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Large distortion of the electric double layer around a charged particle by a shear flow

By D. A. LEVER
Department of Applied Mathematics and Theoretical Physics,
University of Cambridge†

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The distortion by a linear flow of the electric double layer around a small particle is studied for the case of a charge cloud which is thick in comparison with the particle radius and for arbitrary flow strengths, including those which are strong enough to produce a significant distortion of the cloud. For weak flows a second-order-fluid approximation is obtained for the stress contribution for a dilute suspension of such particles. For arbitrarily strong flows integral representations of the charge density and numerical calculations of the stress contribution are given for three representative flows: simple shear, axisymmetric strain and two-dimensional straining motion.

1. Introduction

When a small charged particle is in suspension in an electrolyte it attracts ions of opposite charge and repels ions of like charge, so the particle is surrounded by a charge cloud whose total charge is equal in magnitude and opposite in sign to its own. This charge cloud together with the surface charge is referred to as the electric double layer. A suspension of charged particles whose charge cloud is of comparable size to the particle has noticeably different dynamics to a similar suspension of uncharged particles. Conway & Dobry-Duclaux (1960) describe three ways in which the dynamics are affected, the three electroviscous effects. The first or primary effect arises from the deformation by the flow of the diffuse ion cloud around a single particle, and this leads to a modification of the Einstein term in the viscosity expansion. The second effect arises from particle interactions and has recently been studied theoretically by Russel (1976, 1978*a*). The third or tertiary effect arises from the change in shape of a charged macromolecule in solution.

After a number of earlier theories, Booth (1950) presented a complete analysis of the primary effect for spherical particles with an arbitrarily thick charge cloud in the limits of weak flow and weak electrical effects, and found the correction to the Newtonian viscosity. Russel (1978*b*) has considered the case of a thin double layer and arbitrary flow strength. One of the simplifying features of both these theories is that the deformation of the cloud from its equilibrium shape is small. In this paper the problem of an arbitrary flow strength and thick double layer is considered, as a case when there is a large deformation of the charge cloud and when the electrical contribution to the bulk stress can be comparable with the Einstein $\frac{5}{2}c$ term.

† Present address: Theoretical Physics Division, Atomic Energy Research Establishment, Harwell, Oxfordshire OX 11 0RA.

In the following sections we first review Russel's formulation of the equations for the ion cloud and specialize them to the case of a thick cloud, where we find it convenient to work in Fourier space. For general weak flows the bulk stress is approximated by a second-order-fluid law. For stronger flows the analysis is restricted to three specific flows: simple shear, axisymmetric strain and two-dimensional straining motion. In these cases an integral representation for the charge density and numerical calculations of the stress components are presented. The ideas are developed for a spherical particle, however it is found that the shape is not important, and that the theory holds for particles of arbitrary shape.

2. Basic equations

First the relevant results from Russel (1978*b*) for the model of the charge cloud around a spherical particle are recalled. The ions of species k, with valence z^k, number density n^k and velocity $\mathbf{v}^k$, satisfy the conservation equation

$$\partial n^k/\partial t + \nabla . (n^k \mathbf{v}^k) = 0 \quad \text{(no sum)}. \tag{1}$$

The ions move relative to the local fluid velocity $\mathbf{u}$ under the action of electrostatic and thermal forces. The different ion species are assumed to have the same mobility ω, so

$$\mathbf{v}^k - \mathbf{u} = \omega(-ez^k\nabla\psi - kT\nabla \ln n^k), \tag{2}$$

where $-kT\nabla \ln n^k$ represents Brownian diffusion and ψ is the electrostatic potential. The local fluid properties, such as the dielectric constant ϵ and viscosity μ_0, are taken to be constant throughout the charge cloud, so

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

where $\rho = \Sigma e n^k z^k$ is the local charge density. As the particles under consideration are small the fluid velocity satisfies the Stokes equations modified by the addition of the electrostatic body force $\rho\nabla\psi$:

$$\mu_0 \nabla^2 \mathbf{u} = \nabla p + \rho\nabla\psi, \quad \nabla . \mathbf{u} = 0. \tag{4}$$

The boundary conditions on the particle surface are complicated by the presence of the Stern layer of adsorbed ions, described by Dukhin (1974). However, at the low ionic strengths which are relevant in this analysis, there will be few adsorbed ions, so the no-slip boundary condition on $\mathbf{u}$ and the electrical boundary conditions will be applied at the same surface $r = a$. The appropriate electrical boundary conditions are that there should be no flux of ions normal to the surface, $\mathbf{n}.\mathbf{v}^k = 0$, and that the surface charge is the same as when there is no fluid motion. When the surface potential, the zeta potential ζ, is small, i.e.

$$\Phi_0 = e\zeta/kT \ll 1,$$

these boundary conditions can be combined to give

$$\partial(\rho - \rho_0)/\partial r = 0 \quad \text{at} \quad r = a, \tag{5}$$

where ρ_0 is the equilibrium charge density.

Russel (1978*b*) showed that for small surface potentials, the ionic equation (2) can be summed, to give in the steady state

$$\mathbf{u} . \nabla\rho = \omega kT(\nabla^2\rho - \kappa^2\rho), \tag{6}$$

where κ^{-1}, the Debye length representing the thickness of the charge cloud, is defined by

$$\kappa^2 = \frac{e^2}{\epsilon kT} \Sigma n_0^k (z^k)^2,$$

n_0^k being the equilibrium number density at infinity. Thus, for example, an aqueous solution of a salt consisting of two monovalent ion species has $\kappa^{-1} = 3 \cdot 1 \times C^{-\frac{1}{2}} \times 10^{-10}$ m, where C is the molar concentration. Without the added salt the thickness of the double layer is 10^{-6} m.

Wiersma, Loeb & Overbeek (1966) analysed electrophoresis (i.e. the motion of a charged colloidal particle under an applied electric field) for Φ_0 up to 6 and for arbitrary $a\kappa$. They found that the linear theory for $\Phi_0 \ll 1$ was a good approximation up to $\Phi_0 \sim 2$, which corresponds to $\zeta = 50$ mV, with an error in the electrophoretic mobility of no more than 10 %. For small $a\kappa$ they found that the linear theory was valid for even larger Φ_0, and we expect a similar result in this analysis.

In this paper we shall restrict the analysis to charge clouds that are thick in comparison with the particle radius, i.e. $a\kappa \ll 1$. Thus there will be two length scales in the problem, a and κ^{-1}, and a full solution for ρ would consist of matched asymptotic expansions on these inner and outer scales. We shall be particularly interested in the outer problem where the charge cloud appears to be around a point particle. It is appropriate to work in terms of non-dimensional equations, taking the length scale as κ^{-1} and a typical charge to be Q, the charge on the particle. For $a\kappa \ll 1$

$$Q = 4\pi a\zeta\epsilon. \tag{7}$$

We shall be concerned with linear flows; if the velocity gradient far from the particle is $\mathbf{\Gamma}$, i.e. $\mathbf{u} \sim \mathbf{\Gamma}.\mathbf{x}$ as $r \rightarrow \infty$, with typical value Γ, then the appropriate velocity scale is Γ/κ. Equations (2) and (6) hold only for $r > a$; to make them valid over the whole domain a point charge at the origin is introduced, represented by $\delta(\mathbf{x})$. Denoting the non-dimensional variables by a prime, (3), (4) and (6) become

$$\nabla'^2\psi' = -\rho' - \delta(\mathbf{x}'), \tag{8a}$$

$$\nabla'^2\rho' - \rho' = \gamma\mathbf{u}'.\nabla'\rho' + \delta(\mathbf{x}'), \tag{8b}$$

$$\nabla'^2\mathbf{u}' = \nabla' p' + Ha\rho'\nabla'\psi', \tag{8c}$$

where the Hartmann number Ha and the ion Péclet number γ are given by

$$Ha = \frac{\epsilon a^2 \kappa^4 \zeta^2}{\mu_0 \Gamma} = \frac{Q^2\kappa^4}{16\pi^2\epsilon\mu_0\Gamma}, \quad \gamma = \frac{\Gamma}{\kappa^2 \omega kT}.$$

γ represents the strength of the convective forces on the ions compared with the Brownian forces and Ha represents the strength of the electrostatic body force compared with the viscous term in the Stokes equation, and can be thought of as a rigidity of the charge cloud. For weak flows the appropriate Hartmann number is not Ha but $Ha\gamma$, as then there is only a small change in ρ, and the equilibrium value of $\rho\nabla\psi$ is balanced by an isotropic pressure. Russel found that the Hartmann number for thin double layers is $Ha\gamma/(a\kappa)^3$. In this paper Ha is the relevant parameter and is assumed small. A summary of the dimensionless groups and the restrictions placed on them in this and previous analyses is given in table 1.

		Booth (1950)	Russel (1978b)	This analysis
Φ_0	Dimensionless surface potential	$\ll 1$	$\ll 1$	$\ll 1$
γ	Ion Péclet number	$\ll 1$	Simple shear: arbitrary Pure strain: $\ll a\kappa$	$\ll (a\kappa)^{-2}$
Ha	Hartmann number	$\ll 1$	$\ll 1$	$\ll 1$
$a\kappa$	Cloud thickness	Arbitrary	$\gg 1$	$\ll 1$

TABLE 1. The restrictions on the dimensionless groups in analyses of the primary electroviscous effect.

A typical value of Ha for $\gamma \lesssim O(1)$ is $\Phi_0^2(a\kappa)^2$, thus Ha will be small for small $a\kappa$. For an aqueous solution of NaCl at room temperature $\omega kT \sim 10^{-9}\ \mathrm{m^2\,s^{-1}}$, so γ will not be small only for a combination of thick double layers and strong flows ($\Gamma \gtrsim 10^3\,\mathrm{s^{-1}}$). Chan & Goring (1966) performed experiments to look for a dependence of the shear viscosity on the flow strength, however their experimental values of γ were less than 1.

As both Ha and $a\kappa$ are small, the perturbation to the flow due to both the presence of the particle and the electric forces will be small. So we may take $\mathbf{u}' = \mathbf{\Gamma}'.\mathbf{x}'$ as a solution of (8c), and substitute it into the ρ' equation (8b). The set of equations (8) is then uncoupled.

After solving (8b) for the charge density, the contribution from the charge cloud to the bulk stress $\mathbf{\Sigma}$ of a suspension of such particles will be of particular interest. The volume-averaging method of Batchelor (1970) for evaluating the bulk stress was adapted by Russel (1978b) to the case when both viscous and Maxwell stresses are present. He showed that the bulk stress can be written as

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

where $\mathbf{\Sigma}^p$ is the particle contribution. In the case of a dilute suspension with particle concentration c, the $O(c)$ term in the expansion of $\mathbf{\Sigma}^p$ is

$$\frac{3c}{4\pi a^3}\left\{\int_{r=a} \mathbf{x}\boldsymbol{\sigma}.\mathbf{n}\,dS + \int_{r>a} \mathbf{x}\rho\nabla\psi\,dV\right\}.$$

Here dilute means not only that $c \ll 1$ but also that the charge clouds should not overlap, i.e. $c/(a\kappa)^3 \ll 1$. This expression can be written in terms of non-dimensional variables to give

$$\mathbf{\Sigma}^p = \frac{3c\mu_0\Gamma}{4\pi(a\kappa)^3}\left[\int_{r'=a\kappa} \mathbf{x}'\boldsymbol{\sigma}'.\mathbf{n}\,dS' + Ha\int_{r'>a\kappa} \mathbf{x}'\rho'\nabla'\psi'\,dV'\right]. \tag{9}$$

In the absence of electrical effects the first term gives the $5c\mu_0\mathbf{E}$ Einstein term. In the $a\kappa \ll 1$ limit this integral is over a point particle, so we expect the contribution from the electric forces to be small in comparison with their contribution to the second integral. This assumption will be checked *a posteriori* at the end of §4. Thus the electroviscous contribution to $\mathbf{\Sigma}^p$ can be written as

$$\mathbf{\Sigma}^e = \frac{3c\mu_0\Gamma}{4\pi(a\kappa)^3}\,Ha\,\mathbf{\Sigma}^{e\prime}, \tag{10}$$

where $$\mathbf{\Sigma}^{e\prime} = \int \mathbf{x}'\rho'\nabla'\psi'\,dV'$$

and the integral is now over all space. Even with $Ha \ll 1$ this can be comparable with the Einstein term, as $Ha/(a\kappa)^3$ can be $O(1)$.

So far the theory has been developed for spherical particles. It can now be seen that, as we are dealing with the outer problem on the scale κ^{-1}, the shape of the particle is not important, provided that κ^{-1} is much greater than the largest linear dimension of the particle. The solution of (8*b*) for ρ and the corresponding value of $\mathbf{\Sigma}^e$ from (10) depend only on κ^{-1}, Q and n, the number density of particles ($n = 3c/4\pi a^3$), and not on a. For non-spherical particles equation (7) relating Q and ζ will no longer be valid, and it should be replaced by the appropriate relationship.

Equation (8*b*) for ρ' is similar to a diffusion equation for a point source of heat in a linear flow, with the addition of the electrostatic force term, and it can be solved by a number of methods. However in general it will not be easy to write down the corresponding solution of the Poisson equation for ψ', so evaluation of $\mathbf{\Sigma}^{e\prime}$ will be difficult. To get over these problems the most appropriate method appears to be to take a three-dimensional Fourier transform of (8*a*, *b*), giving

$$\left.\begin{aligned} \gamma\mathbf{k}\,.\,\mathbf{\Gamma}'\,.\,\hat{\nabla}\hat{\rho} &= (1+K^2)\,\hat{\rho}+1, \\ \hat{\psi} &= (1+\hat{\rho})/K^2, \end{aligned}\right\} \tag{11}$$

where $\hat{\rho}(\mathbf{k})$ is the Fourier transform of $\rho'(\mathbf{x}')$, $K = |\mathbf{k}|$ and $\hat{\nabla} = \partial/\partial\mathbf{k}$. This is solved subject to $\hat{\rho}(\mathbf{k}) \rightarrow 0$ as $\mathbf{k} \rightarrow \infty$. The expression for the stress contribution (10) is a convolution and can be written as

$$\mathbf{\Sigma}^{e\prime} = \frac{1}{8\pi^3}\int \mathbf{k}\hat{\nabla}\hat{\rho}\hat{\psi}\,d^3\mathbf{k}, \tag{12}$$

and the condition that the total charge in the charge cloud is -1 becomes $\hat{\rho}(0) = -1$.

Henceforth the quantities $\mathbf{x}'$, ρ', ψ' and $\mathbf{\Sigma}^{e\prime}$ in real space occur only as non-dimensional variables so for convenience the prime will be dropped.

3. Second-order-fluid approximation

When the ion Péclet number γ is small, a power-series solution of (11) can be written down:

$$\hat{\rho} = \sum_{n=0}^{\infty} \gamma^n \hat{\rho}_n, \tag{13}$$

where

$$\hat{\rho}_n = \frac{\mathbf{k}\,.\,\mathbf{\Gamma}\,.\,\hat{\nabla}\,\hat{\rho}_{n-1}}{1+K^2}, \quad \hat{\rho}_0 = -\frac{1}{1+K^2}.$$

Here $\hat{\rho}_0$ corresponds to the well-known equilibrium double layer solution $-e^{-r}/4\pi r$, with $r = |\mathbf{x}|$.

It is convenient to write the deviatoric-stress contribution (12) as

$$\mathbf{\Sigma}^e = \frac{\gamma}{8\pi^3}\int\left(\frac{2\mathbf{k}\mathbf{k}}{(1+K^2)^3}+\frac{\mathbf{k}\hat{\nabla}\hat{\rho}}{(1+K^2)\,K^2}\right)\mathbf{k}\,.\,\mathbf{\Gamma}\,.\,\hat{\nabla}\hat{\rho}\,d^3\mathbf{k}. \tag{14}$$

Equation (14) can be used to provide successive approximations to $\mathbf{\Sigma}^e$. The first is found by substituting $\hat{\rho}_0$; the $\mathbf{k}$ integral is then a symmetric isotropic tensor of rank 4, which can be evaluated to give a correction to the Newtonian viscosity

$$\mu_0^e = 1/240\pi,$$

which agrees with the $a\kappa \ll 1$ limit of the analysis of Booth (1950).

The second approximation to the constitutive relationship must be of the form of a second-order-fluid, namely

$$\boldsymbol{\Sigma}^e = 2\mu_0^e\gamma\mathbf{E} - 2\alpha\gamma^2\delta\mathbf{E}/\delta t + \beta\gamma^2\mathbf{E}.\mathbf{E}, \tag{15}$$

where $\delta\mathbf{E}/\delta t$ is the Oldroyd derivative

$$D\mathbf{E}/Dt - \boldsymbol{\Gamma}.\mathbf{E} - \mathbf{E}.\boldsymbol{\Gamma}^{\mathrm{T}}.$$

In this case the constants α and β are found from (14) to be

$$\alpha = 1/640\pi, \quad \beta = -1/224\pi. \tag{16}$$

These will be used to give the weak-flow limits of the stress components which vanish for a Newtonian fluid, such as the normal-stress differences in a simple shear flow.

4. Simple shear

In the previous section we restricted the analysis to $\gamma \ll 1$. We now look for solutions for arbitrary values of γ. In principle we could look for a solution of (11) for a general flow, however the value of any results will be lost in the complexity of the algebra. So we restrict the analysis to two specific flows, first simple shear and then in §5 pure straining motion. For simple shear

$$\boldsymbol{\Gamma} = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

and then (11) reduces to the ordinary differential equation

$$\gamma k\,\partial\hat{\rho}/\partial l - (1+K^2)\,\hat{\rho} = 1$$

with $\mathbf{k} = (k, l, m)$ and the boundary condition $\hat{\rho}(\mathbf{k}) \to 0$ as $\mathbf{k} \to \infty$. The solution is

$$\hat{\rho}(\mathbf{k}) = -\int_0^\infty dv \exp\{-(1+K^2)\,v - kl\gamma v^2 - \tfrac{1}{3}k^2\gamma^2v^3\}. \tag{17}$$

This is basically a product of three Gaussians in k, $l+\frac{1}{2}\gamma vk$ and m, so it can be inverted to give

$$\rho(\mathbf{x}) = -\frac{1}{8\pi^{\frac{3}{2}}}\int_0^\infty dv\, \frac{\exp\left\{-v - \dfrac{(x-\frac{1}{2}\gamma yv)^2}{4(v+\frac{1}{12}\gamma^2v^3)} - \dfrac{y^2}{4v} - \dfrac{z^2}{4v}\right\}}{v(v+\frac{1}{12}\gamma^2v^3)^{\frac{1}{2}}}. \tag{18}$$

This integral is plotted in figure 1 for three different values of γ, namely 0·5, 2·0 and 10·0. It can be seen that the distortion of the charge cloud from the spherically symmetric equilibrium solution ρ_0 increases with increasing flow strength. The distortion can be understood in terms of the associated quadrupole moment of the charge distribution

$$\mathbf{Q} = (-3\hat{\nabla}\hat{\nabla}\hat{\rho} + \hat{\nabla}^2\hat{\rho}\mathbf{I})_{\mathbf{k}=0} = -\begin{pmatrix} 8\gamma^2 & 6\gamma & 0 \\ 6\gamma & -4\gamma^2 & 0 \\ 0 & 0 & -4\gamma^2 \end{pmatrix}.$$

For weak shear this is a tesseral quadrupole of strength -6γ, arising from the perturbed charge distribution

$$\rho = -(1+\tfrac{1}{4}\gamma xy + O(\gamma^2r^4))\,e^{-r}/4\pi r. \tag{19}$$

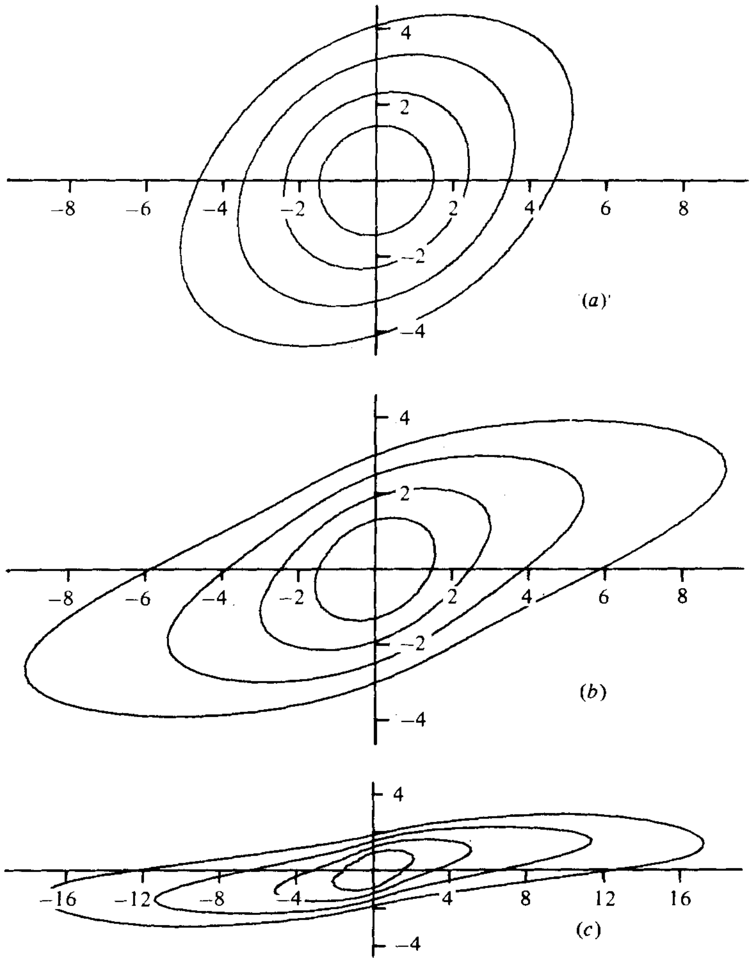

FIGURE 1. Contours of constant ρ in the plane $z = 0$ for simple shear flow. (a) $\gamma = 0{\cdot}5$, (b) $\gamma = 2{\cdot}0$, (c) $\gamma = 10{\cdot}0$. The values of ρ are $-0{\cdot}0128$, $-0{\cdot}0032$, $-0{\cdot}0008$ and $-0{\cdot}0002$.

However for stronger flows ($\gamma \gg 1$) this changes to an axial quadrupole of strength $-8\gamma^2$, corresponding to a long downstream wake in which there is a balance between diffusion in the y and z directions, the electrostatic body force and the strong convective drag on the ions. From the integral (18) it can be seen that for strong flows y and z scale on $O(1)$ whereas x scales on $O(\gamma)$.

As was commented in §2, (18) is a solution of the outer problem and it has been obtained without satisfying the inner boundary condition that there should be no flux of ions at the surface (5). However, from (19) at $r = a\kappa$

$$\partial\rho/\partial r = (1 + O((a\kappa)^2\gamma))\,\partial\rho_0/\partial r,$$

which shows that the inner correction is not important.

In the case of simple shear there are three independent contributions to the deviatoric bulk stress. These are the shear stress Σ^e_{12} and the two normal-stress differences $\Sigma^e_{11} - \Sigma^e_{33}$ and $\Sigma^e_{22} - \Sigma^e_{33}$. The shear stress is obtained by substituting (17) and the corresponding form of $\hat{\psi}$ from (11) into (12). Using spherical polars (K, θ, ϕ), this can be simplified by performing the K integration to give

$$\Sigma_{12}^e = \frac{1}{8\pi^{\frac{3}{2}}}\int_0^\infty dv \int_0^{\frac{1}{2}\pi} d\theta \sin\theta \int_0^\pi d\phi (2\sin\theta\cos\theta\cos\phi v + \cos^2\theta\gamma v^2) \times \left(g(\theta,\phi,v,0) - \int_0^\infty dv' g(\theta,\phi,v,v'\right), \qquad (20)$$

where

$$g(\theta,\phi,v,v') = e^{-v-v'}[v+v'+\gamma\cos\theta\sin\theta\cos\phi(v^2+v'^2)+\tfrac{1}{3}\cos^2\theta\gamma^2(v^3+v'^3)]^{-\frac{3}{2}}.$$

This is computed numerically; the θ and ϕ integrations offer no problems and can be evaluated to within 1% by 8-point Gaussian quadrature. The v and v' integrals have an $O(v^{-\frac{1}{2}})$ singularity as $v \to 0$ which can be subtracted out in the form of the integrand when $\gamma = 0$. These integrals can then be evaluated by 12-point Laguerre quadrature as they decay exponentially as $v \to \infty$. However for $\gamma \gtrsim 10$ this scheme is not appropriate as the algebraic decay of g in v and v' becomes more important than the exponential decay. A substitution $w^2 = \cos\theta\gamma v$, $u = 1/(w+1)$, $w'^2 = \cos\theta\gamma v'$ and

$$u' = 1/(w'+1)$$

is then made, and a 16-point Gaussian quadrature on (0, 1) can be used for u and u'. The high shear form of Σ_{12}^p can also be seen from the transformed form; the $g(\theta,\phi,v,0)$ term contributes an $O(\gamma^{-\frac{1}{2}})$ term and the $g(\theta,\phi,v,v')$ term an $O(\gamma^{-\frac{3}{2}})$ term. Thus

$$\Sigma_{12}^e \sim A/\gamma^{\frac{1}{2}} \quad \text{as} \quad \gamma \to \infty$$

with

$$A = \frac{1}{4\pi^{\frac{3}{2}}}\int_0^\infty dw \int_0^{\frac{1}{2}\pi} d\theta \sin\theta (\cos\theta)^{\frac{1}{2}} \int_0^\pi d\phi \frac{2\sin\theta\cos\phi + w^2}{(1+w^2\sin\theta\cos\phi+\frac{1}{3}\omega^4)^{\frac{3}{2}}} = 0{\cdot}020.$$

The neglect of the second term in (20) is equivalent to writing $\hat{\psi} = 1/K^2$, or $\psi = 1/4\pi r$. Thus the dominant contribution comes from the interaction of the charge cloud with the electric field due only to the charged particle, the stretched diffuse cloud producing a negligible field. In addition, for strong flows the major contribution comes from $K = O(\gamma^{\frac{1}{2}})$, which corresponds to $r = O(\gamma^{-\frac{1}{2}})$, this being the length scale on which diffusion balances convection in (8*b*). This scaling has been found for all stress components in the $\gamma \gg 1$ limit of all the linear flows considered. As the contribution comes from $r = O(\gamma^{-\frac{1}{2}})$ the condition $a\kappa \ll 1$ should be strengthened to $a\kappa \ll \gamma^{-\frac{1}{2}}$ for $\gamma \gg 1$. Σ_{12}^e is plotted in figure 2 and it can be seen that the strong shear region is not reached until $\gamma \sim 50$.

The normal-stress differences are also plotted in figure 2. For weak shear the form can be found from (15) and (16) to give

$$\Sigma_{11}^e - \Sigma_{33}^e \sim \frac{9}{4480\pi}\gamma^2, \quad \Sigma_{22}^e - \Sigma_{33}^e \sim \frac{-1}{896\pi}\gamma^2,$$

whilst for $\gamma \gg 1$

$$\Sigma_{11}^e - \Sigma_{33}^e \sim 0{\cdot}180\gamma^{-\frac{1}{2}}, \quad \Sigma_{22}^e - \Sigma_{33}^e \sim -0{\cdot}025\gamma^{-\frac{1}{2}}.$$

Thus for strong flows the first normal-stress difference is the largest of the stress components by a factor of 9. From the plots it can also be seen that the normal stresses converge more slowly to the asymptotic value than the shear stress: this is because the error is $O(\gamma^{-1})$ rather than $O(\gamma^{-\frac{3}{2}})$.

The magnitude of the stresslet term in (9), which was neglected for $a\kappa \ll 1$, can

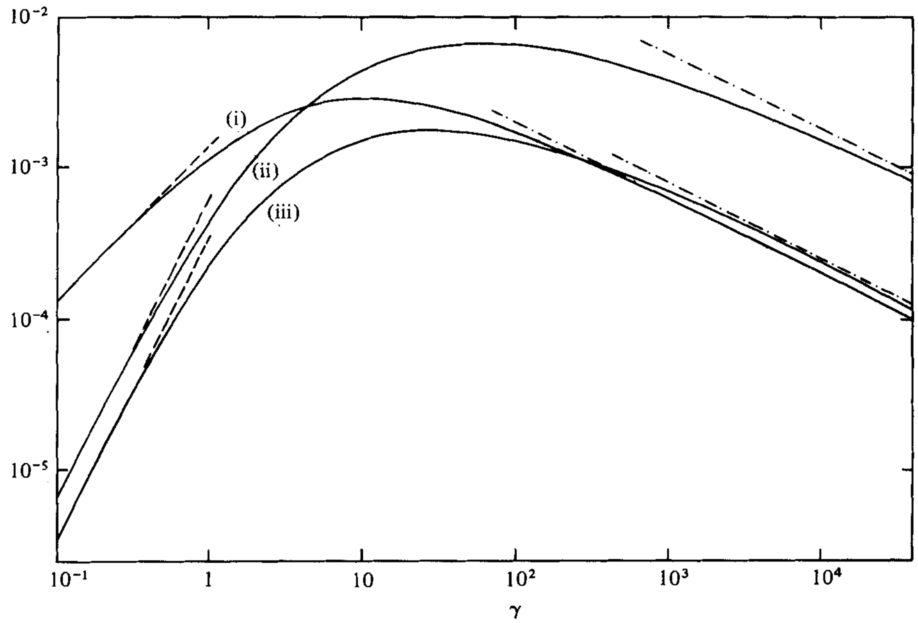

FIGURE 2. Logarithmic plot of the stress components in simple shear as a function of ion Péclet number. (i) Σ^e_{12}, (ii) $\Sigma^e_{11}-\Sigma^e_{33}$, (iii) $-(\Sigma^e_{22}-\Sigma^e_{33})$. ----, $\gamma \ll 1$ limit; -·-·-, $\gamma \gg 1$ limit.

now be estimated. First, from the inner length scale there is a contribution from the velocity perturbation due to the presence of the particle: this gives the $\frac{5}{2}c$ Einstein term. The outer contribution, due to the electrostatic body force, can be found by examining the behaviour of ρ near the origin, which is the same as (19). The equilibrium part gives only an isotropic pressure so the leading term arises from the perturbation to $\rho\nabla\psi$, which is $O(r^{-1})$. This leads to a stress at $r = a\kappa$ which is $O(Ha \ln a\kappa)$, thus the stresslet term is $O(Ha(a\kappa)^3 \ln a\kappa)$. Logarithmic terms arise in Booth's analysis at the same order.

5. Pure straining motion

The second particular flow we consider for arbitrary values of γ is the case of a particle in a pure straining motion. Taking axes along the principal axes of strain, the imposed velocity can be written as $\mathbf{u} = (E_1 x, E_2 y, E_3 z)$ with $E_1+E_2+E_3 = 0$. Then (11) takes the form

$$\gamma \sum_{i=1}^{3} E_i k_i \frac{\partial \hat{\rho}}{\partial k_i} - (1+K^2)\hat{\rho} = 1.$$

This can be integrated by the method of characteristics to give

$$\hat{\rho}(\mathbf{k}) = -\int_0^1 d\lambda \exp\left\{-\sum_{i=1}^{3} \frac{k_i^2(\lambda^{-2E_i\gamma}-1)}{2E_i\gamma}\right\}.$$

This is a product of three Gaussians and can be inverted to give an integral representation of the charge density:

$$\rho(\mathbf{x}) = -\int_0^1 d\lambda \left(\frac{1}{8\pi^3}\prod_{i=1}^{3}\frac{E_i\gamma}{(\lambda^{-2E_i\gamma}-1)}\right)^{\frac{1}{2}} \exp\left\{-\sum_{i=1}^{3}\frac{x_i^2 E_i\gamma}{2(\lambda^{-2E_i\gamma}-1)}\right\}. \quad (21)$$

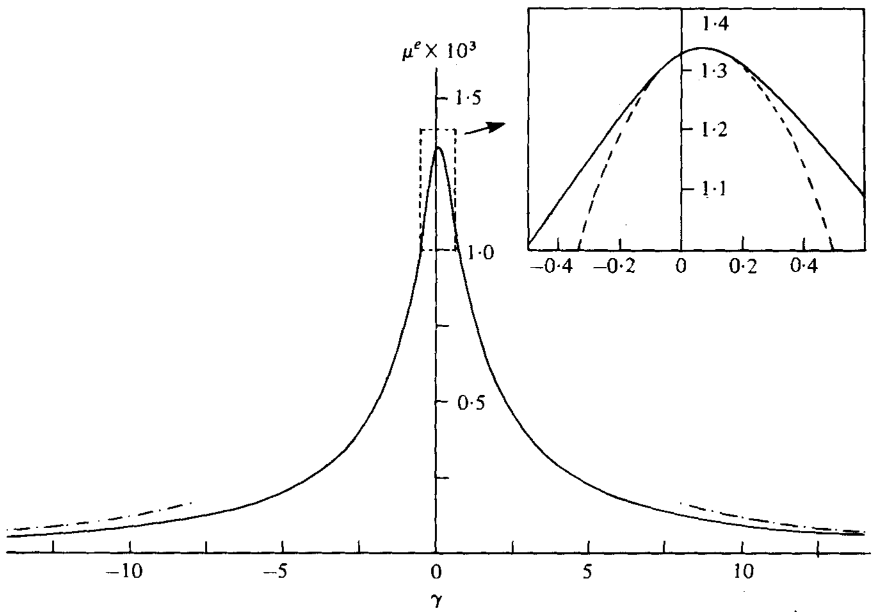

FIGURE 3. Strain viscosity μ^e for axisymmetric straining motion as a function of γ. ----, quadratic approximation from (22) for $|\gamma| \ll 1$ limit; —·—·—, $|\gamma| \gg 1$ limit.

The asymptotic form of ρ for large $\mathbf{x}$ can be found. For simplicity we take the case of uniaxial extensional flow, i.e. $E_1 = 2$ and $E_2 = E_3 = -1$. Working in cylindrical polars (x, s, ϕ), the principal contribution to the integral (21) for large x comes from the neighbourhood of $\lambda = 0$, giving

$$\rho(\mathbf{x}) \sim -\frac{1}{8\pi^{\frac{3}{2}}} \frac{\Gamma(\frac{1}{2}+1/4\gamma)}{\gamma^{1/4\gamma}} \frac{1}{x^{1+1/2\gamma}} \exp\left(-\tfrac{1}{2}\gamma s^2\right) \quad \text{as} \quad x \to \infty,$$

where Γ is the gamma function. Thus there is an algebraic decay in ρ in the direction of extension, instead of the exponential decay in the equilibrium double layer and the simple-shear case. This is because the ions experience an accelerating flow as they are swept downstream. For strong flows ($\gamma \gg 1$), this algebraic decay is very weak and the charge is found on length scales $x = O(e^{\gamma})$ and $s = O(\gamma^{-\frac{1}{2}})$.

The bulk-stress contribution has not been evaluated for the general case of pure strain, calculations having been restricted to axisymmetric strain and two-dimensional strain. For axisymmetric strain ($E_1 = 2, E_2 = E_3 = -1$), both uniaxial and biaxial strain are taken into account by allowing γ to be positive and negative for the respective cases. There is only one independent stress component for this flow and the corresponding viscosity contribution is

$$\mu^e = (2\Sigma^e_{11} - \Sigma^e_{22} - \Sigma^e_{33})/12\gamma.$$

The transform variables in the five-dimensional integral for μ^e obtained from (12) can be integrated out to give the two-dimensional integral

$$\mu^e = \frac{1}{24\pi^2\gamma^2} \int_0^1 du \left(I(u, 1) - \int_0^1 du' I(u, u') \right),$$

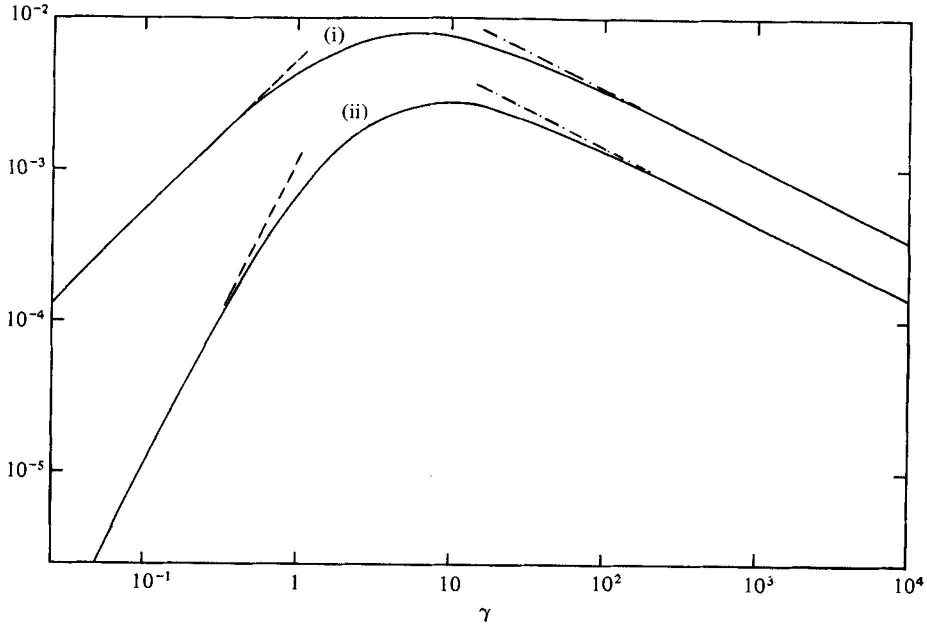

FIGURE 4. Logarithmic plot of the stress components in two-dimensional strain as a function of γ. (i) $\Sigma^e_{11}-\Sigma^e_{22}$, (ii) $\Sigma^e_{11}+\Sigma^e_{22}-2\Sigma^e_{33}$. ----, $\gamma \ll 1$ limit; -·-·-, $\gamma \gg 1$ limit.

where

$$I(u,u') = \begin{cases} \dfrac{\pi^{\frac{1}{2}}}{4}\dfrac{\gamma^{\frac{3}{2}}}{x_3^{\frac{3}{2}}}\left\{x_1 \ln\left(\left(\dfrac{x_3}{x_4}\right)^{\frac{1}{2}}+\left(1+\dfrac{x_3}{x_4}\right)\right)+\dfrac{x_3^{\frac{1}{2}}}{x_4}\dfrac{(x_2x_3-x_1x_4)}{(x_3+x_4)^{\frac{1}{2}}}\right\} & \text{for} \quad \gamma > 0, \\ \dfrac{\pi^{\frac{1}{2}}}{4}\dfrac{|\gamma|^{\frac{3}{2}}}{x_3^{\frac{3}{2}}}\left\{-x_1 \sin^{-1}\left(\left|\dfrac{x_3}{x_4}\right|\right)^{\frac{1}{2}}-\dfrac{x_3^{\frac{1}{2}}}{x_4}\dfrac{(x_2x_3-x_1x_4)}{|x_3+|x_4|^{\frac{1}{2}}}\right\} & \text{for} \quad \gamma < 0, \end{cases}$$

and

$$x_1 = u^{-4\gamma}-u^{2\gamma}, \quad x_2 = u^{2\gamma}-1, \quad x_3 = \tfrac{1}{4}(u^{-4\gamma}+u'^{-4\gamma}+2u^{2\gamma}+2u'^{2\gamma}-6),$$

$$x_4 = \tfrac{1}{2}(2-u^{2\gamma}-u'^{2\gamma}).$$

This is simpler to evaluate than the corresponding integral in the simple-shear case and can be computed to within 1% accuracy by using 8-point Gaussian quadrature for each integral. The results are plotted in figure 3. The dominant contribution for strong flows comes from the $I(u,1)$ integral, which has the same interpretation as in the simple-shear case, namely the interaction of the charge cloud with the field due to the point charge. The asymptotic value of μ^e can be evaluated exactly to give a strain-thinning viscosity

$$\mu^e = \tfrac{1}{48}(\pi|\gamma|)^{-\frac{3}{2}} \quad \text{as} \quad |\gamma| \to \infty$$

for both uniaxial and biaxial flows.

The second-order-fluid approximation from (15) and (16) for weak flows has only a limited range of validity, as the maximum value of μ^e is at $\gamma_{\max} = 0{\cdot}070$. Far better agreement is obtained if the expansion of (14) is extended to the next order, when

$$\mu^e = \frac{1}{240\pi}+\frac{\gamma}{1120\pi}-\frac{27\gamma^2}{4480\pi}+O(\gamma^3), \tag{22}$$

and this approximation is included in figure 3. The coefficient of the $O(\gamma^2)$ term is much larger than that of the $O(\gamma)$ term, and it predicts the maximum well, giving $\gamma_{max} = 0{\cdot}074$.

For the case of two-dimensional strain ($E_1 = -E_2 = 1$ and $E_3 = 0$), the integral representation of the charge density (20) can be written as

$$\rho(\mathbf{x}) = -\int_0^1 d\lambda \, \frac{\gamma\lambda^\gamma}{4\pi^{\frac{3}{2}}(\ln\lambda^{-1})^{\frac{1}{2}}(1-\lambda^{2\gamma})} \exp\left\{-\frac{x^2\gamma}{2(\lambda^{-2\gamma}-1)} - \frac{y^2\gamma}{2(1-\lambda^{2\gamma})} - \frac{z^2}{4\ln\lambda^{-1}}\right\}.$$

The two independent stress contributions are $\Sigma^e_{11} - \Sigma^e_{22}$ and the cross-stress

$$\Sigma^e_{11} + \Sigma^e_{22} - 2\Sigma^e_{33},$$

which for a Newtonian fluid are respectively $4\mu_0\gamma$ and zero. These can be reduced to three-dimensional integrals which can be evaluated numerically and are shown in figure 4. The low strain forms, from (15) and (16), and the high strain forms, obtained numerically, are

$$\Sigma^e_{11} - \Sigma^e_{22} = \begin{cases} \gamma/60\pi, \\ 0{\cdot}034\gamma^{-\frac{1}{2}}, \end{cases} \quad \Sigma^e_{11} + \Sigma^e_{22} - 2\Sigma^e_{33} = \begin{cases} \gamma^2/280\pi & \text{for} \quad \gamma \ll 1, \\ 0{\cdot}014\gamma^{-\frac{1}{2}} & \text{for} \quad \gamma \gg 1. \end{cases}$$

In conclusion we compare the results for a thick charge cloud with the results of Russel (1978*b*) for a thin charge cloud. Russel found for simple shear that the viscosity shear-thins, with a γ^{-2} behaviour as $\gamma \to \infty$, whilst the normal-stress differences tend to constant values for large γ. For pure strain he found a Newtonian behaviour until his expansion of the charge density broke down, when $\gamma \sim a\kappa \gg 1$. The results in this analysis show much less variation. In all the linear flows considered, all the stress components have a $\gamma^{-\frac{1}{2}}$ behaviour as $\gamma \to \infty$, the uniaxial extension strain viscosity first strain-thickening at small γ. Thus we expect the particular flows considered for arbitrary γ to be typical of other linear flows as far as the strong flow limit is concerned. Although there is no difference in the asymptotic behaviour of the bulk-stress contributions in the two cases considered, there is a difference in the far-field behaviour of the charge density. For simple shear we found an exponential decay, whereas for pure strain we found an algebraic decay. Since for general linear flows there will be an accelerating flow in the direction in which the charge cloud is stretched, we expect the algebraic decay to be more typical.

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