Effect of Geometrical Confinement on Depletion Interactions in Colloidal Suspensions *

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(Received 9 November 2004)

The depletion effect between two big hard spheres in a sea of small spheres under a geometrical confinement is studied by Monte Carlo simulations. The numerical results show that both the depletion potential and depletion force are sensitive to the geometrical confinements.

PACS: 82. 70. Dd

It is well known that depletion effects arise at the positions where two big hard spheres are immersed in a sea of small spheres. The mechanism of depletion force was first described by Asakura and Oosawa,[1] and now it has attracted great attention because of the practical importance for understanding the properties of sphere mixtures and the significance in fundamental statistical mechanics. In recent years, many studies on depletion effects have been obtained by computer simulations,[2−4] approximate theories,[5,6] density functional theory[7−9] and experiments.[10,11] These studies have significantly improved our understanding of the structure and equilibrium behaviour of hard sphere fluids, especially in the case without geometrical confinements. However, there is recent experimental evidence that effective interaction between charged-like colloidal particles is sensitively affected by a geometrical confinement between two parallel charged plates.[12−16] This reminds us that the depletion interactions in hard sphere suspensions may also be affected by the geometry confinements. In this Letter, we analyse the effects of the geometrical confinements on depletion interactions.

It is known that the main actors of depletion effects are the depletion potential and depletion force. Among small spheres of radius r, the depletion force on a large sphere of radius R is usually determined by the density integral method,[4,7] i.e.

$$\boldsymbol{f} = -k_B T \int_S \rho \boldsymbol{n} dA, \tag{1}$$

where k_B is Boltzmann's constant, the integration is taken over the surface S of a sphere of radius $R + r$ spanned from the centre of the large sphere, $\boldsymbol{n}$ is the unit normal vector starting from the large sphere. However, the depletion force can also be calculated by the differential of depletion potential which can be conveniently obtained by the acceptance ratio method (ARM) introduced by Bennett,[17] details of the ARM and its implementation can be found in Ref. [4]. For the ARM, different values of the distance between the two large spheres are taken as different systems, if the potential and the partition function of two systems are V_0, Q_0 and V_1, Q_1 respectively, the free energy difference between the two systems is given by[4]

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

where $\beta = k_B T$; T is temperature, N_{10} is the number of samples drawn out from N simulated samples, which are generated from the potential V_0, where V_1 is not infinite; N_{01} is the number of samples drawn out from N simulated samples, which are generated from the potential V_1 where V_0 is not infinite.

The model considered here is a rectangular box of size $L_x \times L_y \times L_z$, with two boundless hard walls represented by $x_1 = -\frac{1}{2}L_x$ and $x_2 = \frac{1}{2}L_x$. In the box, two big hard spheres are placed in the middle of the box along the z direction and small hard spheres are randomly distributed in the box to form a hard sphere fluids, the size ratio R/r is take to be 5, 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, $V_S = \frac{4}{3}\pi r^3$ is the volume of a small sphere, $V_b = \frac{4}{3}\pi R^3$ is the volume of a large sphere. The effects of geometrical confinements can be investigated by changing the width of the box by moving the two boundless hard walls. The width of the boxes studied are $L_x = 20r$, $16r$, and $13r$ respectively. We perform the simulation with volume fractions $\eta = 0.116$, 0.229 and 0.341 respectively, for each η, we set $L_Z = 36r$, $L_y = 18r$. When the parameters η, L_x, L_y, and L_z and the initial configuration of the spheres are given, the configurations of the small

* Supported by the National Natural Science Foundation of China under Grant No 10375024, and the Science Foundation of Hunan Educational Committee.

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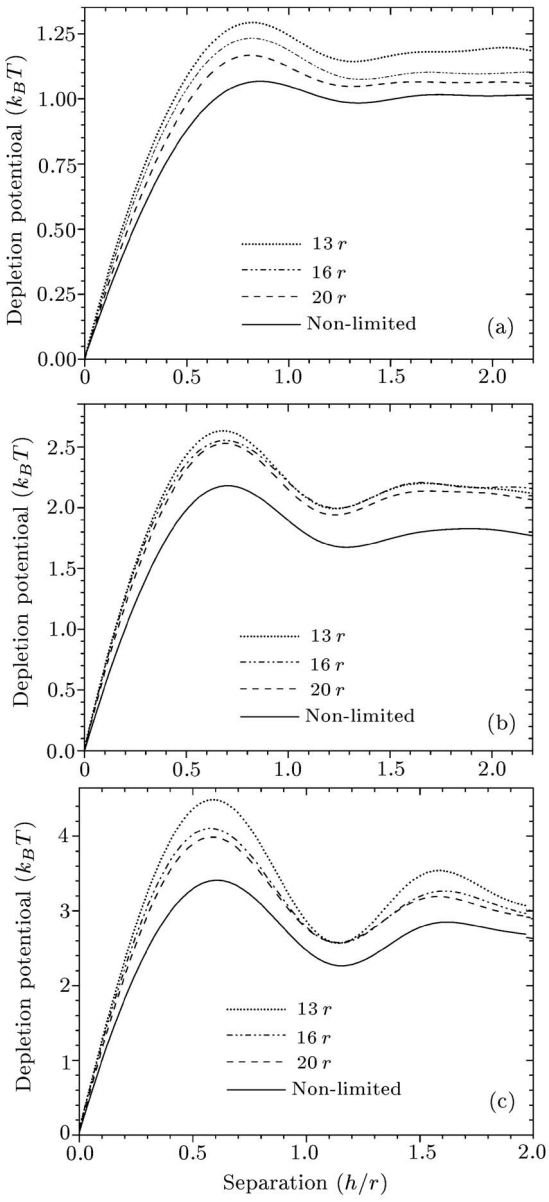


Fig. 1. Depletion potentials between the two large-spheres with different geometrical confinements in different volume fractions (a) $\eta = 0.116$, (b) $\eta = 0.229$, (c) $\eta = 0.341$.

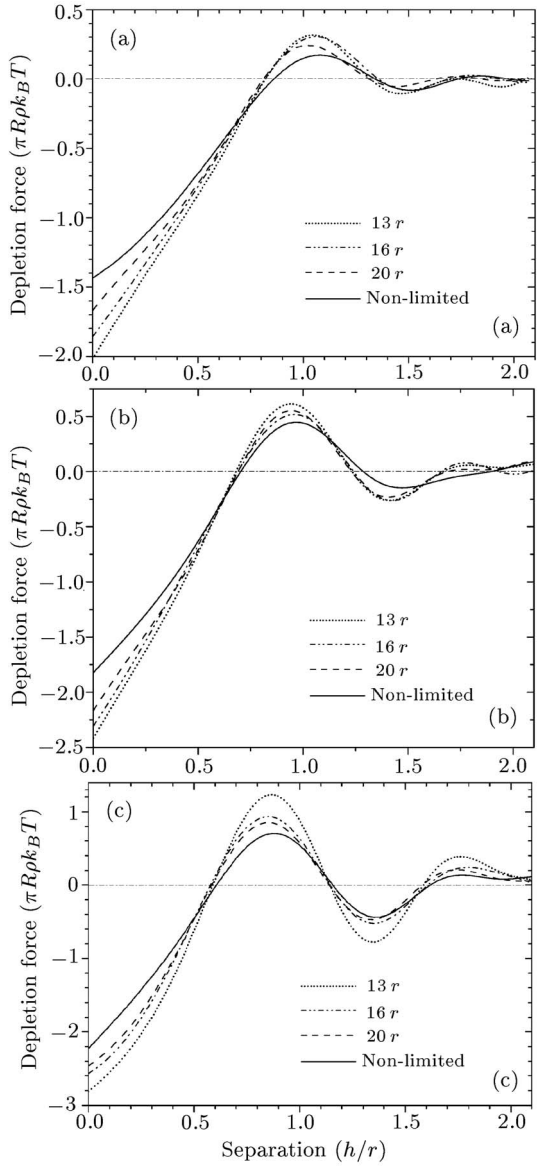


Fig. 2. Depletion forces between the two large-spheres with different geometrical confinements in different volume fractions (a) $\eta = 0.116$, (b) $\eta = 0.229$, (c) $\eta = 0.341$.

spheres are sampled according to the Metropolis algorithm[18] with the two big spheres fixed at 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 big hard spheres, the other small spheres and the walls. To take the geometrical confinements into account, the mirror boundary condition is used in the x direction, but the periodic boundary conditions in the y and z directions. These denote that, except for the two parallel plates placed in the x direction, there are no plates placed in the y and z directions. Therefore, when an attempted moving bring one small sphere out of the box in the x direction, it is brought back to the box by the mirror reflection on the surface of $x_1 = -\frac{1}{2}L_x$ and $x_2 = \frac{1}{2}L_x$. Obviously, when the periodic boundary condition is used in all the three directions, it is just the case without geometrical confinements. Meanwhile, the magnitude of the maximum random displacement is adjusted so that the overall acceptance ratio is about 0.3–0.5. In our simulation, 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. In the calculation of depletion potential between the two big spheres, the separation between them is changed and the free energy difference between different distances is obtained by fixing the potential zero to a reference point. In the present study, the contact of the two big spheres is chosen to be the zero

point of energy, this choice will not affect the depletion force because it is the differentiation of the depletion potential. To demonstrate the effects of geometrical confinement on depletion interactions clearly, all the depletion potentials corresponding to the cases mentioned above are shown in Fig. 1. The depletion potential F in units of k_BT is plotted as a function of h, the length is measured in units of r. Corresponding to the depletion potentials shown in Fig. 1, the depletion forces are plotted in Fig. 2: the unit of depletion force is $\pi R\rho k_BT$, where ρ is the number density of small spheres. In Figs. 1 and 2, the solid lines describe the depletion potentials or depletion forces without geometrical confinements, whereas the other lines are for the geometrical confinements case: the dashed lines for the width between the two plates $L_x = 20r$, the dot-dot-dashed lines for $L_x = 16r$, the dotted lines for $L_x = 13r$. From Figs. 1 and 2, it is evident that, no matter whether the volume fraction is high or low, both the depletion potentials and depletion forces are affected by geometrical confinements from the two parallel plates or by L_x. Furthermore, we also note that, for the same volume fraction, the nearer the two plates are placed, the larger the depletion potential and depletion force will be. Obviously, the nearer the two plates are placed, the larger the geometrical confinement effects will be.

In summary, we have studied the depletion potential and depletion force in the hard sphere mixtures with or without geometrical confinements through Monte Carlo simulation. From the above discussion, we have shown that the depletion interacts are affected by the geometrical confinements, the nearer the two plates are placed, the larger the effects from the geometrical confinements will be.

References

[1] Asakura S and Oosawa F 1954 *J. Chem. Phys.* **22** 1255
[2] Biben T, Bladon P and Frenkel D 1996 *J. Phys: Condens. Matter* **8** 10799
[3] Dickman R, Attard P and Simonian V 1997 *J. Chem. Phys.* **107** 205
[4] Li W H and Ma H R 2002 *Phys. Rev.* E **66** 61407
[5] Mao Y, Cates M E and Lekkerkerker H N W 1995 *Physica* A **222** 10
[6] Götzelmann B, Evans R and Dietrich S 1998 *Phys. Rev.* E **57** 6785
[7] Attard P 1989 *J. Chem. Phys.* **91** 4790
[8] Roth R and Dietrich S 2000 *Phys. Rev.* E **62** 6926
[9] Li W H, Ma H R 2004 *Chin. Phys. Lett.* **21** 1175
[10] Ohshima Y N, Sakagami H, Okumoto K, Tokoyada A, Igarashi T, Shintaku K B, Toride S, H, Kabuto K and Nishio I 1997 *Phys. Rev. Lett.* **78** 3961
[11] Crocker J C, Matteo J A, Dinsmore A D and Yodh A G 1999 *Phys. Rev. Lett.* **82** 4352
[12] Crocker J C and Grier D G 1994 *Phys. Rev. Lett.* **73** 352
[13] Chen Y 2003 *Chin. Phys. Lett.* **20** 1626
[14] Wu J Z, Bratko D, Blanch H W and Prausnitz J M 1999 *J. Chem. Phys.* **111** 7084
[15] Lin Y Z ,Li Y G and Lu J F 2002 *J. Chem. Phys.* **117** 407
[16] Crocker J C and Grier D G 1996 *Phys. Rev. Lett.* **77** 1898
[17] Bennett C H 1976 *J. Comput. Phys.* **22** 245
[18] Metropolis N, Rosenbluth A W, Rosenbluth M N, Teller A N and Teller E 1953 *J. Chem. Phys.* **21** 1087