Depletion interactions in binary mixtures of repulsive colloids*

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Acceptance ratio method, which has been used to calculate the depletion potential in binary hard-sphere mixtures, is extended to the computation of the depletion potential of non-rigid particle systems. The repulsive part of the Lennard–Jones pair potential is used as the direct pair potential between the non-rigid particles. The depletion potential between two big spheres immersed in a suspension of small spheres is determined with the acceptance ratio method through the application of Monte Carlo simulation. In order to check the validity of this method, our results are compared with those obtained by the Asakura–Oosawa approximation, and by Varial expansion approach, and by molecular dynamics simulation. The total effective potential and the depth of its potential well are computed for various softness parameters of the direct pair potential.

Keywords: acceptance ratio method, Monte Carlo, depletion interaction

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1. Introduction

Colloidal suspensions, commonly referred to simply as colloids, are the complex fluids composed of mesoscopic particles dispersed in a solvent of microscopic particles.[1,2] Colloids have widespread industrial and biological applications in nanostrutured materials, including paints, coatings, inks, and drug carriers.[3] The stability of colloidal suspensions, which is very important during these applications, has been intensively studied in the past decades.[4−9] The understanding of the stability and the equilibrium phase behaviours relies on a fundamental knowledge of the effective inter-particle interactions which are a combination of direct interactions (such as electrostatic forces) with indirect interactions mediated through the solvent and the other solute particles.[4−6] Hard-sphere colloids dispersed in a solvent provide a simple model system for the study of fundamental questions in colloidal systems. In the hard-sphere suspensions, the typical indirect potential is the depletion potential. The first successful model to describe the depletion effects was developed by Asakura and Oosawa in 1954.[10,11] This model shows that there is an attractive depletion interaction between two plates immersed in a solution of polymers, and the attractive range is about twice as large as the radius of gyration, $R_{\rm g}$, of the polymer. Later, the same authors, and independently Vrij,[12] derived a depletion potential between two hard spheres by approximating the ideal polymers as penetrable spheres with $R_{\rm g}$. The phase behaviour of colloid-polymer mixtures has been investigated by using a hard-sphere perturbation theory with the depletion potential obtained by this Asakura–Oosawa (AO) model.[13,14]

Binary hard-sphere mixtures, as a standard reference system for determining the properties of more realistic models of mixtures of simple (atomic) fluids, of colloids and polymers, and of other colloidal systems, have attracted much attention. The phase behaviours of asymmetric hard-sphere mixtures are more complicated than those of identical hard-sphere system.[4−6,15,16] When studying the phase behaviours and the structure of asymmetric binary hard-sphere mixtures, Dijkstra *et al.*[4−6] derived a formal expression for the effective Hamiltonian of the large spheres by integrating out the degrees of freedom of the small spheres in the partition function. The prediction of phase behaviours has been justified by comparing with those from the simulations of the true binary mixture.[7] When the binary system is reduced into an effective one-component system according to this way,

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the main task is to determine the depletion potential between two big spheres immersed in a fluid of small spheres. This additive mixtures of hard spheres are different from colloid-polymer mixtures which are usually treated by a model under the assumption of ideal polymer–polymer interactions (hard-sphere diameters are nonadditive).[17,18] The AO model, which gives the depletion potential between two colloidal spheres in a solution of polymers with a reasonable accuracy, can give only an approximate depletion potential to the first order of the density of small spheres in the hard-sphere mixtures, which is also termed AO approximation (or ideal-gas approximation).

Understanding of depletion potentials is not only relevant to bulk phase behaviour, but also of intrinsic interest. In recent years, the depletion interactions in binary hard-sphere mixtures have been intensively investigated in both experiment and theory. In experiment, a variety of techniques, such as video microscopy[19] and optical tweezer techniques,[20,21] have been used to determine depletion forces in binary hard-sphere mixtures. In theory, the density functional[22] approach based on the Rosenfeld fundamental measures functional[23,24] has been proved very efficient and highly accurate when it is used to calculate the depletion potential in binary hard-sphere mixtures. In addition, there are a few semi-analytical approaches available. In these approaches, the depletion potential between two big spheres is determined by the effective direct correlation function of the big spheres which can be estimated with Virial expansion approximation[6,25,26] or integral equation method[27−29] in the Percus Yevick (PY) approximation,[30] or hypernetted chain (HPC) approximation, or other approximations.[31,32]

Computer simulation, as a complementary method to experimental and theoretical measurements, has been widely used to calculate depletion potential. Owing to the rapid development in computer technology, computer simulations become more and more important in research. Two main simulating techniques, molecular dynamics (MD) and Monte Carlo (MC) simulations, are applicable for the computation of depletion potentials.[26−28,33,34] It is straightforward to compute the depletion force acting on the big sphere surrounded by small spheres in MD simulations.[26,27,35,36] For hard-sphere binary systems, the depletion force can be obtained by integrating the contact density profiles of small spheres around the big spheres, and the density profiles can be estimated in MC simulations.[28] However, inaccuracies can be introduced by extrapolation which is usually used to determine the contact density profiles. Another approach to the determination of depletion interactions by means of MC simulations is acceptance ratio method (ARM) developed by Li and Ma.[34] In our previous studies,[34,37−40] it has been proven very efficient for calculating depletion potentials in binary hard-core colloids including nonspherical colloidal systems.[41] It has also been used to calculate the depletion potential in geometrically confined binary colloids by Xiao *et al.*[42] and Guo *et al.*[43]

In more realistic colloidal systems, the direct interactions among colloids are not simple hard-core interactions. Coulombic forces, van der Waals attractions, and other interactions are generally present in colloids. The changes of effective interactions, which are sensitive to the direct interactions, significantly influence the phase behaviours of the binary mixtures.[26,44,45] In recent years, there have been more and more attempts to go beyond pure depletion effects by including non-rigid direct interactions between the particles of a binary mixture.[26,44−50] The depletion effect in non-rigid mixtures is very different from that in the hard-sphere mixtures. For example, Walz and Sharma[46] calculated the depletion force between two charged spheres in a solution of charged spherical macromolecules. They found that the presence of the long-range electrostatic repulsion increases significantly both the magnitude and the range of the depletion effect. Very recently, the similar characteristics were also seen in the soft repulsive-sphere binary mixtures by Cinacchi *et al.*[26] The adding of non-rigid direct interactions enriches the physics in the binary mixtures. However, it also increases the complexity in the computation of the effective potential.

For non-rigid colloidal mixtures, there is no appropriate density functional for the approach proposed by Roth *et al.*[22] The Virial expansion theory is an alternative option which provides a perturbative expansion for the depletion potential in powers of the particle density.[6,25,26] As higher order Virial expansion requires the evaluation of multidimensional integrals which is very time-consuming for high accuracy in numerical procedure, usually the second-order Virial approximation is implemented,[26] and therefore the accuracy of the Virial approximation is limited. Even though the accuracy is limited, Virial expansion as a semi-analytical approach is very useful to guide the measurements of experiments and simulations. When

no accurate theoretical method is available, computer simulation can act as an important role. In the case of calculating depletion forces, MD simulation does not rely on the direct potentials in the binary mixtures, and can accurately calculate depletion forces within statistical errors for any particle density lower than the critical crystalization density.[26,35,36] However, the calculation of depletion interactions is not a dynamic process, it is not necessary to use MD simulation which requires the integrating of the equation of motion which is time costly.

ARM, which has been implemented to calculate the depletion potential by means of MC simulations, can be readily extended to non-rigid particle systems. In this article, the implementation of ARM in MC simulation for the calculating of the depletion potential in the binary repulsive colloidal mixtures is presented. The rest of the article is arranged as follows. In Section 2 we describe the acceptance ratio method and its implementation in MC simulations for non-rigid particle systems. In this section, the AO approximation for non-rigid colloidal mixtures is also briefly described. The results of the depletion potential obtained by the ARM are presented as well as the comparisons between them and other results obtained by Virial expansion approach and MD simulation in Ref. [26] are given in Section 3. In Section 4 our results as well as the comparisons between our results and those from other methods are presented.

2. Theory and model

2.1. Acceptance ratio method and its implementation

In order to check the validity of our method, the similar binary non-rigid particle mixtures considered in this work are used as those in Ref. [26] for the convenience of comparing our results with theirs. The direct inter-particle potential is given by

$$u_{ij}(r) = \begin{cases} 4\epsilon_{ij}\left[(\sigma_{ij}/r)^{2n} - (\sigma_{ij}/r)^{n} + 1/4\right], & r \le 2^{1/n}\sigma_{ij}, \\ 0, & r > 2^{1/n}\sigma_{ij}, \end{cases} \tag{1}$$

where ϵ_{ij} and σ_{ij} ($i,\ j$ = b, s) are the energy and the range parameter, respectively, r is the distance between two interacting particles, n is the measure of the softness of the interactions, and the limit of $n \to \infty$ refers to the hard-sphere. When $n = 6$, the pair potential is the repulsive part of the familiar Lennard–Jones potential.

The acceptance ratio method was first proposed by Bennett,[51] and it is a very powerful method of determining free energy from simulations. Following its implementation in hard-sphere binary mixtures, we extend it to the binary non-rigid particle mixtures. The ARM aims to calculate the free energy difference between two similar systems distinguished by two external potentials V_0 and V_1. For the investigation of the depletion potential between two big spheres in a solution of small spheres, the presence of the two big spheres acts as an external potential of surrounding small spheres. The external potential can be indicated by the distance d between the two big spheres, and d_0 and d_1 indicate the distances between two big spheres for the systems of V_0 and V_1, respectively. With the corresponding partition functions of the two systems being Q_0 and Q_1, the free-energy difference between these two systems is given by

$$\begin{aligned} \beta\triangle F &\equiv \beta F_1 - \beta F_0 \\ &= -\ln\frac{Q_1}{Q_0} \\ &= -\ln\frac{\langle f(\beta(V_1 - V_0))\rangle_0}{\langle f(-\beta(V_1 - V_0))\rangle_1}, \end{aligned} \tag{2}$$

where $f(x) = [1+\exp(x)]^{-1}$ is the Fermi function and $\beta = 1/k_{\rm B}T$.

For the hard sphere systems, equation (2) is simplified into

$$\beta\triangle F = -\ln\frac{N_{10}}{N_{01}}, \tag{3}$$

where N_{10} is the number of samples drawn out from the N simulated samples, which are generated with potential V_0 where V_1 is not infinite; and N_{01} is the number of samples drawn out from N simulated samples, which are generated with potential V_1 where V_0 is not infinite. During the MC simulation, with the two big spheres fixed at the distance of d_0, small spheres are simulated according to the standard Metropolis scheme. As it is ensured that there is no overlap between spheres in any pair, V_0 is always zero. When the system reaches equilibrium, N MC steps are used to sample N_{10}. After each MC step, we check whether or

not there is any overlap between small spheres and big spheres for the distance d_1 of two big spheres. If there is no overlap, then $V_1 = 0$, and $f(\beta(V_1 - V_0)) = 1$, and then N_{10} is added by one; otherwise, $V_1 = \infty$, and $f(\infty) = 0$, and then N_{10} is added by nothing. A similar process can be done to accumulate N_{01}. With the values of N_{10} and N_{01}, the free-energy difference, which is just the difference in depletion potential, can be obtained from Eq. (3).

When the system is changed to non-rigid binary mixtures, the calculating procedure is similar. The main difference is that the external potential is no longer zero or infinity, but a finite value. In each MC step, V_0 and V_1 are calculated with new positions of small spheres. Expression 2 can be evaluated from the difference between V_0 and V_1 for small spheres, and N_{10} (or N_{01}) is not an integer, but a floating number.

2.2. Asakura–Oosawa approximation

The results of depletion potential obtained by the AO approximation are usually used to guide theoretical or experimental results. In Ref. [26], the Virial expansion approach has been developed for the calculation of the depletion potential in soft repulsive-sphere binary mixtures. When only the contribution of the first-order term of the density is considered, the Virial expansion approach gives the AO approximation. In the following, the AO approximation based on Virial expansion is briefly described. More details about this approach can be found in Ref. [26].

The depletion potential between two big spheres immersed in a solvent of small spheres can be expressed in terms of the difference between one-body direct correlation functions

$$\begin{aligned}\beta W(\boldsymbol{r}) = {} & C_{\mathrm{b}}^{(1)}\left(\boldsymbol{r}\to\infty;[\,\rho_{\mathrm{b}}\to 0,\rho_{\mathrm{s}}]\right)\\ & - C_{\mathrm{b}}^{(1)}\left(\boldsymbol{r};[\,\rho_{\mathrm{b}}\to 0,\rho_{\mathrm{s}}]\right).\end{aligned} \tag{4}$$

The big spheres are assumed to be infinitely dilute in the binary mixtures. The correlation function $C_{\mathrm{b}}^{(1)}$ of big spheres under the limit of infinite dilution can be obtained by means of Virial expansion as

$$\begin{aligned}& -C_{\mathrm{b}}^{(1)}\left(\boldsymbol{r};[\,\rho_{\mathrm{b}}\to 0,\rho_{\mathrm{s}}]\right)\\ &= \int \mathrm{d}\boldsymbol{r}'\rho_{\mathrm{s}}(\boldsymbol{r}')f_{\mathrm{bs}}(\boldsymbol{r}-\boldsymbol{r}') + \frac{1}{2}\int \mathrm{d}\boldsymbol{r}'\,\mathrm{d}\boldsymbol{r}''\rho_{\mathrm{s}}(\boldsymbol{r}')\rho_{\mathrm{s}}(\boldsymbol{r}'')\\ &\quad\times f_{\mathrm{bs}}(\boldsymbol{r}-\boldsymbol{r}')f_{\mathrm{bs}}(\boldsymbol{r}-\boldsymbol{r}'')f_{\mathrm{ss}}(\boldsymbol{r}'-\boldsymbol{r}'')+\ldots,\end{aligned} \tag{5}$$

where $f_{ij}(\boldsymbol{r}) = 1 - \exp[-\beta u_{ij}(\boldsymbol{r})]$ is the Mayer function in terms of the pair potential between particles i and j. The density $\rho_{\mathrm{s}}(\boldsymbol{r})$ in Eq. (5) can be expanded in terms of the bulk density ρ_{s} and the pair potential appearing in the Mayer function. Retaining only the first-order contribution of the density on the right-hand side of Eq. (5), and inserting the expression of the correlation function into Eq. (4) we yield the depletion potential between two big spheres in the AO approximation as follows:

$$\beta W^{(\mathrm{AO})}(\boldsymbol{r}) = -\rho_{\mathrm{s}}\int \mathrm{d}\boldsymbol{r}' f_{\mathrm{bs}}(\boldsymbol{r}')f_{\mathrm{bs}}(\boldsymbol{r}-\boldsymbol{r}'). \tag{6}$$

For hard-sphere binary mixtures, the above expression gives the simple geometric excluded volume between two big spheres induced by surrounding small spheres.[22,28,34]

The depletion potential of AO approximation can also be obtained readily by the ARM in MC simulations.[41] During the MC simulations, the AO approximation is realized by neglecting the direct pair potential between small spheres. However, the pair potential between small sphere and big sphere is still considered.

3. Results and discussion

In this work, a fixed size ratio of the big spheres and the small spheres, $\sigma_{\mathrm{bb}}/\sigma_{\mathrm{ss}} = 5$, is considered, and $\sigma_{\mathrm{ss}} = 1$ is chosen as a length unit which gives $\sigma_{\mathrm{bs}} = \sigma_{\mathrm{sb}} = 3$. The energy parameters $\epsilon_{ij} = \epsilon$ for all the cases are used. In our simulation, a canonical ensemble is used by giving the number n of small spheres, the volume of the simulated box, and the rescaled temperature $T^\star = k_{\mathrm{B}}T/\epsilon = 1.0$. Two big spheres with a given distance are put into a box with sizes $L_x \times L_y \times L_z$ as an external potential of small spheres in MC simulations. The average number density of small spheres is defined as $\bar{\rho}_{\mathrm{s}} = n/V$ with $V = L_xL_yL_z$. Periodic boundary conditions are applied along three directions. 2×10^4 MC steps are typically used to equilibrate the systems and other 5×10^5 MC steps to collect data.

First we examine the validity of our ARM by comparing our results with those from the Virial expansion under the AO approximation. The depletion potential of the AO approximation can be calculated by the ARM in MC simulations through neglecting the pair potential between small spheres. However, the pair potential between small spheres and big spheres is still considered. Though it is a non-physical procedure, it is helpful to test the ARM because its results can be compared with the reliable analytical results under the AO approximation. Before presenting the

results, we need to give a simple explanation to a basic concept that the bulk number density ρ_s is different from the average number density $\bar{\rho}_s$.[41] The bulk density, which appears in expression (6) of the Virial expansion, refers to the density where small spheres are so far from the external field formed by the presence of the two big spheres that their density configuration is not influenced. The average density is convenient to be used in our simulations when the simulated box is given. The effective volume to which small spheres can have access is the total volumes subtracted by the volume of the two big spheres and their excluded volume to small spheres, so the bulk density is larger than the average density. Sometimes one can modify the definition of the average density to reduce the discrepancy between the two densities, such as $\bar{\rho}_s = n/(V - 2V_b)$ with $V_b = 4\pi R_b^3/3$ being the volume of the big sphere,[41] but the discrepancy still exists due to the existence of the excluded volume. For a few average densities $\bar{\rho}_s = 0.19$, 0.381, 0.565, and 0.74, the corresponding bulk densities are estimated to be $\rho_s = 0.201$, 0.402, 0.592, and 0.772, respectively, in MC simulations.

The depletion potential $\beta W(h)$ and the total effective potential $\beta U_{tot}(h) = \beta W(h) + \beta u_{bb}(h)$ between two big spheres induced by a solution of non-interacting small spheres for $n = 6$, each as a functions of the surface separation $h = d - \sigma_{bb}$ of the two big spheres, are presented in Fig. 1. The solid lines are for the results obtained from Varial expansion of expression (6), and the symbols are for those obtained from the ARM. From small to big potential depths, the average densities are $\bar{\rho}_s = 0.19$, 0.381, 0.565, and 0.74, for MC simulations, and the corresponding bulk densities are $\rho_s = 0.201$, 0.402, 0.592, and 0.772, respectively, for the calculations in Eq. (6). In our simulations, the number of small spheres varies from about 700 to 2800 for various number densities. The results obtained by the two methods are in excellent agreement with each other, and they are independent of the densities. So far the ARM has been believed to be a reliable method of calculating the depletion potential under AO approximation in the non-rigid binary mixtures.

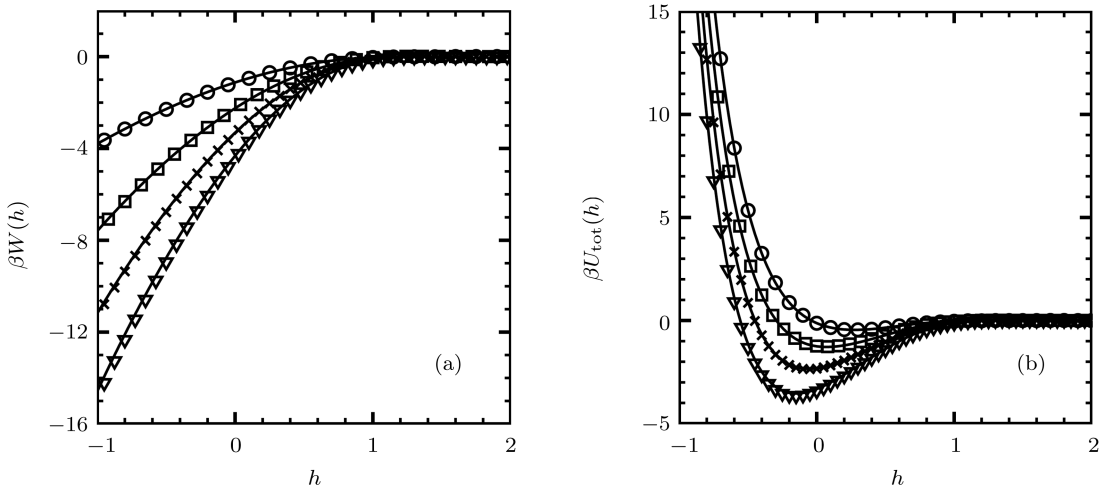


Fig. 1. (a) Depletion potentials and (b) total effective potentials for $n = 6$ between two big repulsive spheres with diameter $\sigma_{bb} = 5$ induced by a solution of non-interacting small spheres with diameter $\sigma_{ss} = 1$. The solid lines are for the results obtained from Eq. (6), and the symbols are for the results obtained from the ARM of MC simulation. From small to big potential depths, the average densities are $\bar{\rho}_s = 0.19$, 0.381, 0.565, and 0.74, for MC simulations, and the corresponding bulk densities are $\rho_s = 0.201$, 0.402, 0.592, and 0.772, for the calculations in Eq. (6).

In order to check the validity of ARM further, we implement ARM to compute the depletion potential in the repulsive-sphere binary mixtures where the particles interact with each other through the pair potential in expression (1), and compare the results with those obtained by MD simulation, Virial expansion approach, and AO approximation. The depletion potentials and the total effective potentials for $n = 6$ with various average densities, $\bar{\rho}_s = 0.19$, 0.381, and 0.74, are shown in Figs. 2 and 3, respectively. The solid lines denote the results calculated with the ARM by means of MC simulations, and the squares repre-

sent the MD simulations from Ref. [26]. From Fig. 2, we can see that the agreement is generally good for all densities. This suggests that our ARM, as well as MD simulation, can give accurate results within the range of their statistical errors which depend on the number of small spheres and the number of samples used to collect data. In Figs. 2 and 3, the results of the first-order (AO approximation) and second-order Virial expansions are indicated by dot lines and dash lines. The second-order Virial expansion can give reasonable accuracy (see Figs. (a) and (b)) when the density is not high, but the accuracy becomes obviously worse when the density increases. However, the AO approximation can be used only for such a low density, lower than 0.05.[26]

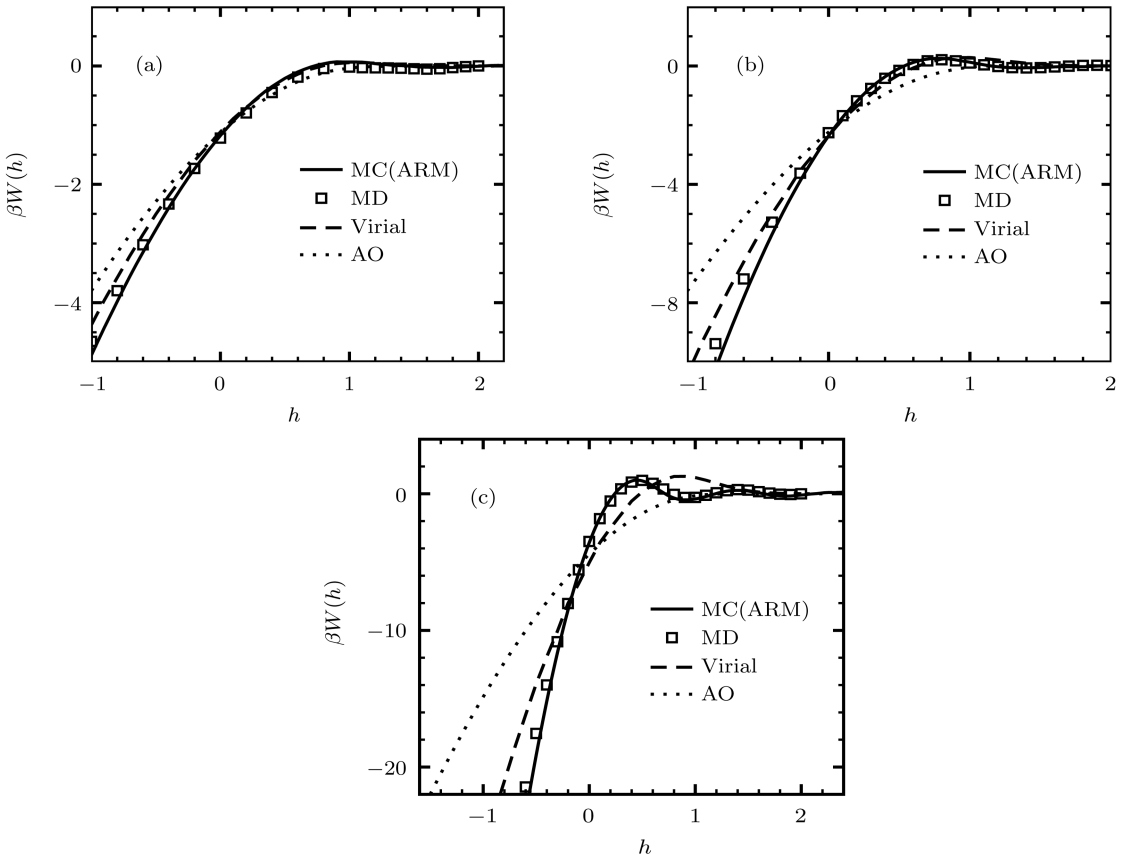
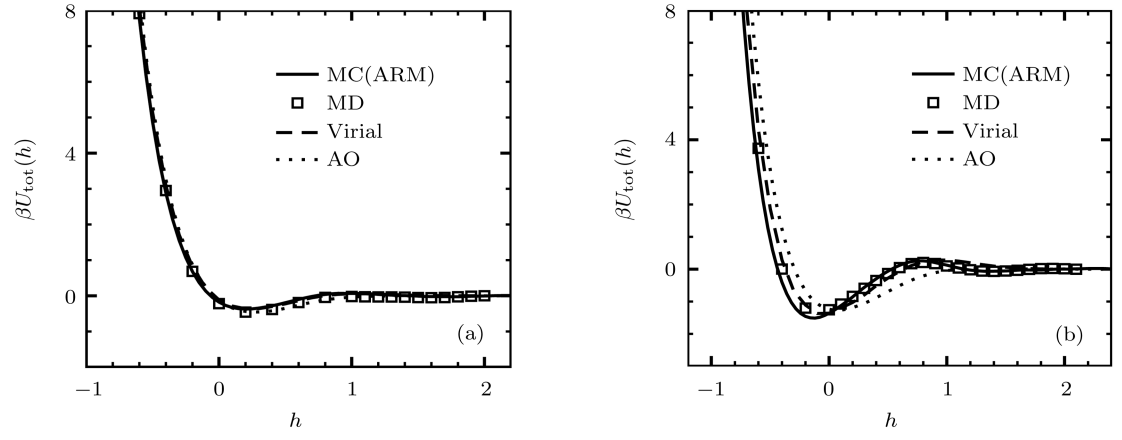


Fig. 2. Depletion potentials between two big repulsive spheres with $n = 6$ and diameter $\sigma_{\rm bb} = 5$ induced by a solution of interacting small spheres with diameter $\sigma_{\rm ss} = 1$ for three average densities $\bar{\rho}_{\rm s} = 0.19$ (a), 0.381 (b), 0.74 (c). The solid lines, symbols, dash lines, and dot lines denote the depletion potential calculated with ARM, MD, Virial expansion, and AO approximation, respectively.



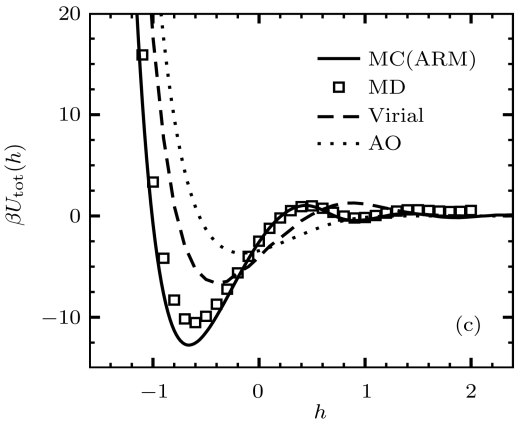


Fig. 3. Total effective potentials in the same situations as those in Fig. 2.

In Fig. 4, we present the total effective potentials between two big spheres for softness $n = 6$ and 12, and the hard-sphere case with the three densities of $\bar{\rho}_{\rm s} = 0.19$, 0.565, and 0.74. The potential well is an indicative characteristic of the total effective potential after including depletion contribution as it acts as a deterministic role in determining the phase behaviours of the mixture. At all densities, we can see that the potential wells become narrow monotonically as the softness parameter increases. For a low density of $\bar{\rho}_{\rm s} = 0.19$, the potential well of the hard-sphere case has the largest depth among the three cases, and that of $n = 6$ has the smallest depth (see Fig. 4(a)). This is consistent with the prediction of AO approximation (see the inset). However, at a higher density of $\bar{\rho}_{\rm s} = 0.565$, the situation is inverted. The depth of the potential well of $n = 6$ is the largest, and that for the hard-sphere case is the smallest (see Fig. 4(b)). This property can be explained by the competition between the pure depletion part and the direct potential part of the total effective potential. For the case of low density, the particles are separated far away from each other, and they cannot feel the long range part of their interactions strongly. The depletion interaction is mainly from the contribution of the hard-core interaction, and therefore, it is hardly influenced by the direct potential. However, after adding the direct potential, the depth of the potential well of $\beta U_{\rm tot}(h)$ is reduced significantly by the long-range repulsive part of $n = 6$, and is invariant for the case of hard sphere. When the density increases, the contribution of the long-range potential part of $n = 6$ to the depletion potential is increased dramatically as the non-additive distances between the small spheres and the big spheres, and separations among the small spheres, become larger. In other words, for the same density, the interacting range of the depletion potential of $n = 6$ in Fig. 4(c) has extended toward closer distance between the two big spheres with larger magnitude than that of hard sphere in Fig. 4(c). After adding the direct potential, $\beta U_{\rm tot}(h)$ of $n = 6$ still has much deeper potential well than that of hard-sphere case, and that of $n = 12$ is intermediate between the two formers. In addition, the minimal positions of the potential of $n = 6$ and $n = 12$ are shifted from $h > 0$ at a low density of $\bar{\rho}_{\rm s} = 0.19$ to $h < 0$ at a high density of $\bar{\rho}_{\rm s} = 0.74$. The shift of the minimal position is due to the dominance of the depletion potential over the direct potential, too.

As the depletion effect increases with density increasing, the depth becomes deeper, and the minimal position moves toward closer distance. To obtain a quantitative knowledge of the change in the depth of the potential well, we estimate the value of the depth for varying density, and present the results in Fig. 5. The symbols of squares, crosses, and triangles represent the results of $n = 6, n = 12$, and the hard-sphere cases, respectively. The thin solid lines are used to connect these points to guide eyes. For comparison, the results under the AO approximation are also given: $n = 6$ (solid lines), $n = 12$ (dash lines), and hard-sphere case (dot lines). For the hard-sphere case, the depth of the potential well is nearly a linear function of density while it is an exact linear function under the AO approximation. When the softness parameter decreases, the linear relation is broken. The depth of $n = 6$ changes from smaller to larger than that of hard-sphere case at $\bar{\rho}_{\rm s} \simeq 0.4$ (see the enlarged part in the inset of Fig. 5), and then at high densities, the depth for $n = 6$ increases much faster than the two others with density increasing. These differences are underestimated in the AO approximation.

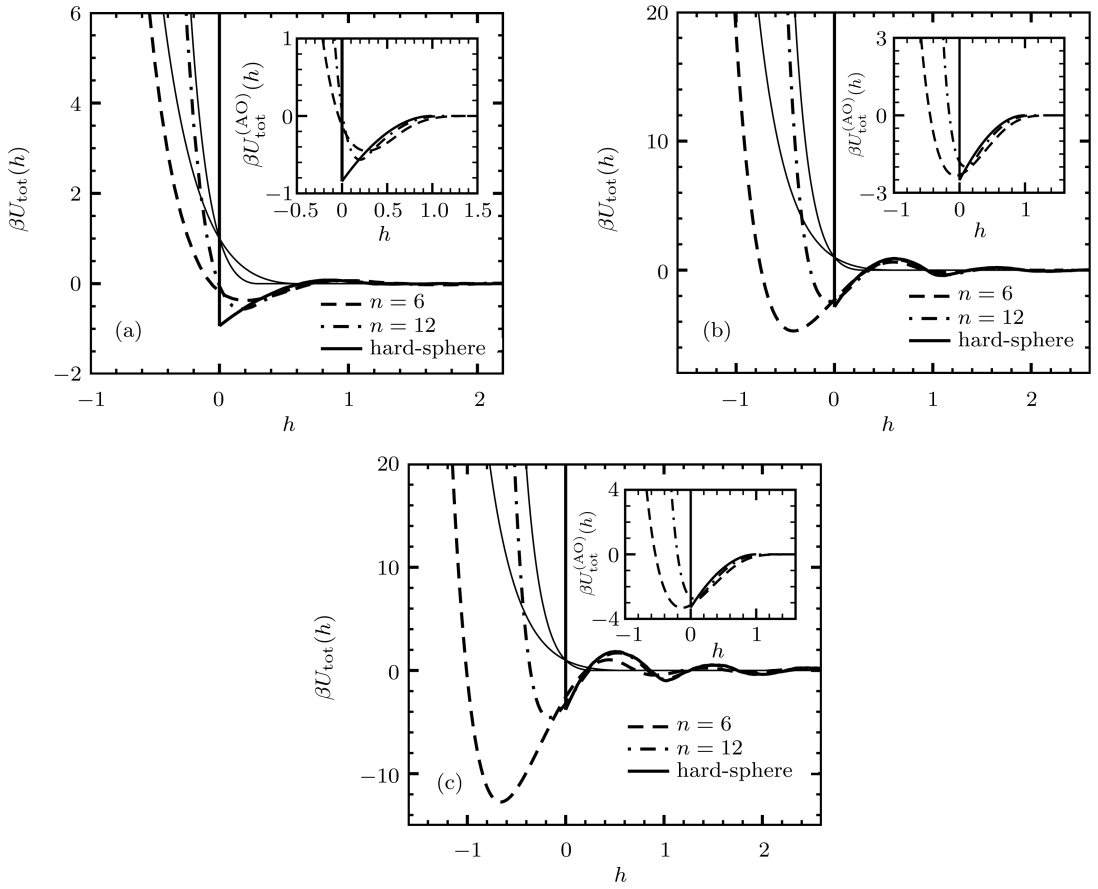


Fig. 4. Total effective potentials between two big spheres for softness $n = 6$ (dash lines), $n = 12$ (dot-dash lines), and hard-sphere case (solid lines). Three nubmer densities of small spheres are presented $\bar{\rho}_{\rm s} = 0.19$ (a), 0.565 (b), 0.74 (c). The thin solid lines denote the direct pair potentials of the two big spheres for $n = 6$ and $n = 12$ (steeper one). Insets show the corresponding total effective potentials under AO approximation.

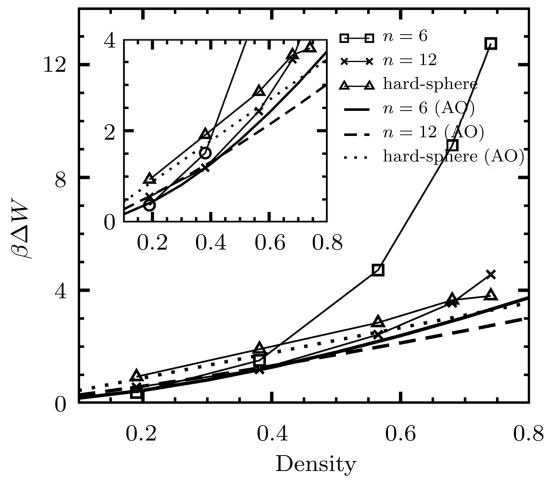


Fig. 5. Attractive potential-well depths of the total effective potential between two big spheres, each as a function of density, for $n = 6$ (squares), $n = 12$ (crosses), and hard-sphere case (triangles). The corresponding results of AO approximation are shown for $n = 6$ (solid lines), 12 (dash lines), and hard-sphere case (dot lines). The inset is the enlarged part for small values of the depth.

4. Conclusion

In this work, the depletion interactions between two big spheres, interacting with the repulsive part of the Lennard–Jones pair potential, are investigated with the acceptance ratio method by means of MC simulation. Three softness parameters of the direct pair potential $n = 6$, $n = 12$, and $n = \infty$ (HS case) are considered. Our results from the ARM are compared with those obtained by AO approximation, second-order Virial expansion theory, and MD simulations. The comparisons show that our ARM can give an accurate depletion potential of this non-rigid particle system as well as MD simulations. The total effective potential has a potential well being the same as that with including of the depletion potential induced by surrounding small spheres. The depth of the potential well depends on the softness of the direct potential among these particles (including big spheres and small spheres) and the density of small spheres. For hard-

sphere case, the relationship between potential depth and density is nearly linear. However, for $n = 6$, the potential depth increases much faster than that of the hard-sphere case at a high density region. It is suggested that the depletion effect in the binary mixtures with softer and longer-range direct pair potential is much larger. This is consistent with the conclusions in the charged colloidal mixtures.[46] When the effective one-component method is used to examine the phase behaviour of the binary non-rigid mixtures, the calculation of the depletion potential is crucial. The ARM is an efficient method of computing an accurate depletion potential of non-rigid colloidal mixtures.

References

[1] Gast A P and Russel W B 1998 *Phys. Today* **51** 24
[2] Likos C N 2001 *Phys. Rep.* **348** 267
[3] Russel W B, Saville D A and Schowalter W R 1992 *Colloidal Dispersions* (Cambridge: Cambridge University Press)
[4] Dijkstra M, van Roij R and Evans R 1998 *Phys. Rev. Lett.* **81** 2268
[5] Dijkstra M, van Roij R and Evans R 1999 *Phys. Rev. Lett.* **82** 117
[6] Dijkstra M, van Roij R and Evans R 1999 *Phys. Rev.* E **59** 5744
[7] Dijkstra M, Brader J M and Evans R 1999 *J. Phys.*: *Condens. Matter* **11** 10079
[8] de Hoog E H A, Kegel W K, van Blaaderen A and Lekkerkerker H N W 2001 *Phys. Rev.* E **64** 021407
[9] Bolhuis P G, Louis A A and Hansen J P 2002 *Phys. Rev. Lett.* **89** 128301
[10] Asakura S and Oosawa F 1954 *J. Chem. Phys.* **22** 1255
[11] Asakura S and Oosawa F 1958 *J. Polym. Sci.* **23** 183
[12] Vrij A 1976 *Pure Appl. Chem.* **48** 471
[13] Gast A P, Hall C K and Russel W B 1983 *J. Colloid Interface Sci.* **96** 251
[14] Gast A P, Hall C K and Russel W B 1986 *J. Colloid Interface Sci.* **109** 161
[15] Wood W W and Jacobson J D 1957 *J. Chem. Phys.* **27** 1207
[16] Alder B J and Wainwright T E 1957 *J. Chem. Phys.* **27** 1208
[17] Roth R, Evans R and Louis A A 2001 *Phys. Rev.* E **64** 051202
[18] Louis A A and Roth R 2001 *J. Phys.*: *Condens. Matter* **13** L777
[19] Dinsmore A D, Wong D T, Nelson P and Yodh A G 1998 *Phys. Rev. Lett.* **80** 409
[20] Dinsmore A D, Yodh A G and Pine D J 1996 *Nature* **383** 239
[21] Crocker J C, Matteo J A, Dinsmore A D and Yodh A G 1999 *Phys. Rev. Lett.* **82** 4352
[22] Roth R, Evans R and Dietrich S 2000 *Phys. Rev.* E **62** 5360
[23] Rosenfeld Y 1989 *Phys. Rev. Lett.* **63** 980
[24] Rosenfeld Y 1993 *J. Chem. Phys.* **98** 8126
[25] Almarza N G and Enciso E 1999 *Phys. Rev.* E **59** 4426
[26] Cinacchi G, Martinez-Raton Y, Mederos L, Navascues G, Tani A and Velasco E 2007 *J. Chem. Phys.* **127** 214501
[27] Biben T, Bladon P and Frenkel D 1996 *J. Phys.*: *Condens. Matter* **8** 10799
[28] Dickman R, Attard P and Simonian V 1997 *J. Chem. Phys.* **107** 205
[29] Li W H and Ma H R 2004 *Chin. Phys. Lett.* **21** 1175
[30] Percus S K and Yevick G J 1958 *Phys. Rev.* **110** 1
[31] Rogers F J and Young D A 1984 *Phys. Rev.* A **30** 999
[32] Ballone P, Pastore G, Galli G and Gazzillo D 1986 *Mol. Phys.* **59** 275
[33] Bolhuis P G, Louis A A, Hansen J P and Meijer E J 2000 *J. Chem. Phys.* **114** 4296
[34] Li W H and Ma H R 2002 *Phys. Rev.* E **66** 061407
[35] Ciccotti G and Ryckaert J P 1986 *Comput. Phys. Rep.* **4** 345
[36] Shinto H, Myiahara M and Higoshitani K 1999 *J. Colloid Interface Sci.* **209** 79
[37] Li W H and Ma H R 2005 *Eur. Phys. J.* E **12** 321
[38] Li W H and Ma H R 2003 *Eur. Phys. J.* **16** 225
[39] Li W H and Ma H R 2003 *J. Chem. Phys.* **119** 585
[40] Zhu D M, Li W H and Ma H R 2003 *J. Phys.*: *Condens. Matter* **15** 8281
[41] Li W H, Yang T and Ma H R 2008 *J. Chem. Phys.* **128** 044910
[42] Xiao C M, Guo J Y and Li C S 2006 *Europhys. Lett.* **73** 443
[43] Guo J Y, Huang L X and Xiao C M 2006 *Chin. Phys.* **15** 1638
[44] Germain P, Malherbe J G and Amokrane S 2004 *Phys. Rev.* E **70** 041409
[45] Germain P, Bouaskarne M, Malherbe J G, Regnaut C and Amokrane S 2004 *Prog. Colloid Polym. Sci.* **126** 102
[46] Walz J Y and Sharma A 1994 *J. Colloid Interface Sci.* **168** 485
[47] Amokrane S 1998 *J. Chem. Phys.* **108** 7459
[48] Malherbe J and Amokrane S 1999 *Mol. Phys.* **97** 677
[49] Clement-Cottuz J, Amokrane A and Regaut C 2000 *Phys. Rev.* E **61** 1692
[50] Méndez-Alcaraz J M and Klein R 2000 *Phys. Rev.* E **61** 4095
[51] Bennett C H 1976 *J. Comput. Phys.* **22** 245
[52] Allen M P and Tildesley D J 1994 *Computer Simulation of Liquids* (Oxford: Clarendon Press) Chap. 7