Journal of Colloid and Interface Science 388 (2012) 92–94

Contents lists available at SciVerse ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

A simpler expression for Henry's function describing the electrophoretic mobility of spherical colloids

James W. Swan *, Eric M. Furst

Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19702, USA

ARTICLE INFO

Article history:
Received 9 June 2012
Accepted 14 August 2012
Available online 28 August 2012

Keywords:
Electrophoresis
Colloidal hydrodynamics

ABSTRACT

An approximate expression for Henry's function, describing the electrophoretic mobility of a spherical colloidal particle in the limit of low surface potentials, is developed through a physical analogy to a colloidal particle with a linearly slipping surface (i.e. satisfies the Navier slip condition). The resulting expression reproduces Henry's function with a relative error of no more than 0.1%. This approach is generalized for the electrophoretic mobility of a particle regardless of surface potential though necessary data for rigorous testing is lacking.

The electrophoretic mobility of an insulating spherical colloid in the low surface potential and weak applied field limits:

$$\mu = \frac{2\epsilon\epsilon_0\zeta}{3\eta} f(\kappa a), \tag{1}$$

relates the velocity of the particle with radius a and zeta potential ζ through a fluid with viscosity η and dielectric permittivity ϵ to the electric field driving the electrophoresis (*viz.* $\mathbf{U} = \mu\mathbf{E}$). $f(\kappa a)$ is Henry's function and depends on the thickness of the Debye or double layer κ^{-1} which acts to screen the electrostatic interactions around the particle [1]. This particular form of the electrophoretic mobility is valid for weak, constant surface potentials so that the electrostatic potential in the fluid is governed by the linearized Poisson–Boltzmann equation.

In the limit of a thick double layer (i.e. $\kappa a \ll 1$), $f(\kappa a)$ approaches unity and the Hückle mobility is recovered [2]. Here, the Stokes drag force on the particle directly balances with the Coulomb force to determine the particle's velocity. In the limit of a thin double layer (i.e. $\kappa a \gg 1$), $f(\kappa a) \to 3/2$ and the Smoluchowski mobility is recovered [3]. In this case, near the particle, an imbalance of cations and anions leads to a flow which relieves the shear stress on the particle as it moves. The full form of the Henry function is

$$f(\kappa a) = 1 + \frac{1}{16}(\kappa a)^2 - \frac{5}{48}(\kappa a)^3 - \frac{1}{8}(\kappa a)^4 \times \left[\frac{1}{12}(1-\kappa a) - \left(1 - \frac{1}{12}(\kappa a)^2\right) e^{\kappa a} E_1(\kappa a)\right], \tag{2}$$

where $E_1(\kappa a)$ is the exponential integral of order one.

Interestingly, we may write the electrophoretic velocity in the form of a hydrodynamic mobility multiplied by an applied force: $\mathbf{U} = M_{UF}\mathbf{F}$ with $M_{UF} = f(\kappa a)(6\pi\eta a)^{-1}$ and $\mathbf{F} = 4\pi\epsilon\epsilon_0 a\zeta\mathbf{E}$. Here, the force $\mathbf{F}$ takes on the form of a Coulomb force while the mobility is a modified Stokes drag law. The limit of thick and thin double layer suggest that the colloid behaves as a particle subject to a no-slip boundary condition ($M_{UF} = (6\pi\eta a)^{-1}$) and a no shear stress condition ($M_{UF} = (4\pi\eta a)^{-1}$) in each case, respectively. That is, the Hückle solution represents the motion of a rigid no-slip particle while the Smoluchowski solution represents the motion of a rigid bubble as if both have charge $4\pi\epsilon\epsilon_0 a\zeta$ in the electric field $\mathbf{E}$. Here, "hydrodynamic," can refer to the forces of the medium (solvent plus ions) acting on the charged particle.

From colloidal hydrodynamics, we know that a smooth transition from the no-slip to the shear stress free mobility can be achieved by hypothesizing a particle for which the fluid undergoes prescribed slip along the particle's surface. The Navier slip condition states that the fluid velocity relative to the particle and tangential to its surface, $\mathbf{t}\cdot\mathbf{u}$ is related linearly to the density of force exerted by the fluid tangential to that surface, $\mathbf{tn}:\boldsymbol{\sigma}$ as $\mathbf{t}\cdot\mathbf{u} = (\lambda/\eta)\mathbf{nt}:\boldsymbol{\sigma}$. The length scale λ is termed the slip length and corresponds physically to the distance below the particle's surface at which $\mathbf{u}$ would reach zero, the no-slip value, were it to continue changing linearly at a rate given by the surface rate of strain. For a spherical particle with $0 < \lambda a < 1$, this interpretation suggests a spherical, no-slip surface at a depth λ within the particle. Regardless of the interpretation, it is simple to show that the mobility of such a particle is $M_{UF} = g(\lambda/a)(6\pi\eta a)^{-1}$ with

$$g\left(\frac{\lambda}{a}\right) = \frac{1 + 3\left(\frac{\lambda}{a}\right)}{1 + 2\left(\frac{\lambda}{a}\right)}. \tag{3}$$

* Corresponding author. Fax: +1 3028311048.
E-mail address: jswan@udel.edu (J.W. Swan).

0021-9797/$ - see front matter © 2012 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jcis.2012.08.026

In the limit of small slip lengths, $g(\lambda/a)$ approaches unity and the particle moves as though subject to the no-slip condition. In the limit of large slip lengths, $g(\lambda/a) \to 3/2$ and bubble-like motion results [4].

Now we are left with a compelling analogy between the mobility of a slipping spherical particle and the electrophoretic mobility in the low potential limit. By doing an admittedly naive thing and equating the two, we find that the slip length can be related to the double layer thickness as

$$\frac{\lambda}{a} = \frac{f(\kappa a) - 1}{3 - 2f(\kappa a)}. \tag{4}$$

In the limit of thick double layers ($\kappa a \ll 1$), we find the scaling relation $\lambda/a = (\kappa a/4)^2$ while in the thin double layer limit ($\kappa a \gg 1$) the slip length scales as $\lambda/a = \kappa a/18$. The equivalent slip length is plotted as a function of κa in Fig. 1.

This equivalence between mobilities allows us to write Henry's function is written in terms of the equivalent slip length as

$$f(\kappa a) = \frac{1 + 3\lambda/a}{1 + 2\lambda/a}. \tag{5}$$

Therefore, in the limit that $\kappa a \ll 1$, $f(\kappa a) \approx (16 + 3(\kappa a)^2)/(16 + 2(\kappa a)^2)$ and in the limit that $\kappa a \gg 1$, $f(\kappa a) \approx (18 + 3\kappa a)/(18 + 2\kappa a)$. These approximations for Henry's function are within 2% of the exact value for $\kappa a < 1$ and $\kappa a > 1$ respectively. The slip length can be interpolated by a rational function which takes on the correct values in the limits of thick and thin double layers: $\lambda/a = (\kappa a/4)^2(1 + 9\kappa a/8)^{-1}$. With this, a deceptively simple empirical approximation to Henry's function, denoted $f_{SF}(\kappa a)$, is

$$f_{SF}(\kappa a) = \frac{16 + 18\kappa a + 3(\kappa a)^2}{16 + 18\kappa a + 2(\kappa a)^2}. \tag{6}$$

For all values of κa, this differs from Henry's formula by less than 0.1%. This is an order of magnitude improvement over the interpolation formula due to Ohshima [5],

$$f_O(\kappa a) = 1 + \frac{1}{2[1 + \delta/(\kappa a)]^3}, \tag{7}$$

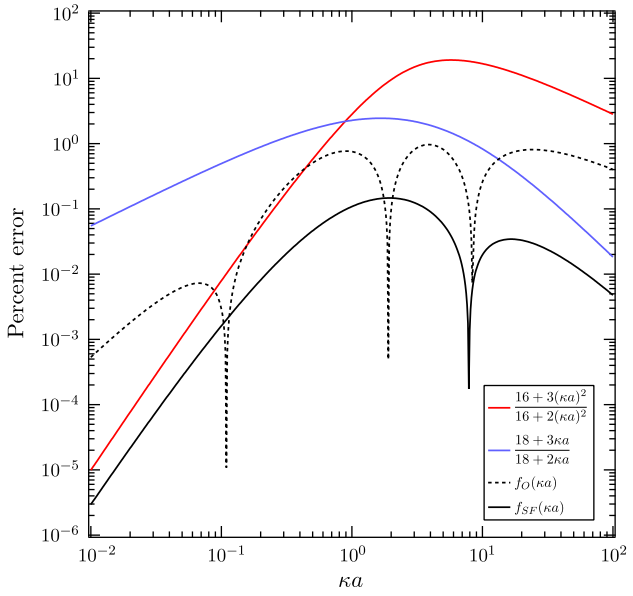

Fig. 2. The error in various approximations to Henry's formula is plotted as a function of double layer thickness. The formula proposed in Eq. (6) out performs that of Ohshima by an order of magnitude.

with $\delta = (5/2)[1 + 2\exp(-\kappa a)]^{-1}$. It is also superior to the limiting forms just discussed over the entire range of κa. The relative error in these approximations is plotted in Fig. 2.

The reason for this fortuitous agreement is made clear partly by examining the limits $\kappa a \ll 1$ and $\kappa a \gg 1$, for which Henry's formula takes on the particular scaling matched exactly by our approximation, *viz.*

$$f(\kappa a \ll 1) = f_{SF}(\kappa a \ll 1) = 1 + \left(\frac{\kappa a}{4}\right)^2, \tag{8}$$

and

$$f(\kappa a \gg 1) = f_{SF}(\kappa a \gg 1) = (3/2)\left(1 - \frac{3}{\kappa a}\right). \tag{9}$$

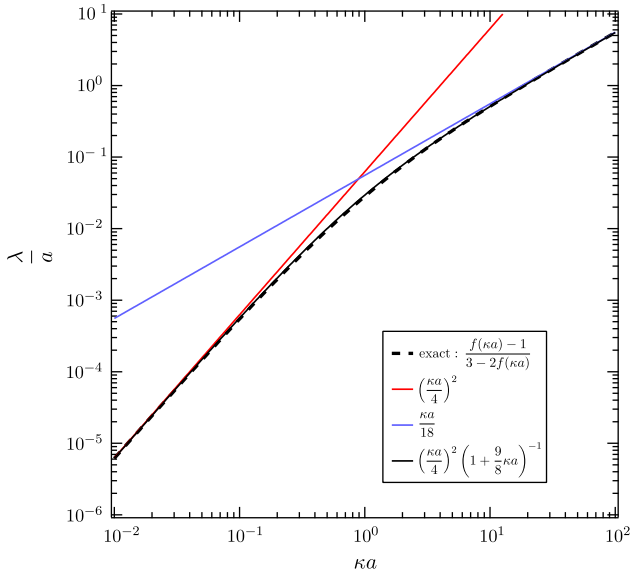

Fig. 1. On proposing an equivalence of mobilities, the slip length corresponding to a particular double layer thickness is plotted. We see that the slip length is quadratic in double layer thickness in the thick double layer limit, but linear in double layer thickness in the thin double layer limit.

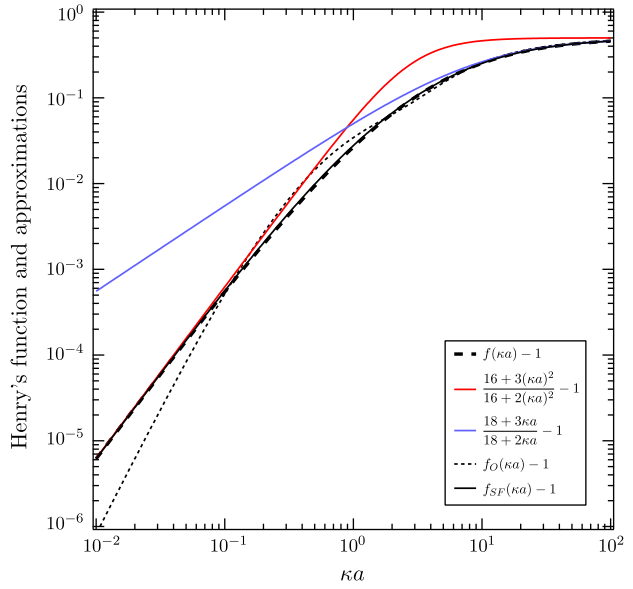

Fig. 3. Henry's formula and various approximations are plotted as a function of the double layer thickness. Eq. (6) is indistinguishable from the exact result over the entire range of κa.

Neither of these are reproduced correctly by the Ohshima interpolation. In fact, an expansion of Eq. (6) in double layer thickness to terms of the next order of magnitude yields coefficients that differ by only a small fraction from the value predicted by Henry's formula (30% for thick double layers, 2% for thin double layers). The result of Henry and the approximates discussed herein are plotted in Fig. 3.

The analogy between electrophoretic mobility and hydrodynamic mobility has its short-comings, however. Chiefly that the flow around a bubble is not irrotational while the flow around an electrophoretic particle in the thin double layer limit is. The contradiction comes from what we considered the origin of the thrust driving the motion. For the slipping particle, if we treat the effective thrust ($4\pi\epsilon\epsilon_0 a\zeta$) as external to the fluid system, then the irrotational flow cannot result. If however, the thrust comes from an appropriate surface flow, the proper flow far-field flow may be modeled as well. Anymore discussion in this vein is too much speculation for a note, however.

If we relax the restriction on the surface potential so that linearization of the electrostatic equations is not possible, the problem is too complex to solve analytically [6]. However, for a 1–1 electrolyte, it must have the form

$$\mu = \frac{2\epsilon\epsilon_0\zeta}{3\eta} f(\kappa a, \hat{\zeta}), \tag{10}$$

where $\hat{\zeta} = \zeta e/kT$ is the zeta potential made dimensionless on the thermal potential. In the limit that $\hat{\zeta} \to 0$, $f(\kappa a, \hat{\zeta})$ becomes Henry's function. Troublingly, this solution has a non-monotonic dependence on double layer thickness. Values of $f(\kappa a, \hat{\zeta})$ less than one are possible when the surface potential is large enough. The double layer polarization retards the electrophoretic motion in a way that is unaccounted for in Henry's approach. Conversely, the Smoluchowksi limit is never exceed.

Contrast that with the function $g(\lambda/a)$ for the slipping particle. For positive slip lengths, it varies monotonically in the range (1,3/2). However, for $\lambda/a > -1/3$, $g(\lambda/a)$ can take on any value in the range (0,3/2). Therefore equivalence of mobilities postulated earlier may still be applicable. A negative slip length corresponding to conditions where the electrophoretic mobility is smaller than the Hückle limit may even make some physical sense as the double layer polarization has the equivalent effect enhancing the Stokes drag.

Drawing on our experience with Henry's formula we might suspect that in the limit of thin double layers, the electrophoretic mobility is $\mu = \epsilon\epsilon_0\zeta/\eta[1 - A(\kappa a, \hat{\zeta})]$, where $A(\kappa a, \hat{\zeta})$ is a function of the surface potential, reduces to $3/(\kappa a)$ as $\hat{\zeta} \to 0$ and scales as $(\kappa a)^{-1}$ in the limit that $\kappa a \to \infty$. A number of asymptotic analyses conducted in the thin double layer limit confirm this form and are suitable approximations for $A(\kappa a, \hat{\zeta})$ [7,8]. There are many other approximations that extend Henry's result asymptotically beyond the limit of small surface potentials [9]. Any of these could be used to formulate an equivalent relationship in the thick double layer limit but with limits on applicability with increasing the zeta potential. A most useful approximation would be an asymptotic expansion of the electrophoretic mobility in powers of κa, in the limit $\kappa a \ll 1$ and valid for all surface potentials. This would have the form $\mu = 2\epsilon\epsilon_0\zeta/(3\eta)[1 + B(\kappa a, \hat{\zeta})]$. However, an exact result for $B(\kappa a, \hat{\zeta})$ valid for arbitrary $\hat{\zeta}$ has not been determined. Certainly, it must agree with Henry's formula, $(\kappa a/4)^2$, in the limit of small zeta potentials. An extension of the thick double layer problem in this manner is complicated by identification of a far-field boundary layer at which the charge neutralization condition is satisfied [10]. The present analysis suggests tantalizingly that this expansion could be used to form a simple and accurate approximation to the exact electrophoretic mobility valid for arbitrary double thickness and surface potential.

Following the same procedure as before (equating this mobility with that of a slipping particle), we find that in the thick double layer limit the slip length is $\lambda/a = B(\kappa a, \hat{\zeta})$ while in the thin double layer limit it is $\lambda/a = [6A(\kappa a, \hat{\zeta})]^{-1}$. We suggest the interpolation formula between thin and thick double layers $\lambda/a = B(\kappa a, \hat{\zeta})[1 + 6C(\kappa a, \hat{\zeta})]^{-1}$, which captures these two limits exactly when the function $C(\kappa a, \hat{\zeta}) \to 0$ as $\kappa a \to 0$ and $C(\kappa a, \hat{\zeta}) \to A(\kappa a, \hat{\zeta})B(\kappa a, \hat{\zeta}) \gg 1$ as $\kappa a \to \infty$. From this we have another simple formula for determining the electrophoretic mobility which may prove valid for arbitrary surface potentials:

$$f_{SF}(\kappa a, \hat{\zeta}) = \frac{1 + 6C(\kappa a, \hat{\zeta}) + 3B(\kappa a, \hat{\zeta})}{1 + 6C(\kappa a, \hat{\zeta}) + 2B(\kappa a, \hat{\zeta})}. \tag{11}$$

Testing this specific interpolation requires more data: the electrophoretic mobility represented as an asymptotic series in κa with $\kappa a \ll 1$ beyond the Hückle solution.

Acknowledgment

The authors gratefully acknowledge funding from NASA (Grant No. NNX10AE44G) and stimulating discussions prompted by the University of Delaware class, CHEG867 – Advanced Colloid Science.

References

[1] D.C. Henry, Proc. R. Soc. London, A 133 (1931) 106–129.
[2] E. Hückel, Phys. Z. 25 (1924) 204–210.
[3] M. von Smoluchowski, Bull. Int. Acad. Sci. Cracovie 8 (1903) 182–200.
[4] J. Happel, H. Brenner, Low Reynolds Number Hydrodynamics, Nijhoff, The Hague, 1983.
[5] H. Ohshima, J. Colloid Interface Sci. 168 (1994) 269–271.
[6] R.W. O'Brien, L.R. White, J. Chem. Soc., Faraday Trans. 2 (74) (1978) 1607–1626.
[7] S.S. Dukhin, B.V. Deryaguin, Surface and Colloid Science, vol. 7, Wiley, New York, 1974.
[8] R.W. O'Brien, R.J. Hunter, Can. J. Chem. 59 (1981) 1878–1887.
[9] R.J. Hunter, Zeta Potential in Colloid Science, Academic Press, London, 1981.
[10] H.A. Hamed, E. Yariv, J. Fluid Mech. 627 (2009) 341–360.