Editors' Suggestion

# Detachment dynamics of colloidal spheres with adhesive interactions

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(Received 23 January 2018; published 23 April 2018)

Escape of colloidal-size particles from various kinds of solids, such as aggregates and surfaces, occurs in a wide variety of settings of both fundamental and applied scientific interest. In this paper an exact solution for the detachment of adhesive spheres from each other by means of diffusion is presented. The solution takes into account repeated detachment and reattachment events in the course of time on the way toward the permanently separated state. For strongly adhesive spheres this state is approached in an exponential manner essentially regardless of how the bound state is specified. The analytical solution is shown to capture semiquantitatively the escape from more realistic potential wells using a mapping procedure whereby equality of second virial coefficients is imposed.

DOI: 10.1103/PhysRevE.97.042610

## I. INTRODUCTION

The distinguishing feature of the colloidal state in liquid dispersions is that diffusion of particles is a mode of transport; particles are not massive enough (for sizes ranging between 1–$10^4$ nm) to be unaffected by the thermal motion of the molecules of the surrounding liquid. Though itself very inefficient at transporting particles over macroscopic distances, diffusion may nevertheless be quite pivotal in that it can cause particles to migrate short distances over (free) energy barriers that tend to keep particles immobilized on larger grains or surfaces via, e.g., van der Waals attractions. Once such barriers are traversed, particles may be free to travel appreciable macroscopic distances by flow.

This mechanism of escape of bound particles is expected to be important in a number of industrial settings, such as in processes dealing with separations, dispersion, and redispersion of dry solids [1–3]. In addition, the mobilization and leaching of colloidal species is nowadays widely recognized as playing an important role in the environment [4]. In this context, the colloidal particles, when liberated, act as a mobile phase on which numerous sparingly soluble compounds can piggyback, which may accelerate the transport of, e.g., sorbed contaminants considerably [5,6]. Of course, sorption of contaminants on colloidal particles need not just be detrimental; it also serves as a key step in water treatment and remediation strategies [7–9]. Yet, in other cases, it is the colloidal species themselves that are harmful [10–12]; pathogens, such as some bacteria, viruses, and protozoa, are generally of colloidal size and may be mobilized and introduced into the environment through the same processes that govern nonbiological particles.

The detachment of colloidal particles from surfaces [13] and other particles [14,15] has been treated in the past by so-called first-passage time theory [16–18]. In this context, the theory governs the time evolution of the probability of a particle detaching for the first time from an initially bound state. There are some complications with using such results as models for detachment of colloidal particles. One concern is the interaction potentials relevant to colloids, which most often do not present a barrier to particles returning to the attached state once detached. Another related complication is associated with the lack of an obvious definition of what should be considered bound and unbound states for colloids subject to such interactions [19]. A third issue concerns the effect of hydrodynamic interaction, mediated by the solvent in which the particles are dispersed. In this paper we will be concerned with the first two of these issues.

In what follows, we begin by presenting results of applying the first-passage time theory to attachment and detachment of colloidal spheres subject to the secondary minimum of a Derjaguin-Landau-Verwey-Overbeek (DLVO) potential. The purpose is to illustrate the need for an alternative approach to dealing with the detachment process. Then, particle escape from a simplified interaction potential of square-well form in three dimensions is analyzed. Taking the so-called adhesive limit further simplifies the interaction, allowing for an analytical solution of the governing diffusion equation. The solution, in terms of the more experimentally relevant escape probability, exhibits a rather complex behavior with a crossover from power-law to exponential in time approach to the detached state as the adhesion is increased. The solution is tested within a second virial coefficient mapping against exact numerical solutions of the escape from the secondary minimum of DLVO potentials.

## II. FIRST-PASSAGE TIME APPROACH

It is tempting to apply first-passage time theory to a particle initially trapped in a potential well even when there is no barrier to prevent its return to the initial state. Chan and Halle [14] employed Deutch's method [20] to derive the mean first-passage time for the separation of particle pairs and Bergenholtz *et al.* [15] solved for the full first-passage time distribution. Although formally exact, problems may arise when first-passage time theory is used to model processes with significant recrossing probabilities. To illustrate this effect we consider in this section a single particle diffusing in the vicinity

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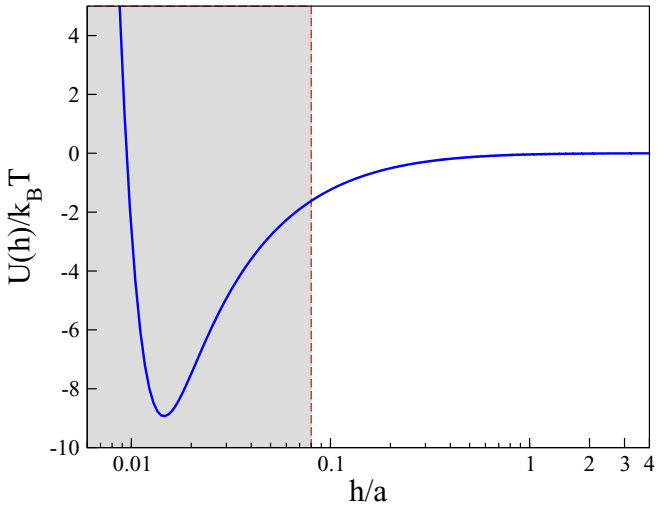


FIG. 1. The wall-sphere interaction potential $U$ as a function of surface-surface separation $h$. At $h/a = 0.08$, marked by the vertical line, an absorbing boundary condition is erected. For short separations corresponding to the shaded region to the left of this boundary, the particle is considered as bound to the wall. For larger separations, $h/a > 0.08$, the sphere is considered detached from the wall.

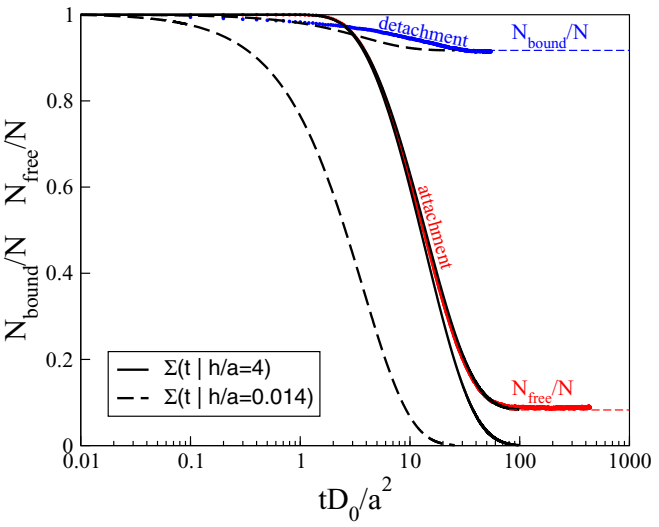


FIG. 2. The fraction of free and bound particles as a function of dimensionless time from BD simulations with $N = 10^3$. The attachment and detachment processes imply having particles in starting positions given by $h/a = 4$ and 0.014, respectively. The lines show results for the survival probability obtained from first-passage time theory, as given by numerical solution of Eq. (1) with an absorbing boundary condition at $h/a = 0.08$ and the same starting positions as in the BD simulations as labeled. These survival probabilities are also shown after they have been shifted to account for the equilibrium reached at long times.

of a plane wall. The corresponding first-passage time problem was treated by Zimmer and Dahneke numerically [13].

A colloidal sphere of radius $a$ is considered. It is allowed to start at a surface-surface separation $h$ from the wall at time $t = 0$. The survival probability, $\Sigma(t|h)$, i.e., the probability that the sphere remains in the domain of interest by time $t$, is given by [17,18]

$$\frac{\partial}{\partial t}\Sigma(t|h) = \mathcal{L}^{\dagger}(h)\Sigma(t|h) = \left(\frac{\partial}{\partial h} - \frac{1}{k_B T}\frac{\partial U}{\partial h}\right) D_{\perp}(h)\frac{\partial}{\partial h}\Sigma(t|h), \quad (1)$$

which is governed by the backward or adjoint Smoluchowski operator $\mathcal{L}^{\dagger}(h)$ involving the mobility $D_{\perp}(h)/k_B T$ with the thermal energy $k_B T$. The above equation is readily solved by an implicit finite differences scheme in a finite spatial domain. Here, a particle in the two domains of Fig. 1 is considered. It is started from $h = 4a$, i.e., where the influence of the interaction potential is negligible, and we ask for the time dependence of the survival probability in the presence of an absorbing boundary condition at $h = 0.08a$ and a reflecting boundary at $h = 4a$ to prevent the particle from escaping altogether. In addition, we perform the corresponding first-passage time analysis for a starting position at the minimum of the interaction potential in Fig. 1 with the same absorbing boundary condition at $h = 0.08a$. Note that the choice of the dividing boundary at $h = 0.08a$ between bound and unbound states has been rather arbitrarily selected at a point where the interaction is of order $k_B T$.

To evaluate how the first-passage time theory fares for the two initial conditions, comparison will be made with Brownian dynamics (BD) simulations of the particle-wall dynamics [21] using the same interaction potential and also with the same reflecting boundary. To study the attachment process a particle is started at $h = 4a$ and its position is tracked as a function of time. As long as it is found at $h > 0.08a$ it is considered a free particle detached from the wall, whereas for $h < 0.08a$ it is considered as a bound particle attached to the wall. The process is repeated under the same conditions $N$ times. Out of these $N$ trials, equivalent to $N$ mutually noninteracting particles, we track the number of free and bound particles, $N_{\text{free}}$ and $N_{\text{bound}}$, as a function of time. The same procedure is followed for the study of the detachment process except that the starting position of the particle is set to the minimum of the interaction potential, in this case at $h \approx 0.014a$.

Figure 2 shows the outcome of BD simulations of particles detaching from the wall, meaning the particles have to diffuse out of the well of the interaction potential to enter the domain $0.08 < h/a < 4$, as well as the reverse process of attachment whereby particles have to cross the dividing boundary at $h/a = 0.08$ from the other direction. For sufficiently long times the fraction of free and bound particles reach equilibrium values.

To see the extent to which the dynamics can be modeled by first-passage time theory, Eq. (1) is solved numerically for the survival probability with an absorbing boundary erected at $h/a = 0.08$. The results for the survival probability for the same two initial conditions as used in the BD simulations are also shown in Fig. 2. As seen, the initial time dependence for the attachment process is reproduced well by this first-passage time theory, whereas the same theory predicts a much more rapid detachment process than seen in the BD simulations. The difference between the two is due to the effect of particles traversing the dividing boundary at $h/a = 0.08$ multiple times in the simulations, which is neglected entirely in applying

the first-passage time theory to the detachment process here. Indeed, by using an absorbing boundary condition in the theory one studies the attachment and detachment processes in isolation, treating both as irreversible. As a consequence, as shown in Fig. 2 and in line with arguments presented by Widom [22], no information about the equilibrium state can be gained from such irreversible dynamics. Since the equilibrium condition in this case is quite trivial, we can supplement the first-passage time theory with this result, i.e., plotting $(1-f_{eq})\Sigma(t)+f_{eq}$ with $f_{eq}$ as the equilibrium fraction of free or bound particles. Figure 2 shows that for the attachment process this quantitatively reproduces the BD simulation results, indicating a negligible flux of particles across the dividing boundary from the opposite direction. However, for the detachment process the first-passage time theory significantly overestimates the rate of detachment compared to the BD simulations, which is caused by particles detaching and reattaching several times before establishing final equilibrium. It follows that unless there is a significant barrier to prevent recrossing of the dividing boundary, first-passage time theory is ill suited to treating detachment dynamics. In what follows, we will pursue an exact analytical solution to the two-sphere detachment problem in three dimensions, subject to a simplified interaction and neglect of hydrodynamic interaction.

## III. EXACT SOLUTION FOR A SIMPLIFIED INTERACTION POTENTIAL

### A. Governing equation and boundary conditions

The Smoluchowski equation for the conditional probability density governing a pair of otherwise isolated particles diffusing under the influence of their mutual interaction $U(r)$ is given as [14]

$$\frac{\partial}{\partial t}p(r,t|r_0)=\frac{2D_0}{r^2}\frac{\partial}{\partial r}\times\left(r^2G(r)e^{-U(r)/k_BT}\frac{\partial}{\partial r}[e^{U(r)/k_BT}p(r,t|r_0)]\right),\tag{2}$$

where $G(r)$ is the mobility along the line of centers, $D_0$ is the single-sphere diffusion coefficient, and $r_0$ is the separation at time $t=0$. Substituting in a new function, defined as $p(r,t|r_0)=e^{-U(r)/k_BT}v(r,t|r_0)$, yields the adjoint equation

$$\frac{\partial}{\partial t}v(r,t|r_0)=e^{U(r)/k_BT}\frac{2D_0}{r^2}\frac{\partial}{\partial r}\left(r^2G(r)e^{-U(r)/k_BT}\frac{\partial}{\partial r}v(r,t|r_0)\right).\tag{3}$$

This equation is made dimensionless using the particle diameter $\sigma$, through $\tau=2D_0t/\sigma^2$ and $x=r/\sigma$, and subsequently Laplace transformed into

$$-v(x,0)+s\tilde{v}(x,s)=\frac{e^{U(x)/k_BT}}{x^2}\frac{\partial}{\partial x}\left(x^2G(x)e^{-U(x)/k_BT}\frac{\partial\tilde{v}(x,s)}{\partial x}\right),\tag{4}$$

where $s$ is the dimensionless Laplace transform variable and the dependence on $x_0=r_0/\sigma$ of the Laplace-transformed function $v$, denoted by $\tilde{v}$, has been suppressed. Equation (4) will be solved for a square-well interaction

$$U(x)=\begin{cases}\infty & 0<x<1\\ -\epsilon & 1<x<\lambda\\ 0 & \lambda<x<\infty\end{cases}\tag{5}$$

subject to the initial condition that the separation satisfy $1<x_0<\lambda$. The probability density must be normalized to unity at all times, which means that $\int_1^\lambda v(x,0)x^2dx=(4\pi\sigma^3e^{\epsilon/k_BT})^{-1}$. This condition can be met by selecting $v(x,0)=a\Theta(\lambda-x)$ in terms of $a=[4\pi\sigma^3e^{\epsilon/k_BT}(\lambda^3-1)/3]^{-1}$ and the unit step function.

The procedure used by Weaver [23] is followed to derive appropriate boundary conditions at the well boundary $x=\lambda$. Integrating Eq. (4) from sphere-sphere contact to an arbitrary separation leads to

$$\int_1^x[-a\Theta(\lambda-y)+s\tilde{v}(y,s)]e^{-U(y)/k_BT}y^2dy=\int_1^x d\left(y^2G(y)e^{-U(y)/k_BT}\frac{\partial\tilde{v}(y,s)}{\partial y}\right)=F(x,s)\tag{6}$$

from which one recognizes that the function $F(x,s)$ must be a continuous function of $x$. The rightmost integral in Eq. (6) can be completed as $F(x,s)=x^2G(x)e^{-U(x)/k_BT}\frac{\partial\tilde{v}(x,s)}{\partial x}$ because the $x=1$ limit vanishes due to the flux vanishing in this limit. The continuity of $F(x,s)$ results in the following boundary condition at the well boundary

$$e^{\epsilon/k_BT}\left(\frac{\partial\tilde{v}(x,s)}{\partial x}\right)_{x\to\lambda-}=\left(\frac{\partial\tilde{v}(x,s)}{\partial x}\right)_{x\to\lambda+}.\tag{7}$$

Rearranging the expression for $F(x,s)$ and integrating it from contact to an arbitrary separation results in

$$\tilde{v}(x,s)-\tilde{v}(1,s)=\int_1^x\frac{e^{U(y)/k_BT}F(y,s)}{y^2G(y)}dy=B(x,s),\tag{8}$$

where $B(x,s)$ is a another continuous function of $x$. This leads to the following, second boundary condition at the well boundary:

$$\tilde{v}(\lambda-,s)=\tilde{v}(\lambda+,s).\tag{9}$$

### B. Solution for the square-well interaction

Applying Eq. (4) with the initial condition $v(x,0)=a\Theta(\lambda-x)$ to the square-well interaction in Eq. (5) under neglect of hydrodynamic interactions $[G(x)=1]$ leads to

$$\frac{\partial^2\tilde{v}(x,s)}{\partial x^2}+\frac{2}{x}\frac{\partial\tilde{v}(x,s)}{\partial x}-s\tilde{v}(x,s)=-a\tag{10}$$

for $1<x<\lambda$ and

$$\frac{\partial^2\tilde{v}(x,s)}{\partial x^2}+\frac{2}{x}\frac{\partial\tilde{v}(x,s)}{\partial x}-s\tilde{v}(x,s)=0\tag{11}$$

for $x > \lambda$. The solutions to these equations read as

$$\tilde{v}(x,s) = -\frac{a\lambda}{sx}\frac{e^{\sqrt{s}\lambda}}{Z(s)}\left[e^{\sqrt{s}x} + e^{2\sqrt{s}}\frac{\sqrt{s}-1}{\sqrt{s}+1}e^{-\sqrt{s}x}\right] + \frac{a}{s} \tag{12}$$

for $1 < x < \lambda$ and

$$\tilde{v}(x,s) = \frac{a\lambda}{sx}e^{\sqrt{s}\lambda}\left[1 - \frac{e^{2\sqrt{s}\lambda}}{Z(s)} - \frac{e^{2\sqrt{s}}}{Z(s)}\frac{\sqrt{s}-1}{\sqrt{s}+1}\right]e^{-\sqrt{s}x} \tag{13}$$

for $x > \lambda$, where $Z(s) = e^{2\sqrt{s}\lambda}(e^{\epsilon/k_BT}\frac{\sqrt{s}\lambda-1}{\sqrt{s}\lambda+1} + 1) - e^{2\sqrt{s}}\frac{\sqrt{s}-1}{\sqrt{s}+1}(e^{\epsilon/k_BT} - 1)$. These solutions satisfy the boundary conditions in Eqs. (7) and (9) as well as a no-flux condition at $x = 1$ and a boundedness condition at $x \to \infty$.

### C. Baxter limit

So far our treatment has mirrored that carried out by Felderhof for the one-dimensional problem [24]. At this stage, however, we look for an even simpler model than the square-well interaction. Baxter's adhesive sphere potential [25] represents such a simplification in that the effects of well depth and well width are subsumed in a single parameter, defined as $\tau_b^{-1} = 12\delta e^{\epsilon/k_BT}$, which takes on finite values in the double limit $\delta \to 0$ and $e^{\epsilon/k_BT} \to \infty$ where $\delta = \lambda - 1$. This limiting procedure applied to Eq. (13) gives

$$\tilde{v}(x,s) = \left[\frac{a}{s + 12\tau_b + 12\sqrt{s}\tau_b}\right]\frac{e^{-\sqrt{s}(x-1)}}{x}. \tag{14}$$

Recognizing that the denominator in Eq. (14) is a quadratic function of $\sqrt{s}$, we can rewrite Eq. (14) as

$$\tilde{v}(x,s) = a\left[\frac{1}{\sqrt{s}-\alpha-\beta} - \frac{1}{\sqrt{s}-\alpha+\beta}\right]\frac{e^{-\sqrt{s}(x-1)}}{2\beta x} \tag{15}$$

for $\tau_b \geqslant \frac{1}{3}$ and as

$$\tilde{v}(x,s) = a\left[\frac{1}{\sqrt{s}-\alpha-i\beta} - \frac{1}{\sqrt{s}-\alpha+i\beta}\right]\frac{e^{-\sqrt{s}(x-1)}}{2i\beta x} \tag{16}$$

for $0 < \tau_b < \frac{1}{3}$. In Eqs. (15) and (16),

$$\alpha = -6\tau_b \tag{17}$$

$$\beta = 2\sqrt{3}\sqrt{|3\tau_b^2 - \tau_b|}. \tag{18}$$

The inverse Laplace transforms of Eqs. (15) and (16) are given as [26]

$$v(x,\tau) = \frac{a}{2\beta x}e^{-\frac{(x-1)^2}{4\tau}}\{(\alpha+\beta)w[i(g+h)] + (-\alpha+\beta)w[i(g-h)]\} \tag{19}$$

for $\tau_b \geqslant \frac{1}{3}$ and as

$$v(x,\tau) = \frac{a}{2i\beta x}e^{-\frac{(x-1)^2}{4\tau}}[(\alpha+i\beta)w(-h+ig) + (-\alpha+i\beta)w(h+ig)] \tag{20}$$

for $0 < \tau_b < 1/3$, where the so-called Faddeeva function is defined as $w(z) = e^{-z^2}\mathrm{erfc}(-iz)$ in terms of the complementary error function. In Eqs. (19) and (20),

$$g = -\alpha\sqrt{\tau} + \frac{x-1}{2\sqrt{\tau}} \tag{21}$$

$$h = -\beta\sqrt{\tau}. \tag{22}$$

For a complex argument, $z = g + ih$, the Faddeeva function can be split into real and imaginary parts, $w(g+ih) = K(g,h) + iL(g,h)$, where $K$ and $L$ are real and imaginary Voigt functions. From this it follows that Eq. (20) can be expressed as

$$v(x,\tau) = \frac{a}{\beta x}e^{-\frac{(x-1)^2}{4\tau}}[\alpha L(-h,g) + \beta K(-h,g)], \tag{23}$$

which, as before, governs the solution for $0 < \tau_b < 1/3$.

### D. Escape probability

In experiments one generally defines a bound state and a corresponding free, unbound state based on the resolution of the detection [27] or some other pragmatic criterion [28]. Here we define $x_1$ ($>1$) as some dimensionless separation beyond which particles are considered as singlets, whereas within this separation particles are considered bound to each other in a doublet. It is assumed that $x_1$ is of order 1. An escape probability, $P_+(\tau,x_1)$, is now defined. This is the probability that by time $\tau$ particles are separated by at least a distance $x_1$, which is given by $P_+(\tau,x_1) = 4\pi\sigma^3\int_{x_1}^{\infty} v(x,\tau)x^2dx$ with $v(x,\tau)$ from either Eq. (19) or (23). It is related to a survival probability, labeled as $P_-(\tau,x_1)$ to distinguish it from the corresponding first-passage time quantity $\Sigma(\tau,x_1)$, simply as $P_-(\tau,x_1) + P_+(\tau,x_1) = 1$. Integration results in

$$P_+(\tau,x_1) = \frac{12\tau_b}{\alpha^2+\beta^2}\mathrm{erfc}\left(\frac{x_1-1}{2\sqrt{\tau}}\right) + \frac{6\tau_b}{\beta}e^{-\frac{(x_1-1)^2}{4\tau}} \times \left\{\left(x_1 + \frac{1}{\alpha+\beta}\right)w[i(g_1+h_1)] - \left(x_1 + \frac{1}{\alpha-\beta}\right)w[i(g_1-h_1)]\right\}, \tag{24}$$

which applies for $\tau_b \geqslant 1/3$, whereas for $0 < \tau_b < 1/3$ the escape probability is given as

$$P_+(\tau,x_1) = \mathrm{erfc}\left(\frac{x_1-1}{2\sqrt{\tau}}\right) + e^{-\frac{(x_1-1)^2}{4\tau}}\left\{-K(-h_1,g_1) + \left(\frac{12\tau_b x_1 + \alpha}{\beta}\right)L(-h_1,g_1)\right\}, \tag{25}$$

where $g_1$ and $h_1$ are the quantities in Eqs. (21) and (22) evaluated at $x = x_1$.

### E. Asymptotic analysis

Here we extract the long-time asymptotic behavior of the escape probability, both for modest adhesion, $\tau_b \geqslant 1/3$, and in the limit of very strong adhesion $\tau_b \to 0$. Starting with Eq. (24), for $\tau_b \geqslant 1/3$, the argument of the Faddeeva function is purely imaginary, which gives the following expansion $w(ih) = \pi^{-1/2}(h^{-1} - h^{-3}/2 + \ldots)$. From this one concludes

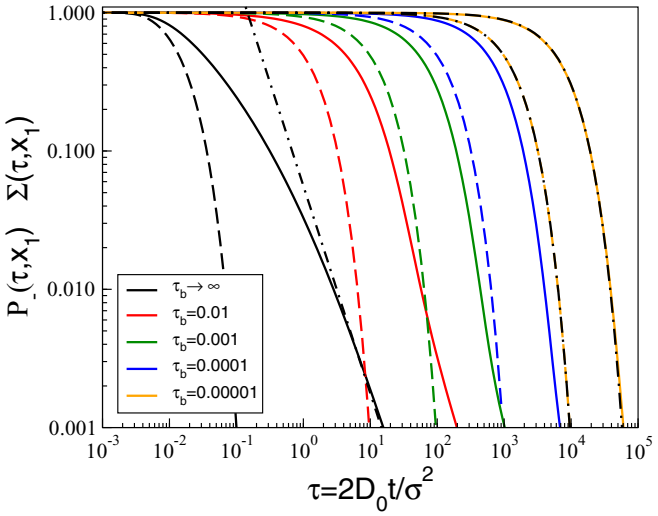


FIG. 3. The survival probability, $P_{-}(\tau,x_1)$, for the detachment of an adhesive sphere doublet with $x_1 = 1.2$, shown as solid lines, and the corresponding first-passage time result, $\Sigma(\tau,x_1)$, as a function of the Baxter stickiness parameter $\tau_b$. Also shown, as the chain curves, are the two leading-order long-time asymptotic terms for $\tau_b = 0.0001$ as well as the $\tau^{-3/2}$ long-time tail for the hard-sphere ($\tau_b \to \infty$) case.

that the escape probability at long times behaves as

$$P_{+}(\tau,x_1) \sim 1 - \pi^{-1/2} A \tau^{-3/2}, \tag{26}$$

where

$$A = \frac{2 - x_1 - 2\tau_b\left(5 - 3x_1 - 3x_1^2 + x_1^3\right)}{24\tau_b} \tag{27}$$

is positive as long as $x_1$ is of order unity as tacitly assumed in setting up the definition of a bound state. For a pair of hard spheres, for which $\tau_b \to \infty$, the above reduces to

$$P_{+}(\tau,x_1) \sim 1 + \left(\frac{5 - 3x_1 - 3x_1^2 + x_1^3}{12\sqrt{\pi}}\right)\tau^{-3/2}. \tag{28}$$

For small values of $\tau_b$ and for large values of the time $\tau$, $-h_1 \sim 2\sqrt{3\tau_b\tau}$ and $g_1 \sim 6\tau_b\sqrt{\tau}$, which leads to the escape probability from Eq. (25) behaving as $P_{+}(x_1,\tau) \sim 1 - K(-h_1,g_1)$. Since, asymptotically, $-h_1 \gg g_1$ as $\tau \to 0$, the Voigt function can be approximated by one of its special values [29], leading to the prediction

$$P_{+}(\tau,x_1) \approx 1 - K(-h_1,0) = 1 - e^{-12\tau_b\tau}. \tag{29}$$

Thus, for strongly adhesive particles the escape probability approaches unity in an exponential manner. As long as $x_1$ is of order 1, the escape probability becomes independent of the definition of the bound state in this limit, which is not the case for the moderately adhesive spheres.

## IV. RESULTS AND DISCUSSION

Figure 3 shows the survival probability, $P_{-}(\tau,x_1) = 1 - P_{+}(\tau,x_1)$, for a range of stickiness parameters $\tau_b$, evaluated for $x_1 = 1.2$. In addition, the figure shows the corresponding results obtained by applying the first-passage time theory to the same problem [15]. Recall that once particles diffuse apart from initial contact, there is no barrier to prevent their returning to adhesive contact even after separating beyond the $x_1 = 1.2$ distance used to define them as single, unbound particles. The choice of $x_1 = 1.2$, which defines separations at which the particles go from being considered part of a doublet to being free or vice versa, has been selected according to the criterion suggested by Zaccone and Terentjev [19]. In practice this amounts to setting $x_1$ equal to the separation at which the effective potential $\frac{U(x)}{k_B T} - 2\ln x$ exhibits a maximum at separations beyond the potential minimum.

The $\tau_b \to \infty$ limit corresponds to the hard-sphere case, which vanishes with a $\tau^{-3/2}$ long-time tail. Similar long-time tails have been noted in related problems involving relative diffusion of hard-sphere colloidal particles [30]. The first-passage time result does not vanish with a similar long-time tail, and it is seen to give a significant overprediction of the rate of doublet breakup. As the particles are made more adhesive by decreasing $\tau_b$, the survival probability remains finite for longer times. This holds also for the first-passage time theory, but it remains a rather poor approximation regardless of the adhesiveness. For smaller $\tau_b$, the qualitative behavior of the survival probability changes. The dynamics crosses over from the power-law decay to an exponential decay. As a consequence, the first-passage time theory comes to agree qualitatively with this decay.

For strong adhesiveness the survival probability behaves, according to Eq. (29), as $P_{-}(\tau,x_1) \approx \exp(-12\tau_b\tau)$. The first-passage time theory, in the same limit, gives instead [15] $\Sigma(\tau,x_1) \approx \exp\left(-12\tau_b\tau\frac{x_1}{x_1-1}\right)$. These two asymptotic predictions are also shown in Fig. 3 for $\tau_b = 0.00001$. They reproduce the full solutions of the two theories quantitatively over the entire time domain. However, as the asymptotic analysis reveals, there is a fundamental difference between the two. Whereas the first-passage time theory exhibits a dependence on how one defines the bound state, via its dependence on $x_1$, the analytical solution becomes independent of this definition. However, this only holds for sufficiently strong attractions [cf. Eq. (26) and the hard-sphere limit in Eq. (28)]. This is a physically intuitive result in that, for strong adhesiveness, particles spend a long time in adhesive contact when one allows for particles revisiting this state and thereby comparatively little time diffusing the distance to reach separation $x_1$. It is also a satisfying result because it shows that the separation dynamics is not sensitive to the definition of the bound state in this limit.

One may wonder how representative the analytical solution is for the detachment dynamics of the adhesive sphere doublets. After all, the interaction does not exhibit a finite attractive range. However, it is well known that the models furnished by applying Baxter's adhesive sphere potential can often be brought into qualitative or even quantitative accord with experimental data for a range of properties [32–35]. Here we examine whether the analytical solution for the adhesive sphere doublets can be used to model detachment of spheres interacting via the secondary minimum of a DLVO potential.

First, however, a way to compute the escape probability for a pair of spheres initially captured by their mutual DLVO interaction potential is needed. Figure 4 shows a comparison of a numerical, finite difference solution of the backward Smoluchowski equation, as described in the Appendix, and BD

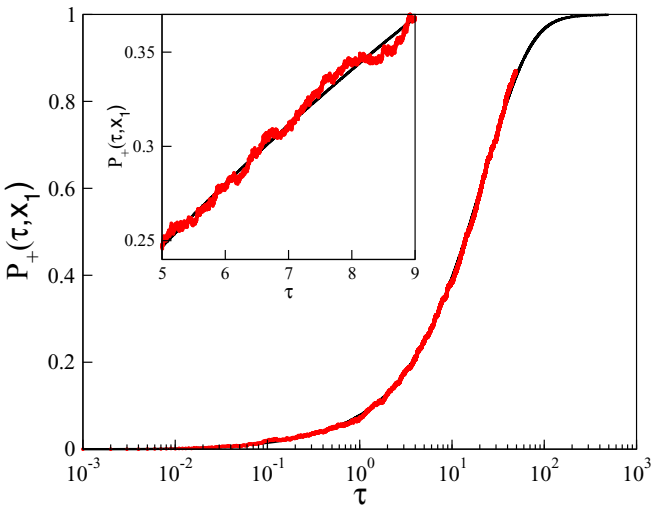


FIG. 4. The escape probability, $P_+(\tau,x_1)$, as a function of dimensionless time for the detachment of a doublet interacting with the DLVO potential in Fig. 5 at 10 mM salt concentration with $x_1 = 1.2$. The solid line is the numerical finite difference solution and the symbols are BD simulation data using the algorithm suggested by Mittal and Hummer [31]. The inset is an enhancement of the same results and data for a smaller range of times.

simulation data. The same DLVO potential for a salt concentration of 10 mM (cf. Fig. 5) has been used for both methods. The agreement between the two is excellent, though, as the inset in Fig. 4 demonstrates, the progression in time of the escape probability for the small number of particles used in the BD simulations, here $10^3$ pairs, is nonmonotonic. This is caused by fluctuations where, intermittently, slightly more particles cross $x_1 = 1.2$ to enter the attached state compared to the opposite direction. In other words, particles clearly undergo multiple crossings of the dividing point between the bound and unbound state on their way toward the permanently unbound state.

The DLVO potentials investigated, shown in Fig. 5, vary in the depth of the attractive minimum, which is achieved by changing the concentration of monovalent electrolyte. More specifically, particles of radius 1 $\mu$m, a surface potential of 50 mV, and a Hamaker constant of $1.37 \times 10^{-20}$ J were considered using a nonretarded van der Waals attraction and a linear superposition approximation for the treatment of the double layer repulsion. As seen in Fig. 5, the variation of the salt concentration results in well depths of $-5.5$, $-8.8$, and $-11.5\ k_BT$. As mentioned already, the description of the numerical method used to compute the true escape probability for doublets interacting via these DLVO potentials is given in the Appendix. The results in Fig. 5 show that the escape is increasingly retarded as the salt concentration is increased as must be the case. Considering the relatively small changes in the DLVO potential, the doublet breakup time appears to be quite sensitive to the strength of the attraction.

The analytical solution for the adhesive sphere doublet can be used in a predictive manner, by determining a stickiness parameter $\tau_b$ such that the second virial coefficient of the adhesive sphere system equals that of the system of interest. In the case of a DLVO potential, this second virial coefficient

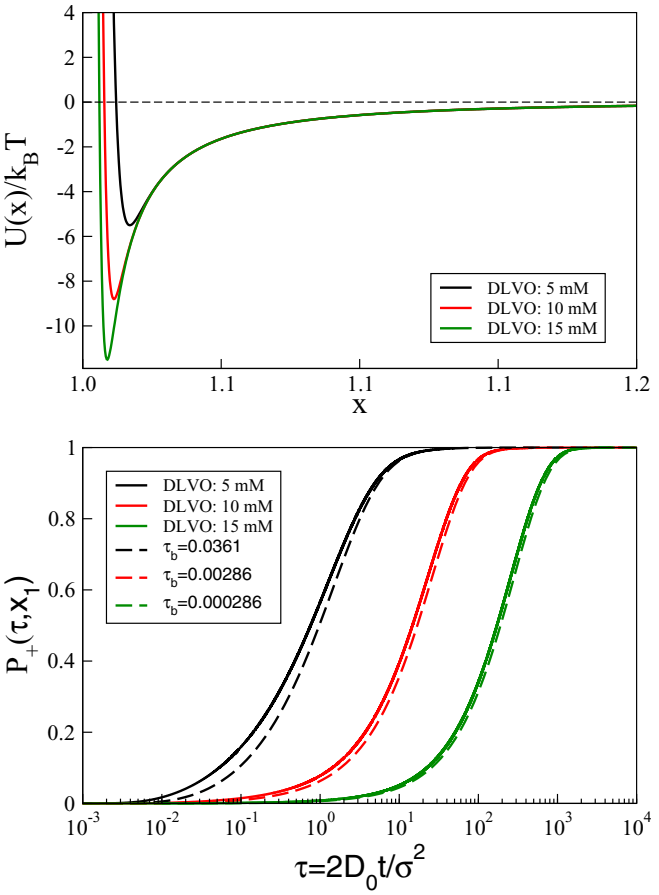


FIG. 5. Top: DLVO potentials as a function of dimensionless separation and salt concentration, as labeled. Bottom: Escape probability as a function of dimensionless time for the three DLVO potentials as obtained from the numerical solution of Eq. (A3) and from the analytical solution for adhesive spheres in Eq. (25) via matching of the second virial coefficients.

mapping leads to

$$B_2^{\mathrm{ahs}}/\sigma^3 = \frac{2\pi}{3}\left(1 - \frac{1}{4\tau_b}\right) = B_2^{\mathrm{DLVO}}/\sigma^3, \qquad (30)$$

where $B_2^{\mathrm{DLVO}}/\sigma^3 = -2\pi \int_0^\infty (e^{-U(x)/k_BT} - 1)x^2 dx$ has been determined by numerical integration. Given the parameters governing the DLVO potential, the above equation can be solved for $\tau_b$. The escape probability is then computed for this $\tau_b$ value using the appropriate choice of Eqs. (24) and (25).

The result of the $B_2$ mapping is shown in Fig. 5. For a salt concentration of 5 mM, giving a rather shallow secondary DLVO minimum, the agreement with the full numerical result is fair. The agreement improves considerably as the minimum is made deeper by increasing the salt concentration. Although not shown, for the 15 mM case the simple asymptotic result in Eq. (29) delivers a result that is almost in as good an agreement as is the solution from Eq. (25).

It is prudent to caution that the results obtained here hold in the infinite dilute limit and applying them at finite particle concentrations needs care. The typical time expended by particles of radius $a$ in reaching a neighboring particle by diffusion is $t_\phi = a^2\phi^{-2/3}/D_0$ [36]. For small but nevertheless

nonzero volume fractions $\phi$, this time scale should be weighed against typical detachment times in order to ascertain whether three-particle effects might be important. For example, in going from $\phi = 0.00001$ to 0.01, $t_\phi$ goes from $10^4$ s to $10^2$ s for the parameters used for the DLVO potentials in Fig. 5. Reading off the dimensionless times for which detachment is complete in Fig. 5, yields roughly $\tau = 10^3$ for 15 mM and 10 for 5 mM. These correspond to actual times of about $9 \times 10^3$ s and 90 s, respectively. It follows that in experiments on thermal breakup of doublets at $\phi = 0.01$, a 5 mM salt concentration should be on the safe side as far as interference from three-particle effects, whereas a 15 mM salt concentration would necessitate a lower particle concentration, $\phi \approx 0.00001$, for the particle size and diffusion coefficient considered here.

## V. CONCLUSIONS

Escape of colloidal particles from doublet states caused by interparticle attractions has been studied with focus on relaxing the restriction of it proceeding by just a single detachment event as imposed by adopting a first-passage time description. This has been achieved by analyzing the two-particle Smoluchowski equation for a sufficiently simple adhesive interaction so that an analytical solution can be worked out for the probability density. The solution obtained is somewhat similar mathematically to the potential-free solution derived by Kim and Shin [37]. However, their solution requires finding the roots of a cubic equation, whereas the solution for adhesive spheres here is based on the roots of a quadratic equation [cf. Eq. (14)].

Thez experimentally more relevant quantities, escape and survival probabilities, were derived by integrating the probability density. The long-time behavior of these has been analyzed and exhibits power-law decay for weaker adhesive interactions that crosses over to an exponential decay for strong adhesion. In the limit of strong adhesion, the escape and survival probabilities were found to become independent of how one assigns a bound state. Finally, this analytical solution for the adhesive sphere doublet was shown to be useful for predicting the detachment dynamics of particles interacting via more realistic interaction potentials, provided the stickiness parameter was determined by matching the second virial coefficients.

## ACKNOWLEDGMENT

A mobility grant (SM12-0013) from the Swedish Foundation for Strategic Research (SSF) is gratefully acknowledged.

## APPENDIX: NUMERICAL SOLUTION FOR THE ESCAPE PROBABILITY FROM A DLVO POTENTIAL

The Smoluchowski equation can be expressed in backward form [17,18], as

$$\frac{\partial}{\partial\tau}p(x,\tau|x_0) = \frac{e^{U(x_0)/k_BT}}{x_0^2}\frac{\partial}{\partial x_0} \times\left(x_0^2G(x_0)e^{-U(x_0)/k_BT}\frac{\partial}{\partial x_0}p(x,\tau|x_0)\right), \tag{A1}$$

where $x_0$ is the initial coordinate. This equation can be integrated over the $x$ coordinate to yield an equation of motion for the escape probability as

$$\frac{\partial}{\partial\tau}P_+(\tau,x_1|x_0) \tag{A2}$$

$$= \frac{e^{U(x_0)/k_BT}}{x_0^2}\frac{\partial}{\partial x_0}\left(x_0^2G(x_0)e^{-U(x_0)/k_BT}\frac{\partial}{\partial x_0}P_+(\tau,x_1|x_0)\right)$$

$$= A(x_0)\frac{\partial P_+(\tau,x_1|x_0)}{\partial x_0} + \frac{\partial^2P_+(\tau,x_1|x_0)}{\partial x_0^2}, \tag{A3}$$

where, in the last step, hydrodynamic interactions were neglected [$G(x_0) = 1$] and $A(x_0) = 2/x_0 - \frac{1}{k_BT}\frac{\partial U(x_0)}{\partial x_0}$ was introduced. This equation is subject to the initial condition: $P_+(0,x_1|x_0) = \Theta(x_0 - x_1)$. In order to determine a solution in the entire radial domain, the starting coordinate is transformed as $q = 1/x_0$, which transforms the governing equation into

$$\frac{\partial P_+(\tau,q_1|q)}{\partial\tau} = (2q^3 - A(q)q^2)\frac{\partial P_+(\tau,q_1|q)}{\partial q} + q^4\frac{\partial^2P_+(\tau,q_1|q)}{\partial q^2}, \tag{A4}$$

where $q_1 = 1/x_1$. This equation is discretized using $q_j = j\Delta q$ and $\tau_i = i\Delta\tau$, such that $0 < q_j < 1$, by introducing a centered finite difference approximation for derivatives with respect to $q$ and a backward finite difference approximation for the time derivative. After imposing the boundary conditions $P_+(\tau,q_1|q = 0) = 0$ and $\frac{\partial}{\partial q}P_+(\tau,q_1|q = 1) = 0$, the partial differential equation is turned into a matrix equation that is tridiagonal. It is solved at every time step using an efficient back substitution method [38]. A further technical detail concerns the removal of the primary DLVO minimum, which otherwise introduces a singularity. It is removed from the problem by imposing a constant repulsive force at the apex of the repulsive DLVO barrier. The finite difference equation was solved using 3500 nodes, equispaced along the transformed radial $q$ coordinate.

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