J. Flnid Mech. (1978), vol. 85, part 4, pp. 673–683
Printed in Great Britain

Bulk stresses due to deformation of the electrical double layer around a charged sphere

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(Received 25 January 1977 and in revised form 13 September 1977)

A charged particle suspended in an electrolyte solution attracts ions of opposite charge and repels those of like charge. The surface charge and the resulting distributed charge in the fluid comprise an electrical double layer. When a shear flow deforms the diffuse part of the double layer from equilibrium, stresses are generated which make the effective viscosity of the suspension greater than it would be if there were no charges present. In this paper these stresses are calculated for a dilute dispersion of spheres which have small surface charges and which are surrounded by thin double layers. The viscosity is predicted to be Newtonian in extensional flow but shear-thinning with non-zero normal-stress differences in shear flow. For more complex flows a constitutive equation couples the bulk stress directly to the microstructural deformation responsible for non-Newtonian effects.

1. Introduction

Suspensions of small charged spheres are more viscous than similar suspensions of uncharged spheres and more strikingly non-Newtonian. The physics has been qualitatively explained for many years in terms of the 'primary' and 'secondary' electroviscous effects (Conway & Dobry-Duclaux 1960). The secondary effect is the result of interparticle repulsions; this has been shown experimentally (Stone-Masui & Watillon 1968) and theoretically (Russel 1976, 1978) for dilute concentrations of particles for which pair interactions dominate. The primary effect arises from the deformation by a shear flow of the diffuse ion cloud attracted to the charged surface of a single particle and hence is linear in the volume fraction of particles ϕ. In the absence of flow the ions distribute themselves so that the Brownian and electrostatic forces balance, producing a Boltzmann distribution. In a shear flow, convection relative to this equilibrium configuration is resisted by the thermal and electrostatic forces, generating body forces in the fluid which translate into additional bulk stresses for the macroscopic suspension.

The first theory for the primary electroviscous effect was presented without proof for the limiting case of thin double layers by Smoluchowski (1916). Later Krasny-Ergen (1936) calculated the viscous dissipation in the same limit to obtain a result similar to Smoluchowski's but differing from it by a numerical factor. Booth (1950), on the other hand, performed a definitive analysis in the low shear limit for arbitrary double-layer thickness, obtaining a Newtonian viscosity with an $O(\phi)$ coefficient which increased with increasing surface charge and double-layer thickness. The predicted enhancement of the coefficient over the Einstein value of 2·5 is generally of the same magnitude as or smaller than 2·5 and hence is difficult to measure accurately; nevertheless, Stone-Masui & Watillon's (1968) experiments with polystyrene latexes show similar effects.

Since the rheology of colloidal suspensions is complex and quite sensitive to their electrochemical state, we have analysed the primary electroviscous effect as one source of non-Newtonian behaviour by extending the classical theories mentioned above to higher flow strengths. In the following sections we first present the full equations governing electrokinetic phenomena and discuss their limitations before taking those limits appropriate for thin double layers. Bulk stresses and a constitutive equation are then derived from the general form of the body force distribution produced by the double-layer deformation. A dilute suspension is predicted to be Newtonian in extensional flow to the current order of approximation but shear-thinning with non-zero normal-stress differences in shear flow, reflecting the critical role of vorticity in reducing deformation at a given strain rate. For more general flows the constitutive equation can be presented as either a pair, illustrating the direct coupling between bulk stress and microstructure, or a single equation of a standard phenomenological form.

2. Governing equations

The equations describing the dynamics of and the conservation of the ions within the diffuse charge cloud incorporate three basic assumptions:

(1) Fluid properties such as the viscosity μ_0 and dielectric constant ϵ remain constant independent of ion concentration and electric field strength.

(2) The ions of species k with valence z^k and number density n^k behave as point charges affected only by electrostatic, thermal and viscous forces.

(3) Inertia can be neglected owing to the small size of the particles.

The velocity field $\mathbf{u}$ and the pressure p must then satisfy the incompressibility condition

$$\nabla.\mathbf{u} = 0, \tag{1}$$

and the Stokes equation with an electrostatic body force

$$\nabla p + \rho \nabla \psi = \mu_0 \nabla^2 \mathbf{u}, \tag{2}$$

where ψ is the electrostatic potential and

$$\rho = e \sum_k z^k n^k$$

is the local charge density, e being the electronic charge. The boundary conditions for a sphere of radius a require the fluid at its surface to rotate with it,

$$\mathbf{u} = \boldsymbol{\omega} \times \mathbf{x} \quad \text{at} \quad r = a,$$

and the fluid velocity must tend to an undisturbed linear flow far away from the sphere,

$$\mathbf{u} = \boldsymbol{\Omega} \times \mathbf{x} + \mathbf{E}.\mathbf{x} \quad \text{as} \quad r \to \infty,$$

where $2\boldsymbol{\Omega}$ is the vorticity and $\mathbf{E}$ the symmetric rate-of-strain tensor. When inertia is negligible, an angular momentum balance on the sphere determines its spin $\boldsymbol{\omega}$ to be half the free-stream vorticity, i.e. $\boldsymbol{\omega} = \boldsymbol{\Omega}$.

The electrostatic potential is related to the charge density by Poisson's equation

$$\nabla^2\psi = -\rho/\epsilon. \tag{3}$$

The appropriate boundary conditions for an insulating particle suspended in an electrolyte solution are continuity of the potential

$$\psi = \psi^* \quad \text{at} \quad r = a, \tag{4}$$

and a specified constant surface charge density q_0,

$$\mathbf{n}\,.\,(\epsilon\nabla\psi - \epsilon^*\nabla\psi^*) = -q_0, \tag{5}$$

at $r = a$, while $\psi \to 0$ as $r \to \infty$. The * denotes values within the particle and $\mathbf{n}$ the unit normal to the surface. In the condition (5) the internal field can be neglected for aqueous systems since $\epsilon^*/\epsilon \ll 1$.

The ion concentrations n^k are governed by the conservation equations

$$\partial n^k/\partial t + \nabla\,.\,(\mathbf{v}^k n^k) = 0, \tag{6}$$

where $\mathbf{v}^k$, the velocity of the kth species, is given by a dynamical equation

$$\mathbf{v}^k = \mathbf{u} + \omega^k(-ez^k\nabla\psi - kT\nabla\ln n^k), \tag{7}$$

in which ω^k is the mobility of the ion and kT the Boltzmann temperature. The dynamical equation (7) says that the ions slip relative to the flow $\mathbf{u}$ owing to the electrical force $-ez^k\nabla\psi$ and the entropic force $-kT\nabla\ln n^k$ (which drives diffusion). The boundary conditions on the ion concentrations are that there is no flux of ions into the particle,

$$\mathbf{n}\,.\,\mathbf{v}^k = 0 \quad \text{at} \quad r = a, \tag{8}$$

and that there is a constant neutral electrolyte solution far from the particle,

$$n^k \to n_0^k \quad \text{as} \quad r \to \infty \tag{9}$$

with

$$\sum_k z^k n_0^k = 0.$$

At high ionic strengths the above model breaks down near the particle surface owing to the formation of a compact Stern layer of adsorbed ions, invalidating the first two basic assumptions. This layer, however, appears to be insignificant dynamically. A detailed analysis of it can be avoided by lumping the adsorbed ions into the surface charge and applying the electrical boundary conditions at a no-slip level $r = a$.

Without flow the ion conservation equations integrate to Boltzmann distributions

$$n^k = n_0^k \exp\{-ez^k\psi/kT\}, \tag{10}$$

from which the Poisson–Boltzmann equation

$$\nabla^2\psi = -(e/\epsilon)\sum_k z^k n_0^k \exp\{-ez^k\psi/kT\} \tag{11}$$

for the potential within the equilibrium double layer follows from the Poisson equation. Knowing (10) allows one to integrate the momentum equation to determine the local osmotic pressure due to the thermal motion of the ions

$$\sum_k n_0^k kT \exp\{-ez^k\psi/kT\}, \tag{12}$$

which leads to an isotropic bulk pressure of no dynamic significance in an incompressible medium. If, however, a shear flow disturbs the equilibrium double layer the altered potential and ion densities create body forces which do generate deviatoric stresses opposing the applied flow and increasing the apparent viscosity above its value for uncharged spheres.

In most studies of dynamical phenomena, the Poisson–Boltzmann equation is simplified by assuming, as we do here, that the potentials are small:

$$e\psi/kT \ll 1. \tag{13}$$

In practice this means restricting attention to surface potentials less than 25 mV. With this assumption the Poisson–Boltzmann equation becomes

$$\nabla^2\psi = \kappa^2\psi, \tag{14}$$

where

$$\kappa^2 = (e^2/\epsilon kT)\sum_k (z^k)^2 n_0^k.$$

The spherically symmetric solution is

$$\psi = a^2 q_0 e^{-\kappa(r-a)}/\epsilon(1+a\kappa)r, \tag{15}$$

demonstrating that the charge cloud shields the surface charge on the Debye–Hückel length κ^{-1}. In this paper we shall assume the charge cloud to be thin relative to the sphere radius, i.e.

$$a\kappa \gg 1, \tag{16}$$

a condition frequently satisfied for aqueous suspensions with $a \gtrsim 0{\cdot}1\ \mu$m.

In the ion conservation equation (6), the linearization (13) corresponds to multiplying the electric force term in $\mathbf{v}^k$ by n_0^k rather than n^k. With the additional assumption that all ion mobilities are equal, i.e. $\omega^k = \omega$ for all k, the ion conservation equations can be summed to produce a single equation for the total electric charge:

$$\partial\rho/\partial t + \nabla.(\rho\mathbf{u}) = \omega kT(\nabla^2\rho - \kappa^2\rho). \tag{17}$$

The boundary conditions follow from (8) and (9):

$$\mathbf{n}.(\mathbf{u} - \omega kT(\epsilon\kappa^2\nabla\psi - \nabla\rho)) = 0 \quad \text{at} \quad r = a, \tag{18}$$

and $\rho \to 0$ as $r \to \infty$.

The charge equation contains an important dimensionless group comparing convection with diffusion, the Péclet number

$$Pe = \gamma/\kappa^2\omega kT \tag{19}$$

with γ the magnitude of $\mathbf{\Omega}$ and $\mathbf{E}$. Note that for thin double layers (16) the appropriate length scale is κ^{-1} rather than the radius a. Actually, as shown in the next section, the charge cloud only distorts by $O(Pe/a\kappa)$ because the normal component of the fluid velocity, which is responsible, is $O(\gamma/a\kappa^2)$, not $O(\gamma/\kappa)$, within the charge cloud.

One further assumption is needed: the electrical body force in (2) must not greatly affect the flow. While this term is $O(\psi_0^2 \epsilon\kappa^3)$ for the equilibrium double layer, it is precisely balanced by the gradient in the osmotic pressure (12). Only the $O(Pe/a\kappa)$ distortion of the charge cloud leads to a modification of the flow. Then from (2) the shear within the double layer is altered by $O(\gamma Ha)$, where Ha is the dimensionless group

$$Ha = (a\kappa)^{-1} \epsilon\psi_0^2/\mu_0 \omega kT. \tag{20}$$

Thus for small Ha the Stokes equation for viscous flow without an electrical body force pertains. Note that of the four independent dimensionless groups, $e\psi_0/kT$, $1/a\kappa$, Ha and Pe, the first three are assumed small here.

3. The deformed charge cloud

For $Ha \ll 1$ the first approximation for the flow is found by solving (1) and (2) (without the electrostatic force) with the appropriate boundary conditions and with $\boldsymbol{\omega} = \boldsymbol{\Omega}$; we obtain

$$\mathbf{u} = \boldsymbol{\Omega}\times\mathbf{x} + \mathbf{E}.\mathbf{x}\left\{1-\left(\frac{a}{r}\right)^5\right\} + \mathbf{x}\frac{\mathbf{x}.\mathbf{E}.\mathbf{x}}{r^2}\frac{5}{2}\left(\frac{a}{r}\right)^3\left\{\left(\frac{a}{r}\right)^2-1\right\}. \tag{21}$$

For $a\kappa \gg 1$ the velocity within the charge cloud can be expanded using the boundary-layer variable

$$\eta = \kappa(r-a) \sim O(1),$$

so that

$$\mathbf{x} = \mathbf{n}(1+\eta/a\kappa)\,a,$$

and

$$\mathbf{u} = \boldsymbol{\Omega}\times\mathbf{x} + 5\frac{\eta}{a\kappa}\left(\mathbf{E}.\mathbf{x} - \mathbf{x}\frac{\mathbf{x}.\mathbf{E}.\mathbf{x}}{r^2}\right)\left(1-3\frac{\eta}{a\kappa}\right) + \frac{15}{2}\left(\frac{\eta}{a\kappa}\right)^2\mathbf{x}\frac{\mathbf{x}.\mathbf{E}.\mathbf{x}}{r^2} + O\left(\mathbf{x}.\mathbf{E}\left(\frac{\eta}{a\kappa}\right)^3\right). \tag{22}$$

To first order the fluid merely rotates as a solid body with half the free-stream vorticity. At higher order the straining motion creates tangential and normal velocities which increase linearly and quadratically, respectively, with distance from the surface. This variation can be understood by noting that the no-slip boundary condition requires that both velocities vanish on the surface. The incompressibility condition then dictates that the normal derivative of the normal velocity also vanishes at the surface leaving a quadratic variation with η.

The charge cloud associated with the equilibrium potential (15) can be calculated from the Poisson equation (3) as

$$\rho_e = \epsilon\kappa^2\psi_0(a/r)\,e^{-\kappa(r-a)}. \tag{23}$$

Owing to its spherical symmetry, solid-body rotation has no effect on (23) and it satisfies the charge equation (17) for purely vortical flows of arbitrary strength. Since the straining motion, which does cause deformation, is an order of magnitude (in $1/a\kappa$) weaker than the rotation, the equilibrium distribution (23) will be only slightly perturbed. Thus

$$\rho = \rho_e + \rho'/a\kappa, \tag{24}$$

where the distortion ρ' must satisfy

$$\partial\rho'/\partial t + \mathbf{\Omega}\times\mathbf{x}\,.\,\nabla\rho' - \kappa^2\omega kT(\partial^2\rho'/\partial\eta^2 - \rho') = \tfrac{15}{2}\epsilon\psi_0 a\kappa^3\eta^2 e^{-\eta}\,\mathbf{x}\,.\,\mathbf{E}\,.\,\mathbf{x}/r^2. \tag{25}$$

The boundary-layer approximation has simplified the left-hand side of (25) by reducing the Laplacian to $\partial^2/\partial\eta^2$, while curvature has been neglected on the right-hand side in the deformation of the equilibrium double layer by the straining motion. Corrections to both are $O(1/a\kappa)$ smaller than the terms retained. The boundary conditions follow directly from (18):

$$\partial\rho'/\partial\eta = 0 \quad \text{at} \quad \eta = 0 \quad \text{and} \quad \rho'\to 0 \quad \text{as} \quad \eta\to\infty.$$

The solution to (25) has a second-harmonic form

$$\rho' = \epsilon\kappa^2\psi_0\,\mathbf{x}\,.\,\mathbf{A}(\eta,t)\,.\,\mathbf{x}/r^2, \tag{26}$$

where

$$\partial\mathbf{A}/\partial t + \mathbf{A}\times\mathbf{\Omega} - \mathbf{\Omega}\times\mathbf{A} - \kappa^2\omega kT(\partial^2\mathbf{A}/\partial\eta^2 - \mathbf{A}) = \tfrac{15}{2}\,\mathbf{E}\eta^2 e^{-\eta}, \tag{27}$$

with

$$\partial\mathbf{A}/\partial\eta = 0 \quad \text{at} \quad \eta = 0 \quad \text{and} \quad \mathbf{A}\to 0 \quad \text{as} \quad \eta\to\infty.$$

In a steady pure straining motion, i.e. one in which $\mathbf{\Omega} = 0$, the solution is

$$\mathbf{A} = \tfrac{15}{8}(\kappa^2\omega kT)^{-1}\,(\tfrac{2}{3}\eta^3 + \eta^2 + \eta + 1)\,e^{-\eta}\,\mathbf{E}. \tag{28}$$

The deformation remains of second order as required provided $Pe/a\kappa \leqslant 1$, limiting the theory to flows which are weak in some sense.

In steady simple shear flow

$$u_1 = \gamma x_2, \quad u_2 = u_3 = 0.$$

The solutions are

$$\begin{aligned} A_{12} &= A_{21} = \tfrac{15}{2}(Pe)^{-1}e^{-\eta}(1-2\eta) + 2\,\mathrm{Im}\,(c\,e^{\alpha\eta}),\\ A_{11} &= -A_{22} = 30(Pe)^{-2}e^{-\eta}(1-\tfrac{1}{8}Pe^2\eta^2) + 2\,\mathrm{Re}\,(c\,e^{\alpha\eta}), \end{aligned} \tag{29}$$

where

$$\alpha = (1+iPe)^{\frac{1}{2}}, \quad c = \frac{15}{4Pe^2}\alpha\,\frac{4+3Pe^2-iPe}{1+Pe^2}$$

and Re and Im denote the real and imaginary parts, respectively. In this case of shear flow with $a\kappa \geqslant 1$, the deformation is small for all flow strengths because the vorticity rotates the charge cloud rapidly from the stretching quadrant to the compressional quadrant. The cloud thus feels in quick succession phases of stretching and compression with neither phase lasting sufficiently long to produce significant distortion. The same phenomena would occur in any flow with the straining motion only in the plane orthogonal to the vorticity. Liquid drops exhibit an analogous behaviour (Cox 1969); droplets with a viscosity much larger than that of the suspending fluid also rotate almost rigidly with half the vorticity, resulting in little overall deformation in a simple shear flow.

From the charge-cloud distortion we can now calculate the perturbation in the electrostatic potential from the Poisson equation (3) with the boundary conditions (4) and (5). Outside the thin double layer, the deformation appears as a surface distribution of charge

$$\epsilon\kappa\psi_0\mathbf{x}\,.\int_0^\infty \mathbf{A}\,d\eta\,.\,\mathbf{x}\Big/r^2.$$

This produces an unshielded quadrupole potential

$$\psi' = \tfrac{1}{3}\psi_0 a^4 \kappa \mathbf{x} . \int_0^\infty \mathbf{A}\, d\eta . \mathbf{x} \Big/ r^5 \tag{30}$$

which dominates the exponentially decaying equilibrium potential in the far field.

Within the charge cloud, i.e. for $\eta \sim O(1)$, the perturbation potential has the form

$$\psi' = \psi_0 \mathbf{x} . \mathbf{B}(\eta, t) . \mathbf{x}/r^2, \tag{31}$$

where

$$\partial^2 \mathbf{B}/\partial \eta^2 = -\mathbf{A} \quad \text{and} \quad \partial \mathbf{B}/\partial \eta = 0 \quad \text{at} \quad \eta = 0.$$

Hence

$$\mathbf{B} = -\int_0^\eta (\eta - \eta') \mathbf{A}(\eta', t)\, d\eta' + \mathbf{C}, \tag{32}$$

where the constant tensor $\mathbf{C}$ is determined by matching with the outer solution (30) as $\eta \to \infty$. As a result

$$\mathbf{C} = \tfrac{1}{3} a\kappa \int_0^\infty \mathbf{A}\, d\eta \tag{33}$$

with errors of $O(1/a\kappa)$.

The electric field outside the charge cloud follows from (30) as

$$\tfrac{1}{3}\psi_0 \frac{a^4 \kappa}{r^5} \left\{ 2\mathbf{x} . \int_0^\infty \mathbf{A}\, d\eta - 5\mathbf{x}\mathbf{x} . \int_0^\infty \mathbf{A}\, d\eta . \mathbf{x} \Big/ r^2 \right\}. \tag{34}$$

Within the double layer the normal and tangential components of the field are of the same order of magnitude in $1/a\kappa$ with the tangential component remaining constant at

$$\tfrac{2}{3}\psi_0 \frac{a^4 \kappa}{r^5} \left\{ \int_0^\infty \mathbf{A}\, d\eta . \mathbf{x} - \mathbf{x}\mathbf{x} . \int_0^\infty \mathbf{A}\, d\eta . \mathbf{x} \Big/ r^2 \right\}. \tag{35}$$

In the next section we show that under these conditions only the tangential component contributes to the bulk stress.

In addition to the single-particle primary electroviscous effect, the rheology of colloidal suspensions depends on electrostatic interactions between particles. Recent calculations of the secondary electroviscous effect for stable suspensions (Russel 1976) and orthokinetic flocculation of unstable or marginally stable systems (Curtis & Hocking 1970; Zeichner & Schowalter 1977; van de Ven & Mason 1976) have relied on electrostatic force laws derived from equilibrium-double-layer theories ($Pe \equiv 0$). Since the electrical quadrupole produces a longer-range repulsive force than does the thin-double-layer field, a brief estimate of its magnitude will be presented. From a far-field approximation

electrical force $\sim$ particle charge $\times$ electric field,

the quadrupole force between two spheres with equal charge at separation r and orientation $\mathbf{x}/r$ in a pure straining flow is

$$15 \frac{\mathbf{x} . \mathbf{E} . \mathbf{x}}{r^2} \frac{\epsilon \psi_0^2 a^2}{\omega k T} \frac{\gamma}{a^2} \left(\frac{a}{r}\right)^4 . \tag{36}$$

Note that the force is repulsive as the spheres approach but attractive as they separate. Without hydrodynamic interactions the opposing viscous force between the two spheres is

$$6\pi \mu_0 a \gamma \mathbf{x} . \mathbf{E} . \mathbf{x}/r, \tag{37}$$

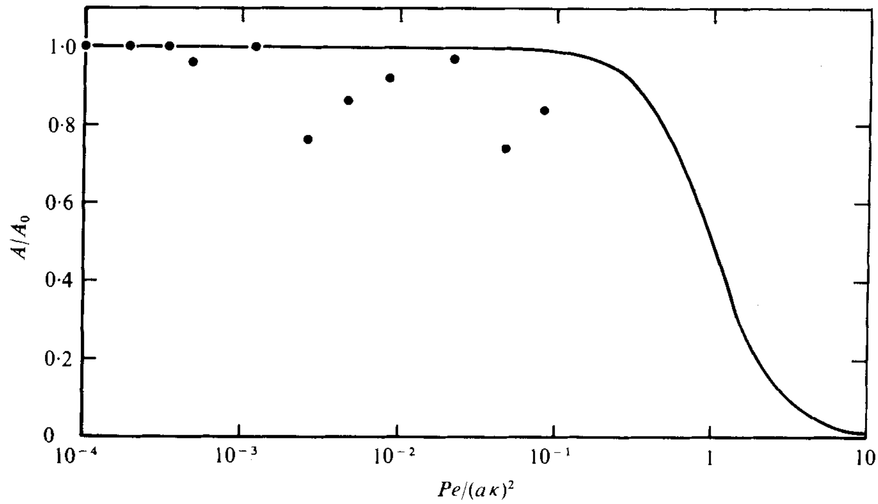

FIGURE 1. Plot of $O(\phi)$ coefficient of reduced-shear viscosity normalized by its zero-shear value *vs.* the dimensionless shear rate. ---, theoretical curve, equation (54); ●, data of Chan & Goring (1966).

so that

$$\frac{\text{electrical force}}{\text{viscous force}} = \frac{5}{2\pi}\frac{\epsilon\psi_0^2}{\mu_0 \omega kT}\frac{1}{a\kappa}\frac{a^5}{r^5}. \tag{38}$$

For moderately charged aqueous suspensions ($\epsilon \sim 80$, $\psi_0 \sim 50$ mV, $\mu_0 \sim 10^{-2}$ poise, $\omega kT \sim 10^{-5}\,\text{cm}^2/\text{s}$, $a\kappa \sim 10$) the ratio in (38) is $\sim 2(a/r)^5$, indicating that the quadrupole force is negligible under ordinary circumstances.

4. The bulk stress

Following Batchelor (1970) we can now calculate the bulk stress $\mathbf{\Sigma}$ by averaging the local stress field within a volume V chosen large enough to contain many particles but small enough for bulk quantities to remain constant. For electroviscous problems, Russel (1976) has noted that the appropriate bulk stress is the sum of the viscous stress and the Maxwell stress, the latter being defined by

$$\mathbf{m} = \epsilon(\nabla\psi\nabla\psi - \tfrac{1}{2}\mathbf{I}\nabla\psi.\nabla\psi),$$

i.e. the bulk stress is

$$\mathbf{\Sigma} = \frac{1}{V}\int_V (\boldsymbol{\sigma}+\mathbf{m})\,dv. \tag{39}$$

The contribution from the homogeneous fluid can be separated from that of the particle as

$$\mathbf{\Sigma} = -p\mathbf{I} + 2\mu_0\mathbf{E} + \mathbf{\Sigma}^p, \tag{40}$$

where the particle stress is

$$\mathbf{\Sigma}^p = \frac{1}{V}\int_V (\boldsymbol{\sigma}+\mathbf{m}+p\mathbf{I}-2\mu_0\mathbf{e})\,dv \tag{41}$$

and the viscous terms cancel outside the particle. A more convenient form can be obtained by using

$$\boldsymbol{\sigma}+\mathbf{m} = \nabla.((\boldsymbol{\sigma}+\mathbf{m}).\mathbf{x}) - \mathbf{x}\nabla.(\boldsymbol{\sigma}+\mathbf{m}) \quad\text{and}\quad \mathbf{m} = \nabla.(\mathbf{m}.\mathbf{x}) - \mathbf{x}\nabla.\mathbf{m}; \tag{42}$$

the last term in the first equation is zero in the absence of inertia from the momentum equation, while $-\mathbf{x}\nabla.\mathbf{m} = \mathbf{xF}$, where $\mathbf{F}$ is the body force on the fluid. With these identities and the divergence theorem we obtain from (41)

$$\mathbf{\Sigma}^p = \frac{1}{V}\sum_{n=1}^{N}\int_{A_n}\mathbf{x}\boldsymbol{\sigma}.\mathbf{n}\,dA + \frac{1}{V}\int_{V-\Sigma V_n}\mathbf{xF}\,dV + \frac{1}{V}\int_A \mathbf{xm}.\mathbf{n}\,dA, \tag{43}$$

where the A_n are the surfaces of the N individual particles and A encloses the control volume. The isotropic pressure has been discarded as irrelevant to the dynamics of an incompressible fluid and the last term in (41) has integrated to zero for a rigid particle. If the surface A is chosen to avoid all particles by the mean separation $a/\phi^{\frac{1}{3}}$, the last integral in (43) can also be neglected to $O(\phi)$ because the unshielded quadrupole potential, which decays as $1/r^3$, contributes at most a term $O(\phi^{\frac{5}{3}})$. Thus there remain only the weighted integral of the viscous traction over the surface of each particle, which Batchelor (1972) identifies as the stresslet $\mathbf{S}$, and the moment of the electrostatic body force integrated over the fluid.

In the preceding section the velocity field was decomposed into that due to Stokes flow around a rigid sphere and that induced by the deformed double layer. The former generates Einstein's well-known result $5\mu_0\phi\mathbf{E}$ through the first term in (43). Rather than calculate the latter velocity field, we can determine the particle stress directly from the distribution of body forces $\mathbf{F}$. Batchelor (1972) has recently derived the stresslet induced in a rigid sphere by an imposed flow (i.e. in the absence of the sphere) as

$$\mathbf{S} = \tfrac{20}{3}\pi a^3\mu_0(\mathbf{e} + \tfrac{1}{10}a^2\nabla^2\mathbf{e})_{\mathbf{x}=0}, \tag{44}$$

where $\mathbf{x} = 0$ corresponds to the sphere centre. Since a point force at position $\mathbf{x}$ in an infinite fluid generates the velocity

$$\mathbf{u} = (8\pi\mu_0)^{-1}\,\mathbf{F}.r^{-1}(\mathbf{I} + \mathbf{xx}/r^2), \tag{45}$$

at the origin, the resultant stresslet follows after some algebra. For body forces distributed only within a thin double layer, the stresslet reduces to

$$\mathbf{S} = \tfrac{1}{3}\{\mathbf{x}.\mathbf{FI} - \tfrac{3}{2}(\mathbf{xF}+\mathbf{Fx}) + \tfrac{15}{2}\eta/a\kappa(\mathbf{xF}+\mathbf{Fx} - 2\mathbf{x}.\mathbf{Fxx}/r^2)\} \tag{46}$$

plus terms $O(1/a\kappa)$ smaller. The complete viscous stress for a volume V containing N identical spheres each having volume V_0 can now be found as N/V times the integral of $\mathbf{S}$ over the double layer around an isolated sphere. Before evaluating this integral let us examine the Maxwell stress, which has a form very similar to $\mathbf{S}$.

The symmetric form of the second integrand in (43), without the isotropic pressure, is

$$\tfrac{1}{2}(\mathbf{xF}+\mathbf{Fx} - \tfrac{2}{3}\mathbf{x}.\mathbf{FI}).$$

This must also be multiplied by N/V and integrated over the volume external to a single sphere, so we can add it directly to (46) to obtain the following simplified particle stress:

$$\mathbf{\Sigma}^p = 5\frac{N}{V}\frac{a^4}{(a\kappa)^2}\int_0^\infty \eta\int_{A_0}\frac{1}{r}\left(\mathbf{xF} - \frac{\mathbf{xx}}{r^2}\mathbf{x}.\mathbf{F}\right)dA\,d\eta. \tag{47}$$

Note that normal forces of the same magnitude as tangential forces do not contribute to leading order.

The electrostatic body force

$$\mathbf{F} = -\rho\nabla\psi \tag{48}$$

within the equilibrium double layer generates an isotropic bulk pressure which can be ignored here. The first dynamically significant term arises from the interaction between the perturbed electric field and the equilibrium charge distribution. Since the field has normal and tangential components of the same order of magnitude, only the former need be retained here, giving

$$\mathbf{F} = -\frac{3\epsilon\psi_0^2}{2a^3}(a\kappa)^2 e^{-\eta}\left(\frac{\mathbf{x}}{r}.\int_0 \mathbf{A}\,d\eta - \frac{\mathbf{x}}{r}\mathbf{x}.\int_0^\infty \mathbf{A}\,d\eta.\mathbf{x}\Big/r^2\right). \tag{49}$$

Now from (47)

$$\mathbf{\Sigma}^p = -2\frac{\epsilon\psi_0^2}{a^2}\phi\int_0^\infty \mathbf{A}\,d\eta. \tag{50}$$

Equation (50) shows that the bulk stress does not depend on the details of the cloud charge distortion, but on the single integral $\int_0^\infty \mathbf{A}\,d\eta$. The constitutive equations can thus be completed by finding an equation for this single quantity by integrating the charge equation (27) with respect to η and using the boundary conditions on A to obtain

$$\left(\frac{\mathscr{D}}{\mathscr{D}t} + \kappa\omega^2 kT\right)\int_0^\infty \mathbf{A}\,d\eta = -15\mathbf{E}, \tag{51}$$

where

$$\mathscr{D}/\mathscr{D}t = \partial/\partial t + \mathbf{u}\nabla + \nabla\times\mathbf{u}\times + (\nabla\times\mathbf{u}\times)^T$$

is the corotational derivative. The constitutive equations thus can be presented as the pair (50) and (51), in a form suggested by Hinch & Leal (1975). The particular form of the time derivative reflects the fact that to a first approximation the charge cloud rotates with the rigid sphere as a solid body with an angular velocity equal to half the vorticity.

It is also possible to eliminate $\int_0^\infty \mathbf{A}\,d\eta$ by combining (50) and (51) to obtain the result

$$\mathbf{\Sigma} + \frac{1}{\kappa^2\omega kT}\frac{\mathscr{D}}{\mathscr{D}t}\mathbf{\Sigma} = -p\mathbf{I} + 2\mu_0\left\{1 + \tfrac{5}{2}\phi\left(1 + 6\frac{\epsilon\psi_0^2 a}{\mu_0\omega kT}\frac{1}{(a\kappa)^2}\right)\right\}\mathbf{E} + \frac{2\mu_0(1+\tfrac{5}{2}\phi)}{\kappa^2\omega kT}\frac{\mathscr{D}}{\mathscr{D}t}\mathbf{E}, \tag{52}$$

which is the Jeffery/Oldroyd equation.

Now the viscosity in the zero-shear limit

$$\mu/\mu_0 = 1 + \tfrac{5}{2}\phi\{1 + 6\epsilon\psi_0^2(a\kappa)^{-2}/\mu_0\omega kT\} \tag{53}$$

agrees with both Krasny-Ergen's theory and the $a\kappa \to \infty$ limit of Booth's. At higher shear rates a shear-thinning viscosity

$$\frac{\mu}{\mu_0} = 1 + \tfrac{5}{2}\phi\left\{1 + 6\frac{\epsilon\psi_0^2}{\mu_0\omega kT}\frac{1}{(a\kappa)^2}\frac{1}{1+Pe^2}\right\} \tag{54}$$

and normal-stress differences

$$N_1 = \Sigma_{11} - \Sigma_{22} = 30\frac{\epsilon\psi_0^2}{a^2}\phi\frac{Pe^2}{1+Pe^2}, \quad N_2 = \Sigma_{33} - \Sigma_{22} = -\tfrac{1}{2}N_1 \tag{55}$$

are predicted.

The magnitude of the perturbation of Einstein's results described by (53) results from the integration of the deviatoric part of the Maxwell stress, $O(Ha)$, over the volume fraction of the charge cloud, $O(\phi/a\kappa)$. Hence the effect is $O(\phi Ha/a\kappa)$, which has been restricted to be small in this theory.

Unfortunately, the literature contains no definitive measurements on the shear-rate dependence of the primary electroviscous effect. Stone-Masui & Watillon (1968) carefully restricted their experiments with monodisperse polystyrene latexes to the low shear limit. Chan & Goring (1966) observed shear-thinning with different latexes but inconsistencies in their data indicate that their particles may have been swollen and deformable. For example, at high ionic strengths when the electrical effect should be small, their $O(\phi)$ coefficient based on the dry particle size was about 5 rather than 2·5. Also as shown in the plot of their data in figure 1 (with A the $O(\phi)$ coefficient and $A_0 = \lim_{Pe\to 0} A$), the shear-thinning occurred at $Pe < 10^{-1}$ and could be within the experimental uncertainty. The small magnitude of the effect and the high shear rates required pose formidable problems for their experimental observation.

The non-Newtonian behaviour characterized by (52) derives from the effect of vorticity on the unshielded quadrupole. In simple shear with vorticity in fixed ratio to straining, the quadrupole aligns with the principal direction of straining at low shear rates but rotates toward the no-flow axis at higher rates. As with drops having high internal viscosities this reduces the effectiveness of the flow, allowing the magnitude of the deformation to achieve a constant asymptote. As a consequence the shear viscosity decreases but the normal stresses become unbalanced. Conversely, for uniform straining the quadrupole remains oriented with the principal directions and increases in magnitude monotonically with increasing flow strength. The constant viscosity is, however, an artifact of truncating the expansion in powers of $1/a\kappa$; in fact, the expansion breaks down when $Pe > a\kappa$.

The work was supported by the National Science Foundation through a NATO Postdoctoral Fellowship and a Research Initiation Grant. The author thanks Dr E. J. Hinch for his generous and patient assistance throughout.

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