Testing the Derjaguin approximation for colloidal mixtures of spheres and disks

S. M. Oversteegen and H. N. W. Lekkerkerker
Van 't Hoff Laboratory for Physical and Colloid Chemistry, Debye Institute, Utrecht University, Padualaan 8, 3584CH Utrecht, The Netherlands

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The depletion potential between two large hard spheres due to the presence of hard disks has been derived up to first order in the number density of disks by Piech and Walz [J. Colloid Interface Sci. **232**, 86 (2000)] using the Derjaguin approximation. Using the generalized Gibbs equation, we compare this depletion potential to the exact solution up to first order in density. The Derjaguin approximation turns out to be surprisingly accurate; for aspect ratios smaller than 0.25 the error is less than 1%.

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I. INTRODUCTION

Mixtures of colloidal particles with different sizes and shapes are ubiquitous in industry (e.g., paints, pharmaceuticals, and drilling fluids), food science, and the biological realm [1,2]. Moreover, there is much interest in understanding the properties of mixed colloidal suspensions at a fundamental microscopic level. It is commonly accepted that mutual asymmetry of the particles in these mixtures alone may induce a net attraction between them by the so-called depletion effect.

For binary mixtures of asymmetric hard spheres this depletion effect has been established both experimentally [3–8] and theoretically [9–16]. When large spheres of diameter σ approach each other up to a distance h smaller than the diameter of a smaller sphere, a, the latter is expelled from the gap. Using the Derjaguin approximation, the resulting depletion potential for $a \ll \sigma$ up to first order in the number density of the smaller spheres, n_s, is given by [17,18]

$$\frac{W_{\rm spheres}}{k_B T} = -\frac{\pi}{4} n_s a^2 \sigma \left(1 - \frac{h}{a}\right)^2. \tag{1}$$

Up to first order in the density of small spheres the exact depletion potential can also be calculated analytically [19]. The relative error introduced by the Derjaguin approximation can from straightfoward algebra be determined as $1/(1+3\sigma/2a)$ at contact of the large spheres. Hence, for a size ratio of the spheres of $a/\sigma = 0.1$ the Derjaguin approximation *underestimates* the depth of the potential by 6%.

Also colloidal mixtures of hard spheres with hard rods give an entropically driven phase separation according to experiments [20,21] as well as theory [22–24]. When placed between two spheres, the orientational entropy of infinitely thin rods of length L decreases. The consequent pressure deficit leads to a depletion potential that reads up to first order in the number density n_r using the Derjaguin approximation [25–27]

$$\frac{W_{\rm rods}}{k_B T} = -\frac{\pi}{12} n_r L^2 \sigma \left(1 - \frac{h}{L}\right)^3. \tag{2}$$

Calculations [28] reveal what error the Derjaguin approximation has introduced for the depletion of large spheres due to rods. For a size ratio of the length L of the rods over the diameter of the sphere of $L/\sigma = 0.1$, the Derjaguin approximation *overestimates* the potential at contact by 7%. The potential turns out to be quite accurate indeed from experiments [29–31].

In contrast to bimodal mixtures of colloidal spheres and mixtures of colloidal spheres with rods, those of colloidal spheres with platelets has received little attention. The phase behavior of platelets may nevertheless be of great interest to phenomena observed in, e.g., soil science, drilling muds, and paints [32,33]. Although the phase behavior of binary mixtures of hard colloidal rods and plates [34–36] as well as plates and nonadsorbing polymer [37–39] have been studied, binary mixtures of hard spheres with plates are still unexplored. Recently, a stable system of hard spheres and platelets has been developed in our laboratory [40], as presented in Fig. 1, which opens up the possibility for fundamental studies underpinning the aforementioned practical applications.

Analogous to rods, the orientation of platelets is restricted when confined between two spheres. Approximating the platelets by disks, i.e., infinitely thin of diameter D, the depletion potential for such systems up to first order in the number density of disks, n_p, reads by applying the Derjaguin approximation [41]

$$\frac{W_{\rm disks}}{k_B T} = -\frac{\pi}{6} n_p D^2 \sigma \left[\frac{3}{2}\frac{h}{D}\arcsin\frac{h}{D} - \frac{3}{4}\pi\frac{h}{D} + \left\{1 + \frac{1}{2}\left(\frac{h}{D}\right)^2\right\}\sqrt{1-\left(\frac{h}{D}\right)^2}\right]. \tag{3}$$

Comparison of the depletion potentials of hard spheres due to disks, Eq. (3), small spheres, Eq. (1), or rods, Eq. (2), reveals that all have the general form

$$\frac{W_i}{k_B T} = -c_i n_i \ell^2 \sigma F_i\left(\frac{h}{\ell}\right), \tag{4}$$

where ℓ is the characteristic length scale of the depletion agent i. The prefactor c_i determines the depth of the potential, whereas F_i determines its distance dependence that equals unity at contact of the large spheres. In terms of volume fractions, it is readily seen that rods are compared to

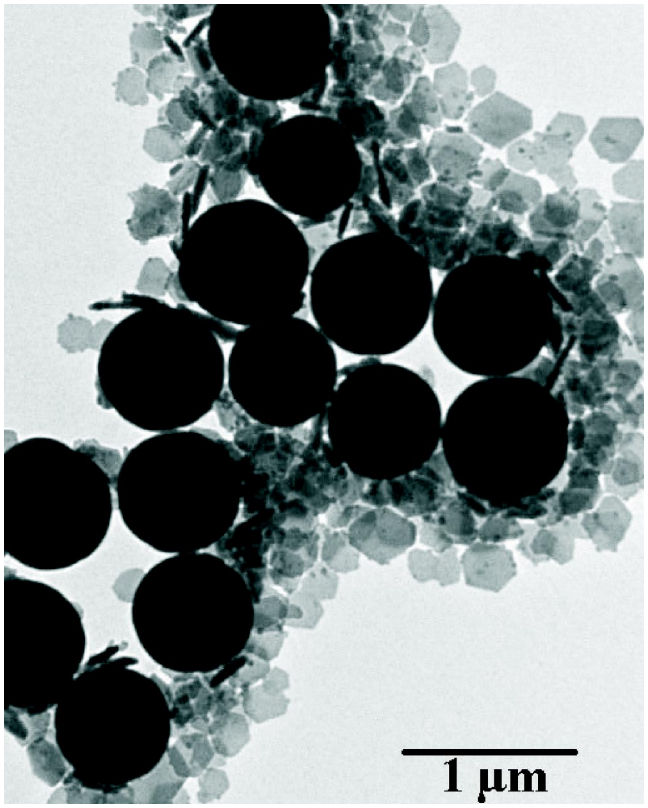


FIG. 1. TEM micrograph of a mixture of silica spheres ($\sigma = 700$ nm) with silica coated gibbsite plates (diameter $D = 200$ nm, thickness $L = 30$ nm).

small spheres already at low volume fractions effective depletion agents, whereas colloidal platelets give rise to attraction at intermediate volume fractions. From the numerical plot, Fig. 2, it is seen that the distance dependence of rods decays fastest, that of spheres the slowest, and disks are in between.

From their top view, disks may be regarded as two-dimensional spheres and from their side view as infinitely thin rods. Consequently, upon rotating the particles at a given number density the apparent volume fraction of disks seems higher than that of spheres but lower than that of rods. This is also exhibited by the depletion potential due to disks of which it was shown above that both the depth and the distance dependence is in between that of rods and small spheres. If we carry this comparison further, the error introduced by the Derjaguin approximation in Eq. (3) may also be assumed to be intermediate. That is, the Derjaguin approximation could be surprisingly accurate for mixtures of thin platelets with large spheres. In this paper we will show that this is indeed the case. To that end, we first rederive Eq. (3) from the Gibbs adsorption equation by applying the Derjaguin approximation and subsequently do the full calculation.

II. THE SPHERE-DISK DEPLETION POTENTIAL

A. The Derjaguin approximation

Consider a dilute dispersion of disks of diameter D. The depletion potential between two spheres due to the presence

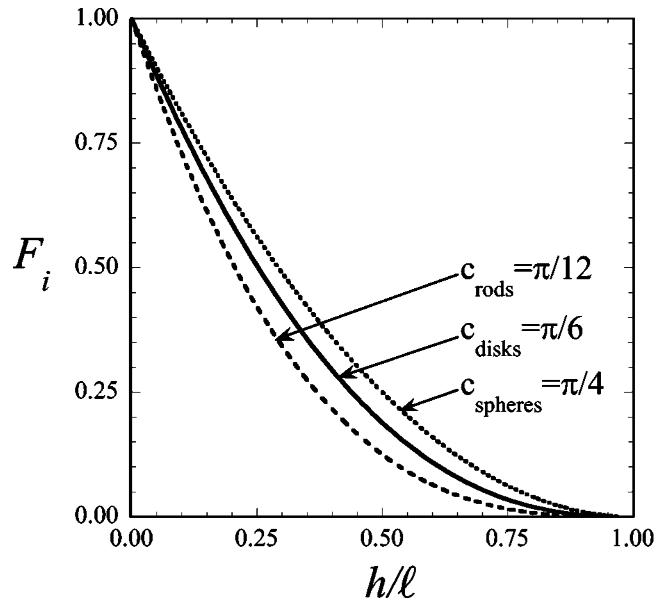


FIG. 2. The distance dependence F_i of the depletion potential of hard spheres due to the presence of other particles, Eq. (4), as a function of the scaled interparticle distance, h/ℓ. The depth of the potential is given by c_i. Disks (full line, $\ell = D$) are intermediate depletion agents compared to rods (dashed line, $\ell = L$) and small spheres (dotted line, $\ell = a$).

of small disks ($D \ll \sigma$) can be derived from the interaction between two walls using the Derjaguin approximation [42]

$$W_{\rm disks}(h) = \frac{1}{2}\pi\sigma\int_h^\infty w(h')dh', \tag{5}$$

where w is the potential of mean force per unit area of disks between two planar walls. Next we will derive an expression for w.

In the vicinity of a wall, at a distance $h < D$ from the other, the disk can no longer assume all configurations, as illustrated in Fig. 3(a). As a consequence of this loss of configurational entropy the number density of disks that are in contact with the walls, $n_i(h)$, is less than the coexisting number density in the bulk, n_p. Hence, there will be a net attraction between the walls according to the generalized Gibbs equation [43–46]

$$-\left(\frac{\partial W}{\partial \mu_p}\right)_h = N(h) - N(\infty). \tag{6}$$

Here $N(h)$ and $N(\infty)$ are the (ensemble averaged) number of disks in the system when the walls are at separation h or infinity, respectively. Expressing Eq. (6) per unit area, we obtain

$$-\left(\frac{\partial w}{\partial \mu_p}\right)_h = \Gamma(h) - \Gamma(\infty), \tag{7}$$

where Γ is the number of disks per unit area adsorbed at both walls,

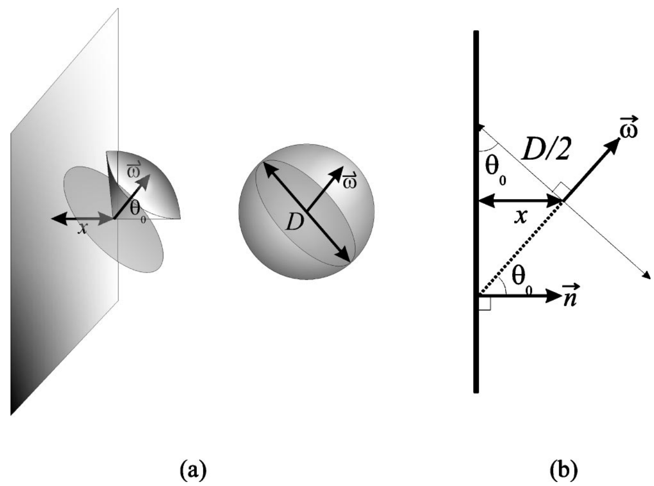


FIG. 3. (a) In the bulk the director $\vec{\omega}$ of a disk with diameter D can describe a full unit sphere (right), whereas a disk at a distance $x<D/2$ to a wall only describes part of it (left). (b) The maximum angle θ_0 between the director $\vec{\omega}$ and the normal on a planar wall $\vec{n}$ follows from $\sin\theta_0 = x/(D/2)$.

$$\Gamma(h) = \int_0^h [n_i(x) - n_p]\, dx. \tag{8}$$

Since we consider a dilute dispersion of disks, we may write the chemical potential of the disks as $\mu_p = \mu_p^0 + k_B T \ln n_p$. Hence, integration of Eq. (7) gives

$$\begin{aligned} w(h) &= -k_B T \int_0^{n_p} [\Gamma(h) - \Gamma(\infty)] \frac{1}{n_p'} dn_p' \\ &= -k_B T [\Gamma(h) - \Gamma(\infty)]. \end{aligned} \tag{9}$$

Here we used that up to first order, Γ is linear in n_p.

The relative number density of disks between the two confining planar walls can be derived from the orientational freedom of the director of the disk. Consider the angle θ of the director of a disk with the normal on one of the walls. In bulk this angle can describe all polar angles, whereas in the vicinity of a wall it is limited to θ_0 which follows from $\sin\theta_0 = x/(D/2)$, as indicated in Fig. 3(b). Hence, for $h<D$ it follows from Eq. (8) that

$$\begin{aligned} \Gamma(h) &= 2\int_0^{h/2} n_p \left(\int_0^{\theta_0} \sin\theta\, d\theta - 1 \right) dx \\ &= -2\int_0^{h/2} n_p \sqrt{1 - \left(\frac{x}{D/2}\right)^2}\, dx \\ &= -\frac{1}{2} n_p D \left[\arcsin\frac{h}{D} + \frac{h}{D}\sqrt{1 - \left(\frac{h}{D}\right)^2} \right]. \end{aligned} \tag{10}$$

If the two walls are infinitely apart, a disk can rotate freely until it approaches the wall up to a distance $x<D/2$. Completely analogous to Eq. (10), we find

$$\Gamma(\infty) = -2\int_0^{D/2} n_p \sqrt{1 - \left(\frac{x}{D/2}\right)^2}\, dx = -n_p \frac{\pi}{4} D. \tag{11}$$

Insertion of Eqs. (10) and (11) into Eq. (9) straightforwardly gives the potential of mean force per unit area of the walls due to disks up to first order in the number density

$$w(h) = -\frac{1}{2} k_B T n_p D \left[\frac{\pi}{2} - \arcsin\frac{h}{D} + \frac{h}{D}\sqrt{1 - \left(\frac{h}{D}\right)^2} \right]. \tag{12}$$

Substitution of Eq. (12) into the Derjaguin approximation, Eq. (5), yields the depletion potential of hard spheres due to hard disks, Eq. (3).

Where Eq. (12) is exact to first order in the number density, Eq. (3) is approximate due to the Derjaguin approach. Although the usefulness of the Derjaguin approximation for depletion forces is questioned [47,48], we believe with Henderson [49] that this analysis is justified in the appropriate limits, i.e., dilute suspensions of small depletion agents. We will show that the Derjaguin approximation for spheres in a dilute suspension of disks is actually very accurate up to relatively large aspect ratios.

B. Exact solution

In order to arrive at the exact depletion potential of dilute suspensions of disks, we may write Eq. (6), in analogy to Eq. (9), as

$$\frac{W}{k_B T} = -[N(h) - N(\infty)] = N_{\rm I} + N_{\rm II} - N_{\rm III}. \tag{13}$$

The $N_{\rm I}$ term accounts for the number of conformations the disks now may assume in the bulk when the two spheres are closer than $h<D$, whereas $N_{\rm II}$ accounts for the actual number of possible orientations in that gap. The number of conformations that used to be accessible when not hindered by the other sphere is denoted by $N_{\rm III}$. The three contributions $N_{\rm I}$, $N_{\rm II}$, and $N_{\rm III}$ are depicted schematically in Fig. 4(a) and made more explicit below. Henceforth we will drop the explicit distance dependence of these terms.

Around each of the two spheres there is a layer of thickness $D/2$ in which the disks are hindered by the spheres; the so-called depletion zone. When two spheres approach each other up to a distance $0<h<D$ the depletion zones of both spheres overlap, which restricts the number of conformations of the disk there further. However, due to the overlap, disks in the bulk have more volume accessible to move freely. This is reflected by the gain $N_{\rm I}$ in the bulk and follows from the volume of a spherical cap of height $(D-h)/2$

$$N_{\rm I} = \frac{\pi}{6} n_p D^2 \sigma \times \left(\frac{3}{2} + \frac{D}{\sigma} + \frac{1}{2}\frac{h}{\sigma} \right) \left(1 - \frac{h}{D} \right)^2. \tag{14}$$

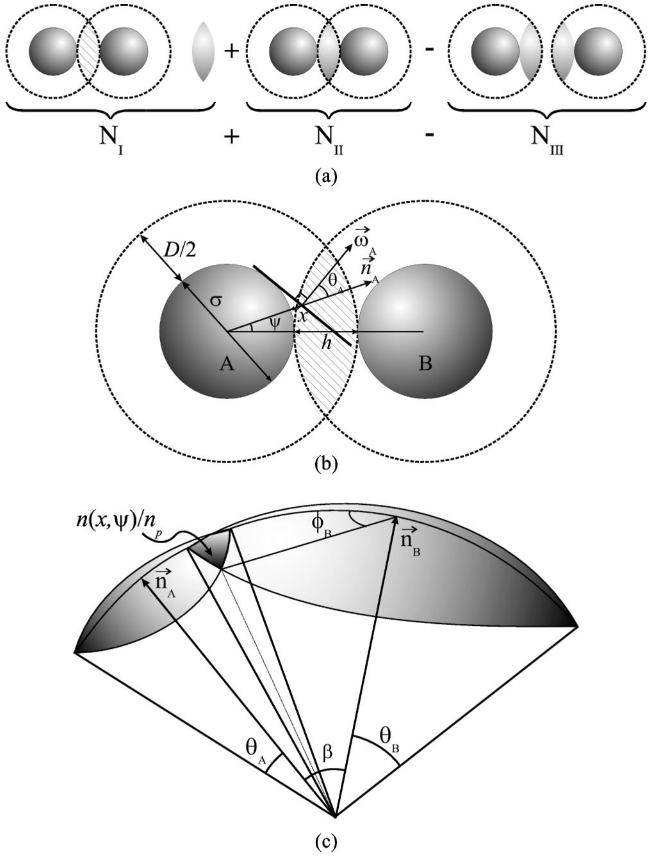


FIG. 4. (a) The three contributions to the excess adsorption density for $h=D/2$. (b) Definitions of the distances and angles of a disk in the overlapping depletion zone relative to sphere A. (c) The overlap of cones relative to spheres A and B [cf. Fig. 3(a)] determines the area accessible to a disk at a certain position between the two spheres.

The number of particles N_{II} that fits in the gap between the two spheres is formally given by the volume integral over the number density of particles that fit in the gap

$$N_{\mathrm{II}}=4\pi\int_{\max(0,h-D/2)}^{D/2}\int_{\psi_i(x)}^{\psi_f(x)}\left(\frac{\sigma}{2}+x\right)^2 n(x,\psi)\sin\psi d\psi dx. \tag{15}$$

The radial integration over x goes from the edge of the overlap volume to the outer shell of a depletion zone. In order to describe the whole volume, for each radial position an integral over the angles ψ that describe the overlap volume is required. From Fig. 4(b) basic trigonometry gives

$$\psi_i(x)=\begin{cases}0 & \text{if } x\leqslant\dfrac{h}{2}\\[2ex] \arccos\left\{\dfrac{\sigma+h}{\sigma+2x}\right\} & \text{if } x>\dfrac{h}{2}\end{cases} \tag{16}$$

and

$$\psi_f(x)=\arccos\left\{\frac{(\sigma+h)^2+\left(\frac{1}{2}\sigma+x\right)^2-\frac{1}{4}(\sigma+D)^2}{(\sigma+h)(\sigma+2x)}\right\}. \tag{17}$$

Remains the actual number of conformations, $n(x,\psi)/n_p$, a disk can assume at a given position x,ψ. As can be seen from Fig. 3, at that position the disk can move within a certain cone around the normal of each of the spheres ignoring the other. From the intersection of both cones follows the possible number of conformations between both spheres, as can be seen from Fig. 4(c),

$$\begin{aligned}\frac{n(x,\psi)}{n_p}&=\frac{1}{\pi}\int_{\beta-\theta_A}^{\theta_B}\sin\theta\phi_B(\theta)d\theta\\&=\frac{1}{\pi}\int_{\beta-\theta_A}^{\theta_B}\sin\theta\arccos\left(\frac{\cos\theta_A-\cos\theta\cos\beta}{\sin\theta\sin\beta}\right)d\theta.\end{aligned} \tag{18}$$

Here θ_A and θ_B give the widths of the accessible cones around the normals on spheres A and B, respectively. Moreover, the angle between these normals is given by β. If $\beta+\theta_A>\pi-\theta_B$, complementary conformations can be assumed, which adds an extra term similar to Eq. (18) but the lower limit equal to $\pi-\beta-\theta_A$. Expression for the angle θ_A can be derived straightforwardly from Fig. 4(b), where we must distinguish the case for $x<x_0$, when the face of the disk touches the sphere first, from $x>x_0$ when the edge of the disk touches the spheres, where $x_0=\frac{1}{2}(\sqrt{D^2+\sigma^2}-\sigma)$. Similarly the expression for θ_B can be derived.

Since the depletion potential requires the excess amount, $N(h)-N(\infty)$, we finally have to subtract the number of conformations of disks when the two depletions zones did not yet overlap, i.e., $h>D$. Analogously to Eq. (15), we find

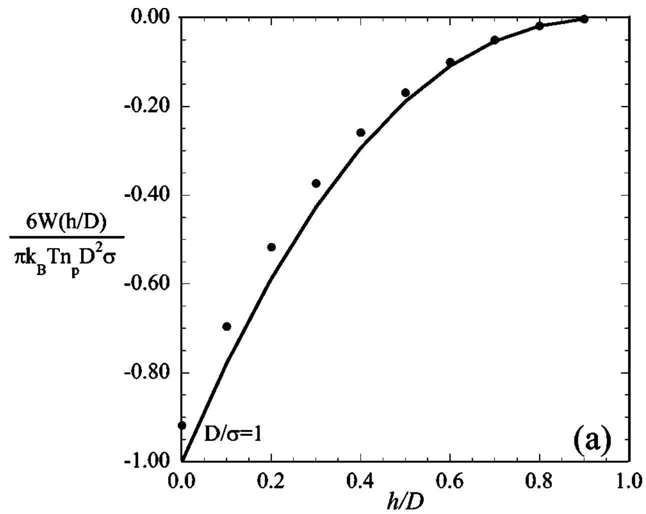
$$N_{\mathrm{III}}=2n_p\int_{\max(0,h-D/2)}^{D/2}A(x)\{1-\cos\theta(x)\}dx. \tag{19}$$

Here the area in the overlap volume at radial distance x is given by

$$A(x)=\frac{\pi\left(\frac{1}{2}\sigma+x\right)}{\sigma+h}\left\{\sigma(x-h)-(x-h)^2+\frac{1}{2}\sigma D+\frac{1}{4}D^2\right\}. \tag{20}$$

The angles $\theta(x)$ follow, like θ_A and θ_B, from

$$\cos\theta(x)=\begin{cases}\dfrac{\sigma}{\sigma+2x} & \text{if } x\leqslant x_0\\[2ex] \sqrt{1-\left\{\dfrac{\left(\frac{D}{2}\right)^2+x(\sigma+x)}{(\sigma+2x)\left(\frac{D}{2}\right)}\right\}^2} & \text{if } x>x_0.\end{cases} \tag{21}$$



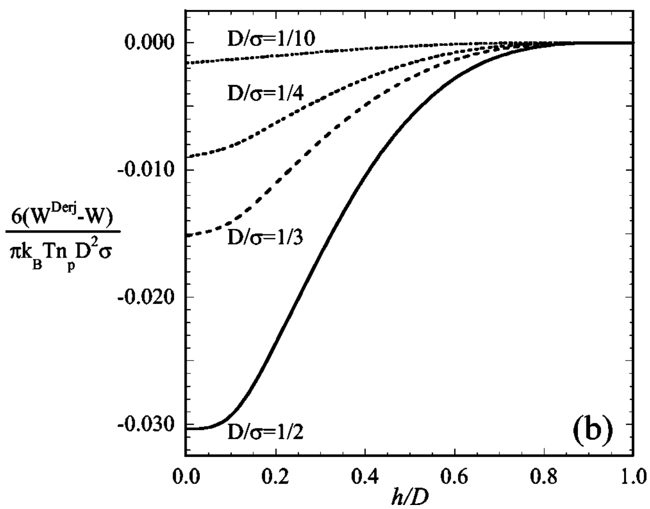


FIG. 5. (a) An actual profile (symbols) and Eq. (3) (solid line) for $D/\sigma=1.0$. (b) The difference of the distance dependence of the depletion potential of the exact solution compared to the Derjaguin approximation for several size ratios.

III. RESULTS

Invoking Eqs. (14), (15), and (19), we determined the depletion potential from Eq. (13). All integrals are solved numerically using Romberg integration [50] up to a numerical accuracy of 5×10^{-5}. As can be seen from Fig. 5(a), even for a size ratio $D/\sigma=1.0$, the resemblance between the exact solution (symbols) and the Derjaguin approximation (line), Eq. (3), of the depletion potential is striking. For smaller aspect ratios the difference is on the scale of the depletion potential hardly visible. We therefore plot the difference between the exact solution and the Derjaguin approximation in Fig. 5(b).

It is seen from Fig. 5 that the discrepancy between the exact solution and the Derjaguin approximation is the largest at contact $(h/\sigma=0)$. In Fig. 6 we show these values for several size ratios. We fitted that data and find

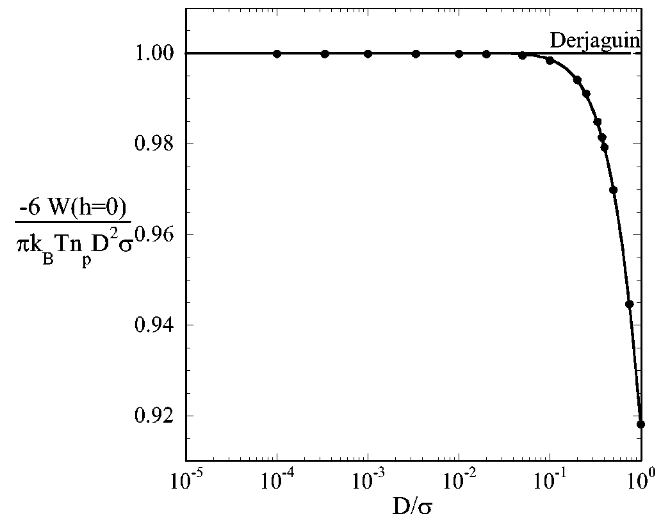


FIG. 6. The value of the exact solution at contact (symbols) may be fitted by Eq. (22) (solid line).

$$\frac{W(h=0)}{k_BT}=-\frac{\pi}{6}n_pD^2\sigma\left\{\frac{1+1.1674\left(\frac{D}{\sigma}\right)}{1+1.1674\left(\frac{D}{\sigma}\right)+0.1938\left(\frac{D}{\sigma}\right)^2}\right\}. \tag{22}$$

From this equation we find that for $D/\sigma<0.25$ the error is less than 1%.

IV. DISCUSSION

We conclude that the Derjaguin approximation for the depletion potential between spheres due to disks, Eq. (3), yields very accurate results. The Derjaguin approximation underestimates the potential for a bimodal mixture of spheres, Eq. (1), while it overestimates it for sphere-rod mixtures, Eq. (2). The generic intermediate behavior of disks leads to the result that the Derjaguin approximation is indeed surprisingly accurate. For instance, an error of -0.2% is found for $D/\sigma=0.1$ at contact, whereas for the same aspect ratios it is $+6\%$ and -7% for mixtures of spheres with small spheres and spheres with rods, respectively.

So far we only considered disks, i.e., infinitely thin platelets. Going to platelets of finite thickness, e.g., oblate ellipsoids, the deviation from the Derjaguin approximation may change sign [41]. We nevertheless reckon the Derjaguin approximation in dilute suspensions to be a useful guide to our experiments of colloidal mixtures of spheres and platelets.

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