On the derivation of the Smoluchowski result of electrophoretic mobility
(Revised version)

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Abstract

One of the most enduring, broadly applicable and widely used theoretical results of electrokinetic theory is the Smoluchowski expression for the electrophoretic mobility. It is a limiting form that holds for any solid particle of arbitrary shape in an electrolyte of any composition provided the thickness of the electrical double layer is "infinitely" thin compared to the particle size and the particle has uniform surface potential. The familiar derivation of this result that is a simplified version of the original Smoluchowski analysis in 1903, considers the motion of the electrolyte adjacent to a planar surface. The theory is deceptively simple but as a result much of the interesting physics and characteristic hydrodynamic behavior around the particle have been obscured. This paper provides a derivation of this key theoretical result by starting from Smoluchowski's original 1903 analysis but brings out overlooked details of the hydrodynamic features near and far from the particle that have not been canvassed in detail. The objective is to draw together all the key physical features of the electrophoretic problem in the thin double layer regime to provide an accessible and complete exposition of this important result in colloid science.

Keywords: Colloid, Smoluchowski theory, Thin double layer, Electrophoretic hydrodynamics, Electrophoresis, Electrophoretic mobility

1. Introduction

A well-established method to characterize the state of charge on colloidal particles in electrolyte is to deduce the so called zeta (ζ) potential, of colloidal particles by measuring the electrophoretic velocity, U, due to a constant applied electric field, E. The ratio between these two quantities is the electrophoretic mobility, μ. The Smoluchowski formula [1, 2, 3, 4] for the mobility takes the form[1]

$$U = (\epsilon\zeta/\eta)E \equiv \mu E \tag{1}$$

where $\epsilon = \varepsilon_0\varepsilon_r$ is the product of the permittivity of free space, ε_0 and the relative permittivity of the solvent, ε_r, and η is the shear viscosity of the electrolyte. This result is applicable to particles with a uniform ζ-potential and to particles of any shape so long as the Debye length, $1/\kappa$ of the electrolyte (of any composition) is negligible compared to the characteristic dimension, a of the particle, that is, $\kappa a \to \infty$, i.e. the thin double layer limit. These conditions have been subject to recent detailed experimental verification, see for example Bakker [5].

The derivation of the Smoluchowski result (1) given in many standard text and monographs on the subject (for example [6, 7, 8, 9, 10, 11]), is based on analysing the tangential flow of the thin layer of fluid adjacent to a planar charged surface that contains the electrical double layer. A conclusion of this analysis is that the tangential fluid velocity varies monotonically from zero at the planar surface to the electrophoretic velocity, U just outside the double layer. Furthermore, the analysis does not make contact with known general results about the velocity field outside the double layer [12]. However, a recent investigation of the electrophoretic velocity field around a spherical particle [13] that is based on the general theory of Overbeek [14], shows that the tangential velocity always has a maximum at some intermediate distance from the sphere for all values of κa. The value of this maximum exceeds the electrophoretic velocity that is attained many radii from the sphere. As κa increases, this maximum velocity approaches a limiting value that is $(3/2)$ times the Smoluchowski velocity, U (1).

In characterizing the state of charge using electrophoresis, one generally also studies variations of the mobility with ionic strength and with the concentration of potential determining ions. Comparison with such data will generally require the construction of models to describe how the particles develop a surface charge. This may include consideration of a Stern layer, surface conductivity and perhaps particle porosity. Theories of such detailed modeling are well established in the literature [6, 7, 8, 9, 10, 11].

The aim of this paper is undertake a consistent analysis of the electrostatic and velocity fields near and far from the particle surface. The starting point is the same as Smoluchowski's original 1903 analysis of the electrophoretic problem in the thin

[1] Smoluchowski worked in CGS units where $\epsilon = \varepsilon_0\varepsilon_r$ (SI) $= \varepsilon_r/4\pi$ (CGS)

double layer limit but we take into account details in the spatial variation of the electrostatic potential and the velocity field near and far from the particle that has a uniform ζ potential. This allows us to draw together all the key physical features of the electrophoretic problem in the thin double layer regime to provide a complete and accessible exposition of the Smoluchowski theory. The discussion will include insight as to whether the applied field can be assumed to be tangential to the surface when the particle can have any shape and why the mobility is independent of the dielectric properties of the particle.

The standard derivation of the Smoluchowski results will be reproduced in the next section to recapitulate a number of open questions about this approach. Technical results needed for this development are given in the appendices and a glossary of symbols is provided for easy reference.

2. The Smoluchowski result

2.1. The standard derivation

The common derivation of the Smoluchowski result presented in textbooks and monographs [6, 7, 8, 9, 10, 11] considers a planar surface with a uniform ζ-potential adjacent to an electrolyte. The applied electric field, E, assumed to be parallel to the surface, drives a tangential flow of the electrolyte because the double layer adjacent to the surface is not neutral. Within the double layer the charge density, ρ and electrostatic potential, ψ vary only in the direction normal to the surface with ρ and ψ related by the Poisson equation. In the reference frame in which the surface is stationary, the electrolyte just beyond the double layer is assumed to move with the constant electrophoretic velocity, U parallel to the surface but in the direction opposite to the applied field, E.

The flow of the electrolyte is described by the Stokes equation: $\eta\, \nabla^2 \boldsymbol{u} - \nabla p = -\rho \boldsymbol{E}$ for the fluid velocity, $\boldsymbol{u}$ and pressure, p with a body force, $-\rho\boldsymbol{E}$ that accounts for the effect of the applied electric field on the net charge in double layer. The planar geometry is depicted in Fig. 1 in which the tangential, t and the normal, s coordinates are defined. By symmetry, the pressure does not vary in the tangential direction and the velocity is tangential so it is only necessary to consider the Stokes equation for the tangential velocity, $u_t(s)$ that depends solely on the normal coordinate, s:

$$\eta \, \frac{d^2 u_t}{ds^2} = \epsilon \frac{d^2 \psi}{ds^2}\, E. \tag{2}$$

where we have used the Poisson equation: $\rho = -\epsilon(d^2\psi/ds^2)$ to express the charge density, ρ in terms of the electrostatic potential, ψ.

A first integral of (2) with the condition that far from the surface, $s \to \infty$, $du_t/ds \to 0$ and $d\psi/ds \to 0$, gives

$$\eta \, \frac{du_t}{ds} = \epsilon E \, \frac{d\psi}{ds}. \tag{3}$$

An immediate consequence of (3) is that if the potential gradient, $d\psi/ds$ is monotonic, then so is the tangential velocity gradient, du_t/ds.

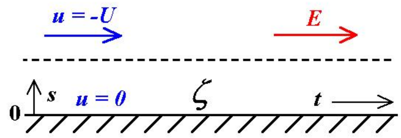

Figure 1: The planar geometry of the charged surface with surface potential ζ (assumed > 0) and the adjacent electrical double layer in the classic derivation of the Smoluchowski result in an applied electric field, $\boldsymbol{E}$. The indicated fluid velocity, $\boldsymbol{u}$ is in the reference frame in which the surface is stationary. The local co-ordinates s and t are, respectively, normal and tangential to the surface. The outer edge of the electrical double layer is indicated by the dashed line.

A second integral from $s = 0$ to ∞ then gives

$$\eta \left[u_t\right]_0^\infty = \eta\Big[-U - 0\Big] = \epsilon E \Big[\psi\Big]_0^\infty = \epsilon E \,\Big[0 - \zeta\Big] \tag{4}$$

since the tangential fluid far from the surface is $(-U)$, the negative of the electrophoretic velocity and $\psi = \zeta$ at the surface $s = 0$. This then gives the Smoluchowski formula for the electrophoretic velocity (1) as found in standard textbooks[2].

2.2. Questions relating to the standard derivation

This standard derivation of the Smoluchowski result has a number of unresolved issues:

1. Is the assumption that the applied field being tangential to the surface valid for particles of any shape in the thin double layer limit?
2. Is the field just outside the double layer equal to the applied field, E for a particle of any shape? And if not, why is the Smoluchowski theory still valid?
3. Why is the electrophoretic velocity and hence the mobility independent of the dielectric properties of the particle?
4. The standard derivation implies that the fluid velocity approaches the constant electrophoretic value, U monotonically just outside the double layer. However, this behavior does not agree with general theoretical result that the fluid velocity, relative to the particle, should approach the electrophoretic value, U with an inverse distance cubed law [12].
5. Recent theoretical results [13] based on the Overbeek model of electrophoresis [14, 15] show that the tangential velocity always attains a maximum value outside the double layer that exceeds the electrophoretic value, U. However, this velocity maximum does not exceed $(3/2)U$ and its occurance is a general consequence of the fact that a particle in electrophoretic motion experiences zero net force. Is the observed maximum in the tangential velocity in disagreement with the standard derivation of the Smoluchowski result in which the velocity near the surface is monotonic?

[2] In original articles in French, Polish and German [1, 2, 3, 4], Smoluchowski derived (1) in a slightly different manner. He started off with the Stokes equations with an electric body force: $\eta\nabla^2\boldsymbol{u} - \nabla p = -\rho\boldsymbol{E}$ (written in our notation). He then subtracted the osmotic pressure from the total pressure and argued that the resulting pressure made a negligible contribution. Integration over the other terms resulted in the electrophoretic velocity.

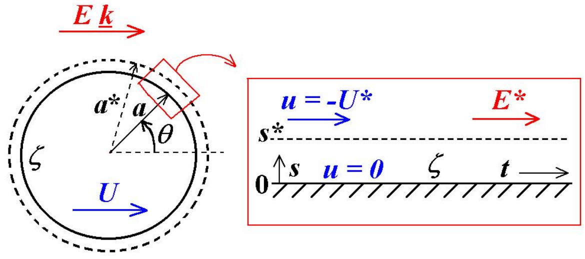

Figure 2: A solid sphere with radius a and uniform (positive) ζ-potential in an external electric field, E. The sphere surface is denoted as S. The extent of the thin double layer is indicated by the dotted spherical surface, S^* with radius, a^*, with $(a^* - a) \ll a$. Inset: A portion of the surface at angular position, θ with local coordinates that are tangent, t and normal, s to the surface. At the outer limit of the double layer at normal coordinate, s^* (dashed line), the fluid velocity is $-U^*$ (in the reference frame in which the surface is stationary) and the electric field, E^*, is tangential to the surface (see text for details).

In the next section, we resolve these issues by analysing the fluid velocity field outside a spherical particle in the thin double layer regime. This keeps the mathematical details simple and explicit although the conclusions can be extended to particles of general shape.

3. Mobility of a sphere in the thin double layer limit

In this section we derive the expression for the electrophoretic velocity in the thin double layer limit that not only gives the mobility, but also the corresponding form of the velocity field in the fluid beyond the extent of the electrical double layer around the particle. To make the development explicit, we will consider a solid spherical particle with a uniform ζ-potential. In the thin double layer limit, we follow the original 1903 approach of Smoluchowski [1] by focusing first on the fluid flow near the surface and within the electrical double layer that has a net charge. However, we go beyond the Smoluchowski analysis by matching this result to the velocity field outside the double layer where the electrolyte is neutral. In this manner, we provide clarity and resolution to the various points about the standard Smoluchowski derivation raised in the preceding section.

In Fig. 2, we show a sphere, S of radius, a in an applied electric field, E in the z-direction. The sphere has a uniform ζ-potential and the extent of the thin electrical double layer around the sphere is indicated by the dotted sphere, S^* of radius, a^*. A portion of the sphere surface and the associated electrical double layer is given in the inset of Fig. 2 with the indicated local coordinates tangent, t and normal, $s = (r - a)$ to the surface.

3.1. Electric field outside the electric double layer

Outside the double layer, the electrolyte is neutral and so the electrostatic potential, ϕ in $r > a^*$, obeys by the Laplace equation: $\nabla^2\phi = 0$ with the condition that $\phi \to -Er\cos\theta$, as $r \to \infty$, where θ is the polar angle measured with respect to the z-axis (see Fig. 2). In the thin double layer limit, we can regard the solid sphere and its electrical double layer inside the sphere of radius a^* as effectively neutral so that by Gauss' Law, the normal component of the electric field at $r = a^*$ vanishes. This then results in the boundary condition: $\partial\phi/\partial r = 0$ at $r = a^*$.

From Appendix A, we see that the potential and the electric field outside the double layer, $r \geq a^*$, have the form

$$\phi = -Er\cos\theta\left(1 + \frac{a^{*3}}{2r^3}\right) \tag{5a}$$

$$\boldsymbol{E} = -\nabla\phi = E\cos\theta\left(1 - \frac{a^{*3}}{r^3}\right)\boldsymbol{n}_r - E\sin\theta\left(1 + \frac{a^{*3}}{2r^3}\right)\boldsymbol{n}_\theta \tag{5b}$$

where $\boldsymbol{n}_r$ and $\boldsymbol{n}_\theta$ are unit vectors in the direction of the spherical coordinates r and θ. Therefore, the electric field at the outer edge of the double layer, $r = a^*$, is

$$\boldsymbol{E}(r = a^*) = -(3/2)E\sin\theta\,\boldsymbol{n}_\theta \equiv -E^*\boldsymbol{n}_\theta. \tag{6}$$

In other words, the field at the spherical surface S^* just outside the electrical double layer, defined by $r = a^*$, is tangential to the sphere since the field there only has a $\boldsymbol{n}_\theta$ component. The magnitude of this tangential field, $E^* \equiv (3/2)E\sin\theta$, defined in (6), varies with position, θ along the surface of the sphere and has a maximum of $(3/2)E$ at $\theta = \pi/2$. The tangency of the electric field follows from the boundary condition: $\partial\phi/\partial r = 0$ at $r = a^*$, which expresses the fact that the normal component of the field is zero. This reflects the assumption that the surface S^*, being just outside the double layer, encloses zero net charge. As this is the only electrical property assumed about the material enclosed by S^*, the result of this derivation is therefore independent of the dielectric property of the sphere.

3.2. Velocity field inside the electric double layer

We now consider the velocity field near the sphere surface, inside the electrical double layer by focusing on a small segment of the sphere at angular position, θ as shown in Fig. 2. As seen from the previous subsection, the electric field at the outer edge of the electric double layer at the local normal coordinate, s is tangential to the surface with magnitude, E^* given by (6).

In the frame of reference in which the surface is stationary, we can integrate the tangential component of the Stokes equation as in the standard derivation of the Smoluchowski results in Section 2.1 to obtain the velocity, U^* at the edge of the double layer as

$$U^* = -(\epsilon\zeta/\eta)E^*. \tag{7}$$

Note that U^* and E^* will in general vary with the angular position of the surface element. For a sphere, we see from (6) that $E^* = (3/2)E\sin\theta$ and so the magnitude of U^* can be up to (3/2) times larger in magnitude than the Smoluchowski velocity, $U = (\epsilon\zeta/\eta)E$.

3.3. Velocity field outside the electric double layer

In the reference frame in which the sphere is stationary, the electrophoretic velocity is the fluid velocity far from the particle. To find this in the far field, we have to determine the velocity variation outside the electrical double layer that is consistent with the velocity at $r = a^*$ given by (7). In addition, the system, comprised of the sphere and it surrounding electrical double layer, moves at a constant velocity under electrophoretic motion and moreover experiences no net external force. These are the physical conditions that determine the velocity, $\boldsymbol{u}$ and pressure, p in $a^* < r < \infty$ that obey the Stokes equation without a body force: $\eta \nabla^2 \boldsymbol{u} - \nabla p = \boldsymbol{0}$, together with the incompressibility condition: $\nabla \cdot \boldsymbol{u} = 0$.

From Appendix B, we find that the required solution for the velocity and pressure in this frame of reference with a vanishing radial velocity at a^* is

$$\boldsymbol{u} = U \cos\theta \left(1 - \frac{a^{*3}}{r^3}\right) \boldsymbol{n}_r - U \sin\theta \left(1 + \frac{a^{*3}}{2r^3}\right) \boldsymbol{n}_\theta \qquad (8a)$$

$$p = 0 \qquad (8b)$$

$$\boldsymbol{F}_h = \boldsymbol{0} \qquad (8c)$$

$$\nabla \times \boldsymbol{u} = \boldsymbol{0}. \qquad (8d)$$

The zero net force condition: $\boldsymbol{F}_h = \boldsymbol{0}$ that can be verified by integrating the stress tensor, see Appendix B, gives the limit $\boldsymbol{u} \to -U\mathbf{k}$ as $r \to \infty$, which is the electrophoretic velocity as given by the Smoluchowski formula (1).

The solution (8) has the unique property that the pressure is identically zero. Such a flow is generally referred to as a zero pressure, zero vorticity (or curl free) Stokes flow.

3.4. Remarks

There are a number of similarities and differences between the standard derivation of the Smoluchowski results as given in Section 2 and the derivation in this Section. In particular, the present treatment resolves issues about the standard derivation that were raised in Section 2.2.

- Both derivations lead to the same expression for the electrophoretic velocity for a particle in the thin electrical double layer limit (1), though the present derivation addresses key physical aspects of the problem from the region near the surface to well outside the electrical double layer.

- In the standard derivation of the Smoluchowski result, an equilibrium electrostatic potential whose magnitude decays monotonically away from the surface will imply that the tangential component of the fluid velocity varies monotonically from zero relative to the solid surface to a constant fluid velocity at the outer edge of the electrical double layer. This velocity is the Smoluchowski value (1) and the fluid retains this constant value far into the bulk electrolyte. In contrast, the present derivation shows that the tangential fluid velocity increases from zero at the solid surface to a value at the outer edge of the electrical double layer that varies with the position on the sphere surface. In particular, at the equators of the sphere at $\theta = \pi/2$ the fluid velocity at the edge of the double layer is (3/2) times the Smoluchowski value and then it decays to the Smoluchowski value far from the sphere[3].

- By analysing and matching the flow field inside the electrical double layer with that outside the electrical double layer we establish that the velocity field association with electrophoresis decreases towards the Smoluchowski value with a $1/r^3$ decay [12] rather than with $1/r$, as in say the velocity field surrounding a steadily sedimenting particle. The physical reason is that electrophoresis is driven by a body force in the fluid which is exactly counteracting the force on the sphere rather than an external force (such as gravity) acting on the sphere. This faster decay of the velocity field has important implications on the hydrodynamic interaction between particles undergoing electrophoresis: since the decay is now $1/r^3$ the hydrodynamic interaction between neighboring particles is much weaker.

- The zero force condition also means that the pressure outside the double layer is identically zero and the flow is irrotational in contrast to the flow associated with say a sedimenting sphere. So the velocity field around a sphere undergoing electrophoresis corresponds to a special case of zero pressure, irrotational Stokes flow and is quite peculiar.

- The velocity field outside the double layer appears to have a "slip velocity" boundary condition given by (7) at $r = a^*$, just outside the electrical double layer. This should not be confused with the traditional "slip plane" in the equilibrium theory of the electrical double layer where the ζ-potential is defined and where continuum electrostatics and hydrodynamic boundary conditions are applied [11].

- By considering a sphere, we see explicitly why the electric field is tangential to the surface in the thin double limit because outside the double layer, at the radius a^*, the particle and the double layer, when taken together, enclose no net charge within the sphere of radius a^*. However, this tangential field is not equal to the applied field, E but has a magnitude that varies with the position on the surface and can be up to (3/2) times larger than E.

4. Comparison with finite κa results and generalizations

4.1. Finite κa results for a sphere

Recently the Overbeek theory of the electrophoretic motion of a spherical particle [14, 15] has been used to calculate the spatial variation of the fluid velocity, pressure and vorticity for a range of κa values [13]. For comparison with the present large κa results we will adopt the Henry [16] approximation that uses the linear Debye-Hückel result for the equilibrium electrostatic properties of the double layer. We note that ion convection effects are omitted in the Henry approximation and also in the Smoluchowski approximation. However, the Henry approximation is valid for all values of κa, albeit limited to low ζ-potentials, nonetheless, it contains the essential information related to variations in κa that is of interest here.

[3] Smoluchowski, in his 1903 paper [1], also mentioned the electrophoretic velocity of a sphere in his §8. He gave the classical formula for the electric potential in his Eq. (18) resulting in a $(3/2)E$ term on the equator of the sphere and then gave, without further proof, the electrophoretic velocity in his Eq. (19) corresponding to our Eq. 1

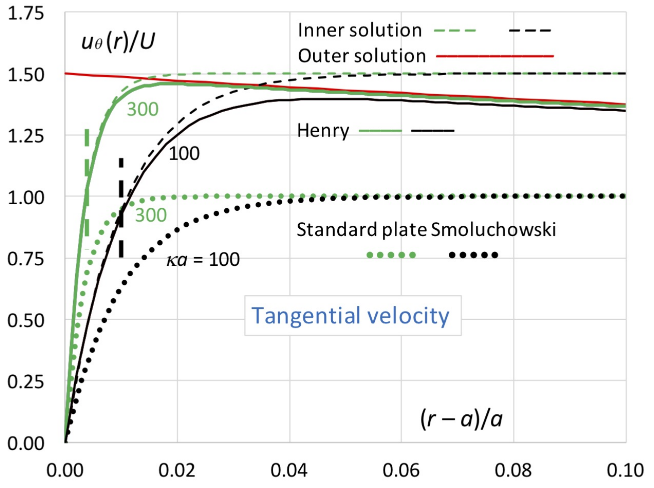

Figure 3: A comparison of the tangential velocity near the particle surface from different derivations of the Smoluchowski result at large values of κa as indicated. Results of the standard derivation of the tangential velocity, $u_t(r)/U$ at a planar surface, given by (10) are shown as dotted lines (• • •, • • •). Results of the present derivation of the tangential velocity, $u_\theta(r)/U$ around a sphere, given by (11) are shown as dashed lines (– – –, – – –). The outer solution for the tangential velocity (12) is shown as the solid red line (—). Results from the Henry theory, valid for all separations are shown in solid lines (—, —). The velocity maximum is at $(r-a)/a = 0.019, 0.048$ for $\kappa a = 100, 300$, respectively. The locations of $1/(\kappa a)$ in each case are indicated by vertical dashed lines.

In the Overbeek theory, where the applied field, $\boldsymbol{E} = E\mathbf{k}$ is along the z-direction, the electrophoretic fluid velocity relative to a stationary sphere has the form:

$$\boldsymbol{u} = u_r(r)\cos\theta\ \boldsymbol{n}_r - u_\theta(r)\sin\theta\ \boldsymbol{n}_\theta, \tag{9}$$

with just r and θ components and their magnitudes only vary with the radial coordinate, r. We show variations of these components scaled by the Smoluchowski velocity: $u_r(r)/U$ and $u_\theta(r)/U$ as functions of the scaled distance from the sphere surface: $s/a = (r-a)/a$ in the inner region, within the electrical double layer, in Fig. 3 and in the outer region over the scale of the sphere in Fig. 4.

Consistent with the Henry theory, we use the Debye-Hückel potential at a planar surface: $\psi(s) = \zeta\exp(-\kappa s)$ in (3) to give an expression for the inner solution of the tangential fluid velocity relative to the surface within the electrical double layer

$$u_t(s) = U\left[1 - \exp\Big(-(\kappa a)[(r-a)/a]\Big)\right]. \tag{10}$$

where U is the Smoluchowski velocity (1). This inner solution holds for the standard derivation of the Smoluchowski formula.

On the other hand, if we follow the present derivation of the inner solution outlined in Section 3 for a sphere, the tangential fluid velocity, $u_\theta(r)$ relative to the surface within the electrical double layer (inside the surface S^*) would take the form

$$u_\theta(r) = (3/2)U\left[1 - \exp\Big(-(\kappa a)[(r-a)/a]\Big)\right]. \tag{11}$$

A number of features are of note in the results for the electrophoretic velocity components relative to a stationary sphere (9) given in Figs. 3 and 4:

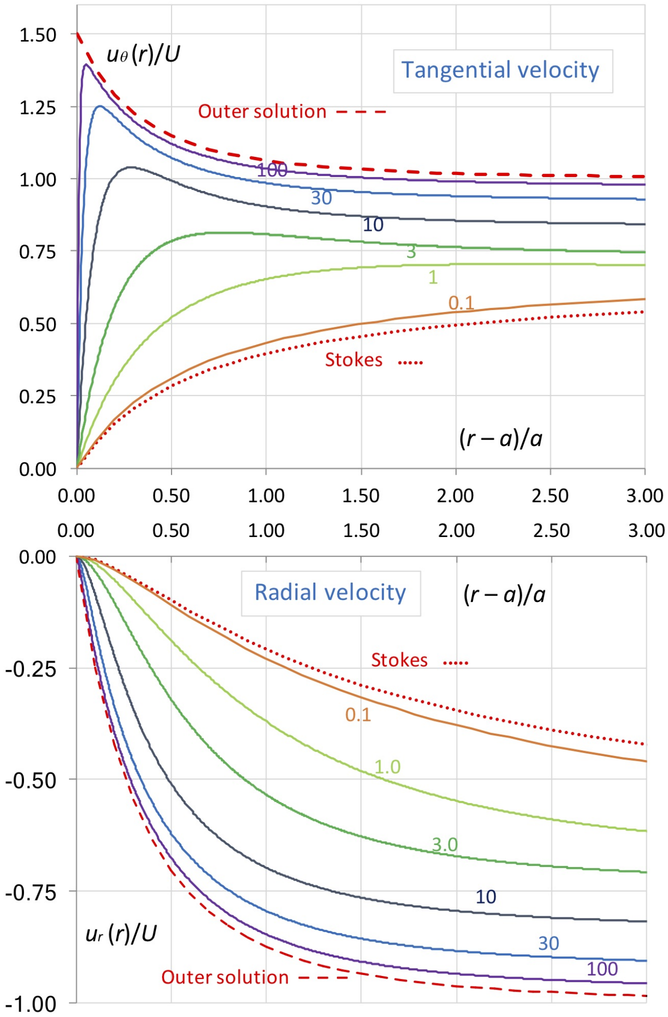

Figure 4: The (a) (upper) tangential velocity, $u_\theta(r)$ and (b) (lower) radial, $u_r(r)$ velocity, see (9), around a sphere in electrophoretic motion according to the Henry model [13, 16] for the indicated values of κa. Shown also are the outer solutions (8a) and the Stokes solution for a solid sphere with $U_\infty = -(2/3)U$, see Appendix B.

1. The Henry results show that the tangential velocity, Fig. 4a, has a maximum that becomes progressively more prominent as κa increases and the location of the maximum moves towards the surface of the sphere.
2. The fundamental physical reason for the existence of this velocity maximum is the requirement that a particle in electrophoretic motion experiences zero net force as it travels at constant velocity. For a detailed technical exposition, see [13].
3. For $\kappa a \gg 1$, there are 2 distinct regions: (i) an inner region, $a < r < a^*$ and (ii) and outer region, $r > a^*$, as can be seen in Fig. 3 where a^* is around the position of the maximum of u_θ/U that extends a few Debye lengths from the sphere surface.
4. The velocity in the inner region ($a < r < a^*$) is well described by the result derived here for the sphere (11), whereas the standard Smoluchowski inner solution (10) does not capture the behavior in the inner region.

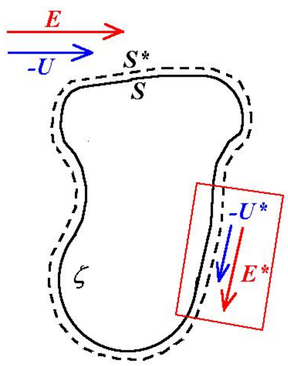

Figure 5: A schematic illustration of a general shaped particle with a uniform ζ-potential ($\zeta > 0$) on its surface, S in an applied electric field E and the resulting electrophoretic velocity, U. The tangential electric field, E^* and the corresponding tangential fluid velocity, U^* (in the reference frame that the particle is at rest) at the outer edge of the electrical double layer at surface, S^* are shown at a general point on the surface.

5. In the outer region ($r > a^*$), the magnitude of the tangential velocity has the limiting form given by (8a), with $a \approx a^*$ for $\kappa a \gg 1$

$$u_\theta(r)/U \to 1 + \frac{a^3}{2r^3}, \qquad \kappa a \to \infty, \tag{12}$$

approaches the Smoluchowski value (1) from above as $r \to \infty$.
6. For $\kappa a \gg 1$, we see from Fig. 3 that the simple inner (11) and outer (12) solutions derived here provide a quantitatively accurate picture of the velocity at all locations.
7. As seen in Fig. 4a the limiting value of $u_\theta(r)$ as $r \to \infty$ is the electrophoretic velocity that varies from the Hückel limit of $(2/3)U$ for small κa to the Smoluchowski limit of U for large κa given by (1).
8. Both the tangential velocity, $u_\theta(r)$ (Fig. 4a) and the radial velocity, $u_r(r)$ (Fig. 4b) lie between the outer solution (12) and the Stokes solution for a solid sphere with $U_\infty = -(2/3)U$, given by (B.4) in Appendix B.
9. The normal velocity, $u_r(r)$ as well as its derivative, du_r/dr are small at the outer edge of the double layer. In particular, the velocity inside the double layer indeed has a very small radial component in the direction normal to the surface and thus justifies the assumption that the flow is predominantly tangential near the surface at large κa.
10. The magnitudes of the pressure and the vorticity are only significant inside the double layer, that is $r < a^*$. Outside $r > a^*$, the pressure and vorticity are exponentially small (see [13] for more details).

4.2. Arbitrarily shaped particles

We generalize our derivation of the electrophoretic velocity of a sphere in the thin double layer limit to particles of arbitrary shape (as in Fig. 5) with a constant ζ-potential and give a physically perspicuous exposition of the theoretical treatment given by Morrison [12].

Outside the thin electrical double layer, the electrolyte is neutral, so the electrostatic potential, ϕ that is generated by the presence of the particle in an applied electric field $\boldsymbol{E} = E\mathbf{k}$ in the z-direction must satisfy the Laplace equation: $\nabla^2\phi = 0$. Far from the particle, $\phi \to -Ez$. The surface, S^* that is just outside the thin electrical double layer around the particle encloses the charged particle and the thin diffuse layer of neutralizing counter-ions and co-ions and is therefore electrically neutral. Therefore, the normal component of the electric field vanishes on S^*, that is, $\partial\phi/\partial n = 0$ on S^* ($\partial/\partial n$ indicating the normal derivative). These conditions are sufficient to determine the electrostatic potential, ϕ outside the thin double layer. In particular, the tangential electric field, E^* at S^* for a particle of arbitrary shape can be determined from ϕ.

Turning now to the velocity field, $\boldsymbol{u}$ in the reference frame in which the particle is stationary. Far from the particle we have the condition $\boldsymbol{u} \to -U_\infty\mathbf{k}$ as $r \to \infty$, but the value of the constant velocity, U_∞ remains to be determined. At the surface S^* the normal velocity is approximately zero in the thin double layer limit. As for the tangential velocity, U^* on S*, it must be proportional to the electric field there according to (7).

As the electrophoretic problem is linear in the applied electric field, E, all transport properties must be proportional to E. So outside the thin double layer we seek a solution of the velocity expressed in terms of a scalar function, Φ where $\boldsymbol{u} = \nabla\Phi$ so that the above velocity boundary conditions for Φ are: $\Phi \to -U_\infty z$ as $r \to \infty$, and $\partial\Phi/\partial n = 0$ on S^*. From the incompressibility condition: $\nabla\cdot\boldsymbol{u} = 0$, the velocity potential, Φ obeys the Laplace equation: $\nabla^2\Phi = 0$.

Now we see that the electrostatic potential, ϕ and the velocity potential, Φ both satisfy the Laplace equation and analogous boundary conditions. Thus in the thin double layer limit, the linearity property of the electrophoretic problem means that the local electric field and the local velocity outside the double layer are proportional to each other. This is a considerable simplification. Since $\boldsymbol{u} = \nabla\Phi$ is also a solution of the Stokes equation in the absence of a body force, we have found the unique solution of the hydrodynamic problem. It also follows that the velocity field is irrotational since $\nabla\times\boldsymbol{u} = \nabla\times\nabla\Phi \equiv \mathbf{0}$.

From the Stokes equation we deduce that the pressure, p is a constant because

$$\nabla p = \eta\nabla^2\boldsymbol{u} = \eta\nabla^2\nabla\Phi = \eta\nabla\nabla^2\Phi = 0. \tag{13}$$

The constant pressure can be set to zero without loss of generality since the pressure is arbitrary up to an additive constant.

The above discussion about the electric and velocity potentials around a particle of any shape with a thin electrical double layer can be summarized as follows:

$$\begin{array}{cc} \underline{\text{Electric potential}} & \underline{\text{Fluid potential}} \\ \nabla^2\phi = 0 & \nabla^2\Phi = 0 \\ \dfrac{\partial\phi}{\partial n} = 0 \quad (\text{on S*}) & \dfrac{\partial\Phi}{\partial n} = 0 \quad (\text{on S*}) \\ \lim\limits_{r\to\infty}\phi = -Ez & \lim\limits_{r\to\infty}\Phi = -U_\infty z \end{array} \tag{14}$$

where S^* is the surface just outside of the thin double layer and thus very close to the 'real' surface S. Both the electric and the fluid potentials obey the same governing equation and boundary conditions on any shaped object with boundary S^*. The electric field, E^* on S^*, which is tangential to the surface, and the apparent slip velocity, U^* just outside the double layer are proportional to each other according to (7). The same proportional relationship must hold between the applied field, E and the velocity at infinity, U_∞ in (14). And therefore the Smoluchowski result (1) follows: $U_\infty = U$.

The fluid dynamics of such a system under electrophoresis is thus indeed quite 'unusual' [13]. This discussion about particles with thin double layers is similar to the analysis by Morrison [12], except for the fact that Morrison did not assume that the pressure outside the double layer is zero, but instead use the Bernoulli equation for pressure: $p \sim u^2$ which is inconsistent with a viscous dominated, low Reynolds flow in electrophoresis. In fact, as demonstrated in Appendix C, the zero pressure condition is related to the fact that a particle in electrophoretic motion experiences zero net force.

For smaller values of κa, the double layer becomes thicker and the condition $\partial\Phi/\partial n = 0$ in Eq. 14 breaks down, because the normal velocity a S^* is no longer zero.

5. Conclusions

In this paper, we revisited the derivation of the Smoluchowski expression for the electrophoretic mobility that is valid in the so-called thin double layer limit in which the thickness of the electrical double layer is small compared to the characteristic dimension of the colloidal particle. This result is valid for any electrolyte composition as long as the particle has a uniform ζ-potential.

By using a sphere as an explicit example, we demonstrate how the flow field close to the particle surface, within the electrical double layer, couples to the flow field outside the extent of the double layer. Whereas the standard derivation of the Smoluchowski result implies that the fluid velocity increases monotonically from zero, relative to the surface, to the electrophoretic velocity U just outside the double layer, results of our present analysis (11) and (12), substantiated by detailed numerical results [13], shows that the fluid velocity actually attains a maximum at the outer edge of the double layer and then decreases towards the electrophoretic velocity U far from the particle Figs. 3 and 4. This velocity maximum approaches $(3/2)U$ as $\kappa a \to \infty$.

Arguments are presented to show that the results for a sphere apply equally to particles of any shape as long as the double layer is thin and the particle ζ-potential is uniform. Although in the thin double layer limit, the electric field is tangential to the surface just outside the double layer with magnitude E^* that varies with the position on the surface, the magnitude of E^* is not that of the applied field $\boldsymbol{E} = E\mathbf{k}$, that is $E^* \neq E$.

In fact, the velocity field, $\boldsymbol{u}$ outside the double layer can be expressed as the gradient of a velocity potential: $\boldsymbol{u} = \nabla\Phi$ [12] and as a result both the pressure outside the double layer and the force on the particle are identically zero. In the reference frame in which the particle is stationary, $\boldsymbol{u} \to -U\mathbf{k}$ far from the particle ($r \to \infty$), and the velocity decays as $1/r^3$ towards this limit. Just outside the double layer where the tangential electric field has magnitude E^*, the fluid has a tangential slip velocity, U^*, where U^* and E^* are related by the formula in (7).

Although there are a number of theoretical studies of the electrophoretic mobility in the literature in the thin double layer limit that take into account other effects such as ion transport and surface conductivity, see for example [10, 17, 18, 19], they all took the approach of eliminating the pressure by taking the curl of the Stokes equation and avoided the need to consider details of the velocity field. Indeed, in the O'Brien-White formulation of the electrophoresis of a sphere [20], the calculation of the electrophoretic mobility does not require explicit evaluation of the fluid velocity,

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Appendix A. A neutral sphere in a constant electric field

The variation of the electric field, $\boldsymbol{E} = -\nabla\phi$, around a neutral sphere of radius, a, placed in a constant uniform electric field far away from the sphere in the z-direction: $E_\infty\ \mathbf{k}$, can be found by solving the Laplace equation: $\nabla^2\phi = 0$ with $\phi \to -E_\infty z = -E_\infty\ r\cos\theta$, as $r \to \infty$, far from the sphere. At the surface of the neutral sphere with a zero surface charge density, we have the boundary condition: $\partial\phi/\partial r = 0$ at $r = a$.

In spherical polar co-ordinates, r, θ and φ, the solution for the potential is $\phi = -E_\infty \cos\theta\ [r + a^3/(2r^2)]$ and the corresponding electric field is [21]

$$\boldsymbol{E} = E_\infty \cos\theta \left(1 - \frac{a^3}{r^3}\right) \boldsymbol{n}_r - E_\infty \sin\theta \left(1 + \frac{a^3}{2r^3}\right) \boldsymbol{n}_\theta \qquad \text{(A.1)}$$

where $\boldsymbol{n}_r$ and $\boldsymbol{n}_\theta$ are unit vectors in the direction of increasing radial, r and angular, θ directions.

At the surface of the sphere, $r = a$, the electric field is tangential to the surface and varies with the polar angle, θ as

$$\boldsymbol{E}(r = a) = -(3/2)E_\infty \sin\theta\ \boldsymbol{n}_\theta \equiv \boldsymbol{E}_{tang}. \qquad \text{(A.2)}$$

The negative sign indicates that the tangential field, $\boldsymbol{E}_{tang}$ points in the direction of decreasing θ (see Fig. 2). The magnitude of the tangential field at the sphere surface varies with position as $\sin\theta$ with an absolute maximum magnitude that is (3/2) times that of the constant applied field, E_∞.

Appendix B. A sphere in a constant velocity field

The velocity field, $\boldsymbol{u}$, and pressure, p, in an unbounded incompressible Newtonian fluid with density, ρ, shear viscosity, η, around a sphere of radius, a, placed in a uniform flow field: $U_\infty\ \mathbf{k}$, can be found by solving the Stokes equation in the absence of a body force:

$$\eta\ \nabla^2\boldsymbol{u} - \nabla p = 0 \qquad \text{(B.1a)}$$

$$\nabla\cdot\boldsymbol{u} = 0 \qquad \text{(B.1b)}$$

in the low Reynolds number regime: $\text{Re} \equiv \rho a U_\infty/\eta \ll 1$ (i.e. neglecting inertial effects).

The general solution of (B.1) with the sphere located at the origin satisfying the condition $\boldsymbol{u} \to U_\infty \mathbf{k}$, as $r \to \infty$, is in Cartesian coordinates [22, 23]:

$$\begin{aligned}\boldsymbol{u} = U_\infty \frac{(\mathbf{k}\cdot\boldsymbol{x})}{r^2}\left[B_1\frac{a}{2r} + B_2\frac{3a^3}{2r^3}\right]\boldsymbol{x} \\ + U_\infty\left[1 + B_1\frac{a}{2r} - B_2\frac{a^3}{2r^3}\right]\mathbf{k}\end{aligned} \qquad \text{(B.2)}$$

where $\boldsymbol{x}$ is the position vector, $r = |\boldsymbol{x}|$. Equivalently, the solution can be expressed in spherical polar coordinates

$$\begin{aligned}\boldsymbol{u} &\equiv u_r(r,\theta)\ \boldsymbol{n}_r + u_\theta(r,\theta)\ \boldsymbol{n}_\theta \\ &= U_\infty \cos\theta\left(1 + B_1\frac{a}{r} + B_2\frac{a^3}{r^3}\right)\boldsymbol{n}_r \\ &\quad - U_\infty \sin\theta\left(1 + B_1\frac{a}{2r} - B_2\frac{a^3}{2r^3}\right)\boldsymbol{n}_\theta \qquad \text{(B.3a)}\end{aligned}$$

$$p = \frac{\eta a}{r^2}\ B_1 U_\infty \cos\theta \qquad \text{(B.3b)}$$

$$\boldsymbol{F}_h = -\ 4\pi\eta a\ B_1 U_\infty\ \mathbf{k} \qquad \text{(B.3c)}$$

$$\nabla\times\boldsymbol{u} = \frac{3a}{2r^2}\ B_1 U_\infty \sin\theta\ \boldsymbol{n}_\varphi \qquad \text{(B.3d)}$$

and the hydrodynamic force, $\boldsymbol{F}_h$, exerted on the sphere is found by integrating the stress tensor: $-p\mathbf{I} + \eta[(\nabla\boldsymbol{u}) + (\nabla\boldsymbol{u})^T]$ over any surface that encloses the sphere using (B.2). The constants B_1 and B_2 are determined by the boundary conditions specified on the sphere surface. Note that only the constant B_1 is present in the pressure, the force and the vorticity, $(\nabla\times\boldsymbol{u})$.

Appendix B.1. Standard Stokes result

At a stationary solid sphere surface, the normal and tangential components of the fluid velocity vanish: $u_r(a,\theta) = 0$, $u_\theta(a,\theta) = 0$, the constants are: $B_1 = -3/2$ and $B_2 = 1/2$ and we have

$$\begin{aligned}\boldsymbol{u} &= U_\infty \cos\theta\left(1 - \frac{3a}{2r} + \frac{a^3}{2r^3}\right)\boldsymbol{n}_r \\ &\quad - U_\infty \sin\theta\left(1 - \frac{3a}{4r} - \frac{a^3}{4r^3}\right)\boldsymbol{n}_\theta \qquad \text{(B.4a)}\end{aligned}$$

$$p = -\frac{3\eta a}{3r^2}\ U_\infty\cos\theta \qquad \text{(B.4b)}$$

$$\boldsymbol{F}_h = \ 6\pi\eta a\ B_1 U_\infty\ \mathbf{k} \qquad \text{(B.4c)}$$

$$\nabla\times\boldsymbol{u} = -\frac{9a}{4r^2}\ U_\infty\sin\theta\ \boldsymbol{n}_\varphi \qquad \text{(B.4d)}$$

where both the pressure, p and $\nabla\times\boldsymbol{u}$ decay as $1/r^2$, while the velocity perturbation from the uniform flow decays as $1/r$.

Appendix B.2. Imposed tangential velocity

If the tangential velocity on the impenetrable sphere in the θ-direction is prescribed as:

$$u_\theta(a,\theta)\ \boldsymbol{n}_\theta = -(3/2)U_\infty \sin\theta\ \boldsymbol{n}_\theta, \qquad \text{(B.5)}$$

the constants are: $B_1 = 0$ and $B_2 = -1$, thus giving

$$\boldsymbol{u} = U_\infty\cos\theta\left(1 - \frac{a^3}{r^3}\right)\boldsymbol{n}_r - U_\infty\sin\theta\left(1 + \frac{a^3}{2r^3}\right)\boldsymbol{n}_\theta \quad \text{(B.6a)}$$

$$p = 0 \qquad \text{(B.6b)}$$

$$\boldsymbol{F}_h = \mathbf{0} \qquad \text{(B.6c)}$$

$$\nabla\times\boldsymbol{u} = \mathbf{0}. \qquad \text{(B.6d)}$$

With this tangential boundary condition, the sphere experiences no hydrodynamic drag force and is vorticity-free. This is referred to as the zero pressure or irrotational (or curl free) solution of the Stokes equation. The velocity perturbation now decays as $1/r^3$.

Although the solution for the velocity, $\boldsymbol{u}$ in (B.6) has the same form as that for a sphere in an inviscid fluid governed by potential flow [22], the underlying physical assumptions embodied in these two cases are at the opposite ends of the spectrum. Whereas (B.6) is a result that holds in the limit of zero Reynolds number where inertial effects are negligible relative to viscous forces and the pressure, p is zero, the potential flow result, in contrast, accounts fully for inertial effects but omits effects due to viscosity with the pressure being given by the Bernoulli equation: $p = \frac{1}{2}\rho u^2$.

Appendix C. The relationship between zero pressure and zero force

The force $\boldsymbol{F}$ on a particle in Stokes flow can be obtained by integrating the stress tensor over any surface, S_0 that encloses the particle [24]

$$\boldsymbol{F} = \int_{S_0}\left[-p\delta_{ij} + \eta\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right)\right] n_j dS. \qquad \text{(C.1)}$$

We have seen that if the velocity, $\boldsymbol{u}$ can be expressed as the gradient of a potential: $\boldsymbol{u} = \nabla\Phi$ then the pressure is zero, $p = 0$. Thus we can write for this force:

$$\begin{aligned}\boldsymbol{F} &= \eta\int_{S_0}\left[\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right]n_j\ dS \\ &= \eta\int_{S_0}\left[\frac{\partial^2\Phi}{\partial x_j\partial x_i} + \frac{\partial^2\Phi}{\partial x_i\partial x_j}\right]n_j\ dS \\ &= 2\eta\int_{S_0}\frac{\partial^2\Phi}{\partial x_j\partial x_i}\ n_j\ dS = 0\end{aligned} \qquad \text{(C.2)}$$

where S_0 is a sphere around the particle with a very large radius, R_0. Then the last equality follows from the fact that for any potential function that dies out faster than $1/r^2$ from a particle, the twice differentiation in the integrand means that as $R_0 \to \infty$, the decrease in the integrand will be faster than the R_0^2 growth in the surface area of S_0.

Appendix D. Glossary of symbols

a radius of a spherical charged colloidal particle or typical length scale of an particle of arbitrary shape

a^* radius of a spherical surface that encloses the particle and its neutralizing diffuse layer ionic cloud.

$\boldsymbol{E}$ constant external applied electric field in the z-direction = $E\mathbf{k}$

E^* magnitude of the tangential component of the electric field just outside the electrical double layer at the surface, S^*

$\boldsymbol{n}_r, \boldsymbol{n}_\theta, \boldsymbol{n}_\varphi$ unit vector in the (r, θ, φ) - (radial, polar, azimuthal) direction of a spherical polar coordinate system centered at the sphere

p pressure

r radial coordinate of the spherical polar system

s local coordinate normal to the particle surface

S the surface of the particle

S^* the surface that just encloses the particle and the neutralizing diffuse double layer

t local coordinate tangential to the particle surface

$\boldsymbol{u}$ velocity field of the fluid

U the electrophoretic velocity given by the Smoluchowski formula (1)

U^* the tangential fluid velocity at the outer edge of the double layer at surface S^* and is related to E^* by (7)

U_∞ the constant velocity at infinity in Appendix B

ε_r relative permittivity of the solvent

ε_0 permittivity of vacuum, 8.852×10^{-12} F/m

$\epsilon \equiv \varepsilon_0 \varepsilon_r$, solvent permittivity

η solvent viscosity

ϕ the local electrostatic potential generated by the presence of the particle in and imposed electric field

Φ the fluid velocity potential: $\boldsymbol{u} = \nabla\Phi$

θ polar angular coordinate of the spherical polar system, i.e. the angle between the radius vector and the electric field

ρ local volume charge density

ψ equilibrium electrostatic potential in the electrical double layer

ζ the zeta potential of the colloidal particle (assumed to be constant everywhere on the surface)

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