the context of anisotropic viscosities.

$$\frac{\eta_{ij}}{\eta_2}=1+\frac{1}{2S_{ijij}}\frac{\phi}{1-\phi}\ ,\quad \frac{\eta_1}{\eta_2}\gg1\ . \tag{31}$$

V. LATTICE MODEL

The mean-field theory developed in the preceding section shows how the effects of particle-particle interaction influence the effective viscosities. The short-range molecular interaction within the microstructure will now be discussed. The difficulty of extending the recent microscopic theories [7–11] to describe nonspherical particles in concentrated suspensions has already been mentioned. It is natural for us to try the free volume or hole theories of the liquid state [19,20]. Lattice models are basically theories of the solid state, and have the advantage of providing good connections between the dense liquid and amorphous solid [21,22]. Consider a lattice consisting of n holes or free volumes and n_x polymer molecules of x monomer segments each. The total number of lattice is written in the form

$$N=n+xn_x\quad \text{and}\quad n=\sum_{i=1}^{L}n_i\ , \tag{32}$$

where n_i denotes configurations and L is the total number of hole configurations. When the internal configurations of holes and molecules are neglected, the lattice partition function is

$$Q=\sum_{n_i}W(n_i)\exp\left[-\frac{E(n_i)}{kT}\right]\ , \tag{33}$$

where $W(n_i)$ is the number of arrangements of n_i holes in state energy $E(n_i)$ and n_x molecules on the lattice, k is Boltzmann's constant, and T is temperature. The Gibbs free energy of the system is

$$G=-kT\ln Q\ . \tag{34}$$

The equilibrium distribution of the hole number (n_i^*) can

be determined by minimizing the Gibbs free energy

$$\frac{\partial G}{\partial n_i}=0\quad (i=1,2,\ldots,L)\ , \tag{35}$$

which gives

$$\frac{\partial\ln W(n_i)}{\partial n_i}=\frac{1}{kT}\left[\frac{\partial E(n_i)}{\partial n_i}\right]\quad \text{at}\ n_i=n_i^*\ . \tag{36}$$

The derivative on the right-hand side is called the energy of hole formation in the ith state,

$$\varepsilon_i=\left[\frac{\partial E(n_i)}{\partial n_i}\right]_{n_i=n_i^*}\ . \tag{37}$$

The derivative on the left-hand side of Eq. (36) is determined from [23]

$$\ln W(n_i)=-\left[n_x\ln(xn_x/N)+\sum_i n_i\ln(n_i/N)\right]\ . \tag{38}$$

Combining Eqs. (36)–(38) gives

$$\frac{n_i^*}{N}=c\,\exp\left[-\frac{\varepsilon_i}{kT}\right]\ ,\quad c=e^{-1+1/x}\ . \tag{39}$$

In later discussions, the equilibrium hole numbers are implied without being mentioned and the asterisk will be dropped. The equilibrium hole fraction is

$$f=\frac{n}{N}=f_r\exp\left[-\frac{\varepsilon}{k}\left[\frac{1}{T}-\frac{1}{T_r}\right]\right]\ , \tag{40}$$

where the subscript r refers to an arbitrary reference condition in the liquid state. The mean energy of hole formation, $\varepsilon=\sum_i\varepsilon_i n_i/n$, characterizes the intermolecular interaction.

The shear viscosity of highly viscous fluids is the product of the high-frequency modulus of rigidity (μ) and the relaxation time (τ): $\eta=\mu\tau$. The instantaneous shear modulus μ can be treated as a constant. The macroscopic relaxation time τ is sometimes called the Maxwellian relaxation time, during which the stresses are damped. This is also the time needed for a hole to penetrate barriers in a dense fluid. Thus we have

$$\eta\propto\tau\propto\exp\left[\frac{\Delta H}{kT}\right] \tag{41}$$

and the activation energy is [21]

$$\Delta H=\frac{\varepsilon N}{\beta n}=\frac{\varepsilon}{\beta f}\ . \tag{42}$$

It is related to the local activation energy (ε/f) and β (≤1), which defines the relaxation-time spectrum. When $\beta=1$, the spectrum is a δ function. Combining Eqs. (40)–(42) yields

$$\frac{\eta}{\eta_r}=\left[\frac{f}{f_r}\right]^{-1/\beta f}\ . \tag{43}$$

When f is chosen to be in the vicinity of f_r, Eq. (43) can be written approximately as

$$\ln\left[\frac{\eta}{\eta_r}\right] = -\frac{1}{\beta f}\ln\left[\frac{f}{f_r}\right]$$

$$= \frac{1}{\beta f}\left[\left[1-\frac{f}{f_r}\right]+\frac{1}{2}\left[1-\frac{f}{f_r}\right]^2+\cdots\right],$$

$$\left|1-\frac{f}{f_r}\right| < 1 . \quad (44)$$

Therefore

$$\eta \propto \exp\left[\frac{1}{\beta f}\right], \quad (45)$$

which has the form of Doolittle's viscosity equation [20], which, however, has not been theoretically derived before. Equation (45) relates the viscosity to the free volume. The present lattice model provides us with useful theoretical basis for a quantitative description of the viscosity of multiphase systems.

VI. CONCENTRATED DISPERSIONS

We are now in a position to analyze the composition-dependent viscosity of liquid mixtures microscopically. It is assumed that the lattice vibration is unaffected by the composition of the system and we need only to focus our attention on the configurational changes in the lattice. In accordance with Eq. (32), let us consider the number of lattice sites for individual component of binary mixture having the form

$$N_j(t) = n_j + x_j n_{xj} , \quad j = 1,2 , \quad (46)$$

where n_j and n_{xj} are the number of holes and polymer molecules, respectively, and x_j is the number of monomer segments for the jth polymer component. The lattice is assumed that each molecule occupying a single lattice site with volume v_j. The total volume V of the mixture is given by

$$V = vN = \sum_j v_j N_j + \Delta V_m , \quad (47)$$

where v and $N = n + x n_x$ are, respectively, the lattice volume and total number of lattice sites of the mixture. The summation is carried out for $j = 1$ and 2, and ΔV_m is the excess volume of mixing. Since the close-packed volumes should remain unchanged, the close-packed volume of the mixture is equal to the sum of the pure component close-packed volumes:

$$vx n_x = \sum_j v_j x_j n_{xj} . \quad (48)$$

Subtracting Eq. (48) from Eq. (47), we get

$$vn = \sum_j v_j n_j + \Delta V_m . \quad (49)$$

The volume fraction of the jth component and the excess volume of mixture can be written, respectively, as

$$\phi_j = \frac{v_j N_j}{vN} \quad \text{and} \quad \frac{\Delta V_m}{vN} = A\phi_1\phi_2 , \quad (50)$$

where A is a nondimensional parameter that measures the strength of the volume interaction between components 1 and 2. From Eqs. (49) and (50), the free volume fraction of the mixture is obtained:

$$f = \frac{vn}{vN} = \sum_j \phi_j f_j + A\phi_1\phi_2 . \quad (51)$$

For rigid particles dispersed in liquid, the subscripts 1 and 2 refer to the particle and liquid, respectively. The excess volume is zero and the free volume of particle (f_1) is negligible in comparison with that of liquid (f_2), i.e.,

$$A = 0 \quad \text{and} \quad f_1/f_2 \ll 1 . \quad (52)$$

Using Eqs. (45), (51), and (52), we obtain

$$\ln\left[\frac{\eta}{\eta_2}\right] \propto \frac{1}{\beta}\left[\frac{1}{f}-\frac{1}{f_2}\right] = \frac{1}{\beta f_2}\frac{\phi}{1-\phi} , \quad (53)$$

where the volume fraction of particles $\phi = \phi_1 = 1-\phi_2$. Thus

$$\frac{\eta}{\eta_2} \equiv \eta_{\text{rel}} = \exp\left[B\frac{\phi}{1-\phi}\right] . \quad (54)$$

Although the focus of this paper has been on concentrated dispersions, the liquid lattice model sets no theoretical restriction on the value of ϕ that can be used in Eq. (54). This helps us to determine the constant **B** by matching Eqs. (54) with (31) at low volume fractions. Expanding the above equation into the series

$$\frac{\eta}{\eta_2} = 1 + \mathbf{B}\frac{\phi}{1-\phi} + \cdots , \quad (55)$$

where η and **B** are tensors for nonspherical particles, we obtain

$$\mathbf{B} = \frac{1}{2\mathbf{S}} . \quad (56)$$

Finally, from Eqs. (54) and (56), the effective shear viscosities are obtained

$$\frac{\eta_{ij}}{\eta_2} = \exp\left[\frac{1}{2S_{ijij}}\frac{\phi}{(1-\phi)}\right] , \quad i\neq j , \quad (57)$$

where the particle-shape tensor S_{ijij} is given in Sec. III.

VII. RESULTS AND DISCUSSION

A. Spherical particles

When the aspect ratio $\rho = 1$, the particle-shape tensor reduces to a single constant given by Eq. (25), and the effective viscosity $\eta = \eta_{ij}$ is isotropic. In the dilute and semidilute dispersions, the expansion of Eq. (57) in powers of the volume fraction ϕ is

$$\eta_{\text{rel}} = 1 + 2.5\phi + 5.6\phi^2 + \cdots . \quad (58)$$

The coefficient of the ϕ term is the well-known constant

calculated by Einstein [1] for a very dilute dispersion. The coefficient 5.6 of the ϕ^2 term in Eq. (58) consists of 2.5 from Eq. (31) as a result of the long-range hydrodynamic interaction of particles, and 3.1 from the short-range intermolecular interaction for the equilibrium microstructure. Equation (58) compares well with Batchelor's equation [2,3]

$$\eta_{rel} = 1 + 2.5\phi + 6.2\phi^2 + \cdots . \tag{59}$$

The coefficient 6.2 in Eq. (59) decreases to 5.2 if the Brownian motion effect is not taken into account. The ϕ^2 coefficient has been recalculated by Cichocki and Felderhof [9] and Russel, Saville, and Schowalter [10]. Their calculated values, which are also expressed in terms of the contributions from the hydrodynamic and intermolecular interactions, are within the error range of that in Eq. (58).

Shear rate has negligible effect on the viscosities of dilute and semidilute solutions. As the concentration of particles increases, the appearance of the shear rate effect [4,5] on the effective viscosity has been observed for $\phi > 0.2$. Equation (57) is derived under the assumption of high shear limit. Figure 3 shows the comparison between Eq. (57) and data for polystyrene latices in water [4] and for silica spheres in cyclohexane [5] ranging from dilute, to semidilute, to concentrated dispersions. We have used experimental data of the high shear limiting viscosity in Fig. 3 in the case of $\phi > 0.2$. The Einstein and Batchelor equations are also included in the figure. Figure 3 and Eq. (57) suggest that (1) the long-range particle-particle interaction is important in semidilute solutions, and (2) the short-range intermolecular interaction within the equilibrium microstructure dominates in concentrated dispersions. Before we move on, it may be worthwhile to mention that the interaction potential can be estimated from Eqs. (41), (42), (53), and (54):

$$\frac{\varepsilon}{f} = 2.5\beta kT , \quad \beta \leq 1 . \tag{60}$$

When the random process for holes is Gaussian, we have

FIG. 4. Calculated [from Eq. (57)] effects of particle shape, orientation, and volume fraction on the anisotropic shear viscosities of rigid spheroids dispersed in an isotropic fluid.

$\beta = 0.5$ [22] and Eq. (60) is very close to the reported interaction potential [11].

B. Nonspherical particles

Both the particle and liquid phases have been assumed to be isotropic; the anisotropic viscosities are due to the nonspherical shape of particles. We have included both the long-range hydrodynamic interaction of particles and the short-range intermolecular interaction for the equilibrium microstructure in Eq. (57). In Fig. 4, this equation is used to calculate the effects of particle shape, shear orientation, and volume fraction on the effective anisotropic viscosities of colloidal dispersions over a broad concentration range. It is customary assumed for dilute rather than for concentrated dispersions that stable flow corresponds to low energy dissipation which is proportional to the effective viscosity. Due to significant higher η_{12} for $\rho < 1$, the shear flow in the 13 direction may be more stable than in the 12 direction for oblate spheroids
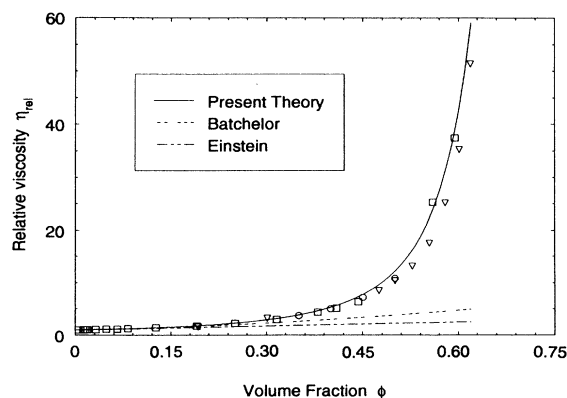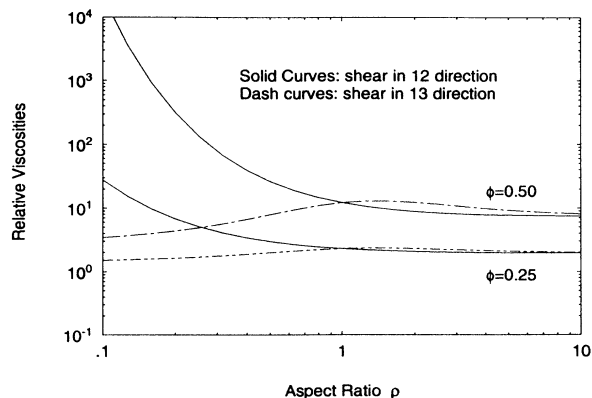

FIG. 3. Present theory [Eq. (57)] is compared with the experimental data for polystyrene latices in water [4] and silica spheres on cyclohexane [5], and the Einstein and Batchelor equations. Points are experimental data.
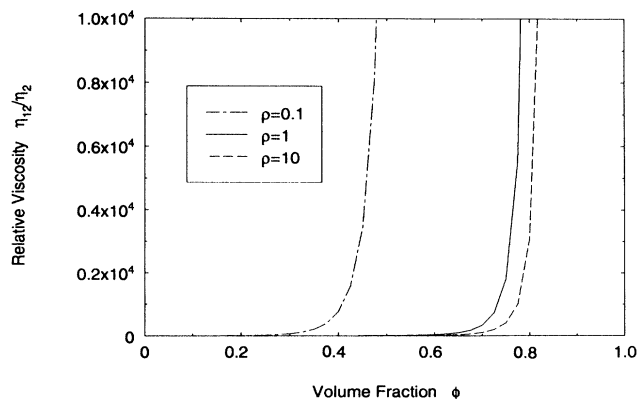

FIG. 5. Drastic change in the effective viscosity as a function of particle shape and volume fraction for shear in the 12 direction. The transition is identified as a particle-shape-dependent percolation threshold.
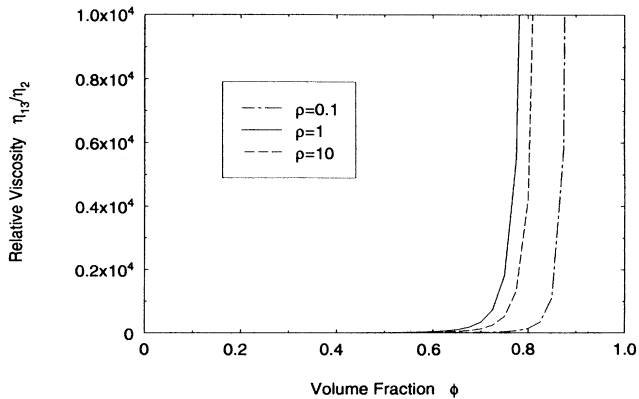
FIG. 6. Drastic change in the effective viscosity as a function of particle shape and volume fraction for shear in the 13 direction. The transition is identified as a particle-shape-dependent percolation threshold.

at low concentrations. When $\rho = 1$, all the calculations in Figs. 3 and 4 agree with each other exactly.

At high concentrations, Figs. 5 and 6 show the drastic change in the effective shear viscosities in the 12 and 13 directions, respectively. The figures reveal that the dispersion undergoes a transition which is identified as a percolation threshold [13,24]. This threshold (ϕ_c) is found to be a strong function of particle shape and shear orientation. In the vicinity of ϕ_c, a drastic change in

viscosity occurs. The critical thresholds (ϕ_c) shown in Figs. 5 and 6 can also be related to the maximum packing fractions [4,25].

VIII. CONCLUSIONS

A theory, which consists of the coupling between a liquid lattice model and hydrodynamics, has been developed to address an unsolved problem in colloidal dynamics—the effects of particle shape and flow orientation on the anisotropic shear viscosities at high ϕ. The modern microscopic theories [7–11] have their limitations [7], and they cannot be generalized to describe nonspherical particles in concentrated dispersions. The short-range intermolecular interaction within the equilibrium microstructure is the dominant interaction mechanism which leads to the drastic increase in the effective viscosities near ϕ_c. Equations have been derived to predict the effective shear viscosities of nonspherical particles dispersed in an isotropic fluid as a function of particle shape, orientation, and volume fraction.

For spherical particles, the predictions of our theory, in which there are no adjustable parameters, are in good agreement with experimental data from dilute, to semidilute, to concentrated dispersions. The values of the ϕ^2 coefficient calculated from our lattice model and from the above-mentioned modern theories are very close. For nonspherical particles at high concentrations, the system undergoes a transition which is identified as a percolation threshold. Our calculation reveals that this threshold is a strong function of particle shape and orientation.

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