Anomalous behavior of the depletion potential in quasi-two-dimensional binary mixtures

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We report an experimental determination of the depletion interaction between a pair of large colloid particles present in a binary colloid mixture that has a high density of large particles and is tightly confined between two parallel plates, as a function of the small colloid particle density. The bare interaction between the large particles in the one component large colloid suspension, and the effective potential between the large particles in the binary colloid suspension represented as a pseudo-one-component fluid, were obtained by inverting the Ornstein-Zernike equation with the hypernetted chain closure. The depletion interaction is defined by subtracting the bare potential from the effective potential at fixed large colloid density. We find that the depletion potential in the quasi-two-dimensional (Q2D) system is purely attractive and short ranged as described by Asakura-Oosawa model. However, the depth of the depletion potential is found to be almost an order of magnitude larger than the counterpart depletion potential predicted for the same density and diameter ratio in a three-dimensional system. Although it is expected that the confining walls in the Q2D geometry enhance the excluded volume effects that generate entropic attraction, the observed enhancement is much larger than predicted for a Q2D binary mixture of hard spheres. We speculate that this anomalously strong confinement-induced depletion potential is a signature of characteristics of the real confined binary colloid mixture that are not included in any extant theory of the depletion interaction, specifically the omission of the role of the solvent in those theories. One such characteristic could be differential wall or particle wetting that generates a wall induced one-particle effective potential that confines the centers of the small particles to lie closer to the midplane between the walls than expected from the wall separation and the direct particle-wall interaction, thereby enhancing the depletion interaction.

I. INTRODUCTION

The work reported in this paper started as a complement to an investigation of the influence of the small particles in a quasi-two-dimensional (Q2D) binary mixture of large (diameter σ_L) and small (diameter σ_S) hard sphere colloid particles on structure [1] and dynamics [2] in that system. In such a binary mixture the excluded volume between a pair of large particles and the surrounding small particles provides an entropic source for an interaction that is often referred to as the depletion potential [3,4]. A qualitative understanding of the depletion potential follows from the observation that the center of a small colloid particle is excluded from a shell with thickness $\sigma_S/2$ that surrounds the large colloid particle. When the distance between two large particles is less than $\sigma_L+\sigma_S$ these excluded volume shells overlap, thereby generating an increase in the space accessible to the small particles and of the system entropy, which results in a purely entropy driven attractive depletion potential between the two large particles. We note that the character of this depletion potential is the same as that of the potential of mean force in a pure hard sphere system.

In a pioneering paper, Asakura and Oosawa (AO) [5,6] analyzed the depletion potential in a binary polymer-colloid system with a theoretical model that assumes that the isolated polymer chains in a dilute solution can be treated as small hard spheres, and that the interactions between the small hard spheres can be neglected. They predicted that the depletion potential is purely attractive for $\sigma_L \le r < \sigma_L+\sigma_S$, with a magnitude proportional to the polymer volume fraction ϕ_S. Subsequent theoretical [7,8] and simulation [9,10] studies have examined the depletion potential when the small particle interactions cannot be neglected [11,12], and for a large particle near a planar wall [12] or a curved surface [13]. And, there have been many recent experiments [14–17] that, using a variety of techniques, have investigated depletion interactions in three-dimensional (3D) colloid mixtures and colloid-polymer mixtures. In general, the results of the experimental studies of the depletion interaction have supported the qualitative aspects of the theoretical predictions: the depletion interaction is found to be purely attractive when the small sphere packing density is small, and to have "structure" as a function of particle separation when the small sphere packing density is large [18].

This paper describes experimental studies of the depletion interaction in Q2D binary colloid mixtures. The Q2D geometry is achieved by confining the binary colloid mixture between two parallel glass walls with separation $d<\sigma_L+\sigma_S$. The systems studied are set up in such a way that small particles cannot pass "over" or "under" the large particles, although they can pass "around" them. A consequence of this restriction is that the excluded volume between a pair of large colloid particles depends both on their separation and their proximity to the walls of the cell. If there were only small and large hard sphere colloid particles present in the cell, collisions between the small particles and a selected pair of large particles will be biased to emphasize those that have

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the larger projections of momentum transfer along the line of centers of the large particles. In that case it is expected that the depletion interaction in the quasi-two-dimensional system will be enhanced relative to that for the same mixture in three dimensions. The presence of solvent, and the substitution of diffusive motion for ballistic motion, does not change the expected enhancement of the depletion interaction since the influence of the walls on the shape of the excluded volume, hence the increase in entropy of the small particles when two large particles are close to each other and to the walls, plays the same role as the restriction on collisions mentioned above.

The existence of a large depletion potential is consistent with the results of our previous studies of freezing of binary colloid mixtures [1]. Those studies showed that the presence of 0.5% small particles ($\phi_S = 0.005$) shifts the density at which the large particles undergo a liquid-to-solid transition from $\eta_L = 0.80$ to $\eta_L = 0.86$, thereby signaling a drastic change in the effective potential between the large particles. The results reported in this paper show that the enhancement of the strength of the depletion interaction signaled by the density dependence of the freezing transition is supported by determination of that potential.

However, the depth of the depletion potential is found to be almost an order of magnitude larger than the counterpart depletion potential predicted for the same densities and diameter ratio in a 3D system. Computer simulations of Q2D binary mixtures of hard spheres, reported elsewhere [19–21], indicate that provided the small spheres can move freely the full distance perpendicular to the confining walls, the restricted-three-dimensional motion of small spheres only accounts for a part of the enhanced depletion potential at the large sphere density considered in this paper. When the motion of the small spheres along the line perpendicular to the walls is subject to a one-body interaction that tends to restrict the amplitude of motion about the midplane, the depletion interaction is greatly enhanced, but is still smaller than that inferred from our experiments. Although a detailed assignment of the origin of the discrepancy between the predicted depletion potential and that which we have found has thus far eluded us, we speculate that it arises from neglected effects in the extant theory. We note that all existing theories of the depletion interaction deal only with the large and small particles, and they omit from any consideration the solvent that suspends both the large and small particles. When the colloid suspension is three-dimensional and the role of the bounding walls is inconsequential, omission of any role played by the solvent is reasonable. However, when the colloids are confined to a Q2D domain, and the separation of any colloid particle and a wall is a small fraction of the particle diameter, the character of the wall-solvent and colloid-solvent interactions can affect the effective interaction between the large colloid particles. Thus we have previously reported [22] that in a one-component Q2D or Q1D assembly of what are thought to be very nearly hard sphere colloid particles there is an effective interaction that is weakly attractive. That attraction has been shown to be dependent on the geometry of the confining walls (different in Q1D and Q2D), and it has been shown to be independent of the salt concentration in the suspending solvent. The latter

observation rules out a Coulombic origin for the interaction. Given that in the experiments carried out the walls of the cell are hydrophobic whilst the colloid particles are hydrophilic, and that a colloid particle nearly spans the distance between the cell walls, it was suggested that the nonwetting of the walls, coupled with the wetting of the particles, generated a capillary attraction between large particles. This interpretation is an illustration of an effect that can arise that is not accounted for by any theory of the depletion interaction that omits consideration of the solvent that suspends the colloid particles.

II. EXPERIMENTAL PROCEDURE

The binary colloid mixtures we have studied consist of water suspensions of nearly monodisperse large silica spheres (Duke Scientific, $\sigma_L = 1.58 \pm 0.04$ μm) and nearly monodisperse small polystyrene spheres with modified hydroxyl end groups to minimize surface charges (Bangs Laboratory, PS/R-OH $\sigma_S = 0.34 \pm 0.01$ μm). The silica particles carry a very small amount of negative charge on their surfaces, while the small polystyrene spheres carry no measurable charge. Earlier studies [22] of Q1D one-component suspensions of the same silica particles, carried out with varying ionic strength of the host liquid, show that the very small charge on the particles has no discernable effect on their interaction. In those earlier experiments we found, by inversion of the experimental pair correlation function (Q2D one component system) a very weak attraction ($\approx 0.5 k_B T$) between the silica particles. As noted in the previous section, we have speculated that this attraction arises from capillary interactions generated by differential wetting of the walls and colloid particles by the solvent water.

The binary mixtures made as described above were confined between two parallel walls of a glass cell coated with chlorine terminated polydimethylsiloxane telomer (Glassclad 6C, United Chemical Products). Because of this hydrophobic coating of the glass walls, they are not wetted by the aqueous colloid suspension and sticking of colloid particles to the glass walls is prevented. The details of the cell construction have been described in previously published papers [23]. A handheld vacuum pump was used to adjust the hydrostatic pressure inside the cell and thus control the distance between the two glass walls to ~ 1.76 μm, which is less than $\sigma_L + \sigma_S = 1.92$ μm. With the vertical confinement defined by the glass walls, the large silica particles move only in the xy plane determined by the depth of focus of our optics. The small polystyrene particles have a mass density of 1.027 g/ml, which is very close to that of the surrounding water, hence their thermal motion prevents any significant sedimentation in the experimental cell.

Measurements of the binary mixture with size ratio $s \equiv \sigma_L / \sigma_S = 4.6$ were made at small particle volume fractions of $\phi_S = 0$, 0.005, 0.05, and 0.10. The trajectories of the large particles were measured by digital video microscopy using an Olympus BH2 metallurgical microscope with a 100X objective. The small colloid particles are not resolved by our optics, but they do contribute to background scattering that appears as noise in the images. Using previously developed
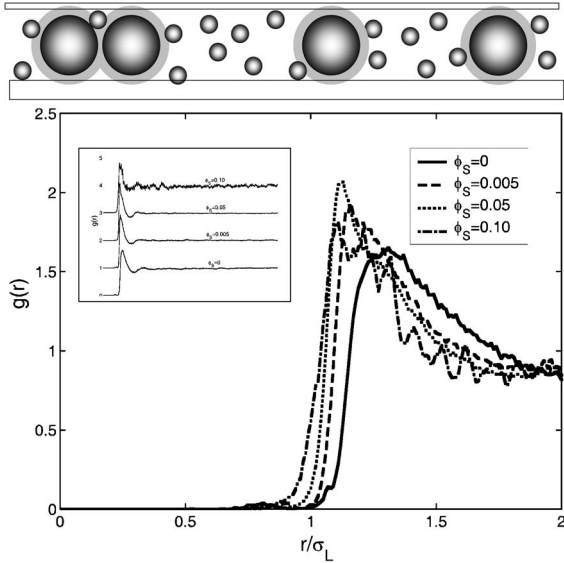
FIG. 1. A comparison of the nearest neighbor peaks in the pair correlation functions of binary systems with approximately the same large particle density but different small particle volume fractions. The upper panel shows a schematic side view of the experimental cell. The inset figure shows $g_2(r)$ over the full range of measurement, with curves shifted vertically for clarity.

image process routines [23,24], we were able to locate the center of a large particle in the focal plane within ± 0.02 μm.

III. RESULTS

The effective interaction between the large colloid particles was determined by inverting the Ornstein-Zernike equation with the hypernetted chain approximation, using the measured pair correlation function and the static structure factor as input data. Although the Percus-Yevick approximation is often preferred for the description of the hard sphere fluid, calculation of the effective potential using the inverse Monte Carlo simulation method yields agreement with those found with the method used in this paper. The pair correlation function was calculated from a histogram of the equilibrium pair separations determined from the digitized images using the definition

$$g_2(r) = \rho^{-1} \left\langle \sum_i \sum_{j \neq i} \delta(r_i) \delta(r_j - r) \right\rangle. \qquad (3.1)$$

To avoid introduction of edge effect artifacts due to image size limitation, we used only those colloid particle positions that are at least a distance r from the edges of the image in our reduction of the experimental data. The positional data from $\sim 10^9$ pairs were averaged for each set of large particle and small particle densities. The two-dimensional density of the large particles, defined in this paper by the relation $\eta_L = N_L \sigma_L^2 / A$ where N_L is the number of large spheres inside the field of view of the microscope and A is the total area of the image, cannot be exactly controlled by preparation because of the method used to fill the cell. So as to compare the effective potentials at different small particle densities with fixed large particle density, we choose data sets with approxi-
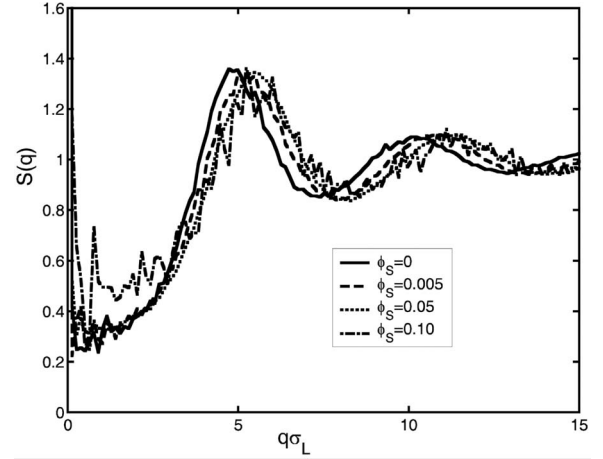

FIG. 2. A comparison of the static structure factors calculated from Eq. (3.3) for systems with different small particle volume fractions.

mately the same large particle density. Figure 1 displays the calculated pair correlation functions with $\phi_S = 0$, 0.005, 0.05, and 0.10 when $\eta_L = 0.32$, 0.34, 0.37, and 0.30, respectively. These pair correlation functions display the same characteristic features at all of the small particle densities considered: there is a well-defined first peak in $g_2(r)$ at about one large particle diameter, some weak structure for larger separation, and the correct asymptotic limit, namely $g_2(r) = 1$ for large separation. Note that the experimentally determined $g_2(r)$ extends to about $r \approx 12\sigma_L$. Note also that the first peaks of $g_2(r)$ shift to smaller particle-particle separation as the small particle concentration increases.

The method we have chosen to calculate the effective potential of the binary colloid mixture treated as a pseudo-one-component system requires the static structure factor, $S(q)$. For a two-dimensional isotropic liquid, $S(q)$ is related to the pair correlation function by

$$S(q) = 1 + 2\pi\rho \int_0^\infty (g_2(r) - 1) J_0(qr) r \, dr, \qquad (3.2)$$

where $J_0(qr)$ is the Bessel function of zero order. $S(q)$ can also be obtained directly from the colloid suspension image via the definition

$$S(q) = N^{-1} \langle \rho(q) \rho(-q) \rangle, \qquad (3.3)$$

where

$$\rho(q) = \sum_{i=1}^N \exp(i\mathbf{q} \cdot \mathbf{r}) \qquad (3.4)$$

is the Fourier transform of the two-dimensional colloid suspension image. Figure 2 shows calculated $S(q)$ corresponding to the same large and small particle densities as in Fig. 1. An obvious effect of the presence of the small particles in the colloid binary mixture is to shift the phases of the peaks of $S(q)$ to larger q with increasing small particle density.

In principle, $S(q)$ obtained from Eq. (3.2) must be the same as $S(q)$ obtained from Eq. (3.3), as the information
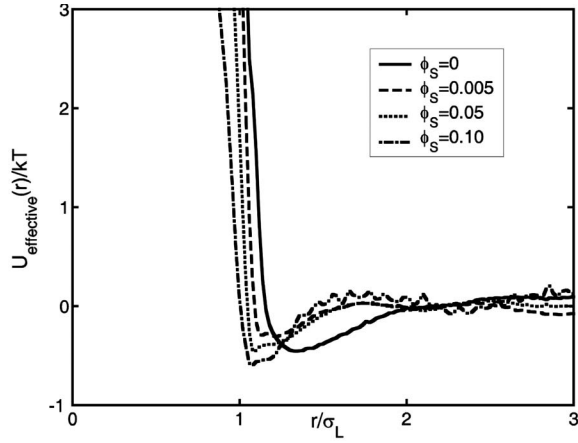
FIG. 3. Effective interaction potential between two large particles, obtained from the pair correlation function and the static structure factor using the Ornstein-Zernike equation and the hypernetted chain closure.

used comes from the same set of images. We note that the pair correlation functions were calculated from histograms of the distances between centers of pairs of large particles for distances up to $12\sigma_L$. The spatial resolution of the center position data, with image deconvolution, is 0.015 μm. The limit to the range of the calculated $g_2(r)$ was determined by the statistical quality of the accumulated data. We also note that when $S(q)$ is calculated using Eq. (3.3) all the possible large particle pair separations in an image can be employed, but with the poorer spatial resolution of 0.169 μm that is determined by the pixel size in the CCD camera. Then, overall, comparing the two methods of calculation, $S(q)$ obtained from Eq. (3.3) provides more accurate information at small q, while $S(q)$ obtained from Eq. (3.2) provides more accurate information at large q. In our determination of the effective pair interaction in the pseudo-one-component system, we used $S(q)$ calculated from Eq. (3.3) for small q($q\sigma_L < 5$) and $S(q)$ calculated from Eq. (3.2) for large q($q\sigma_L \geqslant 5$).

The Ornstein-Zernike equation relates the pair correlation function to the total correlation function, $h(r)=g_2(r)-1$, and the direct correlation function, $c(r)$, by the q-space definitions

$$\hat{h}(q) = \frac{\hat{c}(q)}{1 - \rho\hat{c}(q)}, \qquad (3.5)$$

$$S(q) = 1 + \rho\hat{h}(q). \qquad (3.6)$$

We have adopted the hypernetted chain approximation

$$\beta u_{\text{eff}}(r) = g_2(r) - 1 - c(r) - \ln g_2(r) \qquad (3.7)$$

to close the equation set and thereby calculate the effective pair potential $u_{\text{eff}}(r)$ from $g_2(r)$ and $S(q)$. The effective interaction, displayed in Fig. 3 at every small particle density we studied, shows a weak attractive well ranging from $0.3k_BT$ to $0.8k_BT$. As ϕ_S increases, the depth of the well increases slightly, the position of the repulsive branch shifts noticeably

to smaller distance, as does the position of the minimum of the potential well.

We note that there is an attractive potential ($\approx 0.5k_BT$) well for the large spheres even in the absence of the small spheres. This attractive potential is described in our previous paper [22] and has also been observed by Han and Grier [25] with the same sample of colloid particles used in our experiments. We found that this attractive potential depends on the geometry of the system; using the same colloid particles, it is somewhat deeper and longer ranged in the Q2D system than in the Q1D system. We have shown that this attractive potential well does not arise from charge-charge interactions by demonstrating its insensitivity to the salt concentration in the system. Furthermore, the glass walls of our Q2D chamber were rendered uncharged by coating with a hydrophobic polymer layer. Han and Grier [25] found that the distance between the confining walls had a significant effect on their inferred colloid-colloid pair interaction; the pair interaction is purely repulsive when the confining walls are very far away (more than $100\sigma_L$), but a pronounced attractive well develops and continuously strengthens as the confining wall separation is reduced ($\sim 0k_BT$ at about $130\sigma_L$ and $\sim 0.3k_BT$ at about $6\sigma_L$). The origin of this confinement-induced attractive potential remains unclear.

IV. THE DEPLETION POTENTIAL

The general theory of the depletion interaction can be presented as an application of the McMillan-Mayer theory of solutions [26]. The usual formal definition of the depletion interaction is

$$W_{\text{depl}}^{\infty}(\mathbf{r}) \equiv k_BT[\lim_{\mu_b\to-\infty} c_b^{(1)}(\mathbf{r}\to\infty;\{\mu_{i\neq b}\},\mu_b\to-\infty) - c_b^{(1)}$$

$$\times(\mathbf{r};\{\mu_{i\neq b}\},\mu_b\to-\infty)], \qquad (4.1)$$

which describes the situation in which one particle of species i is fixed at the origin and another particle of species b is fixed at $\mathbf{r}_b$. In Eq. (4.1) $c_b^{(1)}$ is the one particle direct correlation function. Note that taking the infinite dilution limit of the chemical potential, $\mu_b\to-\infty$, implies that we are considering the case in which the two particles between which the depletion potential is calculated are at infinite dilution in the mixture. The measured effective potential contains contributions from (i) the bare interaction between the colloid particles, (ii) the direct effect of the small particles on the selected pair of large particles, and (iii) the indirect effect of the small particles on the selected pair of large particles due to the existence of other large particles in the system. In the limit of $\mu_b\to-\infty$ contribution (iii) vanishes and the conventional definition of the depletion potential refers only to contribution (ii).

Our experimental situation is different from that usually envisaged for the definition of the depletion interaction in that we are particularly interested in the case that the large particle density is high. In order to reduce the binary mixture system with high density of large particles to an effective one-component system, we are interested in the part of the pair interaction that is in excess of the bare pair potential between the same large particles at the same density in the
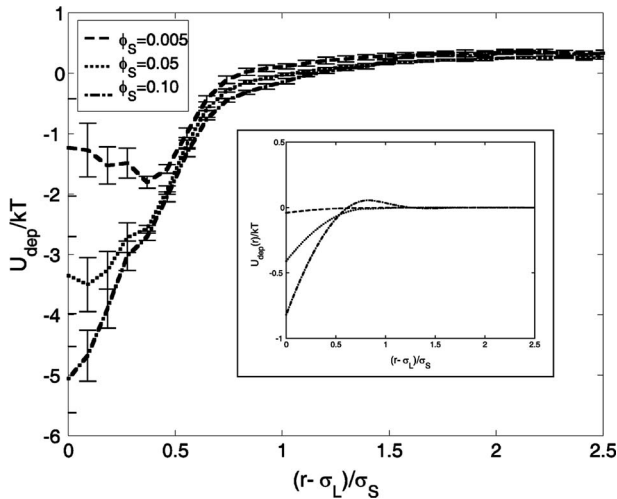
FIG. 4. The calculated depletion potential between a pair of large particles at fixed large particle density for several small particle volume fractions ϕ_S. The error bars are estimated by considering the experimental uncertainty in the pair correlation function and the static structure factor as manifest during the inversion process. The inset figure is the theoretical prediction of the depletion potential for size ratio $s \equiv \sigma_L/\sigma_S = 4.6$ and the same value of ϕ_S in a three-dimensional binary hard sphere mixture.

same state of aggregation but without any small particles. Therefore, we define the depletion potential by subtracting the bare potential from the effective potential:

$$W_{\text{dept}}(r) = u_{\text{eff}}(r, \phi_S) - u_{\text{eff}}(r, \phi_S = 0). \quad (4.2)$$

The depletion potential defined in this way is a sum of all contributions arising from the presence of the small particles; it can have contributions associated with Q2D boundary effects other than excluded volume effects. The resultant depletion potentials for small colloid particle volume fractions of 0.005, 0.05, and 0.10 are shown in Fig. 4. The accuracy of the measured depletion potentials was estimated by considering all sources of error in the measurement technique and in the calculation process. We used a well-established method [24] to locate the center of mass of each particle in an image with an accuracy of 15 nm. However, as the small particle density increases the image quality degrades somewhat, and there is greater background noise. We estimate that the uncertainty in location of large sphere centers is about 25 nm for the sample with $\phi_S = 0.10$. Also, when $\phi_S = 0.10$, the large particle motions are slower than $\phi_S = 0$. Then, for the same duration trajectories, the sampling of thermodynamic states is less extensive when $\phi_S = 0.10$ than when $\phi_S = 0$, which gives rise to a larger uncertainty in the experimentally inferred pair distribution function. We have estimated the error in the calculated depletion potential by adding or subtracting the statistical error in the experimental $g_2(r)$ before computing $u_{\text{eff}}(r)$.

The inset of Fig. 4 shows the depletion potential calculated for a 3D binary hard sphere mixture with the same size ratio and with the corresponding small particle density as in our experiment. Clearly, the Q2D depletion interaction is attractive and has a range comparable to the diameter of the small colloid particle, which is in agreement with general expectations for this interaction. However, the depths of the depletion potentials at the several small colloid particle volume fractions are much greater, by almost an order of magnitude, than predicted for the case that each colloid is a hard sphere and that there is no dispersion in the distribution of diameters of the hard spheres.

V. DISCUSSION

We have reported measurements of the depletion potential, as defined by Eq. (4.2), between a pair of large colloid particles in binary mixtures of large and small hard sphere colloids confined to be in a Q2D fluid state. Elsewhere we have reported studies of the influence of the small colloid particles in the binary mixture on the density of freezing of the large particles [1], and on the relationship between local ordering and dynamical heterogeneity in the dense fluid state [2]. Changes in the freezing density and the dynamical heterogeneity indicate the influence of large depletion potentials. Quantitative estimates of the error in the inferred depletion potentials ensure that they are indeed clearly resolved. Variations in $g_2(r)$ within subsets of the full sample data set are consistent with expected equilibrium fluctuations. However, the large depletion potential observed in our experiment cannot be explained by the predictions of available depletion potential theories.

As discussed earlier, the depletion potential due to purely excluded volume effects arises from the fact that small particles are expelled from the inter particle space of the large particles due to the hard-core repulsion. The geometric constraints imposed by the confining walls amplify this effect and deepen the depletion potential [27]. We have carried out detailed simulation studies of the effect of degree of confinement on the properties of Q2D binary hard sphere mixtures, reported elsewhere [19,21]. Our results indicate that the effective potential and other properties of the binary colloid system are modified by the presence of the confining boundaries but we do not find an enhancement comparable to that found in the experiments reported in this paper. We have also carried out simulations of Q2D binary hard sphere mixtures including polydispersity of the large particle diameter [20]. The results of these simulations were used to determine the influence of polydispersity on $g_2(r)$ and on the conversion of $g_2(r)$ to $u_{\text{eff}}(r)$ using the inverse Monte Carlo technique [28]. It is found that polydispersity has an important influence on the calculated $u_{\text{eff}}(r)$ only when the large particle density is much higher than that used in the experiments reported in this paper. The experimental data we and Han *et al.* [25] have obtained for $u_{\text{eff}}(r)$ can be taken to imply that there is some interaction in a real Q2D binary colloid mixture that has not been captured by the models used in current computer simulations; it appears to have the form of a wall induced colloid-colloid interaction that is independent of any excluded volume effects.

A possible clue as to the character of the unknown interaction described in the last paragraph comes from our study of colloid motion in a Q1D system [22]. In that system, as in the Q2D system, the walls that confine the colloid suspen-

sion are hydrophobic, which prevents the suspension from wetting them. In the Q1D case it was found that the colloid displacement distribution along the line perpendicular to the walls differed from the *a priori* expected (near hard sphere–hard wall like) wall-particle interaction. The one particle effective potential energy as a function of displacement from the center line of the Q1D channel, obtained by inverting the displacement distribution, keeps the centers of the large particles much closer to the center line than expected. We have not been able to measure the distribution of large particle displacements from the midplane of the Q2D cell, but there is reason to believe, because of the aqueous character of the suspension and the hydrophobic character of the walls, that there may be a similar one body potential acting. Presumably there will also be a one body potential of similar character acting on the small colloid particles. Accordingly, we have examined the consequences of restricting the motion of the small colloid particles along the line perpendicular to the walls. It is to be expected that, for a given volume fraction of small particles, the depletion interaction between large particles will be enhanced since the midplane concentration of small particles is thereby increased. In the same simulation we have taken account of the weak large colloid-large colloid attraction found in the pure large colloid fluid. Specifically, the large colloid–large colloid interaction was taken to be that for $\phi_S=0$ in Fig. 3 (which we fit to an analytic form), while the small colloid-large colloid and the small colloid-small colloid interactions had hard sphere form. The ratio of colloid diameters used in the simulations was $\sigma_L/\sigma_S=5$, close to that characteristic of the experiments reported in this paper. The different curves displayed in Fig. 5 correspond to a fixed Q2D plate separation of $1.00\sigma_L$ and restriction of the extent of motion along the z axis by the small colloid particles to $H_S=1.00\sigma_L$, $0.80\sigma_L$, $0.60\sigma_L$, and $0.40\sigma_L$. The centers of the large colloid particles were constrained to lie in the midplane of the Q2D cell with density $\eta_L=0.7$. When the degree of confinement of the small particles is changed, the number of small particles is held fixed; it always corresponds to $\phi_S=0.05$ when $H_S=1.00\sigma_L$. The results, shown in Fig. 5, indeed indicate that the depletion interaction is greatly enhanced relative to the case that the motion of the small particles along the line perpendicular to the walls is unconstrained, but the calculated depletion interaction is still smaller than that inferred from our experiments. The inset in Fig. 5 shows how the effective pair potential between large
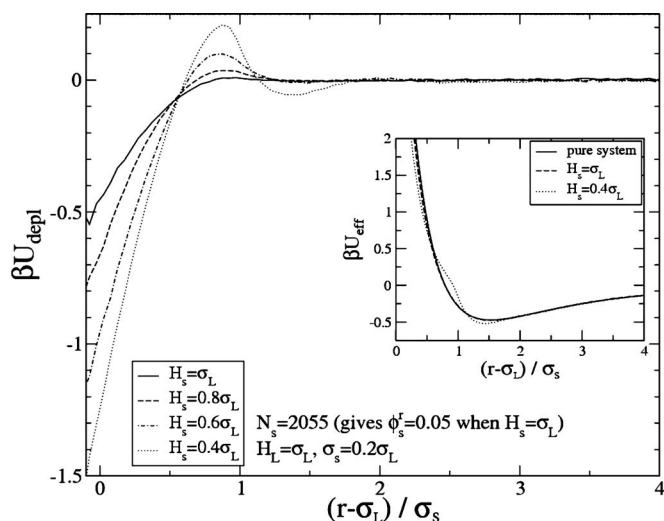

FIG. 5. The depletion potential inferred from simulations of a Q2D binary colloid mixture as a function of constraint of the small particle motion along the line perpendicular to the simulation cell walls. In this simulation the large colloid-large colloid interaction was taken to be that shown for $\phi_S=0$ in Fig. 3, while the small colloid–large colloid, and the small colloid–small colloid interactions had hard sphere form. The different curves shown correspond to a fixed Q2D plate separation of $1.00\sigma_L$ and restriction of the domain in which the small hard spheres can move to $1.0\sigma_L$, $0.8\sigma_L$, $0.6\sigma_L$, and $0.4\sigma_L$. The densities of the large and small colloid particles are $\eta_L=0.7$ and $\phi_S=0.05$, respectively.

colloid particles, obtained by the inverse Monte Carlo method [28], changes as small colloid particles are added to the suspension.

The true nature of the strong depletion potential we have found in the experiments reported in this paper remains unknown to us.

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