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Motion of a particle generated by chemical gradients Part 1. Non-electrolytes

By J. L. ANDERSON, M. E. LOWELL
AND D. C. PRIEVE
Department of Chemical Engineering, Carnegie-Mellon University,
Pittsburgh, PA 15213, U.S.A.

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When a particle is placed in a fluid in which there is a non-uniform concentration of solute, it will move toward higher or lower concentration depending on whether the solute is attracted to or repelled from the particle surface. A quantitative understanding of this phenomenon requires that the equations representing conservation of mass and momentum within the fluid in the vicinity of the particle are solved. This is accomplished using a method of matched asymptotic expansions in a small parameter L/a, where a is the particle radius and L is the length scale characteristic of the physical interaction between solute and particle surface. This analysis yields an expression for particle velocity, valid in the limit $L/a \to 0$, that agrees with the expression obtained by previous researchers. The result is cast into a more useful algebraic form by relating various integrals involving the solute/particle interaction energy to a measurable thermodynamic property, the Gibbs surface excess of solute Γ. An important result is that the correction for finite L/a is actually $O(\Gamma/C_\infty a)$, where C_∞ is the bulk concentration of solute, and could be $O(1)$ even when L/a is orders of magnitude smaller.

1. Introduction

A physical interaction between solute molecules and the interface separating two immiscible phases, one of which is fluid, can cause motion of one phase relative to the other when there is a concentration gradient of the solute parallel to the surface. One example is the 'Marangoni effect' experienced by drops placed in a fluid having a non-uniform concentration of a surfactant or a non-uniform temperature field, which alters the tension at the drop/continuous fluid interface. The surfactant or temperature gradient creates a stress on the drop surface which propels the drop toward regions of lower surface tension; that is, toward higher surfactant concentration or higher temperature (Young, Goldstein & Block 1959; Ruckenstein 1964). Another example involves ionic solutes, whose gradients usually generate electric fields, causing electrophoretic motion of charged drops or particles (Prieve *et al.* 1979).

Although the usual Marangoni motion is precluded by the no-slip condition at a fluid/solid interface, it has been argued theoretically that gradients of non-electrolytes can propel rigid particles through fluids (Dukhin & Derjaguin 1974) or generate osmotic flow through capillaries (Derjaguin, Dukhin & Koptelova 1972; Anderson & Malone 1974; Anderson 1981). The origin of such flows is the diffuse nature of the force field between solute molecules and solid surface, which enters directly in the fluid momentum equations, whereas this interaction is lumped into a boundary condition in the usual analysis of the Marangoni effect. That a rigid particle placed in a solute gradient should move can be understood by considering the case of attraction between solute and particle. Because of the gradient, there are more solute molecules interacting with one side of the particle compared to the opposite side, and hence the particle feels a pull toward higher solute concentration. Another way of looking at this motion is to consider the thermodynamic state of the particle: by moving toward higher concentration, the particle can adsorb more solute, thereby lowering its surface energy (Ruckenstein 1981).

Derjaguin, Dukhin & Korotkova (1961) and Derjaguin & Dukhin (1971) introduced the term 'diffusiophoresis' to denote the relative motion generated between two phases by a gradient in solute concentration. For the case in which the gradient is tangent to a plane solid/liquid interface and in which the potential energy $\phi(h)$ of any solute molecule depends solely on its normal distance h from the interface they obtained

$$U_{\text{rel}} = -\alpha\frac{kT}{\eta}\int_0^\infty h[\exp(-\phi/kT)-1]\,dh \tag{1.1}$$

for the tangential component of velocity of distant fluid relative to the solid, where α is the magnitude of the concentration gradient, η is the fluid viscosity, k is Boltzmann's constant and T is the temperature. The flow described by (1.1) is driven by a pressure gradient which balances the force field $-C(d\phi/dh)$ within the thin fluid layer ($h \lesssim L$), where C is the solute concentration. Because ∇C has a non-zero component parallel to the surface, the pressure gradient will also have a non-zero parallel component which can only be balanced by viscous forces generated by flow in that direction.

This result is expected to correctly predict the rate of osmotic flow through a cylindrical capillary, provided that the smallest radius of curvature is much larger than the range L of the solute–solid interaction. However, the applicability of (1.1) to the motion of a large solid sphere through an infinite fluid is less apparent: in this geometry, the curvature causes profound disturbances in the velocity and concentration fields which extend into the fluid a distance comparable to the sphere's radius. For example, the velocity field now has both normal and tangential components. Such disturbances were not considered in the analysis leading to (1.1).

In this paper we attempt a more rigorous analysis of the motion of a rigid spherical particle induced by the gradient in concentration of a non-electrolyte. In § 2, the solute concentration field is determined to $O(L/a)$ using matched asymptotic expansions, where L is the range of the solute–particle interaction and a is the particle radius. This analysis is done under conditions of small Péclet number, where convection can be neglected. Then Stokes's equation, modified to include the body force on fluid elements within range of the solute–particle interaction, is solved in § 3 to obtain the velocity of the particle. In § 4 this result is recast in terms of the Gibbs excess surface concentration Γ – an independently measurable quantity.

The leading term of our result coincides with the right-hand side of (1.1), indicating that the disturbances to the concentration and velocity fields caused by curvature do not alter the difference in velocity of the solid and distant fluid in the limit as $L/a \to 0$. The next higher-order term contains $\Gamma/C_\infty a$, where C_∞ is the undisturbed concentration of solute in the absence of the particle. This ratio can be comparable to unity even when $L/a \ll 1$. To neglect curvature effects, the particle must be large compared to both the range of the solute interaction and to the 'adsorption length' Γ/C_∞.

In part 2 of this work we shall analyse the motion of charged rigid spheres through fluids that are non-uniform in electrolyte concentration.

2. Concentration field about the particle

When a rigid particle of radius a is placed in a fluid that has a non-uniform concentration of solute, the solute concentration field is disturbed because (i) the solute molecules cannot penetrate the particle, and (ii) the solute molecules experience a short-range force near the surface of the particle. Let ϕ be the potential of mean force describing this short-range physical interaction between solute and particle such that $-\nabla\phi$ is the force exerted by the particle on the solute molecule located at position $\mathbf{x}$ relative to the centre of the particle. We shall assume throughout this paper that ϕ is only a function of $r = |\mathbf{x}|$, and that it decays to zero as $r-a$ approaches a characteristic distance L which is much smaller than the particle radius. The ratio of these two length scales is given the symbol λ:

$$\lambda \equiv L/a \ll 1. \tag{2.1}$$

If the undisturbed solute concentration field C_∞ is *uniform*, then by definition of ϕ

$$C_{\text{eq}}(r) = C_\infty \exp[-\phi/kT] \quad (r > a), \tag{2.2}$$

where C_{eq} is the equilibrium solute concentration. Thus C_{eq} differs appreciably from C_∞ only in the thin region $0 \leqslant r-a \lesssim L$, near the surface of the particle where ϕ is non-zero.

The situation of interest occurs when the undisturbed solute concentration depends on $\mathbf{x}$. We assume that the undisturbed field is linear over distances $O(a)$:

$$C_\infty = C_\infty(\mathbf{0}) + \mathbf{x}.(\nabla C_\infty)_0, \tag{2.3}$$

and define the z-axis to be directed along $(\nabla C_\infty)_0$. Owing to this gradient, the particle is expected to move at some constant but yet unknown velocity $\mathbf{U} = U\mathbf{i}_z$. In terms of a co-ordinate system moving at velocity $\mathbf{U}$, the mass-conservation equation for the solute is

$$\frac{\partial C}{\partial t} + \nabla.\mathbf{N} = 0, \tag{2.4a}$$

$$\mathbf{N} = -D\nabla C - \frac{D}{kT}C\nabla\phi + C\mathbf{v}, \tag{2.4b}$$

where C is the disturbed solute concentration, $\mathbf{v}$ is the velocity field of the fluid relative to the particle, and D is the solute diffusion coefficient, which is assumed independent of position. The boundary conditions associated with the above equation are

$$\mathbf{i}_r.\mathbf{N} = 0 \quad (r = a), \tag{2.5a}$$

$$C \rightarrow C_\infty(0) + \alpha z + \alpha U t \quad (r \rightarrow \infty), \tag{2.5b}$$

where $\alpha .= |(\nabla C_\infty)_0|$. The time-dependent term in (2.5*b*) makes the problem inherently unsteady; (2.4) and (2.5) cannot be transformed into a steady-state problem merely by defining a new concentration variable equal to $C - \alpha U t$ because an explicit time dependence would be introduced into (2.4*b*) through the $C\nabla\phi$ term.

To simplify (2.4) we make two assumptions. First, the connective term $C\mathbf{v}$ is negligible compared with the two other terms of (2.4*b*). This will be true if the Péclet number is very small:

$$\frac{aU}{D} \ll 1. \tag{2.6}$$

Secondly, the time $C_\infty/\alpha U$ for a significant change in concentration is much longer than the time a^2/D for the profile to relax to its pseudosteady state. In addition to (2.6), this requires

$$\frac{\alpha a}{C_\infty(0)} \lesssim 1. \tag{2.7}$$

Given these two constraints, the statement of solute conservation becomes

$$\nabla^2 C + (kT)^{-1}\nabla.(C\nabla\phi) = 0, \tag{2.8}$$

$$\frac{\partial C}{\partial r} + (kT)^{-1} C\frac{d\phi}{dr} = 0 \quad (r = a),$$

$$C \to C_\infty(0) + \alpha z \quad (r \to \infty).$$

Besides the removal of time dependence, the fluid velocity has been eliminated, which means that the equation for solute conservation is uncoupled from the fluid dynamics and, in principle, can now be solved directly for $C(\mathbf{x})$.

Further simplifications are possible. The radial co-ordinate and the potential energy are made dimensionless by

$$\rho \equiv r/a, \quad \Phi \equiv \phi/kT. \tag{2.9}$$

A concentration perturbation C^* is defined as the difference between the actual concentration and the equilibrium value that would exist if $\alpha = 0$ (given by (2.2)):

$$C^* \equiv C - C_\infty(0)\exp(-\Phi). \tag{2.10}$$

Recognizing the axisymmetric nature of the problem, we propose a solution of the form

$$C^* = \alpha a F(\rho)\cos\theta. \tag{2.11}$$

Substituting (2.9)–(2.11) into (2.8) gives

$$F'' + \left[\frac{d\Phi}{d\rho} + \frac{2}{\rho}\right]F' + \left[\frac{d^2\Phi}{d\rho^2} + \frac{2}{\rho}\frac{d\Phi}{d\rho} - \frac{2}{\rho^2}\right]F = 0, \tag{2.12}$$

$$F' + \frac{d\Phi}{d\rho}F = 0 \quad (\rho = 1),$$

$$F \to \rho \quad (\rho \to \infty).$$

Even though (2.12) is linear, a solution for F for arbitrary Φ is not apparent. The equation seems to have two distinct regions: very near the particle surface all terms involving Φ are important; but at distances much greater than L from the surface, Φ and its derivatives are zero, and hence the solution to F should be of the form $\rho + B\rho^{-2}$. This dichotomy suggests the strategy of matched expansions with a power series in the small parameter λ.

In what follows, we assume that Φ has the form

$$\Phi = \Phi(y) = O(y^{-n}) \quad \text{as} \quad y \to \infty, \tag{2.13a}$$

where

$$y \equiv (r-a)/L = (\rho-1)/\lambda, \tag{2.13b}$$

and n is a positive number that represents the order of the decay. Using y as the inner variable, we seek a solution to (2.12) in the inner region that, in the limit $\lambda \to 0$, has the form

$$F = F^{i} = f_0^{i}(y) + f_1^{i}(y)\lambda + f_2^{i}(y)\lambda^2 + \dots \quad (\rho - 1 \lesssim \lambda). \tag{2.14}$$

In the outer region, a similar asymptotic expansion is assumed, except that the coefficients are functions of the outer variable ρ instead of y:

$$F = F^{o} = f_0^{o}(\rho) + f_1^{o}(\rho)\lambda + f_2^{o}(\rho)\lambda^2 + \dots \quad (\rho - 1 \gg \lambda). \tag{2.15}$$

The inner solution F^{i} must satisfy the boundary condition at $\rho = 1$, while F^{o} must satisfy the condition at $\rho \to \infty$. The two solutions will later be matched to eliminate the remaining integration constants of each and obtain a composite solution.

We consider the outer region first. From (2.13*a*) $d\Phi/d\rho$ and $d^2\Phi/d\rho^2$ are $O(\lambda^n)$ as $\lambda \to 0$ for constant ρ. Substitution of (2.15) into (2.12) and matching terms of like order in λ gives, for $j < n$,

$$\frac{d^2 f_j^{o}}{d\rho^2} + \frac{2}{\rho}\frac{df_j^{o}}{d\rho} - \frac{2}{\rho^2} f_j^{o} = 0, \tag{2.16}$$

$$\left.\begin{aligned} &f_0^{o} \to \rho \quad (j = 0), \\ &f_j^{o} \to 0 \quad (1 \leqslant j < n) \end{aligned}\right\} \quad (\rho \to \infty).$$

These equations are easily solved; combining the results gives the outer solution

$$F^{o} = \rho + [B_0 + B_1\lambda + B_2\lambda^2 + \dots]\rho^{-2}, \tag{2.17}$$

where B_j are the remaining integration constants.

The equations for the inner coefficients are obtained by substituting (2.14) into (2.12) and collecting terms of like order in λ:

$$\frac{d}{dy}\left[\frac{df_m^{i}}{dy} + \frac{d\Phi}{dy} f_m^{i}\right] = \Lambda_m, \quad \frac{df_m^{i}}{dy} + \frac{d\Phi}{dy} f_m^{i} = 0 \quad (y = 0), \tag{2.18}$$

where

$$\Lambda_0 = 0,$$

$$\Lambda_1 = -2\left[\frac{df_0^{i}}{dy} + \frac{d\Phi}{dy} f_0^{i}\right],$$

$$\Lambda_2 = -y\Lambda_1 + 2f_0^{i} - 2\left[\frac{df_1^{i}}{dy} + \frac{d\Phi}{dy} f_1^{i}\right].$$

The above equations are solved with $m = 0, 1, 2$ and combined to obtain

$$F^{i} = [b_0 + b_1\lambda + (b_2 + b_0 I(y))\lambda^2 + \dots]\exp(-\Phi), \tag{2.19}$$

where

$$I = 2\int_0^{y} \exp\Phi(\xi)\,d\xi \int_0^{\xi} \exp[-\Phi(u)]\,du,$$

and b_m are the remaining integration constants.

The function I arises from the particular solution for f_2^{i} and becomes unbounded as $y \to \infty$. Adding and subtracting unity to the integrands, this integral can be related to a bounded integral:

$$I(y) = y^2 + 2yK/L + J(y), \tag{2.20}$$

where

$$J(y) \equiv 2\int_0^y \left\{\xi\,[\exp \Phi(\xi) - 1] + \exp(\Phi(\xi)) \int_0^\xi [\exp(-\Phi(u)) - 1]\,du - \frac{K}{L}\right\} d\xi, \tag{2.21a}$$

and

$$K \equiv L \int_0^\infty [\exp(-\Phi(y)) - 1]\,dy \tag{2.21b}$$

is a characteristic length associated with the 'Gibbs excess' to be discussed later. The integral $J(y)$ remains bounded as $y \to \infty$ provided that $n > 2$ (see 2.13a).

Using Van Dyke's (1964) method to match the three-term inner and outer expansions yields the following three relations among the integration constants:

$$\lambda^0{:}\quad b_0 = 1 + B_0,$$

$$\lambda^1{:}\quad b_1 = B_1 + (1 - 2B_0)\,y,$$

$$\lambda^2{:}\quad b_2 + b_0\left[y^2 + 2\left(\frac{K}{L}\right)y + J(\infty)\right] = B_2 - 2B_1 y + 3B_0 y^2.$$

Matching terms having like powers of y yields

$$b_0 = 3B_0 = \tfrac{3}{2},$$

$$b_1 = B_1 = -\frac{3K}{2L},$$

$$b_2 = B_2 - \tfrac{3}{2}J(\infty).$$

While four of the six integration constants are determined uniquely by this method, only a relation between b_2 and B_2 is obtained. To get a second relation between them, another term in the inner and outer expansion would be required. Substituting the known constants into (2.17) and (2.19) gives

$$F(\rho, \lambda) \simeq F^{\mathrm{i}}(y, \lambda) = \frac{3}{2}\left(1 - \frac{K}{L}\lambda\right)\exp(-\Phi(y)) + O(\lambda^2) \tag{2.22a}$$

as $\lambda \to 0$ for $y \lesssim 1$, and

$$F(\rho, \lambda) \simeq F^{\mathrm{o}}(\rho, \lambda) = \rho + \frac{1}{2}\left(1 - 3\frac{K}{L}\lambda\right)\rho^{-2} + O(\lambda^2) \tag{2.22b}$$

as $\lambda \to 0$ for $\rho - 1 \gg \lambda$.

For the purpose of comparison, the boundary-value problem (2.12) was also solved numerically for each of two assumed forms of $\Phi(y)$:

$$\Phi(y) = A_1 \exp(-y), \tag{2.23a}$$

$$\Phi(y) = A_2[(y+1)^{-9} - (y+1)^{-3}]. \tag{2.23b}$$

A fourth-order Runge–Kutta method was used. Some of the results are summarized in figure 1. If (2.22a) is correct, the intercept of this plot should equal

$$-\tfrac{3}{2}(K/L)\exp\Phi(0).$$

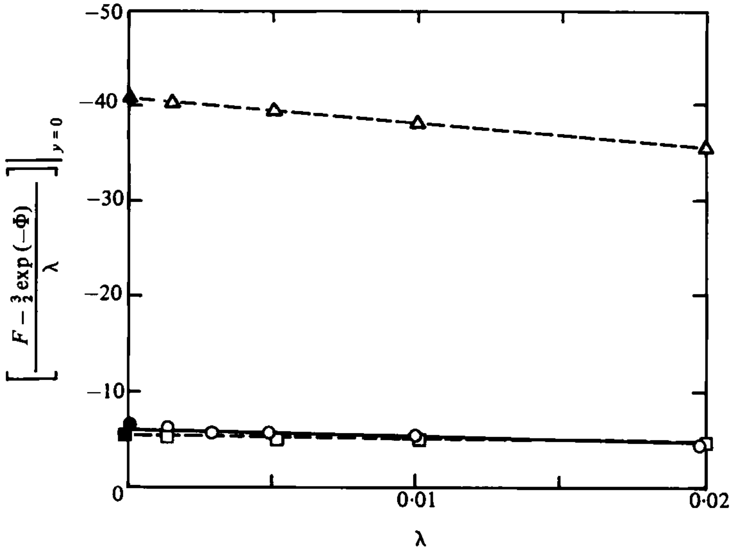

FIGURE 1. A comparison of the solution to (2.12) at $y = 0$ obtained numerically for finite λ (plotted as open symbols), with $-\frac{3}{2}(K/L)\exp[-\Phi(0)]$ predicted by (2.22*a*) for the asymptote $\lambda \rightarrow 0$ (plotted as filled symbols). Squares and triangles are results obtained using (2.23*a*) with A_1 equal to -1 and -2 respectively; circles are results obtained using (2.23*b*) with $A_2 = 5.09$ (yields the same K/L as for $A_1 = -2$).

The predicted intercepts agree with the corresponding values extrapolated from the numerical solution. Furthermore, the linearity of the curves in figure 1 confirms that the next-higher term in (2.22*a*) is $O(\lambda^2)$, as predicted. Comparison between the numerical solution and (2.22*a*) at other values of y shows the same agreement, thereby supporting our analytical solution to $O(\lambda)$.

It is possible to obtain the leading term of (2.22*a*) using a more intuitive approach. Recognizing that the solute–particle interaction is negligible nearly everywhere, (2.8) is first solved with $\Phi = 0$ to obtain

$$C_0(\rho,\theta) = C_\infty(0) + \alpha a[\rho + \tfrac{1}{2}\rho^{-2}]\cos\theta. \tag{2.24}$$

Next, it is assumed that the solute within the thin layer on the surface of the sphere (where $\Phi \neq 0$) is in equilibrium with solute just outside the layer, or

$$C = C_0(1,\theta)\exp(-\Phi). \tag{2.25}$$

Substituting (2.24), one obtains

$$C = [C_\infty(0) + \tfrac{3}{2}\alpha a\cos\theta]\exp(-\Phi). \tag{2.26}$$

If (2.26) is used with (2.10) and (2.11) to evaluate F, the leading term (i.e. $\lambda = 0$) of (2.22*a*) is obtained. Although this derivation is successful in arriving at the correct zeroth-order expression for F, it is not clear how it can be extended to obtain the first-order term.

The appearance of K/L as the coefficient of the $O(\lambda)$ term is significant, because it can be rather large even if λ is quite small. In reality, then, the first correction is $O(K/a)$. In figure 2 we show the mathematical meaning of K as an integral. In physical

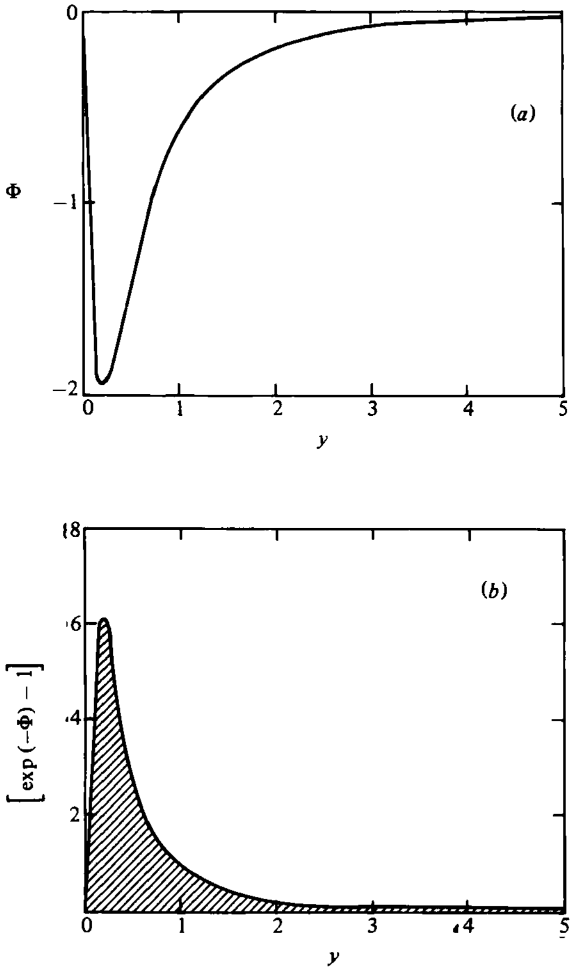

FIGURE 2. (*a*) Potential-energy profile of (2.23*b*) with $A_2 = 5.09$. (*b*) Local surface excess of solute for the same potential. Area under curve equals K/L.

terms, it is proportional to the excess amount of solute per area that accumulates near the particle owing to the potential Φ, as discussed in §4. The value of K can often be determined experimentally by straightforward material balances, and a value as large as 10^{-4} cm is not uncommon for surface-active agents (Berg 1972). In general, K and L are uncorrelated, and each represents an important parameter characterizing Φ; K depends primarily on the depth of the energy well of a potential as shown in figure 2. However, if the interaction between solute and particle is repulsive on the average, so that $K < 0$, then K and L should be of comparable magnitude.

3. Derivation of the particle velocity

The coupling between the disturbed concentration field and the force field $-\nabla\phi$ produces stresses near the particle surface that result in motion of the fluid. This is because $-C\nabla\phi$ is a body force which depends on θ through C. The fluid equations at negligibly small Reynolds number are

$$\nabla . \mathbf{v} = 0, \tag{3.1}$$

$$\eta\nabla^2\mathbf{v} - \nabla p - C\nabla\phi = 0, \tag{3.2}$$

$$\mathbf{v} = 0 \quad (r = a),$$

$$\mathbf{v} \to -U\mathbf{i}_z \quad (r \to \infty),$$

where U is the unknown particle velocity. A stream function defined by

$$\mathbf{v} = \frac{\mathbf{i}_\phi}{r\sin\theta} \times \nabla\psi(r,\theta) \tag{3.3}$$

automatically satisfies (3.1). This expression is substituted into (3.2), and the curl of both sides is taken to eliminate the pressure. A solution of the form

$$\psi = G(\rho)\sin^2\theta \tag{3.4}$$

is sought. The resulting equation for G that must be solved is

$$\left.\begin{aligned} S'' - \frac{2}{\rho^2}S &= \frac{\alpha a^4 kT}{\eta}\frac{d\Phi}{d\rho}F, \\ G'' - \frac{2}{\rho^2}G &= S, \end{aligned}\right\} \tag{3.5}$$

$$G = G' = 0 \quad (\rho = 1),$$

$$G \to \tfrac{1}{2}Ua^2\rho^2 \quad (\rho \to \infty).$$

Since our objective is to derive a relationship for U in terms of the other parameters, another physical constraint is needed. This is achieved by considering a spherical surface at $r = R^*$ that encloses the particle and surrounding fluid. If $R^* - a \gg L$ then there is no interaction between solute molecules and particle surface when $r > R^*$; hence the net force acting on the body contained within $r < R^*$ is zero, and the total fluid force must also be zero:

$$\iint_{r=R^*} \mathbf{i}_r . \mathbf{\Pi}\, dA = \mathbf{0}, \tag{3.6}$$

where $\mathbf{\Pi}$ is the fluid stress tensor. This zero-force constraint means that the velocity field is irrotational outside the interaction layer, as is the case for electrophoretic flows (Morrison 1970). In terms of the radial part of the stream function, (3.6) can be written as (Happel & Brenner 1965)

$$\lim_{\rho\to\infty}\left[\frac{G - \frac{1}{2}Ua^2\rho^2}{\rho}\right] = 0. \tag{3.7}$$

By forcing the solution of (3.5) to satisfy (3.7) one can find the particle velocity U.

The solution of (3.5) is obtained directly by first solving the homogeneous case ($\Phi = 0$) and then using the method of variation of parameters to find a particular solution:

$$G = A_1 \rho^{-1} + A_2 \rho + A_3 \rho^2 + g, \tag{3.8}$$

$$g = \tfrac{1}{3} \int_{\rho_0}^{\rho} [\rho^2 t^{-1} - \rho^{-1} t^2]\, s(t)\, dt, \tag{3.9a}$$

$$s = \tfrac{1}{3} \Lambda \int_{\rho_0}^{t} [t^2 u^{-1} - t^{-1} u^2] \frac{d\Phi}{du} F(u)\, du, \tag{3.9b}$$

$$\Lambda = \frac{\alpha a^4 kT}{\eta},$$

where ρ_0 is an arbitrary integration limit. Applying the boundary conditions as well as (3.7), an expression for the particle velocity results:

$$U = -\tfrac{2}{3} a^{-2} \left\{ \left[g + \frac{dg}{d\rho} \right] \bigg|_{\rho=1} - 2 \lim_{\rho \to \infty} \left(\frac{g}{\rho} \right) \right\}. \tag{3.10}$$

We propose a regular expansion for s and g:

$$g = g_0(y) + g_1(y)\, \lambda + g_2(y)\, \lambda^2 + \ldots, \tag{3.11a}$$

$$s = s_0(y) + s_1(y)\, \lambda + s_2(y)\, \lambda^2 + \ldots. \tag{3.11b}$$

We anticipate that $g \to 0$ for $y \gg 1$, but there are problems for certain types of potential functions, as discussed later. Substituting (3.11b) and (2.22a) into (3.9b) and changing the integration variable from ρ to y, one obtains

$$s = \tfrac{3}{2} \Lambda \lambda \left[1 - \frac{K}{L} \lambda \right] \int_{y_0}^{y} (y - x)\, \Phi'(x) \exp[-\Phi(x)]\, dx + O(\lambda^3). \tag{3.12}$$

After integrating by parts and setting $y_0 = \infty$, the above becomes

$$s = \tfrac{3}{2} \Lambda \lambda \left[1 - \frac{K}{L} \lambda \right] \int_{y}^{\infty} [\exp[-\Phi(x)] - 1]\, dx + O(\lambda^3). \tag{3.13}$$

This expression is now substituted into (3.9a) to obtain

$$g = -\tfrac{3}{2} \Lambda \lambda^3 \left[1 - \frac{K}{L} \lambda \right] \int_{y}^{\infty} (y - w)\, dw \int_{w}^{\infty} [\exp[-\Phi(x)] - 1]\, dx + O(\lambda^5). \tag{3.14}$$

The particle velocity is found by substituting (3.14) into (3.10):

$$U = U_0 \left[1 - \left(\frac{K}{L} + H \right) \lambda + O(\lambda^2) \right], \tag{3.15}$$

$$U_0 = \frac{\alpha L^2 kT}{\eta} \int_0^{\infty} y\, [\exp[-\Phi(y)] - 1]\, dy, \tag{3.16a}$$

$$H = \frac{\displaystyle\int_0^{\infty} \tfrac{1}{2} y^2\, [\exp[-\Phi(y)] - 1]\, dy}{\displaystyle\int_0^{\infty} y\, [\exp[-\Phi(y)] - 1]\, dy}. \tag{3.16b}$$

Equation (3.16*a*) is the same as the result obtained by Dukhin & Derjaguin (1974) for the limit $\lambda \rightarrow 0$. Their derivation is based on analogy with osmosis through a membrane having capillary pores whose radius r_0 is much greater than L. In the osmotic system, ϕ is the interaction potential between solute and pore wall (Anderson & Malone 1974). The osmotic velocity of the fluid, which is caused by the solute gradient along the pore axis, equals $-U_0$, since in osmosis the solid surface (membrane) is fixed and the solution flows. Osmotic flow and the particle motion considered here are simply related by a change in reference in the limit $\lambda \rightarrow 0$; however, the analogy between these two phenomena fail when the $O(\lambda)$ correction is considered. If y is defined as the distance from the pore wall normalized by L, then straightforward expansion in powers of λ of the relevant formula for osmotic flow in a circular capillary (Anderson 1981) gives

$$U_{\text{osmosis}} = -U_0[1 - \tfrac{3}{2}H\lambda + O(\lambda^2)], \tag{3.17}$$

where U_0 and H are given by (3.16*a*, *b*). The K/L term, which is extremely important, does not exist in the case of osmotic flow.

Equation (3.15) has an important mathematical limitation: the integral for H only converges if $\lim (y^3\Phi) = 0$ as $y \rightarrow \infty$. Thus, our result for the first-order term is valid for exponential functions such as (2.23*a*), but not Lennard-Jones-type potentials such as (2.23*b*), whose far-field exponent is 3. This limitation is perhaps an artefact, however, of assuming $\Phi(y)$ to be independent of λ. An actual potential arising from van der Waals forces should depend on both y and λ and, in fact, should go as y^{-6} when $\rho \gg 1$ since the particle begins to appear as a point mass. As discussed in §4 the dependence of Φ on y is never known in practice, so that the result (3.15)–(3.16) still has significant utility in that a wide variety of potential functions can be examined in an effort to relate U to some average of the solute/particle interaction. Discussion of this approach is given in §4.

4. Discussion

The usefulness of (3.16*a*) for computing U_0 is limited by the fact that the precise form of $\Phi(y)$ is not known or measurable. One measurable physical property is the Gibbs excess surface concentration Γ (solute molecules/area of particle surface), which is related to K under equilibrium conditions by

$$\Gamma = C_\infty K,$$

where K is given by (2.21*b*), and C_∞ is uniform far from the particle (when $\alpha = 0$). Γ is an *equilibrium* property of the solute/particle interaction. If we define a new length L^* by

$$L^* \equiv L \frac{\displaystyle\int_0^\infty y[\exp(-\Phi) - 1]\,dy}{\displaystyle\int_0^\infty [\exp(-\Phi) - 1]\,dy}, \tag{4.1}$$

the zeroth-order particle velocity is rewritten as

$$U_0 = \frac{\alpha kT}{\eta} L^* K, \tag{4.2}$$

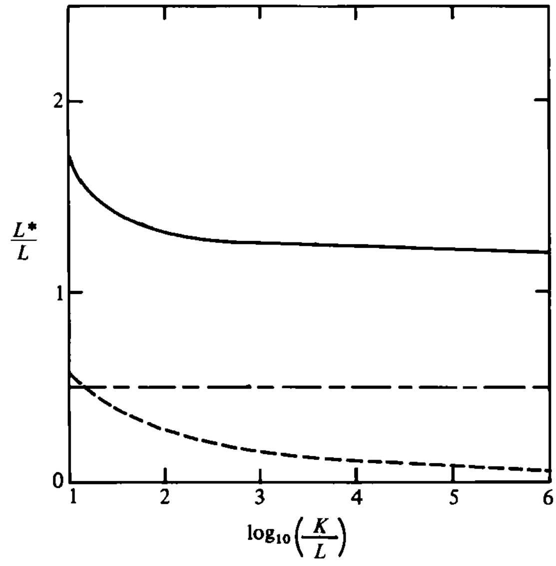

FIGURE 3. Dependence of L^*/L (see (4.1)) on surface excess parameter K. Attractive potentials ($K > 0$). ——, Lennard-Jones ((4.3c), $n = 9$, $m \doteq 3$); — — —, square well (4.3a); - - - -, exponential (4.3b).

Figures 3 and 4 show that L^*/L does not differ much from unity over a large range in K for the following forms of the potential energy function:

$$\left.\begin{aligned} \Phi &= \Phi_0 \quad (0 \leqslant y < 1) \\ &= 0 \quad (1 < y), \end{aligned}\right\} \tag{4.3a}$$

$$\Phi = \Phi_0 \exp(-y), \tag{4.3b}$$

$$\Phi = \Phi_0 [y^{-n} - y^{-m}] \quad (\Phi_0 > 0). \tag{4.3c}$$

For the case of (4.3c), if $\Phi_0 \gg 1$ then

$$\frac{L^*}{L} \simeq \left(\frac{n}{m}\right)^{1/(n-m)} \simeq 1{\cdot}2,$$

as long as $n > m$. For the square-well form (4.3a), $L^*/L = \frac{1}{2}$ for all Φ_0.

An example calculation demonstrates that U_0 can be large relative to other transport phenomena. Consider a 1 μm particle of specific gravity 1·1 in aqueous solution at 20 °C ($\eta = 0{\cdot}01\,\mathrm{g\,cm^{-1}\,s^{-1}}$). Suppose that $K = 0{\cdot}1\,\mu\mathrm{m}$, $\alpha = 10^{-3}\,\mathrm{mol\,cm^{-4}}$ and $L^* \simeq 10\,\mathrm{Å}$. Equation (4.2) predicts $U_0 = 24\,\mu\mathrm{m\,s^{-1}}$. For comparison, the sedimentation velocity by gravity is only $0{\cdot}2\,\mu\mathrm{m\,s^{-1}}$, and the Brownian diffusion velocity for distances of $100\,\mu$m is only $0{\cdot}002\,\mu\mathrm{m\,s^{-1}}$.

In many physical systems the solute/particle interaction is governed by a Langmuir adsorption isotherm

$$\Gamma = \frac{K_0 C_\infty}{1 + K_0 C_\infty / \Gamma_{\mathrm{sat}}}, \tag{4.4}$$

which is linear at low solute concentrations but displays saturation at higher concentrations. The analyses in §§2 and 3 implicitly assume that Φ is independent of local

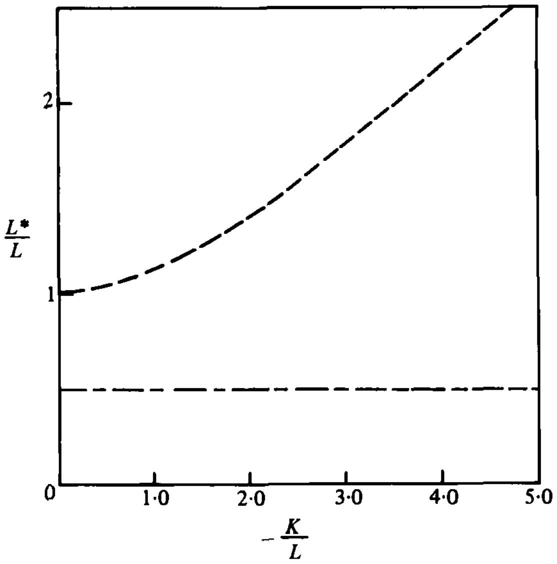

FIGURE 4. Dependence of L^*/L (see (4.1)) on surface excess parameter K. Repulsive potentials ($K < 0$). - - -, exponential (4.3*b*); — — —, square well (4.3*a*).

solute concentration, while (4.4) can only result if the opposite is true. However, our results are valid, even for a Langmuir isotherm, if concentration changes in the vicinity of the particle are sufficiently small that locally Φ is only a function of y. This condition is satisfied as long as the macroscopic (undisturbed) solute gradient is small:

$$|\alpha| \ll \Gamma_{\text{sat}}/3K_0 a. \tag{4.5}$$

For the example in the previous paragraph and $\Gamma_{\text{sat}} = 1{\cdot}7 \times 10^{-10}\,\text{mol cm}^{-2}$ (one molecule 'adsorbed' per 100 Å^2), the gradient must be smaller than about 0·05 mol cm^{-4}, which is probably the case in most situations. An interesting consequence of (4.4) is the concentration dependence of K:

$$K = \frac{K_0}{1+(K_0/\Gamma_{\text{sat}})C_\infty}. \tag{4.6}$$

From (4.2) we see that at low solute concentrations U_0/α is constant but goes as C_∞^{-1} at high concentrations. Since both K_0 and Γ_{sat} are measurable the veracity of (4.2) can be determined experimentally by measuring the dependence of particle velocity on solute concentration at constant gradient.

Our result for U_0 can be related to changes in interfacial energy by recalling that K is given by the following formula derived by Gibbs (Adamson 1967), which is valid when the solution is thermodynamically ideal:

$$K = -\frac{1}{kT}\frac{\partial\gamma}{\partial C_\infty}, \tag{4.7}$$

where γ is the interfacial excess energy (or 'surface tension') between solution and particle surface. Substituting this expression into (4.2) gives

$$U_0 = \frac{L^*}{\eta}\left(-\frac{\partial\gamma}{\partial C_\infty}\right)\alpha. \tag{4.8}$$

This relationship resembles that for the velocity of a small spherical *fluid* drop moving through a second fluid containing a surface-active solute having concentration gradient α. Young *et al.* (1959) solved the fluid equations for this system in the zero-Péclet-number limit and obtained the following:†

$$U_{\mathrm{M}} = \frac{1}{3\sigma+2}\frac{a}{\eta}\left(-\frac{\partial\gamma}{\partial C_\infty}\right)\alpha. \tag{4.9}$$

The subscript M denotes 'Marangoni effect', and $\sigma = \eta_{\mathrm{i}}/\eta$, where η_{i} is the viscosity of the fluid inside the drop. There are two important differences between (4.8) and (4.9). First, $U_0 \sim L^*$ while $U_{\mathrm{M}} \sim a$, and these two length scales differ by orders of magnitude in general. Second, $U_{\mathrm{M}} \rightarrow 0$ for the case of a rigid drop ($\sigma \rightarrow \infty$). These two differences result from the same source, namely, that in the Young *et al.* analysis all interfacial effects (solute–surface interactions) are assumed to be included in the tension γ that acts within an infinitely thin plane at the interface. The gradient of this tension appears only in the stress balance on the drop surface; that is, in the boundary condition and not in the momentum equation itself. As shown below, this treatment results in the omission of a stress term that is distributed throughout the thin region of thickness L where the solute feels the presence of the interface.

We now reconsider our analysis of §3 in the $\lambda \rightarrow 0$ limit for the case of a particle which is fluid. The subscript i refers to the region $r < a$, or $\rho < 1$. We assume that the solute cannot enter the inside of the drop, so the previous results for F remain valid. The equation for the radial part of the internal stream function $G_{\mathrm{i}}(\rho)$ is

$$\left.\begin{aligned} S_{\mathrm{i}}'' - \frac{2}{\rho^2}S_{\mathrm{i}} &= 0, \\ G_{\mathrm{i}}'' - \frac{2}{\rho^2}G_{\mathrm{i}} &= S_{\mathrm{i}}. \end{aligned}\right\} \tag{4.10}$$

The equation for the stream function $G(\rho)$ outside the drop ($\rho > 1$) is still given by (3.5). The boundary conditions for the two stream functions are

$$\left.\begin{aligned} G_{\mathrm{i}} = G = 0, \quad G_{\mathrm{i}}' = G' = 0, \\ (\rho^{-2}G_{\mathrm{i}}')' = (\rho^{-2}G')' \quad \text{(stress balance at particle surface)}, \end{aligned}\right\} \quad (\rho = 1)$$

$$G \rightarrow \tfrac{1}{2}Ua^2\rho^2 \quad (\rho \rightarrow \infty).$$

The solution of (3.5) and (4.10) in the limit $\lambda \rightarrow 0$ with these boundary conditions and the constraint (3.7) yields the following:

$$\begin{aligned} U_0 &= \frac{\alpha kT}{\eta}\frac{3\sigma L^* + a}{3\sigma+2}K \\ &= \frac{1}{\eta}\frac{3\sigma L^* + a}{3\sigma+2}\left(-\frac{\partial\gamma}{\partial C_\infty}\right)\alpha. \end{aligned} \tag{4.11}$$

Because $L^* \ll a$, when $\sigma \simeq 1$ this result is equivalent to U_{M}, while (4.2) or (4.8) is obtained in the limit $\sigma \rightarrow \infty$. We see that if the particle interior is a fluid of viscosity comparable to that of the surrounding fluid, then collapsing all the interfacial forces into an equivalent tension acting at the surface is a valid strategy, but when the particle is rigid the distributed nature of the solute–surface interaction (i.e. $\Phi(y)$) must

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† Young *et al.* actually consider a spherical drop in a fluid with a temperature gradient. The result here is for the case of an insulated drop; that is, no solute can enter the fluid inside the drop.

be included explicitly in the fluid equations. Colloid physicists have long recognized the essential nature of distributed surface forces in their dealings with the electrical double layer and associated electrokinetic phenomena. More recently, Brenner & Leal (1977, 1978) have emphasized this point in developing two-dimensional conservation equations from a three-dimensional analysis of transport near interfaces.

The parameter H appearing in the $O(\lambda)$ term of (3.15) should be approximately unity or less. For the square-wall potential given by (4.3a) its value is exactly $\frac{1}{2}$. Thus the K/L factor probably dominates the $O(\lambda)$ term. As emphasized at the end of § 2, this means that the correction to U_0 for curvature is $O(K/a)$, and could be about unity or greater in many cases, even when the particle is quite large. For attractive solute–particle interactions ($K > 0$) the $O(\lambda)$ term reduces U below U_0, while in the case of repulsion ($K < 0$) the $O(\lambda)$ term augments U_0. However, for repulsive interactions one can show that the magnitude of K/L is around unity, and hence the $O(\lambda)$ term is probably not important in these cases for particles $10^{-1}\,\mu$m or larger.

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