Vol 15 No 7, July 2006
1009-1963/2006/15(07)/1638-07

Chinese Physics

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Effects of unsymmetrical geometric confinements on depletion interactions in colloidal suspensions*

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(Received 22 July 2005; revised manuscript received 3 April 2006)

The depletion interactions between two large-spheres immersed in a fluid of small spheres under unsymmetrical geometrical confinement are studied through the acceptance ratio method. The numerical results show that no matter whether the volume fraction is large or small, both the depletion potential and depletion force are affected by the presence of the two plates; the closer the two large spheres are to the plate, the larger the effects of the unsymmetrical confinements.

Keywords: depletion interactions, colloidal, acceptance ratio method
PACC: 8270D, 7115Q

1. Introduction

Depletion interactions arise when two large-spheres are immersed in a fluid of small spheres. The fact that the depletion attraction between the two large-spheres comes from the unbalanced osmotic pressure exerted by small spheres was first described by Asakura and Oosawa.[1] In the last few years, focusing on the force acting on the colloidal spheres as well as on the phase separation of the colloidal suspensions, hard sphere mixtures were the subject of experimental and theoretical studies.[2−4] Many interesting results on depletion interactions have been obtained through computer simulations,[5−7] theory analyses,[8−15] and experimental measurements.[16−19] These studies have significantly improved our understanding of the structure and the equilibrium behaviour of the hard sphere fluids. Recent research work shows that the depletion interactions are affected by the presence of geometric confinements. For example, we can confine the colloidal system between two parallel plates. Generally speaking, according to the influence of the two plates on the depletion interaction, a geometric confinement can be of the symmetrical or unsymmetrical type: if the distances between the two large-spheres and the two plates are equal, the influences of the two plates on the depletion interaction are the same, then the influence is the symmetrical confinement; otherwise, the confinement will be unsymmetrical, i.e., the influences of the two plates on the depletion interaction are different (see Fig.1).

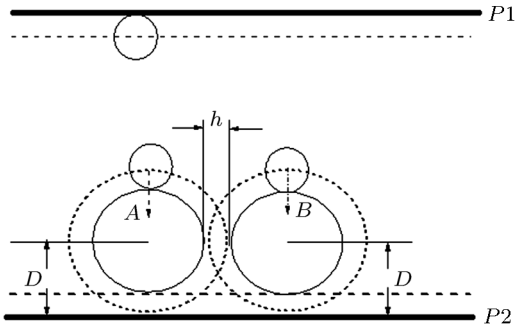


Fig.1. Schematic diagram of the model under unsymmetrical geometric confinement. $h \geq 0$ is the minimal gap between the two fixed hard large-spheres, and D is the distance from the large-spheres' centre to the plate $P2$. The zones between the dashed line and plate or large-sphere are the forbidden regions for the small spheres.

Investigations on the cases under the symmetrical confinement show that the depletion interactions are sensitive to the confinement.[20] However, we note that the symmetrical confinement is a very special one. Usually a system is found to be confined under the unsymmetrical confinement. Therefore further investigations on the effect of the unsymmetrical confinements are needed. In addition, we note that, if a system is confined under an unsymmetrical confinement,

*Project supported by the National Natural Science Foundation of China (Grant No 10375024) and the Science Foundation of Hunan Educational Committee, China

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the density distribution of the small-spheres near the two large-spheres is different from that if the system is confined under the symmetrical confinement: for the symmetrical confinement, the symmetric distribution of small-spheres in the direction along the line of the two large-spheres' centres is kept, but for the unsymmetrical confinement, this symmetry is broken down. Obviously the depletion force between the two large-spheres under unsymmetrical confinements cannot be determined through the density integration method. So some new questions arise in the calculations of depletion forces in the cases of unsymmetrical confinements. Fortunately, we will see that, for unsymmetrical confinements, the acceptance ratio method (ARM) is still valid and can be used in calculations. In this paper, we use the ARM to study the depletion interactions between the two large-spheres in the fluid of small spheres under unsymmetrical geometric confinements.

This paper is organized as follows. A brief review of the theory of ARM is given in Section 2, and the numerical results about the unsymmetrical confinements will be given in Section 3, then in Section 4, we will summarize our conclusions.

2. Simulation method

We know that the depletion force is usually determined through the differentiation of the depletion potential, which can be conveniently obtained through the ARM introduced by Bennett,[21] and details of the ARM and its implementation can be found in Refs.[7,22–25]. In the ARM, two systems of the hard-sphere fluid in an external potential characterized by two large spheres located in the simulated cell 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

$$\beta\Delta F = \beta F_1 - \beta F_0 = -\ln\frac{Q_1}{Q_0}, \tag{1}$$

where $\beta = (k_{\rm B}T)^{-1}$. Introducing a weight function $W(r)$, the ratio of the partition functions of the two systems shifts to

$$\frac{Q_1}{Q_0} = \frac{Q_1}{Q_0}\frac{\int {\rm d}r W(r)\exp[-\beta(V_1+V_0)]}{\int {\rm d}r W(r)\exp[-\beta(V_1+V_0)]} = \frac{\langle W\ \exp(-\beta V_1)\rangle_0}{\langle W\ \exp(-\beta V_0)\rangle_1}, \tag{2}$$

where r represents the coordinates of all particles in the system and the subscripts 0 and 1 denote the averages with respect to the Boltzmann factor of V_0 and V_1, respectively. Since the weight function is arbitrary, it therefore can be chosen in such a way that the calculations will be reduced. If we choose it as

$$W \propto \left[\frac{Q_0}{n_0}\exp(-\beta V_1) + \frac{Q_1}{n_1}\exp(-\beta {\rm V}_0)\right]^{-1}, \tag{3}$$

where n_0 and n_1 are two arbitrary numbers to be determined later. Equation (2) then reduces to

$$\frac{Q_1}{Q_0} = \frac{n_0Q_1}{n_1Q_0}\frac{\left\langle\left[1+\frac{n_0Q_1}{n_1Q_0}\exp[-\beta(V_0-V_1)]\right]^{-1}\right\rangle_0}{\left\langle\left[1+\frac{n_1Q_0}{n_0Q_1}\exp[-\beta(V_1-V_0)]\right]^{-1}\right\rangle_1}, \tag{4}$$

Assuming $\frac{n_0Q_1}{n_1Q_0} = {\rm e}^{-C}$, we have

$$\frac{Q_1}{Q_0} = \frac{\langle f[\beta(V_1-V_0)+C]\rangle_0}{\langle f[-\beta(V_1-V_0)-C]\rangle_1}{\rm e}^{C},$$

$$\ln\frac{Q_1}{Q_0} = \ln\frac{\langle f[\beta(V_1-V_0)+C]\rangle_0}{\langle f[-\beta(V_1-V_0)-C]\rangle_1} + C,$$

where $f(x) = [1+\exp(x)]^{-1}$ is the Fermi function. For hard sphere potential, we choose C=0, then we obtain

$$\begin{aligned}\beta\Delta F &= -\ln\frac{Q_1}{Q_0}\\ &= -\ln\frac{\langle f[\beta(V_1-V_0)+C]\rangle_0}{\langle f[-\beta(V_1-V_0)-C]\rangle_1}\\ &= -\ln\frac{N_{10}}{N_{01}},\end{aligned} \tag{5}$$

where N_{10} is the number of samples drawn out from N simulated samples, generated under the potential V_0, with V_1 being not infinite; N_{01} is the number of samples drawn out from N simulated samples generated under the potential V_1, with V_0 being not infinite. From Eq.(5), we see that the free energy difference ΔF is only related to the number of samples drawn out from the N simulated samples, therefore the depletion interaction is determined through the ARM conveniently even under the unsymmetrical confine-

ments, then the ARM is the basis of force calculation in this paper.

3. Numerical results

To show the effects on the depletion forces from the unsymmetrical geometric confinements, 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 (see Fig.1). In the cell, two large hard spheres of radius R are placed close to plate $P2$ and far away from $P1$, and the small hard spheres of radius r are randomly distributed to form hard-sphere fluids. D is the distance between the line connecting the centres of the two large-spheres and the plate $P2$. The size ratio of the large- to small-sphere R/r is 5, and the number of the small spheres N is determined by the given volume fraction η, defined as $\eta = NV_{\rm s}/(V - 2V_{\rm b})$, where $V = L_x \times L_y \times L_z$ is the total volume, $V_{\rm s} = \frac{4}{3}\pi r^3$ is the volume of a small sphere, and $V_{\rm b} = \frac{4}{3}\pi R^3$ is the volume of a large sphere. The effects of the unsymmetrical geometric confinements can then be investigated in the systems with the same L_x but different D, or with a fixed D but different L_x. In the whole process of our simulations, the distance between the plate $P1$ and the line connecting the two large spheres' centres is larger than D, therefore, the influences on the depletion interactions from $P1$ and $P2$ are different. That is why we call this model unsymmetrical confinement. In this way, we study the depletion potentials and depletion forces not only in the systems with the same L_x and different D, but also in the systems with the same D and different L_x. For each case, we take $L_y = 18r$ and $L_z = 36r$, and the simulations are performed in the systems with volume fractions $\eta = 0.116$ and 0.229; for each η, the cases with $D = 5r, 6r$ and $8r$ are studied separately. When the parameters η, D, 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[26] with the two large spheres fixed at a separation h. Each small sphere is chosen in an orderly way involving a trial displacement and the new position is accepted so long as it does not result in an overlap with the large hard spheres, the other small spheres and the plates. The geometric confinements are taken into account by using the fixed boundary condition in the x direction. Obviously, the periodic boundary condition should be used in y and z directions. When the periodic boundary condition is used in all the three directions, it is just the case without geometric confinement. Meanwhile the magnitude of the maximum random displacement is adjusted so that the overall acceptance ratio is about 0.3–0.5. In our simulations, to minimize the finite size effects and the statistical errors, L_y is enlarged when the distance between the two plates decreases, and the number of Monte Carlo (MC) steps is also enlarged, i.e. 2.5×10^5, MC steps are used for obtaining equilibrium of the system and other 2.5×10^5 MC steps to collect data. If the free energy difference for different separations between the two large-spheres is obtained through ARM, then the depletion potential can be obtained by fixing the potential zero to a reference point. In this paper, the contact point of the two large-spheres is chosen to be the zero point of energy. Obviously, this choice will not affect the depletion force because it is obtained by the differentiation of the depletion potential. In this way, all the depletion potentials and depletion forces corresponding to the cases mentioned above are determined and the results are shown in Figs.2 and 3. The depletion potentials F in units of $k_{\rm B}T$ and the corresponding depletion forces in units of $\pi R\rho k_{\rm B}T$ are plotted as functions of h, where h is measured in units of $2r$, and ρ is the number density of small spheres. In both Figs.2 and 3, the solid lines describe the depletion potentials or depletion forces in the systems without geometric confinements, i.e., D=unconfined, whereas the other lines are those under unsymmetrical confinements: the dashed lines for $D = 8r$, the dot-dashed lines for $D = 6r$, and the dotted lines for $D = 5r$. From Figs.2 and 3, it is evident that, no matter whether the volume fraction is large or small, both the depletion potential and depletion force are affected by the presence of the two plates. Meanwhile, we also see from Figs.2 and 3 that, for the same L_x, the nearer the large-spheres are placed on the plate, the larger the influence on the depletion interaction by the plates.

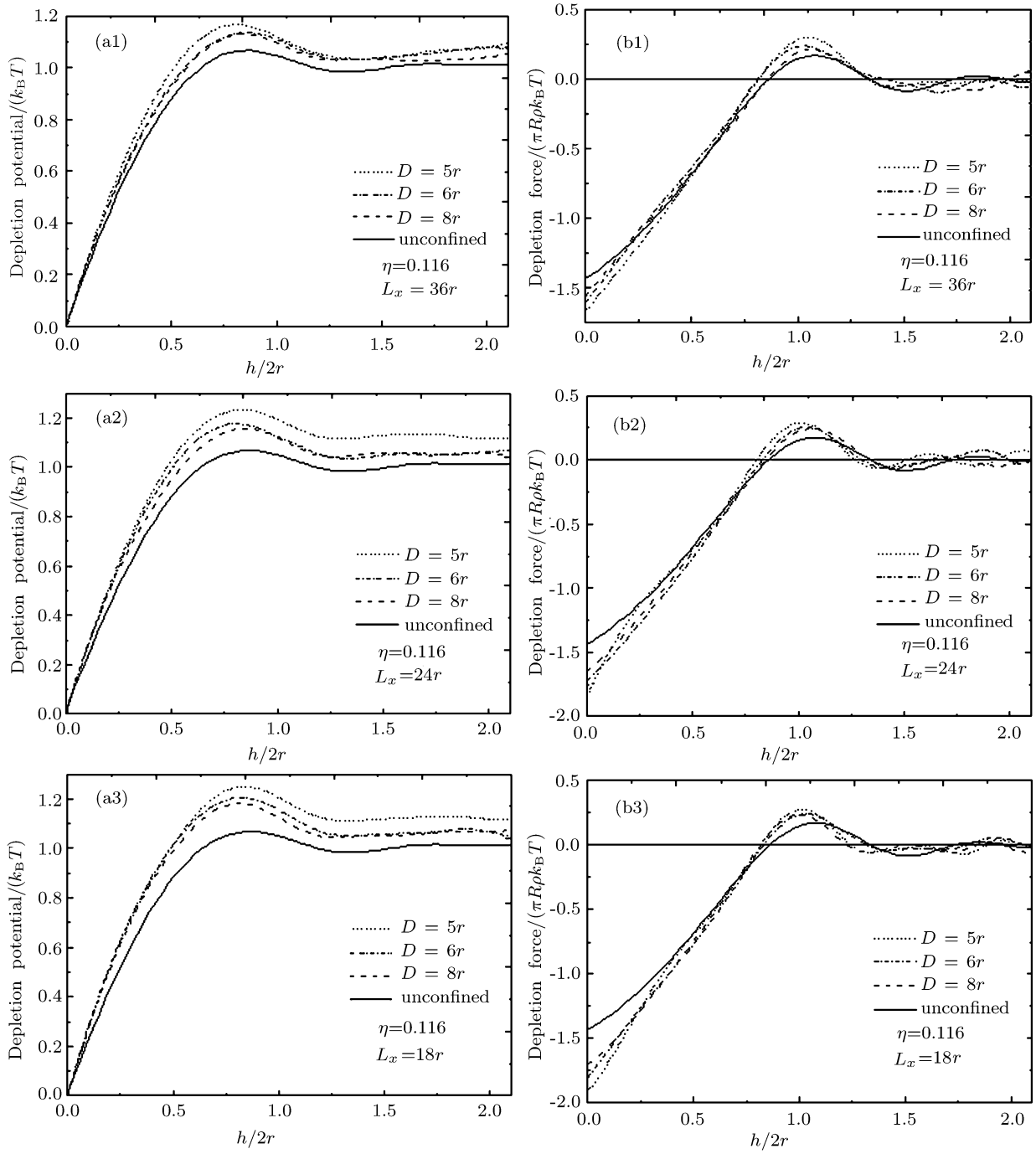


Fig.2. Depletion potentials (a1)–(a3) and the corresponding depletion forces (b1)–(b3) in the systems of $\eta = 0.116$ under the unsymmetrical confinements with different D.

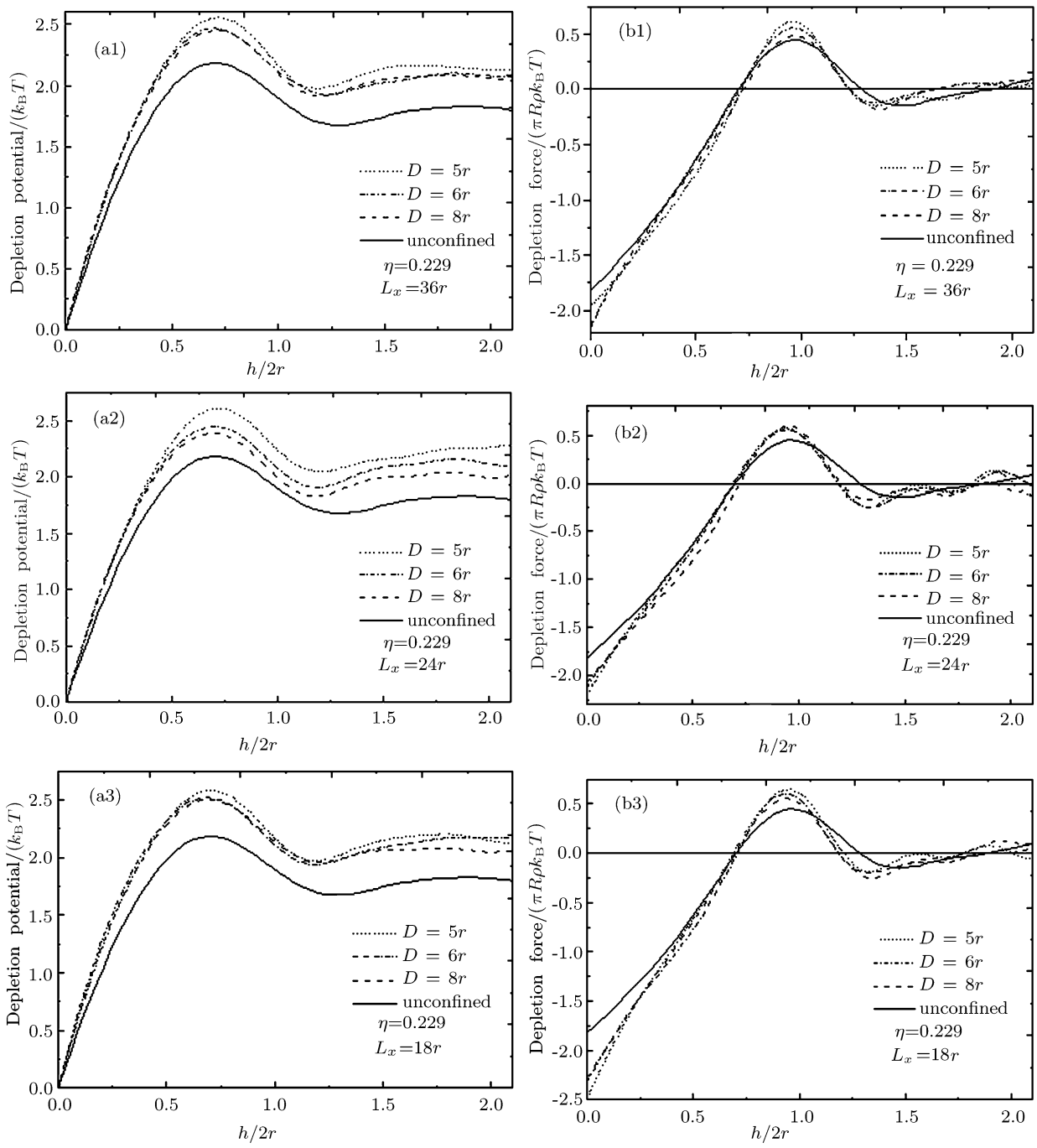


Fig.3. Depletion potentials (a1)–(a3) and the corresponding depletion forces (b1)–(b3) in the systems of $\eta = 0.229$ under the unsymmetrical confinements with different D.

In addition, the depletion forces of the systems with the same D but different L_x are shown in Fig.4, in which the solid lines describe the depletion forces with $L_x = 36r$, the dashed lines those with $L_x = 24r$, and the dotted lines those with $L_x = 18r$. From Fig.4, we also note that, for the same D, the larger the width of the box L_x, the smaller the effect on the depletion potential or the depletion force by the geometric confinements. If L_x is very large, the influence of $P1$ on the depletion interactions will be very small and can be neglected as compared with the other plate $P2$: i.e., the system is confined only by one plate. Besides the cases discussed above, we can gain more information about the geometrical confinements if the depletion forces in the systems under the unsymmetrical geometric confinements are compared with that under the symmetric confinements.

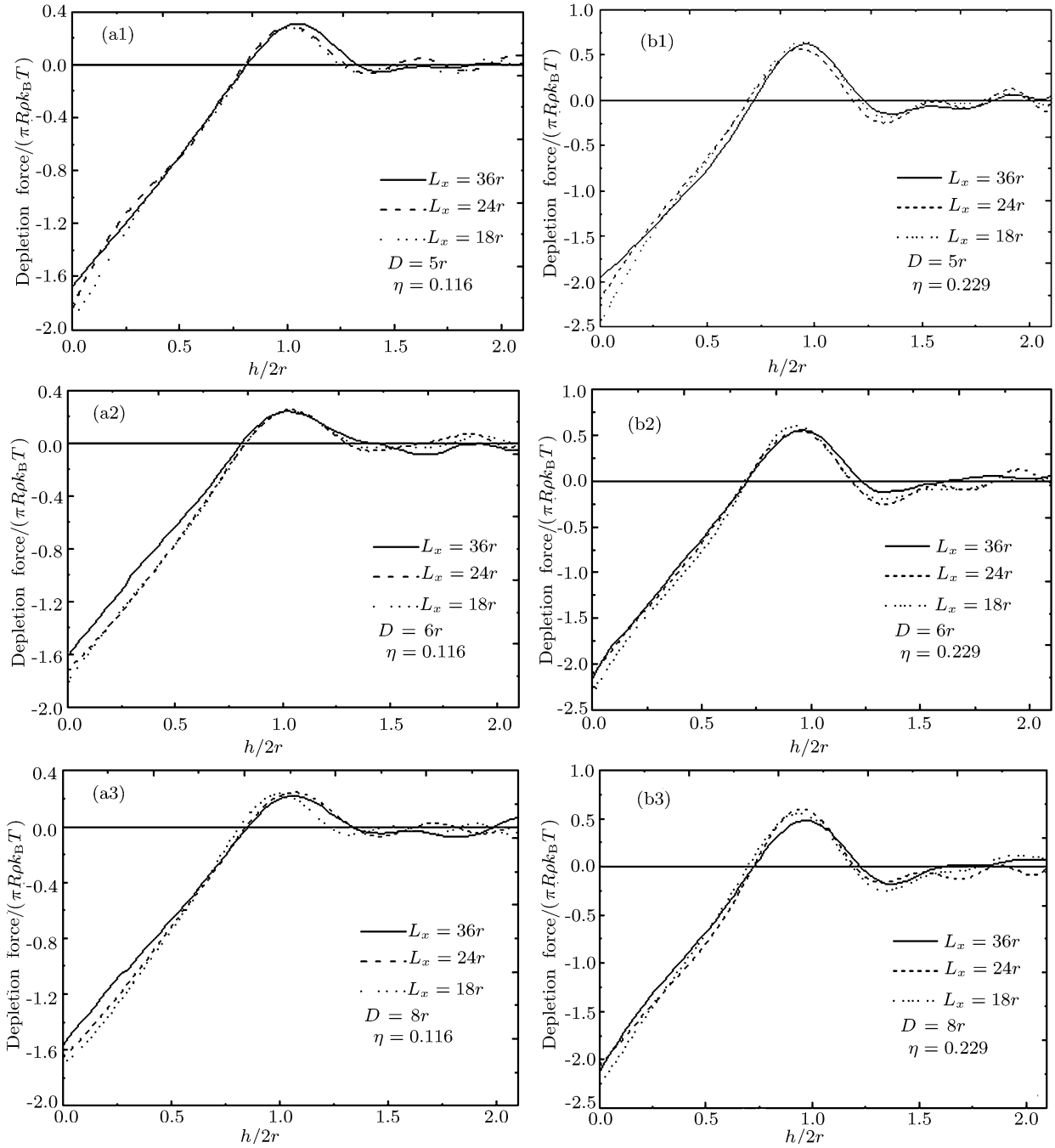


Fig.4. Depletion forces in the systems of (a) $\eta = 0.116$ and $\eta = 0.229$ (b) under the unsymmetrical geometry confinements with L_x.

Our simulations are performed in this way, and the results are shown in Fig.5, in which the solid and the dashed lines describe the systems under the unsymmetrical confinements with $L_x = 36r$, $18r$ respectively, and the dotted lines describe the systems under symmetrical confinement. From Fig.5, it is evident that, for the same distance between the large sphere and the plate, the effects of the unsymmetrical confinements on the depletion forces are smaller than that of the symmetrical confinements; we can also find from Fig.5 that the influence of the unsymmetrical confinements on the depletion forces becomes stronger with the decrease of L_x. It is of benefit to point out that all the simulations are performed in the canonical ensembles with a fixed number of colloidal spheres. There can be some difference between our results and the experimental results from which are obtained the grand canonical ensembles with fixed chemical potentials. We believe that the difference may be very small, and our simulations reflect the real physical features about the depletion interactions in the confined situation to some extent. Simulations performed in the grand canonical ensembles are under way.

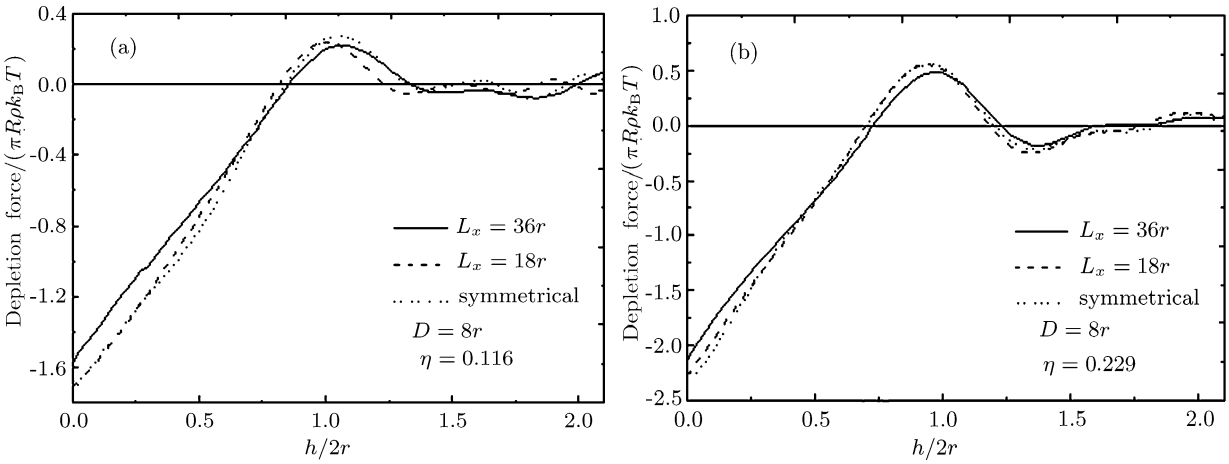


Fig.5. Depletion forces in the systems under the symmetrical and unsymmetrical geometry confinements with (a) $\eta = 0.116$ and (b)$\eta = 0.229$.

4. Conclusion

In summary, we have studied the depletion potentials and depletion forces in hard sphere mixtures confined under unsymmetrical geometric confinement through Monte Carlo simulations. From the discussion above, we find that the depletion interactions are affected by the unsymmetrical geometric confinements. Furthermore, the closer the two large spheres to the plate, the larger the effects of the unsymmetrical geometric confinements. On the other hand, for the same D, the larger the L_x, the smaller the influence of the other plate.

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