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The electroacoustic equations for a colloidal suspension

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The term 'electroacoustic' is used in connection with phenomena that involve the interaction of sound waves and electric fields, such as the voltage difference generated across a transducer by the passage of a sound wave. This paper is concerned with electroacoustic effects in suspensions of electrically charged colloidal particles. The existing methods for calculating electroacoustic effects in suspensions are limited either to the dilute case, or to one particular effect, namely the open-circuit voltage generated between two parallel wire probes by a locally plane sound wave, propagating perpendicular to the wires. In this paper we present a procedure for calculating any electroacoustic effects in suspensions of arbitrary concentration. The only restriction on the method is that the particles must be small compared with the sound wavelength. The procedure involves the solution of a set of differential equations – referred to here as the 'electroacoustic equations' – for the macroscopic pressure, velocity and electrical potential in the suspension. The derivation of these equations and the associated boundary conditions form the major part of this paper. General features of the solution are also discussed, and an application is given involving a novel electroacoustic measurement.

1. Introduction

This paper is concerned with electroacoustic effects in colloidal dispersions. The aim is to set up the differential equations and boundary conditions which govern the distribution of the macroscopic pressure, velocity and electric field in a suspension and to discuss general features of the solutions to these equations. With the aid of these equations it will be possible to predict electroacoustic effects in terms of suspension transport properties, or conversely to obtain transport properties from electroacoustic measurements. Since the transport properties are related to the suspension microstructure, this latter application could provide a new way of probing the microstructure of colloidal suspensions.

To get some idea of the sort of microstructural information which might be obtained in this way, it is instructive to consider one particular electroacoustic effect, namely the generation of electric fields by sound waves in a suspension.

These fields arise from the electric charge on the colloidal particles. This charge is balanced in equilibrium by an excess of oppositely charged ions which form a diffuse cloud around each particle. This cloud, and the layer of charge on the particle are referred to as the electrical double layer.

As the sound waves pass through the suspension they generate a relative motion between the particles and the surrounding liquid. The magnitude of this motion depends on the density difference between the particle and the solvent, on the size and shape of the particle, and on the frequency of the sound wave. As a result of this relative motion, the diffuse layer distorts, and its centre of charge is displaced from that of the particle. Hence each particle generates an alternating electric dipole field, and the superposition of these fields leads to the macroscopic electric field referred to earlier.

From this discussion it can be seen that the field generated by a sound wave in a suspension depends on the density difference between the particle and solvent, on the particle charge, size, shape and concentration. Measurements of this field can therefore be used to provide information about these variables.

In general, the electroacoustic measurements will depend not only on the transport properties of the suspension, but also on the geometry of the device and the means by which the sound wave and electric fields are generated and measured. Thus the first step in the determination of the microstructure is the extraction of the transport properties from the electroacoustic measurement. It is this step which forms the subject of this paper. The next step, of relating the transport properties to the microstructure, has already received some preliminary attention (Booth & Enderby 1952; O'Brien 1988; Marlowe, Fairhurst & Pendse 1988), and will no doubt form the subject of future papers in this area.

2. Outline of the paper

In the following two sections we derive the macroscopic momentum and mass conservation equations for a suspension. In §5 we introduce two constitutive relations for the electric current density and the particle velocity in the suspension. By adding the macroscopic charge conservation equation we obtain a complete set of equations for the determination of the macroscopic pressure, velocity and electric field in the suspension. It is these equations that are referred to here as the electroacoustic equations.

The associated boundary conditions are derived in §6. In §§7 and 8 we discuss general features of the solution procedure for the case when the fields are generated by the motion of a boundary, and by an applied electric field respectively. Finally in §9 an application is presented, involving the interpretation of measurements for a novel electroacoustic device.

3. The momentum equation

The macroscopic quantities of interest in a suspension can usually be written as spatial averages over volumes large enough to enclose a large number of particles but small in comparison with the macroscopic lengthscales (Batchelor 1970). In this problem the smallest macroscopic lengthscale is likely to be the sound wavelength λ, which at a typical frequency of 1 MHz† is around 1.5 mm in water. For this averaging procedure to be valid, the particles must be much smaller than λ, a restriction which is usually satisfied in practice.

On applying the momentum equation to such a sample volume, and neglecting products of the various macroscopic disturbances, we obtain

$$\langle \rho_0 \rangle \frac{\partial \bar{\boldsymbol{u}}}{\partial t} = -\boldsymbol{\nabla} \cdot \boldsymbol{\Sigma} \tag{3.1}$$

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† The existing commercial electroacoustic devices by Matec Applied Sciences and Penkem operate at 1 MHz and 200 kHz respectively.

where $\langle \rho_0 \rangle$ is the equilibrium suspension density, $\mathbf{\Sigma}$ is the bulk stress tensor, and

$$\bar{\boldsymbol{u}} = \frac{1}{\langle \rho_0 \rangle V} \int_V \rho \boldsymbol{u} \, \mathrm{d}V \tag{3.2}$$

is the macroscopic momentum per unit mass of suspension.

The stress tensor can be written as the sum

$$\mathbf{\Sigma} = -\langle p \rangle \boldsymbol{I} + \langle \boldsymbol{\sigma}' \rangle + \mathbf{\Sigma}_{\mathrm{p}}, \tag{3.3}$$

where the angle brackets denote volume averages of the local pressure p and deviatoric stress $\boldsymbol{\sigma}'$ in the suspension, and $\mathbf{\Sigma}_{\mathrm{p}}$ is the contribution from interparticle forces. Of these three components, the pressure term dominates, as demonstrated by following order of magnitude estimates.

Consider first the pressure term. If this really is dominant, then the pressure gradient must balance the inertia term in (3.1). Assuming $\langle p \rangle$ varies on a lengthscale of order λ, we get the estimate

$$\langle \rho_0 \rangle \, \omega U \lambda \tag{3.4}$$

for the pressure, where U is a typical suspension velocity.

An estimate for the local deviatoric stresses can be obtained by dividing the typical viscous force on the particle by its surface area. In the case when the electroacoustic effects arise from the motion of a boundary, the viscous force and the interparticle forces are driven by the inertia forces on the particle. It therefore seems reasonable to assume that the viscous force will be the same order of magnitude, or less than, the inertia force. Dividing the inertia force by the particle area, we obtain the estimate

$$\rho_{\mathrm{p}} \, \omega a U$$

for the viscous stresses. Here ρ_{p} is the density and a the radius of the particle. In making this estimate it has been assumed that the particle velocity is of the same order as that of the suspension. On dividing this quantity by the estimate (3.4) for the pressure, we obtain the ratio a/λ, which is assumed to be small in this study.

The interparticle forces will presumably also be of the same order as the particle inertia force $\rho_{\mathrm{p}} a^3 \omega U$, since they must balance the inertia and viscous forces. Taking the lengthscale of the interaction to be $O(a)$, and assuming that each particle interacts with one or so neighbours, we find that the particle stress term $\mathbf{\Sigma}_{\mathrm{p}}$ will be of order

$$\phi \rho_{\mathrm{p}} \, \omega a U.$$

Once again, this is negligible in comparison with the pressure estimate (3.4) if a/λ is small.

Thus we can approximate the bulk stress in the suspension by the volume average of the local pressure. With this approximation, the momentum equation (3.1) becomes

$$\langle \rho_0 \rangle \frac{\partial \bar{\boldsymbol{u}}}{\partial t} = -\boldsymbol{\nabla} \langle p \rangle. \tag{3.5}$$

4. The mass conservation equation

Applying the principal of mass conservation to a sample volume V, and again neglecting the products of small terms, we get

$$\langle \rho_0 \rangle \boldsymbol{\nabla} \cdot \bar{\boldsymbol{u}} = -\frac{\partial \langle \rho \rangle}{\partial t}. \tag{4.1}$$

This equation, and the momentum equation (3.5) in the previous section have the same form as the sound equations in a pure liquid. In the latter case the equations are completed by evoking an equilibrium relation between the density and the pressure. In a suspension the situation is more complicated however, for the density depends on the particle concentration as well as the pressure.

To find the relation between density, pressure and concentration changes, we must first write $\partial\langle\rho\rangle/\partial t$ as an integral over the particles and the solvent. This step contains an interesting subtlety, which arises from the fact that the local density changes discontinuously at a point when it is crossed by a particle surface. Thus $\partial\rho/\partial t$ involves delta functions at the particle surface. When this is taken into account the expression for $\partial\langle\rho\rangle/\partial t$ becomes

$$\frac{\partial\langle\rho\rangle}{\partial t}=\left\langle\frac{\partial\rho}{\partial t}\right\rangle+\frac{1}{V}\sum_{\mathrm{p}}\int_{A_{\mathrm{p}}}\Delta\rho\boldsymbol{U}\cdot\hat{\boldsymbol{n}}\,\mathrm{d}A, \tag{4.2}$$

where the first term on the right-hand side is the average of $\partial\rho/\partial t$ over the sample volume excluding the particle surfaces. The second term, which arises from the delta functions, involves a sum over the particle surfaces lying within the sample volume. $\Delta\rho$ denotes the particle density minus that of the liquid, and $\hat{\boldsymbol{n}}$ is the unit outward normal at the particle surface.

It is convenient to rewrite the sum in (4.2) as

$$\sum_{\mathrm{p}}\frac{1}{V}\oint_{A_{\mathrm{p}}}\Delta\rho\boldsymbol{U}\cdot\hat{\boldsymbol{n}}\,\mathrm{d}A-\frac{1}{V}\sum_{\mathrm{p}'}\int_{A'_{\mathrm{p}}}\Delta\rho\boldsymbol{U}\cdot\hat{\boldsymbol{n}}\,\mathrm{d}A, \tag{4.3}$$

where the first term extends over *closed* particle surfaces. Those particle surfaces that are cut by the sample volume boundary are closed in this sum by the addition of the surface A'_{p}, formed by the intersection of the particles and the sample volume. The second sum is included to cancel these added terms.

This second term can be written as

$$-\phi\Delta\rho\boldsymbol{\nabla}\cdot\langle\boldsymbol{U}\rangle$$

where $\langle\boldsymbol{U}\rangle$ is the average particle velocity and ϕ is the particle volume fraction, assumed to be uniform. On applying the mass conservation equation to the individual particles, we find that the first term in (4.3) becomes

$$-\phi\frac{\Delta\rho}{\rho_{\mathrm{p}}}\left\langle\frac{\partial\rho_{\mathrm{p}}}{\partial t}\right\rangle,$$

where the average extends over the particle volume only.

Combining these expressions with (4.2), we find

$$\frac{\partial\langle\rho\rangle}{\partial t}=\left\langle\frac{\partial\rho}{\partial t}\right\rangle-\phi\frac{\Delta\rho}{\rho_{\mathrm{p}}}\left\langle\frac{\partial\rho_{\mathrm{p}}}{\partial t}\right\rangle-\phi\Delta\rho\boldsymbol{\nabla}\cdot\langle\boldsymbol{U}\rangle. \tag{4.4}$$

The first two terms on the right-hand side depend on the pressure, while the third term is related to the rate of change of the particle number density.

Since the macroscopic pressure $\langle p\rangle$ varies on a lengthscale large compared with the sample volume, we may take $\langle p\rangle$ to be spatially uniform in calculating the first two terms on the right-hand side of (4.4). The calculation of these two terms thus involves the determination of the local density changes caused by a uniform pressure change throughout the sample volume. Since we are neglecting products of small disturbances in this analysis, these terms in (4.4) should be a linear functional of $\langle p(t)\rangle$. Thus in the case of an oscillating pressure field, (4.4) can be written in the form

$$\mathrm{i}\omega\rho' = \mathrm{i}\omega\chi p' - \phi\Delta\rho\nabla\cdot\langle U\rangle, \tag{4.5}$$

where ρ' and p' are the variations in $\langle\rho\rangle$ and $\langle p\rangle$ respectively, and an $\mathrm{e}^{\mathrm{i}\omega t}$ form has been assumed for these variations.

Although the calculation of suspension properties, such as χ, is beyond the scope of this paper, there are two interesting aspects to the calculation of χ which deserve mention.

First, the compression and expansion of a suspension causes the particles and fluid to heat up or cool down at different rates. If the fluid heats up more than the particles, heat will pass into the particles. As a result, the density changes in the particle and in the liquid will differ from the values for an adiabatic compression. Furthermore, if the period of the pressure field is of the same order as the time required for heat to diffuse through a distance of the order of the particle radius, there will be a phase difference between the pressure and density changes. This leads to dissipation in the suspension. Allegra & Hawley (1971) calculated this thermal dissipation effect for a dilute suspension and found it to be unimportant compared to the viscous dissipation, except in the case of suspensions in which the particle density is nearly equal to that of the solvent. In the latter case, the viscous dissipation, which arises from a velocity difference between the particles and solvent, is small. This viscous dissipation effect will be discussed in §5.

The second interesting feature of the χ calculation, arises from the possibility that the surface charge – which often involves the dissociation of some surface group – may depend on the pressure. In this case the sound wave would cause a fluctuation in the surface charge. If the dissociation reaction involves a volume change, or if the fluid is locally heated by the reaction, the compressibility will be altered. This gives rise to another type of dissipation at frequencies around the characteristic frequency for the surface reaction. In pure electrolytes this effect is called Ultrasonic Relaxation Spectroscopy (Slutsky 1981), and measurements of the dissipation are used to study electrolyte reactions. Judging by the typical volumetric changes involved in such reactions (Slutsky 1981, p. 201) it seems unlikely that this dissipation effect will be significant in suspensions, except again in the case of particles with density near that of the solvent.

5. The electroacoustic equations

At present we have three equations, (3.5), (4.1) and (4.5) with four unknowns, viz. ρ', p', $\bar{u}$ and $\langle U\rangle$. To complete the set we must invoke constitutive relations for the suspension.

For the small disturbances assumed here, the macroscopic fluxes will be linear functions of the applied macroscopic electric field and pressure gradient. Hence the average particle velocity $\langle U\rangle$ will be given by an expression of the form

$$\langle U\rangle = \alpha\nabla\langle p\rangle + \mu_{\mathrm{E}}\langle E\rangle, \tag{5.1}$$

where α and μ_{E} are suspension transport properties. In the case of dilute suspensions with steady fields, μ_{E} is called the electrophoretic mobility (Hunter 1981, §3.3). This term will also be used for the μ_{E} defined here, but it should be born in mind that μ_{E} is a function of frequency in this case, and that it is defined as the velocity per unit field with zero pressure gradient. As we shall show in §8, the application of an electric field to a concentrated suspension gives rise to pressure gradients which make a substantial contribution to the particle motion. Thus μ_E is not simply equal to the velocity per unit field, as might be expected by readers who are familiar with the definition for dilute suspensions.

Although the constitutive relation (5.1) provides us with an extra equation, it also contains another unknown, namely the field $\langle \boldsymbol{E} \rangle$. To complete the set we must add the constitutive relation

$$\langle \boldsymbol{i} \rangle = K^* \langle \boldsymbol{E} \rangle + \gamma \nabla \langle p \rangle, \tag{5.2}$$

for the total current density $\langle \boldsymbol{i} \rangle$, together with the charge conservation equation (O'Brien 1982, §3)

$$\nabla \cdot \langle \boldsymbol{i} \rangle = 0, \tag{5.3}$$

where K^* is the complex conductivity of the suspension.

In my earlier paper on this topic, I showed that the quantities γ and μ_E are linked by the reciprocal relation

$$\gamma = \frac{\Delta\rho}{\rho} \phi \mu_E \tag{5.4}$$

in the case of dilute monodisperse suspensions, where ρ is the solvent density. In the appendix to this paper it is shown that the relation (5.4) holds for any suspension of solid particles with fixed charge, provided only that the radius is small compared with the wavelength. Judging by the general nature of other reciprocal relations, it seems likely that this restriction to solid particles and fixed charge is an artifact of the proof, and that the relation (5.4) should apply to any suspension of particles small compared with λ.

The equation (4.5) for the macroscopic density fluctuations contains the term $\nabla \cdot \langle U \rangle$. On taking the divergence of the formula (5.1) for $\langle U \rangle$, and using (5.2) and (5.3), we find

$$\nabla \cdot \langle U \rangle = \alpha \nabla^2 \langle p \rangle \left(1 - \frac{\mu_E}{\alpha K^*} \gamma\right).$$

With the aid of the reciprocal relation (5.4) we can write this as

$$\nabla \cdot \langle U \rangle = \alpha \nabla^2 \langle p \rangle \left(1 - \frac{\phi \Delta\rho (\mu_E)^2}{\alpha \rho K^*}\right). \tag{5.5}$$

Assuming that the particle velocity due to the pressure gradient is the same order of magnitude as the macroscopic velocity, we obtain the estimate $1/\rho\omega$ for the quantity α. Using typical values of 10^{-8} M^2 V^{-1} s^{-1} for μ_E and 10^{-2} Ω^{-1} M^{-1} for K^*, we find that the quantity

$$\frac{\phi \Delta\rho (\mu_E)^2}{\alpha \rho K^*} = O\left(10^{-4} \phi \frac{\Delta\rho}{\rho}\right) \tag{5.6}$$

at a frequency of 1 MHz with water as the solvent.

Thus, to a good approximation, we may write

$$\nabla \cdot \langle U \rangle = \alpha \nabla^2 \langle p \rangle$$

in place of (5.5).

Combining this result with the mass conservation equations (4.1) and (4.5) we get

$$\langle \rho_0 \rangle \nabla \cdot \bar{\boldsymbol{u}} = -\mathrm{i}\omega \chi \langle p \rangle + \phi \Delta\rho \alpha \nabla^2 \langle p \rangle, \tag{5.7}$$

where the pressure $\langle p \rangle$ is now measured relative to the equilibrium value.

The above equation and the force balance equation (3.5) provide the complete set for the determination of $\langle p \rangle$ and $\bar{\boldsymbol{u}}$, provided appropriate boundary conditions are supplied.

Combining (5.7) with (3.5), we obtain an equation for the macroscopic pressure, viz.

$$(1+\mathrm{i}\omega\phi\Delta\rho\alpha)\nabla^2\langle p\rangle+\omega^2\chi\langle p\rangle = 0.$$

This equation yields plane-wave solutions of the form $p_0\,\mathrm{e}^{\mathrm{i}(\omega t-kx)}$, where

$$k^2 = \omega^2\chi/(1+\mathrm{i}\omega\phi\Delta\rho\alpha).$$

If α has a real component, the plane wave will decay in amplitude. From (5.1) and the momentum equation (3.5) it can be seen that a real component to α corresponds to a particle velocity out of phase with the bulk, indicating a relative motion between the particle and fluid. This relative motion leads to the viscous dissipation which is responsible for the decay in the wave amplitude. Judging by results for dilute suspensions (Temkin 1981, §§6.9, 6.10) the real part of α peaks at a frequency ω around ν/a^2, where ν is the kinematic viscosity and a is the particle radius, and that peak value is of order $1/\rho\omega$. Thus at these frequencies, the decay in amplitude of a plane-wave per wavelength will be of order $\phi\Delta\rho/\rho$. Unless the suspension is dilute, or $\Delta\rho/\rho$ is small, sound waves will tend to be confined within a few wavelengths of the boundaries at these frequencies.

In addition to the dissipation mechanisms discussed so far there may also be a very significant dissipation caused by bubbles in the suspension (Lighthill 1978, §1.6). Provided the bubbles are small, this effect can be incorporated into the bulk compressibility factor χ, which will then have an imaginary component at frequencies near the resonant frequency of the bubbles.

6. The electroacoustic boundary conditions

The boundary conditions for electroacoustic problems are obtained by applying conservation equations to slab-shaped boundaries lying on the macroscopic surface of the suspension.

From the current conservation equation

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

we find that

$$\langle \boldsymbol{i}\rangle\cdot\hat{\boldsymbol{n}} \tag{6.1}$$

is continuous at an interface, where $\hat{\boldsymbol{n}}$ is the unit normal to that surface.

An application of the mass conservation equation to the slab yields (O'Brien 1988, §5)

$$\left(\bar{u}-\phi\frac{\Delta\rho}{\langle\rho_0\rangle}\langle U\rangle\right)\cdot\hat{\boldsymbol{n}} = \boldsymbol{u}_{\mathrm{B}}\cdot\hat{\boldsymbol{n}} \tag{6.2}$$

where $\boldsymbol{u}_{\mathrm{B}}$ is the velocity of the boundary.

Finally, from a force balance on the slab, we find that

$$\boldsymbol{\sigma}\cdot\hat{\boldsymbol{n}} = \langle p\rangle\,\hat{\boldsymbol{n}},$$

where $\boldsymbol{\sigma}$ is the stress tensor in the material that forms the boundary.

7. Electroacoustic effects caused by the motion of a solid boundary

The electroacoustic equations can be simplified in the case when the effects are caused by either a boundary motion, or an applied electric field acting separately.

In this section we shall consider the case of excitation by boundary motion; we shall turn to the electric field excitation in §8. Since the electroacoustic equations and boundary conditions are linear, any excitation can be written as a superposition of these two modes.

From the current balance equation (5.3) and the constitutive formula (5.2) for the current density, we find that the field generated by a boundary motion is of order

$$\left| \phi \frac{\Delta\rho}{\rho} \frac{\mu_E}{K^*} \nabla\langle p \rangle \right|.$$

Thus in the formula (5.1) for the average particle motion, the ratio of the term $\mu_E \langle \boldsymbol{E} \rangle$ to $\alpha \nabla \langle p \rangle$, is of order

$$\phi \frac{\Delta\rho}{\rho} \frac{(\mu_E)^2}{K^* \alpha}.$$

In §5 it was shown this ratio is typically very small. To a good approximation we can therefore neglect the effect of the macroscopic electric field on the particle motion in this case.

Since the equations (3.5) and (5.7) for $\bar{\boldsymbol{u}}$ and $\langle p \rangle$ do not involve $\langle \boldsymbol{E} \rangle$, the only way that the field can affect these quantities is through its effect on the particle velocity in the boundary condition (6.2), but as we have seen, this effect is negligible. Hence when the waves are generated by the motion of a boundary, the velocity and pressure field can be calculated independently of the electric field.

Once $\langle p \rangle$ has been determined, the electric field can then be obtained from the solution of Poisson's equation

$$\nabla^2 \langle \psi \rangle = \phi \frac{\Delta\rho}{\rho} \frac{\mu_E}{K^*} \nabla^2 \langle p \rangle,$$

obtained from the current conservation equation (5.3) and the formula (5.2) for the current density.

Rather than solve Poisson's equation directly however, it is more convenient to introduce a modified potential ψ', defined by

$$\psi' = \langle \psi \rangle - \phi \frac{\Delta\rho}{\rho} \frac{\mu_E}{K^*} \langle p \rangle.$$

This quantity satisfies Laplace's equation and, on a conducting surface, it satisfies the boundary condition

$$\psi' = V - \phi \frac{\Delta\rho}{\rho} \frac{\mu_E}{K^*} \langle p \rangle, \tag{7.1}$$

where V is the true potential of the conductor. Clearly the pressure on a conducting surface is equivalent electrically to an applied voltage. That equivalent voltage is usually quite small; using the values of μ_E and K^* quoted earlier, we find that a one atmosphere pressure amplitude is equivalent to about

$$10^{-1} \phi \frac{\Delta\rho}{\rho} \text{volts.}$$

In this analysis we have so far neglected electroacoustic effects that arise directly from the background electrolyte. If we regard the electrolyte ions as suspended particles, their contribution to the equivalent voltage in (7.1) will be

$$\sum_{j=1}^{N} \phi_j \frac{\Delta\rho_j}{\rho} \frac{\mu_j}{K^*} \langle p \rangle.$$

The ionic mobilities μ_j are typically of the same order as that of the particle, so the electrolyte contribution is significant if the electrolyte mass is comparable with the particle mass in the suspension. For 10^{-3} M KCl, the electrolyte accounts for roughly 10^{-4} of the total mass, while the particle contribution is $\phi\Delta\rho/\rho$. Thus in most cases the particles provide the dominant electroacoustic effect.

8. An applied electric field

The phenomenon of sound waves generated by an alternating electric field in a suspension was only recently discovered by Cannon and his coworkers (Cannon, Oja & Petersen 1985).

Mathematically speaking, the macroscopic motion arises for the particle term in the boundary condition (6.2); the particles generate a mass flux at the boundaries. With the estimate $\mu_E E$ for $\langle U\rangle$, we find from (6.2) that the macroscopic velocity in this case is of order

$$\phi\frac{\Delta\rho}{\rho}\mu_E E,$$

and hence the pressure gradients due to the electric field are of order

$$\omega\phi\Delta\rho\mu_E E.$$

Using the estimate of μ_E given in §5, we see that a field of 10^4 V M^{-1} at 1 MHz will produce a pressure amplitude of order $10^5(\phi\Delta\rho/\rho)$ N M^{-2}, or $\phi\Delta\rho/\rho$ atmospheres: not a pressure that is likely to cause any damage, but a measurable effect, nonetheless. Using the above estimate for the pressure gradient, we find that the current formula (5.2) can be approximated by the usual relation

$$\langle \boldsymbol{i}\rangle = K^*\langle \boldsymbol{E}\rangle$$

in this case.

The current conservation equation (5.3) therefore reduces to Laplace's equation for the potential, and hence the electric field distribution is unaffected by the sound waves that are excited by that field.

Although the current is unaffected by the sound waves, the same is not true of the particle motion. For if we use the above estimate for the pressure gradient, we find that the ratio of the pressure term to the field term in the expression (5.1) for the particle velocity is of order $\phi\Delta\rho/\rho$.

Thus when an alternating electric field is applied to a concentrated suspension, the particle velocity is not simply equal to $\mu_E\langle \boldsymbol{E}\rangle$ as might be expected. Instead the particle velocity will depend on position in the sound wave field, which in turn depends on the device geometry. This is a point which was raised in §5, when the quantity μ_E was defined, for μ_E is not simply the particle velocity per unit field, it is the particle velocity per unit field with zero pressure gradient. The simplest way to measure that mobility is not by direct observation of particle motion (since the pressure gradient will usually be non-zero), but by making electroacoustic measurements, as illustrated in the following example.

9. An application

Until recently, electroacoustic research has focused on a quantity known as the Colloid Vibration Potential† (CVP). This is defined as the open-circuit voltage

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† In the case of a pure electrolyte, the term Ionic Vibration Potential is used.

between two parallel fine-wire probes aligned perpendicular to the direction of propagation in a plane-wave field (Zana & Yaeger 1981).

The calculation of the CVP involves the solution of Laplace's equation for the modified potential ψ' subject to the boundary condition (7.1) on each electrode, together with the requirements that no current passes on to the electrodes, and $\psi' \rightarrow 0$ far from the electrodes. The solution to this problem is of course given by $\psi' \equiv 0$. From (7.1) it follows that the CVP is given by

$$\phi \frac{\Delta\rho}{\rho} \frac{\mu_{\mathrm{E}}}{K^*} \Delta\langle p\rangle, \tag{9.1}$$

where $\Delta\langle p\rangle$ is the pressure difference between the two wires. This result is equivalent to the formula obtained by the traditional method of summing the electric fields due to the individual particle dipoles (O'Brien 1988, §4), a procedure that is limited to open-circuit measurements in a plane-wave field.

Suppose now that instead of measuring the open-circuit voltage, the probes are wired up to measure the short-circuit current. To determine this current, we must again solve Laplace's equation for ψ', subject to the same boundary conditions, except that now the potential V is the same on each wire.

Mathematically, this problem is identical to that of determining the electrostatic potential around two parallel wires held at a known potential difference. In this case the 'potential' difference arises from a pressure difference between the two wires. By representing the wires as a two-dimensional source–sink pair, we find that the potential is given by

$$\psi' = \phi \frac{\Delta\rho}{\rho} \frac{\mu_{\mathrm{E}}}{K^*} \frac{\Delta\langle p\rangle}{2\ln(a/d)} \{\ln r_1 - \ln r_2\},$$

where r_1 and r_2 are distance from the centre of each wire, a is the wire radius and d the wire separation. From this it follows that the current passing between the wires is

$$\pi\phi \frac{\Delta\rho}{\rho} \mu_{\mathrm{E}} \frac{\Delta\langle p\rangle}{\ln(a/d)}.$$

Unlike the CVP, this quantity is independent of the suspension conductivity, and therefore provides a more direct measure of the mobility μ_{E} than the traditional electroacoustic devices.

Appendix. The electroacoustic reciprocal relation

The microscopic disturbances caused by a sound wave, or an alternating electric field are governed by the equations (O'Brien 1988, §2)

$$\nabla^2 \delta\psi = -\frac{\delta\rho_{\mathrm{E}}}{\epsilon}, \tag{A 1}$$

$$\nabla \cdot \boldsymbol{f}_j = -\mathrm{i}\omega\delta n_j, \tag{A 2}$$

$$\nabla \cdot \boldsymbol{\sigma} - \delta\rho_{\mathrm{E}} \nabla\psi^0 - \rho_{\mathrm{E}}^0 \nabla\delta\psi = \mathrm{i}\omega\rho\boldsymbol{u} \tag{A 3}$$

and

$$\nabla \cdot \boldsymbol{u} = 0. \tag{A 4}$$

Here ψ^0 refers to the local equilibrium electrical potential and

$$\rho_{\mathrm{E}}^0 = \sum_{j=1}^{N} e z_j n_j^0 \tag{A 5}$$

is the equilibrium charge density, where n_j is the number density and ez_j the charge on the jth ionic species, and N the number of such species. $\boldsymbol{\sigma}$ is the local hydrodynamic stress tensor, and $\boldsymbol{f}_j$ is the flux density of the jth ionic species, given by

$$\boldsymbol{f}_j = -D_j\left[\nabla\delta n_j + \frac{n_j^0\, ez_j}{kT}\nabla\delta\psi + \frac{\delta n_j\, ez_j}{kT}\nabla\psi^0\right] + n_j^0\,\boldsymbol{u}. \tag{A 6}$$

As usual, D_j denotes the ionic diffusivity, and ϵ is the permittivity of the solvent. At the frequencies of interest here, ϵ is approximately equal to the static permittivity.

The incompressibility constraint (A 4) is invoked on the assumption that the wavelength is much greater than the particle radius and any other lengthscales associated with the microscopic disturbances.

The reciprocal relation is obtained from an analysis of the expression

$$\frac{1}{V}\int_A \left\{\boldsymbol{u}^a\cdot\boldsymbol{\sigma}^b - \boldsymbol{i}^a\delta\psi^b - \sum_{j=1}^{N}\frac{kT}{n_j^0}\delta n_j^b\,(\boldsymbol{f}_j^a - n_j^0\,\boldsymbol{u}^a)\right\}\cdot\hat{\mathbf{n}}\,\mathrm{d}A, \tag{A 7}$$

where the superscripts a and b denote two solutions with different macroscopic pressure gradients and electric fields. V is the volume enclosed by the surface A.

If the radii of curvature of A are much greater than the average particle separation, then A can be subdivided into portions that are small enough to be treated as flat, but large enough to pass through a representative sample of suspension (O'Brien 1979, §3). By using this fact, together with the statistical homogeneity of the various disturbances, it can be shown (O'Brien 1988, §3) that the term (A 7) is equal to

$$-\langle\boldsymbol{u}\rangle^a\cdot\nabla\langle p\rangle^b + \langle\boldsymbol{i}\rangle^a\cdot\langle\boldsymbol{E}\rangle^b, \tag{A 8}$$

in the limit of large V.

To establish the reciprocal relation we must first show that (A 7) and (A 8) are unaffected by an exchange of the superscripts a and b.

With the aid of the Divergence Theorem and (A 1)–(A 6), we can write (A 7) as

$$\begin{aligned}\frac{1}{V}\int_{V_\ell}\Bigg[&\mathrm{i}\omega\left\{\boldsymbol{u}^a\cdot\boldsymbol{u}^b + \nabla\delta\psi^a\cdot\nabla\delta\psi^b + \sum_{j=1}^{N} kT\frac{\delta n_j^a\,\delta n_j^b}{n_j^0}\right\}\\ &+2\mu\boldsymbol{e}^a:\boldsymbol{e}^b + \sum_{j=1}^{N} kTn_j^0D_j\left(\nabla\left(\frac{\delta n_j^b}{n_j^0}\right)+\frac{ez_j}{kT}\nabla\delta\psi^b\right)\\ &\times\left(\nabla\left(\frac{\delta n_j^a}{n_j^0}\right)+\frac{ez_j}{kT}\nabla\delta\psi^a\right)\Bigg]\mathrm{d}V + \frac{1}{V}\sum_p\int_{A_p}\left\{\boldsymbol{u}^a\cdot\boldsymbol{\sigma}^b - \boldsymbol{i}^a\delta\psi^b - \sum_{j=1}^{N}\frac{kT}{n_j^0}\delta n_j^b\,(\boldsymbol{f}_j^a - n_j^0\,\boldsymbol{v}^a)\right\}\cdot\hat{\boldsymbol{n}}\,\mathrm{d}A\end{aligned} \tag{A 9}$$

Here $\boldsymbol{e}$ denotes the rate of strain tensor and μ is the solvent viscosity. Σ_p represents a sum over the particles enclosed by A, and A_p denotes a particle surface. For those particles cut by A, A_p is the particle surface within A, plus the portion of A intersecting the particle. Finally, V_ℓ is the liquid volume within V.

Clearly, the volume integral in (A 9) is unaffected by an exchange of a and b. The difficult part of the proof lies in showing that the particle sum is also unaffected by an exchange of a and b.

In the long-wavelength approximation used here, the solid particles can be treated as rigid bodies. Hence the particle integral in (A 9) can be written as

$$\boldsymbol{U}^a\cdot\boldsymbol{F}^b + \boldsymbol{\Omega}^a\cdot\boldsymbol{T}^b - \int_{A_\mathrm{p}}\boldsymbol{i}^a\delta\psi^b\cdot\hat{\boldsymbol{n}}\,\mathrm{d}A, \tag{A 10}$$

where $\boldsymbol{F}$ and $\boldsymbol{T}$ are the net hydrodynamic force and torque on the particle, $\boldsymbol{\Omega}$ is the angular velocity, and $\boldsymbol{U}$ the translational velocity of the particle centre of mass. The term involving $\boldsymbol{f}_j - n_j^0 \boldsymbol{u}$ has been dropped on the assumption that the particle has a fixed charge; hence in a frame of reference moving with the particle the flux of ions into the surface is zero.

With the aid of Newton's second law, we can write (A 10) in the form

$$\mathrm{i}\omega[M\boldsymbol{U}^a\cdot\boldsymbol{U}^b+\boldsymbol{\Omega}^a\cdot\boldsymbol{I}\cdot\boldsymbol{\Omega}^b]-\left\{\boldsymbol{U}^a\cdot\boldsymbol{F}_{\mathrm{E}}^b+\boldsymbol{\Omega}^a\cdot\boldsymbol{T}_{\mathrm{E}}^b+\int_{A_{\mathrm{p}}}\boldsymbol{i}^a\delta\psi^b\cdot\hat{\boldsymbol{n}}\,\mathrm{d}A\right\}, \tag{A 11}$$

where M is the particle mass, and $\boldsymbol{I}$ the inertia tensor. The quantities $\boldsymbol{F}_{\mathrm{E}}$ and $\boldsymbol{T}_{\mathrm{E}}$ are the force and torque on the particle due to non-hydrodynamic forces such as electrical or Van der Waals forces between particles.

The term in square brackets in (A 11) has the required symmetry property. The symmetry of the remaining term can be demonstrated by the following thermodynamic argument.

To begin with we note that the terms $\boldsymbol{F}_{\mathrm{E}}$ and $\boldsymbol{T}_{\mathrm{E}}$ depend only on the instantaneous particle configuration and on the electric field distribution at the particle surface, since the Maxwell stresses are determined by that field. Furthermore, that electric field is in turn uniquely determined by the instantaneous particle orientation and position, and the potential over the particle surface; a result which follows from the uniqueness theorem for Poisson's equation (Protter & Weinberger 1967, §2.4)

$$\nabla^2\delta\psi = -\delta\boldsymbol{\chi}\cdot\nabla\rho_{\mathrm{E}}^0$$

for the potential inside the fixed charge particle, where $\delta\boldsymbol{\chi}$ is the local displacement of the particle from its equilibrium position.

Thus $\boldsymbol{F}_{\mathrm{E}}$ and $\boldsymbol{T}_{\mathrm{E}}$ are determined by the instantaneous particle configurations and the potential on the particle surfaces, irrespective of how that configuration and potential distribution are achieved. They could for example be set up in a reversible manner by the application of forces to the particles, and by the transfer of charge to conducting surfaces arranged around each particle in a way to achieve the desired potential distribution.

In the latter case $\boldsymbol{F}_{\mathrm{E}}$ and $\boldsymbol{T}_{\mathrm{E}}$ can be written as derivatives of the free energy $\mathscr{F}$ with respect to particle displacement and orientation. Similarly the potential $\delta\psi$ on the particle surface can be written as the derivative of the free energy with respect to charge σ, where

$$\sigma = -\frac{\boldsymbol{i}\cdot\hat{\boldsymbol{n}}}{\mathrm{i}\omega}\mathrm{d}A.$$

Since the system is only slightly perturbed from equilibrium, $\mathscr{F}$ can be approximated by the quadratic form

$$\mathscr{F} = \mathscr{F}_0+\frac{1}{2}\frac{\partial^2\mathscr{F}}{\partial x_j\,\partial x_k}x_j\,x_j,$$

where x_j denotes the generalized displacement, and the repeated subscripts imply a summation.

In this notation, the square bracketed term in (A 11) becomes

$$\mathrm{i}\omega\frac{\partial^2\mathscr{F}}{\partial x_j\,\partial x_k}x_j^a\,x_k^b,$$

which clearly has the required symmetry property.

Hence (A 8) is unaffected by an exchange of a and b. By choosing $\nabla\langle p\rangle^a$ and $\langle\boldsymbol{E}\rangle^b$ to be zero, we obtain

$$-\langle\boldsymbol{u}\rangle^a\cdot\nabla\langle p\rangle^b = \langle\boldsymbol{i}\rangle^b\cdot\langle\boldsymbol{E}\rangle^a. \tag{A 12}$$

The left-hand side can be rewritten in terms of the average particle velocity, by using the fact that

$$\bar{u} = \frac{\rho}{\langle \rho_0 \rangle} \langle u \rangle + \frac{\Delta\rho}{\langle \rho_0 \rangle} \phi \langle U \rangle,$$

a result which follows directly from the definitions of the momentum and volume-averaged velocities. In case (*a*), $\bar{u}$ is zero, since there is no pressure gradient to drive the momentum. Thus (A 12) can be written as

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

On substituting (5.1) and (5.2) for $\langle U \rangle$ and $\langle E \rangle$ in the above result we get the required relation, viz.

$$\gamma = \frac{\Delta\rho}{\rho} \phi \mu_{\mathrm{E}}. \tag{A 13}$$

In deriving this result it has been assumed that the particle charge is fixed. Although it seems likely that the result (A 13) applies to all suspensions, any attempt to allow for charge variation in the particle seems to require the use of some specific model – such as surface site dissociation (Hunter 1981, §6.3) – to describe that charge variation. I have been deterred from attempting such a proof by the increase in complication which would accompany such a model, and by the fact that the result would still not be completely general.

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