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Depletion interactions in a cylindric pipeline*

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In a colloidal system confined by a small cylindric pipeline, the depletion interaction between two large spheres is different to the system confined by two plates, and the influence on depletion interaction from the pipeline is related to both the size and shape of it. In this paper, the depletion interactions in the systems confined by pipelines of different sizes or different shapes are studied by Monte Carlo simulations. The numerical results show that the influence on depletion force from the cylindric pipeline is stronger than that from two parallel plates, and the depletion force will be strengthened when the diameter of the cylinder is decreased. In addition, we also find that the depletion interaction is rather affected if the shape change of the pipeline is slightly changed, and the influence on depletion force from the shape change is stronger than that from the size change.

Keywords: depletion interactions, cylindric pipeline, colloidal system
PACC: 8270D, 7115Q

1. Introduction

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It is well known that, in binary colloidal suspensions, the depletion forces among large-spheres are the central issues of the stability of colloids[1] and were well studied through computer simulations, approximation theories, integral equation theory, density functional theory and experiments,[2−18] etc. Recent investigations show that the depletion interactions are sensitive to the geometry confinements.[19−32] It is known that the depletion interactions are strengthened if the colloidal systems are confined between two parallel plates.[25−31] These results are very important for us to get the special characters of the colloids confined by geometrical factor, and is therefore useful for industrial application or for our real life. For example, investigations on depletion interactions in the system confined by a cylindric pipeline may provide us with the information about a jam taking place in it. It is certainly interesting because very little is known about the effect of a confining capillary slit on e.g. the gas-liquid phase behavior of such binary hard sphere mixtures or other systems. In addition, stressed by external forces, the shape of the pipeline may be changed. Then a new question arises, how about the depletion interaction when the shape of the pipeline is changed: it is almost unaffected or is strongly affected? Usually we cannot prohibit the shape of a pipeline to be changed, so investigations on the influence from the shape change are needed. In this paper, we aim to study the depletion interactions in the pipelines of different sizes and different shapes respectively.

2. Models

We consider the system consisting of two large spheres immersed in the fluid of small spheres, which is further confined by a small cylindric pipeline (see Fig.1(a)) or by a small elliptic pipeline (see Fig.1(b)). In these systems, the potential between two hard spheres may be written as

$$u(d) = \begin{cases} \infty, & \text{if } d < \sigma_{ij}, \\ 0, & \text{if } d > \sigma_{ij}, \end{cases} \tag{1}$$

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where d is the distance between the two spheres in diameters of σ_i, σ_j, respectively, and $\sigma_{ij} = (\sigma_i + \sigma_j)/2$. Usually, the Acceptance Ratio Method (ARM), which was first introduced by Bennett,[33] is used to determine the depletion force between the two large spheres. For ARM, two different separations of the two large spheres are taken as two different systems, denoted by the potentials of V_0 and V_1 respectively, and the partition functions of them are Ω_0 and Ω_1 respectively, then the free energy difference between these two systems is given by

$$\beta\Delta F = \beta F_1 - \beta F_0 = -\ln\left(\frac{\Omega_1}{\Omega_0}\right), \tag{2}$$

where $\beta = 1/(k_{\mathrm{B}}T)$, k_{B} is Boltzmann's constant, and T is the absolute temperature. With the aid of the weighting function $W(r)$, it is easy to get

$$\beta\Delta F = -\ln\frac{\Omega_1}{\Omega_0} = -\ln\frac{N_{10}}{N_{01}}, \tag{3}$$

where N_{10} is the number of samples drawn form N simulated samples 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 generated with potential V_1 (where V_0 is not infinite).

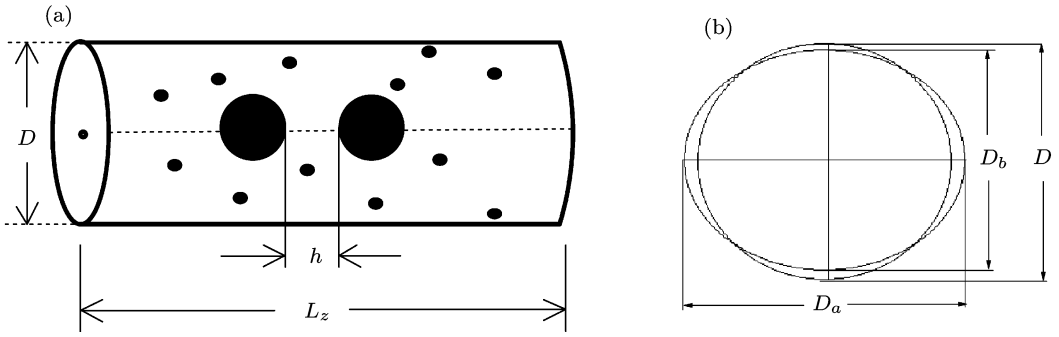


Fig.1. (a) Colloidal particles confined in the cylindrical pipeline; (b) Section of the colloidal particles confined in the cylindric and the elliptic pipelines with the same section area. The diameter of the cylinder is D, the long and short radii of the elliptic pipeline are $D_a/2$ and $D_b/2$.

3. Simulation details

In our study, the two large spheres of radius R are placed along the center symmetric axis of the cylindric pipeline (see Fig.1(a)); the length and diameter of the simulating cell for the cylindric pipeline are $L_z = 36r$ and $D = 20r$ respectively, where r is the radius of the small spheres; the size ratio of the large sphere to the small one is $R/r = 5.0$. Obviously, the number of small spheres N can be determined through the given volume fraction η defined as $\eta = NV_s/(V - 2V_b)$, where $V = \pi\rho^2 L_z, V_s = 4\pi r^3/3$ and $V_b = 4\pi R^3/3$ are the total volume of the simulating cell, the small sphere's volume and the large sphere's volume, respectively. In the simulations, corresponding to the wall of the pipeline, the fixed boundary condition is used, and the magnitude of the maximum random displacement is adjusted so that the overall acceptance ratio is about $0.3 - 0.5$. In addition, 1.0×10^5 Monte Carlo steps (MCS) are used for the equilibrium of the system and the other 3.0×10^5 MCS to collect data. Then the depletion potentials and depletion forces in the above systems of $\eta = 0.1$ and 0.2 are obtained by ARM, and the simulation results are shown in Figs.2 and 3, respectively. To show the influence on depletion interaction from the cylindric pipeline, a comparison between the systems without confinement or confined between two parallel plates is needed. So, the results of them are also shown in Figs.2 and 3.

Furthermore, the influence on the depletion interaction from size change or the shape change of the pipeline should also be considered. So the depletion interactions in cylinders with different sizes, such as $D = 18r$, $D = 20r$, $D = 24r$, are studied and the corresponding results are shown in Figs.4 and 5, respectively; Meanwhile the depletion interactions in the systems confined by the cylindric or by the elliptic pipelines are studied (see Fig.1(b)). In fact, if a cylindric pipeline is changed into an elliptic one, the long and short axes of the ellipse,

$D_a/2$, $D_b/2$, are used to describe the character of it. Supposing the shape change is very small, and the cross-sectional areas of the cylindric and the elliptic pipelines are the same, then the relation among D, D_a and D_b is $D^2 = D_a D_b$. In our simulations, the systems confined by the cylindrical pipeline of $D = 20r$, or confined by the elliptic ones of $D_b = 19r$, $18r$, are studied, and the results are shown in Figs.6 and 7, respectively.

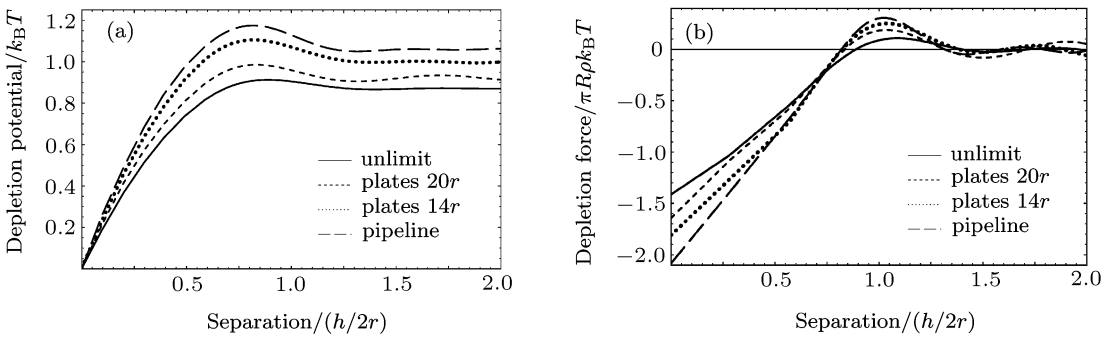


Fig.2. Depletion potentials in unit of k_BT between the two large spheres with different h for the volume fraction $\eta = 0.1$; (b) Depletion forces in unit of $\pi R\rho k_BT$ between two large spheres with different h for the volume fraction $\eta = 0.1$. The solid lines in both (a) and (b) describe the case without confinement; the dotted lines and the short dashed lines for the cases confined between two plates with separation $D = 14r$ and $D = 20r$ respectively, and the long dashed lines for the cases confined by cylinder.

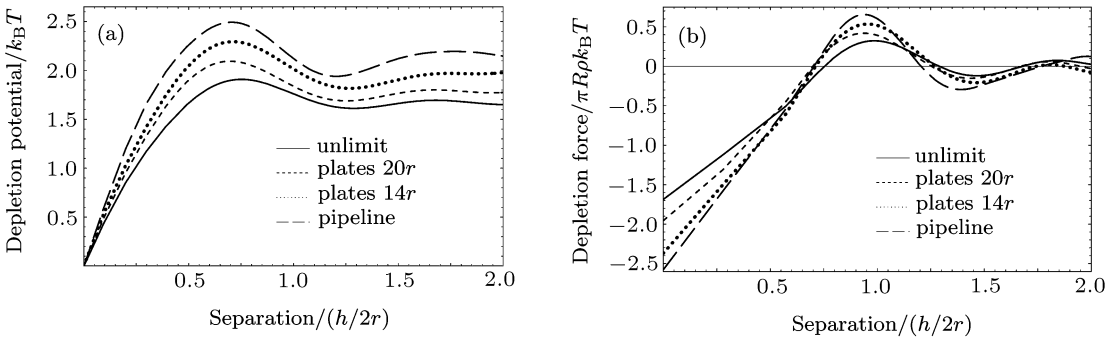


Fig.3. (a) The same as Fig.2(a) but for $\eta = 0.2$. (b) The same as Fig.2(b) but for $\eta = 0.2$

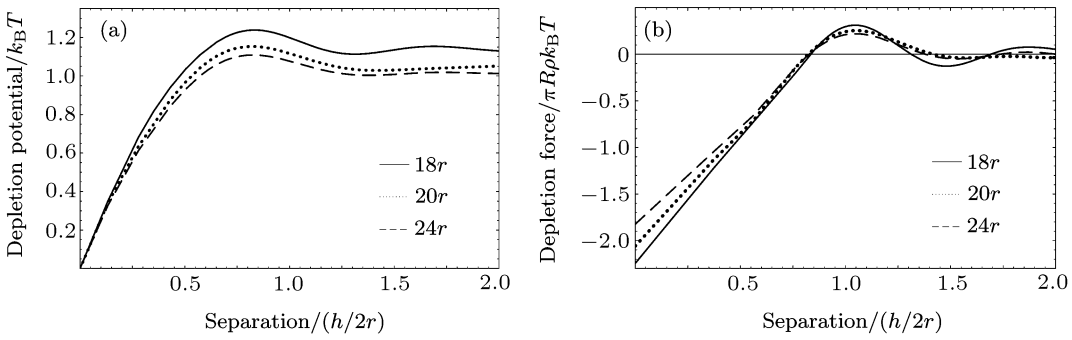


Fig.4. (a) Depletion potentials in unit of k_BT of the two large spheres with different h for the volume fraction $\eta = 0.1$; (b) Depletion forces in unit of $\pi R\rho k_BT$ between two large spheres with different h for the volume fraction $\eta = 0.1$. The solid lines, the dotted lines and the dashed lines in both (a) and (b) describe the cases confined by cylinder with diameters of $18r$, $20r$ and $24r$, respectively.

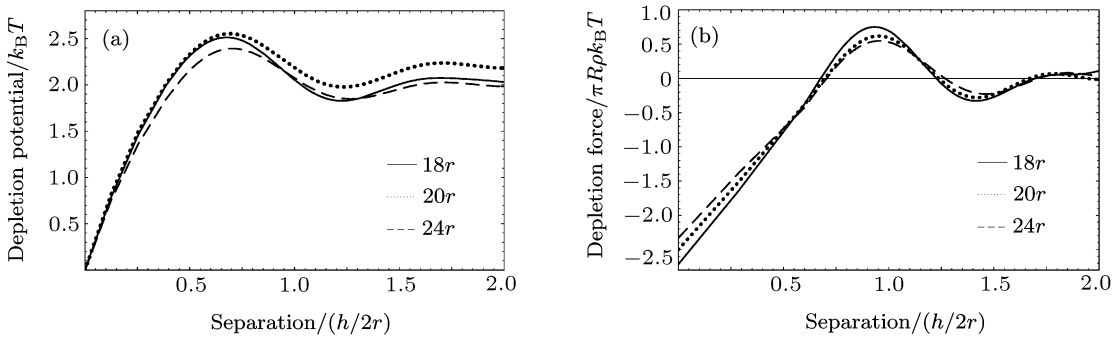


Fig.5. The same as Fig.4 but for $\eta = 0.2$.

4. Results and discussion

In all the figures mentioned above, the depletion potential F is measured in units of k_BT, the depletion force f in units of $\pi R\rho k_BT$, and h is measured in units of $2r$, ρ is the number density of small spheres. We firstly analyze Figs.2 and 3, in which the solid lines in both (a) and (b) describe the cases without confinement; while the dotted, short dashed lines describe the cases confined between two plates with separation $14r$ and $20r$ respectively; and the long dashed lines for the cases confined by the cylinder. From Figs.2 and 3, we find that the depletion force in the cylindric pipeline is the largest one: it is not only larger than that of the system without confinement but also larger than that of the systems confined between two plates. Obviously, the influence on depletion interaction from the pipeline is larger than that from the two plates. Due to the fact that the freedom of the system in the pipeline is confined in two directions while only one direction is confined by the two plates, our result is reasonable.

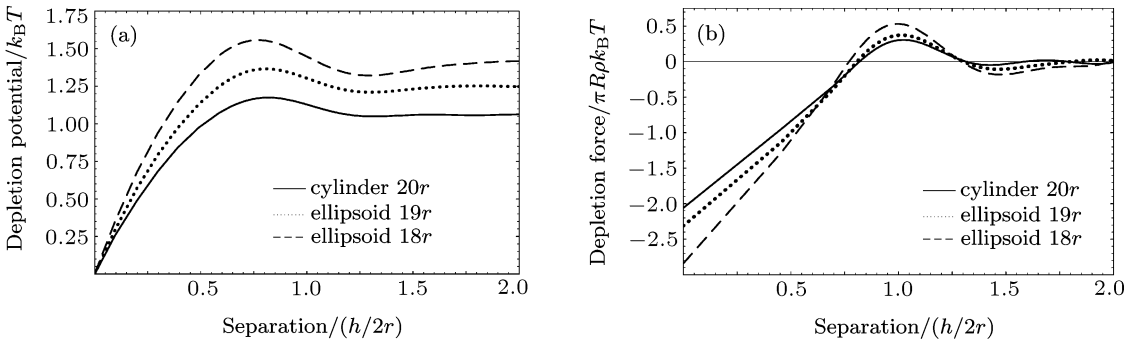


Fig.6. (a) Depletion potentials in unit of k_BT in the cylindric pipeline with diameter of $D = 20r$, and in the elliptic pipelines with their short shafts $D_B = 19r$, $D_b = 18r$, respectively. (b) The corresponding depletion forces of the depletion potentials shown in (a). In both (a) and (b), the solid lines, the dotted lines and the dashed lines denote the results for $D = 20r$, $D_b = 19r$ and $D_B = 18r$, respectively. They describe for the systems with volume fraction $\eta = 0.1$.

Figures 4 and 5 show the depletion interactions in cylinders of different sizes, in which the solid lines, dotted-lines and dashed-lines are described for the systems of $D = 18r$, $20r$, $24r$ respectively. From Figs.4 and 5, we find that, with the increase of the diameter, the influence on the depletion interactions from the cylinder decreases. It tells us that a jam will easily take place in the smaller cylinder. Beside the size change, figures 6 and 7 show the depletion interactions in the pipelines of different shapes. In Figs.6 and 7, the solid lines are for the cases that the systems are confined by the cylindric pipeline of $D = 20r$, the dotted lines and the long dashed lines are for the systems confined by the elliptic pipelines of $D_B = 19r$, $18r$, respectively. From Figs.6 and 7, we find that, no matter whether the volume fraction is large or small, the depletion forces in the cylindric pipeline are smaller than those in the elliptic pipelines. Meanwhile, we also note that, for the same volume fraction, the smaller the short axis, the larger the depletion forces will be. It tells us clearly that, the depletion

interactions are strongly affected when the shape of the pipeline is changed; the larger the shape change, the larger the influence on the depletion interaction will be.

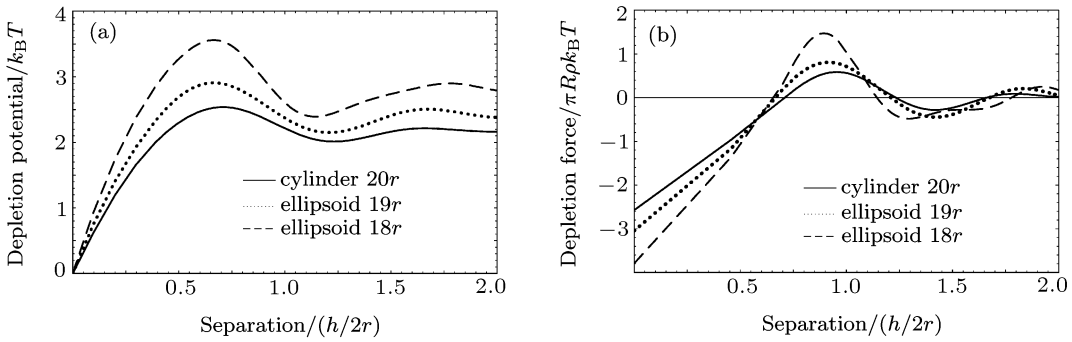


Fig.7. The same as Fig.6 but for the volume fraction $\eta = 0.2$.

In order to measure the influence on the depletion interaction from the size change or from the shape change of the pipeline, a quantity Δf, defined as the difference between the maximum and minimum of the depletion force is introduced. From Figs.4 and 5, we get that, for $\eta = 0.1$, the values of Δf confined in the cylindric pipelines are $\Delta f_{\rm C}^{18} = 2.54$, $\Delta f_{\rm C}^{20} = 2.35$, $\Delta f_{\rm C}^{24} = 2.02$, and the relative values are $(\Delta f_{\rm C}^{18} - \Delta f_{\rm C}^{20})/\Delta f_{\rm C}^{20} = 8\%$, $(\Delta f_{\rm C}^{20} - \Delta f_{\rm C}^{24})/\Delta f_{\rm C}^{24} = 16\%$ respectively, where the subscript C denotes for the cylindric pipeline, and the superscripts 18, 20, and 24 represent the diameter of the cylinders. For $\eta = 0.2$, $\Delta f_{\rm C}^{18} = 3.48$, $\Delta f_{\rm C}^{20} = 3.15$, $\Delta f_{\rm C}^{24} = 2.90$, and the relative values are $(\Delta f_{\rm C}^{18} - \Delta f_{\rm C}^{20})/\Delta f_{\rm C}^{20} = 10.5\%$, $(\Delta f_{\rm C}^{20} - \Delta f_{\rm C}^{24})/\Delta f_{\rm C}^{24} = 8.6\%$ respectively. From Figs.6 and 7, we obtained that, for $\eta = 0.1$, the values of Δf confined in the cylindric and elliptic pipelines are $\Delta f_{\rm C} = 2.34$, $\Delta f_{\rm E}^{19} = 2.69$, $\Delta f_{\rm E}^{18} = 3.35$, and the relative values are $(\Delta f_{\rm E}^{19} - \Delta f_{\rm C})/\Delta f_{\rm C} = 15\%$, $(\Delta f_{\rm E}^{18} - \Delta f_{\rm C})/\Delta f_{\rm C} = 43\%$ respectively; for $\eta = 0.2$, $\Delta f_{\rm C} = 3.2$, $\Delta f_{\rm E}^{19} = 3.83$, $\Delta f_{\rm E}^{18} = 5.22$, and the relative values are $(\Delta f_{\rm E}^{19} - \Delta f_{\rm C})/\Delta f_{\rm C} = 20\%$, $(\Delta f_{\rm E}^{18} - \Delta f_{\rm C})/\Delta f_{\rm C} = 63\%$ respectively, where the subscripts C and E denote the cylindric and elliptic pipelines respectively, the superscript 18 and 19 represent the short diameter of the elliptic pipeline. From the above data, it is clear that, in the systems confined by the cylindric pipelines of different sizes, Δf increases as the diameter decreases or as the volume fraction increases. However, for an elliptic pipeline, both the value Δf and its relative value increase with the decrease of D_b. Furthermore, the value Δf and its relative value caused by the shape change of the pipeline are far more larger than those caused by the size change, i.e., the influence on depletion interaction from the shape change is larger than that from the size change.

5. Conclusion

In conclusion, we have studied the depletion interactions between two large hard spheres immersed in the sea of small spheres which is further confined by a pipeline through Monte Carlo simulations, and the numerical results show that both the depletion potential and depletion force are more sensitive to the cylindric pipeline than those to the two plates, and the influence on depletion interactions decreases with the increase of the diameter of the cylinder. Furthermore, the depletion interaction is obviously strengthened if the shape of the pipeline is slightly changed, so, for a pipeline, the shape change plays a more important roles to the depletion force than that of the size change.

References

[1] Asakura S and Oosawa F 1954 *J. Chem. Phys.* **22** 1255
[2] Derjaguin B V and Landau L 1941 *Acta Physicochim.* USSR **14** 633
[3] Croker J C and Grier D G 1994 *Phys. Rev. Lett.* **73** 352
[4] Overbeek J T G 1987 *J. Chem. Phys.* **87** 4406
[5] Roij R and Hansen J P 1997 *Phys. Rev. Lett.* **79** 3082
[6] Bliben T, Bladon P and Frenkel D 1996 *J. Phys: Condens. Matter* **8** 10799

[7] Dickman R, Attard P and Simonian V 1977 *J. Chem. Phys.* **107** 205
[8] Li W H and Ma H R 2002 *Phys. Rev.* E **66** 061407
[9] Mao Y, Cates M E and Lekkerkerker H N W 1995 *Physica* A **222** 10
[10] Kinoshita M 2002 *J. Chem. Phys.* **116** 3493
[11] Henderson D, Wasan D T and Trokhymchuk A 2003 *J. Chem. Phys.* **119** 11989
[12] Trokhymchuk A and Henderson D 2004 *Langmuir* **20** 7036
[13] Kinoshita M 2006 *Chem. Eng. Sci.* **61** 2150
[14] Götzelman B, Evans R and Dietrich S 1988 *Phys. Rev.* E **57** 6785
[15] Attard P 1989 *J. Chem. Phys.* **91** 4790
[16] Roth R and Dietrich S 2000 *Phys. Rev.* E **62** 6926
[17] Egorov S A 2004 *Phys. Rev.* E **70** 031420
[18] Zhou S 2004 *Chem. Phys. Lett.* **399** 323
[19] Zhou S 2004 *Chem. Phys. Lett.* **392** 110
[20] Ohshima Y N, Sakagami H, Okumoto K, Tokoyada A, Igarashi T, Shintaku K B, Toride S H, Labuto K and Nishio I 1997 *Phys. Rev. Lett.* **78** 3981
[21] Crocker J C, Matteo J A, Dinsmore A D and Yodh A G 1999 *Phys. Rev. Lett.* **82** 4352
[22] Han Y and Grier D G 2003 *Phys. Rev. Lett.* **91** 038302
[23] Li Y Z, Li Y G and Lu J F 2002 *J. Chem. Phys.* **117** 407
[24] Crocker J C and Grier D G 1996 *Phys. Rev. Lett.* **77** 1898
[25] Xiao C M, Guo J Y and Li C S 2006 *Europhys. Lett.* **73** 443
[26] Xiao C M, Guo J Y and Hu P 2006 *Phys. Rev.* E **73** 061403
[27] Zhang C Y, Jin G J and Ma Y Q 2007 *Phys. Rev.* E **75** 041406
[28] Shi X Q and Ma Y Q 2007 *J. Chem. Phys.* **126** 125101
[29] Chen K and Ma Y Q 2005 *J. Phys. Chem.* B **109** 17617
[30] Zhang C Y, Jin G J and Ma Y Q 2008 *J. Phys.* C **20** 075111
[31] Zhang C Y, Jin G J and Ma Y Q 2007 *Europhys. Lett.* **80** 48003
[32] Huang L X, Xiao C M, Hu P and Gao H X 2009 *Chin. Phys.* B **18** 1287
[33] Bennett C H 1976 *J. Comput. Phys.* **22** 245