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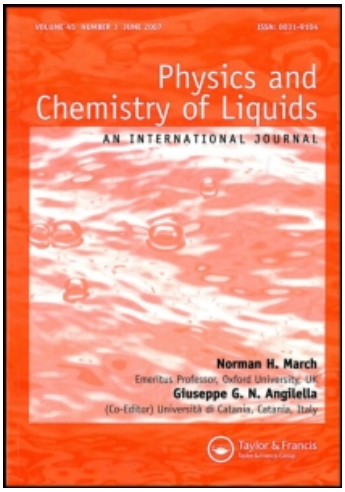

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Dynamics of Colloidal Dispersions

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Review Article

Dynamics of Colloidal Dispersions

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We review the essential physics underlying the dynamics of colloidal dispersions. The development of the theoretical techniques is discussed in the context of calculations done for both diffusion coefficients and viscosities.

1 INTRODUCTION

The dynamic and rheological properties of colloidal dispersions are of considerable importance and a comprehensive review of many aspects of these systems was given by Goodwin in 1975.[1] These properties control many aspects of processing of importance to the chemical engineer such as materials handling, pumping and transfer in pipes, mixing and stirring. They also determine important properties relating to behaviour in use such as is found in paints, many food dressings such as sauces, detergent products, etc. Often the dispersion is concentrated and imposed flows can be complex. For example the shear rate may be high to produce turbulent flow thereby aiding heat transfer into our out of the system.[2] The dispersion particles may have a complex shape and interact directly via van der Waals, electrical double layer and solvation forces[3] as well as indirectly via hydrodynamic effects.[4] Given this complexity, it is not surprising that the literature abounds with empirical and semi-empirical expressions that describe the properties of such systems in various regimes. However, despite this, a

number of authors have attempted to analyse the dynamics of dispersions from a fundamental point of view.

The basic model is one which considers spherical, rigid, neutrally buoyant particles of mass m immersed in a solvent. If the concentration of particles is sufficiently dilute that all interactions can be neglected then the well-known Fokker–Planck equation for the single particle distribution function $f_1(\mathbf{r}_1 p; \mathbf{t})$ is valid:

$$\frac{\partial f_1}{\partial t} + \frac{P}{m} \cdot \nabla f_1 = kT\zeta \frac{\partial}{\partial \mathbf{p}}\left(\frac{\partial}{\partial \mathbf{p}} + \frac{p}{mkT}\right) f_1$$

where ζ is the friction constant. Assuming that the momenta of the Brownian particles relax to equilibrium values instantaneously through interaction with the surrounding solvent, the equation for the one particle spatial distribution function $n_1(\mathbf{r}, t)$ can be obtained:

$$\frac{\partial n_1}{\partial t} = \frac{kT}{\zeta} \nabla^2 n_1$$

Thus we identify the one particle diffusion coefficient $D = kT/\zeta$.

When considering a system of N Brownian particles which interact directly, or indirectly via the solvent, it is necessary to deal with the diffusion tensors $\mathbf{D}_{\alpha\beta}$ and friction tensors $\zeta_{\alpha\beta}$ which relate the flow of solvent at the location of one particle and the hydrodynamic force at the location of another. In addition the interparticle forces of molecular origin must also be considered. The appropriate many particle Fokker Planck and Smoluchowski equations have been derived by a number of authors.[5,6] In the next section we give a relatively simple derivation of the Smoluchowski equation which forms the formal basis for much of colloidal dynamics. Section 3 discusses the problem of evaluating the diffusion tensors and fluid flows in dispersions using classical hydrodynamics within the framework of a diagrammatic perturbation theory which is used in later sections. Calculations of the one particle diffusion coefficient are discussed in Section 4. The nature of the bulk stress and viscosities of dispersions for both dilute and concentrated systems are discussed in Sections 5 and 6. We close with a brief discussion.

2 THE GENERALISED SMOLUCHOWSKI EQUATION

This equation has been derived for the case of no imposed flow by Deutch and Oppenheim[5] and Murphy and Asquire.[6] Beginning with the Liouville equation for the total system (fluid molecules plus N Brownian particles)

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they used a fairly lengthy method using Zwangzig's projection operators which derived en route the generalised Fokker–Planck equation and also proved the fluctuation dissipation theorem for this particular system. Thus they showed that the friction tensor:

$$\zeta_{\alpha\beta} = \frac{1}{k_B T} \int_0^\infty dt' \langle \mathbf{f}_\alpha(0)[\mathbf{f}_\beta(-t') - \langle \mathbf{f}_\beta \rangle] \rangle \tag{2.1}$$

where $\mathbf{f}_\alpha$ is the force on particle α and the average is taken over the fluid with the particles at fixed positions (r_α).

If we recognise at the outset that the mass of our particles is large and they are essentially Brownian particles we can obtain the Smoluchowski equation relatively simply. Note first that the particle distribution function $\mathbb{P}(\{r_\alpha, v_\alpha\}; t)$ satisfies the Liouville equation:

$$\frac{\partial \mathbb{P}}{\partial t} + \sum_\alpha \frac{\partial}{\partial \mathbf{r}_\alpha} (\mathbf{v}_\alpha \mathbb{P}) + \sum_\alpha \frac{\partial}{\partial \mathbf{f}_\alpha} \left\{ \left(\frac{\mathbf{F}_\alpha}{m} \right) \mathbb{P} \right\} = 0 \tag{2.3}$$

where $\mathbf{F}_\alpha$ is the total force on particle α (including Brownian forces). Integrating over particle velocities and noting the third term, which may be transformed into a surface integral, vanishes we obtain:

$$\frac{\partial P}{\partial t} + \sum_\alpha \frac{\partial}{\partial \mathbf{r}_\alpha} \bar{\mathbf{v}}_\alpha P \tag{2.4}$$

where

$$P = P(\{\mathbf{r}_\alpha\}, t) = \int \mathrm{d}\{\mathbf{v}_\alpha\} \mathbb{P}(\{\mathbf{r}_\alpha, \mathbf{v}_\alpha\}; t) \tag{2.5}$$

and

$$\bar{0} = \int \mathrm{d}\{\mathbf{v}_\alpha\} 0 \frac{\mathbb{P}}{P} \tag{2.6}$$

To obtain an expression for $\bar{\mathbf{v}}_\alpha$ we multiply Eq. (2.3) by $\mathbf{v}_\alpha$ and again integrate over particle velocities:

The third term may again be integrated by parts and noting the surface integral vanishes we obtain:

$$\frac{\partial}{\partial t} (\bar{\mathbf{v}}_\alpha P) + \sum_\beta \frac{\partial}{\partial r_\beta} \overline{\mathbf{v}_\alpha \mathbf{v}_\beta} P - \int \mathrm{d}\{\mathbf{v}_\alpha\} F_{\alpha/m} \mathbb{P} = 0 \tag{2.7}$$

We now observe that the total force on our Brownian particles is:

$$\mathbf{F}_\alpha = -\sum_\beta \zeta_{\alpha\beta} \cdot (\mathbf{v}_\beta - \mathbf{U}_B) + \mathbf{f}_\alpha + \mathbf{f}_\alpha^B \tag{2.8}$$

where $\mathbf{f}_\alpha$ is the body force from inter-particle and external forces and $\mathbf{f}_\alpha^\beta$ is the force due to Brownian fluctuations. U_B is the velocity of the particles

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in the absence of inter-particle forces, external forces and diffusion. It is the motion which would obtain for non-interacting massless particles governed by hydrodynamics alone; this itself presents a difficult calculation in hydrodynamics but the solution can at least be represented as a functional of the bare macroscopic flow, $\mathbf{U}^0$, and the particle positions:

$$\mathbf{U}_\alpha = H_\alpha(\{\mathbf{r}_\alpha\}, [\mathbf{U}^0(\mathbf{r})]) \tag{2.9}$$

Now if the velocities satisfy a local equilibrium distribution then we further have:

$$\overline{\mathbf{v}_\alpha \mathbf{v}_\beta} = \left(\frac{k_B T}{m}\right)\mathbf{1}\delta_{\alpha\beta} + \bar{\mathbf{v}}_\alpha \bar{\mathbf{v}}_\beta \tag{2.10}$$

It is generally the case that the momenta of the particles relax to their equilibrium distribution values much more rapidly than do their positions although work by Hinch[7] and Zwanzig[8] suggests we should have some reservations about this. Nevertheless if we consider the system over a time scale which is consistent with this assumption and neglect terms $0(\bar{\mathbf{v}}^2)$ we obtain from Eqs (2.7)–(2.9)

$$k_B T \frac{\partial P}{\partial \mathbf{r}_\alpha} + \int \mathrm{d}\{\mathbf{v}_\alpha\}[\zeta_{\alpha\beta}(\mathbf{v}_\beta - \mathbf{U}^0(\mathbf{r}_\beta) - \mathbf{f}_\alpha]\mathbb{P} \tag{2.11}$$

i.e.

$$\bar{\mathbf{v}}_\alpha P = \mathbf{U}^0(\mathbf{r}_\alpha)P + \sum \mathbf{D}_{\alpha\beta}\left[\frac{\mathbf{f}_\beta}{k_B T} - \frac{\partial}{\partial \mathbf{r}_\beta}\right]P \tag{2.12}$$

where we have introduced the diffusion tensor

$$\mathbf{D}_{\alpha\beta} = k_B T \zeta_{\alpha\beta}^{-1} \tag{2.13}$$

Substituting Eq. (2.11) into the continuity Eq. (2.4) gives the required result:

$$\frac{\partial P}{\partial t} - \sum_{\alpha\beta} \frac{\partial}{\partial \mathbf{r}_\alpha} \mathbf{D}_{\alpha\beta}\left[\frac{\partial}{\partial \mathbf{r}_\beta} - \frac{\mathbf{f}_\beta}{k_B T}\right]P + \sum_\alpha \frac{\partial}{\partial \mathbf{r}_\alpha} \mathbf{U}_\alpha P = 0 \tag{2.14}$$

3 DIAGRAMMATIC HYDRODYNAMICS

To calculate the diffusion tensor $\mathbf{D}$, the convective motion $\mathbf{U}_\alpha$ of the particles and other properties such as the viscosity of the suspension, requires a solution for the fluid flow around the particles. If we take the linear Stokes' equations to govern the fluid flow (thus neglecting fluid inertia in the micro

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hydrodynamics) the solution may be written as a linear response to the bare flow U^0 and the forces on the particles f^α

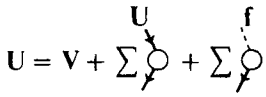
$$\mathbf{U}(\mathbf{r}) = \mathbf{U}^0(r) + \int d r' \mathbf{h}_N(\mathbf{r}\mathbf{r}') \cdot \mathbf{U}^0(r') + \sum_\alpha \mathbf{g}_N(\mathbf{r}, \alpha) \cdot \mathbf{f}_\alpha .$$

We do not include applied couples, assuming the particles to be couple-free. $\mathbf{g}_N$ and $\mathbf{h}_N$ both depend upon the positions of all the particles and

$$\mathbf{H}_\alpha = \mathbf{h}_N(r_\alpha)$$

$$\frac{1}{kT} \mathbf{D}_{\beta\alpha} = \mathbf{g}_N(r_\beta, \alpha)$$

$\mathbf{h}_N(\mathbf{r}, \mathbf{r}')$ gives the flow perturbations, or scatterings due to all the particles; where each particle individually scatters according to the total flow as perturbed by all the others. We may represent this diagrammatically as



where $\mathbf{U}$ represents the total flow field $\mathbf{U}(r)$ and $\mathbf{V}$ the bare field or vacuum term, $\mathbf{U}^0(\mathbf{r})$. The two diagrams represent each particle creating a disturbance (which contributes to $\mathbf{U}$) due to the field $\mathbf{U}$ and the body force respectively infringing upon the particle. The scattering here is the isolated single particle scattering because interactive effects are included explicitly by the self-consistent form of the above equation. Simple iteration of the above equation generates the "method of reflections"[9] for calculating the flows; in the iteration, diagrams giving direct self interactions must be counted zero.

Even for the single particle scattering, however, we do not have a complete closed-form result. For a sphere, Stokes' drag calculation[10] gives exactly

i.e. the flow due to the application of a steady force to the particle.

Faxen's theorem[11] gives the net translation of a sphere when an arbitrary flow impinges upon it, denoted by the diagram:

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Notice that we have introduced here the notation that a line terminating on a particle represents a calculation of only the resulting motion of that particle, not the surrounding flow.

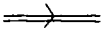
We only know the resulting flow perturbation

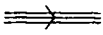
$$\int \mathbf{h}_1(\mathbf{r}\mathbf{r}')\mathbf{U}^0(\mathbf{r}')\mathrm{d}r'$$

as an expansion in the gradients of U_0 at the particle centre r_α

$$\mathbf{h}^{(0)} \cdot \mathbf{U}^0(\mathbf{r}_\alpha) + \mathbf{h}^{(1)} : [\nabla \mathbf{U}^0]\mathbf{r}_\alpha + h^{(2)} : [\nabla\nabla\nabla \mathbf{U}^0]\mathbf{r}_\alpha + \text{etc.}$$

Of this, the first term is zero, the second was obtained by Einstein[12] for a sphere and is known for an ellipsoid[13] but few explicit calculations have been made of higher terms even for spheres. Consequently it is convenient to be able to represent separately the flow $\mathbf{U}(r)$ —→— and all its derivatives:

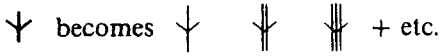
$\nabla \mathbf{U}(\mathbf{r})$ 

$\nabla\nabla \mathbf{U}(\mathbf{r})$ 

etc.

The particle scattering is a linear function of these values at the particle centre, rather than a functional of the flow field over the particle volume.

In the diagrams we may now replace the thick lines by this infinite series of fields so that



Of course we are forced to truncate this series in most cases, but it will be seen below that, if the number of scatterings or "reflections" is also truncated, it is entirely consistent to do this.

Einsteins calculation can now be exhibited diagrammatically as

Note that particles scatter only on response to flow gradients, i.e.

≡ zero.

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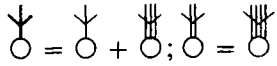
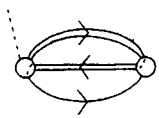
Also even though higher ordered fields all cause a particle to generate a disturbance only two cause any net translation of the particle itself


= all higher orders = zero.

The order of a field is the order of its tensor form, represented by the multiplicity of its line; the dotted line for an applied force is counted of order one.

It is very important to note that the way in which a flow propagates depends upon what caused it. The scattered flows (and gradients) decay as sums of inverse powers of distance and there is a very simple rule for calculating the leading term. Each line decays as r^{1-p-q} where p and q are the respective orders of the line in question and its predecessor. Thus the emerging line in the diagram:

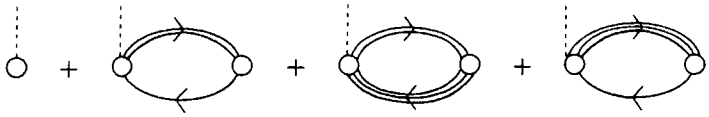
decays as $r^{1-3-2} = r^{-4}$ and the most complex of Felderhof's diagrams (see next section) is counted as

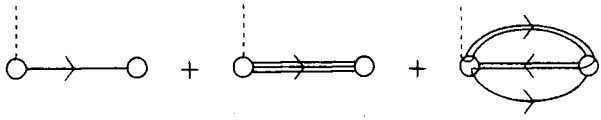


$$r^{-2} \times r^{-3} \times r^{-2} = r^{-7}$$

4 THE DIFFUSION COEFFICIENT

The effect of interparticle interactions on the single particle diffusion coefficient D have been studied by a number of authors. Felderhof[14] has calculated this effect to first order in the particle volume fraction ϕ, by evaluating the equation of motion for the one particle distribution function $p(\mathbf{r}t)$ from the Smoluchowski Eq. (2.14) using a density expansion. The bare flow $\mathbf{U}^0(r_\alpha)$ and hence $\mathbf{U}_\alpha$ is zero. In terms of the diagrammatic scheme given previously, Felderhof's approximation to $\mathbf{D}$ is

$D_{11} =$ 

$D_{12} =$ 

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and terms of order $1/r^8$ and greater are neglected. The contracted Smoluchowski equation is then reduced to a simple diffusion equation with coefficient $D = D_0(1 + \lambda\phi)$. Felderhof obtains, for the case of hard sphere interparticle forces and the usual "stick" hydrodynamic boundary conditions, $\lambda = 1.56$.

Batchelor[15] has obtained D using a generalised Einstein relation:

$$D(\phi) = \frac{\phi}{1-\phi}\frac{(\partial\mu/\partial\phi)pt}{f(\phi)}$$

where μ is the particle chemical potential and $f(\phi)$ is the friction coefficient for sedimenting particles in a uniform force field, e.g. gravity. He obtained $f(\phi)$ by integrating numerically the hydrodynamic equations of motion for a pair of hard sphere particles and obtained $\lambda = 1.45$. Felderhof discusses the shortcomings of other earlier calculations. The authors are not aware of any calculations of D in the higher volume fraction regime.

Comparison of the results with experimental data based on light scattering techniques[16] have been made but at present only qualitative agreement can be claimed.

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5 BULK STRESS AND VISCOSITY

a) Bulk stress

The effective viscosity η of a suspension is given by:

$$\langle\sigma\rangle = 2\eta\langle\varepsilon\rangle$$

where the averages of stress σ and strain rate ε are volume averages. That these are indeed the observed macroscopic quantities is justified by considering an experiment in which a large volume of suspension has *exactly* linear flow imposed at its outer boundaries:

$$U(r) = \mathbf{E}\cdot\mathbf{r} \quad \text{on boundary} \quad S_0$$

The volume averaged strain rate is then given by:

$$\frac{1}{V}\int_{\substack{\text{Total}\\\text{Suspension}\\\text{Volume}}} \nabla\mathbf{U}\,dV = \frac{1}{V}\int_{S\delta} d\mathbf{S}\;\mathbf{U} = \frac{1}{V}\int_{S\delta} d\mathbf{S}\;\mathbf{E}\cdot\mathbf{r} = \frac{\mathbf{E}}{V}\cdot\int dV(\nabla\mathbf{r})\cdot = \mathbf{E}$$

and the total work done on the system is

$$\int_{S_0} \mathbf{dS} \cdot \sigma \cdot \mathbf{U} = \int \mathbf{dS} \cdot \sigma \cdot \mathbf{E} \cdot \mathbf{r} = \int \mathrm{d}V\, \nabla \cdot (\sigma \cdot \mathbf{E} \cdot r) = \int \mathrm{d}V\, \sigma : \mathbf{E} = V\langle \sigma \rangle : \mathbf{E}$$

where we have used the Stokes' flow limit, $\nabla \cdot \sigma = 0$.

Macroscopic stress is due, at the microscopic level, to interparticle forces. As a result it is much easier to focus upon the divergence of the stress tensor, giving the net force on unit volume, as this is a quantity to which individual particles respond.

The short range forces between fluid molecules are easy to handle if we assume equilibrium continuum mechanics for the fluid. This gives:

$$\sigma^f = 2\eta_0 \varepsilon_{\text{fluid}}$$

and a contribution to the bulk stress of:

$$(1 - \phi)\langle \sigma^f \rangle_{\text{fluid}} = 2\eta_0 (1 - \phi)\langle \varepsilon \rangle_{\text{fluid}} = 2\eta_0 \langle \varepsilon \rangle_{\text{suspension}}$$

For the forces associated with the particles it suffices to partially deine a stress field by

$$\nabla \cdot \sigma^p + \mathbf{F}^p = 0 \tag{5.1}$$

where $\mathbf{F}^p$ is the density of force exerted by the fluid on the particles and $-\sigma^p \cdot \mathrm{d}S$ is the force exerted by particles on an element $\mathbf{dS}$ of the outer boundary of the suspension. This definition ensures that we may write $\nabla \cdot \sigma = 0$, where the total stress σ is given by $\sigma = \sigma^p + \sigma^f$; thus σ incorporates all the forces within the suspension.

Multiplying, e.g. (5.1) by r and integrating by parts we obtain

$$\int \mathrm{d}V_{\text{suspension}}\, \sigma^P = \int \mathrm{d}V\, \mathbf{r}\mathbf{F}^p + \int_{S_0} \mathbf{dS} \cdot \sigma^p \mathbf{r}$$

The forces $\mathbf{F}^p$ can be written in terms of the surface stresses on the particles due to the fluid to give

$$\sum_\alpha \int_{\text{Particle surface}} \mathbf{r}\sigma^f \cdot \mathrm{d}S_\alpha + \int_{S_0} \mathbf{dS} \cdot \sigma^p \mathbf{r} = \sum_\alpha \int (\mathbf{r} - \mathbf{r}_\alpha)\sigma^f \cdot \mathbf{dS}_\alpha$$
$$- \sum_\alpha \mathbf{r}_\alpha \mathbf{f}_\alpha^* + \int_{S_0} \mathbf{dS} \cdot \sigma^p \mathbf{r}$$

where $\mathbf{r}_\alpha$ is the centre of each particle and

$$\mathbf{f}_\alpha^* = -\int \sigma^f \cdot \mathbf{dS}_\alpha \tag{5.2}$$

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is the force on the particle required to balance the surface stresses. Thus f_α^* is given by the actual body force on the particle together with the force that would be required to produce the motion due to diffusion

$$\mathbf{f}_\alpha^* = \mathbf{f}_\alpha - kT \frac{\partial}{\partial r_\alpha} \ln P(\{\mathbf{r}_\beta\})$$

This provides some justification for the inclusion of the latter, included *ad hoc* by Batchelor.[17]

However, the contribution of the diffusion forces to

$$-\sum_\alpha \mathbf{r}_\alpha \, \mathbf{f}_\alpha^*$$

gives exactly, on averaging over the full N-body distribution, the perfect gas term $-NkT$: this point is rather obscured in Ref. 18. The true interparticle forces then give:

$$-\sum_\alpha \mathbf{r}_\alpha \, \mathbf{f}_\alpha + \int \mathbf{dS} \cdot \sigma^p \mathbf{r} = \frac{1}{2} \sum_{\alpha\beta} (\mathbf{r}_\alpha - \mathbf{r}_\beta) \, \mathbf{f}_{\alpha/\beta} - \sum_\beta \int \mathrm{d}S(\mathbf{r}(s) - \mathbf{r}_\beta) f_{S/\beta}$$

where $f_{\alpha/\beta}$ is the force on particle α due to particle β and $\mathrm{d}S\mathbf{f}_{s/\beta}$ is the force on $\mathrm{d}S$ due to particle β. The extension to n-body forces is trivial and the surface terms are irrelevant as $V \to \infty$. Now we return to the term:

$$\sum_\alpha \int (\mathbf{r} - \mathbf{r}_\alpha) \sigma^f \cdot \mathbf{dS}$$

which may in fact be identified with the contribution due to continuum solid stress on the particles.

Since for a given configuration of the particles the Stokes' equations for the fluid flow are *linear* we may decompose the fluid stress into

$$\sigma^f = \sigma^H + \sigma^F \tag{5.3}$$

where the first term is associated with the pure hydrodynamic shear flow $\mathbf{U}^H$. The remainder σ^F is associated with the flow $\mathbf{U}^F$ due to net forces on the particles and diffusion. Batchelor[17] has proved a powerful identity which gives the bulk stress contribution of the latter flow in terms of the force-free flow.

If we have two Stokes' flows $\mathbf{U}_1$ and $\mathbf{U}_2$ with associated stress fields σ_1 and σ_2 then

$$\int \mathbf{dS} \cdot \sigma_1 \cdot \mathbf{U}_2 = \int \mathbf{dS} \cdot \sigma_2 \cdot \mathbf{U}_1 \text{ both giving } \int \mathrm{d}V(\sigma_1 : \sigma_2 - 3P_1P_2) \text{ by parts} \tag{5.4}$$

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Flow 1 is taken to be the deviation part of the hydrodynamic flow round the particles.

$$\mathbf{U}_1 = \mathbf{U}^H - \mathbf{E}\cdot\mathbf{r}$$

$$\sigma_1 = \sigma^H - 2\eta\mathbf{E}_s;\ 2\mathbf{E}_s = \mathbf{E} + \mathbf{E}^T \tag{5.5}$$

and flow 2 is the flow due to forces on (+diffusion of) the particles

$$\mathbf{U}_2 = \mathbf{U}^F;\ \sigma_2 = \sigma^F \tag{5.6}$$

The surface is that enclosing a large volume of suspension together with surfaces excluding all the particles. If exact linear shear flow is imposed at the outer boundary, U_2 and U_1 vanish there so only the particle surface terms contribute.

On the surface of particle α centred at $\underline{r}_\alpha$,

$$\mathbf{U}_2 = \mathbf{U}^F(\mathbf{r}_\alpha) + \mathbf{\Omega}_\alpha^F \wedge (\mathbf{r} - \mathbf{r}_\alpha)$$

and

$$\mathbf{U}_1 = \mathbf{U}^H(\mathbf{r}_\alpha) + \mathbf{\Omega}_\alpha^H \wedge (\mathbf{r} - \mathbf{r}_\alpha) - \mathbf{E}\cdot\mathbf{r} \tag{5.7}$$

Neither rotational part contributes to the surface integrals since the particles are couple-free.

Also

$$\int \mathbf{U}^F(\mathbf{r}_\alpha)\cdot(\sigma^H - 2\eta_0\mathbf{E}_s)\cdot d\mathbf{S} = 0$$

since in flow H the particles are force-free. Then if we write

$$\mathbf{U}^H(\mathbf{r}_\alpha) = \mathbf{E}\cdot\mathbf{r}_\alpha + \mathbf{E}:\mathbf{C}_\alpha \tag{5.8}$$

we obtain

$$0 = \sum_\alpha \int \mathbf{U}_1\cdot\sigma_2\cdot d\mathbf{S}_\alpha$$

$$= \sum_\alpha E\cdot(\mathbf{r}_\alpha - \mathbf{r})\cdot\sigma_F\cdot d\mathbf{S}_\alpha + \sum_\alpha \mathbf{E}:\mathbf{C}_\alpha\cdot\int\sigma_F\cdot d\mathbf{S}_\alpha \tag{5.9}$$

Since this holds for arbitrary (traceless) E we can deduce

$$\sum_\alpha \int(\mathbf{r} - \mathbf{r}_\alpha)\cdot\sigma_F\cdot d\mathbf{S}_\alpha = \mathbf{C}_\alpha\cdot\int\sigma_F\cdot d\mathbf{S}_\alpha = -\mathbf{C}_\alpha\cdot\mathbf{f}_\alpha^* \tag{5.10}$$

where $\mathbf{f}_\alpha^*$ is given by Eq. (5.2).

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The bulk stress is thus given by:

$$\langle\sigma\rangle_{\text{suspension}} = 2\eta_0\langle\varepsilon\rangle_{\text{suspension}} + \frac{1}{V}\sum_\alpha \int (\mathbf{r} - \mathbf{r}_\alpha)\sigma^H \cdot \mathbf{dS}_\alpha$$
$$- \frac{1}{V}\sum_\alpha \mathbf{C}_\alpha \cdot \mathbf{f}_\alpha^* - \frac{1}{2}\frac{1}{V}\sum_\alpha\sum_\beta (\mathbf{r}_\alpha - \mathbf{r}_\beta)\mathbf{f}_{\alpha/\beta} + \text{isotropic terms} \tag{5.11}$$

where $\mathbf{f}_{\alpha/\beta}$ is the force on α due to β and $\mathbf{f}_\alpha^*$ is the force on α *including* $-kT(\partial/\partial\mathbf{r}_\alpha)\ln p\,(\{r_\beta\})$.

It should be noted that to include electro-viscous effects[18] in the above formulation, each ion must be interpreted as a separate particle.[19] Alternatively the flow around each solid inclusion has to be treated as that of the appropriate inhomogeneous medium.

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b) Viscosity at low volume fractions

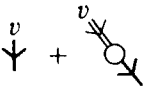
Evaluating the terms in the stress formula (5.11) is in practice not at all easy. Various simplifying approximations have been explored, the chief being the limit of a dilute suspension. In this regime it is natural to seek an expansion of the viscosity on the volume fraction of particles ϕ:

$$\eta = \eta_0(1 + C_1\phi + C_2\phi^2 + \cdots)$$

Contributions of order ϕ^p are due to effects involving at most p particles, so that the first correction involves only the response of an isolated particle. In this case the only suspension correction to the stress is:

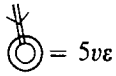
$$\frac{N}{V}\int (\mathbf{r} - \mathbf{r}_1)\sigma^H \cdot \mathbf{dS}_1 \tag{5.12}$$

and the flow is given by:

$W =$ 

as calculated by Einstein.[13] He then proceeded to evaluate not the stress but the dissipation, but his results are equivalent to obtaining $5\phi\varepsilon/2$ for the above force dipole (Eq. 5.12) and hence $C_1 = \frac{5}{2}\phi$. We may denote the evaluation of just the hydrodynamic force dipole on a particle by

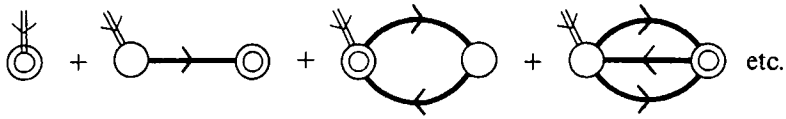
whereupon Einstein's result is



$= 5v\varepsilon$

where v is the particle volume.

Over sixty years passed before Batchelor and Green[20] presented a direct calculation of the corresponding pure hydrodynamic contribution to the bulk stress to order ϕ^2. Their calculation is equivalent to the infinite series of diagrams.



but they also had to take account of the corresponding modification to the shear rate in the fluid to obtain integrals. (Jeffrey and others,[21] including one of the present authors, discuss this last issue at some length.) In the approach the hydrodynamic equations were integrated using a numerical procedure.

For the thermal equilibrium distribution they obtained:

$$C_2^H = 5.2$$

where the superscript denotes the hydrocarbon contribution. For pure extension rates $E > D_0/a^2$ (where a is the particle radius and D_0 the diffusion constant) they found the resulting steady state correlation function from Eq. (2.14) with $D = 0$. This gave:

$$C_2^H = 7.6$$

For the case of low Peclet number, $Ea^2/D_0 \ll 1$, Batchelor[17] has evaluated the direct Brownian contribution to C_2 given by the stress

$$\frac{kT}{V}\sum_\alpha \mathbf{C}_\alpha \cdot \frac{\partial}{\partial r_\alpha} \ln P \quad \text{(see equation 5.11)}$$

obtaining $C_2^B = 1.0$.

To obtain the contribution due to inter-particle forces requires first the solution of (5.11) to at least first order in the flow term, for two particles. Neglecting hydrodynamic interactions this was carried through by Russel[22] for spheres with screened colomb forces.

6 VISCOSITY AT HIGH VOLUME FRACTIONS

Serious attempts to extend the formalism of the preceding sections to more concentrated dispersions have not been made but are likely to prove difficult. However other methods have been successful to some degree. Frankel and

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Acrivos[23] have used a cell model to obtain the viscosity in the limit as the volume fraction ϕ approaches its maximum value ϕ_∞. Assuming viscous dissipation arises primarily from flow in the fluid between the particles via lubrication their result for hard spheres is

$$\frac{\eta}{\eta_0} \to c\left\{\frac{(\phi/\phi_\infty)^{1/3}}{1-(\phi/\phi_\infty)^{1/3}}\right\} \quad \text{as} \quad \frac{\phi}{\phi_\infty} \to 1 \tag{6.1}$$

and c is a number which depends on the assumed cell geometry. A particularly fruitful approach can be developed using the notion of a mean field. Consider first the Einstein result for dilute suspension which may be expressed in differential form

$$\delta\eta = \eta_0 \tfrac{5}{2}\delta\phi \tag{6.2}$$

Now consider increasing the volume fraction ϕ of a concentrated suspension by an amount of $\delta\phi$. Within a mean field treatment one argues that the increase in viscosity $\partial\eta$ should be given by

$$\delta\eta = \tfrac{5}{2}\eta\phi \quad \text{i.e. } \eta = \eta_0 e^{5\phi/2} \tag{6.3}$$

This result was first proposed by Arrhenius.[24] However, as he recognised, this equation omits the correlations between spheres due to their finite size. One can argue in one of two ways:

On increasing the volume fraction by an amount $\delta\phi$, the spheres that were already present suffer a crowding effect. This gives rise to an additional incremental increase in viscosity $(k\phi\,\delta\phi) \times \delta\eta/\delta\phi$. The "crowding" factor k will in general be a function of ϕ and also for multimodel dispersions, a function of the polydispersity. We shall argue elsewhere[26] that it varies only slowly with these parameters and set it equal to a constant in what follows. Thus the differential equation now reads:

$$\delta\eta = \tfrac{5}{2}\eta\delta\phi + k\phi\delta\eta \tag{6.4}$$

Alternatively one can argue that because particles are already present, the free volume available to the added particles is reduced by a factor $1 - k\phi$. Thus we obtain

$$\delta\eta = \frac{5}{2}\frac{\eta\delta\phi}{1-k\phi} \tag{6.5}$$

Clearly both approaches give the same equation and a net viscosity

$$\eta = \eta_0(1-k\phi)^{-5/2k} \tag{6.6}$$

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This result was first reported by Krieger.[25] Mooney[27] has published a derivation of η in which both of the above effects are included simultaneously. This leads to an exponential expression:

$$\eta = \eta_0 \exp\left(\frac{2.5\phi}{1 - k\phi}\right) \tag{6.7}$$

However this approach appears to be inconsistent and double count the crowding effect. By exploring polydispersity both experimentally and theoretically Farris[28] was able to show that the result of Krieger has a high degree of merit. Indeed, generalisation of the Krieger result to a bimodal distribution of particles with radii R_1 and R_2 is exact in the limit $R_1/R_2 \to 0$ and ∞ which casts further doubt on Mooney's result.

More recently De Gennes[29] has published a calculation of the effect on the viscosity of aggregation of particles which occurs from hydrodynamic interactions. De Gennes argues that above a critical volume fraction an infinitely large cluster or aggregates could form which give rise to a cusp in the viscosity $v\phi$ data. Such a phenomenon has not so far been reported but it is interesting to note that such a distribution may behave similarly to the multimodal distributions studied by Farris[28] for which case cusps are predicted and observed experimentally.

In relating these results to experiment, it has been common practice to set $1/k = \phi_\infty$, the volume fraction at which the viscosity is infinite. Precise identification of this point is not easy for two reasons. Firstly, the measurement of viscosity in this region is not simple, spurious effects can and do occur which must be corrected for. Secondly, the calculation of volume fraction ϕ is itself subject to uncertainties since the particles may swell, adsorb surface active agents or aggregate for a variety of reasons. In some respects the situation is analogous to that in critical phenomenon where one has to obtain an unknown exponent near to the vicinity of the critical point which is itself uncertain (at least to the degree of accuracy necessary).

We would like to point out here another simple method for obtaining k which avoids this difficulty. Note that Eq. (6.6) must be valid over the whole range of volume fractions. Thus expanding in a power series in ϕ we obtain:

$$\frac{\eta}{\eta_0} = 1 + \frac{5\phi}{2} + C_2\phi^2 + \cdots \tag{6.8}$$

where $C_2 = \frac{5}{4}(\frac{5}{2} + k)$.

Now an accurate value for C_2 has been obtained by Batchelor and Green,[21] i.e. $C_2 = 5.2$. Care must be taken not to add the Brownian contribution to C_2 later calculated by Batchelor[18] since this has not been included in the mean field approach. This now yields $\phi_\infty = 0.60$ and which as expected lies

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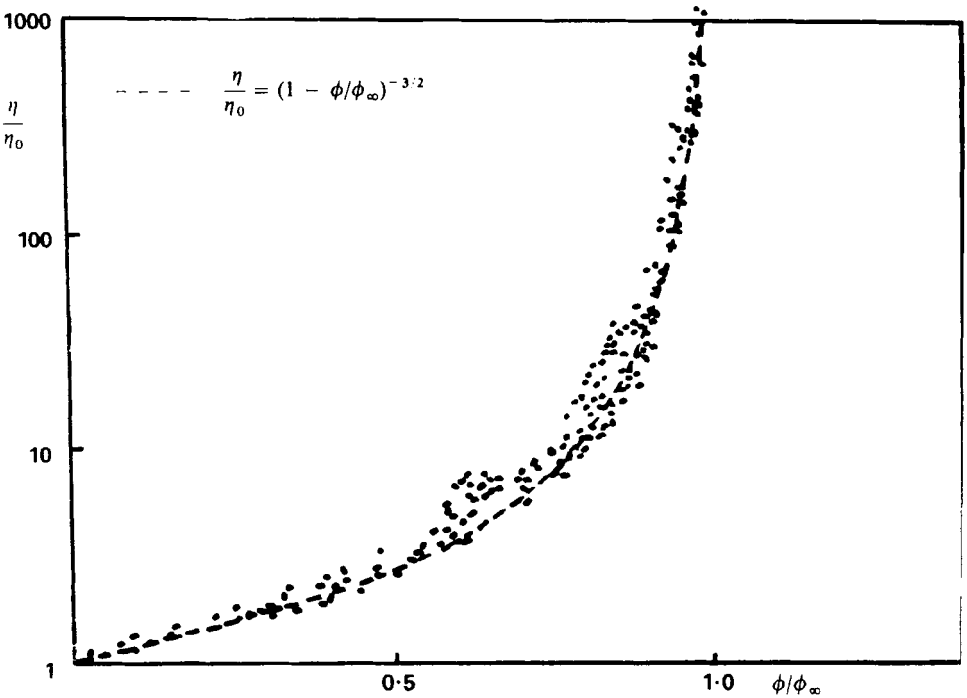

FIGURE 1 The points in the Figure are experimental values for shear viscosity *vs.* volume fraction (relative to the locking volume fraction, ϕ^∞) for many colloids compiled by Chong, Christiansen and Baer.[31] The dotted line represents the theoretical predictions of equation (6.6) derived in the text.

below the value 0.64 for random close packing.[30] Chong, Christiansen and Baer[31] have compiled viscosity data from many sources. Their data which includes viscosities of different suspensions are reproduced in Figure 1 and Eq. (6.6) using $\phi_\infty = 0.6$ is shown for comparison. The agreement is good. If now we add the direct Brownian contribution to the viscosity the theoretical values for η/η_0 in the region $\phi/\phi_\infty \lesssim 0.7$ are increased slightly thus improving further the agreement between theory and experiment. The Brownian contribution will be relatively negligible at higher volume fractions.

7 DISCUSSION

The essential foundation for a comprehensive treatment of colloidal dynamics is the Smoluchowski equation deduced in Section Two. Given the diffusion tensor D and the response H, from classical hydrodynamics the Smoluchowski equation yields complete equilibrium and diffusion controlled

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dynamical information. The latter includes diffusion controlled aggregation kinetics as well as the quantities discussed here. To progress with understanding of the diffusion coefficient more experimental data on well characterised dispersions are needed to compare with theoretical predictions, as well as to stimulate further work. Dilute systems may be studied using light scattering techniques;[17] radioactive tracers or neutron scattering may aid the study of concentrated systems.

With regard to the viscosity within the linear regime the situation is quite different. Here mean field theories, whose parameters can be determined by ensuring they predict viscosities of dilute systems, can be used over the whole range of concentrations. Furthermore Farris[28] has shown how such theories can be extended to cover polydisperse systems.

There are many aspects of colloidal dynamics we have not discussed in this relatively brief review. Electroviscous effects,[1] non-Newtonian behaviour such as may arise from particle deformation or aggregation, the consequences of anisotropic particles[32,33] are all important aspects of the subject. Currently much experimental data is being obtained on systems that are better characterised than was the case a few years ago and it seems clear that theoretical techniques able to analyse less ideal, more complex systems are also being developed. This bodes well for a more fruitful interaction of theory and experiment and, in our opinion, theoreticians particularly should now take seriously the many challenges which have long been present in this field.

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