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用积分方程方法决定胶粒之间的空耗势 *

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摘 要: 用硬球模中性胶体粒子,数值求解双组分 Ornstein-Zernike 积分方程(当大的中性胶体粒子的浓度为零时),用来决定悬浮在溶剂(用小的硬球模拟)中两个胶粒之间的空耗势. 所预言的空耗势与文献的模拟数据和实验数据能很好地符合. 研究发现,基于空耗势的有效一组分 Hansen-Verlet 一相相变标准完全不能预言双组分系统的液-固相变. 讨论了导致这种现象的原因:Hansen-Verlet 一相相变标准不能自洽地处理有效一组分系统中固相与液相的体积能.

关键词: 空耗势;胶体;积分方程理论
中图分类号: O64 **文献标识码:** A

Integral Equation Method for the Determination of the Depletion Potential Between Two Colloidal Particles *

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Abstract Binary components Ornstein-Zernike integral equation with the concentration of large particle component being set to zero was employed to study the depletion potential behavior between two large neutral colloid particles (modeled as hard spheres) immersed in a sea of small neutral solvent particles. The prediction for the depletion potential behavior compared well with simulation data and experimental data available in the literature. It is found that the Hansen-Verlet one phase criterion, based on the effective one component system with the present depletion potential, for the freezing transition is completely not suitable for the real binary components system. It is disclosed that the unsuitability is due to the volume term of the solid phase and liquid phase which can not be treated self-consistently in the Hansen-Verlet one phase criterion.

Keywords Depletion potential, Colloids, Integral equation theory

1 Introduction

The depletion potential is of fundamental significance to issues of colloidal stability[1]. It arises between two larger particles suspended in a sea of smaller particles such as the nonadsorbing polymers, micelles, or small hard spheres. The idealized system (two isolated large hard spheres suspended in the solution of small hard spheres) provides a natural reference system for determining the properties of more realistic models of mixtures of simple atomic fluids, of colloids and polymers, and of other colloidal systems[2]. It is

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the expulsion or depletion of the small particles from the space of two large particles that leads to the so-called depletion potential whose basic properties are the attractive depletion force when the separation h of two surfaces of the two large particles is less than the diameter of the small ones[3]. Recently the depletion effect is identified as the mechanism of possible phase separation of binary components hard sphere fluid[4] whose phase instability can not be predicted in the framework of Percus-Yevick (PY) approximation Ornstein-Zernike (OZ) integral equation theory[5]. With the role of the small particles being taken into account by the depletion potential, the phase behaviors of the real binary components system can be calculated on the basis of the effective one component system[6] with the component particles (large particles) interacting by the depletion potential. So a good understanding of the depletion potential is very helpful to the unclosing of many practical phenomena. Napper and coworkers[7] argued some years ago that depletion effect can also lead to a repulsive interaction at larger distances and at depletant concentration. The resulting potential barrier might be large enough to kinetically stabilize colloid particles against flocculation. This claim, though partially supported by experiment, was not considered theoretically convincing, and has since been disregarded. However, recent papers[8] gave results for the depletion potential whose repulsive energy barrier could in principle be large compared with k_BT for large size ratios of large particle diameter to small particle diameter. Therefore it seems necessary to investigate in detail the depletion potential behavior. Theoretically, two apparently different approaches are proposed, one is in a virial expansion to order ϕ^2 and ϕ^3[8,9] whose predictions about the depletion potential doesn't compare with simulation data very well. Furthermore the virial expansion method to third order meets with the great mathematical obstacle. The other[10] is by the density functional approach predicted in very good agreement with the simulation data but is computationally complicated. Furthermore, the depletion potential between particles with arbitrary interaction potential suspended in the sea of particles with arbitrary interaction potential can not be treated in a unified way, that is to say, the above-mentioned two theoretical methods are devised originally for the hard sphere interaction potential, their extension to non-hard sphere interaction potential system is not straightforward.

It is the aim of the present contribution to propose a simple theoretical method for the predictions of the depletion potential behavior, which is based on the two components version of the OZ integral equation[11]. Then with regard to the success of the effective one component method for the freezing transition of the original binary components system, we investigate the suitability of the Hansen-Verlet one phase criterion[12] for the freezing transition of the original binary components system based on the present depletion potential.

2 Method

We consider a hard sphere mixture of two components in which the diameter of large particle is denoted by σ_l, that of small particle by σ_s, and the size ratio is denoted by $s=\sigma_s/\sigma_l$. To describe the structure of two components hard sphere fluid, we employ the OZ integral equation for a uniform mixture

$$g_{ij}(r)-1=c_{ij}(r)+\rho_k\times\sum_{k=l,s}\int d\mathbf{r}'(g_{ik}(r')-1)c_{kj}(|\mathbf{r}-\mathbf{r}'|) \quad (1)$$

To provide predictions, Eq. (1) has to be combined with the closure equation

$$g_{ij}(r)=\exp[-\beta u_{ij}(r)+\gamma_{ij}(r)+B_{ij}(\gamma_{ij})] \quad (2)$$

where $g_{ij}(r)$ is the radial distribution function, $c_{ij}(r)$ the direct correlation function, $\gamma_{ij}(r)$ the indirect correlation function and B_{ij} the bridge function for i and j component pair. For the hard sphere fluid considered here, the interaction potential $\beta u_{ij}(r)$ is of the following form

$$\beta u_{ij}(r)=\begin{cases}\infty, & r<\sigma_{ij}\\ 0, & r>\sigma_{ij}\end{cases} \quad (3)$$

We consider the additive hard sphere, thus $\sigma_{ij}=(\sigma_i+\sigma_j)/2$. The Eqs. (1) ~ (3) can be solved by the algorism by Labik *et al.*[13] which is actually an extension of Gillan's algorism[14]. The depletion potential between two large hard spheres $\beta W(h)$ is related by the Boltzmann distribution to the radial distribution

function $g_{ll}(r)$ of the infinitely dilute large hard sphere

$$\beta W(h) = -\ln(g_{ll}(r)) \quad (4)$$

where $h = r - \sigma_{ll}$ is the surface separation of the two large hard spheres. Thus, to obtain the depletion potential, we firstly solve the OZ equation with the large hard sphere density being set to a very small numerical value (tending to be zero).

To test the predictions of the present method, in Fig. 1 ~ 8 we compare the present predictions with the corresponding computer simulation data, the DFT predictions by Evans and Dietrich, experimental data by Ref [15] and the predictions of three analytical expressions for the depletion potential by Asakura and Oosawa[16], by Gotzelmann[17] and by Almarza and Enciso[18] respectively.

$$\beta W^{AO}(r) = -\frac{1+s}{2s}3\lambda^2\eta_s\left[\frac{1+(1+\lambda/3)s}{1+s}\right], \quad -1 < \lambda < 0 \quad (5)$$

$$\beta W^{G}(r) = -\frac{1+s}{2s}\left[3\lambda^2\eta_s + (9\lambda+12\lambda^2)\eta_s^2 + (36\lambda+30\lambda^2)\eta_s^3\right], \quad -1 < \lambda < 0 \quad (6)$$

$$\beta W^{AE}(r) = f_1(r,s)\eta_s + f_2(r,s)\eta^2 \quad (7)$$

where $\lambda = \frac{r}{s} - \frac{1}{s} - 1$, $\eta_s = P_s\sigma_s^3\frac{\pi}{6}$ is the small packing fraction, r is the center distance of two large hard spheres, in the units of σ_l.

$$f_0(s) = \left[1 + \frac{9}{8}\left(\frac{s}{1+s}\right) - \frac{1}{4}\left(\frac{s}{1+s}\right)^3\right]^{1/3} \quad (8)$$

$$f_1(r,s)\begin{cases} = -\frac{1}{2s^3}(1+s-r)^2[2(1+s)+r], & 1 < r < 1+s \\ = 0, & r > 1+s \end{cases} \quad (9)$$

$$f_2(r,s)\begin{cases} = 8f_1(r,s) + \frac{2}{s^3}[(1+s)f_0(s) - r]^2 \times [2(1+s)f_0(s)+r], & 1 < r < (1+s)f_0(s) \\ = 0, & r > (1+s)f_0(s) \end{cases} \quad (10)$$

In Fig. 1, the theoretical predictions are based on the HNC approximation[11] for $l-l$, $l-s$ and $s-s$ component pairs. Good agreement with the simulation data is obtained, and the potential barrier could be larger compared with the kinetical energy denoted by kT, thus to stabilize colloid particles against flocculation.

In Fig. 2 the scaled depletion force between two big hard spheres

$$\beta f^*(h) = \frac{2\beta F(h)(\sigma_s/2)^2}{(\sigma_l+\sigma_s)/2}$$

in a sea of small hard sphere with packing fractions $\eta_s = 0.3$ for a size ratio $s = 0.1$ is made. According to the relationship between force and potential, the depletion force $F(h)$ can be calculated from the following formula

$$F(h) = -\frac{\partial W(h)}{\partial h} \quad (11)$$

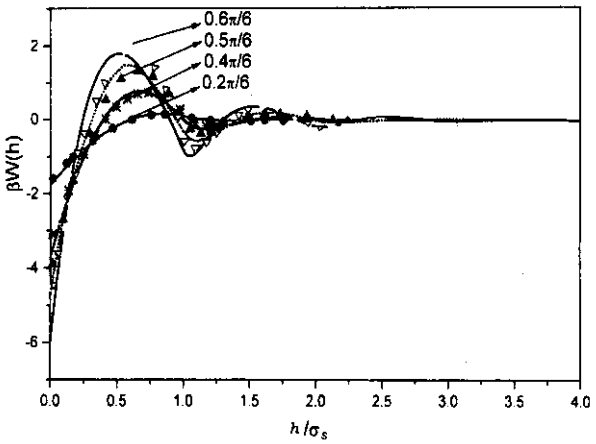

Fig. 1 The depletion potential between two large hard spheres in a sea of small hard spheres calculated for various packing fractions η_s of small spheres and a fixed size ratio $s = 0.1$ The symbols are from computer simulation results from Ref [21], the solid lines are from the present OZ theory (HNC approximation).

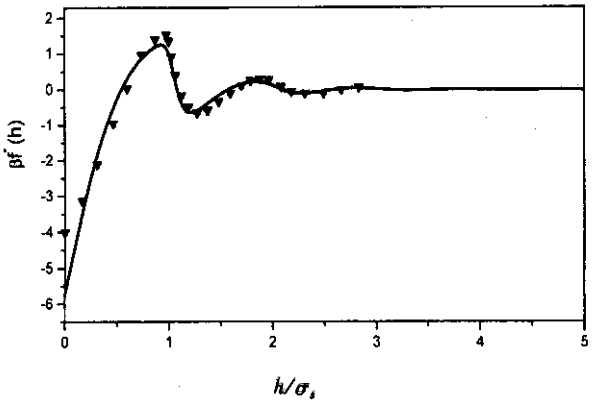

Fig. 2 The scaled depletion force between two big hard spheres $\beta f^*(h) = \frac{2\beta F(h)(\sigma_s/2)^2}{(\sigma_l+\sigma_s)/2}$ in a sea of small hard spheres with $\eta_s = 0.3$ for $s = 0.1$

The solid line is from the present OZ theory (HNC approximation), the symbols are from the density functional theory of Ref [10].

The theoretically obtained solid line is also based on the HNC approximation for all of the component pairs. Again the agreement with the simulation data is also good. In Fig. 3, in order to mimic the experimental condition of Ref [18], the diameters are chosen to be $\sigma_l = 1.1$ μm and $\sigma_s = 0.083$ μm so that the size ratio is $s = 0.0755$. With regard to the attractive interaction actually included in the experimental material as shown in Ref [18], the present agreement with the experimental data should be good (the experimental data are not shown in the Fig. 3. For clarity). In Fig. 4, it is found that as the size difference of the large and small sphere increases, the potential barrier increases. We can explain the phenomenon as follows. The depletion potential arises from the smaller particle, and when the size difference increases, there are more small particles being forced out of the space between the two larger particles, thus the depletion potential bahavior is strengthened quantitatively. This combined with the Fig. 1 gave us the method to stabilize the colloidal system, i. e. , decreasing the size and increasing the concentration of the depletant. In Fig. 5, it is shown that upon the increasing of the size difference, the position of the first (exactly the maximum) repulsive barrier decreases. This is due to the fact that as the size of the smaller particles decreases compared with the larger particles, relatively there is more space between the two larger particles for the smaller particles, and one can arrive at the first repulsive barrier at smaller distance between two larger particles.

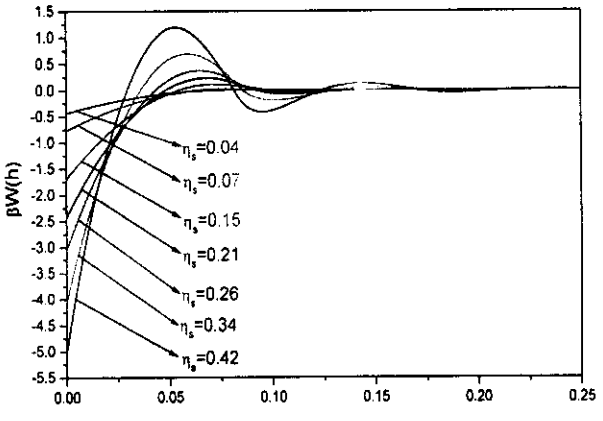

Fig. 3　The depletion potential between two large hard spheres in a sea of small hard spheres calculated for various packing fractions η_s of small spheres
In order to mimic the experiment of Ref [15], the diameters are chosen to be $\sigma_l = 1.1$ μm and $\sigma_s = 0.083$ μm $s = 0.0755$.
The theoretical predictions are from the OZ-PY approximation.

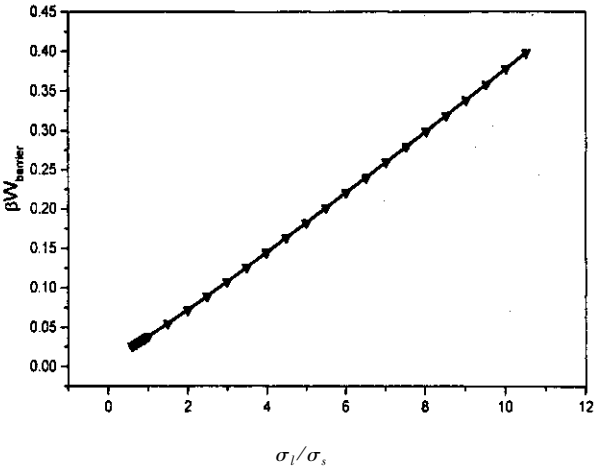

Fig. 4　The effect of s on the first (exactly the maximum) repulsive barrier βW_{barrier} with the small spheres $\eta_s = 0.3\pi/6$ (PY approximation)

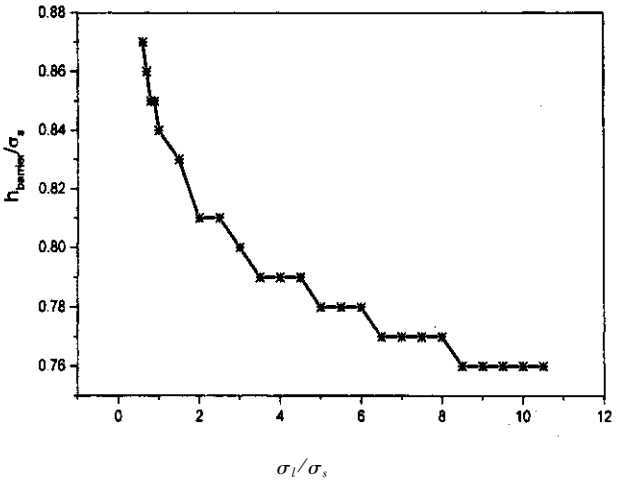

Fig. 5　The effect of s on the position of the first (exactly the maximum) repulsive barrier h_{barrier} with the small spheres $\eta_s = 0.3\pi/6$ (PY approximation)

In Fig. 6 ~ 8, the behavior of the different depletion potential $\beta W(r)$ with different s and η_s is plotted, it is shown that the predictions from OZ-HNC is similar to that from $\beta W^G(r)$, $\beta W^{AE}(r)$ and $\beta W^{AO}(r)$, so we conclude that the prediction accuracy of OZ-HNC is higher than that of OZ-PY. In fact, in Fig. 1 ~ 5 we choose the one of OZ-HNC and OZ-PY which can com-

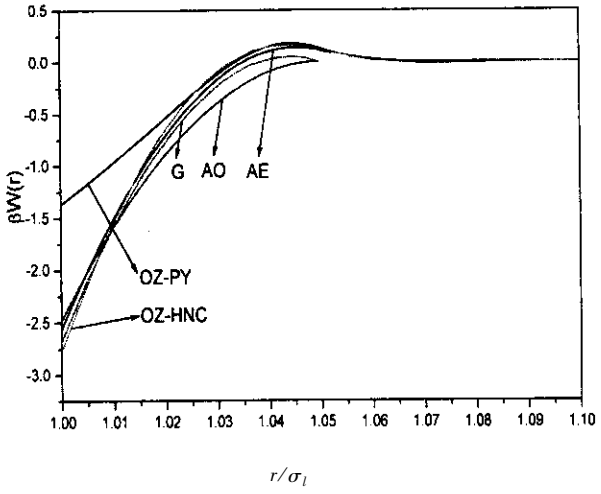

Fig. 6 The behavior of the different depletion potential with $\beta W(r)$ with $s=0.05$ and $\eta_s=0.08$

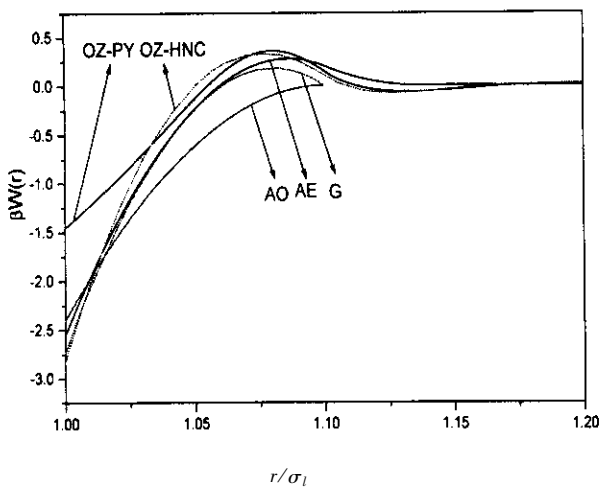

Fig. 7 The same as Fig. 6 but with $s=0.1$ and $\eta_s=0.15$

pare more favorably with the simulation data, and only when simulation data is not available, we choose the OZ-PY, because the PY approximation is generally regarded as appropriate for the hard sphere fluid. As in Ref [6], one can study on phase behavior of the above colloid mixtures by treating the two components colloid mixture as an effective one component system with the large hard sphere interacting through the depletion potential as well as the hard core potential by employing the first-order perturbation approach for the Helmholtz energy $F(\rho)$

$$F(\rho)=F_{HS}(\rho)+2\pi\rho^2\int_{\sigma_l}^{\infty}\mathrm{d}r r^2\tilde{g}_{HS}(r)W(r) \quad (12)$$

The meaning of the notation in Eq. (12) can be

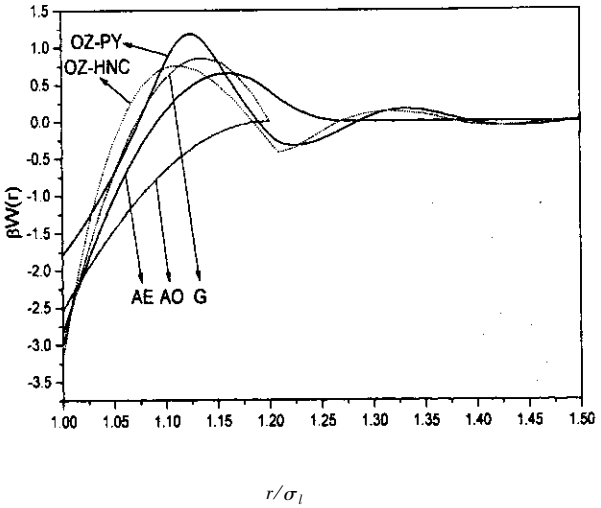

Fig. 8 The same as Fig. 6 but with $s=0.2$ and $\eta_s=0.3$

found[6]. With the above-explained procedure[6] studied the phase behavior of binary components hard sphere mixture based on the $\beta W^G(r)$, $\beta W^{AE}(r)$ and $\beta W^{AO}(r)$, the calculated phase diagram based on the $\beta W^G(r)$, $\beta W^{AE}(r)$ and $\beta W^{AO}(r)$ depletion potential are similar to each other and also in good agreement with the simulation data based on the real binary components hard sphere mixtures. Because the present predictions (OZ-HNC) are similar to the predictions of $\beta W^G(r)$, $\beta W^{AE}(r)$ and $\beta W^{AO}(r)$ depletion potential, we can expect that the calculated phase diagram is also similar to that based on $\beta W^G(r)$, $\beta W^{AE}(r)$ and $\beta W^{AO}(r)$ depletion potential, but we do not repeat the procedure here. Instead, we investigate whether the well-known one component one phase freezing criterion is applicable to real binary components system by mapping the original binary component system into the effective one component system by employing the present depletion potential. The investigated one component one phase freezing criterion is Hansen-Verlet criterion[12] which states that at freezing the maximum in the structure factor $S_{\max}\approx 2.85$ is found to hold remarkably for systems interacting with a $1/r^n$ potential. In Fig. 9, we plot the structure factor $S(k)$ for the effective one component system based on the present depletion potential with $s=0.1$ at four different liquid-solid freezing state points. Fig. 9 shows that the maximum in the structure factor $S_{\max}$ increases as the volume fraction of

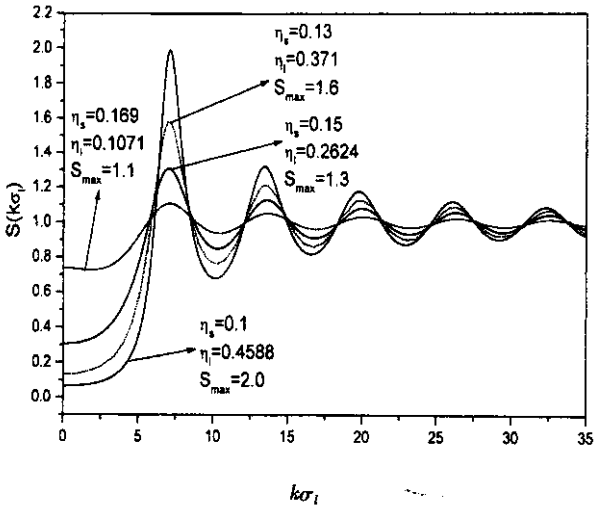

Fig. 9　$S(k)$ for the effective one component system based on the present depletion potential with $s=0.1$ and the parameters of four solid-liquid transition points

the larger particle increases, and the maximum in the structure factor $S_{\max}$ is not fixed at a constant as it is in the case of the real one component $1/r^n$ potential system. Even we try to build some relationship between the $S_{\max}$ at freezing points with the freezing state parameters s, η_s and η_l, but we fail completely.

A recent paper[22] discussed the effective one component model of binary component system and many component colloid mixture from first principle of statistical methanics and found that the total free energy of the mixture system is the sum of a so-called volume energy and the free energy of the equivalent effective one component pseudoparticles system interacting by the depletion potential. The indicated failure of the Hansen-Verlet one phase criterion for predicting freezing of the present binary component mixture based on the effective one component model signals the important influences of the volume energy on the phase behavior of the mixture. But how does one explain the success of the first-order perturbation approach for the Helmholtz energy which is also based on the effective one component model for the binary component system to predict the freezing ?One possible explanation is that the volume energy, which depends on the average large particles density, is smaller compared with the the free energy of the equivalent effective one component pseudoparticles system interacting by the depletion potential. Furthermore the influence of the small volume energy can be weakened to a large extent in the first-order perturbation approach for the Helmholtz energy which consistently treats the fluid and solid with complete neglect of the volume energy of fluid and solid. But in the Hansen-Verlet one phase criterion, only the information of the fluid side is employed to predict the freezing and the information of the solid side is not employed, so the errors resulting from the neglect of the volume energy of the fluid side can not be compensated for by the same neglect of the volume energy of the solid side.

3　Concluding remarks

The most advantage of the present OZ equation method lies in that different interaction potential systems can be treated in a unified way contrary to the previous two types which are devised for hard sphere interaction potential. With the standard algorism by Labik *et al.* [13], the predictions of the present method can be done fast and easily for two components case. Especially a recently proposed algorism[19], which makes numerical solution of many components (more than three components) OZ equation very easy, enables the present method for depletion suitable for more practical cases.

The relationship $\beta W(h) = -\ln(g_{ll}(r))$ on which the present method is based, is exact in principle, and all of the approximations of the present method come from the approximation for the bridge function, so the predictions accuracy can be improved with the more sophisticated and accurate bridge function approximation. With the present method, one can study the effect of long-range interaction potentials among the small and large particles on the depletion potential between the two large particles, then with the effective one component method, one can study the effect of the long-range interaction potential on the phase behaviors and structural properties of the n-component system ($n \geqslant 2$) by means of recently proposed density functional theory by the present author[20].

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