Coupling effects of depletion interactions in a three-sphere colloidal system*

Chen Ze-Shun(陈泽顺)[a)b)], Dai Gang(戴 刚)[a)], Gao Hai-Xia(高海峡)[a)b)], and Xiao Chang-Ming(肖长明)[a)†]

[a)] *Department of Physics, Hunan Normal University, Changsha* 410081, *China*

[b)] *Department of Electronic Engineering, Hunan University of Science and Engineering, Yongzhou* 425100, *China*

(Received 1 November 2012; revised manuscript received 18 December 2012)

In a three-sphere system, the middle sphere is acted upon by two opposite depletion forces from the other two spheres. It is found that, in this system, the two depletion forces are coupled with each other and result in a strengthened depletion force. So the difference of the depletion forces of the three-sphere system and its corresponding two two-sphere systems is introduced to describe the coupling effect of the depletion interactions. The numerical results obtained by Monte–Carlo simulations show that this coupling effect is affected by both the concentration of small spheres and the geometrical confinement. Meanwhile, it is also found that the mechanisms of the coupling effect and the effect on the depletion force from the geometry factor are the same.

Keywords: three-sphere system, coupling effect of depletion interactions

PACS: 82.70.Dd, 64.70.qd **DOI:** 10.1088/1674-1056/22/5/058202

1. Introduction

It is well known that the depletion interaction arises when two large spheres are immersed in a sea of small spheres. The mechanism of the depletion force was first described by Asakura and Oosawa (AO) with the concept of excluded volume.[1] According to the AO approximation, the depletion force is monotonously attractive. However, both the experimental and simulation results show that besides the attractive part, there is also a repulsive part in the depletion interaction. So the mechanism for the depletion interaction is not as simple as that described in the AO model. Due to the fact that the depletion force is very important to the colloidal system, many investigations have been carried out all these years, and knowledge about the depletion interactions is significantly improved.[2–14] In fact, it was found that the depletion force between two spheres will be strengthened if they are confined between two parallel plates.[3] Recently, more and more research works were carried out on the three-body depletion interactions. For example, the equilateral triplets, where three large spheres are dispersed in equilateral-triangular configurations, were studied and the results showed that the three-body interaction is attractive when the distance among them is small.[4–7] Obviously, the depletion interaction is not the additive one. We also found that when two spheres are perpendicularly placed in two parallel plates, the depletion forces between the two spheres and between the spheres and the plates can couple with each other, and finally result in a strengthened depletion force.[10,11] As a new finding, the coupling effect is very interesting and is significant to the colloidal system, since the dynamic behavior of the particles and the structure of the system will be affected by the strengthened depletion interactions. In this paper, we will study the depletion interactions of the three-sphere system schematically illustrated in Fig. 1(a). In this system, the large sphere B is placed between two spheres A and C. Apparently it suffers two opposite depletion forces from A and C. However, it will be found that in this three-sphere system, the depletion forces acted on B are larger than that of the two-sphere system described by Fig. 1(b), where sphere C is taken out of the three-sphere system. To describe this coupling effect of depletion interactions clearly, a parameter should be introduced. According to the definition of the three-body interaction, the difference of the depletion forces in the three systems demonstrated in Figs. 1(a)–1(c) can be used to describe the coupling effect. On the other hand, the sphere C can be also taken as a geometrical factor to the depletion force of spheres A and B, so there are some relationships between the coupling effect and the effect on the depletion force from geometrical confinements. That is why the corresponding confined three-sphere system and two-sphere systems described by Fig. 1(a′)–1(c′) will also be taken into consideration, and the relationships between the coupling effect and the effect of geometrical confinement can be studied through the depletion forces from the plates.

In this paper, the model and the theory are presented in Section 2, and the numerical results and a simple discussion are given in Section 3. Finally a summary of our study will be given in Section 4.

*Project supported by the Scientific Research Fund of Hunan Provincial Education Department, China (Grant Nos. 08B028 and 10A075) and the Natural Science Foundation of Hunan Province, China (Grant No. 08jj6043).

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

© 2013 Chinese Physical Society and IOP Publishing Ltd

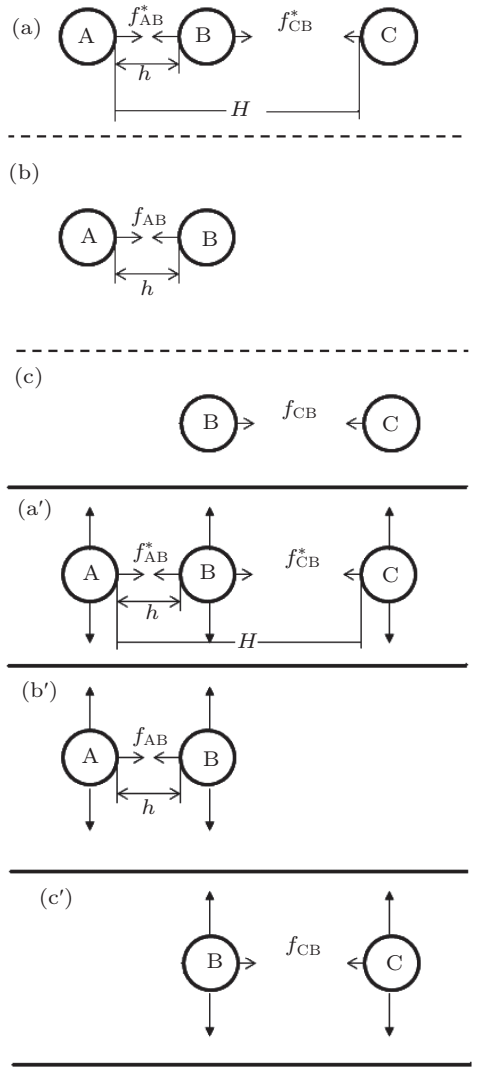


Fig. 1. (a) Schematic diagram of a three-sphere system consisting of spheres A, B, and C; panels (b) and (c) show the two-sphere systems where C and A are taken out from the three-sphere system, respectively; panels (a′)–(c′) show the confined systems corresponding to those in panels (a)–(c), respectively. The dashed lines in panels (a)–(c) denote the separation of the systems, the solid lines in panels (a′)–(c′) denote the confinement plates. Here h is the separation of spheres A and B, H is the separation of A and C, and the vertical arrows in panels (a′)–(c′) denote the depletion forces on the spheres from the plates.

2. Theory and model

It is well known that a hard-sphere mixture is characterized by the pair potential

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

where d is the distance between two spheres of diameters σ_i and σ_j, respectively. The force exerted on the big sphere of radius R by a small sphere of radius r can then be written as $k_B T \delta(d - d_{ij})$. Consequently, the depletion force is the total force acted on the large sphere from the small spheres, and can usually be determined through the acceptance ratio method (ARM).

In the ARM, if the potential and the partition function of two systems are V_0, Q_0 and V_1, Q_1, respectively, where V_0 and V_1 are the external potentials corresponding to the two large spheres located at different positions, the free energy difference between these two systems is given by[3,8,15]

$$\begin{aligned} \beta\Delta F &= -\ln\frac{Q_1}{Q_0} = -\ln\frac{\langle f[\beta(V_1 - V_0) + C]\rangle_0}{\langle f[-\beta(V_1 - V_0) - C]\rangle_1} \\ &= -\ln\frac{N_{10}}{N_{01}}, \end{aligned} \tag{2}$$

where N_{10} is the number of samples drawn out from N simulated samples generated with potential V_0, and V_1 is not infinite; N_{01} is the number of samples drawn out from N simulated samples generated with potential V_1, and V_0 is not infinite; $f(x) = [1 + \exp(x)]^{-1}$ is the Fermi function; and C is a constant which is usually set to 0 for a hard-sphere system. Since the change of potential is only related to the number of samples drawn out from the N simulated samples, therefore the depletion interaction can be obtained through the ARM conveniently. Furthermore, we note that if many depletion forces act on a sphere at the same time, instead of the component force, only the resultant force will be determined by the ARM.

In general, when two or many depletion forces act on a sphere at the same time, these forces will couple with each other. To expose the coupling effect among the depletion interactions in this three-sphere system, a parameter should be introduced. If the two component forces acted on large sphere B are f^*_{AB} and f^*_{CB}, and the resultant force is f, apparently,

$$f = f^*_{AB} - f^*_{CB}. \tag{3}$$

On the other hand, the resultant force f can be easily obtained by the ARM for the three-sphere system, the uncoupled component forces of spheres A and B, B and C (f_{AB}, f_{CB}) should be determined through the two-sphere systems described in Figs. 1(b) and 1(c), respectively, then the difference between the resultant and the two component forces is

$$\Delta f = f - f_{AB} - f_{CB}. \tag{4}$$

Obviously, if there is no coupling effect between f_{AB} and f_{CB}, $\Delta f = 0$, otherwise $\Delta f \neq 0$, so Δf can be used to describe the coupling effect. In addition, in the confined systems demonstrated by Figs. 1(a′)–1(c′), Δf can also be defined in the same way through Eq. (4). For the sake of simplicity, we suppose that in all the systems mentioned above, the positions of spheres A and C are fixed, only B moves from the contact position with A to the middle of A and C. Parameter h is the separation of A and B, and H is the separation of A and C.

3. Results and discussion

In this section, according to Eq. (4), the six systems described in Fig. 1 are studied respectively. In the simulations, the two or three large hard spheres are placed along the z direction of a cell box of sizes $L_x \times L_y \times L_z$, and the small spheres are randomly distributed around the macro spheres to

form a fluid; the size ratio of the macro sphere to the micro sphere R/r is 5, and the number of micro-ions N is determined by the given volume fraction η, which is defined as $\eta = NV_c/(V - 3V_m)$ and $\eta = NV_c/(V - 2V_m)$ for the three- and two-sphere systems, respectively, where $V = L_x \times L_y \times L_z$ is the total volume of the cell box, $V_c = 4\pi r^3/3$ is the volume of the micro sphere, and $V_m = 4\pi R^3/3$ denotes the volume of the macro sphere. For the unconfined systems, the period boundary condition is applied to all three directions of x, y, and z in the Monte–Carlo simulations. However, for the confined systems, the fixed boundary condition is applied to the direction (such as the x direction) in which the two parallel plates are placed; the other two directions y and z still have the period boundary conditions. Then the configurations of the micro spheres will be sampled according to the Metropolis algorithm with the two macro spheres A and C fixed while B is moved from the contact position with A to the middle of A and C. Each micro sphere is orderly chosen involving a trial displacement. Except for an overlap with the macro spheres and the other micro spheres, the new position of the micro sphere is randomly accepted. In our simulations, 1.0×10^5 Monte–Carlo steps (MCS) are used to reach the equilibrium state of the system, and another 3.0×10^5 MCS are used to collect data. The depletion potential is set as 0 while the two macro spheres A and B are at contact, i.e., $h = 0$. In this way, the depletion potentials then the corresponding depletion forces in both the confined and the unconfined two- and three-sphere systems are determined by the ARM respectively. For the sake of simplicity, only the cases of $\eta = 0.116$ and 0.229 are studied, and the corresponding depletion forces in the confined and the unconfined systems are shown in Figs. 2–5, respectively. In these figures, the depletion force F is plotted as a function of h, and F and h are in units of $\pi R\rho k_B T$ and $2r$, respectively, where ρ is the number density of the small spheres, k_B is the Boltzmann constant, and T is the absolute temperature. In Figs. 2–5, the short-dashed lines denote the depletion forces of the three-sphere system, the solid and long-dashed lines denote the two-sphere systems described by Figs. 1(b) and 1(c) or Figs. 1(b′) and 1(c′), respectively. From Figs. 2–5, it is evident that no matter whether the system is confined or unconfined, the volume fraction is large or small, (i) the depletion force between spheres B and C is almost 0; (ii) the depletion force of the three-sphere system is larger than that of the two-sphere system (consisting of A and B); and (iii) the depletion forces of the confined systems are larger than those of the corresponding unconfined systems. Furthermore, according to Eq. (4), Δf in both the confined and the unconfined systems are determined, the results for the systems of $\eta = 0.116$ and 0.229 are shown in Figs. 6 and 7, where the dashed and the solid lines are for the confined and the unconfined systems, respectively. From Figs. 6 and 7, it is evident that $\Delta f \neq 0$, so the two depletion forces acted on sphere B are coupled with each other. In addition, from Figs. 6 and 7 we also find that, for the same volume fraction, the difference of depletion force in the confined system is larger than that in the unconfined system. For both the confined and the unconfined systems, Δf is enlarged when the volume fraction of the system increases from 0.116 to 0.229.

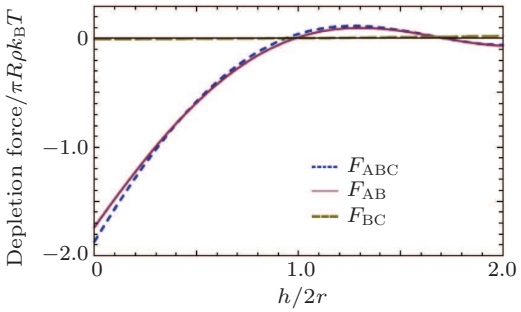


Fig. 2. (color online) Depletion forces of the unconfined three-sphere system (solid lines) and the two-sphere systems (dotted and dot-dashed lines). The volume fraction is $\eta = 0.116$.

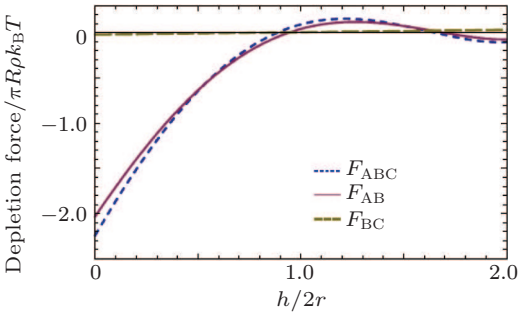


Fig. 3. (color online) Depletion forces of the confined three-sphere system (solid lines) and the two-sphere systems (dotted and dot-dashed lines). The volume fraction is $\eta = 0.116$.

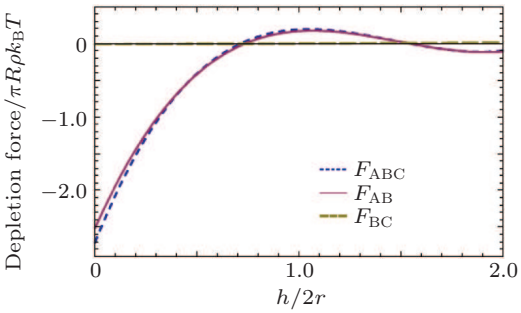


Fig. 4. (color online) Depletion forces of the unconfined three-sphere system (solid lines) and the two-sphere systems (dotted and dot-dashed lines). The volume fraction is $\eta = 0.229$.

We now discuss the results obtained above. From Fig. 1(a′), it is known that both the coupling effect and the effect on the depletion force from the geometry factor have been brought together in the confined three-sphere system. Though the mechanisms for the two effects are still unknown, we believe that there are some relations between them. Firstly, it is known that the depletion force between two spheres will be strengthened if they are confined by geometry factors, such as by two plates,[3] by a cylinder,[12] or by other spheres.[13]

Based on this fact, it is easy to understand that, in the three-sphere system discussed in this paper, if the large sphere C is taken as a geometry factor for the system consisting of two large spheres A and B, the depletion force of this system must be strengthened due to the presence of large sphere C. Secondly, the effect of geometrical confinement can be taken as a special case of the coupling effect: in the confined systems shown in Figs. 1(a′)–1(c′), we know that, besides the depletion interactions among spheres A, B, and C, there are also two opposite depletion forces acted on each of the three spheres from the two plates. Though the values of the two opposite depletion forces from the plates are equal and will cancel out each other, their influence on the depletion force of the two spheres in the parallel direction is obvious, in other words, the depletion forces from the spheres and from the plates can couple with each other. Meanwhile, in the three-sphere system, though the depletion force on the middle sphere from C is also very small, it couples with the depletion force between A and B, and results in a strengthened depletion interaction. So, the coupling effect of the three-sphere system is the coupling of two depletion forces in opposite directions, but the effect of geometry confinement is the coupling of the depletion interactions in the vertical and the parallel directions. Obviously, the nature of the coupling effect and the effect on the depletion interactions from a geometry factor is the same. That is why the depletion interaction can be enlarged by both the coupling effect and the geometrical effect of depletion, and will be further enlarged when the volume fraction of the system increases.

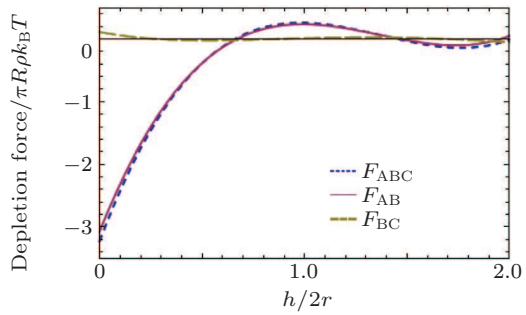


Fig. 5. (color online) Depletion forces of the confined three-sphere system (solid lines) and the two-sphere systems (dotted and dot-dashed lines). The volume fraction is $\eta = 0.229$.

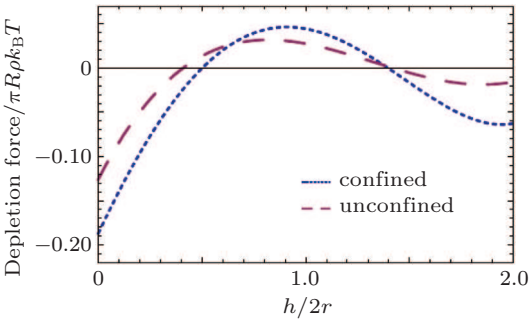


Fig. 6. (color online) Differences of the depletion forces of the unconfined and the confined three-sphere system and two-sphere system, where $\eta = 0.116$.

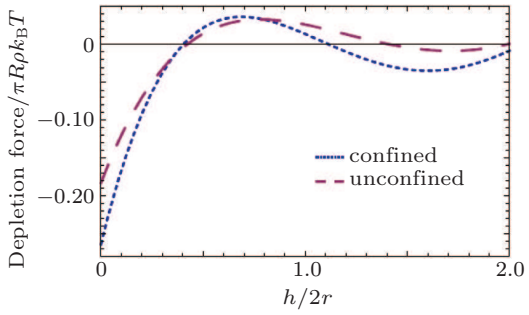


Fig. 7. (color online) Differences of the depletion forces of the unconfined and the confined three-sphere system and two-sphere system, where $\eta = 0.229$.

4. Conclusion

We have studied the depletion interactions in the confined and the unconfined three-sphere systems through Monte–Carlo simulations. The difference of the depletion forces of the three-sphere system and the two corresponding two-sphere systems has been introduced to describe the coupling effect. It is found that the depletion interactions may couple with each other and result in a strengthened total depletion force; the coupling effect of the depletion force will increase when the volume fraction of the system is increased. In addition, it is also found that the nature of the effect on the depletion interactions from a geometry factor and the coupling effect is the same, or the effect of geometry confinement can be taken as a special case of the coupling effect, and both of them are affected by the concentration of the small spheres and the geometrical confinements.

References

[1] Asakura S and Oosawa F J 1954 *J. Chem. Phys.* **22** 1255
[2] Götzelmann B, Evans R and Dietrich S 1998 *Phys. Rev. E* **57** 6785
[3] Xiao C M and Guo J Y 2006 *Europhys. Lett.* **73** 443
[4] Wu J Z, Bratko D, Blanch H W and Paausnitz J M 2000 *J. Chem. Phys.* **113** 3360
[5] Goulding D and Melchionna S 2001 *Phys. Rev. E* **64** 011403
[6] Brader J M, Dijkstra M and Evans R 2001 *Phys. Rev. E* **63** 041405
[7] Zhu D M, Li W H and Ma H R 2003 *J. Phys.: Condens. Matter* **15** 8281
[8] Li W H and Ma H R 2002 *Phys. Rev. E* **66** 61407
[9] Triplett D A and Fichthorn K A 2010 *J. Chem. Phys.* **133** 144910
[10] Xiao C M, Guo J Y and Hu P 2006 *Phys. Rev. E* **73** 061403
[11] Wang L X, Gao H X and Xiao C M 2009 *Acta Phys. Sin.* **58** 5865 (in Chinese)
[12] Gao H X and Xiao C M 2007 *Phys. Lett. A* **362** 234
[13] Xiao C M, Guo J Y and Hu P 2006 *Chin. Phys. Lett.* **23** 1038
[14] Gu L Y, Xu S H and Sun Z W 2011 *Acta Phys. Sin.* **60** 126402 (in Chinese)
[15] Bennett C H 1976 *J. Comput. Phys.* **22** 245