Geometrical confinements and depletion interactions

Changming Xiao,[1,*] Jiyuan Guo,[1,2] and Ping Hu[1]
[1]*Department of Physics, Hunan Normal University, 410081 China*
[2]*College of Mathematics and Physics, Jiangsu University of Science and Technology, 212003 China*
(Received 1 November 2005; revised manuscript received 23 March 2006; published 8 June 2006)

In the system with two large spheres confined between two parallel plates, there are depletion interactions between the two large spheres and between one large sphere and the closely placed plate. Obviously, the depletion interactions exerted on one large sphere will be strongly affected by the presence of the closely placed plate or the other large sphere. This prediction is confirmed by the numerical results obtained through the acceptance ratio method (ARM) or density integration method (DIM), i.e., they are strengthened when two large spheres are contacted. Furthermore, it is found that the influences on the depletion forces are also sensitive to the angle of the centers' connection line between the two large spheres and the confining walls. In addition, the numerical results show that the total depletion force exerted on one large sphere from both the other large sphere and the closely placed plate can be determined through ARM or DIM from the interactions between the two large spheres or between one large sphere and the corresponding closely placed plate.

DOI: 10.1103/PhysRevE.73.061403 PACS number(s): 82.70.Dd

It is well known that the depletion forces play very important roles in the colloidal suspensions [1–4]. Many interesting results on depletion interactions have been obtained through computer simulations [5–7], theory analyses [8–14], and experimental measurements [15–18]. These studies have significantly improved our understanding of the structure and the equilibrium behavior of the hard-sphere fluids. In fact, based on the geometrical consideration, the mechanism of depletion forces was firstly proposed by Asakura and Oosawa (AO) [1]. Recent investigations show that the depletion force comes from the unbalanced osmotic pressure between the two large spheres and the relation between the depletion forces and geometrical factors is very complex [2–4]. As we know, immersed in a fluid of small spheres, the depletion forces between two large spheres or between a large sphere and a closely placed plate are well studied [5–7]. On the other hand, the effect of the geometrical confinement on the depletion interaction is currently interesting [19–23]. In Refs. [22,23], the depletion interactions between two large spheres, which are placed in the middle plane of the two plates, in which the pair distance vector of the two large spheres is parallel to the wall, were studied, and the results show that the depletion interaction is strongly affected. It is found that the depletion interactions of a large sphere and a plate between two large spheres are also affected by another closely located large sphere. So it will be better if the study on the relation of the depletion force and geometrical factors is carried out in the context including the influences from both the plates and the closely placed large sphere. Fortunately, we can accomplish this aim through an interesting model discussed in this paper.

The model considered here consists of two large spheres A and B of radius R immersed in a fluid of small spheres of radius r confined between two parallel plates $P1$ and $P2$ [see Figs. 1(a) and 1(b)]. Obviously there are depletion interactions between the two large spheres A and B, or between the large sphere A (or B) and the plate $P1$ (or $P2$). When the two large spheres are closely placed, the depletion force between them will play a dominating role; however, the depletion force between the large sphere A (or B) and the closely placed plate $P1$ (or $P2$) will gradually surpass the initial depletion force when both A and B are moved to $P1$ and $P2$ respectively. One may think that this model is very simple, and take it for granted that the depletion force between A and B counteracts to that between A (or B) and $P1$ (or $P2$). Based on the followed two factors, we do not think that the case is as simple as that: Not only is the depletion force between the two large spheres affected by the presence of the two plates, but the depletion force between the large sphere A (or B) and the corresponding closely placed plate $P1$ (or $P2$) is affected due to the presence of the other large sphere B (or A). To demonstrate the influence on the depletion interactions from the geometrical factors, further investigations on this simple model are needed. Usually the depletion force is determined through the density integration method (DIM) or the acceptance ratio method (ARM). To make our conclusions credible, both DIM and ARM are used in our investigations.

As is known, the hard-sphere mixture can be characterized by the following pair potentials:

$$u(d) = \begin{cases} \infty & D < d_{ij} = (\sigma_i + \sigma_j)/2 \\ 0 & D > d_{ij} \end{cases}, \tag{1}$$

where D is the distance between two spheres of diameters σ_i and σ_j. The force exerted by a small sphere on a large sphere can then be written as $k_B T \delta(D - d_{ij})$. Consequently, the volume integral that gives the small-sphere force acting on each large sphere reduces to a surface integral [7,10],

$$\vec{f} = -k_B T \int_S \rho(S) \vec{n}\, dS, \tag{2}$$

where k_B is the Boltzmann's constant and T the temperature, $\vec{n}$ is the outward normal unit vector at the surface, $\rho(S)$ is the contact density of small spheres on the surface of the large-sphere, and dS is an infinitesimal area element on the sur-

*Corresponding author. E-mail address: cmxiao@hunnu.edu.cn

 ©2006 The American Physical Society

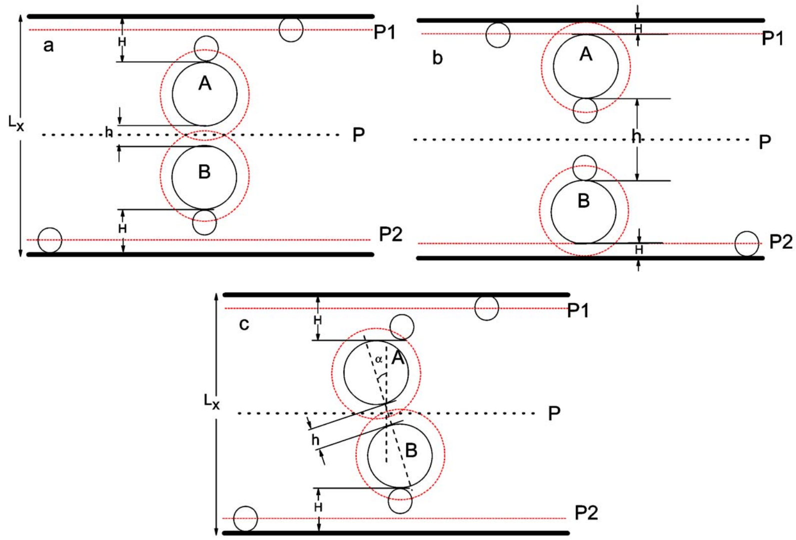

FIG. 1. (Color online) Schematic representation of the model considered in this paper. h and H measure the minimal distances between the two large spheres A and B, between A (or B) and $P1$ (or $P2$) respectively. The dashed zones are the forbidden regions of the small spheres. The dotted line P is the center plane of the two plates $P1$ and $P2$.

face. For the symmetrical arrangements considered here, only f_x is nonzero, and is given by

$$f_x = -2\pi k_B T(R+r)^2 \int \rho(R+r,\theta)\cos\theta \sin\theta d\theta, \tag{3}$$

where the integration part $I=\int\rho(R+r,\theta)\cos\theta\sin\theta d\theta$ is usually obtained according to the following practice by extrapolating data near contact: The space around the large sphere is divided into shells of thickness d, $2d,\ldots$, etc. By evaluating $I_i\langle\Sigma\cos\theta_i\rangle$, where the sum is over all particles in shell i and the brackets denote a thermal average, the force can be obtained by extrapolating I_i to $d=0$ using the spline method [6,7]. On the other hand, the depletion force can also be determined through the differential of the depletion potential, which can be conveniently obtained through the ARM introduced by Bennett [24], and details of the ARM and its implementation can be found in Refs. [7,25–27]. For ARM, two systems of the hard-sphere fluid in an external potential characterized by two large spheres or a large sphere and a closely placed plate should be considered. If the potential and the partition function of the two systems are V_0, Q_0 and V_1, Q_1 respectively, the free energy difference between these two systems is given by

$$\beta\Delta F = -\ln\frac{Q_1}{Q_0} = -\ln\frac{\langle f[\beta(V_1-V_0)+C]\rangle_0}{\langle f[-\beta(V_1-V_0)-C]\rangle_1} = -\ln\frac{N_{10}}{N_{01}}, \tag{4}$$

where C is a constant, $\beta=(k_BT)^{-1}$, N_{10} is the number of samples drawn out from N simulated samples, which is generated with the potential V_0 where V_1 is not infinite, N_{01} is the number of samples drawn out from N simulated samples, which is generated with potential V_1 where V_0 is not infinite.

To get the influences on the depletion interactions from the geometrical confinements through this special model, a simulated cell of size $L_x\times L_y\times L_z$ with two boundless hard plates placed at $x_1=0$ and $x_2=L_x$ is considered here [see Figs. 1(a) and 1(b)]. In the cell, the two large spheres A and B are symmetrically placed besides the center plane P of the two plates $P1$ and $P2$; furthermore, the connecting line of the centers of A and B is vertical to the plates $P1$ and $P2$. Obviously, the small hard spheres are randomly distributed in the cell to form a hard-sphere fluid. In this paper, the size ratio R/r is taken to be 5, and the number of small spheres N is determined by the given volume fraction η, defined as $\eta=NV_s/(V-2V_b)$, where $V=L_x\times L_y\times L_z$ is the total volume of the simulated cell, $V_s=4/3(\pi r^3)$ stands for the volume of a small sphere, and $V_b=4/3(\pi R^3)$ is the volume of a large sphere. The law of the depletion potential and the depletion force between the two large-spheres, or between the large-sphere A (or B) and the plate $P1$ (or $P2$), is usually described as a function of the distance h or H, where h is the distance between the surfaces of the two large spheres, H the distance between the large sphere A (or B) and $P1$ (or $P2$). Obviously the relation between h and H is given by

$$h = L_x - 4R - 2H. \tag{5}$$

In all the process of our simulations, the two large spheres A and B are moved in the contrary direction towards the plates $P1$ and $P2$ with the same magnitude value at the same time respectively. To avoid finite size effect, we take $L_y=20r$, $L_Z=20r$, and $L_x=32r$, and perform the simulations in the systems with volume fractions $\eta=0.116$, 0.229, and 0.341. When the parameters η, L_x, L_y, L_z, and the initial configuration of the spheres are given, the configurations of the small spheres are sampled according to the Metropolis algorithm [28] with the two large spheres fixed at a separation h. Each small sphere is orderly chosen involving a trial displacement and the new position is accepted as long as it does not result in an overlap with the large spheres, the other small spheres, and the plates. To take the two plates into account, the fixed boundary condition is used in the x direction, but the periodic boundary conditions in the y and z directions. Meanwhile, the magnitude of the maximum random displacement is adjusted so that the overall acceptance ratio is about 0.3 to ~0.5. In our simulations, 1.0×10^5 Monte Carlo steps (MCS) are used for equilibrium of the system and other 3.0×10^5 MCS to collect data. Through ARM, in the calcu-

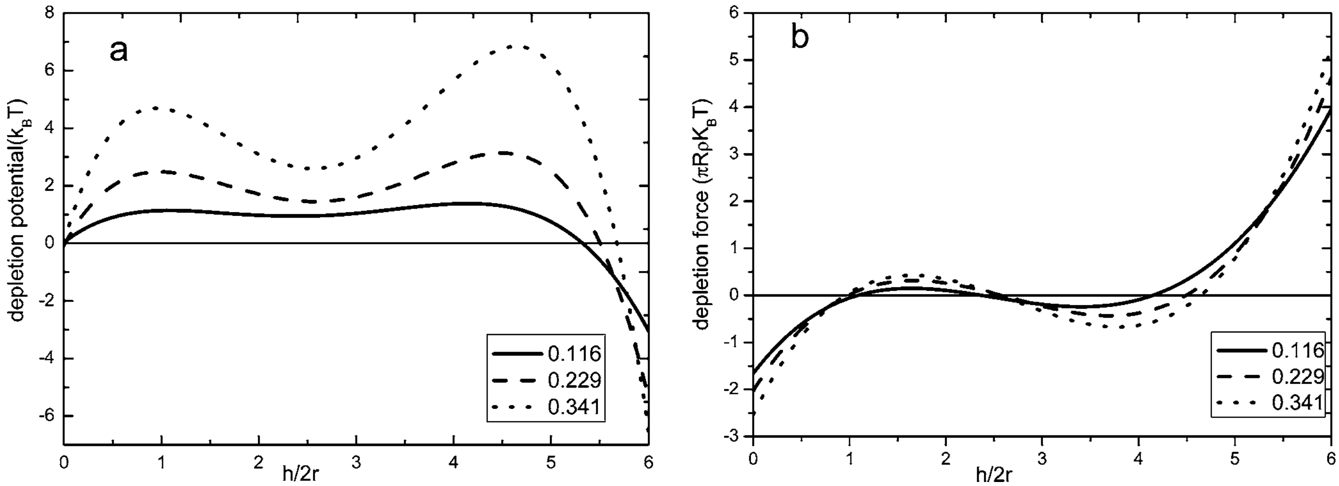

FIG. 2. (a) Depletion potentials between the two large spheres confined between the two plates in different volume fractions. (b) The depletion forces corresponding to the depletion potentials shown in (a). The depletion interactions are affected by the presence of the two plates.

lation of the depletion potential between the two large spheres A and B, or between the large sphere A (or B) and the plate $P1$ (or $P2$), the separation between them (h or H) is changed and the free energy differences between different distances are obtained by fixing the potential zero to a reference point. In the present study, including the depletion potentials between the two large spheres A and B, and between the large sphere A and plate $P1$ (or $P2$), the contact of A and B (or $h=0$ and $H=3$) is chosen to be the zero point of energy. Obviously, this choice will not affect the depletion force because it is the differential of the depletion potential.

In this way, all the depletion potentials and the corresponding depletion forces between the two large spheres A and B, and between A (or B) and $P1$ (or $P2$) in the systems mentioned above, are obtained and shown in Fig. 2 and Fig. 3 respectively. In order to make a comparison with our model to the unconfined systems that were well studied [5–7], the depletion interactions between two large spheres, or between a large sphere and the closely placed plate, in systems without geometrical confinements are demonstrated in Fig. 4 and Fig. 5 respectively. In Figs. 2–5, the depletion potentials F in units of k_BT and the corresponding depletion forces in units of $\pi R\rho k_BT$ are plotted as a function of h or H; here, ρ is the number density of small spheres, the length h or H is measured in units of $2r$. In these figures, the solid lines, the dashed lines, and the dotted lines describe the depletion potentials or depletion forces with volume fraction $\eta=0.116$, 0.229, and 0.341 respectively. We firstly consider the case of $\eta=0.229$ in Fig. 2(a), described by the dashed line, and get that the depletion potential between the two large spheres increases with the increasing h. After it gets to its extremum near $h=0.8$, a little decrease appears. Compared with Fig. 4(a), in the region of $0<h<3$, it behaves as the similar trend of the depletion potential between two large spheres without geometrical confinement. As h keeps increasing, the interaction between A and B is weakened; how-

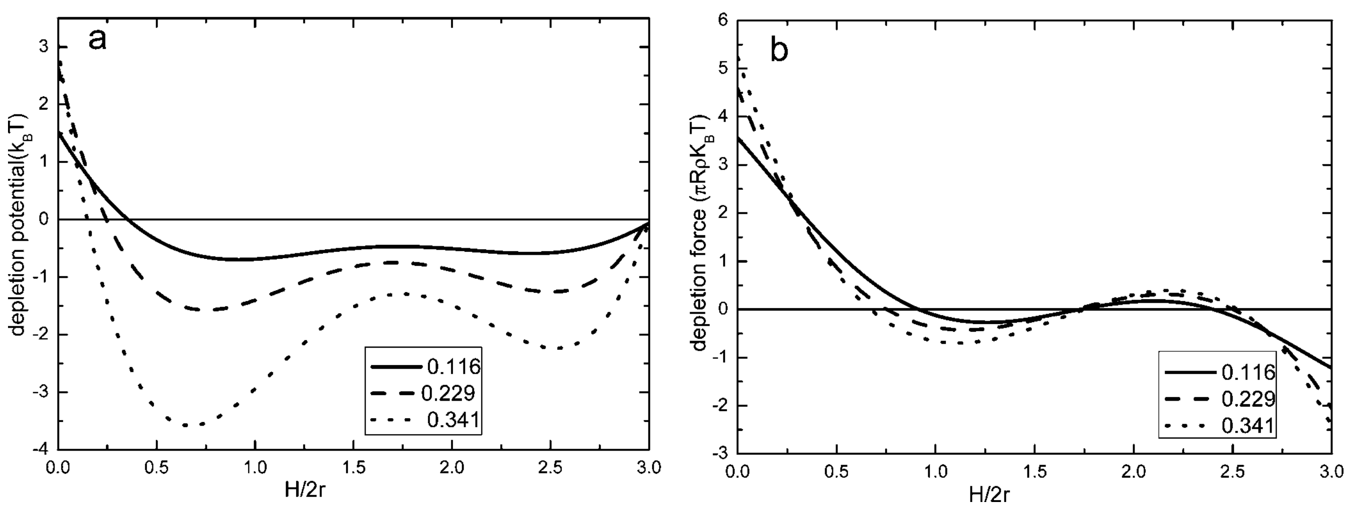

FIG. 3. (a) Depletion potentials between the large sphere A (or B) and the plate $P1$ (or $P2$) in different volume fractions. (b) The depletion forces corresponding to the depletion potentials shown in (a). The depletion interactions are affected by the presence of the large sphere B (or A).

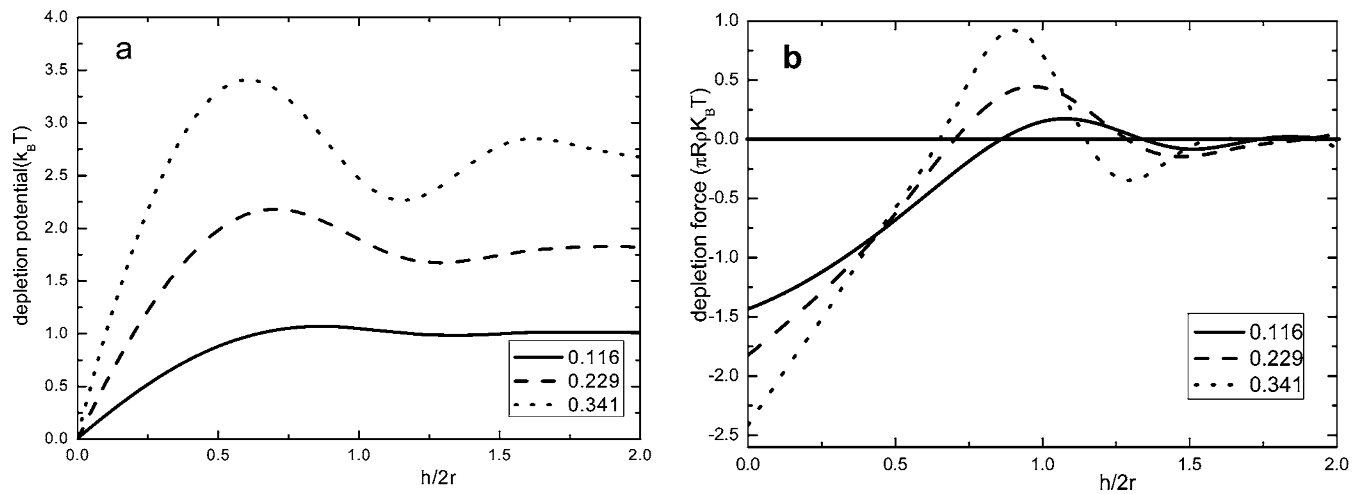

FIG. 4. (a) Depletion potentials and (b) the corresponding depletion forces between two large spheres in different volume fractions without other geometrical factors. The size ratio is $R/r=5$. h is the distance between the two large spheres, and $h=0$ is chosen to be the zero point of energy.

ever, at this time, the distance H is small enough for A (or B) and $P1$ (or $P2$) to form another interacting system, so the depletion potential increases rapidly and get to a larger extremum at $h \approx 5.0$; then it decreases rapidly, and finally gets to its minimum at $h=6.0$. It tells us clearly that, according to the value of h, the depletion interaction can be roughly divided into two parts: From 0 to 3, it mainly describes the depletion potential between A and B, and from 3 to 6, it is that between A (or B) and $P1$ (or $P2$). If we compare Fig. 2(a) and Fig. 4(a) in more detail, it is easy to find the influence on the depletion potential from the plates $P1$ and $P2$; for the dashed lines, the extremum value shown in Fig. 2(a) is about 2.5, which is larger than that shown in Fig. 4(a); furthermore, corresponding to the extremum mentioned above at $h \approx 0.8$, it is also larger than that shown in Fig. 4(a). So the position and the magnitude of the extremum of the depletion potential in our model are different from that in the unconfined systems. In other words, both the position and value of the extremum of the depletion potential are affected by the presence of the two plates. The same trend is also found in the systems of $\eta=0.341$, 0.116 respectively. The influence on the depletion interactions from the geometrical factors is further confirmed through the corresponding depletion forces shown in Fig. 2(b). Comparing Figs. 2(b) with 4(b), for the dashed line, it is normal that the absolute value of the depletion force of our model is smaller than that without geometrical confinements show in Fig. 4(b), because the depletion force between A and B counteracts that between A (or B) and $P1$ (or $P2$), but the abnormal behavior is found as $h \rightarrow 0$, i.e., the absolute value of the depletion force between the two large spheres is larger than that without geometrical confinements when $h \rightarrow 0$. The abnormal behavior as $h \rightarrow 0$ exposes the influence on the depletion interaction from the geometrical confinements. The same phenomenon is found in the solid and dotted lines when $h \rightarrow 0$. Comparing Fig. 3 with Fig. 5, we find that the depletion interactions between A (or

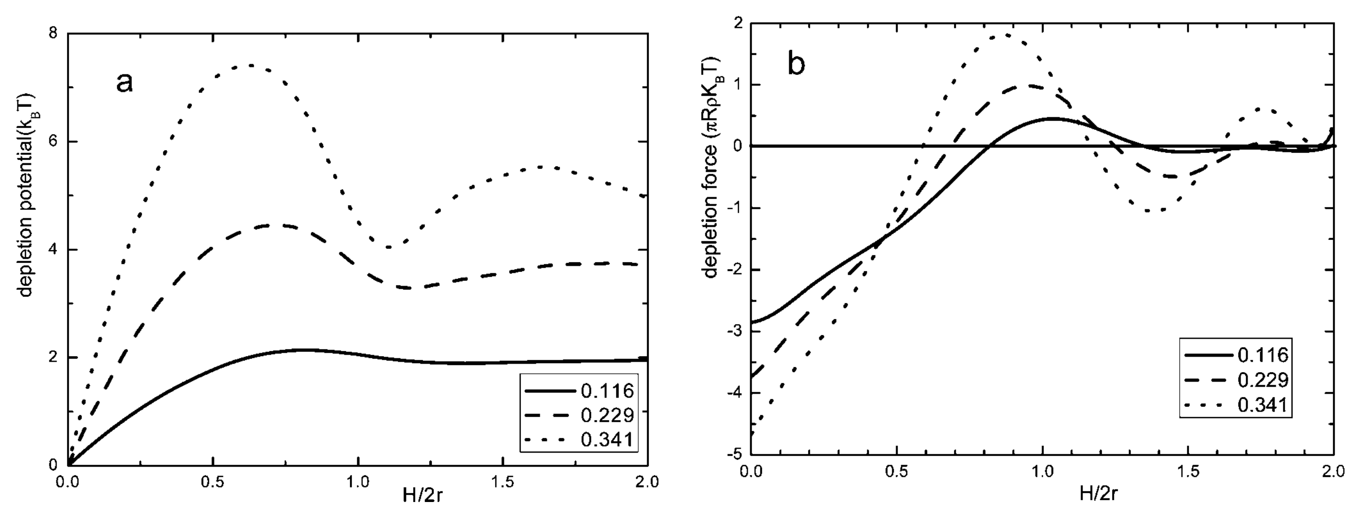

FIG. 5. (a) Depletion potentials and (b) the corresponding depletion forces between a large sphere and a closely placed plate in different volume fractions without other geometrical factors. The size ratio is $R/r=5$. H is the distance between the large sphere and the plate, and $H=0$ is chosen to be the zero point of energy.

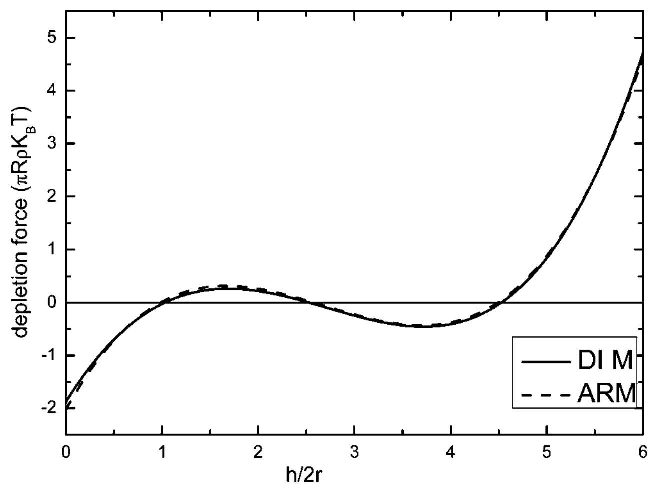

FIG. 6. Depletion force exerted on the large sphere A (or B) in the system of η=0.229. The solid and dashed lines are for the depletion forces determined through DIM and ARM respectively.

B) and $P1$ (or $P2$) are also affected by the presence of the other large sphere B (or A). As the zero potential is set at H=3; therefore, the depletion potentials between A (or B) and $P1$ (or $P2$) shown in Fig. 3(a) are negative and different from that shown in Fig. 5(a), which H=0 is set as the zero potential. Compared Fig. 3(b) with Fig. 5(b), it is easy to find that the absolute values of the depletion forces in the solid, dashed, and dotted lines are larger than that in Fig. 5(b) when $H \to 0$. Now we see that the depletion forces in our model are really affected by the presence of the two plates or the other large sphere; They are strengthened when two large spheres are very closely placed to each other h=0 or to the plate H=0, but are weakened if they are placed with a little distance. This point is very interesting and useful for us to get the stability of the confined colloidal system: instead of distributed randomly in the colloidal suspension, a large-sphere would rather stays closely to the plate or closely to the other large-spheres. Furthermore, though the depletion potentials shown in Fig. 3(a) are different to that shown in Fig. 2(a), the depletion forces between A and B shown in Fig. 2(b) are symmetrical to that between A (or B) and $P1$ (or $P2$) shown in Fig. 3(b). Comparing Fig. 2(b) with Fig. 3(b), it is reasonable for us to suppose that the depletion force determined through ARM is the total force acted on the large sphere. As we know, for DIM, the depletion force is determined through the surface integral of the corresponding large sphere; therefore, it reflects the composition interactions exerted on it. So it is reasonable to confirm this conjecture and the conclusion about the influences on depletion interaction from the geometrical confinements by comparing the depletion force on A (or B) determined through both ARM and DIM. The depletion forces determined through both DIM and ARM are shown in Fig. 6, from which the conjecture and the conclusions are confirmed.

Obviously, above discussions is about the case that the pair distance vector of the two large spheres is perpendicular to the plates. It is useful to study the effect of the angle between the distance vector and the wall α [see Fig. 1(c)]. For simplicity, we consider here the case with a small angle $\alpha = 5^0$, and the results about the depletion forces and geometrical confinements are shown in Fig. 7. It shows that the geometrical effect on the depletion interaction is still notable for the off-perpendicular pair-wall configurations.

As the small differences of the contact depletion forces between the confined and unconfined configurations cannot be easily read from the graph intercepts, the contact depletion forces in different configurations are given in Table I. From Table I, one can understand that the influences on the depletion forces are more sensitive to the angle between the centers' connection line of the two large spheres and the

TABLE I. The contact depletion forces in units of $\pi R\rho k_B T$ between two large spheres in different configurations.

		Confined cases	
Volume fraction	Unconfined cases	Perpendicular configuration	Tilted configuration
η=0.116	−1.43608	−1.66465	−1.68312
η=0.229	−1.82251	−2.03405	−2.10882
η=0.341	−2.41632	−2.53760	−2.60002

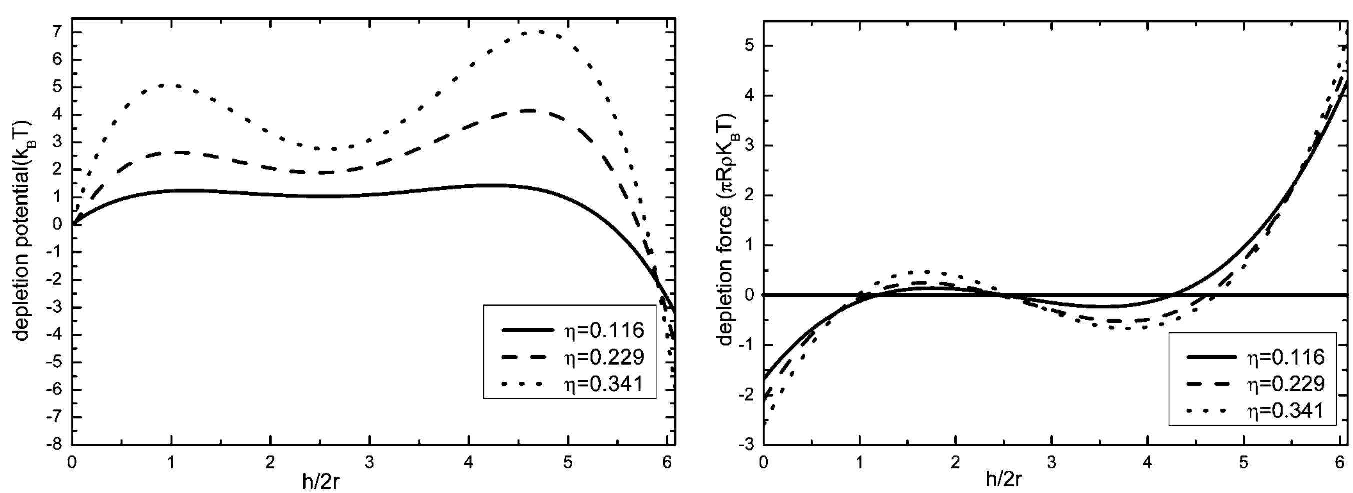

FIG. 7. (a) Depletion potentials and (b) the corresponding depletion forces between the two large spheres when α=5°.

confining walls than to that of the volume fraction. We believe that, in both the perpendicular and the tilted cases, the anomalous increase of the contact forces between the two large spheres comes from the confining walls, since the distribution of the small spheres around the large spheres is different from that without the two confining walls.

As a whole, we have studied the depletion potentials and depletion forces in the model through Monte Carlo simulations. From above discussion, we have shown that the total depletion force exerted on one large sphere from both the other large sphere and the closely placed plate can be determined through ARM or DIM from the interactions between the two large spheres or between one large sphere and the corresponding closely placed plate. Though the depletion forces between the two spheres and between a large sphere and the corresponding closely placed plate are counteracted, the total force is strengthened when the distance between the two large spheres $h \rightarrow 0$ or the distance between a large sphere and the corresponding plate $H \rightarrow 0$. It tells us clearly that the depletion interaction on a large sphere is strongly affected by the presence of geometrical confinements.

The authors acknowledge support by the National Natural Science Foundation of China under Grant No. 10375024 and the Science Foundation of the Hunan Educational Committee.

[1] S. Asakura and F. Oosawa, J. Chem. Phys. **22**, 1255 (1954).
[2] R. Roth, R. Evans, and S. Dietrich, Phys. Rev. E **62**, 5360 (2000).
[3] M. Kinoshita, J. Chem. Phys. **116**, 3493 (2002).
[4] P. Bryk, R. Roth, M. Schoen, and S. Dietrich, Europhys. Lett. **63**, 233 (2003).
[5] T. Biben, P. Bladon, and D. Frenkel, J. Phys.: Condens. Matter **8**, 10799 (1996).
[6] R. Dickman, P. Attard, and V. Simonian, J. Chem. Phys. **107**, 205 (1997).
[7] W. Li and H. R. Ma, Phys. Rev. E **66**, 061407 (2002).
[8] Y. Mao, M. E. Cates, and H. N. W. Lekkerkerker, Physica A **222**, 10 (1995).
[9] B. Götzelmann, R. Evans, and S. Dietrich, Phys. Rev. E **57**, 6785 (1998).
[10] P. Attard, J. Chem. Phys. **91**, 4790 (1989).
[11] R. Roth and S. Dietrich, Phys. Rev. E **62**, 6926 (2000).
[12] W. H. Li and H. R. Ma, Chin. Phys. Lett. **21**, 1175 (2004).
[13] Y. Rosenfeld, Phys. Rev. Lett. **72**, 3831 (1994).
[14] H. Grunberg and R. Klein, J. Chem. Phys. **110**, 5421 (1999).
[15] Y. N. Ohshima, H. Sakagami, K. Okumoto, A. Tokoyada, T. Igarashi, K. B. Shintaku, S. H. Toride, K. Kabuto, and I. Nishio, Phys. Rev. Lett. **78**, 3963 (1997).
[16] J. C. Crocker, J. A. Matteo, A. D. Dinsmore, and A. G. Yodh, Phys. Rev. Lett. **82**, 4352 (1999).
[17] D. Rudhardt, C. Bechinger, and P. Leiderer, Phys. Rev. Lett. **81**, 1330 (1998).
[18] C. Bechinger, D. Rudhardt, P. Leiderer, R. Roth, and S. Dietrich, Phys. Rev. Lett. **83**, 3960 (1999).
[19] Y. Han and D. G. Grier, Phys. Rev. Lett. **91**, 038302 (2003).
[20] E. Allahyarov, I. D'Amico, and H. Lowen, Phys. Rev. Lett. **81**, 1334 (1998).
[21] E. Allahyarov, I. D'Amico, and H. Lowen, Phys. Rev. E **60**, 3199 (1999).
[22] J. Y. Guo, C. S. Li, and C. M. Xiao, Chin. Phys. Lett. **22**, 1267 (2005).
[23] C. M. Xiao, J. Y. Guo, and C. S. Li, Europhys. Lett. **73**, 443 (2006).
[24] C. H. Bennett, J. Comput. Phys. **22**, 245 (1976).
[25] W. H. Li, S. Song, and H. R. Ma, J. Shanghai Jiao Tong University **E-6**, 126 (2001).
[26] W. H. Li and H. R. Ma, Eur. Phys. J. E **16**, 225 (2005).
[27] D. Frenkel and B. Smit, *Understanding Molecular Simulation: From Algorithms to Applications* (Academic Press, New York, 1996).
[28] N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. N. Teller, and E. Teller, J. Chem. Phys. **21**, 1087 (1953).