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Interfacial Resistance to Interphase Mass Transfer in Quiescent Two-Phase Systems

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Interfacial resistance to solute mass transfer between two unstirred immiscible fluids is theoretically calculated. Solute molecules are modeled as Brownian particles, bathed by homogeneous fluid continua when wholly immersed in either fluid, or else by heterogeneous fluid continua when instantaneously straddling the interface. These diffusing particles are assumed to be subjected to either repulsive or attractive conservative forces exerted on them by the interface. Additionally, their mobility is supposed affected by proximity to the interface. Circumstances are found to exist under which the interface may offer significant resistance to interphase transport. Surprisingly, conditions also exist in which the interface may actually offer a negative resistance to such solute transfer. In such cases, the presence of the interface enhances the overall interphase mass transfer rate.

SCOPE

Solute mass transfer between two immiscible fluids is of fundamental importance in a variety of industrial operations and research activities. Little is known, however, of the resistance offered by the interface itself to solute transfer across it, except that it can be appreciable in some systems (Davies and Rideal, 1963; Chandrasekhar and Hoelscher, 1975) compared with that offered by the individual bulk fluids. This paper reports upon a theoretical study of interphase mass transfer in a quiescent unstirred system, across which a steady concentration gradient is maintained, normal to the interface. This represents the simplest class of such transport problems.

The diffusing solute molecules are modeled as spherical Brownian particles, subject to external forces exerted on them by the interface. Independently, their Brownian diffusivity is decreased by their relative proximity to the interface. Such anomalous effects are important only in the domain extending several sphere radii a on either side of the interface. Beyond this region, ordinary unhindered bulk diffusion concepts apply. In this sense, the anomalous region immediately surrounding the interface plays the role of a transition layer, smoothly and continuously joining together the otherwise discontinuous bulk properties associated with the particles in each of the two fluids bounding the layer.

Local equilibrium is not assumed to exist at the interface. Indeed, at the microscopic level of description of the problem, appropriate to an observer able to resolve concentration variations on length scales of order a, the solute concentration varies continuously across the interface, from one bulk value to the other. As such, the conventional concept of interphase solute equilibrium is devoid of meaning. Rather, the concept is meaningful only at a macroscopic or bulk level, corresponding to a macroscopic length scale $L >> a$. Viewed from this length scale, the local solute concentration will appear discontinuous across the interface. The origin of interfacial resistance, which is a macroscopic concept, resides in viewing particle transport through the transition region from the vantage point of a macroscopic observer at the length scale L.

The object of this investigation consisted of developing a quantitative theory of the phenomenon, in which the resistance offered by the interface itself could be related to the fundamental microscopic physical parameters of the system, namely, the potential energy function characterizing the repulsive and/or attractive forces and the position-dependent particle diffusivity.

CONCLUSIONS AND SIGNIFICANCE

The interfacial resistance to solute mass transfer across a two-fluid layer of specified thickness $L = L_1 + L_2$ was defined as the difference between the overall resistance and the sum of the diffusional resistances of the individual bulk fluid layers of thicknesses L_1 and L_2, respectively. This led ultimately to a quantitative expression for the interfacial resistance containing two parametric functions: the position-dependent potential energy function, governing the repulsive or attractive forces exerted on the Brownian solute molecules by the interface, and the variation of the Brownian diffusion coefficient with distance of the sphere center from the interface.

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Neither of these two functions are presently available, either theoretically or experimentally. Hence, numerical values of the interfacial resistance are not yet available for comparison with existing data (Davies and Rideal, 1963; Chandrasekhar and Hoelscher, 1975). Nevertheless, the theory clearly shows that one may expect to encounter positive interfacial resistance in circumstances where the interface derived force exerted on a Brownian particle is repulsive in nature.

Conversely, in situations where the force is attractive (that is, adsorptive), the interfacial resistance may actually be negative, indicating an enhanced, rather than diminished, interphase transport rate. Though this interfacial enhancement effect does not yet appear to have been observed experimentally, the a priori circumstances under which it may be expected to occur are delineated. Experimental detection of such an effect would do much to lend credence to the present theory.

The normal continuum description of the interphase transport of a solute between two immiscible fluids is that appropriate to the length scale L which characterizes the bulk concentration gradient normal to the interface. Empirical observations on this (macro) scale (Davies, 1963; Davies and Rideal, 1963; Chandrasekhar and Hoelscher, 1975) reveal that the apparent resistance to solute transport is frequently greater than the sum of the resistances in the individual phases, and it is customary to attribute the difference to the existence of an appreciable barrier to transport at the interface itself. However, little is known of the underlying molecular sources of such interfacial resistance to mass transfer. This paper is addressed to an analysis of the phenomenon in quiescent, unstirred systems, which are appropriately dilute.

This examination of the phenomenon of molecular transport perpendicular to an interface represents a natural extension of our prior studies (Brenner and Leal, 1977, 1978*a*, 1978*b*) of molecular transport parallel to interfaces, that is, surface diffusion. As in this earlier work, we shall adopt a spherical Brownian particle as a model for a diffusing molecule. The radius a, of this particle is assumed to be much smaller than the scale L of bulk concentration gradients but much greater than the thickness of the interfacial region between the two pure solvents, which is therefore regarded as a locally plane, singular surface. With the exception of possible interactions between the particle and the interface, the particles are assumed to be physicochemically inert, and the theory which we shall discuss is thus restricted to ideal solutions. Although we have limited our attention to spherical particles in the present paper, the analysis is readily extended to nonspherical particles as well.

STATEMENT OF THE PROBLEM

Imagine a steady state, interphase transport process, as in Figure 1, where specified solute concentrations

$$c = C_1 \quad \text{at} \quad y = -L_1 \tag{1}$$

and

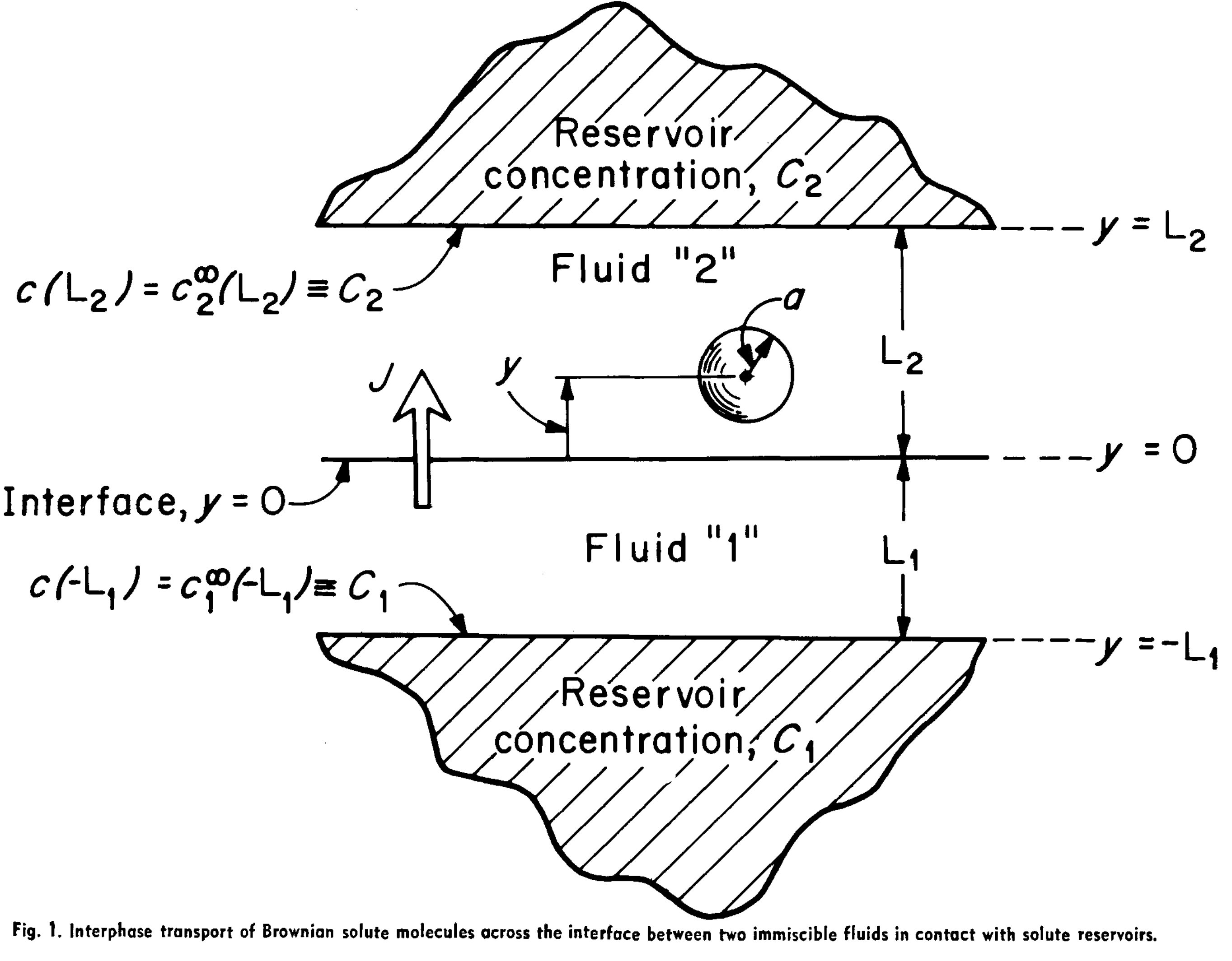

Fig. 1. Interphase transport of Brownian solute molecules across the interface between two immiscible fluids in contact with solute reservoirs.

$$c = C_2 \quad \text{at} \quad y = L_2 \tag{2}$$

are maintained across planes situated at distances L_1 and L_2 units below and above, respectively, the interface $y = 0$ between two immiscible Newtonian fluids. It will be assumed that $L_i >> a$ $(i = 1, 2)$. This steady state may be imagined as sustained by means of well-stirred reservoirs maintained at concentrations C_1 and C_2. If B denotes the thermodynamic interphase equilibrium distribution coefficient (assumed to be of the linear Henry's law form), it will be supposed that

$$C_1 > B\, C_2 \tag{3}$$

Thus, the direction of solute transfer is from phase 1 into phase 2. The objective of the present study is to identify the role of interfacial resistance in this process and to obtain a predictive description of its magnitude as a function of the various system parameters.

The fundamental assumption of our investigation is that there are two distinct scales of resolution which may be applied to the diffusive transport process for our model system. The first is characteristic of the localized concentration variations which are due to the presence of short-range forces of attraction or repulsion between individual particles and the interface. For subsequent discussion, we shall term this the microscale description and denote the associated length scale as l. As discussed in our previous studies of (surface) diffusion parallel to the interface (Brenner and Leal, 1977, 1978*a*), there is no need, at this microlevel, for concepts such as interfacial resistance which are specifically associated with the plane $y = 0$. Any influence of the interface on the solute diffusion process is manifested only by a localized, but continuous, transition in particle concentration from phase 1 to phase 2, and the whole problem for dilute solutions reduces to a classical investigation of Brownian diffusion, applied to particles which are either in close proximity to, or actually straddling, the solvent interface. The second level of description is termed macroscale and is characterized by the scale $O(L_i)$, where $L_i >> l$. It is this description which is most common in technological applications. Here, the whole region of $O(l)$ on either side of the plane $y = 0$ is indistinguishable from the plane itself, so that any nonuniformities in the solute concentration which occur in this very local domain remain completely unresolved. In particular, from the macroscopic point of view, the concentration distribution may actually appear to be discontinuous at $y = 0$, and any local excess in solute flux or solute mass, relative to that predicted from the macroscale concentration profiles which are relevant to an inert surface, will be missed altogether. In order to make the macroscale description consistent with the more fundamental microscale description of the system, it is thus necessary to assign these excess quantities to the interface itself; that is, $y = 0$ as seen from the macroscale point of view. We have suggested, in previous papers (Brenner and Leal, 1977, 1978*a*), that the excess solute mass and excess diffusive flux of solute parallel to the interface, which occur in the presence of an attractive potential between the particle and the interface, are the origin of the macroscopic concepts of physical adsorption and surface diffusion. Similarly, we suggest in the present paper that interfacial resistance is a purely macroscopic concept, which is required in order to reconcile the macrodescription of diffusive transport normal to the interface with its more fundamental, microscopic counterpart.

In order to provide a definite predictive relationship between interfacial resistance and the parameters which characterize the system at the scale of individual particles, we adopt the micromechanical procedure that was used (and discussed at length) in our earlier papers (Brenner and Leal, 1977, 1978*a*). Specifically, we start with a rigorous description of the system at the microscale and then deduce the desired macroscopic result by averaging over the domain of significant interaction between the interface and particle, where differences exist between the micro and macroconcentration profiles.

A MICROSCALE DESCRIPTION OF THE INTERPHASE MASS TRANSFER

Choose the center of each spherical particle as its locator point, and let y be the distance from the interface to the center of a sphere. Denote by $c \equiv c(y)$ the local number density (surface averaged, see Brenner and Leal, 1977*a*) of sphere centers at a distance y from the interface. This includes those particles which may instantaneously be straddling the interface. With A an areal surface element whose plane parallels that of the interface, the number of sphere centers in the volume element $dV = A\, dy$ is $cA\, dy$.

The Influence of the Interface on the Diffusive Transport of Solute Particles

The presence of the interface is regarded as having two distinct effects on the diffusive transport of solute molecules (particles) from phase 1 into phase 2.

1. The diffusing molecule will experience physicochemical repulsive (or attractive) forces exerted on it by the interface. This is tantamount to the existence of a potential energy barrier at the interface, which would have to be overcome by the thermal energy of the solute molecule in order for the latter to penetrate it.* If this interaction force varies too rapidly with respect to spatial position, the familiar Fickian description of the diffusion process must be abandoned in favor of the complete Fokker-Planck equation in $(\mathbf{x}, \mathbf{u})$ space (see Brenner and Leal, 1977, for an explicit statement of the condition in which this becomes necessary). Although this poses no difficulty in the case of diffusion parallel to the interface (again, see Brenner and Leal, 1977) where the concentration distribution normal to the boundary can be shown to be in the equilibrium, Boltzmann form, one would be forced in the present case to solve the full nonequilibrium, nonlinear Fokker-Planck equation. In order to avoid this complexity, we shall assume, throughout the remainder of this paper, that the interaction force varies slowly enough to allow use of the simple Fickian constitutive law in all directions.

2. The diffusion coefficient $D_\perp$ of the Brownian particle normal to the interface is dramatically decreased by the presence of the interface in proximity to it. This effect may be regarded as a hydrodynamic wall effect, no different in principle from the enhanced hydrodynamic resistance experienced by a small sphere when approaching a free surface or plane wall (Brenner, 1961; Cox and Brenner, 1967) in the Stokes regime. The net effect of this phenomenon is that if

$$D^\infty = kT/6\pi\mu a \tag{4}$$

represents the Stokes-Einstein diffusivity of the Brownian particle, far from the interface, then $D_\perp/D^\infty << 1$ for close approach of the sphere to the interface.

Let us denote the force exerted in the positive y direction by the interface on a Brownian particle whose center is situated at y as $F(y)$. This force will be assumed to be

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* These remarks refer to solute transfer across clean, uncontaminated interfaces If, however, a mono or polymolecular surfactant film existed at the interface, the transport-rate effects induced by their presence (Davies and Rideal, 1963; Sherwood et al., 1975) would be in addition to those already cited. It is possible that such effects may be lumped into that of the potential energy barrier.

conservative and hence derivable from a potential energy function $V(y)$

$$F = -kT\, dE/dy \tag{5}$$

where

$$E(y) = V(y)/kT \tag{6}$$

is a nondimensional dependent variable, representing the ratio of the particle's potential energy to its mean thermal energy. This function approaches constant limiting values (Brenner and Leal, 1978*a*)

$$E \rightarrow \begin{cases} E_1^\infty & \text{for } -y >> l \\ E_2^\infty & \text{for } \quad y >> l \end{cases} \tag{7}$$

far from the interface, when the particle is wholly immersed in fluid 1 or 2, respectively. That is, provided that

$$|y| >> l \tag{8}$$

E will attain a constant value which is independent of y but dependent upon whether the Brownian particle is present in fluid 1 or 2. Since $l/L_i << 1$ (that is, the ratio of micro to macroscale), it follows that the limiting values (7) may be regarded as asymptotically achieved when y satisfies the inequalities

$$L_i >> |y| >> l \tag{9}$$

The equilibrium interphase distribution coefficient is related to these limiting potentials by the expression (Brenner and Leal, 1978*a*)

$$B = \exp\left[-(E_1^\infty - E_2^\infty)\right] \tag{10}$$

The Local Flux Density

From the microscale point of view, the problem of diffusive transport across a fluid-fluid interface can be rigorously described, for a dilute suspension with not too rapid variations of F, as a combination of classical (Stokes-Einstein) bulk-phase hindered diffusion and particle advection under the action of the external force F. Thus, the complete constitutive equation for the normal flux component is

$$j = -D_\perp(y)\frac{dc}{dy} + M_\perp(y)\,Fc \tag{11}$$

with $c(y)$ the local number density of sphere centers. At steady state, this local flux density is a constant, independent of y; that is

$$j = \text{constant} \tag{12}$$

In contrast with the bulk (macroscale) concentrations $c_i^\infty(y)$, which we will consider in the next section, the function c is continuous throughout the entire range

$$-L_1 < y < L_2 \tag{13}$$

(as is j, too). In particular, this range of continuity includes the region $|y| < a$, where the sphere straddles the interface. The position-dependent quantities $D_\perp(y)$ and $M_\perp(y)$ are, respectively, the diffusion and mobility coefficients for motion of the center of the Brownian particle normal to the plane interface. They, too, are continuous functions of y. The mobility coefficient is not an independent parameter in consequence of the Nernst-Planck-Einstein equation

$$M_\perp = D_\perp/kT \tag{14}$$

In general, the diffusivity-distance function would be expected to possess the form shown in Figure 2.

Equations (11) and (12) apply to all diffusing particles, including those which instantaneously straddle the interface. Therefore, we have purposely avoided affixing indexes 1 and 2 to c or j or, indeed, to any of the other dependent parameters, such as $D_\perp$. In so doing, we have intended to emphasize the continuous variation of properties associated with the Brownian particles in the region (13). This continuous microscopic view is in sharp contrast to the macroscopic or bulk viewpoint, which we discuss in the next section. In particular, whereas the bulk concentrations $c_1^\infty(0)$ and $c_2^\infty(0)$ are discontinuous across the interface, the true microscale concentration $c(y)$ is not (see Figures 5*a*, *b*, and *c*). In addition, the concepts of bulk and surface resistance to mass transfer do not occur in the rigorous microscale description, which is summarized by the Equations (11) and (12).

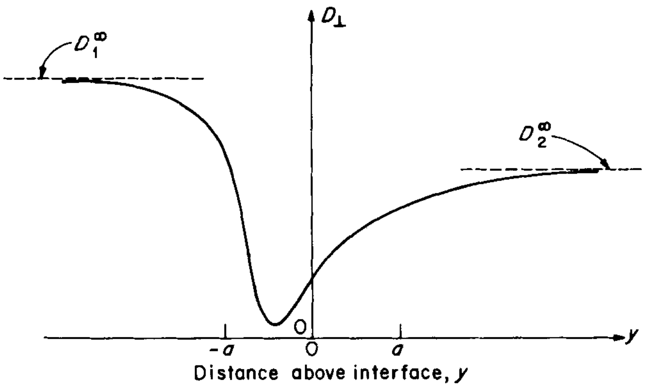

Fig. 2. Diffusivity coefficient as a function of the distance y of the sphere center from the interface. The bulk diffusivities D_i^∞ are given by Equation (1) and hence are in the ratio $D_2^\infty/D_1^\infty = \mu_1/\mu_2$. Thus, the sketch is predicated on the assumption that fluid 2 is more viscous than fluid 1.

A MACROSCALE DESCRIPTION OF INTERPHASE MASS TRANSFER

Let us now turn to the bulk or macroscale description of the transport of solute from reservoir 1 to reservoir 2. This is the standard textbook description which is prescribed for normal engineering or technological applications.

In this approach, the flux of solute is related to the macroscopic driving force $C_1 - BC_2$ through an overall mass transfer coefficient K_1^* (Davies and Rideal, 1963); that is

$$j = \frac{J}{A} = K_1^*(C_1 - BC_2) \tag{15}$$

with J the number of Brownian particles crossing an area A of the interface per unit time. Equation (15) serves as the definition of K_1^*, which in this case is based on fluid 1. At the same time, it expresses the linearity between the flux and the driving force $C_1 - BC_2$. The latter vanishes at equilibrium.

The flux can also be expressed in terms of the individual mass transfer coefficients k_1 and k_2, appropriate to phases 1 and 2, respectively, as

$$J/A = k_1[C_1 - c_1^\infty(0)] \tag{16}$$

and

$$J/A = k_2[c_2^\infty(0) - C_2] \tag{17}$$

where $c_i^\infty \equiv c_i^\infty(y)$ denotes the bulk concentration of spheres in phase i ($i = 1, 2$) at the position y[*]. In particular, $c_i^\infty(0)$ denotes the number density prevailing at the

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[*] For the relationship between these bulk concentrations $c_i(y)$ and the true concentration $c(y)$ at the same value of y, see Equations (53) to (56)

interface, $y = 0$, in phase i.

With

$$D_i^\infty = kT/6\pi\mu_i a \tag{18}$$

the position-independent bulk particle diffusivity in phase i, normal textbook arguments suggest that K_1^* may be theoretically calculated by the following procedure. The local flux density j in the y direction in each of the two phases is given by Fick's law as

$$j = -D_i^\infty\, dc_i^\infty/dy \quad (i = 1, 2) \tag{19}$$

At steady state, this flux density is a constant $(= J/A)$, independent of y, as noted in Equation (12). Thus, the bulk (macroscale) concentration profiles $c_i(y)$ are linear in y and satisfy the constraint

$$D_1^\infty\, dc_1^\infty/dy|_{y=0} = D_2^\infty\, dc_2^\infty/dy|_{y=0} \tag{20}$$

Moreover, if equilibrium is assumed to prevail at the interface, it is further required that

$$c_1^\infty(0)/c_2^\infty(0) = B \tag{21}$$

Additionally, one has to satisfy the boundary conditions

$$c_1^\infty(-L_1) = C_1 \quad \text{and} \quad c_2^\infty(L_2) = C_2 \tag{22}$$

Equations (20), (21), and (22), applied to the linear profiles $c_1^\infty(y)$ and $c_2^\infty(y)$, yield expressions for the individual mass transfer coefficients (that is,

$$(-1)^{i+1} D_i^\infty (dc_i^\infty/dy)/[c_i^\infty(0) - C_i])$$

$$k_1 = D_1^\infty/L_1, \quad \text{and} \quad k_2 = D_2^\infty/L_2 \tag{23}$$

and for the interfacial bulk concentrations

$$c_1^\infty(0) = \frac{C_1 + (k_2/k_1)C_2}{1 + B^{-1}(k_2/k_1)} \tag{24}$$

and

$$c_1^\infty(0) = Bc_2^\infty(0) \tag{25}$$

in terms of the prescribed bulk parameters of the problem. It follows from (22) to (25) that the overall mass transfer coefficient K_1^*, in the absence of any direct interfacial barrier to mass transfer, is

$$1/K_1^* = 1/k_1 + B/k_2 \tag{26}$$

Following the notation of Davies and Rideal (1963), it is convenient to define the mass transfer resistances

$$R_1^* = 1/K_1^* \tag{27}$$

and

$$r_1 = 1/k_1 \qquad r_2 = B/k_2 \tag{28}$$

so that the preceding relation may be expressed as

$$R_1^* = r_1 + r_2 \tag{29}$$

This is, of course, the classical result (Davies and Rideal, 1963), corresponding to resistances in series.

When compared to the microscale analysis of the preceding section, the macroscopic approach which we have just described is both naive and inaccurate. In the first place, it fails to take account of the diminution of the particle diffusivity with decreasing distance from the interface. Furthermore, it does not reflect in any way the fact that the interface may exert short-range attractive or repulsive body forces on the Brownian particle. These two effects are logically independent, and it is therefore not surprising that their inclusion in an improved macroscale description of the system should take different forms. Specifically, the variation in diffusivity with distance from the interface is completely due to the spatial dependence of the hydrodynamic mobility and has no connection with the presence or absence of short-range interaction forces between the particles and the interface. Thus, it is properly included as a direct modification of the expressions for the individual mass transfer coefficients k_1 and k_2 which were originally given by (23) in the crude, textbook version of the macroscale theory. Indeed, the theory of such hindered diffusion processes is straightforward and has, in fact, been developed rather completely for the case of a fluid/solid wall configuration (Prieve and Ruckenstein, 1974). The appropriate generalization of (23), expressed in terms of the resistance factors r_1 and r_2, is

$$r_1 = \int_0^{L_1} \frac{dy}{D_\perp(y)} \quad \text{and} \quad r_2 = B\int_0^{L_2} \frac{dy}{D_\perp(y)} \tag{30}$$

Interfacial Resistance

So far, the concept of interfacial resistance has not appeared in either the microscopic or macroscopic descriptions of the transport of solute from fluid 1 to fluid 2, even with the latter modified as indicated above to account for spatial variations in the bulk-phase diffusivities. It is only when we attempt to reconcile the rigorous microscale expression (11) for the rate of solute transfer in the presence of short-range forces of attraction or repulsion, with the macroscopic expression (15) [plus (27) to (30)], that it becomes necessary to introduce the idea of an additional (macroscale) resistance to mass transfer which is associated with (or, more accurately, assigned to) the fluid/fluid interface. Specifically, when the system is viewed from the macroscopic scale $O(L)$, the changes in concentration at the microscale $O(l)$ that are caused by the presence of an interaction force cannot be resolved. As a result, the solute concentration appears discontinuous across the interface in the macroscopic theory, and the rate of solute transfer which is predicted from (15) and (27) to (30) is different from the exact rate, Equation (11). The two theories, microscopic (exact) and macroscopic, can be reconciled only by the assignment in the macroscopic theory of an added resistance at the interface itself. Since the difference between the macroscale and microscale expressions for solute flux is associated with the inability to distinguish the two short-range effects at the scale $O(L)$, the attempt to reconcile the micro and macroexpressions by assigning any difference to the interface may be viewed as incorporating the short-range factors into the macroscopic analysis.

RESULTS

To proceed with the calculation of interfacial resistance, we compare the micro and macroexpressions for solute flux from the previous section. At the microlevel, Equations (5), (11), (14), and (12) (with $j = J/A$), combine to yield

$$J/A = -D_\perp(y)\, e^{-E(y)} \frac{d}{dy}[c\, e^{E(y)}] \tag{31}$$

with the left-hand side independent of y. Integration between the limits (13) gives, with use of (1) and (2)

$$J/A = (C_1 - B_L C_2)/R_1(L) \tag{32}$$

in which

$$R_1(L) = \exp(-E_1) \int_{-L_1}^{L_2} \frac{\exp E(y)}{D_\perp(y)}\, dy \tag{33}$$

with

$$B_L = \exp[-(E_1 - E_2)] \tag{34}$$

and

$$E_1 \equiv E(-L_1), \quad E_2 \equiv E(L_2) \tag{35}$$

Equation (32) is exact within the context of our model system, and it follows by comparison with the corresponding macroscale expressions (15) and (27) to (30) that $R_1(L)$, defined by Equation (33), is an exact expression for the overall resistance to mass transfer in a fluid layer extending from $-L_1$ to L_2. Being exact, it obviously encompasses both the individual resistance coefficients for the two bulk phases and the interfacial resistance (if any exists) associated with the domain $-L_1$ to L_2. As previously suggested, if a macroscopically meaningful interfacial resistance does exist, it is defined by the relation

$$r_I = R_1 - r_2 - r_1 \tag{36}$$

in which R_1 is the exact macroscopic resistance factor, namely, (33) with $|L_1|, |L_2| \to \infty$, and r_1 and r_2 are the individual bulk-phase resistances as defined in Equation (30).

To obtain a definite result for r_I, we first rewrite (33) in the alternative form

$$R_1(L) = \int_{-L_1}^{0} \frac{\exp[E(y) - E_1]}{D_\perp(y)}\,dy + B_L \int_0^{L_2} \frac{\exp[E(y) - E_2]}{D_\perp(y)}\,dy \tag{37}$$

Now, the macroscopic resistance, relevant to an inert interface, is[(29), (30)]

$$R_1{}^* \equiv \int_{-L_1}^{0} \frac{dy}{D_\perp(y)} + B \int_0^{L_2} \frac{dy}{D_\perp(y)} \tag{38}$$

and we may thus define the function

$$r_I(L) \equiv R_1(L) - R_1{}^* \tag{39}$$

analogous to (36). It follows from (37) to (39) that

$$r_I(L) = \int_{-L_1}^{0} \left[\frac{\exp[E(y) - E_1] - 1}{D_\perp(y)}\right] dy + \int_0^{L_2} \left[\frac{B_L \exp[E(y) - E_2] - B}{D_\perp(y)}\right] dy \tag{40}$$

Note that the numerators of each of these integrals vanish at the integration limits $-L_1$ and L_2 in consequence of the definitions (35). Moreover, these numerators are necessarily bounded throughout their respective integration domains. Thus, as long as $D_\perp$ does not vanish anywhere in the range of integration, the above integrals will be convergent, no matter how large L_1 and L_2 may be chosen to be.

As discussed in connection with Equations (7) to (10), since $L_i >> l$, no appreciable error will accrue by letting L_1 and L_2 tend to infinity in the preceding expression. In this limit, (40) passes over to the equation

$$r_I = \int_{-\infty}^{0} \left[\frac{\exp[E(y) - E_1{}^\infty] - 1}{D_\perp(y)}\right] dy + B \int_0^{\infty} \left[\frac{\exp[E(y) - E_2{}^\infty] - 1}{D_\perp(y)}\right] dy \tag{41}$$

Finally, for convenience, we reexpress $D_\perp(y)$ in the form

$$D_\perp(y) \equiv \beta_1(y) D_1{}^\infty \quad \text{with} \quad \beta_1(y) \leq 1 \quad \text{for} \quad -\infty \leq y < 0$$

and

$$D_\perp(y) \equiv \beta_2(y) D_2{}^\infty \quad \text{with} \quad \beta_2(y) \leq 1 \quad \text{for} \quad 0 < y \leq \infty$$

so that

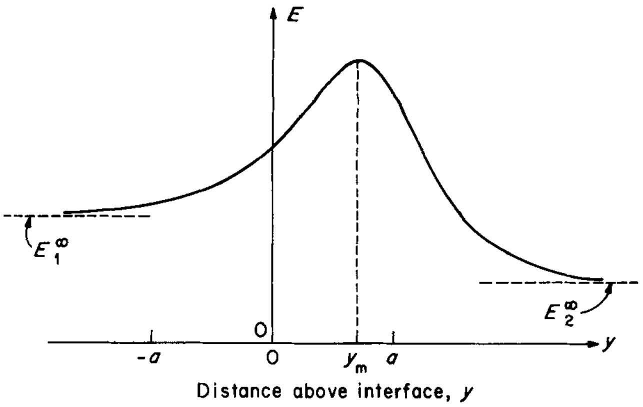

Fig. 3a. Potential energy curve for a case where the solute molecules are repulsed by the interface.

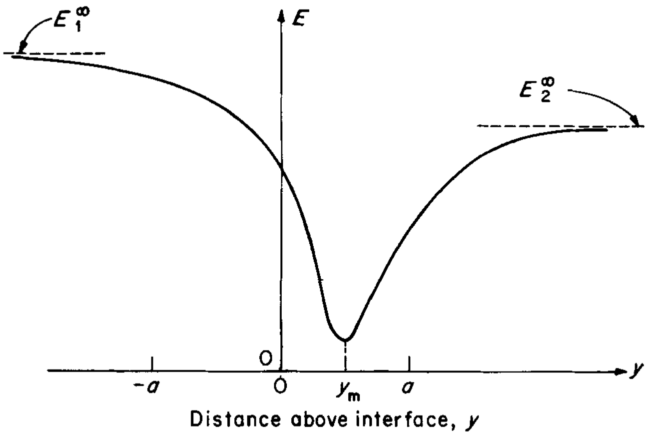

Fig. 3b. Potential energy curve for a case where the solute molecules are attracted by the interface.

$$r_I = \frac{1}{D_1{}^\infty} \int_{-\infty}^{0} \left[\frac{\exp[E(y) - E_1{}^\infty] - 1}{\beta_1(y)}\right] dy + \frac{B}{D_2{}^\infty} \int_0^{\infty} \left[\frac{\exp[E(y) - E_2{}^\infty] - 1}{\beta_2(y)}\right] dy \tag{42}$$

The first portion of (42) represents the contribution to the interfacial resistance arising from fluid 1, the second portion arising from fluid 2. The asymmetry of these respective contributions, that is, the appearance of B as the multiplier of the second term, stems from the fact the R_1 represents the overall mass transfer resistance based upon phase 1.

Algebraic Sign of the Interfacial Resistance

The algebraic sign of the interfacial resistance may be either positive or negative, depending upon whether the force exerted by the interface on the diffusing particles is repulsive or attractive and upon the magnitude and functional form of $\beta_i(y)$. This may be demonstrated by reference to Figures 3*a* and *b*, which represent idealized potential energy-distance plots for two possible situations. The point y_m corresponds to a minimum or maximum in the curve, at which $dE/dy = 0$. In view of (5), it follows from the slopes dE/dy of the potential energy curve for the respective cases $y < y_m$ and $y > y_m$ that the value y_m represents a plane of repulsion for the centers of the Brownian spheres in the case where Figure 3*a* obtains. That is, particles whose midpoints lie on either side of the plane y_m will be repelled by it. As is evident from the plot

$$E(y) - E_1{}^\infty > 0 \quad \text{for} \quad -\infty < y < 0 \tag{43}$$

and

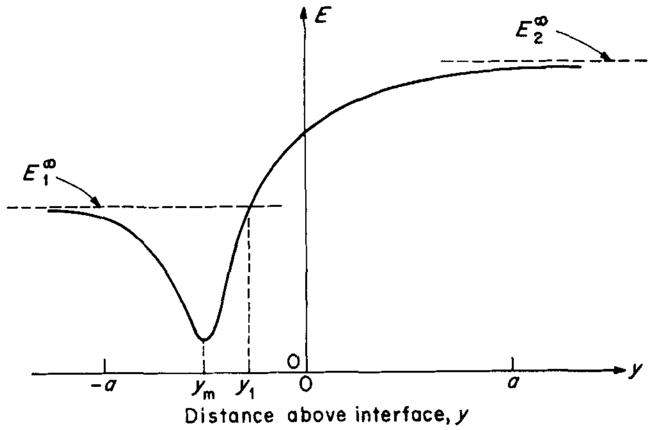

Fig. 4. Potential energy curve for a case where the solute molecules are attracted by the interface.

$$E(y) - E_2^\infty > 0 \quad \text{for} \quad 0 < y < \infty . \qquad (44)$$

Accordingly, since $\beta_i(y) \leq 1$, it follows that

$$\frac{\exp[E(y) - E_i^\infty] - 1}{\beta_i(y)} \geq 0 \quad (i = 1, 2) \qquad (45)$$

for all values of y. The equality holds only as $|y| \rightarrow \infty$. Finally, since D_1^∞, D_2^∞, and B are all positive, it is evident from (42) that

$$r_1 > 0 \qquad (46)$$

Hence, in this case, the physical effect of the interface is to increase the resistance to solute mass transfer beyond the value R_1^*, which is the apparent macroscopic value with no account taken of the hydrodynamic or physicochemical influences of the interface. Examination of (42) reveals two distinct contributions to interfacial resistance: the local increase in $D_\perp(y)$ near the interface, which is reflected by $\beta_i(y) < 1$ for small y, and the potential force interaction, which either increases or decreases the local equilibrium concentration near the interface relative to its bulk value, depending on whether the force is attracting or repelling. Regardless of the sign of $E(y) - E_i^\infty$, the influence of the hydrodynamic factor is always to increase the first term in the integrands of (42) and thus to increase the interfacial resistance. In particular, for $E(y)$ satisfying (43) and (44), r_I is made more positive by the fact that $\beta_i < 1$. The decrease in the local equilibrium concentration associated with the repulsive potential of Figure 3*a* has the effect of decreasing the diffusive flux of particles compared with the flux which would exist if $E(y) \equiv E_i^\infty$, and so again tends to yield positive values for r_I.

Conversely, when the situation depicted in Figure 3*b* obtains, wherein y_m corresponds to an attractive or adsorptive locus, the following inequalities obtain:

$$E(y) - E_1^\infty < 0 \quad \text{for} \quad -\infty < y < 0 \qquad (47)$$

and

$$E(y) - E_2^\infty < 0 \quad \text{for} \quad 0 < y < \infty \qquad (48)$$

Consequently, it is possible that the presence of the interface may actually give

$$r_I < 0 \qquad (49)$$

corresponding to a decrease in the overall resistance to mass transfer.

It may be seen from (42) that the value of r_I, in the presence of an attractive (or repulsive) potential, is dominated by the accumulation (or deficit) of particles in the vicinity of the interface. In particular, for the relatively simple cases represented by (43) to (44) and (47) to (48), the functional form of the hydrodynamic factor

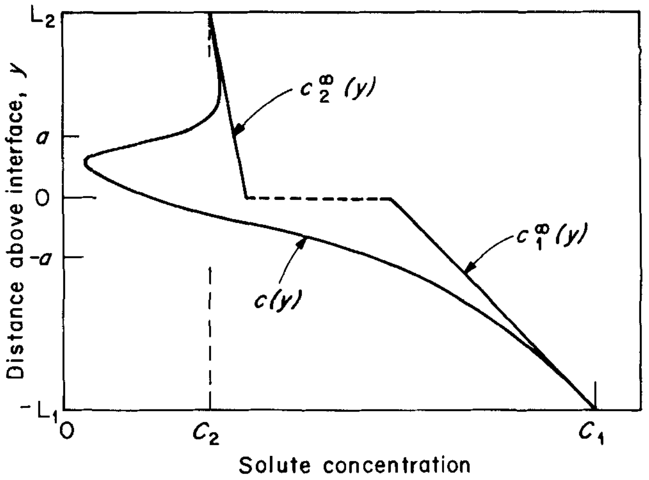

Fig. 5a. Bulk and true concentration profiles for a case where the solute molecules are repelled by the interface. The true concentrations in the neighborhood of the interface tend to be less than those in bulk owing to the solute deficit arising from the repulsive forces.

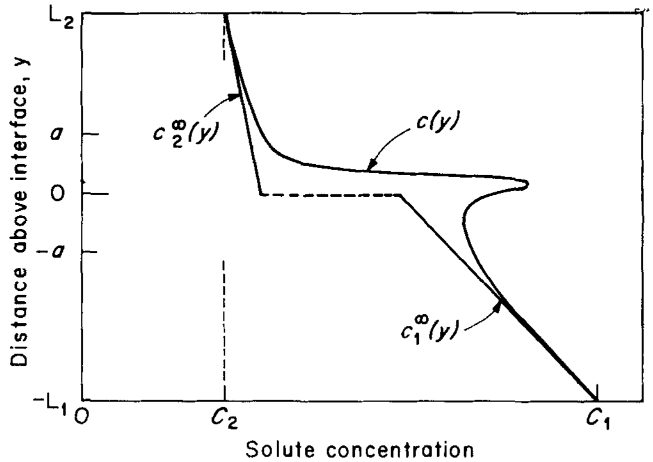

Fig. 5b. Bulk and true concentration profiles for a case where the solute molecules are attracted to the interface. The true concentrations in the neighborhood of the interface tend to be greater than those in bulk owing to the solute excess arising from the attractive forces.

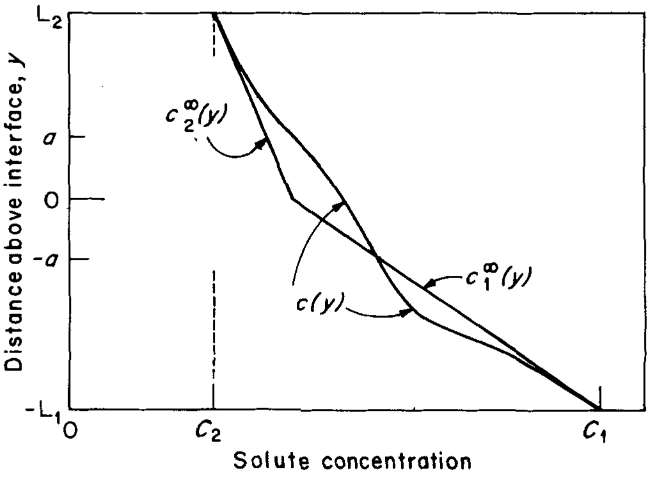

Fig. 5c. Bulk and true concentration profiles for the case $E = 0$ everywhere, corresponding to the absence of any attractive or repulsive forces. In this case $B = 1$, so that the bulk concentration profile is necessarily continuous across the interface. However, the slopes D_1^∞ and D_2^∞ of these bulk profiles are discontinuous across the interface.

$\beta_i(y)$ will affect the magnitude but not the sign of the interfacial resistance. It is important to note that the influence of the potential function is not a consequence of its asymmetry or of any direct dynamic effect on the motion of a particle. This fact explains the contradiction, which might otherwise seem to exist, between the trapping of particles by a deeper (attractive) potential well and the decreased interfacial resistance which would be predicted by (42).

Though experiments performed to date (Davies and Rideal, 1963; Chandrasekhar and Hoelscher, 1975) have identified a number of systems for which $r_I > 0$, none to our knowledge has provided evidence for the converse case $r_I < 0$. This may be either a manifestation of the smallness of the effect in the latter case or simply the failure of prior investigations to examine ternary systems capable of displaying such atypical behavior.

If any such systems actually exist, they clearly must be in the class for which

$$E(y) - E_i^{\infty} < 0 \tag{50}$$

over at least some of the domain $-\infty < y < \infty$. In general, systems in which the solute is surface active (with respect to the pair of immiscible fluids) would be expected to satisfy this condition. For, by definition, surfactant systems are those for which the solute tends to be adsorbed at the interface, a manifestation of the existence of attractive forces at the interface. More generally, if Γ_s denotes the surface excess (Davies and Rideal, 1963; Adam, 1968) solute concentration at the interface, one would expect those systems for which $\Gamma_s > 0$ to satisfy (50). Such systems would thus appear to be good candidates for an experimental investigation of the existence of negative interfacial resistance; that is, $r_I < 0$. Conversely, systems are known (Davies and Rideal, 1963; Adam, 1968) for which $\Gamma_s < 0$, corresponding to a deficiency of solute at the interface or, equivalently, a negative adsorption coefficient. Clearly, solute molecules are repelled by the interface in this case. It is for such systems that one would expect to observe $r_I > 0$.

Figures 3*a* and *b* do not exhaust the possible variety of potential energy curves. Thus, Figure 4 illustrates a situation involving the existence of purely attractive forces, akin to that of Figure 3*b*. However, unlike the latter case, the monotonicity condition (47) is no longer fulfilled for all $-\infty < y < 0$. Rather, as follows from the sketch

$$\begin{cases} E(y) - E_1^{\infty} < 0 & \text{for} \quad -\infty < y < y_1 \\ E(y) - E_1^{\infty} > 0 & \text{for} \quad y_1 < y < 0 \end{cases} \tag{51}$$

Hence, the numerator of the first term of (42) is negative for $-\infty < y < y_1$ but positive for $y_1 < y < 0$. Consequently, it is not generally possible to establish the algebraic sign of r_I without specific and detailed knowledge of the functional dependence of E and $D_\perp$ upon y.

DISCUSSION

Computational Aspects of the Problem

Numerical evaluation of the integral (42), governing the magnitude and algebraic sign of the interfacial resistance to mass transfer, awaits determination of the diffusion coefficient $D_\perp$ for motion of the center of a Brownian particle normal to the interface, when the particle is in close proximity to, or straddling, the latter. In principle, such a calculation can be made by utilizing the mobility relation (14) in conjunction with a knowledge of the low Reynolds number hydrodynamic particle resistance or mobility for movement of the sphere normal to the interface. Computations along these lines are currently being pursued via techniques derived from the solutions of several related problems (Brenner, 1961; Cox and Brenner, 1967; Schneider et al., 1973; Majumdar et al. 1974). On the supposition that the interface may be regarded as plane despite the interfacial stresses generated by the sphere's motion, this necessarily leads to an expression for the diffusion coefficient having the form

$$D_\perp = \frac{kT}{\mu_1 a} \,\text{function}\left(\frac{y}{a}, \frac{\mu_1}{\mu_2}\right) \tag{52}$$

Computation of r_I also requires information regarding the form of the potential energy function, as well as the numerical values of the phenomenological coefficients appearing therein. This same function enters into calculations of the equilibrium interfacial adsorption coefficient K_a (Brenner and Leal, 1977, 1978*a*), relating surface excess to bulk concentrations, as well as into calculations of the heat of adsorption ΔH_a. It also figures in computations of the interfacial surface diffusivity D_s (Brenner and Leal, 1977, 1978*a*, 1978*b*). Thus, it may prove possible to develop macroscopic correlations relating r_I, inter alia, to some of these variables.

Relationship Between Bulk and True Concentrations

Further elaboration of the fundamental distinction between the true and bulk number densities is in order for completeness. The bulk concentrations appropriate to the problem at hand are readily established to be

$$c_1^{\infty}(y) = C_1 - \frac{J}{AD_1^{\infty}}(L_1 + y), \quad (-L_1 < y < 0) \tag{53}$$

and

$$c_2^{\infty}(y) = C_2 - \frac{J}{AD_2^{\infty}}(L_2 - y), \quad (0 < y < L_2) \tag{54}$$

In contrast, integration of (31), subject to the boundary conditions (1) and (2), yields

$$c(y) = C_1 \exp[E_1 - E(y)] - \frac{J}{A}\int_{s=-L_1}^{y} \frac{\exp[E(s) - E(y)]}{D_\perp(s)}\,ds \tag{55}$$

or, equivalently

$$c(y) = C_2 \exp[E_2 - E(y)] + \frac{J}{A}\int_{s=y}^{L_2} \frac{\exp[E(s) - E(y)]}{D_\perp(s)}\,ds \tag{56}$$

each of which applies over the complete range (13).

Depending upon the explicit variation of E and $D_\perp$ with y, the latter concentration profiles may display a variety of different shapes, especially in the immediate neighborhood $|y| = 0(a)$ of the interface. Several possibilities are shown in Figures 5*a*, *b*, and *c*. While the true profiles may differ quite radically from the (discontinuous) bulk profiles in proximity to the interface, they are necessarily asymptotically equivalent for $|y| >> l$.

Relationship between Interfacial Adsorption and Interfacial Resistance

Finally, it is perhaps useful to comment briefly upon the relationship between interfacial adsorption and interfacial resistance as it appears in the context of the present model system. More specifically, it has been shown by other authors that the presence of surface adsorption can confer structure upon the interfacial region if the surface density of adsorbed molecular species is sufficiently large (Morel, 1974; Phillips and York, 1976; Ohnishi and Tsubomura, 1976) as, for example, in the case of monomolecular coverage, and thus contributes a substantial interfacial resistance ($r_I > 0$). Although this may well represent an important mechanism in more concentrated systems, it is completely irrelevant in the dilute regions which we have considered, as may be seen by examination of Equation (42). Here, the phenomenon of interfacial resistance stems from the existence of potential energy barriers, namely, a repulsive interaction force between particle and interface. On the other hand, interfacial adsorption is clearly associated with an attractive interaction force (Brenner and Leal, 1978*a*). In the dilute system which we have investigated, it is the deficit of particles in the vicinity of the interface which leads to positive interfacial resistance.

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NOTATION

a = sphere radius
A = area parallel to interface
B = thermodynamic interphase equilibrium distribution coefficient
$c(y)$ = solute (particle) concentration; local number density of sphere centers at distance y from interface
$c_i^\infty(y)$ = solute (particle) concentration; number density of sphere centers in fluid i at a distance y from the interface, as seen from the macroscopic point of view
C_1, C_2 = solute (particle) concentrations at $y = -L_1$ and L_2
$D_\perp$ = component of the bulk diffusivity tensor for diffusion normal to the interface
D_s = surface diffusivity
D_i^∞ = Brownian diffusivity for a particle far from the interface in fluid i
$\mathrm{E}(y)$ = dimensionless potential energy function, $V(y)/kT$
E_i = potential energy function at a distance $y = |L_i|$ from interface
E_i^∞ = interaction potential energy far from the interface in fluid i
$F(y)$ = physicochemical interaction force between a particle and the interface, $F = -kT\ dE/dy$
j = local particle (solute) flux normal to the interface per unit area
J = local particle (solute) flux normal to the interface through an interfacial area, A
k = Boltzmann constant
k_i = individual mass transfer coefficient appropriate to fluid i, Equations (16) and (17)
K_1^* = overall mass transfer coefficient for solute transport from fluid 1 to fluid 2, Equation (15)
l = microscopic length scale, characteristic of interaction potential energy gradients
L = macroscopic length scale characteristic of bulk concentration gradients
L_1, L_2 = thickness of the fluid layer on either side of the interface
$M_\perp$ = component of hydrodynamic mobility tensor for particle motion normal to the interface
r_i = individual phase bulk resistance factor for fluid i
r_I = interfacial resistance to solute mass transfer
R_1^* = sum of individual phase bulk resistances to solute mass transfer
R_1 = overall resistance factor for solute transport from fluid 1 to fluid 2
T = absolute temperature
$V(y)$ = interaction potential energy function
y = distance from interface, reckoned as positive when going from phase 1 towards phase 2
y_m = position of minimum (or maximum) in the potential energy profile, $E(y)$
β_i = ratio of bulk diffusivity for diffusion normal to the interface to the bulk diffusivity, D_i^∞, in unbounded fluid i
Γ_s = surface-excess solute concentration
μ_i = solvent viscosity, fluid i

Subscripts

a = adsorbed solute
i = phase 1 or 2
I = interface
m = maximum or minimum
s = surface

Superscripts

∞ = bulk value

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