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Hydrodynamics of electrophoretic motion in an alternating electric field

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Electrophoresis in an alternating electric field is the basis for electroacoustical measurements. These measurements provide new means of investigating the electrokinetic properties of colloidal systems. In order to relate electroacoustical signals to the charge and the size of colloidal particles, an expression is required for the dynamic electrophoretic mobility of colloidal particles in a continuous fluid. In this paper, an exact analytical solution to the problem is given for an arbitrary ratio between the particle radius and the electric double-layer thickness, in the case where the electrokinetic potential of the uniformly charged particle is small and unaffected by the alternating field.

1. Introduction

Electrophoretic measurements are an important tool for determining the electrokinetic ζ-potential of colloidal particles. The ζ-potential, in turn, is one of the parameters determining colloidal stability. Traditionally, electrokinetic potentials are determined by measuring the particle's velocity in a direct electric field applied to the colloidal system, where the continuous phase is usually an electrolyte solution.

The particle velocity $\boldsymbol{u}$ and the electric field $\boldsymbol{E}$ are proportional to each other: that is,

$$\boldsymbol{u} = \mu_E \boldsymbol{E}. \tag{1.1}$$

The constant of proportionality μ_E is called the electrophoretic mobility; it can be expressed as (Overbeek 1952)

$$\mu_E = \frac{2\epsilon\zeta}{3\mu} f(\kappa a, \zeta), \tag{1.2}$$

where ϵ and μ are the dielectric permittivity and the viscosity of the liquid phase respectively, a is the particle radius and $1/\kappa$ is the double-layer thickness, which depends on the chemistry of the liquid phase.

In 1903 Smoluchowski showed that $f(\kappa a, \zeta) \to \frac{3}{2}$ when the electrical double layer is thin compared with the size of the particle, the case where $\kappa a \gg 1$ (see Overbeek 1952). As was demonstrated by Henry (1931), Smoluchowski's solution is independent of the shape of the particle. Hückel's solution, which is valid for spherical particles possessing double layers that are thick compared with the size of the particle, corresponds to $f \to 1$ when $\kappa a \ll 1$. Thus changes in $f(\kappa a, \zeta)$ are $O(1)$, and cannot be neglected when interpreting experimental results (Overbeek 1952).

For large ζ-potentials, the function $f(\kappa a, \zeta)$ should include the effects of double-layer polarization. In order to obtain an analytical solution for the electrophoretic

mobility in this case, the Navier–Stokes equations must be coupled with the Nernst-Planck equations for the convective ionic fluxes (Dukhin & Shilov 1974). This poses a complicated mathematical problem.

The general case has not been solved analytically. Within the framework of the Debye–Hückel theory for electrolytes, the problem has been treated numerically by Wiersema, Loeb & Overbeek (1966) and later by O'Brien & White (1978). However, there are limitations to the validity of the results obtained from the numerical solutions. The accuracy of the solutions is doubtful when the surface potential of the colloidal particles becomes sufficiently high. This difficulty is not related to the numerical procedures that were employed in solving the problem. Rather, it appears as a result of the fundamental assumptions underlying the Debye–Hückel theory and the Poisson–Boltzmann equation that forms part of this theory. The use of the Poisson–Boltzmann equation in electrokinetic transport models is based on an ideal bulk-solution behaviour of the solute and solvent (Gur, Ravina & Babchin 1978; Guzmán-Garcia *et al.* 1990). The equation fails to take into account finite ion size, dependence of the dielectric constant for the continuous phase on the electric field, and ion hydration forces; at high surface potentials these effects may have an important influence on the polarization of the double layer.

Recently, electrokinetic models have been proposed to include some of these features of the problem (Guzmán-Garcia *et al.* 1990). For example, Gur *et al.* (1978) took into account hydration forces acting on individual ions within the double layer. In this case the mathematical description of the polarization effects becomes highly nonlinear. This introduces a significant degree of difficulty, and one that remains to be overcome, to the problem of developing a self-consistent analytical theory for double-layer polarization at arbitrary surface potential.

The standard method for avoiding polarization effects is to consider the case of small potentials, $\zeta \leqslant 25$ mV. It has been demonstrated by Overbeek (1952) that in the case of small and constant surface potential the function $f(\kappa a, \zeta)$ reduces to the function $f(\kappa a)$ obtained by Henry (1931). The Henry function provides a smooth transition from the Hückel to the Smoluchowski solutions. It ranges from $f(\kappa a) = 1$ when $\kappa a \ll 1$ to $f(\kappa a) = \frac{3}{2}$ when $\kappa a \gg 1$. In calculating the function $f(\kappa a)$ for small ζ-potentials, Henry (1931) provided the exact analytical solution describing the electrophoretic motion of a spherical particle in a direct electric field for arbitrary κa.

The problem we pose in this paper is the dynamic version of Henry's problem. We want to find, for arbitrary κa, an exact analytical formula for the electrophoretic mobility of a spherical particle in an alternating electric field. In order to avoid complications, intrinsic to the double-layer polarization, we retain the assumption that the ζ-potential is small, and therefore that the double layer is radially symmetric about the particle.

The formula for the high-frequency electrophoretic mobility $\mu_E(\omega)$ that we derive here will serve as a theoretical basis for electrokinetic measurements by electroacoustical methods (see O'Brien 1988; Babchin, Chow & Sawatzky 1989). Electroacoustical instruments for the analysis of colloid systems have only recently become commercially available (Matec Applied Sciences). Measurements can be made in two modes. When sound waves are applied to a colloid, the oscillatory motion of the charged colloidal particles generates an ultrasound vibrational potential (UVP), as predicted by Debye (1933). The reciprocal mode is based on measurements of the acoustical pressure when sound waves are generated by the oscillatory motion of the particles; in this mode, the particle motion is caused by the application of a high-frequency electric field to the colloid. The latter mode of

measurement was invented by Oja, Peterson & Cannon (1985). Following the name given by its inventors, this mode of measurement is called ESA (electrokinetic sonic amplitude).

As demonstrated by O'Brien (1988), electroacoustical signals for monodispersed colloids measured in either mode are proportional to the high-frequency electrophoretic mobility of the colloidal particles. The dependence of the mobility on inertia is the principal distinction between high-frequency and static electrophoresis. This dependence provides new opportunities for applications of electrophoresis, inasmuch as coagulation/coalescence phenomena can be directly monitored, even in non-polar and non-transparent media (Babchin *et al.* 1989; Isaacs *et al.* 1990). The applicability of electroacoustical measurements to a broad range of colloidal systems, in which the liquid continuous phase can vary from a strong electrolyte to a crude oil, makes it important for practical as well as theoretical reasons to develop a rigorous derivation of $\mu_E(\omega)$ for arbitrary κa.

The aim of this paper is to present an expression for high-frequency mobility that is valid for arbitrary κa. The formula developed here will be compared with the results on high-frequency mobility that have appeared previously in the literature, and used to unify these results.

2. Electric field and hydrodynamic equations

We formulate the problem as follows. Consider an isolated, rigid, insulating spherical particle of radius a, with a surface potential ζ, immersed in a fluid of viscosity μ and permittivity e. Suppose that an external electric field is present in the fluid, alternating at fixed frequency. Far from the particle, the field is uniform. The charged particle oscillates in the fluid at the frequency of the external field, along a straight line that is parallel to the direction of the field far from the particle. The calculation of the electrophoretic mobility of the moving charged particle requires the solution of equations that describe the distribution of electric potential, as well as the velocity and pressure in the surrounding fluid.

We take the particle as our frame of reference, and use spherical polar coordinates r, θ, ϕ whose origin is at the centre of the particle. The line of oscillation is the polar axis $\theta = 0$; it coincides with the positive x-axis in Cartesian coordinates. The particle velocity $\boldsymbol{u}$ and the external electric field $\boldsymbol{E}$ are proportional to $\mathrm{e}^{-\mathrm{i}\omega t}$, where $\omega/2\pi$ is the frequency of oscillation.

In the fluid surrounding the sphere, the electric potential ψ satisfies Poisson's equation

$$\epsilon \nabla^2 \psi = -\rho_E, \tag{2.1}$$

where ρ_E is the volume density of charge in the electrical double layer around the particle. It is assumed that the external electric field can be simply superimposed on the electric field arising from the double layer. The distortion of the double layer induced by the motion of the particle is not taken into account. This is a reasonable assumption when, in the absence of the external electric field, the potential ζ at the particle surface is sufficiently small (Overbeek 1952; Hunter 1981; O'Brien 1988). When the charge on the particle is small, changes in charge density due to the external field do not significantly affect the field around the particle. Therefore, we take for ρ_E the distribution of charge density that exists when there is no external electric field and we decompose the electric potential ψ into the sum of two potentials (Henry 1931),

$$\psi = \psi_E + \psi_F;$$

ψ_E is the potential produced by the double layer in the absence of the external field while ψ_F is the potential produced by the external field in the absence of the double layer.

The potential ψ_E satisfies Poisson's equation

$$\epsilon \nabla^2 \psi_E = -\rho_E. \tag{2.2}$$

When ψ_E is small everywhere in the double layer, it can be shown that (Hunter 1981)

$$\rho_E = -\epsilon \kappa^2 \psi_E, \tag{2.3}$$

where

$$\kappa^2 = \frac{1}{\epsilon k_B T} \sum_{i=1}^{N} n_i^0 e^2 z_i^2; \tag{2.4}$$

in (2.4) n_i^0 is the number density and ez_i the charge for the ith species of ion in the bulk of the fluid beyond the double layer, N is the number of ionic species in the fluid, k_B is the Boltzmann constant and T is the absolute temperature. The result (2.3) is known as the Debye–Hückel approximation and κ is referred to as the Debye–Hückel parameter.

The substitution of (2.3) into (2.2) yields the following equation for ψ_E:

$$\nabla^2 \psi_E = \kappa^2 \psi_E. \tag{2.5}$$

It is evident from this equation that the potential ψ_E and the charge density ρ_E decay exponentially with distance from the isolated charged particle. The decay length $1/\kappa$ is the double-layer thickness referred to in §1. Beyond the double layer the potential ψ_E is zero.

The boundary conditions associated with (2.5) are

$$\psi_E = \zeta \quad \text{at} \quad r = a \tag{2.6}$$

and

$$\psi_E \to 0 \quad \text{as} \quad r \to \infty. \tag{2.7}$$

Equations (2.5)–(2.7) completely determine ψ_E.

As ψ_F is the potential produced by the external electric field in the absence of the double layer, this potential satisfies Laplace's equation

$$\nabla^2 \psi_F = 0 \tag{2.8}$$

in the fluid surrounding the sphere. Since we are treating the particle as an insulator the normal component of electric current at the particle surface is zero. In this case the boundary condition for ψ_F at the surface of the particle is

$$\frac{\partial \psi_F}{\partial r} = 0 \quad \text{at} \quad r = a. \tag{2.9}$$

Under most circumstances, the need to take particle conductivity into account is doubtful (Overbeek 1952), due to the electrochemical overpotential at the particle surface. Otherwise, the conductivity of the particle can be included in our results with minor modifications to the analysis (see Henry 1931). Far from the particle the external electric field is uniform, so the other boundary condition for ψ_F is

$$\frac{\partial \psi_F}{\partial x} \to -E \quad \text{as} \quad r \to \infty. \tag{2.10}$$

In the vicinity of the particle, the pressure p and the velocity v in the fluid will vary on a lengthscale that is of the order of the particle radius. This lengthscale is much

smaller than the wavelength of a sound wave in the fluid. For example, at a typical oscillation frequency of 1 MHz, the length of a sound wave in water is of the order of 1 mm. The typical particle radius is of the order of 1 μm. Therefore the fluid can be treated as incompressible. Then the equations of fluid motion have the form

$$\nabla \cdot \boldsymbol{v} = 0 \tag{2.11}$$

and

$$\rho\left(\frac{\partial \boldsymbol{v}}{\partial t}+\frac{\partial \boldsymbol{u}}{\partial t}\right) = -\nabla p+\mu\nabla^2\boldsymbol{v}-\rho_E\nabla(\psi_E+\psi_F), \tag{2.12}$$

where ρ is the fluid density. The term involving the particle velocity $\boldsymbol{u}$ arises from our choice of the sphere as the frame of reference for our coordinate system. The final term on the right-hand side of (2.12) represents the electrical body force per unit volume. The convective inertia term has been omitted from this equation under the following two assumptions: the amplitude of the oscillation of the particle is much smaller than the particle radius; and the Reynolds number based on the particle is small (O'Brien 1988).

At the particle surface, the velocity of the fluid must be the same as the velocity of the particle. Far from the particle the fluid is assumed to be at rest. In our coordinate system, these boundary conditions are represented as

$$\boldsymbol{v} = 0 \quad \text{at} \quad r = a \tag{2.13}$$

and

$$\boldsymbol{v} \to -\boldsymbol{u} \quad \text{as} \quad r \to \infty. \tag{2.14}$$

Equations (2.5)–(2.14) complete the mathematical specification of the problem. They describe the distribution of electric potential, and the pressure and velocity in a viscous fluid surrounding a moving charged particle.

3. Solution of the governing equations

The solutions for the potentials ψ_E and ψ_F can be given immediately, as they are well known. From (2.5)–(2.7) for ψ_E, it follows that

$$\psi_E = \zeta(a/r)\exp[-\kappa(r-a)]. \tag{3.1}$$

The solution to (2.8)–(2.10) for ψ_F is

$$\psi_F = -E(r+a^3/2r^2)\cos\theta. \tag{3.2}$$

The simplicity of these results demonstrates the convenience of being able to decompose the electric potential into the components ψ_E and ψ_F.

The solution for p and $\boldsymbol{v}$ to the fluid equations (2.11)–(2.12) and the boundary conditions (2.13)–(2.14) is well-known for the case in which there is no body force in the momentum equation (2.12). The procedure developed by Landau & Lifshitz (1959) to obtain the solution for that case can be applied equally well in the present case in which there is a body force resulting from the charge in the electrical double layer. The calculations are straightforward, but somewhat lengthy. Here, we present only the principal results.

The fluid velocity $\boldsymbol{v}$ is obtained by solving the vorticity equation, the curl of (2.12):

$$\rho\frac{\partial}{\partial t}[\nabla\times(\boldsymbol{v}+\boldsymbol{u})]-\mu\nabla^2(\nabla\times\boldsymbol{v}) = -\nabla\times(\rho_E\nabla\psi_F). \tag{3.3}$$

With the introduction of the following representation for $\boldsymbol{v}$ (Landau & Lifshitz 1959):

$$\boldsymbol{v}+\boldsymbol{u} = \boldsymbol{\nabla}\times(\boldsymbol{\nabla}f\times\boldsymbol{u}) = \boldsymbol{\nabla}\times\boldsymbol{\nabla}\times f\boldsymbol{u}, \tag{3.4}$$

where f is a scalar function of r, (3.3) can be reduced to

$$(\nabla^2+k^2)\nabla^2(\mathrm{d}f/\mathrm{d}r) = G_0(r), \tag{3.5}$$

where

$$k^2 = \mathrm{i}\omega\rho/\mu \tag{3.6}$$

and

$$G_0(r) = \frac{1}{\mu}\frac{E}{u}\left(1+\frac{a^3}{2r^3}\right)\frac{\mathrm{d}\rho_E}{\mathrm{d}r}. \tag{3.7}$$

Equation (3.5) differs from the corresponding equation for an uncharged oscillating sphere only in the appearance of the forcing term $G_0(r)$. From the solution of (3.5) for $\mathrm{d}f/\mathrm{d}r$, the radial, polar and azimuthal components of $\boldsymbol{v}$ can be calculated:

$$\left.\begin{aligned} v_r &= \frac{1}{r^3}\left[\frac{3a}{k^2}((1-\mathrm{i}kr)\,\mathrm{e}^{\mathrm{i}k(r-a)}-(1-\mathrm{i}ka))-(r^3-a^3)-2G(r)\right]u\cos\theta,\\ v_\theta &= \frac{1}{r^3}\left[\frac{3a}{2k^2}((1-\mathrm{i}kr)\,\mathrm{e}^{\mathrm{i}k(r-a)}-(1-\mathrm{i}ka))+(r^3+\tfrac{1}{2}a^3)\right.\\ &\qquad \left.-\tfrac{3}{2}ar^2\,\mathrm{e}^{\mathrm{i}k(r-a)}-\left(G(r)-r\frac{\mathrm{d}G(r)}{\mathrm{d}r}\right)\right]u\sin\theta,\\ v_\phi &= 0, \end{aligned}\right\} \tag{3.8}$$

where

$$k = (1+\mathrm{i})/\delta, \tag{3.9}$$

$$\delta = (2\mu/\rho\omega)^{\frac{1}{2}}, \tag{3.10}$$

and

$$G(r) = \int_a^r r_4\,\mathrm{e}^{\mathrm{i}k(r_4-a)}\,\mathrm{d}r_4\int_a^{r_4}\mathrm{e}^{-2\mathrm{i}k(r_3-a)}\,\mathrm{d}r_3\int_\infty^{r_3} r_2\,\mathrm{e}^{\mathrm{i}k(r_2-a)}\,\mathrm{d}r_2\int_\infty^{r_2} G_0(r_1)\,\mathrm{d}r_1. \tag{3.11}$$

The corresponding pressure distribution is obtained directly by integrating (2.12). The result is

$$\begin{aligned} p-p_0 = &-\int_\infty^r \rho_E\frac{\mathrm{d}\psi_E}{\mathrm{d}r_1}\mathrm{d}r_1+\frac{1}{r^2}\left[\tfrac{3}{2}a(1-\mathrm{i}kr)\,\mathrm{e}^{\mathrm{i}k(r-a)}+r^2\frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{1}{r^2}\frac{\mathrm{d}G(r)}{\mathrm{d}r}\right)\right]\mu u\cos\theta\\ &+\frac{1}{r^2}\left[\frac{3a}{2k^2}((1-\mathrm{i}kr)\,\mathrm{e}^{\mathrm{i}k(r-a)}-(1-\mathrm{i}ka))+\tfrac{1}{2}a^3-G(r)\right]\rho\frac{\mathrm{d}u}{\mathrm{d}t}\cos\theta-\tfrac{3}{2}Ea^3r\cos\theta\int_\infty^r\frac{\rho_E}{r_1^4}\mathrm{d}r_1, \end{aligned} \tag{3.12}$$

where p_0 is the pressure in the fluid far from the particle.

The terms in (3.8) and (3.12) that appear in addition to those from the corresponding solution for the case of an uncharged oscillating sphere reflect the influence of the electrical double layer on the motion of the fluid. Without the double layer, the velocity and pressure vary over a lengthscale defined by δ, the characteristic distance over which disturbances generated by the oscillating particle decay (Landau & Lifshitz 1959). In the presence of the double layer, variations in velocity and pressure occur over another lengthscale as well, the characteristic double-layer thickness $1/\kappa$. It is evident from (3.11) that the double layer induces variations in the fluid motion over both lengthscales, and that the effects of the two scales are coupled. The relative magnitude of the lengthscales depends primarily on

the extent of the double layer. For fluids whose viscosity and density are comparable with that of water, δ is of the order of 1 μm at a frequency of 1 MHz. When the particle radius is of the order of 1 μm, $1/\kappa$ is two or more orders of magnitude smaller than δ for thin double layers, of the same order of magnitude as δ for intermediate double layers, and one or more orders of magnitude greater than δ for thick double layers. Thick double layers generally occur in non-polar media, but they can appear in polar media as well. For example, a thick double layer is present around very fine particles (with a radius of less than 10^{-2} μm) in distilled water. Although electroacoustical methods have been applied more commonly in polar media, they also have been used successfully to study the electrokinetic properties of colloidal particles in non-polar media (Babchin *et al.* 1989; Isaacs *et al.* 1990).

In §5, the impact of the two lengthscales for fluid motion on the high-frequency electrophoretic mobility will be discussed.

4. Force exerted on the particle

From the solutions to the governing equations obtained in the previous section, the total force exerted on the charged spherical particle by the surrounding fluid can be calculated. As is the case for an uncharged particle, the force exerted on the charged particle is parallel to the particle velocity $\boldsymbol{u}$. Therefore the oscillating particle experiences a drag force but no lift.

The total drag force exerted on the particle is obtained from the formula

$$F_{\text{drag}} = \int_S [\sigma_{rr}\cos\theta - \sigma_{r\theta}\sin\theta]_{r=a}\,\mathrm{d}S, \tag{4.1}$$

where the integration is taken over the whole surface of the sphere. The stress components σ_{rr} and $\sigma_{r\theta}$ can be evaluated at the surface of the sphere from the solution for the fluid velocity and pressure given in (3.8) and (3.12). The result is

$$\left.\begin{aligned}\sigma_{rr} = -\Bigg[p_0 - \int_\infty^a \rho_E \frac{\mathrm{d}\psi_E}{\mathrm{d}r}\,\mathrm{d}r - \tfrac{3}{2}Ea^4\cos\theta\int_\infty^a \frac{\rho_E}{r^4}\,\mathrm{d}r \\ + \frac{\mu}{a}\left(\tfrac{3}{2}(1-\mathrm{i}ka) + \int_\infty^a G_1(r)\,\mathrm{d}r\right)u\cos\theta + \tfrac{1}{2}a\rho\frac{\mathrm{d}u}{\mathrm{d}t}\cos\theta\Bigg], \\ \sigma_{r\theta} = \frac{\mu}{a}\left[\tfrac{3}{2}(1-\mathrm{i}ka) + \int_\infty^a G_1(r)\,\mathrm{d}r\right]u\sin\theta \quad \text{at} \quad r=a,\end{aligned}\right\} \tag{4.2}$$

where

$$G_1(r) = r\,\mathrm{e}^{\mathrm{i}k(r-a)}\int_\infty^r G_0(r_1)\,\mathrm{d}r_1. \tag{4.3}$$

Hence the integral (4.1) becomes

$$F_{\text{drag}} = -\left[6\pi a\mu u(1-\mathrm{i}ka) + \tfrac{2}{3}\pi a^3\rho\frac{\mathrm{d}u}{\mathrm{d}t} + 4\pi a\mu u\int_\infty^a G_1(r)\,\mathrm{d}r - 2\pi a^6 E\int_\infty^a \frac{\rho_E}{r^4}\,\mathrm{d}r\right].$$

To the expression (4.4) must be added the force on the particle due to its fixed surface charge. This force is parallel to the particle velocity and its magnitude is qE. By Gauss' theorem,

$$qE = -4\pi\epsilon E a^2\left(\frac{\mathrm{d}\psi_E}{\mathrm{d}r}\right)_{r=a}.$$

Therefore the total force exerted on the spherical particle is

$$F_{\rm sp} = -\Big[6\pi a\mu u(1-{\rm i}ka)+\tfrac{2}{3}\pi a^3\rho\frac{{\rm d}u}{{\rm d}t}+4\pi a\mu u\int_\infty^a G_1(r)\,{\rm d}r$$
$$-2\pi a^6 E\int_\infty^a\frac{\rho_E}{r^4}{\rm d}r+4\pi a^2\epsilon E\left(\frac{{\rm d}\psi_E}{{\rm d}r}\right)_{r=a}\Big]. \quad (4.5)$$

The first two terms in (4.5) represent the drag exerted on the particle by the fluid in the absence of a double layer. These terms can be written as

$$F_{\rm fl} = -[6\pi a\mu(1+a/\delta)\,u+\tfrac{2}{3}\pi a^3\rho(1+9\delta/2a)\,({\rm d}u/{\rm d}t)]. \quad (4.6)$$

This is Stokes' formula for the drag on an uncharged oscillating sphere (Landau & Lifshitz 1959).

The remaining terms in (4.5) represent the contribution to the total force on the particle by the electrical charge on the particle surface and the corresponding charge in the surrounding double layer. With the use of (4.3), (3.7) and (2.2), and integrating by parts appropriately, these terms can be expressed as

$$F_{\rm el} = 4\pi aE\Big[\tfrac{1}{2}a^3\int_\infty^a\Big[\frac{3}{k^2r^4}((1-{\rm i}kr)\,{\rm e}^{{\rm i}k(r-a)}-(1-{\rm i}ka))-\frac{1}{r^2}{\rm e}^{{\rm i}k(r-a)}\Big]\rho_E\,{\rm d}r$$
$$+\tfrac{1}{2}a^5\int_\infty^a\frac{\rho_E}{r^4}{\rm d}r-\epsilon\Big(k^2\int_\infty^a r\,{\rm e}^{{\rm i}k(r-a)}\psi_E\,{\rm d}r-(1-{\rm i}ka)\,\zeta\Big)\Big]. \quad (4.7)$$

In the limit as $k\to 0$ (i.e. as $\omega\to 0$), we find that

$$F_{\rm el} = 4\pi aE\Big[\epsilon\zeta+\tfrac{1}{4}a^3\int_\infty^a\frac{(r^2-a^2)}{r^4}\rho_E\,{\rm d}r\Big]. \quad (4.8)$$

The formula (4.8) agrees with the formula obtained by Henry (1931) for the corresponding steady-state problem.

When the solution (3.1) for ψ_E is put into (4.7), the definite integrals in the formula for $F_{\rm el}$ can be represented by the exponential integrals E_n, defined in Abramowitz & Stegun (1972). The result is

$$F_{\rm el} = 4\pi a\epsilon\zeta f_1(\kappa a, a/\delta)\,E, \quad (4.9)$$

where

$$f_1(\kappa a, a/\delta) = 1-\frac{{\rm i}ka\kappa a}{\beta a}+\kappa^2a^2\,{\rm e}^{\kappa a}\Big[\tfrac{1}{2}(E_5(\kappa a)-{\rm e}^{-{\rm i}ka}E_3(\beta a))$$
$$+\frac{3}{2k^2a^2}({\rm e}^{-{\rm i}ka}(E_5(\beta a)-{\rm i}kaE_4(\beta a))-(1-{\rm i}ka)\,E_5(\kappa a))\Big] \quad (4.10)$$

and

$$\beta = \kappa-{\rm i}k = \kappa+(1-{\rm i})/\delta. \quad (4.11)$$

In the limit as $k\to 0$, the function f_1 reduces to

$$f_1(\kappa a, 0) = 1-\tfrac{1}{4}\kappa^2a^2\,{\rm e}^{\kappa a}(E_5(\kappa a)-E_3(\kappa a)). \quad (4.12)$$

The function $f_1(\kappa a, 0)$ is the well-known Henry function (Henry 1931) that we denoted by $f(\kappa a)$ in § 1. The formula for $f(\kappa a)$ given by Henry contains a small error that is corrected in Hunter (1981). The corrected formula and the one presented in (4.12) are identical, as can be demonstrated by an appropriate integration by parts.

5. Dynamic electrophoretic mobility

The dynamic electrophoretic mobility $\mu_E(\omega)$ is determined from the equation of motion for the charged particle:

$$\tfrac{4}{3}\pi a^3 \rho_0 \, \mathrm{d}u/\mathrm{d}t = F_{\mathrm{sp}} = (F_{\mathrm{fl}} + F_{\mathrm{el}}), \tag{5.1}$$

where ρ_0 is the particle density. With the use of (4.6) and (4.9), (5.1) becomes

$$\tfrac{4}{3}\pi a^3 \rho_{\mathrm{eff}} \, \mathrm{d}u/\mathrm{d}t = -6\pi a\mu(1 + a/\delta)\, u + 4\pi a\epsilon\zeta f_1(\kappa a, a/\delta)\, E, \tag{5.2}$$

where ρ_{eff}, the effective particle density for the oscillatory motion, is given by

$$\rho_{\mathrm{eff}} = \rho_0 + \tfrac{1}{2}\rho(1 + 9\delta/2a). \tag{5.3}$$

Since the particle oscillates at a fixed frequency, it follows from (5.2) that the ratio u/E is

$$\frac{u}{E} \equiv \mu_E(\omega) = \frac{2\epsilon\zeta f_1(\kappa a, a/\delta)}{3\mu[(1 + a/\delta) - \frac{4}{9}\mathrm{i}(a/\delta)^2 \rho_{\mathrm{eff}}/\rho]}. \tag{5.4}$$

It is evident from (5.4) that $\mu_E(\omega)$ is complex-valued. It can be expressed in terms of its modulus and argument as

$$\mu_E(\omega) = |\mu_E(\omega)|\, \mathrm{e}^{\mathrm{i}\alpha_\mu}, \tag{5.5}$$

where

$$|\mu_E(\omega)| = \frac{2\epsilon\zeta |f_1(\kappa a, a/\delta)|}{3\mu[(1 + a/\delta)^2 + (\frac{4}{9}(a/\delta)^2 \rho_{\mathrm{eff}}/\rho)^2]^{\frac{1}{2}}} \tag{5.6}$$

and

$$\alpha_\mu = \alpha_1 + \alpha_2, \tag{5.7}$$

with

$$\tan\alpha_1 = \frac{4(a/\delta)^2 \rho_{\mathrm{eff}}/\rho}{9(1 + a/\delta)}, \quad \tan\alpha_2 = \frac{\mathrm{Im}\,(f_1(\kappa a, a/\delta))}{\mathrm{Re}\,(f_1(\kappa a, a/\delta))}. \tag{5.8}$$

When $\alpha_\mu > 0$, u lags behind E; conversely, when $\alpha_\mu < 0$, E lags behind u. The function $f_1(\kappa a, a/\delta)$ in the numerator of (5.4) is the dynamic analogue of the Henry function $f(\kappa a)$. The remainder of (5.4) is the dynamic analogue of the Hückel formula for electrophoretic mobility; it appears as the result of the time-dependent Stokes drag on the particle.

In the limit as $\omega \to 0$, the function $f_1(\kappa a, a/\delta)$ reduces to the Henry function $f(\kappa a)$, and the denominator of (5.4) reduces to 3μ, so that we recover the steady-state result

$$\mu_E = (2\epsilon\zeta/3\mu) f(\kappa a). \tag{5.9}$$

Next, we compare our formula for the dynamic electrophoretic mobility with the formulae obtained by Babchin *et al.* (1989) and O'Brien (1988). In the notation we are using in this paper, these two formulae can be expressed as

$$\mu_E(\omega)_{\mathrm{BCS}} = \frac{2\epsilon\zeta f(\kappa a)}{3\mu[(1 + a/\delta) - \frac{4}{9}\mathrm{i}(a/\delta)^2 \rho_{\mathrm{eff}}/\rho]}, \tag{5.10}$$

and

$$\mu_E(\omega)_{\mathrm{OB}} = \frac{2\epsilon\zeta[\frac{3}{2}(1 + (1 - \mathrm{i}a/\delta)]}{3\mu[(1 + a/\delta) - \frac{4}{9}\mathrm{i}(a/\delta)^2 \rho_{\mathrm{eff}}/\rho]}, \tag{5.11}$$

respectively. The formula (5.11) is obtained by specializing the result given by O'Brien to the case where relaxation effects can be ignored, and is derived under the assumption of a thin double layer, where $\kappa a \gg 1$. It can be shown that

$$f_1(\kappa a, a/\delta) \to \tfrac{3}{2}(1 + (1 - \mathrm{i})\, a/\delta) \quad \text{as} \quad \kappa a \to \infty,$$

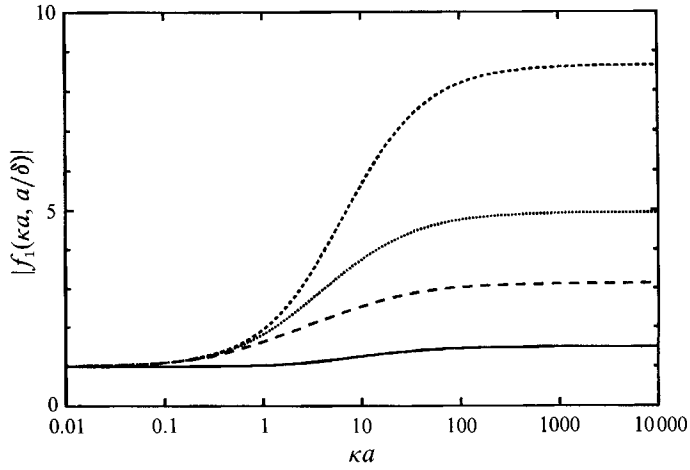

FIGURE 1. The magnitude of $f_1(\kappa a, a/\delta)$ versus κa for $a/\delta = 0$ (——), $\frac{1}{2}\pi^{\frac{1}{2}}$ (– –), $\pi^{\frac{1}{2}}$ (....), $2\pi^{\frac{1}{2}}$ (– –).

and hence our result (5.4) agrees with O'Brien's (5.11). However, the result (5.10) obtained by Babchin *et al.* (1989) does not agree with (5.11) when $\kappa a \gg 1$, and we conclude that it is not correct for double layers of arbitrary thickness. For thick double layers, it can be shown that

$$f_1(\kappa a, a/\delta) \to 1 \quad \text{as} \quad \kappa a \to 0;$$

in this case our result agrees with the one of Babchin *et al.*

For intermediate values of κa, the function $f_1(\kappa a, a/\delta)$ may be evaluated numerically. In figure 1 we have plotted the magnitude of f_1 versus κa for several values of a/δ. It is evident from this graph that the shape of $|f_1(\kappa a, a/\delta)|$ is very similar to that of $f(\kappa a)$. Thus, the function $f_1(\kappa a, a/\delta)$ plays the same role in the dynamic problem that the Henry function $f(\kappa a)$ plays in the static problem. It supplies a smooth transition from the result for thick double layers through double layers of intermediate thickness to the result for thin double layers.

An important feature of the graph in figure 1 is that it indicates clearly the range of κa for which $|f_1|$ is very nearly at its asymptotic limit for $\kappa a \to \infty$. Over this range of κa, the mobility formula given by O'Brien (1988) agrees with ours. It can be seen from figure 1 that as a/δ increases, greater values of κa are necessary before agreement occurs. This observation is consistent with one of the assumptions underlying O'Brien's theory for thin double layers; namely, that the condition $\kappa a \gg a/\delta$ must be satisfied (O'Brien 1988).

In experiments for obtaining electrophoretic measurements from electroacoustical instruments, the theoretical ratio of the dynamic and static mobilities can be a useful quantity. For example, this ratio has served as a basis for the calibration of dynamic electrokinetic measurements (James, Texter & Scales 1991). For the theory proposed in this paper, the ratio of the dynamic and static electrophoretic mobilities is, from (5.4) and (5.9),

$$\frac{\mu_E(\omega)}{\mu_E(0)} = \frac{f_1(\kappa a, a/\delta)/f(\kappa a)}{[(1+a/\delta) - \frac{4}{9}\mathrm{i}(a/\delta)^2 \rho_{\mathrm{eff}}/\rho]}. \tag{5.12}$$

The mobility ratio in (5.12) depends on three dimensionless parameters: $\kappa a, a/\delta$ and the density ratio ρ_0/ρ. In figure 2, the dependence of $|\mu_E(\omega)/\mu_E(0)|$ on κa is illustrated

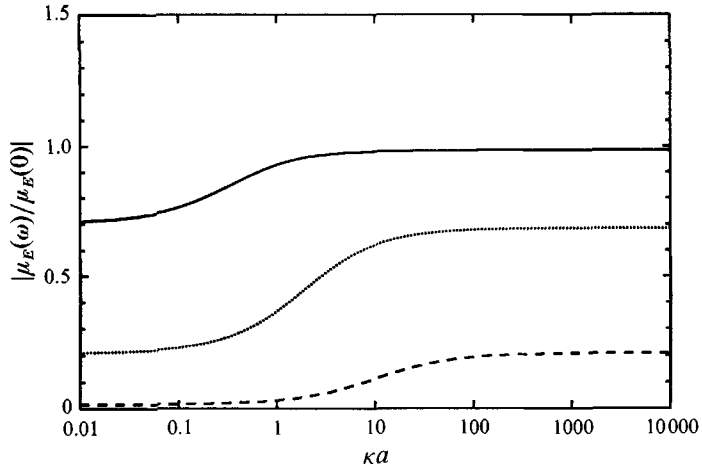

FIGURE 2. The magnitude of the dynamic to static mobility ratio $\mu_E(\omega)/\mu_E(0)$ versus κa for $a/\delta = \frac{1}{5}\pi^{\frac{1}{2}}$ (——), $\pi^{\frac{1}{2}}$ (....), $5\pi^{\frac{1}{2}}$(—), with $\rho_0/\rho = 1.05$.

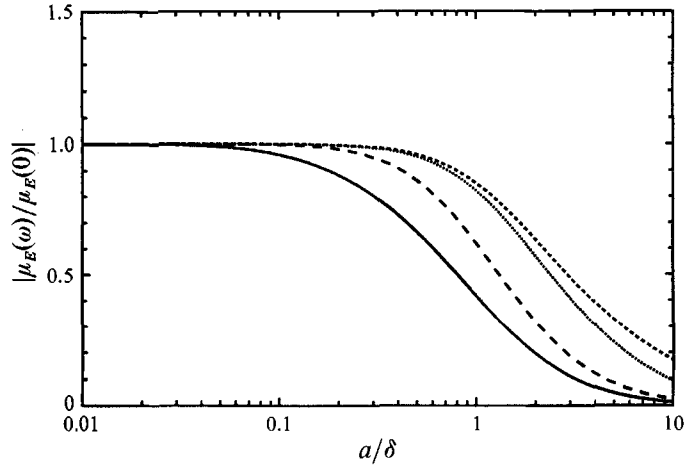

FIGURE 3. The magnitude of the dynamic to static mobility ratio $\mu_E(\omega)/\mu_E(0)$ versus a/δ for $\kappa a = 0.1$ (——), 1.0(—), 10.0 (....), 100.0 (- -), with $\rho_0/\rho = 1.05$.

for several values of a/δ. This graph demonstrates that the mobility ratio $|\mu_E(\omega)/\mu_E(0)|$ reaches its asymptotic limit for $\kappa a \to \infty$ at smaller values of κa than does $|f_1|$. Thus there is a range of κa for which the ratio of the dynamic and static mobilities is approximated well by the thin-double-layer theory, but where the dynamic mobility itself is not represented accurately by this theory.

The graph in figure 2 also indicates that the mobility ratio $|\mu_E(\omega)/\mu_E(0)|$ decreases significantly with increasing a/δ. This behaviour can be observed in more detail in figure 3, where $|\mu_E(\omega)/\mu_E(0)|$ is plotted as a function of a/δ for several values of κa. At small values of a/δ the mobility ratio is flat, but as a/δ increases, the ratio drops sharply towards zero. For example, if $a/\delta = 5\pi^{\frac{1}{2}}$, as it would in a colloidal system where the fluid viscosity is 1 cP, the fluid density is 1 g/cm^3, the particle radius is 5 μm and the oscillation frequency is 1 MHz, the ratio $|\mu_E(\omega)/\mu_E(0)|$ is roughly 0.2 when the double layer is thin compared with the particle radius. The mobility ratio becomes even smaller as the double-layer thickness increases. This means that there is an upper limit to the particle size for which electroacoustical methods can be used

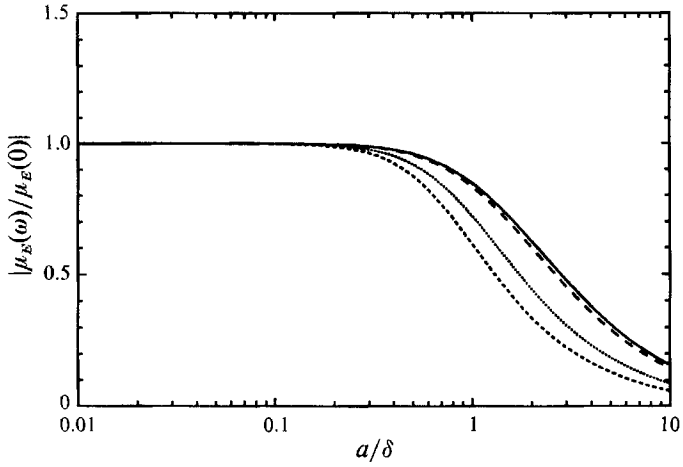

FIGURE 4. The magnitude of the dynamic to static mobility ratio $\mu_E(\omega)/\mu_E(0)$ versus a/δ for $\rho_0/\rho = 1.05$ (——), 1.2 (– –), 2.5 (....), 4.0 (- -), with $\kappa a = 50$.

effectively to obtain electrophoretic measurements. This limit depends on the properties of the colloidal system in question, through the values of the dimensionless parameters κa, a/δ and ρ_0/ρ.

The dependence of $|\mu_E(\omega)/\mu_E(0)|$ on frequency can be seen directly from figure 3, since a/δ is proportional to $\omega^{\frac{1}{2}}$. For example, at a frequency of 1 MHz, if the fluid viscosity is 1 cP, the fluid density is 1 g/cm^3 and the particle radius is 1 μm, $a/\delta = \pi^{\frac{1}{2}}$ and the ratio $|\mu_E(\omega)/\mu_E(0)|$ is roughly 0.7. In the vicinity of this value of a/δ the variation of the mobility ratio with frequency is most pronounced, since the ratio drops steeply there. The variation of $|\mu_E(\omega)/\mu_E(0)|$ with the density ratio ρ_0/ρ is also greatest over the range of a/δ where the mobility ratio drops sharply, as is depicted in figure 4. Over this range of a/δ the mobility ratio decreases with increasing ρ_0/ρ; for smaller a/δ the mobility ratio is independent of ρ_0/ρ.

Recently, James *et al.* (1991) published the results of a set of experiments in which they examined the application of critical methods of instrument calibration to electrokinetic sonic amplitude (ESA) measurements in colloidal dispersions. They were concerned with calibrating the ESA measurements by converting the signals to dynamic electrophoretic mobilities in terms that could be related to the static mobilities of the dispersions. Since electroacoustical signals are proportional to the dynamic mobility of the colloidal particles (O'Brien 1988), this conversion requires a theoretical basis for the correspondence between static mobilities and dynamic mobilities. In their paper, James *et al.* (1991) examined the self-consistency of dynamic and static electrophoretic measurements in several colloidal dispersions for the three theoretical descriptions of the electrophoretic mobility ratio that have appeared in the literature: ours, as represented here by (5.12); and those of Babchin *et al.* (1989) and O'Brien (1988).

Four colloidal dispersions were used in the electrophoretic and electroacoustical measurements reported by James *et al.* (1991). They consisted of two fairly monodisperse latex (PS and PMMA) dispersions, a polydisperse alumina (AKP) dispersion and a fairly monodisperse silica (TM) dispersion. All electrophoretic measurements were performed on samples with the continuous phase adjusted to 0.01M KNO_3. A summary of the physical properties of the four dispersions, as reflected in the dimensionless parameters κa, a/δ and ρ_0/ρ, is given in table 1.

Dispersion	κa	a/δ	ρ_0/ρ
PS	99	0.57	1.057
PMMA	53	0.30	1.195
AKP	55	0.32	3.99
TM	3.8	0.02	2.21

TABLE 1. Physical properties of sample dispersions

The experimental procedure was designed to judge the consistency of the three theoretical treatments of the mobility ratio $|\mu_E(\omega)/\mu_E(0)|$ in converting the ESA signal to a dynamic mobility. The two latex dispersions and the alumina dispersion were used to determine a calibration constant for the ESA instrument. For each dispersion, the instrument constant was calculated from the measured static electrophoretic mobility, the measured ESA signal, and the theoretical correspondence between the static and dynamic mobilities. The results for the theory of O'Brien and the theory presented in this paper were identical. Both theories predicted the same calibration constants for each of the dispersions. For the two monodisperse latex dispersions the calibration constants were nearly equal, while the calibration constant for the polydisperse alumina dispersion was roughly 20% smaller, although this discrepancy was not likely caused by the polydispersity of the particles (James *et al.* 1991). All three constants were greater than unity, as discussed by James *et al.* The results for the formula of Babchin *et al.* were not consistent with the results of the other two theories. This is not surprising, since we see from table 1 that the experimental values of κa were large, and consequently the Babchin *et al.* results were not correct under these conditions.

The experimental results reported by James *et al.* (1991) support the theoretical results discussed in our paper. However, their experiments were carried out effectively under thin-double-layer conditions, even though they presented experimental data for a range of materials with considerable differences in particle size and density. In further experimental tests of the theories for the dynamic electrophoretic mobility, a broader range of operating conditions should be sought to include colloidal dispersions with thick double layers and dispersions with double layers of intermediate thickness.

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After submission of our manuscript, we learned that an equivalent expression for the dynamic electrophoretic mobility had been published previously, without derivation, by O'Brien (1986) in a patent application. Our formula was developed independently, and published initially without derivation in a conference proceedings (Babchin *et al.* 1990). We wish to acknowledge, however, Dr O'Brien's priority in calculating a dynamic mobility formula for an arbitrary double layer thickness with low zeta potential.

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