Dissociation Kinetics of Secondary-Minimum Flocculated Colloidal Particles

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The first passage time method is used to calculate the mean association time of a pair of secondary-minimum flocculated colloidal particles. This approach circumvents the need to solve the Smoluchowski diffusion equation, without invoking any additional approximations. It is shown that the pair association time is a very sensitive probe of the interaction between the particles. A comparison with measured association times of secondary-minimum flocculated monodisperse polystyrene spheres reveals large discrepancies between experiment and theoretical predictions based on exact hydrodynamics and the Derjaguin–Landau–Verwey–Overbeek (DLVO) potential for colloidal interactions. © 1984 Academic Press, Inc.

INTRODUCTION

Under suitably chosen conditions, the interaction potential between a pair of electrostatically stabilized colloidal particles can develop a significant ($\geq 1kT$) secondary minimum, while maintaining a large ($\gg 1kT$) primary maximum. Although the primary maximum will prevent irreversible coagulation into the primary minimum, the particles can undergo reversible flocculation into the secondary minimum. Detailed information about the flocculation process in colloidal dispersions with particle sizes in the μm range can be obtained by direct microscopic observation (1).

After the transient phase following upon preparation of the system (e.g., addition of electrolyte), the colloidal particles exist in a dynamic equilibrium with secondary-minimum flocculated aggregates continuously being formed, rearranged, and dissociated. If the dispersion is sufficiently dilute and if the electrolyte concentration is not too high, nearly all particles will be either unassociated or flocculated into pairs. It is then possible to determine experimentally the distribution of association times, or lifetimes, of pairs of

secondary-minimum flocculated particles. Cornell *et al.* thus reported mean lifetimes of the order of a few minutes for pairs of polystyrene particles of radius 1 μm (1).

The pair lifetime is a useful quantity, not only for the information it furnishes about the rate of redispersion under various conditions, but also, and perhaps more importantly, because it provides us with an exceedingly sensitive probe of the interaction (mechanical and hydrodynamic) between colloidal particles. (In contrast, the association rate does not depend nearly as sensitively on the pair interaction.) It is therefore important to have access to a theory which enables the mean lifetime to be calculated for any given form of the interaction. Comparison with experimental lifetimes then provides a critical test of the assumed form of the interaction. It is our aim in this paper to present such a theory.

One theoretical approach to the space–time evolution of a collection of Brownian particles is based on the many-particle Smoluchowski equation (2). At this level of description, the Brownian particles diffuse through an incompressible viscous medium while being mutually coupled via the conser-

vative forces, e.g., of the traditional DLVO type (3), as well as via configuration-dependent hydrodynamic interactions. A computer simulation algorithm, referred to as Brownian dynamics, has been developed whereby this many-particle diffusion equation can be solved (4).

A difficulty associated with the many-particle diffusion approach is the current incomplete knowledge concerning many-particle hydrodynamics. However, for the case of interest here, namely the dynamics of a system of two spherical colloidal particles, the prospects are brighter. For this case, the exact form of the hydrodynamic interaction is known, whereas accurate expressions are available for the electrical double-layer and van der Waals interactions. Furthermore, the two-particle diffusion equation can be (numerically) solved to any desired accuracy by a number of standard techniques.

The mean lifetime of a pair of colloidal particles may be obtained by solving the two-particle diffusion equation, with the appropriate boundary conditions, and then integrating the resulting propagator over time and space (cf. Eq. [8]). In this paper, however, we shall use the first passage time method, which provides a mathematically simple and *exact* recipe for calculating the mean lifetime. The advantage of this procedure is that it circumvents the need to actually solve the diffusion equation.

The first passage time concept has been widely used in the dynamic description of a variety of physical processes (5). As applied to translational diffusion, as done first by Schrödinger (6) and von Smoluchowski (7), the mean first passage time, τ, gives the mean time taken for a diffusing particle to reach a given spatial coordinate for the first time. If, as in the present case, this coordinate is a suitably defined radial separation, r_b, beyond which the colloidal particles are no longer considered to be associated, then τ may be interpreted as the mean lifetime of secondary-minimum flocculated colloidal particles.

The first passage time method reduces the numerical effort required to obtain the mean lifetime to the mere evaluation of a double integral involving the separation-dependent diffusion coefficient and the DLVO potential. As a result, τ can be readily calculated for any desired set of values of the system parameters.

RELATIVE DIFFUSION OF TWO INTERACTING PARTICLES

In the Smoluchowski picture, the space–time evolution of two Brownian particles in the absence of external fields, can be described in terms of the relative diffusion of the particles. Let $f(\mathbf{r}, t|\mathbf{r}_0)d\mathbf{r}$ be the probability of having a relative displacement vector $\mathbf{r}$ (connecting the centers of the two particles) in the range $\mathbf{r}$ to $\mathbf{r} + d\mathbf{r}$ at time t, given that the displacement vector was $\mathbf{r}_0$ initially, i.e.

$$f(\mathbf{r}, 0|\mathbf{r}_0) = \delta(\mathbf{r} - \mathbf{r}_0). \qquad [1]$$

The propagator $f(\mathbf{r}, t|\mathbf{r}_0)$ satisfies the diffusion equation

$$\frac{\partial}{\partial t} f(\mathbf{r}, t|\mathbf{r}_0)$$
$$= \nabla \cdot \mathbf{D}(r) \cdot [\nabla f(\mathbf{r}, t|\mathbf{r}_0) + f(\mathbf{r}, t|\mathbf{r}_0)], \quad [2]$$

where $\mathbf{D}(r)$ is the relative diffusion tensor. It depends on the interparticle separation because of the hydrodynamic coupling.

We assume that the mechanical force between the particles derives from a DLVO-type potential of mean force

$$V(r) \equiv kT\phi(r) \equiv V_R(r) + V_A(r), \qquad [3]$$

with a component $V_R(r)$ due to electrical double-layer repulsion and a component $V_A(r)$ due to van der Waals attraction.

The two colloidal particles are considered as being associated whenever they are less than a distance r_b apart. The value of r_b will subsequently be chosen so as to coincide with the operational definition of a flocculated pair (dictated by the optical resolution of the microscope), namely $r_b - 2a = 0.5$ μm for a particle radius $a = 1$ μm (1).

In order to determine the evolution of a

pair with initial separation r_0 ($<r_b$), we have to solve [2] in the interval $r_a < r < r_b$ subject to the initial condition [1], the "absorbing" boundary condition

$$f(r_b, t|r_0) = 0, \qquad [4]$$

and the "reflecting," or zero-flux, boundary condition

$$[\nabla f(\mathbf{r}, t|r_0) + f(\mathbf{r}, t|r_0)\nabla\phi(r)]_{r=r_a} = 0. \qquad [5]$$

Equation [5] is a statement of the fact that the two particles are prevented from coming into direct contact ($r = 2a$) by the very large primary potential barrier at $r = r_a$. The precise value of r_a ($2a < r_a < r_0$) is unimportant as long as $\phi(r_a) \gg 1$.

The mean lifetime, $\tau(r_0)$, of a pair with initial separation r_0 is given by

$$\tau(r_0) = \int_0^\infty dt\, t F(t|r_0), \qquad [6]$$

where $F(t|r_0)dt$ is the probability that the pair dissociates (for the first time) between t and $t + dt$. It is related to the propagator through

$$F(t|r_0) \equiv -\frac{\partial}{\partial t} Q(t|r_0)$$

$$\equiv -\frac{\partial}{\partial t} \int d\mathbf{r} f(\mathbf{r}, t|r_0). \qquad [7]$$

Combining [6] and [7], performing an integration by parts and noting that $f(\mathbf{r}, \infty|r_0) = 0$, we obtain

$$\tau(r_0) = \int_0^\infty dt \int d\mathbf{r} f(\mathbf{r}, t|r_0). \qquad [8]$$

For two spherical particles of radii a_1 and a_2 in an unbounded incompressible fluid of shear viscosity η, the exact form of the relative diffusion tensor $D(r)$ in the low-Reynolds-number regime is (8)

$$D(r) = D_0[G(r)\hat{\mathbf{r}}\hat{\mathbf{r}} + H(r)(1 - \hat{\mathbf{r}}\hat{\mathbf{r}})], \qquad [9]$$

where

$$D_0 = \frac{kT}{6\pi\eta}\left(\frac{1}{a_1} + \frac{1}{a_2}\right). \qquad [10]$$

The radial functions $G(r)$ and $H(r)$ both

approach unity as $r \to \infty$, so that $D(r \to \infty) = D_0 I$.

Combining [2] and [9] and assuming central forces, i.e., that ϕ is a function only of $r = |\mathbf{r}|$, we find

$$\frac{1}{D_0}\frac{\partial f}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2 G e^{-\phi}\frac{\partial}{\partial r}(e^\phi f)\right]$$

$$+ \frac{H}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right) + \frac{H}{r^2 \sin^2\theta}\frac{\partial^2 f}{\partial\psi^2}, \qquad [11]$$

which has solutions of the general form

$$f(\mathbf{r}, t) = \sum_l \sum_m f_{lm}(r, t)Y_{lm}(\theta, \psi), \qquad [12]$$

where the $Y_{lm}(\theta, \psi)$ are spherical haromonics. When this expression is substituted into [8], only the isotropic part ($l = 0$, $m = 0$) will survive the angular integrations. For the purpose of calculating the mean lifetime, τ, we need therefore consider only the isotropic propagator, $f(r, t|r_0)$, which satisfies the radial diffusion equation

$$\frac{\partial}{\partial t} f(r, t|r_0)$$

$$= \frac{D_0}{r^2}\frac{\partial}{\partial r}\left\{r^2 G(r)e^{-\phi(r)}\frac{\partial}{\partial r}[e^{\phi(r)}f(r, t|r_0)]\right\}. \qquad [13]$$

In the Appendix, we show how direct integration of [13], using the initial condition [1], the boundary conditions [4] and [5] as well as [8], leads to the following exact expression for the mean lifetime

$$\tau(r_0) = \frac{1}{D_0}\int_{r_0}^{r_b} dr \frac{e^{\phi(r)}}{r^2 G(r)}\int_{r_a}^r ds\, s^2 e^{-\phi(s)}, \qquad [14]$$

which shows the dependence of τ on the mechanical interaction potential, $\phi(r)$, and on the hydrodynamic interaction, via the function $G(r)$. These two functions are discussed in detail in the following sections. Equation [14] also shows the explicit dependence of τ on the initial pair separation, r_0, and on the separation, r_b, at which the pair is said to dissociate.

The previous development is valid for arbitrary radii of the two colloidal spheres. In the following, however, we shall focus on two special cases, namely that of two identical spheres ($a_1 = a_2 = a$) and that of a sphere and a plane ($a_1 = a$, $a_2 \rightarrow \infty$). The emphasis will be placed on the case of identical spheres, for which there exists experimental data (1).

HYDRODYNAMIC INTERACTION

Identical Spheres

The hydrodynamic function $G(r)$ for two identical spheres of radius a has been obtained by Brenner (9) in the form of an infinite series. For computational convenience, we represent this exact result by a rational fraction approximation of the form

$$G(r) = \frac{c_1 x + c_2 x^2 + x^3}{c_3 + c_4 x + c_5 x^2 + x^3}, \quad [15]$$

where

$$x \equiv \frac{h}{a}, \quad [16]$$

h being the surface-to-surface separation; $h = r - 2a$. The coefficients c_1–c_5 are given in Table I. The rational fraction approximation [15] reproduces the exact result with 4 figure accuracy for all interparticle separations $x \geq 0.1$ and with 3 figure accuracy for $0.01 \leq x < 0.1$.

Sphere and Plane

The exact hydrodynamic function for a sphere moving perpendicular to a plane wall (9) has also been represented by a rational fraction approximation of the form [15], the coefficients of which are given in Table I. This approximation is accurate to 3 or 4

figures for $x \geq 0.1$ and to 2 figures for $0.01 \leq x < 0.1$.

ELECTRICAL DOUBLE-LAYER REPULSION

We shall be concerned with aqueous solutions of colloidal particles of radius $a = 1$ μm and of 1:1 electrolyte at concentrations $c \geq 10^{-4}$ mole dm^{-3}. Consequently, we have $\kappa a > 30$, where κ^{-1} is the Debye length. Furthermore, under these conditions the secondary minimum occurs at surface-to-surface separations $h \ll a$. It follows that the interaction between two spheres can be accurately constructed from the interaction between parallel planes using the Derjaguin approximation (10). Accordingly, we write the double-layer repulsion between two spheres of radii a_1 and a_2 as

$$V_R(h) = 2\pi \left(\frac{1}{a_1} + \frac{1}{a_2} \right)^{-1} \int_h^\infty dh' E_R(h'), \quad [17]$$

where $E_R(h)$ is the interaction free energy per unit area between parallel planes.

Since, typically, $\kappa h \sim 10$ at the secondary minimum, we shall be interested only in the regime $\kappa h \gg 1$. We may then use the superposition, or weak-overlap, approximation (3), according to which

$$E_R(h) = \frac{64nkT\gamma^2}{\kappa} e^{-\kappa h}, \quad [18]$$

where n is the number density of the z:z electrolyte and where $\gamma \equiv \tanh(ze\psi_0/4kT)$, ψ_0 being the electrostatic potential on the surface of the spheres (assumed to be the same on both spheres). Note that, as long as the superposition approximation remains valid, no assumption has to be made about whether the spheres approach under constant

TABLE I

Coefficients in Rational Fraction Approximations to the Hydrodynamic Function $G(r)$

	c_1	c_2	c_3	c_4	c_5
Sphere–sphere	0.154030	1.29993	0.0782416	1.10529	2.81955
Sphere–plane	2.04185	5.60414	2.06393	8.59190	6.72180

surface charge or under constant surface potential (3). Combining [17] and [18] and performing the integration, we have

$$V_R(h) = 64\pi \left(\frac{1}{a_1} + \frac{1}{a_2}\right)^{-1} \epsilon_0\epsilon_r \left(\frac{kT\gamma}{ze}\right)^2 e^{-\kappa h}, \quad [19]$$

where $\epsilon_0\epsilon_r$ is the static dielectric permittivity of the solvent.

VAN DER WAALS ATTRACTION

For polystyrene spheres in water, the secondary minimum typically occurs at surface-to-surface separations in the range 5–50 nm, depending on the surface potential and on the electrolyte concentration. At these separations, it is necessary to include retardation effects in the van der Waals interaction. Since $h \ll a$, we can again use the Derjaguin approximation [17] to construct the interaction between spheres from the interaction free energy per unit area, $E_A(h)$, between parallel planes

$$E_A(h) = -\frac{A(h)}{12\pi h^2}. \quad [20]$$

The Hamaker function, $A(h)$, is given by the Lifshitz theory (11) as an infinite sum over imaginary frequencies and requires knowledge about the frequency-dependent dielectric permittivity of the colloidal particles and of the solvent medium. In the separation regime of interest, where $\kappa h \gg 1$, the "zero-frequency" term in $A(h)$ is completely negligible as a result of screening by the electrolyte (12). We therefore omit this term. In calculating the Hamaker function, $A(h)$, we have used standard permittivity data for water and polystyrene (13, 14).

For computational convenience, we have represented the Hamaker function by rational fraction approximations of the form

$$A(h) = \frac{c_0 + c_1 y + c_2 y^2}{1 + c_3 y + c_4 y^2 + c_5 y^3}$$

$$\times 10^{-21} \text{ J.} \quad [21]$$

The definition of the quantity y depends on the separation regime as follows

$$y \equiv \log(h/\text{nm}) + 1.0;$$

$$-1.0 \leqslant \log(h/\text{nm}) \leqslant 1.9$$

$$y \equiv \log(h/\text{nm}) - 1.9;$$

$$1.9 \leqslant \log(h/\text{nm}) \leqslant 2.7$$

$$y \equiv \log(h/\text{nm}) - 2.7;$$

$$2.7 \leqslant \log(h/\text{nm}) \leqslant 3.2. \quad [22]$$

The coefficients c_0–c_5 for each separation regime are given in Table II.

The Derjaguin approximation [17] is accurate only for $h/a \leqslant 0.1$. Fortunately, for the range of system parameters of interest here, the magnitude of the van der Waals attraction falls below $0.1kT$ when $h/a \sim 0.1$ so that any error due to the breakdown of the Derjaguin approximation at larger separations is unimportant. In our calculations, we have set $A(h) = 0$ for $h > 10^{3.2}$ nm.

The Derjaguin approximation yields an estimate of the van der Waals interaction which always exceeds the exact result in magnitude (3). It is therefore noteworthy that a recently proposed ansatz for the van der Waals interaction between spheres (15) predicts an attraction whose magnitude is larger than that predicted by the Derjaguin approximation by as much as 50%. We have consequently refrained from using this ansatz.

RESULTS AND DISCUSSION

Comparison with Simulation Data

The dynamics of secondary-minimum flocculated pairs and triplets of colloidal particles was recently studied by the computer simulation technique of Brownian dynamics (16). In this section, we compare the pair lifetimes obtained in that study with the predictions of the first passage time theory.

In the simulation study, the double-layer repulsion between two spherical particles of radius a was taken to be

$$V_R(h) = 2\pi\epsilon_0\epsilon_r a\psi_0^2 \ln(1 + e^{-\kappa h}), \quad [23]$$

while the van der Waals attraction was described by an empirical formula due to Schenkel and Kitchener (17)

TABLE II

Coefficients in Rational Fraction Approximations to the Hamaker Function $A(h)$

log (h/nm)	c_0	c_1	c_2	c_3	c_4	c_5
−1.0–1.9	6.38790	−3.57341	0.515324	−0.549089	0.0610292	0.0155967
1.9–2.7	1.19360	−1.03183	0	1.41471	1.74380	0
2.7–3.2	0.114740	−0.174856	0	2.11158	4.80144	0

$$V_A(h) = \frac{-aA}{12h(1 + 1.77p)}, \quad [24]$$

with

$$p \equiv \frac{2\pi h}{\lambda_L}. \quad [25]$$

Like Eq. [20], Eq. [23] is based on the Derjaguin approximation. However, [23] also assumes that it is permissible to use a linearized approximation to the interaction between parallel planes. This is the case for $ze\psi_0/kT \lesssim 1$.

The parameter values used in the simulation study were as follows: $a = 1\ \mu m$, $A = 5 \times 10^{-21}$ J, $\lambda_L = 100$ nm, $\psi_0 = 25$ mV, $T = 300$ K, $\epsilon_r = 80$, and $\eta = 8.65 \times 10^{-4}$ kg $(ms)^{-1}$. An accurate representation of the exact hydrodynamic function $G(r)$ was used. The initial separation, r_0, of the flocculated pair corresponded to the position of the secondary minimum in the DLVO potential and the pair was taken to dissociate at $r_b/a = 2.2$.

In the first three columns of Table III, we compare the mean lifetimes, at three concentrations of 1:1 electrolyte, obtained in the simulation study (16) with those calculated from [14] with the *same* interaction potential [23]–[25] and the *same* parameter values. If carried out correctly, the two computational methods should give identical results. This appears to be the case (within the statistical uncertainty of the simulation) at the two lowest electrolyte concentrations. However, at $c = 120$ mmole dm^{-3}, the simulated mean lifetime is too short by an order of magnitude. This discrepancy is probably due to the poor statistics in the simulation at $c = 120$ mmole dm^{-3}; only two dissociation events were recorded. We note that the mean lifetime can

be calculated from [14] to four significant figures in less than a second (on a Univac 1100 computer), whereas the Brownian dynamics results in Table III required of the order 1 hr CPU time (on a CDC 7600 computer).

In the simulation study (16), not only the mean lifetime, τ, but also the distribution of lifetimes was reported. Let $P(t|r_0; \Delta)$ be the probability that a flocculated pair, with initial separation r_0, dissociates in a time interval Δ around t. For sufficiently small Δ,

$$P(t|r_0; \Delta) = \Delta F(t|r_0) = -\Delta \frac{\partial}{\partial t} Q(t|r_0), \quad [26]$$

where the second equality follows from [7]. Many restricted diffusion processes are accurately described by the exponential approximation (18)

$$Q(t|r_0) = e^{-t/\tau}. \quad [27]$$

The physical basis of [27] is the assumption that the diffusing particles become essentially Boltzmann distributed in a time short compared to τ. Combining [26] and [27], we find

$$P(t|r_0; \Delta) = \frac{\Delta}{\tau} e^{-t/\tau}. \quad [28]$$

TABLE III

Mean Lifetime of Secondary-Minimum Flocculated Pairs of Polystyrene Spheres ($a = 1\ \mu m$, $\psi_0 = 25$ mV) in Aqueous 1:1 Electrolyte at 25°C

Electrolyte concentration (mmole dm^{-3})	τ (sec)		
	Ref. 16	Eqs. [14], [23]–[25]	Eqs. [14], [19]–[22]
10	0.258	0.2524	0.3046
50	1.49	1.381	10.08
120	20 ± 5	163.6	31950

In Fig. 1, we compare [28] with the simulation data (16) for the case $c = 10$ mmole dm^{-3}. The agreement is reasonable except at very short times, where the exponential approximation [27] is bound to fail. (A finite time is always required for diffusion from $r = r_0$ to $r = r_b$.) We expect the accuracy of [28] to improve at high electrolyte concentrations, where the secondary minimum is deeper.

The last column of Table III contains mean lifetimes calculated from [14] with the more accurate representation [19]–[22] of the DLVO potential. The parameter values were as given above, except that we used H$_2$O data for 25°C ($\epsilon_r = 78.54$, $\eta = 8.904 \times 10^{-4}$ kg(ms)$^{-1}$. At the two higher electrolyte concentrations, there are striking differences between the mean lifetimes calculated from the two representations of the DLVO potential.

For a surface potential of 25 mV, there is little difference between the two expressions [19] and [23] for the double-layer repulsion in the region of the secondary minimum. However, the depth of the secondary minimum is quite sensitive to the representation of the van der Waals attraction. This is illustrated in Table IV, in which we compare the depths and positions of the secondary minimum as predicted by the two representations of the DLVO potential. The potential
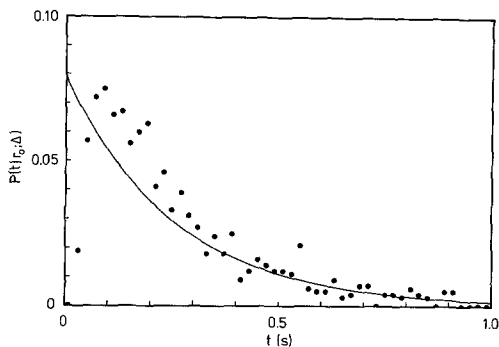
TABLE IV

Positions and Depths of the Secondary Minimum in the DLVO Potential between Polystyrene Spheres ($a = 1$ μm, $\psi_0 = 25$ mV) in Aqueous 1:1 Electrolyte at 25°C

Electrolyte concentration (mmole dm^{-3})	Eqs. [23]–[25]		Eqs. [19]–[22]	
	h_{min} (nm)	$-V_{min}/kT$	h_{min} (nm)	$-V_{min}/kT$
10	24	0.87	22	1.30
50	8.4	4.68	7.5	7.24
120	4.6	10.67	4.1	16.28

curves for the case $c = 50$ mmole dm^{-3} are displayed in Fig. 2, from which it is clear that the discrepancy lies mainly in the van der Waals attraction. (A Hamaker constant $A = 5 \times 10^{-21}$ J was used in the simulation study (16). This may be compared with the contact value of the Hamaker function given by [21] and [22]: $A(0) = 6.39 \times 10^{-21}$ J.) Since the pair potential appears in the exponent in the expression [14] for τ, relatively small discrepancies in the depth of the secondary minimum can produce large varia-
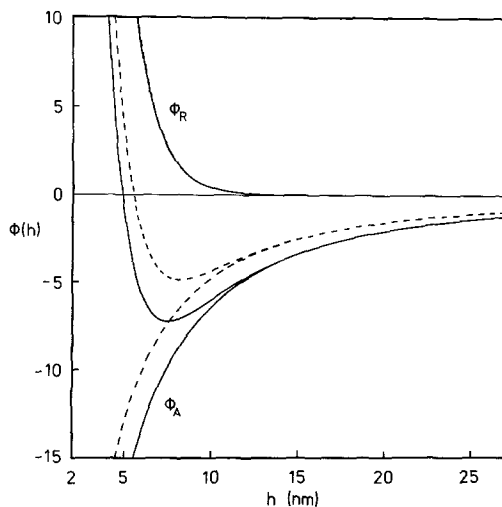

FIG. 1. Distribution of lifetimes of flocculated pairs with initial separation, r_0, corresponding to the secondary minimum. $\Delta = 0.02$ sec, $c = 10$ mmole dm^{-3}, and other parameters as given in the text. The data points are from a Brownian dynamics simulation (16) and the curve is obtained from Eq. [28] with $\tau = 0.2524$ sec.

FIG. 2. DLVO pair potential versus surface-to-surface separation for polystyrene spheres ($a = 1$ μm, $\psi_0 = 25$ mV) in aqueous 50 mmole dm^{-3} 1:1 electrolyte at 25°C. The primary minimum is not shown. Solid curves are calculated from Eqs. [19]–[22], dashed curves from Eqs. [23]–[25]. The solid and dashed curves for ϕ_R are not distinguishable in the figure.

tions in the predicted lifetime. It is this circumstance which makes the lifetime of flocculated pairs an ideal probe of the DLVO potential in the region of the secondary minimum.

Comparison with Experimental Data

The mean lifetime of two identical secondary-minimum flocculated polystyrene spheres ($a = 1$ μm) in aqueous 1:1 electrolyte at 25°C is shown in Fig. 3 as a function of surface potential and electrolyte concentration. These results were obtained from [14], using the exact hydrodynamic interaction [15] and the representation [19]–[22] of the DLVO potential. The latter is accurate over the entire range of parameter values in Fig. 3. The spheres start out in the secondary minimum and are considered to remain associated as long as the surface-to-surface separation does not exceed 0.5 μm. This dissociation criterion is the same as that used in the experimental study (1). It is seen from Fig. 3 that the effect of neglecting the hydrodynamic coupling between the spheres (i.e., setting $G(r) = 1$), would be to shorten the mean lifetime by a factor of 5. The mean

lifetime resulting from the representation [23]–[25] of the DLVO potential at $\psi_0 = 25$ mV (not shown) is virtually identical to that based on [19]–[22] at $\psi_0 = 50$ mV (curve c in Fig. 3).

In the case of a sphere and a plane ($a_1 = a$, $a_2 \rightarrow \infty$), [14] should be replaced by (see Appendix)

$$\tau(r_0) = \frac{1}{D_0} \int_{r_0}^{r_b} dr \frac{e^{\phi(r)}}{G(r)} \int_{r_a}^{r} ds e^{-\phi(s)}. \quad [29]$$

Results for this case are shown in Fig. 4. The qualitative trends are very similar to those in Fig. 3, although the absolute lifetimes are longer. The effect of the hydrodynamic coupling is a factor of 6.3. Again, curve c nearly coincides with the result for the potential [23]–[25] at $\psi_0 = 25$ mV.

The experimental study (1), involving direct microscopic observation of spherical ($a = 1$ μm) polystyrene particles, resulted in lifetimes *of the order of a few minutes* for zeta potentials of 50–75 mV and 1:1 electrolyte concentrations of 5×10^{-5}–6×10^{-3} mole dm^{-3}. As judged from Fig. 3, the theory predicts a mean lifetime of *less than 1 sec* under these conditions. From the upper scale in Fig. 3, we can deduce that the experimental results imply the existence of a secondary minimum which is deeper by about $10kT$ than that predicted by the representation [19]–[22] of the DLVO potential. This difference cannot be accounted for by any reasonable adjustment of system parameters to alter the pair interaction. For instance, for electrolyte concentrations of $<10^{-2}$ mole dm^{-3}, doubling the particle size only increases the association time by about a factor of 2. The effect of other changes in system parameters can be readily deduced from the curves in Fig. 3.

The glaring discrepancy between theory and experiment warrants a closer scrutiny of the results. One difference between the two is in the choice of initial separation for a flocculated pair. However, since the experimental r_0 exceeds the secondary-minimum
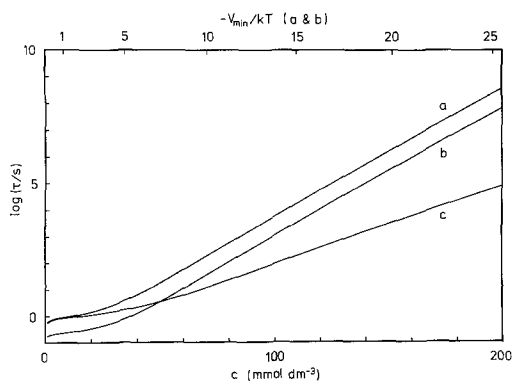

FIG. 3. Mean lifetime of a pair of secondary-minimum flocculated polystyrene spheres ($a = 1$ μm) in aqueous solution at 25°C versus concentration of 1:1 electrolyte. The spheres are initially in the secondary minimum and remain associated as long as $h < 0.5$ μm. The calculations are based on Eqs. [14], [15] and [19]–[22]. The curves refer to (a) $\psi_0 = 25$ mV, exact $G(r)$, (b) $\psi_0 = 25$ mV, $G(r) = 1$, and (c) $\psi_0 = 50$ mV, exact $G(r)$.
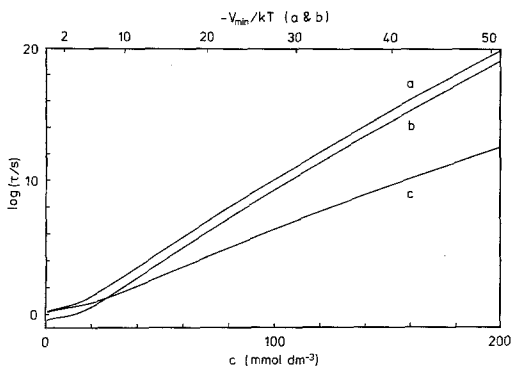
FIG. 4. Mean lifetime of a secondary-minimum associated polystyrene sphere ($a = 1$ μm) at a planar wall (of the same material and with the same surface potential) in aqueous solution at 25°C versus concentration of 1:1 electrolyte. The sphere is initially in the secondary minimum and remains associated as long as $h < 0.5$ μm. The calculations are based on Eqs. [29], [15], and [19]–[22]. The curves refer to (a) $\psi_0 = 25$ mV, exact $G(r)$, (b) $\psi_0 = 25$ mV, $G(r) = 1$, and (c) $\psi_0 = 50$ mV, exact $G(r)$.

separation, we would expect the experimental lifetimes to be shorter, rather than longer, than the calculated ones.

A check on the internal consistency of the experimental data is provided by the reported equilibrium size distribution of flocculated aggregates. Thus, at $c = 3$ mmole dm^{-3} and $\psi_0 = 75$ mV, it was found that 91% of the particles were unassociated (1). For the purpose of the following rough estimate, we may assume that the remaining 9% are all flocculated pairs (rather than higher aggregates). The number density of unassociated particles, n_1, evolves in time according to

$$\frac{dn_1}{dt} = -k_+ n_1^2 + k_- n_2, \qquad [30]$$

where $k_- = 1/\tau$ and where the diffusion-controlled association rate constant may be approximated by $k_+ = 8\pi a D_0$. At equilibrium, [30] yields

$$k_+ x_1^2 n = 1/2 k_- (1 - x_1), \qquad [31]$$

where x_1 is the fraction of unassociated particles and where n is the total particle density. The mean lifetime may thus be estimated from

$$\tau = \frac{3\eta(1 - x_1)}{16kTnx_1^2}, \qquad [32]$$

where we have also used [10]. With $x_1 = 0.91$ and $n = 10^{14}$ m^{-3} we obtain $\tau \approx 1$ min, which is consistent with the values of τ determined by direct observation.

We are consequently led to the somewhat disconcerting conclusion that, even for such a well-characterized model system as monodisperse polystyrene spheres of radius 1 μm and zeta potential 50–75 mV in $\sim 10^{-4}$ mole dm^{-3} aqueous 1:1 electrolyte, the magnitude of the colloidal interaction potential in the region of the secondary minimum, as inferred from measurements of the doublet association time, is of the order of $10kT$ larger than that predicted by the best DLVO potential.

APPENDIX: THE MEAN FIRST PASSAGE TIME

An expression for the mean first passage time can be derived from the Smoluchowski diffusion equation in several ways, the simplest being the direct integration method due to Deutch (19). For convenience, we here reproduce that derivation in the notation of the main text.

The radial diffusion equation [13], generalized to a d-dimensional space, reads

$$\frac{\partial}{\partial t} f(r, t|r_0) = D_0 r^{1-d} \frac{\partial}{\partial r}$$

$$\times \left\{ r^{d-1} G(r) e^{-\phi(r)} \frac{\partial}{\partial r} [e^{\phi(r)} f(r, t|r_0)] \right\}. \quad [A1]$$

Multiplying [A1] by r^{d-1}, integrating from r_a to r and using the boundary condition [5], we get

$$\int_{r_a}^{r} du\, u^{d-1} \frac{\partial}{\partial t} f(u, t|r_0)$$

$$= D_0 r^{d-1} G(r) e^{-\phi(r)} \frac{\partial}{\partial r} [e^{\phi(r)} f(r, t|r_0)]. \quad [A2]$$

Rearranging and integrating from r to r_b, using the other boundary condition [4], we find

$$f(r, t|r_0) = -\frac{1}{D_0} e^{-\phi(r)} \int_r^{r_b}$$

$$\times ds \frac{s^{1-d}e^{\phi(s)}}{G(s)} \int_{r_a}^s du u^{d-1} \frac{\partial}{\partial t} f(u, t|r_0). \quad [A3]$$

The d-dimensional radial version of [8] is

$$\tau(r_0) = \int_0^\infty dt \int_{r_a}^{r_b} dr r^{d-1} f(r, t|r_0) \quad [A4]$$

and of the initial condition [1]

$$f(r, 0|r_0) = r^{1-d}\delta(r - r_0). \quad [A5]$$

Combination of Eqs. [A3]–[A5] yields

$$\tau(r_0) = \frac{1}{D_0} \int_{r_a}^{r_b} dr r^{d-1} e^{-\phi(r)}$$

$$\times \int_r^{r_b} ds \frac{s^{1-d}e^{\phi(s)}}{G(s)} H(s - r_0), \quad [A6]$$

where $H(x)$ is the unit step function. Interchanging the order of integration, we obtain the desired result

$$\tau(r_0) = \frac{1}{D_0} \int_{r_0}^{r_b} dr \frac{r^{1-d}e^{\phi(r)}}{G(r)} \int_{r_a}^r ds s^{d-1} e^{-\phi(s)}.$$

$$[A7]$$

Equations [14] and [29] of the main text are obtained by setting $d = 3$ and $d = 1$, respectively.

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