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Electro-acoustic effects in a dilute suspension of spherical particles

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Sound waves can be generated in a colloid by the application of an alternating electric field. In this paper we describe the method for calculating this and the related electro-acoustic phenomenon of electric fields generated by sound waves. As an illustration of the procedure, we obtain formulae for these two effects for a suspension of spherical particles with thin double layers, in a parallel plate geometry.

1. Introduction

The effects to be described in this paper arise from the presence of electric charges on the suspended particles. In equilibrium such particles are surrounded by a diffuse cloud of ions carrying a total charge equal and opposite to that of the particle. This arrangement of surface charge and diffuse charge is known as a 'double layer'.

When sound waves pass through such a suspension, the density difference between the particles and the liquid leads to relative motion between the two phases. As a result macroscopic electric currents are set up and these lead to electric fields which alternate at the sound-wave frequency.

The idea that sound waves could generate electric fields in a suspension of charged particles arose in a paper by Debye (1933), in connection with electrolyte solutions. The first measurements of the effect in suspensions were reported in 1938 by Rutgers, and in that year the first theoretical paper appeared (Hermans 1938). The paper dealt with the case of a suspension in which the particle radius is much smaller than the double layer thickness, a situation which occurs rarely in practice. In 1951 Enderby studied the more important case of a dilute suspension of weakly-charged spheres in an electrolyte of arbitrary double layer thickness, with the proviso that the ions have equal diffusivities. This restriction on the electrolyte was removed in the following year by Booth & Enderby (1952).

Since that time there have been no theoretical developments in this area, presumably because of the difficulties associated with measuring pressure waves and electric fields in suspensions. Fortunately, these difficulties have now been overcome, and Matec Instruments are marketing a device which is capable of accurately measuring this effect in the megahertz range. The device is also capable of measuring the reverse effect of sound waves generated by electric fields, an effect which has hitherto escaped notice in the scientific literature.

In this paper these two phenomena will be referred to as 'electro-acoustic' effects. The aim of the paper is to provide a theoretical basis for relating both effects to the microstructure of a dilute suspension.

In the following section we set out the microscopic differential equations which

must be solved in the calculation of these effects. These equations govern the distribution of ions, electrical potential, fluid velocity and pressure in the suspension. In § 3 we set out the macroscopic constitutive equations required for the calculation of electro-acoustic effects and we derive a reciprocal relation between two of the coefficients in these expressions. This relation provides a link between the electric field generated by a sound wave, and the sound waves generated by an electric field.

Formulae for these two effects are obtained in §§ 4 and 5 for the case of a dilute suspension confined by two parallel plates. In § 4, which is concerned with electric fields generated by sound waves, we discuss Enderby's work in more detail, pointing out a number of flaws in his solution of the electrokinetic equations and in his subsequent calculation of the electric field.

The formulae derived in §§ 4 and 5 both involve the electrophoretic mobility of the particles in an alternating electric field. In § 6 we calculate this mobility for particles with radii much greater than the double layer thickness.

2. The electrokinetic equations

The calculation of colloidal transport properties involves the solution of the 'electrokinetic equations', equations which describe the microscopic variations in the ion density, electrical potential, velocity and pressure in the suspension. The derivation of these equations is described in a number of papers (see for example O'Brien & White 1978, or Sherwood 1980), so only a brief outline will be given here.

The electrical potential ψ satisfies Poisson's equation, which in SI units takes the form

$$\nabla^2\psi = -\sum_{j=1}^{N} \frac{ez_j n_j}{\epsilon} \tag{2.1}$$

in the liquid. Here ϵ is the permittivity of the electrolyte, ez_j is the charge and n_j the number density of the jth species of ion, and N is the number of ionic species in the electrolyte. In the absence of any chemical reactions each species satisfies the conservation equation

$$\frac{\partial n_j}{\partial t} = -\nabla \cdot \boldsymbol{f}_j, \tag{2.2}$$

where $\boldsymbol{f}_j$ is the flux density of the jth ionic species. In a dilute electrolyte

$$\boldsymbol{f}_j = -D_j\left(\nabla n_j + \frac{n_j ez_j \nabla\psi}{kT}\right) + n_j \boldsymbol{v}, \tag{2.3}$$

where $\boldsymbol{v}$ is the fluid velocity and D_j the ion diffusivity. The terms on the right-hand side represent the fluxes due to Brownian motion, the local electric field, and convection with the flow respectively.

The microscopic quantities of interest will presumably vary in the liquid on a lengthscale of the order of the particle radius. On the assumption that the wavelength of the sound wave is much greater than the particle radius, we will treat the fluid as incompressible in the calculation of these microscopic variations. Thus the equations of fluid motion take the form

$$\nabla \cdot \boldsymbol{v} = 0, \tag{2.4}$$

and

$$\rho\frac{\partial \boldsymbol{v}}{\partial t} = -\nabla p + \mu\nabla^2\boldsymbol{v} - \sum_{j=1}^{N} ez_j n_j \nabla\psi. \tag{2.5}$$

As usual ρ, μ and p are the fluid density, viscosity and pressure respectively. The convective inertia term has been omitted on the grounds that the particle Reynolds number is very small. The final term on the right-hand side represents the electrical body-force per unit volume.

In a suspension in thermodynamic equilibrium, the ionic and fluid fluxes are identically zero. From (2.3) it follows that the ion densities are given by the Boltzmann expression

$$n_j = n_j^\infty \exp(-ez_j\psi/kT),$$

for $j = 1, \ldots, N$, where the n_j^∞ are constants. Substitution of these formulae in Poisson's equation yields a differential equation for the equilibrium potential. From the equation it can be shown (Hunter 1981, chapter 2) that both the potential and the charge density in the electrolyte decay to zero exponentially with distance from an isolated particle, with a decay length κ^{-1} given by

$$\kappa^{-1} = \left(\sum_{j=1}^{N} \frac{e^2 z_j^2 n_j^\infty}{\epsilon kT}\right)^{\frac{1}{2}}, \tag{2.6}$$

κ^{-1} is the 'double layer thickness' referred to in the introduction. Beyond the double layer the potential is zero and $n_j = n_j^\infty$.

The form of the equilibrium potential and ion density fields around a spherical particle depend on the relative ion densities beyond the double layer, on κa, (the ratio of particle radius to double layer thickness) and on the potential ζ at the particle surface. The latter quantity in turn depends on the nature of the particles and on the type and density of the ions beyond the double layer (Hunter 1981, chapter 2.2). In this paper ζ will be treated as a given quantity.

We now turn to the case of a suspension of uniform particles disturbed from equilibrium by the application of an alternating electric field or pressure gradient. As in nearly every other electrokinetic study it will be assumed here that the local ion densities and electric fields are only slightly perturbed from their equilibrium values.

To calculate the electro-acoustic effects we will need to determine these perturbations over regions of the suspension which are large compared with particle spacing, but much smaller than the macroscopic lengthscales. Since the particles are uniform and the suspension is dilute the particle velocities will be uniform over such a region. For convenience we take a frame of reference moving with the particles. A superscript 'o' will be used to denote the equilibrium ion densities and potential, and the departures from those equilibrium values will be indicated by δ prefix.

Neglecting products of the various deviations from equilibrium in (2.1)–(2.3) and (2.5), we obtain the approximate forms

$$\left.\begin{aligned} \nabla^2 \delta\psi &= -\sum_{j=1}^{N} \frac{ez_j \delta n_j}{\epsilon}, \\ -\mathrm{i}\omega \delta n_j &= D_j \nabla\cdot\left(\nabla \delta n_j + n_j^o \frac{ez_j}{kT}\nabla \delta\psi + \delta n_j \frac{ez_j}{kT}\nabla\psi^o\right) - \nabla n_j^o \cdot \boldsymbol{v}, \\ \text{and} \qquad -\mathrm{i}\omega\rho(\boldsymbol{v}+\boldsymbol{U}) &= -\nabla \delta p + \mu \nabla^2 \boldsymbol{v} - \sum_{j=1}^{N} ez_j(n_j^o \nabla \delta\psi + \delta n_j \nabla\psi^o), \end{aligned}\right\} \tag{2.7}$$

where an $\mathrm{e}^{-\mathrm{i}\omega t}$ time dependence has been assumed for each of the perturbed quantities. The term involving the particle velocity $\boldsymbol{U}$ arises from our choice of the particles as the frame of reference.

Inside the particle, the velocity and ion densities are zero, and $\delta\psi$ satisfies Laplace's equation, assuming fixed charge density within the particle. At the particle surface, the boundary conditions are

$$\boldsymbol{v} = \boldsymbol{0}, \quad [\epsilon \nabla \delta\psi \cdot \hat{\boldsymbol{n}}] = 0,$$

and

$$\boldsymbol{f}_j \cdot \hat{\boldsymbol{n}} = 0 \quad (j = 1, 2, \ldots, N). \tag{2.8}$$

where $\hat{\boldsymbol{n}}$ is the unit outward normal and the square brackets denote the jump at the particle surface.

At large distances $\boldsymbol{x}$ from the particle

$$\delta n_j = 0, \quad \boldsymbol{v} = -\boldsymbol{U}, \quad \delta\psi = -\boldsymbol{E} \cdot \boldsymbol{x}, \tag{2.9}$$

and

$$\delta p = -\nabla P \cdot \boldsymbol{x}, \tag{2.10}$$

where $\boldsymbol{E}$ and ∇P are the uniform electric field and pressure gradient far from the particles. For the dilute suspension which is of interest here, these quantities may be equated to the macroscopic electric field and pressure gradient.

The mathematical specification of the problem is completed by the requirement that the net external force on any particle and its double layer is zero. This follows from the fact that in equilibrium, the net charge on the particle and double layer is zero. Since the net external force on this region is the charge × the field, we conclude that to $O(E)$, this force is zero.

3. A useful reciprocal relation

For the calculation of the electro-acoustic effects we will require formulae for the particle velocity $\boldsymbol{U}$ and the volume average current density $\langle \boldsymbol{i} \rangle$ in the suspension where the local current density $\boldsymbol{i}$ is given by

$$\boldsymbol{i} = \boldsymbol{i}_f + i\omega\epsilon \nabla \delta\psi. \tag{3.1}$$

For readers who are unfamiliar with the colloidal dielectric literature, this formulae for $\boldsymbol{i}$ will require some explanation. The term $\boldsymbol{i}_f$ represents the contribution from ionic fluxes in the electrolyte. The second term in (3.1) takes into account the current due to the alternating dipole moments of the dielectric molecules in the system. This current is given by

$$-i\omega \boldsymbol{P},$$

or equivalently by

$$i\omega(\epsilon - \epsilon_0) \nabla \delta\psi,$$

where $\boldsymbol{P}$ is the polarization vector and ϵ_0 is the permittivity in vacuum. Although it does not represent a true current, an extra term

$$i\omega\epsilon_0 \nabla \delta\psi,$$

is added to (3.1) to provide a current density with zero divergence, a result which may be verified by combining Poisson's equation (2.1) with the ion conservation equation (2.2) (see O'Brien 1982, § 3 for more details).

Since the problem (2.7)–(2.10) for the various perturbation quantities is linear, these quantities must be linear functions of the applied field $\boldsymbol{E}$ and the pressure gradient ∇P. For a statistically isotropic suspension it follows that the particle velocity and the average current density are related to ∇P and $\boldsymbol{E}$ by expressions of the form

$$\left.\begin{aligned} \boldsymbol{U} &= \alpha \nabla P + \mu_E \boldsymbol{E}, \\ \text{and} \quad \langle \boldsymbol{i} \rangle &= \beta \nabla P + K^* \boldsymbol{E}. \end{aligned}\right\} \tag{3.2}$$

The coefficient μ_E which relates particle velocity to field strength is normally termed the electrophoretic mobility, while K^* is called the complex conductivity. Our choice of symbols for these quantities is in accordance with standard notation. As yet there is no standard nomenclature and notation for the remaining coefficients α and β.

In the following sections it will be shown that the coefficient β determines the electric field generated by a sound wave, while μ_E determines the form of the sound waves generated by an alternating electric field. The calculation of β and μ_E involves the solution of the electrokinetic equations for zero electric field and zero macroscopic pressure gradient respectively.

Fortunately we only need to solve one of these problems, for μ_E and β are linked by a reciprocal relation.

This relation arises from an integral identity involving two solutions to the electrokinetic equations with different prescribed macroscopic pressure gradients and electric fields. The two solutions will be indicated by superscripts a and b respectively.

Consider the integral

$$\int_A \left\{ \boldsymbol{v}^b \cdot \left(\boldsymbol{\sigma}^a + i\omega\rho \boldsymbol{U}^a \cdot \boldsymbol{x}I + kT \sum_{j=1}^{N} \delta n_j^a I \right) + i\omega\, \delta\psi^a\, \delta\boldsymbol{D}^b - \sum_{j=1}^{N} \left(\frac{kT}{n_j^o} \delta n_j^a + ez_j\, \delta\psi^a \right) \boldsymbol{f}_j^b \right\} \cdot \hat{\boldsymbol{n}}\, dA, \tag{3.3}$$

where A is a closed surface lying in the fluid, $\delta\boldsymbol{D} = -\epsilon\nabla\,\delta\psi$, and $\boldsymbol{\sigma}$ is the usual hydrodynamic stress tensor. Applying the divergence theorem, and using the electrokinetic equations we obtain the volume integral

$$\int_V \left\{ \sum_{j=1}^{N} \frac{D_j n_j^o}{kT} \nabla \left(\frac{kT}{n_j^o} \delta n_j^a + ez_j\, \delta\psi^a \right) \cdot \nabla \left(\frac{kT}{n_j^o} \delta n_j^b + ez_j\, \delta\psi^b \right) + 2\eta \boldsymbol{e}^a : \boldsymbol{e}^b \right\} dV$$

$$- i\omega \int_V \left\{ \sum_{j=1}^{N} kT \frac{\delta n_j^a}{n_j^o} \delta n_j^b + \epsilon\nabla\,\delta\psi^a \cdot \nabla\,\delta\psi^b + \rho \boldsymbol{v}^a \cdot \boldsymbol{v}^b \right\} dV.$$

where V is the volume enclosed by A, and $\boldsymbol{e}$ denotes the rate of strain tensor. Since the volume integral is unaltered by an interchange of a and b, it follows that the surface integral (3.3) is similarly unaffected.

This result concerning the surface integral applies to any closed surface in the suspension, for since $\boldsymbol{v}$ and $\boldsymbol{f}^j \cdot \hat{\boldsymbol{n}}$ are zero at the particle surface, the contribution to (3.3) from a particle surface is given by

$$\int_{A_P} i\omega\, \delta\psi^a\, \delta\boldsymbol{D}^b \cdot \hat{\boldsymbol{n}}.$$

By appling the divergence theorem and using the fact that $\delta\boldsymbol{D} \cdot \hat{\boldsymbol{n}}$ and $\delta\psi$ are continuous across the particle surface we once again obtain a volume integral which is unaffected by an interchange of a and b.

It is convenient to choose A to be a 'macroscopic surface', that is a surface with radii of curvature which are everywhere much greater than the particle radius; since we are treating the fluid as incompressible, we must also add the proviso that A be much smaller than the sound wavelength.

The quantities δn_j, $\boldsymbol{v}$, $\delta\boldsymbol{D}$ and the deviatoric part of the stress tensor will fluctuate with position around spatially uniform mean values, while $\delta\boldsymbol{D}$ and $\delta\psi$ fluctuate about mean values $\nabla P \cdot \boldsymbol{x}$ and $-\boldsymbol{E} \cdot \boldsymbol{x}$ respectively.

On expressing each of the quantities in (3.3) as the sum of their mean and

fluctuating parts, and dividing by the enclosed volume V, we obtain integrals involving products of averages, and products of fluctuating quantities. For example, the contribution to (3.3) from the $\delta\psi^a\,\delta\boldsymbol{D}^b$ term becomes

$$\int_A -\boldsymbol{E}^a\cdot\boldsymbol{x}\langle\delta\boldsymbol{D}^b\rangle\cdot\hat{\boldsymbol{n}}\,\mathrm{d}A+\int_A\langle\delta\psi^{a'}\cdot\delta\boldsymbol{D}^{b'}\rangle\cdot\hat{\boldsymbol{n}}\,\mathrm{d}A, \tag{3.4}$$

where the dashes denote the fluctuating quantities. In deriving this result we have used the fact that since the surface A is macroscopic, any integral over A can be written in terms of surface averages. This is why the angle brackets appear in the second integral in (3.4), and why products of average and fluctuating quantities do not appear, for the average of the fluctuating quantities is zero.

Since the fluctuations are statistically homogeneous functions of position the quantities $\langle\delta\boldsymbol{D}^b\rangle$ and $\langle\delta\psi^{a'}\cdot\delta\boldsymbol{D}^{b'}\rangle$ in (3.4) are uniform. As the surface A increases the first term in (3.4) begins to dominate, thanks to the $\boldsymbol{E}^a\cdot\boldsymbol{x}$ term. On dividing (3.4) by the volume enclosed by A and formally letting that volume become infinite, we obtain

$$-\boldsymbol{E}^a\cdot\langle\delta\boldsymbol{D}^b\rangle.$$

Applying similar arguments to the other components of the integral (3.3) we find that the integral, divided by the volume of A tends to

$$-\langle\boldsymbol{v}^b\rangle\cdot(\nabla P^a-\mathrm{i}\omega\rho\boldsymbol{U}^a)+\boldsymbol{E}^a\cdot\langle\boldsymbol{i}^b\rangle.$$

Since (3.3) is unaffected by an exchange of α and β, we see that the expression (3.4) is equal to

$$-\langle\boldsymbol{v}^a\rangle\cdot(\nabla P^b-\mathrm{i}\omega\rho\boldsymbol{U}^b)+\boldsymbol{E}^b\cdot\langle\boldsymbol{i}^a\rangle.$$

Thus in the case when $\nabla P^a=\boldsymbol{0}$ and $\boldsymbol{E}^b=\boldsymbol{0}$, we find

$$\langle\boldsymbol{v}^b\rangle\cdot\langle\mathrm{i}\omega\rho\boldsymbol{U}^a\rangle+\boldsymbol{E}^a\cdot\langle\boldsymbol{i}^b\rangle=-\langle\boldsymbol{v}^a\rangle\cdot(\nabla P^b-\mathrm{i}\omega\rho\boldsymbol{U}^b). \tag{3.5}$$

By using the second of the formulae (3.2) we can express $\langle\boldsymbol{i}^b\rangle$ in terms of β. To find the required reciprocal relation we must also express $\langle\boldsymbol{v}^a\rangle$ in terms of μ_{E}. To this end, we begin by noting that since the net electrical force on the suspension enclosed by A is zero, we have

$$\int_A\boldsymbol{\sigma}\cdot\hat{\boldsymbol{n}}\,\mathrm{d}A=-\mathrm{i}\omega\int_{V_{\mathrm{f}}}\rho(\boldsymbol{v}+\boldsymbol{U})\,\mathrm{d}V-\mathrm{i}\omega\int_{V_{\mathrm{p}}}(\rho+\Delta\rho)\,\boldsymbol{U}\,\mathrm{d}V,$$

where V_{f} is the fluid volume and V_{p} is the particle volume enclosed by A, and $\rho+\Delta\rho$ is the particle density. On dividing both sides of the above expression by V, we find, in the limit of infinite V that

$$-\nabla P=-\mathrm{i}\omega\rho(\langle\boldsymbol{v}\rangle+\boldsymbol{U})-\mathrm{i}\omega\phi\,\Delta\rho\,\boldsymbol{U}, \tag{3.6}$$

where ϕ is the particle volume fraction.

On writing $\langle\boldsymbol{v}\rangle$ in terms of ∇P and $\boldsymbol{U}$ with the aid of the above relation for both the α and β problems, and combining with (3.5) we get

$$\boldsymbol{E}^a\cdot\langle\boldsymbol{i}^b\rangle=\phi\frac{\Delta\rho}{\rho}\boldsymbol{U}^a\cdot\nabla P^b.$$

Combining this result with the formulae (3.2) for $\boldsymbol{U}^a$ and $\langle\boldsymbol{i}^b\rangle$ we obtain the required result, viz.

$$\beta=\frac{\phi\,\Delta\rho}{\rho}\mu_{\mathrm{E}}. \tag{3.7}$$

The above argument can be applied to any suspension in which the particles move with uniform velocity without any rotation. Thus it is valid for a concentrated suspension of spheres in a cubic array and for a dilute suspension of spheroids with uniform ζ-potential.

4. Electric fields generated by sound waves

By combining the macroscopic version of Poisson's equation with the charge conservation equation it can be shown that

$$\nabla \cdot \langle \boldsymbol{i} \rangle = 0,$$

(see O'Brien 1982, § 3). Replacing $\langle \boldsymbol{i} \rangle$ by the second of the constitutive formulae (3.2), and using the reciprocal relation (3.7) we obtain a differential equation for the field $\boldsymbol{E}$ generated by a sound wave, viz.

$$K^* \nabla \cdot \boldsymbol{E} = -\frac{\phi \Delta\rho}{\rho} \mu_{\mathrm{E}} \nabla^2 P. \tag{4.1}$$

Since the quantity on the right-hand side of this expression involves the particle volume fraction, we may obtain $\boldsymbol{E}$ correct to $O(\phi)$ by solving this equation with P and K^* replaced by the values for a pure liquid with ion densities n_j^∞.

Thus the first step in the calculation of the electric fields involves the determination of the pressure waves that would be set up if the pure solvent were subjected to the same boundary conditions as the suspension.

The mathematical problem for $\boldsymbol{E}$ is completed by the addition of the equation

$$\nabla \times \boldsymbol{E} = \boldsymbol{0},$$

and appropriate boundary conditions.

One obvious solution to these equations is

$$\boldsymbol{E} = -\phi \frac{\Delta\rho \mu_{\mathrm{E}}}{\rho K^*} \nabla P. \tag{4.2}$$

This is the solution corresponding to zero current throughout the suspension, which applies in the case when

$$\langle \boldsymbol{i} \rangle \cdot \boldsymbol{n} = 0, \tag{4.3}$$

on the boundaries. For other boundary conditions it is necessary to superpose a solution to Laplace's equation.

As an illustration of the calculation of this electro-acoustic effect, consider the case of a suspension enclosed between two infinite parallel plates. From the solution of the sound wave equations for a pure liquid in this geometry, we find

$$P = \frac{\mathrm{i}c\rho V_0}{\sin\left(\dfrac{\omega L}{c}\right)} \cos\left(\frac{\omega x}{c}\right),$$

where c is the speed of sound and L is the distance between the plates. x represents the distance from the fixed plate, and V_0 is the transverse velocity of the other plate.

Although the suspension is a conductor there will be no current flow unless the plates are wired together to complete the circuit. If this is not the case, the boundary condition (4.3) applies, and the field between the plates is given by (4.2).

With the aid of the above expression for P we therefore find that the potential difference $\Delta\psi$ between the plates is given by

$$\Delta\psi = \frac{\mathrm{i}\phi\,\Delta\rho\, c V_0 \mu_{\mathrm{E}}}{K^*} \frac{(1-\cos\omega L/c)}{\sin(\omega L/c)}. \tag{4.4}$$

Clearly, the effect is most pronounced at the resonant frequencies, where $\sin(\omega L/c)$ is zero. Unfortunately our formula, which neglects viscous and nonlinear forms, is not valid at these frequencies.

Enderby's (1951) calculation of the electric field was based on the observation that the distortion of the double layer caused by the sound wave gives rise to an electric dipole field at some distance from the particle. He obtained the macroscopic field by summing the dipole fields produced by all the particles in the suspension. Unfortunately, this sum is non-absolutely convergent, that is, the value obtained for an infinite suspension depends on the order in which the particles are summed. Enderby chose to sum over the particles lying in thin slabs perpendicular to the direction of wave propagation. This led to the result

$$\boldsymbol{E} = N_{\mathrm{P}} \boldsymbol{S}, \tag{4.5}$$

where N_{P} is the particle number density, and $\boldsymbol{S}$, which is proportional to the dipole moment, is obtained from the far field form

$$\delta\psi \sim \frac{\boldsymbol{S}}{4\pi} \cdot \boldsymbol{\nabla} \frac{1}{r},$$

at large distances r from the particle.

Enderby's result can also be derived directly from the formula (DeLacey & White 1982)

$$\langle \boldsymbol{i} \rangle = K^*(\boldsymbol{E} - N_{\mathrm{P}} \boldsymbol{S}),$$

relating macroscopic current to particle dipole moment. By putting $\langle \boldsymbol{i} \rangle = \boldsymbol{0}$ we recover Enderby's formula, without the need for evaluating a non-convergent integral. Thus although Enderby's method was wrong in principle, it led to the right result.

Since the formulae (4.2) and (4.5) both apply to the zero-current case, we may equate the two expressions and thereby obtain

$$\boldsymbol{S} = -4\pi a^3 \frac{\Delta\rho}{\rho K^*} \mu_{\mathrm{E}} \boldsymbol{\nabla} P.$$

This relation would enable us to determine μ_{E} from Enderby's formula for $\boldsymbol{S}$, were it not for the fact that Enderby's result is incorrect, owing to two errors in the derivation: to begin with, he assumed (equation (4.5)) that the field inside the particle is uneffected by the applied field. Although this assumption is valid for a conducting particle, the surface charge balance condition (equation (3.14)) is not, for it neglects the current from within the particle. Furthermore, the quantity β, which appears in Enderby's dipole moment expression, is incorrectly given in (4.7) as a real quantity. This cannot be so, for it would mean that the ionic diffusivities do not affect the phase of the dipole moment, a result at variance with our understanding of double layer dynamics (see e.g. §6 of O'Brien 1986). Booth & Enderby made the same errors in their 1952 study of this problem.

The correction of these errors, and the extension to other types of particles with low charge will form the basis of a subsequent paper.

5. Sound waves generated by electric fields

This calculation is less straightforward than the previous one, for in this case the pressure field is $O(\phi)$ and (4.1) simply reduces to

$$\nabla \cdot \boldsymbol{E} = 0. \tag{5.1}$$

Although this equation serves for the determination of the macroscopic field, it provides no information about the pressure or velocity fields. To obtain this information we must turn to the macroscopic equations of motion.

Since the net electrical force on each particle and double layer is zero, the macroscopic version of Newton's second law reduces to a balance between the inertia and the hydrodynamic forces, viz.

$$\mathrm{i}\omega\langle\rho^o\rangle\,\bar{\boldsymbol{v}} = \nabla P. \tag{5.2}$$

Here $\langle\rho^o\rangle$ is the equilibrium volume-average density and $\bar{\boldsymbol{v}}$ is the macroscopic momentum per unit mass of suspension. In deriving this result we have used the fact that the pressure forces dominate the viscous forces on the macroscopic scale. This can be seen by the following argument: the viscous stresses in the neighbourhood of a particle are $O(\mu U/a)$, and the nett viscous stress per unit volume is $O(\phi\mu U/a\lambda)$, where λ is the wavelength. The velocity $\bar{\boldsymbol{v}}$ will presumably be $O(\phi U)$, so the ratio of viscous forces to inertia forces is $O(\nu/a\lambda\omega)$. For a 1 MHz sound wave in water with a particle radius of 0.1 μm this ratio is approximately 10^{-3}.

As is usual in sound-wave studies, we assume that the flow is macroscopically isentropic. In a pure liquid this implies that the density is a function of the local pressure only. In a suspension, however, the picture is more complicated, for the density also depends on the particle and bulk ionic concentrations. Fortunately, however, these variations in concentration are not significant in this case. This follows from the fact that $\boldsymbol{E}$ has zero divergence; from the expression (3.2) for $\boldsymbol{U}$ we then find that

$$\nabla \cdot \boldsymbol{U} = 0,$$

and hence the particle concentration in the bulk of the fluid is not affected by the electric field; similar arguments apply to the ionic concentrations.

Thus the macroscopic mass conservation equation takes the familiar form

$$\frac{\mathrm{i}\omega P}{c^2} = \langle\rho^o\rangle\,\nabla \cdot \bar{\boldsymbol{v}}, \tag{5.3}$$

where c, the speed of sound in the suspension is given by

$$c = 1\Big/\frac{\partial\langle\rho\rangle}{\partial P},$$

the derivative being taken with the entropy and the particle and ion concentrations held fixed.

The boundary condition which accompanies (5.2) and (5.3) is derived from the mass conservation principle, applied to a slab-shaped volume adjacent to the boundary. If the thickness of the slab is much smaller than λ (but much greater than the particle radius), we may treat the enclosed suspension as incompressible. For a rigid boundary, we therefore obtain the boundary condition

$$\langle\boldsymbol{v}\rangle \cdot \hat{\boldsymbol{n}} = 0, \tag{5.4}$$

at the boundary. This does not imply that $\bar{\boldsymbol{v}}\cdot\hat{\boldsymbol{n}}$ is also zero, for if the electric field has a component normal to the boundary, $\boldsymbol{U}\cdot\hat{\boldsymbol{n}}$ will be non-zero at the boundary, and thus if the particle density is different from that of the fluid there will be a normal momentum flux at the boundary.

The formula for this flux follows from the definition of $\bar{\boldsymbol{v}}$, namely

$$\langle\rho\rangle\,\bar{\boldsymbol{v}} = \frac{1}{V}\int_V \rho\boldsymbol{v}\,\mathrm{d}V.$$

By using the fact that the momentum density in the particles is $(\rho+\Delta\rho)\,\boldsymbol{U}$, we find

$$\langle\rho\rangle\,\bar{\boldsymbol{v}} = \rho\langle\boldsymbol{v}\rangle + \phi\,\Delta\rho\boldsymbol{U}.$$

Combining with (5.4) we obtain the boundary condition

$$\bar{\boldsymbol{v}}\cdot\hat{\boldsymbol{n}} = \phi\frac{\Delta\rho}{\rho}\mu_{\mathrm{E}}\boldsymbol{E}\cdot\hat{\boldsymbol{n}}, \tag{5.5}$$

where we have used the fact $\bar{\boldsymbol{v}}$ is $O(\phi)$ in replacing $\langle\rho\rangle$ by ρ, and in neglecting the pressure term in the formula (3.2) for $\boldsymbol{U}$.

Hence the driving term for the sound waves appears in the boundary condition, rather than the differential equations (5.2) and (5.3). This boundary condition can also be derived by another argument which, although less direct, sheds more light on the mechanism for sound-wave generation. The starting point for this alternative derivation can be found in § 1.7 of Lighthill's (1978) book on waves in fluids. In that section it is shown that an incompressible compact body radiates a dipole pressure field, where the dipole strength is given by

$$\boldsymbol{F}+\rho V\dot{\boldsymbol{U}},$$

where $\boldsymbol{F}$ is the hydrodynamic force which the body exerts on the fluid and V is the volume of the body. In our problem the force $\boldsymbol{F}$ must be supplemented by the electric force which the double layer ions exert on the fluid. As mentioned at the end of § 2, the latter force is equal and opposite to the electric force on the particle. Hence by Newton's second law, the dipole strength of the particle and double layer is given by

$$-\Delta\rho V\dot{\boldsymbol{U}}.$$

With the aid of the first of the constitutive equations (3.2) we can approximate this expression by

$$\mathrm{i}\omega\,\Delta\rho\mu_{\mathrm{E}}\boldsymbol{E},$$

a result obtained by neglecting the $O(\phi)$ pressure gradient term. The pressure at any point in the liquid can be written as a sum of dipole contributions together with a surface integral involving $\langle\boldsymbol{v}\rangle\cdot\hat{\boldsymbol{n}}$ and p on the boundary of the suspension. The dipole sum can be approximated by a volume integral which in turn can be expressed as an integral involving sources spread over the macroscopic boundary of the suspension. The resulting expression is equivalent to a Green function formulation for the pressure in the case when the velocity satisfies the boundary condition (5.5). Thus the momentum flux at the boundaries arises from summing the dipole fields of each of the particles in the suspension.

For the parallel plate geometry described in the previous section we find, from (5.1), that the electric field acts perpendicular to the plates and has uniform magnitude

$$E_0 = \Delta\psi_0/L,$$

where $\Delta\psi_0$ is the applied potential difference between the plates. (We are here neglecting 'electrode polarization' the drop in potential caused by the build-up of charge around the plates. This is usually a valid assumption if the frequency of the applied field is more than a few kilohertz.)

From the solution to equations (5.2) and (5.3) with boundary conditions (5.5) at $x = 0$ and L, we find that the pressure P_0, on the plate at $x = 0$ is given by

$$P_0 = \mathrm{i}c\,\Delta\rho\,\phi E_0 \mu_{\mathrm{E}} \left(1 - \cos\frac{\omega L}{c}\right) \Big/ \sin\frac{\omega L}{c}. \tag{5.6}$$

Comparing this result with the formula (4.3) for the potential difference $\Delta\psi$ induced by the motion of the boundary, we obtain

$$\frac{P_0}{E_0 K^*} = \frac{\Delta\psi}{V_0}. \tag{5.7}$$

Since the conductivity of the background electrolyte K^* increases with electrolyte concentration, we see from the above result that at high concentrations the pressure P_0 is the approprate variable to measure, while at low electrolyte concentrations the potential difference $\Delta\psi$ should be measured. Unfortunately, this reciprocal relation appears to be limited to the parallel-plate geometry.

6. Calculating μ_{E} for a thin double layer system

The formulae (4.4) and (5.6) for the electro-acoustic effects involve the electrophoretic mobility μ_{E}. In this section we will calculate μ_{E} for a particle with a radius much greater than the double layer thickness κ^{-1}.

The calculation involves the solution of the electrokinetic equations for an isolated particle in a uniform ambient field with zero pressure gradient. This is a problem which has been studied in connection with the dielectric response of a dilute suspension of spheres. For thin double layer systems, two asymptotic analyses have emerged from these studies, one valid for $\omega/\kappa^2 D \ll 1$, and the other for $\omega a^2/D \gg 1$, where a is the particle radius.

The $\omega/\kappa^2 D \ll 1$ analysis was pioneered by Dukhin & Shilov (1974), who showed that in this limit the thin double layer is in a local equilibrium with the neighbouring electrolyte. With the aid of this observation, Dukhin was able to obtain a local solution of the electrokinetic equations in the double layer. This solution provided boundary conditions which were then used in the calculation of ion densities and electric potential beyond the double layer. In 1984 Hinch *et al.* extended the analysis to include the calculation of the electrophoretic mobility for $\omega a^2/\nu \ll 1$, where, as usual, ν denotes kinematic viscosity. Since κa must also be large, this analysis is restricted to very small particles at high electrolyte concentrations.

In this section we will be concerned with the other asymptotic limit, $\omega a^2/D \gg 1$. For a frequency of 1 MHz, and a typical ion diffusivity of $10^{-5}\,\mathrm{cm^2\,s^{-1}}$, this restriction holds if $a \gg 0.01\,\mu\mathrm{m}$; a condition which is frequently satisfied in practice.

The physical significance of the restriction $\omega a^2/D \gg 1$ can best be appreciated by studying the form of the ion conservation equations in (2.7). Beyond the double layer, the gradients in n_i^o and ψ^o are zero, and thus in this region the equations are diffusion-like. Since there are no source terms, the disturbances in ion density must diffuse out from the double layer. Thus if $\omega a^2/D \gg 1$, these disturbances will be confined to a layer of thickness $(D/\omega)^{\frac{1}{2}}$ beyond the double layer.

In calculating the local flow in this layer and the underlying double layer we can neglect the inertia term in the equation of motion (2.7) provided $\nu/D \gg 1$, and $\omega/\kappa^2\nu \ll 1$; the first condition is always satisfied in practice, while the second is satisfied at a frequency of 1 MHz if the electrolyte concentration $\gg 10^{-6}$ M, as is usually the case.

The problem of calculating the local flow is further simplified by the fact that at these frequencies the electrical force term in the flow equation (2.7) involving the perturbation in ion density is negligible. To show that this is so, we must first estimate the magnitude of the charge density perturbations. Following O'Brien (1986) we apply the principle of charge conservation to the portion of the double layer lying over one half of the particle surface. The applied field sweeps charge into this region at a rate $O(aK^sE)$ where K^s is the 'surface conductivity' of the double layer – the quantity which relates the local tangential current to the tangential field at the surface. The resulting variations in charge over the particle surface give rise to a back-field $\boldsymbol{E}_b$ which opposes the applied field in the double layer. For the important case of a particle whose dielectric constant is much smaller than that of the liquid, the normal component of $\boldsymbol{E}_b$ beyond the double layer is given by

$$\boldsymbol{E}_b \cdot \hat{\boldsymbol{n}} = \frac{\delta\sigma}{\epsilon},$$

where $\delta\sigma$ is the change in the double layer charge per unit area. Thus $\boldsymbol{E}_b$ is $O(\delta\sigma/\epsilon)$. This back field produces a tangential current out of the region of $O(K^s a E_b)$, while the normal component causes a current of $O(K^\infty a^2 E_b)$ to flow out to the surrounding electrolyte where K^∞ is the conductivity of the electrolyte beyond the double layer. On putting the net current flow equal to $\omega a^2 \delta\sigma$ we find

$$\delta\sigma = \frac{K^s}{K^\infty a}\epsilon E \Big/ \left(1 + O\left(\frac{\omega\epsilon}{K^\infty}\right) + O\left(\frac{K^s}{K^\infty a}\right)\right).$$

For most applications $K^s/K^\infty a$ is of order 1 or less, and $\omega\epsilon/K^\infty$ is $O(\omega/\kappa^2 D)$ which will also be typically of $O(1)$ in the MHz range. Thus we may take $\delta\sigma$ to be $O(\epsilon E)$.

By the usual lubrication theory type arguments it can be shown that the flow in the thin double layer is locally tangential to the surface. The electrical force

$$\sum_{j=1}^{N} e z_j \delta n_j \nabla\psi^o \tag{6.1}$$

due the change in ion density acts normal to the surface, and is balanced by normal pressure gradients. Thus tangential variations in this force will give rise to tangential pressure gradients. Assuming that the perturbations in charge density are spread fairly uniformly across the double layer, we find that the force term (6.1) is $O(\delta\sigma\kappa\nabla\psi^o)$, and thus the force gives rise to a pressure difference of $O(\delta\sigma\kappa\zeta)$ across the thickness of the double layer. In the tangential direction quantities vary on the lengthscale of the particle radius. Hence the ratio of the tangential pressure gradient to the other electric force component

$$\sum_{j=1}^{N} n_j^o e z_j \nabla\delta\psi, \tag{6.2}$$

is $O(1/\kappa a)$, where we have used the estimates ϵE for $\delta\sigma$, and $\epsilon\kappa^2\zeta$ for

$$\sum_{j=1}^{N} e z_j n_j^o,$$

the equilibrium charge density in the double layer. Similarly, it can be shown that the tangential pressure gradients due to the component of $\nabla\delta\psi$ normal to the surface are also negligible when compared with the tangential component of (6.2).

Thus the equation of motion (2.7) reduces to

$$\mu\frac{\partial^2 \boldsymbol{v}}{\partial x^2} = \sum_{j=1}^{N} ez_j n_j^o \nabla_s \delta\psi, \tag{6.3}$$

in the double layer, where ∇_s is the tangential gradient operator, and x denotes distance from the surface. In this frequency regime the tangential applied field is approximately uniform across the double layer (O'Brien 1986). Integration of (6.3) therefore yields the result that the velocity rises from zero at the particle surface to the limiting value

$$\frac{\epsilon\zeta}{\mu}\nabla_s \delta\psi \tag{6.4}$$

beyond the double layer. This expression is well known in colloid science, having been derived by Smoluchowski (see Hunter 1981, chapter 3) for a particle in a steady field, under the restriction that $K^s/K^\infty a \ll 1$. We now see that this result also applied to an alternating field, without the restriction on K^s.

The calculation of the particle motion involves the solution of the equations of motion beyond the double layer, where there are no electrical forces, subject to the conditions that the velocity takes the uniform value $-\mu_E \boldsymbol{E}$ far from the particle, and is given by (6.4) in the region beyond the double layer and close to the surface. The required mobility μ_E is determined from the condition that the net electrical force on the particle and double layer is zero.

Following the usual boundary-layer matching we shall take the 'outer' velocity field to be given by (6.4) at the particle surface, and use the zero-electric force constraint in the form

$$\int_{A_p} \boldsymbol{\sigma}\cdot\hat{\boldsymbol{n}}\,\mathrm{d}A = -\mathrm{i}\omega M_p \boldsymbol{U}, \tag{6.5}$$

where A_p denotes the particle surface, M_p is the particle mass, and $\boldsymbol{\sigma}$ is the hydrodynamic stress tensor, calculated using the outer solution. The required mobility μ_E is determined from the condition of zero electrical force on the particle and double layer.

To complete the specification of the velocity boundary condition at the particle surface we require a formula for the potential $\delta\psi$ in the electrolyte. Since the changes in ion density are confined to the neighbourhood of the particle surface, the potential satisfies Laplace's equation beyond that region. By applying the charge conservation principle to a part of the double layer O'Brien (1986) obtained a boundary condition to be satisfied by the potential beyond the double layer. The solution to Laplace's equation with this boundary condition is given by (O'Brien 1986, equation (4.2)),

$$\delta\psi = -\boldsymbol{E}\cdot\boldsymbol{r} + a^3 f \boldsymbol{E}\cdot\nabla\frac{1}{r}, \tag{6.6}$$

where

$$f = \frac{1-\mathrm{i}\omega' - (2\lambda - \mathrm{i}\omega'\epsilon_p/\epsilon)}{2(1-\mathrm{i}\omega') + (2\lambda - \mathrm{i}\omega'\epsilon_p/\epsilon)}. \tag{6.7}$$

Here $\omega' = \omega\epsilon/K^\infty$, and $\lambda = K^s/Ka^\infty$. The calculation of the relationship of K^s to the ζ-potential is discussed in the Appendix to O'Brien's paper; there it is shown that

$$\lambda \approx \frac{n_i^\infty z_i^2 D_i \sqrt{2}}{\sum_{j=1}^{N} z_j^2 n_j^\infty D_j}\left(1+\frac{3m_i}{z_i^2}\right)\frac{\exp(-ez_i\zeta/2kT)}{\kappa_i a}, \tag{6.8}$$

provided
$$\exp(-ez_i\zeta/2kT) \gg 1, \tag{6.9}$$

where
$$\kappa_i^2 = \frac{z_i^2 e^2 n_i^\infty}{\epsilon kT}.$$

Here the subscript i refers to the counterion of highest charge, and

$$m_i = 2\epsilon(kT)^2/3\mu e^2 D_i.$$

If the condition (6.9) is not satisfied, an analytic formula for λ can only be obtained in the case of a symmetric electrolyte. For other electrolytes, the evaluation of λ requires the numerical solution of the problem for the equilibrium potential in the locally flat double layer. With the aid of the above formulae we can write the velocity (6.4) at the particle surface in terms of the non-dimensional surface conductivity λ.

The particle velocity $\boldsymbol{U}$ can be conveniently calculated with the aid of the reciprocal identity

$$\int_A (\boldsymbol{v}\cdot\boldsymbol{\sigma}' - \boldsymbol{v}'\cdot\boldsymbol{\sigma})\cdot\hat{\boldsymbol{n}}\,\mathrm{d}A = 0,$$

linking any two solutions $(\boldsymbol{v}, \boldsymbol{\sigma})$ and $(\boldsymbol{v}', \boldsymbol{\sigma}')$ to the force-free linearized Navier–Stokes equations in the region enclosed by surface A. In this case we take $\boldsymbol{v}$ to be the required velocity field, in the laboratory frame of reference, and $\boldsymbol{v}'$ to be the velocity field around an uncharged sphere of the same radius, which executes translational oscillations in a liquid at rest as a result of an external force $\boldsymbol{F}'e^{-i\omega t}$. We take the surface A to be composed of the particle surface A_p and a large sphere, centred on the particle. As the radius of the large sphere tends to infinity, the integral over that surface approaches zero, and the above identity reduces to

$$\boldsymbol{U}\cdot\boldsymbol{F} = \int_{A_p} (\boldsymbol{v}-\boldsymbol{U})\cdot\boldsymbol{\sigma}'n\,\mathrm{d}A.$$

On replacing $\boldsymbol{v}-\boldsymbol{U}$ by the formula (6.4) and using (6.5), together with the expressions for $\boldsymbol{F}'$ and $\boldsymbol{\sigma}'$ given in §24 of Landau & Lifshitz (1966) we obtain

$$\mu_E = \frac{2\epsilon\zeta}{3\mu}(1+f)G(\omega a^2/\nu), \tag{6.10}$$

where
$$G(\alpha) = (1-\tfrac{1}{9}i\alpha(3+2\Delta\rho/\rho)/[1+(1+i)(\tfrac{1}{2}\alpha)^{\frac{1}{2}}])^{-1}. \tag{6.11}$$

In figures 1 and 2 we show the variation of $|\mu_E|$ and $\arg\mu_E$ with frequency for a particle with $\kappa a = 30$, $D/\nu = 2\times10^{-3}$, $\rho_p/\rho = 2$ and $\epsilon_p/\epsilon = 0$, where ρ_p and ϵ_p are the density and dielectric constant of the particle respectively; these values apply approximately to a suspension of 0.3 μm radius dielectric particles in 10^{-3} M KCl solution. The curves in figure 1 represent the case of a particle with $e\zeta/kT = 1$. The particle charge is so small in this case that the changes in charge density due to the applied field do not significantly affect the field around the particle. Thus the flow in the double layer relative to the particle is in phase with the applied field, and the

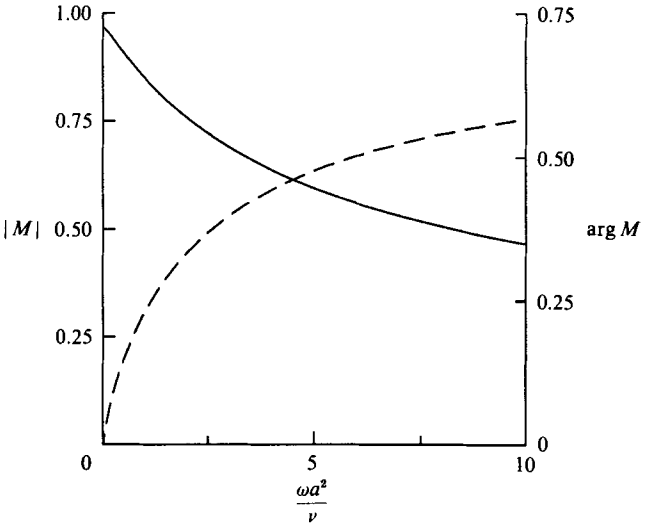

FIGURE 1. ——, the magnitude and – – – –, argument of the non-dimensional electrophoretic mobility $M = \mu e \mu_E / \epsilon kT$, for a spherical particle as a function of the frequency of the applied field. The parameters in this case are $\kappa a = 30$, $\epsilon_p/\epsilon = 0$, $\rho_p/\rho = 2$, $D/\nu = 2 \times 10^{-3}$, and $e\zeta/kT = 1$.

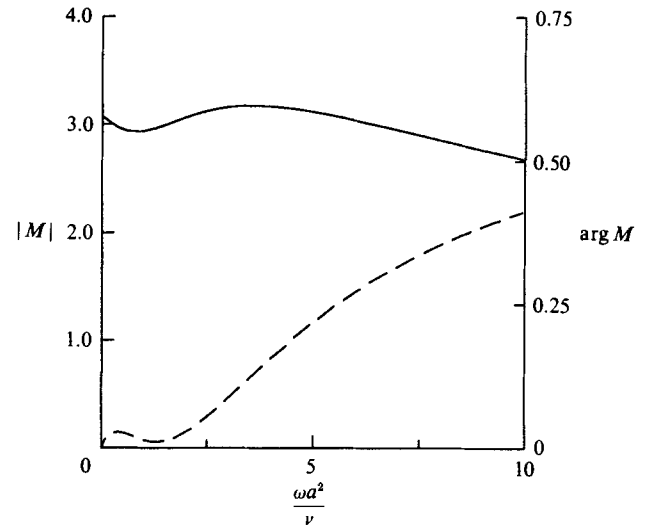

FIGURE 2. The mobility of a highly-charged particle. The parameters in this case are the same as in figure 1, with the exception of $e\zeta/kT$, which is now 6.

phase difference in μ_E arises entirely from the particle and fluid inertia. In figure 2 we show the frequency dependence of the mobility for a highly-charged particle, $e\zeta/kT = 6$. In this case the back field due to the distorted double layer has a significant effect. Since this field lags the applied field, the net tangential field – which determines the relative flow in the double layer – leads the applied field. This is the reason why the phase angle is smaller than in the low-ζ case. The back field is also responsible for the increase in mobility amplitude with frequency, for as the frequency increases, the back field, which opposes the motion, diminishes.

Ideally, the results presented in this section should be compared with experiment, but to date no experiments on such suspensions have appeared in the literature. Hopefully this work will provide the stimulus for such an investigation.

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