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Particle migration in suspensions by thermocapillary or electrophoretic motion

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Two problems of similar mathematical structure are studied: the thermocapillary motion of bubbles and the electrophoresis of colloidal particles. The thermocapillary motion induced in a cloud of bubbles by a uniform temperature gradient is investigated under the assumptions that the bubbles are all the same size, that the surface tension is high enough to keep the bubbles spherical, and that the bubbles are non-conducting. In the electrophoresis problem, the particles, identical spheres having a uniform zeta potential, are suspended in an electrolyte under conditions that make the diffuse charge cloud around each particle small when compared with the particle radius. For both problems, it is shown that in a cloud of n particles surrounded by an infinite expanse of fluid, the velocity of each sphere under creeping flow conditions is equal to the velocity of an isolated particle, unchanged by interactions between the particles. However, when the cloud fills a container, conservation of mass shows that this result cannot continue to hold, and the average translational velocity must be calculated subject to a constraint on the mass flux. The computation requires 'renormalization', but it is shown that the renormalization procedure is ambiguous in both problems. An extension of Jeffrey's (1974) second group expansion, together with the constraint of conservation of mass, removes the ambiguity. Finally, it is shown that the average thermocapillary or electrophoretic translational velocity of a particle in the cloud is related to the effective conductivity of the cloud over the whole range of particle volume fractions, provided that the particles are identical, non-conducting and, for the thermocapillary problem, inviscid.

1. Introduction

If a temperature gradient is applied to a viscous fluid containing bubbles, the bubbles move towards the hotter fluid, owing to the dependence of surface tension on temperature. Similarly, if an electric field is applied to an electrolytic solution containing charged particles, the particles move in directions dictated by their charge. Under conditions described below, the problems of thermocapillary motion and electrophoresis are mathematically similar, the governing equations being the same except for one boundary condition. We wish to calculate the average velocity of a particle in a cloud (we shall understand the word 'particle' to encompass bubbles as well) when the cloud is placed in a uniform gradient of temperature or electric potential and the particle concentration is low. The problem has several features in common with that of calculating the average settling velocity of a particle in a sedimenting cloud, a problem that was the subject of a paper by Professor Batchelor (Batchelor 1972) that gave a strong stimulus to research on the mechanics of suspensions. Its significance lay not just in its calculation of a sedimentation velocity, but equally in the way it addressed wider themes, such as the use of statistical methods to calculate average properties of suspensions and the solution of a subtle technical problem, namely how to express the average properties of a suspension of particles in terms of convergent integrals. The success of this and later work on the mechanics of suspensions, together with parallel progress on other flow systems containing small lengthscales, lead Batchelor (1976) to identify a new branch of specialization in fluid mechanics: microhydrodynamics.

One of the technical difficulties that must be solved during a calculation of the bulk properties of a suspension is the appearance of non-convergent integrals in various formal expressions for the quantities of interest, such as the average sedimentation velocity of the particles or the effective viscosity of a suspension. Earlier workers had already noted and tackled this difficulty (Burgers 1942; Pyun & Fixman 1964; see also references in Jeffrey 1977) and so its widespread occurrence was known when Batchelor (1972) published his method for overcoming it. Because of this, the new method, later called renormalization, was quickly applied to other problems (for example, Batchelor & Green 1972; Jeffrey 1973; Chen & Acrivos 1978). In addition, the method attracted a great deal of examination for its own sake, and was later refined and extended in many different ways (Jeffrey 1974; Willis & Acton 1976; McCoy & Beran 1976; Goddard 1977; O'Brien 1979; Felderhof, Ford & Cohen 1982).

Several concerns can be identified in the papers that reanalysed Batchelor's method of renormalization. The first was whether renormalization was of physical or mathematical significance. It must be remembered that both Rayleigh (1892) and Einstein (1906) had evaluated non-convergent sums or integrals in the course of deriving firmly established results, and consequently non-convergence seemed to some to be a purely mathematical issue and to others a detail requiring just some additional physical justification. Thus the first notable feature of the new approach was its stress on the *necessity* of renormalization. In this regard, an important benefit of tackling the sedimentation problem first (rather than, say, the viscosity problem) was the fact that the integrals were always infinite, and a discussion of 'physically significant' evaluations was impossible.

A second concern, closely related to the first, was a desire to simplify a key step in the original analysis which entailed looking 'for a quantity whose mean is known exactly from some overall condition or constraint in the specification of the problem and whose value at $\boldsymbol{x}_0$ [the position of a test particle – notation similar to Batchelor's is defined in §3] has the same long-range dependence on the presence of a sphere at $\boldsymbol{x}_0+\boldsymbol{r}$ as the velocity of the test sphere; and, once found, the difference between $\bar{\boldsymbol{U}}$ [the sedimentation velocity] and the mean of this quantity can be expressed as an integral...which can be legitimately...evaluated explicitly.' This description and the finding of renormalizing quantities were not easy to grasp, and even rereading Batchelor (1972) today, one is struck by the difficulty of some of the ideas; who, for example, would find it obvious to choose the divergence of the deviatoric stress for use in Batchelor's equation (3.10)?

In fact, a discussion of the physical differences between a cloud of particles that fills a container and one that is surrounded by clear fluid appears as early as the second paragraph of Batchelor (1972), and this is the essence of a physical interpretation. Nevertheless, renormalization was presented as a means of removing a convergence problem which had a physical interpretation, rather than as a means of accounting for backflow that had a mathematical formulation. Similarly, although it was clearly expected that the renormalizing quantity would be physically related to the integrand being renormalized, it was not until Jeffrey (1974) that a methodology was introduced that enforced this requirement systematically. The inadequacy of the purely mathematical interpretation was clearly displayed when a problem was discovered in which several choices of the renormalizing quantity appeared to be possible (Chen & Acrivos 1978), a problem we discuss below.

Another reason why Batchelor's method was re-examined stemmed from issues connected with the distinction between the value of the external field applied to the suspension and the mean value of that field within the suspension. Ever since the investigation of effective viscosity by Einstein (1906), the possible difference between the applied field – in other words, the field 'at infinity' – and the mean field had been a point of debate. Investigators studying the electrostatic and elastostatic properties of dispersions of particles could formulate problems in which the suspension was surrounded by clear fluid or matrix, and thereby they could separate the applied and the mean fields. For sedimentation, however, the very nature of the problem made it necessary to deal with a space-filling suspension from the outset, leaving these issues unresolved. They were addressed in subsequent work (cited above) and the results obtained by Batchelor verified; and although the original method has now been filled out in completeness and rigour, it has yet to be replaced by an approach that is simpler or more direct, at any rate for problems to which it is suited.

Batchelor's 1972 paper stimulated work in other ways as well. It drew attention to the difference between the sedimentation of a random dispersion of freely moving spheres, the sedimentation of a periodic array of spheres and the flow through a random array of fixed spheres. The last case is a 'strong interaction' problem that cannot be solved by Batchelor's method, and the efforts to understand this and find an alternative method lead to the averaged-equation approach (Childress 1972; Saffman 1973; Howells 1974; Hinch 1977). It is interesting to note that the new approach had first to explain Batchelor's method in its own terms (Hinch 1977). Finally, it is instructive to list the topics not treated in the original paper which received attention in later years. For example, the paper contains comments on the importance of particle motions for the probability distribution for the particle positions, even though in the actual calculation, specific distributions were simply assumed. This lead was taken up by many later papers, and the motions of pairs of particles under the influence of hydrodynamic and non-hydrodynamic forces have been explored in detail. Other extensions to the original investigation include the addition of non-hydrodynamic effects, such as Brownian motion, the effects of unequal sizes and of inhomogeneous conditions.

It is a tribute to Batchelor's idea that a new problem should be discovered that leads us to re-examine the basis of his method. This problem, which concerns the thermocapillary motion or electrophoresis of particles, brings a new element into the analysis and adds another example of a well-known difficulty. The new element concerns the 'applied field'. Specifically, when Jeffrey (1974) presented a general treatment of Batchelor's renormalization, all the problems known at that time could be summarized symbolically in terms of a quantity $\boldsymbol{S}$ to be averaged and a quantity $\boldsymbol{H}$ – the applied field – whose average was known. In the thermocapillary and electrophoretic problems, however, there are two quantities whose averages are specified and which determine the velocities of the particles, because both the applied field (electric or thermal) and the volume flux across any boundary spanning the suspension are known and can be used as renormalizing quantities. The well-known difficulty is the possibility, first discovered by Chen & Acrivos (1978), that a study of two-particle interactions may not be sufficient to prove which of several choices gives the correct renormalization strategy.

The study of thermocapillary phenomena has taken on new significance with the development of the space shuttle and the opportunities for experimenting and manufacturing under near-weightless conditions. For example, unwanted gas bubbles in a mixture are usually removed by buoyancy forces, but this force is not available in an orbiting laboratory. In fact, even on Earth a viscous fluid can retain bubbles for a significant length of time if the bubbles are small enough, and under near-weightless conditions forces other than buoyancy must be found to move bubbles, which is why thermocapillary forces are of interest. The motion of a single bubble was studied by Young, Goldstein & Block (1959) and the motion of two bubbles by Meyyappan, Wilcox & Subramanian (1983), Meyyappan & Subramanian (1984), Anderson (1985*a*) and Feuillebois (1989). All of these two-bubble papers noted the remarkable result that two equi-sized bubbles move with the same velocity as one bubble; Meyyappan *et al.* (1983) showed this numerically for the case of axisymmetric motion and Feuillebois proved it analytically, while Meyyappan & Subramanian and Anderson showed that, for bubbles at any angle to the applied temperature gradient, the result was true to the order to which they carried out their approximations. The study of electrophoretic phenomena, on the other hand, has important applications in areas concerned with the fractionation of mixtures of proteins or biological cell populations. Recall that electrophoresis has a venerable history, beginning with the work of Smoluchowski in the early part of this century; see Hunter (1981) for an extensive discussion of particle electrophoresis. But, for our purpose, the work of Reed & Morrison (1976) is especially noteworthy in that they showed that two identical spheres with thin double layers would move with the same velocity in an electric field as one sphere (the Smoluchowski velocity), irrespective of their separation and orientation in the electric field.

In what follows, we shall extend the studies referred to above and explore their consequences for the averaging of thermocapillary and electrophoretic velocities in clouds of particles. The presentation is organized as follows. For the sake of simplicity, we first concentrate on the thermocapillary problem and then show how the electrophoresis problem can be addressed using the same mathematics. Thus, in §2 thermocapillary motion is discussed in detail and we show how particles in a cloud translate with the same velocity that one bubble would have if it were all alone. Thermocapillary motion of a space-filling cloud and the effect of backflow are then taken up in §3 where the renormalization ambiguity is set forth in detail. Next, the formal series for the many-body interactions is developed in §4, where we discover how to reduce the integral based on three-body interactions to one based on two-body interactions. Once the thermocapillary problem has been discussed, it is a simple matter to show how the analysis can be adapted for electrophoresis. This is done in §5 where we show that particles in a cloud of identical spheres move at the same velocity as an isolated sphere. In §6, we derive a surprising result which relates uniquely the average thermocapillary or electrophoretic velocity of a test particle to the effective conductivity of the suspension over the whole range of the particle concentration c. The paper concludes with a discussion in §7.

2. Equations of motion

Consider, first, a bubble in an infinite expanse of fluid of viscosity μ and density ρ, in which a uniform, constant temperature gradient $\boldsymbol{H}$ far from the bubble is imposed. Let the surface tension of the interface between the bubble and the fluid be γ, and assume that γ decreases linearly with temperature T, and that the surface tension is high enough to keep the bubble spherical (of radius a). Then, as shown by Young *et al.* (1959), the bubble moves with a velocity

$$U_{\mathrm{YGB}} = -a\frac{\mathrm{d}\gamma}{\mathrm{d}T}\frac{\boldsymbol{H}}{2\mu},$$

under the assumptions of low Reynolds number

$$R = \rho a U_{\mathrm{YGB}}/\mu,$$

and small Marangoni number

$$Ma = \frac{aU_{\mathrm{YGB}}}{\alpha} = -H\frac{\mathrm{d}\gamma}{\mathrm{d}T}\frac{a^2}{2\mu\alpha},$$

where α is the thermal diffusivity of the fluid.

We can use these results to non-dimensionalize the equations governing the temperature and velocity fields in this limit. Distances are scaled using the bubble radius a, the temperature is scaled using aH and the bubble centre is placed at the origin. We shall denote the dimensionless temperature gradient by $\boldsymbol{h} = \boldsymbol{H}/H$. The temperature field T is then determined by

$$\nabla^2 T = 0, \tag{2.1}$$

together with the boundary conditions

$$\boldsymbol{\nabla} T \rightarrow \boldsymbol{h} \quad \text{as} \quad |\boldsymbol{x}| \rightarrow \infty, \tag{2.2}$$

and

$$\boldsymbol{n}\cdot\boldsymbol{\nabla} T = 0 \quad \text{on} \quad |\boldsymbol{x}| = 1. \tag{2.3}$$

The velocity and pressure fields are scaled with the Young–Goldstein–Block velocity, giving

$$-\boldsymbol{\nabla} p + \nabla^2 \boldsymbol{u} = 0, \tag{2.4}$$

and

$$\boldsymbol{\nabla}\cdot\boldsymbol{u} = 0, \tag{2.5}$$

together with the boundary conditions

$$\boldsymbol{u} \rightarrow 0 \quad \text{as} \quad |\boldsymbol{x}| \rightarrow \infty, \tag{2.6}$$

$$\boldsymbol{u}\cdot\boldsymbol{n} = U\boldsymbol{h}\cdot\boldsymbol{n} \quad \text{on} \quad |\boldsymbol{x}| = 1, \tag{2.7}$$

and

$$\boldsymbol{\sigma}\cdot\boldsymbol{n} - \boldsymbol{nn}\cdot\boldsymbol{\sigma}\cdot\boldsymbol{n} = 2\boldsymbol{\nabla} T \quad \text{on}\, |\boldsymbol{x}| = 1. \tag{2.8}$$

In (2.7) the unknown velocity of the bubble is written as $U\boldsymbol{h}$, but since we have scaled velocities with the known solution, U will equal 1 for the single-bubble problem. The boundary condition (2.8) has been simplified from its usual form using (2.3). The solution to these equations, for $|\boldsymbol{x}| \geqslant 1$, is

$$T = \boldsymbol{h}\cdot\boldsymbol{x} - \tfrac{1}{2}\boldsymbol{h}\cdot\boldsymbol{\nabla}|\boldsymbol{x}|^{-1}, \tag{2.9}$$

and

$$\boldsymbol{u} = -\tfrac{1}{4}\boldsymbol{h}\cdot\nabla^2 \boldsymbol{J}, \tag{2.10}$$

where $\boldsymbol{J}$ is the Green function for the Stokes equations:

$$\boldsymbol{J}(\boldsymbol{x}) = \boldsymbol{I}/|\boldsymbol{x}| + \boldsymbol{xx}/|\boldsymbol{x}|^3.$$

The solution can be interpreted as follows. From (2.9) we see that the response of the bubble to the temperature gradient is equivalent to adding a thermal dipole at the bubble centre. Also, a bubble held fixed in a temperature gradient exerts a force on the fluid (Subramanian 1985), but our problem requires the bubble to be force free, and therefore it translates with whatever velocity is needed to create a cancelling force. The difference between the two flow fields is a Stokes quadrupole, which is represented by (2.10).

We now wish to consider the problem of n interacting bubbles, all of the same size, in an infinite expanse of fluid. We shall suppose that the centre of bubble p is at $\boldsymbol{r}_p$ and let $\boldsymbol{x}_p$ be a vector from the centre of that bubble to an arbitrary point $\boldsymbol{x}$, so that $\boldsymbol{x} = \boldsymbol{r}_p + \boldsymbol{x}_p$. Boundary conditions must now be applied on each surface $|\boldsymbol{x}_p| = 1$. We shall denote the velocity of bubble p by $\boldsymbol{U}_p$. The case of two bubbles (centres at $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$) was studied by Anderson (1985*a*) using the method of reflections, and he found that the velocities were given by

$$\boldsymbol{U}_1 = \boldsymbol{U}_2 = \boldsymbol{h} + O(|\boldsymbol{x}_1 - \boldsymbol{x}_2|^{-8}).$$

In other words, the velocity of one sphere was unaltered by the presence of a second to the indicated order of the approximation. We begin by extending Anderson's analysis to three spheres and arrive at the equivalent result. In order to do so, we first rewrite some of his intermediate expressions in a more compact form. Anderson found that in addition to (2.9) and (2.10) he needed the velocity and temperature fields around a bubble in a quadratic temperature field, obtained from the ambient field T by evaluating $\boldsymbol{\nabla\nabla} T$ at the point $\boldsymbol{r}_p$. In dimensional variables, we can write

$$T = (\boldsymbol{\nabla\nabla} T)_p : (\boldsymbol{xx} + \tfrac{1}{9}\boldsymbol{\nabla\nabla}|\boldsymbol{x}|^{-1}), \tag{2.11}$$

$$\boldsymbol{u} = \frac{-\mathrm{d}\gamma}{\mathrm{d}T}\frac{1}{6\mu}(\boldsymbol{\nabla\nabla} T)_p : \boldsymbol{\nabla}(1 + \tfrac{1}{6}\nabla^2)\boldsymbol{J}. \tag{2.12}$$

As with the constant-temperature-gradient case, we can interpret these results using multipoles. A bubble responds to a linear temperature gradient by generating a quadrupole thermal disturbance and a stresslet (Stokes dipole) velocity disturbance. It should be noted that the stresslet flow field decays only as $|\boldsymbol{x}|^{-2}$ whereas the flow field (2.10) decays as $|\boldsymbol{x}|^{-3}$, which is why it cannot be neglected in interaction calculations.

We now consider three bubbles with centres at $\boldsymbol{r}_1, \boldsymbol{r}_2$ and $\boldsymbol{r}_3$. Starting with the bubble $\boldsymbol{r}_1$ in the temperature gradient $\boldsymbol{h}$, we find the disturbance temperature field at bubble $\boldsymbol{r}_2$ from (2.9). Letting $\boldsymbol{r}_{21} = \boldsymbol{r}_2 - \boldsymbol{r}_1$, we find

$$\boldsymbol{\nabla} T_{21} = \tfrac{1}{2}\boldsymbol{h}\cdot(3\boldsymbol{r}_{21}\boldsymbol{r}_{21}/|\boldsymbol{r}_{21}|^5 - \boldsymbol{I}/|\boldsymbol{r}_{21}|^3).$$

This ambient temperature gradient induces a thermal dipole in sphere $\boldsymbol{r}_2$ and gives it an additional velocity equal to $\boldsymbol{\nabla} T_{21}$. However, the velocity field (2.10) around sphere $\boldsymbol{r}_1$ creates an ambient velocity field at bubble $\boldsymbol{r}_2$ equal to

$$\boldsymbol{u}_{21} = -\tfrac{1}{2}\boldsymbol{h}\cdot(3\boldsymbol{r}_{21}\boldsymbol{r}_{21}/|\boldsymbol{r}_{21}|^5 - \boldsymbol{I}/|\boldsymbol{r}_{21}|^3).$$

Thus the total change in the velocity of bubble $\boldsymbol{r}_2$ is $\boldsymbol{\nabla} T_{21} + \boldsymbol{u}_{21} = 0$. We now continue the method of reflections to sphere $\boldsymbol{r}_3$.

The velocity of bubble $\boldsymbol{r}_3$ will consist of contributions from the disturbances arising from the applied temperature gradient being reflected from bubble $\boldsymbol{r}_1$ and from $\boldsymbol{r}_2$ together with the disturbances being reflected from bubble $\boldsymbol{r}_1$ to $\boldsymbol{r}_2$ and then on to $\boldsymbol{r}_3$. The last effect is the one we are interested in. We saw above that bubble $\boldsymbol{r}_1$ induces a thermal dipole in bubble $\boldsymbol{r}_2$. This will produce a change in the ambient gradient near $\boldsymbol{r}_3$ equal to

$$\tfrac{1}{2}\boldsymbol{\nabla} T_{21}\cdot(3\boldsymbol{r}_{32}\boldsymbol{r}_{32}/|\boldsymbol{r}_{32}|^5 - \boldsymbol{I}/|\boldsymbol{r}_{32}|^3).$$

Bubble $\boldsymbol{r}_3$ will therefore pick up a velocity equal to this. Also there is a relative velocity between bubble $\boldsymbol{r}_2$ and the ambient flow at $\boldsymbol{r}_2$ equal to ∇T_{21}, and this will cause a velocity disturbance at $\boldsymbol{r}_3$. The ambient velocity at $\boldsymbol{r}_3$ will be changed by

$$-\tfrac{1}{2}\nabla T_{21}\cdot(3\boldsymbol{r}_{32}\boldsymbol{r}_{32}/|\boldsymbol{r}_{32}|^5-\boldsymbol{I}/|\boldsymbol{r}_{32}|^3),$$

which cancels the temperature-gradient contribution. Finally we must consider the perturbations due to the Stokes dipole field given in (2.12). There are two contributions to this, of which the first comes from the second derivative of the temperature field (2.9) and the other from the rate-of-strain field obtained from the flow field (2.10). It has been shown by Anderson that these also cancel.

We have seen then that two and three spheres move in an applied temperature gradient with velocities unchanged from the single-sphere case. We now wish to extend this to n spheres. Returning to (2.10), we can rewrite it using standard identities as

$$\boldsymbol{u} = \tfrac{1}{2}\boldsymbol{h}\cdot\nabla\nabla|\boldsymbol{x}|^{-1} = \nabla(\tfrac{1}{2}\boldsymbol{h}\cdot\nabla|\boldsymbol{x}|^{-1}). \tag{2.13}$$

From this, we see that if we write (2.9) for the temperature field as

$$T = \boldsymbol{h}\cdot\boldsymbol{x}+\phi,$$

we can rewrite (2.10) as $\boldsymbol{u} = -\nabla\phi$. We now postulate that the last two expressions hold true for the flow around n spherical bubbles, and replace (2.1)–(2.8) with the equations

$$T = \boldsymbol{h}\cdot\boldsymbol{x}+\phi, \tag{2.14}$$

and

$$\boldsymbol{u} = -\nabla\phi, \tag{2.15}$$

where

$$\nabla^2\phi = 0, \tag{2.16}$$

together with the boundary conditions

$$\nabla\phi\rightarrow 0 \quad \text{as} \quad |\boldsymbol{x}|\rightarrow\infty, \tag{2.17}$$

$$\boldsymbol{n}\cdot\nabla\phi = -\boldsymbol{h}\cdot\boldsymbol{n} \quad \text{on} \quad |\boldsymbol{x}_p| = 1. \tag{2.18}$$

The velocity field (2.15) will automatically satisfy the Stokes equations with the pressure equal to zero. In addition, the kinematic condition on the spheres' surfaces, that sphere p moves with velocity $\boldsymbol{U}_p$, is

$$\boldsymbol{u}\cdot\boldsymbol{n} = \boldsymbol{U}_p\cdot\boldsymbol{n} = -\boldsymbol{n}\cdot\nabla\phi = \boldsymbol{h}\cdot\boldsymbol{n} \quad \text{on} \quad |\boldsymbol{x}_p| = 1, \tag{2.19}$$

meaning $\boldsymbol{U}_p = \boldsymbol{h}$ for all p. The boundary condition left to verify is the stress boundary condition

$$-\boldsymbol{n}\cdot(\nabla\nabla\phi)+\boldsymbol{n}\boldsymbol{n}\cdot(\nabla\nabla\phi)\cdot\boldsymbol{n} = \boldsymbol{h}+\nabla\phi \quad \text{on} \quad |\boldsymbol{x}_p| = 1 \tag{2.20}$$

To prove this we use an expansion of ϕ about $\boldsymbol{r}_p$, the centre of sphere p. To introduce this expansion we consider first the special case of just two spheres. The method of twin multipole expansions calculates ϕ for this case by expressing it as a superposition of multipole expansions (Jeffrey 1973). The expression for ϕ is valid everywhere outside the spheres, but it is expressed in more than one coordinate system (Jeffrey 1973, equation 5.2). The coefficients in the expansion are found by transforming it entirely into the coordinate system of one sphere using addition theorems for spherical harmonics (Jeffrey 1973, equation 5.3) and applying boundary conditions. Here, although our aim is not to calculate coefficients, but rather to verify (2.20), we can still use the transformation idea extended to n spheres. Now ϕ will be a superposition of n multipole series in decaying harmonics, with each series centred on one of the n spheres. But each multipole series can be transferred to the centre of sphere p, where it will become a series of growing harmonics, just as can be seen in the two-sphere case. Thus ϕ can be expanded about $\boldsymbol{r}_p$ in an expansion of growing and decaying harmonics valid in a spherical shell centred at $\boldsymbol{r}_p$ whose inner surface is $|\boldsymbol{x}_p| = 1$ and whose outer surface touches the surface of the nearest neighbour to $\boldsymbol{r}_p$.

Let us denote a general decaying harmonic of order $-n-1$ by ϕ_{-n-1}. Then $|\boldsymbol{x}|^{2n+1}\phi_{-n-1}$ will be a growing harmonic of order n. We now write the expansion of ϕ about $\boldsymbol{r}_p$ as

$$\phi = -\tfrac{1}{2}\boldsymbol{h}\cdot\nabla|\boldsymbol{x}_p|^{-1} + \sum_n [(n+1)|\boldsymbol{x}_p|^{2n+1} + n]\,\phi_{-n-1}. \tag{2.21}$$

In this form, (2.18) is automatically satisfied. Using the identity

$$\boldsymbol{x}_p\cdot\nabla\phi_{-n-1} = (-n-1)\,\phi_{-n-1}, \tag{2.22}$$

together with the fact that $\boldsymbol{x}_p = \boldsymbol{n}$ on $|\boldsymbol{x}_p| = 1$, one obtains, on $|\boldsymbol{x}_p| = 1$,

$$\nabla\phi = -\tfrac{3}{2}\boldsymbol{n}\boldsymbol{h}\cdot\boldsymbol{n} + \tfrac{1}{2}\boldsymbol{h} + \sum_n (2n+1)(n+1)\,\boldsymbol{n}\phi_{-n-1} + (2n+1)\,\nabla\phi_{-n-1},$$

$$\boldsymbol{n}\cdot(\nabla\nabla\phi) = \tfrac{9}{2}\boldsymbol{n}\boldsymbol{h}\cdot\boldsymbol{n} - \tfrac{3}{2}\boldsymbol{h} + \sum_n (2n+1)(n+1)(n-1)\,\boldsymbol{n}\phi_{-n-1} - (2n+1)\,\nabla\phi_{-n-1},$$

and

$$\boldsymbol{n}\boldsymbol{n}\cdot(\nabla\nabla\phi)\cdot\boldsymbol{n} = 3\boldsymbol{n}\boldsymbol{h}\cdot\boldsymbol{n} + \sum_n (2n+1)(n+1)\,\boldsymbol{n}\boldsymbol{n}\phi_{-n-1},$$

whence one can easily verify that (2.20) holds. Thus the general result is proved. Incidentally, since ϕ is harmonic, (2.15) satisfies the full Navier–Stokes equations, with the pressure given by Bernouilli's equation, as long as the Marangoni number remains small. This exact solution to the thermocapillary problem was also noted earlier for the single bubble case by Crespo & Manuel (1983) and Balasubramaniam & Chai (1987).

3. The average velocity of a bubble in a cloud

Since the velocity of a bubble is unaltered by the presence of other bubbles, it might seem that there is no averaging problem to perform. Thus the first renormalization strategy would be to suppose that $\bar{U} = U_{\mathrm{YGB}}$. This is unsatisfactory, however, as can be shown by a physical argument. If the cloud of bubbles fills a closed container, conservation of volume (the fluid is incompressible) shows that the velocity must change, for if we take a surface through the suspensions perpendicular to the applied temperature gradient, the rate at which volume is displaced by the bubbles equals cU_{YGB}, where c is the volume concentration of the bubbles. Since the net flux across the surface must be zero, there must be a net backflow of fluid reducing the velocity of the bubbles by a factor $(1-c)$.

A second argument in support of renormalization comes from noting that the exact cancellation of the two velocity perturbations only occurs for non-conducting bubbles of the same size, because, as Anderson (1985*a*) showed, if the bubbles (or drops) have any conductivity, or if they differ in size, there is a familiar $1/|\boldsymbol{x}|^3$ non-convergent interaction between them. Thus, for the more general conducting-drop problem, we must renormalize, and then if we take the limit of zero conductivity, we are led to a renormalized integral, not the result $\bar{U} = U_{\mathrm{YGB}}$. However, although these arguments help to settle the question of whether or not renormalization is needed, we must still decide on the renormalization procedure. Recall that from the overall specification of the problem we have constraints on $\boldsymbol{u}(\boldsymbol{r})$, the velocity at the origin due to a bubble at $\boldsymbol{r}$, and $\nabla T(\boldsymbol{r})$, the temperature gradient at the origin. They are

$$\int \boldsymbol{u}P(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r} = 0 \quad \text{and} \quad \int (\nabla T - \bar{\boldsymbol{H}})P(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r} = 0.$$

Both of these are non-convergent integrals that cannot be evaluated. From the results above, however, it can be shown that the two integrands have the same dependence on r when the bubbles do not overlap the origin ($r > 1$), but they are different when the bubbles overlap the origin. Therefore the integral

$$\int ([\boldsymbol{U}(r) - \boldsymbol{U}_{\mathrm{YGB}}]P(\boldsymbol{r}|0) - [\lambda_1 \boldsymbol{u} + \lambda_2(\nabla T - \bar{\boldsymbol{H}})]P(\boldsymbol{r}))\,\mathrm{d}\boldsymbol{r}$$

will be convergent for any value of λ_1, provided $\lambda_1 = \lambda_2$, since both terms in brackets will then be zero for $r > 2$. The expression evaluates to $-\frac{3}{2}\lambda_1 c\bar{\boldsymbol{H}}$ and therefore the mean velocity of the particles in the suspension is

$$(1 - \tfrac{3}{2}\lambda_1 c)\,\boldsymbol{U}_{\mathrm{YGB}}$$

if the particles are non-conducting. Anderson's result is obtained by setting $\lambda_1 = 1$. In fact, even when the particles are conducting or have different sizes, there still exists an indeterminacy, because λ_1 and λ_2 must satisfy only one equation, namely that the non-convergent terms in the two sets of brackets cancel. Analogous considerations hold for particles undergoing electrophoresis (Anderson 1986).

Chen & Acrivos (1978) discovered a similar indeterminate situation, by finding several possible convergent two-body integrals. As here, the integral could apparently be put in a convergent form without renormalization and two renormalized integrals were found. Since these authors were able to resolve the indeterminacy by considering three-body interactions, where only one choice gave a convergent integral, we now extend the group expansion approach of Jeffrey (1974) to include the extra field present, in order to investigate the properties of the expansion and resolve the indeterminacy.

4. Formal series for three-body interactions

In order to write down the integral for three-body interactions, we must add to the notation in Jeffrey (1974) the fact that the velocity of a bubble in the laboratory frame now depends upon two applied fields, viz. the ambient temperature gradient and the ambient velocity. We begin by considering a test bubble at the origin surrounded by n others, the whole cloud being immersed in a temperature gradient $\bar{\boldsymbol{H}}$ and an ambient velocity $\bar{\boldsymbol{u}}$. At the end of the calculation, we shall set $\bar{\boldsymbol{u}}$ to zero, but we have seen in the method-of-reflections solution above that we must consider changes in the ambient flow. We shall write $\boldsymbol{U}(\mathscr{C}_n; \bar{\boldsymbol{H}}; \bar{\boldsymbol{u}})$ as the general notation for the velocity of the test bubble, $\mathscr{C}_n$ being the set of position vectors $\boldsymbol{r}_p$ of the other bubbles. We define incremental velocities in the manner of Jeffrey (1974). Thus $\boldsymbol{U}_0(;\bar{\boldsymbol{H}};\bar{\boldsymbol{u}})$ is the velocity of a single sphere in an ambient temperature gradient $\bar{\boldsymbol{H}}$ and a velocity field $\bar{\boldsymbol{u}}$. With suitable non-dimensionalization we know

$$\boldsymbol{U}_0(;\bar{\boldsymbol{H}};\bar{\boldsymbol{u}}) = \bar{\boldsymbol{H}} + \bar{\boldsymbol{u}}.$$

We next consider the test bubble at the origin with a second bubble (a first neighbour) at $\boldsymbol{r}_1$. The velocity of the test bubble is now $\boldsymbol{U}(\boldsymbol{r}_1;\bar{\boldsymbol{H}};\bar{\boldsymbol{u}})$. From this we define the increment $\boldsymbol{U}_1$ due to the second sphere as

$$\boldsymbol{U}_1(\boldsymbol{r}_1;\bar{\boldsymbol{H}};\bar{\boldsymbol{u}}) = \boldsymbol{U}(\boldsymbol{r}_1;\bar{\boldsymbol{H}};\bar{\boldsymbol{u}}) - \boldsymbol{U}_0(;\bar{\boldsymbol{H}};\bar{\boldsymbol{u}}).$$

Now since two bubbles respond to an ambient velocity $\bar{\boldsymbol{u}}$ by each increasing its velocity by the same speed $\bar{\boldsymbol{u}}$, it follows that U_1 is independent of $\bar{\boldsymbol{u}}$. Therefore

$$U_1(\boldsymbol{r}_1;\bar{\boldsymbol{H}};\bar{\boldsymbol{u}}) = U_1(\boldsymbol{r}_1;\bar{\boldsymbol{H}};0) = U(\boldsymbol{r}_1;\bar{\boldsymbol{H}};0)-U_0(;\bar{\boldsymbol{H}};0).$$

In addition we have seen that two bubbles move at the same speed as one, so in this problem $U_1 = 0$, but in general this would not be so.

The continuation to a third bubble (neighbours at $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$) uses the obvious notation

$$U_2(\boldsymbol{r}_1\boldsymbol{r}_2;\bar{\boldsymbol{H}};\bar{\boldsymbol{u}}) = U(\boldsymbol{r}_1\boldsymbol{r}_2;\bar{\boldsymbol{H}};\bar{\boldsymbol{u}})-U_1(\boldsymbol{r}_1;\bar{\boldsymbol{H}};\bar{\boldsymbol{u}})-U_1(\boldsymbol{r}_2;\bar{\boldsymbol{H}};\bar{\boldsymbol{u}})-U_0(;\bar{\boldsymbol{H}};\bar{\boldsymbol{u}}).$$

Again we see that U_2 is independent of $\bar{\boldsymbol{u}}$ and, for our bubble problem, is actually identically zero.

The first group expansion is the generalization of the non-renormalized integral. It consists simply of averaging the velocity increments just defined:

$$\bar{U} = U_0+\int U_1(\boldsymbol{r}_1;\bar{\boldsymbol{H}};\bar{\boldsymbol{u}})\,P(\boldsymbol{r}_1\,|\,0)\,\mathrm{d}\boldsymbol{r}_1+\iint U_2 P(\boldsymbol{r}_1\boldsymbol{r}_2\,|\,0)\,\mathrm{d}\boldsymbol{r}_1\,\mathrm{d}\boldsymbol{r}_2+\dots.$$

Since $U_1 = U_2 = 0$, etc. we again arrive at the unphysical result $\bar{U} = U_0 = U_{\mathrm{YGB}}$. This is different from the previously known case of Chen & Acrivos (1978) in which the expansion broke down visibly at the three-body term by giving a non-convergent integral.

The second group expansion corresponds to generalizing the renormalized integral. To introduce the notation required to write this down, we shall ignore for the moment the fact that $U_1 = U_2 = 0$. It is not true in the more general case of drops with non-zero conductivity, and we need to write down the general asymptotic relations which hold when the spheres are far apart in order to obtain the second expansion. The latter is obtained by rewriting the method-of-reflections results above in a general notation. To do this we need a notation for fields near the origin produced by distant spheres. Consider first a sphere by itself at $\boldsymbol{r}_1$. The temperature gradient at the origin is $\boldsymbol{H}(\boldsymbol{r}_1;\bar{\boldsymbol{H}})$, meaning the field produced by a sphere at $\boldsymbol{r}_1$ immersed in an ambient gradient $\bar{\boldsymbol{H}}$. When there are no spheres present, the field at the origin is just the applied field $\bar{\boldsymbol{H}}$, so we can define an increment in $\boldsymbol{H}$ to be $\boldsymbol{H}_1(\boldsymbol{r}_1;\bar{\boldsymbol{H}}) = \boldsymbol{H}(\boldsymbol{r}_1;\bar{\boldsymbol{H}})-\bar{\boldsymbol{H}}$. This is the field $\frac{1}{2}\nabla(1/|\boldsymbol{x}|)$ given in (2.9). The velocity field at the origin is $\boldsymbol{u}(\boldsymbol{r}_1;\bar{\boldsymbol{H}};\bar{\boldsymbol{u}})$, meaning a sphere at $\boldsymbol{r}_1$ moving because of the field $\bar{\boldsymbol{H}}$ and ambient flow $\bar{\boldsymbol{u}}$. Again there will be a velocity increment:

$$\boldsymbol{u}_1(\boldsymbol{r}_1;\bar{\boldsymbol{H}};\bar{\boldsymbol{u}}) = \boldsymbol{u}(\boldsymbol{r}_1;\bar{\boldsymbol{H}};\bar{\boldsymbol{u}})-\bar{\boldsymbol{u}}.$$

This will be independent of $\bar{\boldsymbol{u}}$, so

$$\boldsymbol{u}_1(\boldsymbol{r}_1;\bar{\boldsymbol{H}};\bar{\boldsymbol{u}}) = \boldsymbol{u}_1(\boldsymbol{r}_1;\bar{\boldsymbol{H}};0).$$

The two-body integral of the second group expansion is now the obvious generalization of Jeffrey (1974):

$$\int\{U_1(\boldsymbol{r}_1;\bar{\boldsymbol{H}};\bar{\boldsymbol{u}})\,P(\boldsymbol{r}_1\,|\,0)-U_0(;\boldsymbol{H}_1(\boldsymbol{r}_1;\bar{\boldsymbol{H}});\boldsymbol{u}_1(\boldsymbol{r}_1;\bar{\boldsymbol{H}};0))\,P(\boldsymbol{r}_1)\}\,\mathrm{d}\boldsymbol{r}_1.$$

This is the integral evaluated by Anderson. Since U_1 is zero, it reduces to a one-particle integral and gives the result

$$\bar{U} = (1-\tfrac{3}{2}c)\,U_{\mathrm{YGB}}.$$

We now need to consider two spheres far from the test sphere. We can extend our notation in the obvious way. $\boldsymbol{H}_2(\boldsymbol{r}_1\boldsymbol{r}_2;\bar{\boldsymbol{H}})$ is the increment at the origin due to spheres at $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$, while $\boldsymbol{u}_2(\boldsymbol{r}_1\boldsymbol{r}_2;\bar{\boldsymbol{H}};\bar{\boldsymbol{u}})$ is the increment in the fluid velocity at the origin.

We shall not repeat the elaborate asymptotic arguments needed to establish the three-body term in the second (renormalized) expansion, but write it down as the obvious extension of Jeffrey (1974). It is

$$\int \{ \boldsymbol{U}_2(\boldsymbol{r}_1 \boldsymbol{r}_2; \bar{\boldsymbol{H}}; \bar{\boldsymbol{u}}) P(\boldsymbol{r}_1 \boldsymbol{r}_2 \,|\, 0) - \boldsymbol{U}_1(\boldsymbol{r}_1; \boldsymbol{H}_1(\boldsymbol{r}_2; \bar{\boldsymbol{H}}); \boldsymbol{u}_1(\boldsymbol{r}_2; \bar{\boldsymbol{H}}; 0)) P(\boldsymbol{r}_1 \,|\, 0) P(\boldsymbol{r}_2)$$
$$- \boldsymbol{U}_0(\,; \boldsymbol{H}_2(\boldsymbol{r}_1 \boldsymbol{r}_2; \bar{\boldsymbol{H}}); \boldsymbol{u}_2(\boldsymbol{r}_1 \boldsymbol{r}_2; \bar{\boldsymbol{H}}; 0)) P(\boldsymbol{r}_1 \boldsymbol{r}_2)$$
$$+ \boldsymbol{U}_0(\,; \boldsymbol{H}_1(\boldsymbol{r}_1; \boldsymbol{H}_1(\boldsymbol{r}_2; \bar{\boldsymbol{H}})); \boldsymbol{u}_1(\boldsymbol{r}_1; \boldsymbol{H}_1(\boldsymbol{r}_2; \bar{\boldsymbol{H}}); 0)) P(\boldsymbol{r}_1) P(\boldsymbol{r}_2) \} \, \mathrm{d}\boldsymbol{r}_1 \, \mathrm{d}\boldsymbol{r}_2.$$

We can now integrate over $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ and obtain the $O(c^2)$ term. First we simplify. We know that $\boldsymbol{U}_2 = \boldsymbol{U}_1 = 0$. So we need consider only the last two terms.

Since $\boldsymbol{u} = -\nabla\phi$ outside the particles, the third term $\boldsymbol{U}_0(\,; \boldsymbol{H}_2; \boldsymbol{u}_2)$ will be zero unless one of the particles overlaps the origin, and in that case $\boldsymbol{u}_2 = 0$ because the velocity of two bubbles equals the velocity of one particle. Therefore the third term is non-zero only if $|\boldsymbol{r}_1| \leqslant 1$, when we have

$$-\boldsymbol{U}_0(\,; \boldsymbol{H}_2; \boldsymbol{u}_2) P(\boldsymbol{r}_1 \boldsymbol{r}_2) = -\boldsymbol{H}_2(\boldsymbol{r}_1 \boldsymbol{r}_2; \bar{\boldsymbol{H}}) P(\boldsymbol{r}_2 \,|\, \boldsymbol{r}_1) P(\boldsymbol{r}_1).$$

Now we perform the integration by fixing $\boldsymbol{r}_2 - \boldsymbol{r}_1 = \boldsymbol{s}$ and integrating first over $\boldsymbol{r}_1$ followed by integration over $\boldsymbol{s}$. The integral over $\boldsymbol{r}_1$ is just the volume integral of $\boldsymbol{H}_2$ over the spherical bubble, which equals the thermal dipole strength of the bubble $\boldsymbol{S}_1$. The integral becomes

$$\iint \boldsymbol{H}_2(\boldsymbol{r}_1 \boldsymbol{r}_2; \bar{\boldsymbol{H}}) P(\boldsymbol{r}_1 \boldsymbol{r}_2) \, \mathrm{d}\boldsymbol{r}_1 \, \mathrm{d}\boldsymbol{r}_2 = \int \boldsymbol{S}_1(\boldsymbol{r}_2; \bar{\boldsymbol{H}}) P(\boldsymbol{r}_2 \,|\, \boldsymbol{r}_1) \, \mathrm{d}\boldsymbol{r}_2.$$

Finally the last term in the three-body integral can be treated the same way to become

$$\int \boldsymbol{S}_0(\,; \boldsymbol{H}_1(\boldsymbol{r}_2; \bar{\boldsymbol{H}})) P(\boldsymbol{r}_2) \, \mathrm{d}\boldsymbol{r}_2.$$

Hence the three-body velocity problem reduces to the two-body heat conduction problem. In §6, we shall show that this is part of a more general result.

5. The electrophoresis problem

To show that much of the analysis and all of the conclusions derived thus far for thermocapillarity apply equally well to charged spheres moving through an electrolyte in an electric field we first recall that a single, non-conducting sphere moves in a uniform electric field $\boldsymbol{E}$ at the Smoluchowski velocity

$$\boldsymbol{U}_{\mathrm{s}} = \frac{\epsilon\epsilon_0 \zeta}{\mu} \boldsymbol{E} \tag{5.1}$$

as long as the double layer is thin (cf. Hunter 1981). Here ϵ is the dielectric constant of the suspending fluid, ϵ_0 is the permittivity of free space, ζ is the electrostatic potential at the surface of the particle (the zeta potential), and μ is as before the viscosity of the suspending electrolyte. Equation (5.1) applies when the particle motion is slow and the diffuse charge thickness (the Debye length κ^{-1}) is small compared with the particle radius a. Viewed on the lengthscale of the particle, fluid appears to slip past the surface at a speed known as the electro-osmotic slip velocity. However, when the details within the thin region adjacent to the surface are resolved by, for example, singular perturbation methods, the no-slip condition holds and the velocity in the diffuse region joins smoothly to that outside. Inside the diffuse layer the Stokes equations must be modified by adding a term to account for the electrostatic body force on the fluid due to the action of the field on the space charge.

For thin double layers and non-conducting particles, however, we can avoid analysing events within the diffuse layer in a consistent fashion by replacing the no-slip condition by

$$U = u - \frac{\epsilon\epsilon_0 \zeta}{\mu} \nabla\psi \tag{5.2}$$

and using the Stokes equations without the extra body force. Here U denotes the particle velocity, u is the fluid velocity, and $-\nabla\psi$ is the local value of the electric field (Anderson 1985*b*; Russel, Saville & Schowalter 1989).

The electric field is governed by solutions of Laplace's equation with the normal gradient equal to zero at a particle surface (non-conducting particles). Inside each particle, Laplace's equation applies and the two fields are continuous at the interface. The potential gradient is constant, i.e. $-\nabla\psi \rightarrow Eh$, far from the particle, while the velocity and pressure fields follow from solutions of Stokes equations with the velocity vanishing far from the particle. The boundary condition at the particle surface, (5.2), shows that the normal velocity of fluid and particle match at the surface.

Now, the electrophoresis problem can be restated in a form analogous to that used in §2 for thermocapillary motion. First, scale the potential on $(-aE)$ and recover (2.1)–(2.3) to describe the dimensionless potential outside the sphere. Next scale the velocity on the Smoluchowski velocity, $\epsilon\epsilon_0 \zeta E/\mu$, to obtain (2.4) and (2.5). The boundary condition (2.6) still holds but in place of (2.7) and (2.8) we use the dimensionless form of (5.2), namely

$$U = u + \nabla T. \tag{5.3}$$

It follows immediately that the dimensionless potential and velocity are given by (2.9) and (2.10).

With these results for a single sphere in hand we can investigate the electrophoresis of two identical spheres. Here, as long as the separation exceeds the Debye thickness, the spheres move at the Smoluchowski velocity irrespective of their separation and orientation (Reed & Morrison 1976). This result also holds for n identical spheres (Zukoski 1984), as can be seen using the arguments given at the end of §2 if (2.8) is replaced by

$$U_p h = u + \nabla T \quad \text{on} \quad |x_p| = 1. \tag{5.4}$$

It follows that $U_p = 1$ and the expansion for ϕ in the harmonic series noted earlier holds. Accordingly, we have the somewhat surprising result that each particle in a cloud of spheres undergoing electrophoresis moves at the same velocity.

6. Equivalence of the migration velocity and the effective conductivity

It was shown in §4 that the integral giving the three-body correction to the thermocapillary or the electrophoretic migration velocity can be reduced to the integral giving the two-body correction to the effective conductivity of the suspension. Here we shall derive a remarkable result that the migration velocity can be obtained simply from the effective thermal conductivity of the suspension of non-conducting particles for all particle concentrations. Specifically, taking the gradient of (2.14), we observe that

$$\nabla T = h + \nabla\phi, \tag{6.1}$$

and averaging this over the volume of the suspension V, we obtain

$$\frac{1}{V}\int_V \nabla T \, \mathrm{d}V = h. \tag{6.2}$$

Splitting the domain of integration into V_f, the part of V occupied by fluid, and V_p, the part occupied by particles, we arrive at

$$\boldsymbol{h} = (1-c)\,\boldsymbol{h} + \frac{1}{V}\int_{V_f} \nabla\phi \, \mathrm{d}V + \frac{1}{V}\int_{V_p} \nabla T \, \mathrm{d}V. \tag{6.3}$$

In the notation of Jeffrey (1973), the last integral is simply equal to $-c\bar{\boldsymbol{S}}$, the average thermal dipole strength of the particles.

Before we can average (2.15) we must remember that this is for particles in an infinite fluid, whereas in a container a backflow $\boldsymbol{U}_B$ will exist which must be included in the equation. Thus (2.15) is replaced by

$$\boldsymbol{u}(\boldsymbol{x}) = -\nabla\phi + \boldsymbol{U}_B, \quad \text{when } \boldsymbol{x} \text{ is outside a particle,} \tag{6.4a}$$

$$\boldsymbol{u}(\boldsymbol{x}) = \bar{\boldsymbol{U}} = \boldsymbol{h} + \boldsymbol{U}_B, \quad \text{when } \boldsymbol{x} \text{ is inside a particle.} \tag{6.4b}$$

Averaging this equation, we obtain

$$\bar{\boldsymbol{u}} = 0 = -\frac{1}{V}\int_{V_f} \nabla\phi \, \mathrm{d}V + (1-c)\,\boldsymbol{U}_B + c\bar{\boldsymbol{U}}. \tag{6.5}$$

Using (6.3) to eliminate the unknown integral from (6.5) and then using (6.4b) to eliminate $\boldsymbol{U}_B$ from (6.5), we obtain

$$\bar{\boldsymbol{U}} = \boldsymbol{h} + c\bar{\boldsymbol{S}} = \boldsymbol{K}^* \cdot \boldsymbol{h},$$

where $\boldsymbol{K}^*$ is the effective conductivity of the medium. It should be noted that this result holds for any particle concentration, and allows us to use not only the existing direct calculations of $\boldsymbol{K}^*$ but also bounds on the effective conductivity, such as the Hashin–Shtrikman bounds (Hashin & Shtrikman 1962) or more recently developed expressions (Torquato 1987). For example, using the results for an isotropic well-mixed suspension given in Jeffrey (1973), we obtain

$$\bar{\boldsymbol{U}} = (1 - \tfrac{3}{2}c + 0.59c^2 + \ldots)\,\boldsymbol{h}$$

for the same suspension.

7. Discussion

The problems of electrophoresis and thermocapillarity provide an interesting challenge to the established methods for calculating the average properties of suspensions. Although it is possible to take refuge in the more general cases of conducting particles or particles of different sizes to distinguish between the alternatives here (in conjunction with the three-body problem), this is an unsatisfying solution from a general point of view since there is no guarantee that such generalizations will always be possible. Moreover, special cases are usually chosen for study because they are simpler than the general problem, so it is disappointing to have to return to a general situation in order to address the special case. One argument used successfully in the past to choose between alternative schemes consisted of appealing to higher approximations. Thus, conflicting convergent integral expressions for the two-body interaction were resolved by extending the analysis to three-body schemes. It seemed from the case of Chen & Acrivos (1978) that the second group expansion of Jeffrey (1974) would always be able to distinguish between different possible treatments of the two-body problem by jumping to the three-body problem (another example of generalizing the problem). The particle problems studied here, however, show that this is not so, because the entire series for the first and second group expansions can be searched without finding an integral that converges in one case but not the other. Thus if we do not wish to leave the confines of the non-conducting particle problem, there is only the argument based on conservation of mass to choose between the mathematically possible alternatives.

Experimental tests of the theory for the thermocapillary or electrophoretic velocity of particles in a suspension are extremely difficult. To begin with, problems arise because of buoyancy and polydispersity. In addition most systems become opaque well before the particle number density is large enough to influence the average translational velocity and this makes it hard to measure the speed of individual particles. Nevertheless, Zukoski & Saville (1987, 1989) were able to prepare neutrally buoyant, transparent suspensions by removing the hemoglobin from red blood cells. A variety of particle shapes could be formed. Then tracer particles with the same electrokinetic properties as the red-blood-cell ghosts could be tracked microscopically over a wide range of particle concentrations. Zukoski & Saville measured the electrophoretic mobility of individual particles and the effective conductivity of the suspension over volume fractions ranging between 0 and 0.8. The effective conductivity was found to follow the Maxwell relation for slightly conducting particles while the mobility varied as $(1-c)$ up to the highest volume fractions. The reasons for the difference between their results and the theory developed here are unclear. It may be due to the slight conductivity of the particles, but further work is obviously necessary.

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Postscript

The references in the text acknowledge formally the influence Professor Batchelor had on this work, but, less formally, the interplay between physical and mathematical arguments discussed in this paper brings to the mind of one of us (D.J.J.) an exchange that took place during a seminar at Cambridge in the mid 1970s.

SPEAKER (justifying elaborate mathematical argument): The trouble with a physical argument is that you may not get all the terms.

GKB: No, that is the trouble with a *bad* physical argument.

SEVERAL VOICES: How do you tell a good physical argument from a bad one?

GBK: That's easy: you *think*.

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