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Depletion forces in colloidal mixtures

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Depletion forces are accounted for by a contraction of the description of colloidal mixtures based on the integral equations theory of simple liquids. The applicability of this treatment is illustrated for binary mixtures of hard spheres, in the bulk and near a hard wall. The Asakura and Oosawa potential is obtained as the dilute limit of our equations. At higher concentrations the depletion potential has an oscillatory behavior and becomes more long ranged. If charge is put on the small particles there are energy-driven depletion forces in addition to those of entropic origin, which result in repulsive interaction at contact.

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I. INTRODUCTION

The phase of a colloidal suspension can be changed by adding a macromolecular solution. Although this knowledge has been applied for centuries, the mechanisms according to which this happens are nowadays subject of intensive research. In the case of nonadsorbing macromolecules effective depletion forces between the colloidal particles may occur. As first predicted by Asakura and Oosawa [1], such forces result from the expulsion of added macromolecules from the gap between two approaching particles, giving rise to a decrease of the free energy, and thus to an effective attraction. This may induce an entropy driven phase separation of asymmetric binary hard-sphere fluids [2], which has been taken as a model for colloid-polymer mixtures. This hard spheres model has been extensively studied using integral equations theory [3,4], perturbation theories [5,6], and density functional theories [7,8]. The measured phase diagrams have been qualitatively reproduced by these approaches.

Some attempts to account for polymer nonideality beyond the hard spheres model have recently been reported in several papers using extensions of perturbation theories [9,10] and self-consistent mean field calculations [11]. Indeed, in many cases the macromolecules are charged, or interact softly with one another. Thus, energetic corrections to the entropic forces have to be considered. If, for example, charge is put on the small particles of a mixture of hard spheres, these like to be at contact with the big particles, since the latter represent a large volume without charge. Therefore, the energy of the system increases when two big spheres approach each other expelling the small spheres from the gap between them. This can lead to repulsive contributions to the depletion forces. In this paper we present a general formulation of depletion forces based on the integral equations theory of simple liquids, which allows for a simultaneous study of entropic and energetic effects.

The basic idea of this approach is that depletion forces are a special case of the more general effective interactions resulting from a contraction of the description of liquid mixtures. Thus, if we do not consider certain components of a mixture as separate species, their influence on the structure of the remaining particles has to be included in the interaction potential. This is obtained by demanding the spacial distribution of the remaining particles to be the same as in the original mixture. Technically, this is done by rewriting the Ornstein-Zernike equation for the original mixture as an effective Ornstein-Zernike equation for the remaining particles, and connecting the latter with the effective interaction potential using one of its closure relations. This idea was first implemented by Medina-Noyola and McQuarrie in order to calculate the interaction between two charged macroions immersed in a bath of small counterions and salt ions [12]. We consider here the case of large hard spheres immersed in a bath of charged or uncharged small hard spheres in order to describe depletion forces, in the bulk and near a hard wall.

In the following section the general formulation of depletion forces in multicomponent systems is presented. Its applicability is then illustrated in the third and fourth sections studying binary mixtures of charged and/or uncharged hard spheres. Also the case of the enhanced depletion potential near a hard wall is considered. Finally, the paper is closed with a section of conclusions.

II. GENERAL FORMULATION

The structure of an homogeneous liquid mixture of p components is given by the Ornstein-Zernike (OZ) equations [13]

$$\tilde{h}_{ij}(q)=\tilde{c}_{ij}(q)+\sum_{k=1}^{p} n_k\tilde{h}_{ik}(q)\tilde{c}_{kj}(q);\ i,j=1,\ldots,p, \quad (1)$$

written here in the Fourier space (this feature is indicated by the tilde, and by the functional dependence on the wave number q). The functions $\tilde{h}_{ij}(q)$ and $\tilde{c}_{ij}(q)$ are the total and direct correlation functions, respectively. The coefficients n_k are the partial number densities. This equation can be rewritten as

$$\tilde{h}_{ii}(q)=\tilde{c}_{ii}^{\mathrm{eff}}(q)+n_i\tilde{h}_{ii}(q)\tilde{c}_{ii}^{\mathrm{eff}}(q);\ i=1,\ldots,p, \quad (2)$$

with $\tilde{c}_{ii}^{\text{eff}}(q)$ given by

$$\begin{aligned}\tilde{c}_{ii}^{\text{eff}}(q)=\tilde{c}_{ii}(q)&+\sum_{k\neq i}^{p}\frac{n_k\tilde{c}_{ik}(q)\tilde{c}_{ki}(q)}{[1-n_k\tilde{c}_{kk}(q)]}\\&+\sum_{k\neq i}^{p}\sum_{l\neq k,i}^{p}\frac{n_kn_l\tilde{c}_{il}(q)\tilde{c}_{lk}(q)\tilde{c}_{ki}(q)}{[1-n_l\tilde{c}_{ll}(q)][1-n_k\tilde{c}_{kk}(q)]}\\&+\sum_{k\neq i}^{p}\sum_{l\neq k,i}^{p}\sum_{m\neq l,i}^{p}\\&\times\frac{n_kn_ln_m\tilde{c}_{im}(q)\tilde{c}_{ml}(q)\tilde{c}_{lk}(q)\tilde{c}_{ki}(q)}{[1-n_m\tilde{c}_{mm}(q)][1-n_l\tilde{c}_{ll}(q)][1-n_k\tilde{c}_{kk}(q)]}\\&+\cdots.\end{aligned}\tag{3}$$

The total correlation function $\tilde{h}_{ii}(q)$ in Eq. (1) is the same as in Eq. (2), but in Eq. (2) the species $k=1,\ldots,p\neq i$ no longer appear as separate species. Instead, their effects on the structure of the component i are included in $\tilde{c}_{ii}^{\text{eff}}(q)$. Equation (3) can be written in closed form by using matrix notation [14]. Its present form however makes easier its application in the following sections, since it straightforwardly takes a very simple closed form in the case of binary mixtures. Therefore, Eq. (2) represents an effective OZ equation for the component i. In addition, an effective pair interaction potential $u_{ii}^{eff}(r)$ can be obtained from Eqs. (2) and (3) by using a closure relation. Taking for example the mean spherical approximation (MSA) [13], the result is

$$\begin{aligned}\beta u_{ii}^{\text{eff}}(r)&=+\infty\quad\text{if } r<\sigma_i,\\&=f_d(r)\quad\text{if } r\geqslant\sigma_i,\end{aligned}\tag{4}$$

with $f_d(r)=-c_{ii}^{\text{eff}}(r)$ being the depletion potential, and σ_i the diameter of the particles of species i. The distance between the centers of the particles is denoted by r. In the following we use Eq. (4) together with other closure relations used to obtain the direct correlation functions of the uncontracted system.

As we can see from the previous equations, an evaluation of $u_{ii}^{\text{eff}}(r)$ requires a complete knowledge of the structure functions $h_{ij}(r)$ and $c_{ij}(r)$ of the original mixture. To proceed along these lines makes sense when the contraction of the description is imposed, for example, by experimental techniques unable to detect all the components. Then Eq. (4) allows for an interpretation of the results in terms of models including the experimentally ''invisible'' species. On the other hand, our approach apparently makes no sense when the goal of the contraction of the description is to simplify the problem. However, we can learn much about depletion forces just evaluating $u_{ii}^{\text{eff}}(r)$ in the cases in which the complete problem can be solved. Furthermore, simple approximation for $h_{ij}(r)$ and $c_{ij}(r)$ could lead to useful expressions for $u_{ii}^{\text{eff}}(r)$, as we show in the next sections.

III. BINARY MIXTURES

In the case of binary mixtures Eqs. (2) and (3) reduce exactly to

$$\tilde{h}_{11}(q)=\tilde{c}_{11}^{\text{eff}}(q)+n_1\tilde{h}_{11}(q)\tilde{c}_{11}^{\text{eff}}(q)\tag{5}$$

and

$$\tilde{c}_{11}^{\text{eff}}(q)=\tilde{c}_{11}(q)+\frac{n_2\tilde{c}_{12}^{2}(q)}{1-n_2\tilde{c}_{22}(q)}.\tag{6}$$

These equations describe the structure of particles of species 1 immersed in a bath of particles of species 2, but the latter do not appear as a separate species; their effects are included in $\tilde{c}_{11}^{\text{eff}}(q)$. The effective pair interaction potential $u_{11}^{\text{eff}}(r)$ can be obtained from Eq. (4) using Eq. (6). For binary mixtures of hard spheres, one obtains in the infinite dilute limit of n_1, up to linear terms in n_2,

$$f_d(r)=-n_2\mathcal{F}^{-1}\{\tilde{c}_{12}^{2}(q)\},\tag{7}$$

with $c_{12}(r)=-1$ for $r<\sigma_{12}=(\sigma_1+\sigma_2)/2$, and 0 elsewhere ($\mathcal{F}^{-1}$ denotes an inverse Fourier transform). Thus, the Asakura and Oosawa (AO) potential is obtained:

$$f_d(r)=-\varphi_2\left[(\eta+1)^3-\frac{3}{2}(\eta+1)^2\frac{r}{\sigma_2}+\frac{1}{2}\frac{r^3}{\sigma_2^3}\right]\tag{8}$$

for $\sigma_1\leqslant r<\sigma_1+\sigma_2$, and 0 for larger distances. Here, $\varphi_2=\pi n_2\sigma_2^3/6$ is the volume fraction of particles of species 2, and $\eta=\sigma_1/\sigma_2$ the ratio of diameters. This potential is purely attractive with a minimum of amplitude $f_d(\sigma_1+)=-\varphi_2(1+3\eta/2)$ at contact. Equation (8) was first derived by Vrij just calculating the difference of the osmotic pressures acting on the inner and outer faces of two big particles separated by a gap thinner than the diameter of the small particles, modeling the latter as an ideal gas [15]. It is here recovered as the dilute limit of our equations.

In order to extend the previous result to higher orders in the densities, Eq. (6) has to be expanded in powers of n_2 to give

$$\begin{aligned}f_d(r)=-c_{11}(r)-n_2\mathcal{F}^{-1}\{\tilde{c}_{12}^{2}(q)[1&+n_2\tilde{c}_{22}(q)\\&+n_2^2\tilde{c}_{22}^{2}(q)+\cdots]\}.\end{aligned}\tag{9}$$

In addition, expansions of $c_{11}(r)$, $\tilde{c}_{12}(q)$, and $\tilde{c}_{22}(q)$ in terms of n_1 and n_2 are required as inputs. For these, the analytic Percus-Yevick direct correlation functions obtained by Hiroike could be used [16]. However, to avoid the rather complicated expressions we obtain them instead by solving the complete problem of Eq. (1) numerically by means of a five parameters version of the Ng method [17], together with the Percus-Yevick (PY) [13] and the Rogers-Young (RY) [18] closure relations.

We consider first corrections on n_2, for the infinite dilute limit of n_1. The results are shown in Fig. 1, which displays $f_d(r)$ for three systems with $\eta=5$, and $\varphi_2=0.05$, 0.1, and 0.2. The full lines correspond to PY, and the dashed lines to the AO potential. As expected, the attraction at contact becomes deeper with increasing concentration of small particles. In addition, a potential barrier develops in front of the attractive well, and the interaction becomes more long-ranged, oscillating around zero, at larger separations. This is

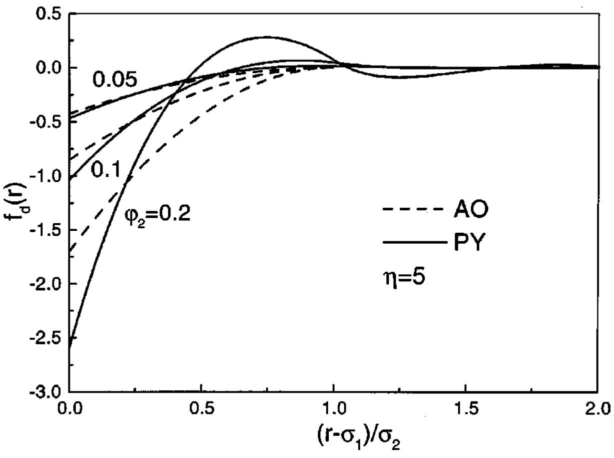

FIG. 1. The figure shows $f_d(r)$ for three binary mixtures of hard spheres with $\eta=5$, and $\varphi_2=0.05$, 0.1, and 0.2, for the infinite dilute limit of n_1. The full lines correspond to PY, and the dashed lines to the AO potential.

due to the correlation between the small particles, which is not included in the AO approximation, but it is in PY.

We now consider the effects of increasing n_1; results for two systems with $\eta=5$, $\varphi_2=0.2$ and $\varphi_1=0.05$ and 0.15 are shown in Fig. 2. Comparison with the PY result of Fig. 1 for $\varphi_2=0.2$ shows that an increase of φ_1 gives rise to deeper contact values and to increasing barriers. The dashed lines in Fig. 2 have been obtained by using the previous results for the infinite dilute limit of n_1, but replacing the volume fraction φ_2 by $\varphi_2'=\varphi_2/(1-\varphi_1)$, as if the only effect of putting more particles of species 1 into the system were to decrease the volume accessible to the particles of species 2 in a quantity equal to the volume occupied by the first; $\pi\sigma_1^3 N_1/6$ (N_1 is the number of particles of species 1). The differences between the full and dashed lines in Fig. 2 show that the correlations including the particles of species 1 become important.

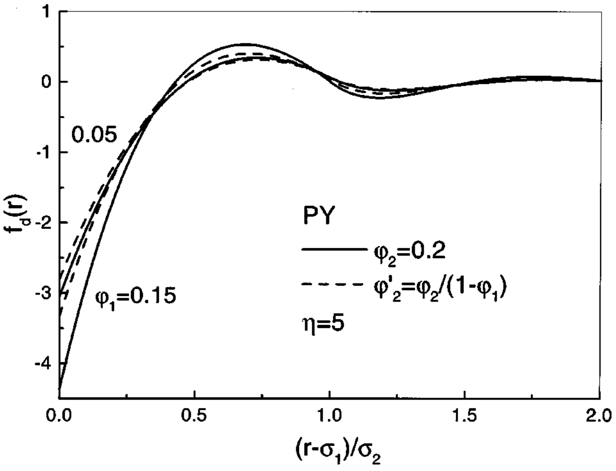

FIG. 2. The figure shows $f_d(r)$ for two binary mixtures of hard spheres with $\eta=5$, $\varphi_2=0.2$, and $\varphi_1=0.05$ and 0.15. All lines correspond to PY, but the dashed lines were obtained taking the volume fractions $\varphi_2'=\varphi_2/(1-\varphi_1)$ and $\varphi_1'\rightarrow 0$, as if the only effect of putting more particles of species 1 into the system were to decrease the volume accessible to the particles of species 2 in a quantity equal to the volume occupied by the first; $\pi\sigma_1^3 N_1/6$ (N_1 is the number of particles of species 1).

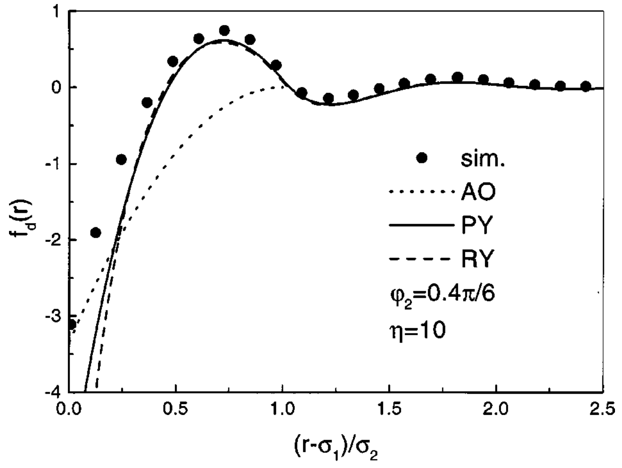

FIG. 3. The figure displays a comparison between computer simulations results of Biben *et al.* [4] (circles) and integral equations theory for a binary mixture of hard spheres with $\eta=10$ and $\varphi_2=0.4\pi/6$, for the infinite dilute limit of n_1. The full line corresponds to PY, the dashed line to RY, and the dotted line to the AO potential.

The accuracy of our approximations for $f_d(r)$ has been tested by a comparison with computer simulation results of Biben *et al.* [4]. This is shown in Fig. 3 for a system with $\eta=10$ and $\varphi_2=0.4\pi/6$, for the infinite dilute limit of n_1. The full line corresponds to PY, the dashed line to RY, and the dotted line to the AO potential. It is seen that there are considerable differences at very small separations but that the present approximation reproduces the effective interaction very well at larger distances, including the oscillatory part.

We now investigate the effects of replacing the hard core interaction among the small particles by long-range repulsions; the repulsive Yukawa potential

$$u_{22}(r)=+\infty,\quad \text{if } r<\sigma_2,$$

$$=\frac{Q^2}{\varepsilon}\left[\frac{\exp(\kappa\sigma_2/2)}{1+\kappa\sigma_2/2}\right]^2\frac{\exp(-\kappa r)}{r},\quad \text{if } r\geqslant\sigma_2, \tag{10}$$

with

$$\kappa^2=\frac{4\pi}{k_B T\varepsilon}\sum_{\text{si}} n_s q_s^2, \tag{11}$$

is taken instead, keeping hard core for $u_{11}(r)$ and $u_{12}(r)$. Such systems represent a simple model of colloidal mixtures of charged and uncharged particles [19,20]. The charge on the small spheres is denoted by Q, and the dielectric constant of the solvent by ε. In expression (11) for the Debye-Hückel screening parameter κ the sum runs over the small ions (si) in the system, i.e., counterions and salt ions. It should be noted that $u_{22}(r)$ is itself an effective potential resulting from the contraction of the small ions and of the solvent molecules from the description of the original system [12,14]. Their effects are contained in κ and in ε, respectively.

In order to calculate the depletion forces between two large uncharged hard spheres immersed in a bath of small charged particles the direct correlation functions of the bi-

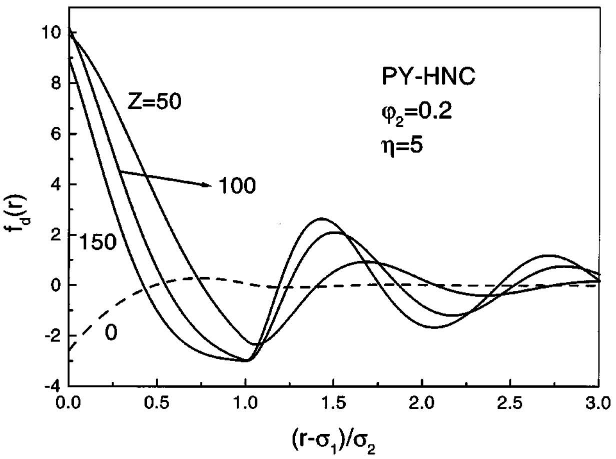

FIG. 4. The figure shows $f_d(r)$ for four binary mixtures of charged and uncharged hard spheres with $\eta = 5$, $\varphi_2 = 0.2$ and valence $Z = 0,50,100$, and 150, in the infinite dilute limit of n_1. All lines correspond to PY-HNC.

nary mixture are calculated solving Eq. (1) together with PY for $c_{11}(r)$ and $c_{12}(r)$, and the hypernetted chain approximation (HNC) for $c_{22}(r)$ (this hybrid closure relation is known as PY-HNC [20]), and they are then used in Eq. (6) to obtain $f_d(r)$ from Eq. (4). Only the infinite dilute limit of the density of large spheres n_1 is considered. Monovalent counterions and no salt are assumed. The values $\sigma_2 = 50$ nm, $T = 300$ K, and $\varepsilon = 78.2$ (water) are used in all cases.

Figure 4 shows $f_d(r)$ for four systems with $\eta = 5$, $\varphi_2 = 0.2$ and valence $Z = 0,50,100$, and 150. The charging of the small spheres has dramatic effects on the depletion potential. As the comparison of results for uncharged and for charged small spheres shows, the depletion potential between the large spheres is now strongly repulsive at contact, but it is attractive for separations such that one small sphere fits in between two large ones. At somewhat larger separations it is again repulsive. In contrast to binary mixtures of hard spheres, where the depletion forces are entirely of entropic nature, energetic corrections have been included here because of the range of the Yukawa potential. When charge is put on the small particles, they try to be at contact with the big particles, because the latter represent a large volume without charge. Thus, the energy of the system increases when two uncharged spheres approach each other expelling the charged spheres from the gap between them, leading to repulsive contributions to the depletion forces. The influence of the energetic corrections on the phase behavior of binary mixtures of hard spheres has been studied in a previous paper [21].

IV. TERNARY MIXTURES AND WALL EFFECTS

Also for ternary mixtures it is straightforward to contract Eq. (1), if at least one of the components is extremely dilute. Thus, if $n_1 \to 0$, the effective OZ equation describing the crossed correlation function $h_{12}(r)$ of particles of species 1 and 2 immersed in a bath of particles of species 3 reads

$$\tilde{h}_{12}(q) = \tilde{c}_{12}^{\mathrm{eff}}(q) + n_2 \tilde{h}_{12}(q) \tilde{c}_{22}^{\mathrm{eff}}(q), \tag{12}$$

with

$$\tilde{c}_{12}^{\mathrm{eff}}(q) = \tilde{c}_{12}(q) + \frac{n_3 \tilde{c}_{13}(q) \tilde{c}_{32}(q)}{1 - n_3 \tilde{c}_{33}(q)} \tag{13}$$

and

$$\tilde{c}_{22}^{\mathrm{eff}}(q) = \tilde{c}_{22}(q) + \frac{n_3 \tilde{c}_{23}^2(q)}{1 - n_3 \tilde{c}_{33}(q)}. \tag{14}$$

The effective interaction potential $u_{12}^{\mathrm{eff}}(r)$ can again be approximated by applying MSA:

$$\begin{aligned} \beta u_{12}^{\mathrm{eff}}(r) &= +\infty, \text{ if } r < \sigma_{12}, \\ &= f_d(r), \text{ if } r \geqslant \sigma_{12}, \end{aligned} \tag{15}$$

with $f_d(r) = -c_{12}^{\mathrm{eff}}(r)$.

When the ternary mixtures consist of hard spheres, we get for the infinite dilute limit of n_2, up to linear terms in n_3,

$$f_d(r) = -n_3 \mathcal{F}^{-1}\{\tilde{c}_{13}(q) \tilde{c}_{32}(q)\}, \tag{16}$$

with $c_{13,32}(r) = -1$ for $r < \sigma_{13,32}$, and 0 elsewhere. Thus, the AO potential is extended to particles of different diameters

$$\begin{aligned} f_d(r) = &-\varphi_3 \left[(\bar{\eta}+1)^3 - \frac{3}{2}(\bar{\eta}+1)^2 \frac{r}{\sigma_3} + \frac{1}{2}\frac{r^3}{\sigma_3^3} \right] \\ &+ \frac{3\varphi_3}{8(r/\sigma_3)} (\eta_1 - \eta_2)^2 \left[(\bar{\eta}+1) - \frac{r}{\sigma_3} \right]^2 \end{aligned} \tag{17}$$

for $\sigma_{12} \leqslant r < \sigma_{12} + \sigma_3$, and 0 for larger distances. Here, $\eta_i = \sigma_i / \sigma_3$ and $\bar{\eta} = (\eta_1 + \eta_2)/2$. The contact value is $f_d(\sigma_{12}+) = -\varphi_3[1 + 3\eta_1\eta_2/(\eta_1+\eta_2)]$. Therefore, fixing the value of η_2 and comparing with the contact value of Eq. (8), we find that the leading effect of the size asymmetry is to increase (reduce) the depletion attraction if $\eta_1 > \eta_2$ ($\eta_1 < \eta_2$). Furthermore, taking $\eta_1 \to \infty$, the AO potential for a particle near a hard wall is obtained, a result also derived by Götzelmann *et al.* [6] by a rather different method:

$$f_d(h) = -\varphi_3 \left(\frac{h}{\sigma_3} - 1 \right)^2 \left(1 + 3\eta_2 + 2\frac{h}{\sigma_3} \right) \tag{18}$$

for $0 \leqslant h < \sigma_3$, and 0 for larger distances. Here, $h = r - \sigma_{12}$ is the distance from the surface of one particle of species 2 to the wall. The contact value $f_d(h = 0+) = -\varphi_3(1 + 3\eta_2)$ is the maximal depletion attraction between two particles of different diameters immersed in a bath of other particles, up to linear order in the volume fraction of the latter. In the opposite limit, $\eta_1 \to 0$, the expected contact value $f_d(r = \sigma_{12}+) = -\varphi_3$ is recovered; the energy lost by filling a hole of volume $\pi\sigma_3^3/6$ between particles 1 and 2 . If $\sigma_1 = \sigma_2$ Eq. (17) reduces to Eq. (8). Recently, expression (18) has been found to be an excellent approximation by comparison with direct measurements of depletion potentials in mixtures of colloid and nonionic polymers [22].

V. CONCLUSIONS

It has been shown how depletion potentials arise from contracting the full integral equation theory of a *p*-component mixture to an effective description on a level which includes explicitly less than *p* components. In the simplest case of a binary mixture $(p=2)$ one obtains as effective description a one-component system of particles interacting through a potential depending parametrically on the contracted component. The approach developed in this paper is of the same spirit as the one used by Mao *et al.* [10]. Instead of integrating over the degrees of freedom of the small particles in the partition function we rewrite the full set of coupled Ornstein-Zernike equations (1) in the form of Eqs. (2). The effects of the contracted components is then taken care of in the direct correlation function $c_{11}^{\mathrm{eff}}(r)$ of the contracted system. The depletion potential is obtained from $c_{11}^{\mathrm{eff}}(r)$ by employing a closure relation; for reasons of simplicity we have used the mean-spherical approximation (MSA), but any other more sophisticated closure relation could have been used as well.

The effective direct correlation function $c_{11}^{\mathrm{eff}}(r)$ is given in terms of the direct correlation functions of the contracted components. Introducing simple approximations for the latter, it has been shown that the Asakura-Oosawa results follow immediately. But our main interest has been to show how these results change when the assumptions of the AO theory no longer apply. From the numerical solution of the full set of OZ equations it is possible to calculate the depletion potentials for arbitrary concentrations of all components of the mixture. Furthermore, energetic corrections to the entropic forces can also be included in order to describe more realistic systems than that composed by only hard spheres.

The integral equation approach can straightforwardly be extended to mixtures of more than $p=2$ components as demonstrated in Sec. IV. In addition to giving results for the depletion potentials between two kinds of large particles in a sea of small particles it is also possible to obtain the depletion potential of one kind of large particles near a wall, in a sea of small particles.

Finally, our approach assumes that depletion forces are pairwise additive. Direct computer simulations by Dijkstra *et al.* [23] have recently shown the correctness of this assumption for hard spheres mixtures, even in regimes where one might expect the approximation of pairwise additivity to fail. Although it was still not proven for mixtures of charged and uncharged particles, we also neglect effective triplet interactions in that case.

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