

Distribution of porous colloidal particles in an energy field

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Received 28 July 1998

Abstract

The spatial distribution of colloidal particles in an energy field is evaluated theoretically. The field may be established by a relatively large object such as a rigid wall, a closed boundary, and a particle. The set of nonlinear hypernetted chain equations describing the variations of the correlation functions for particle–particle and particle–object interactions is solved. A numerical scheme based on the discrete Fourier transform is proposed for the former, and a Newton–Raphson iterative method for the latter. Three cases are examined to illustrate the method proposed, namely, particles in a planar slit, cylindrical pore, and square duct. The qualitative behavior of the spatial variation of the concentration of colloidal particles predicted by the present study is consistent with that observed experimentally by D.H. Van Winkle and C.A. Murray [J. Chem. Phys. 89 (1988) 3885]. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

If a suspension of colloidal particles is placed in an energy field, the dispersed particles will follow a certain distribution as a response to the applied field. The energy field can be generated, for instance, by a rigid wall, or by relatively large nearby entities [1–4]. The phenomenon under consideration has potential applications in various problems in practice. For example, knowing the distribution of colloidal particles in an electrolyte solution is essential to the estimation of the long-range depletion force between two relatively large particles [5–8]. The distribution coefficient, which is a function of the distribution of colloidal particles, plays a significant role in exclusion chromatography [9,10].

Relevant studies are ample in the literature. Van Winkle and Murray [1], for example, observed experimentally the spatial distribution of the concentration of monodispersed latex particles under the influence of a smooth repulsive glass wall. It was found that the concentration of particles decreases oscillatory away from the surface. Gonzalez-Mozuelos et al. [2] considered the distribution of colloidal particles in a planar slit. The one-dimensional problem was solved by applying a rescaled mean spherical approximation to calculate the direct correlation function between two particles, and a hypernetted chain approximation to evaluate the radial distribution function between particle and wall. The result derived was found to be similar to that obtained through a Monte Carlo simulation. In a subsequent study [3], they also used a rescaled mean spherical approximation to estimate the radial distribution function, and concluded that the result obtained is close to that based on the

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hypernetted chain approximation. The analysis was extended to the problem of the adsorption of particles to a planar slit [4]. It was proposed that if the concentration of colloidal particles is low, their distribution can be approximated by the Boltzmann distribution [5,6]. However, since the volume of a colloidal particle is neglected, this assumption may lead to some deviation in the prediction of the behavior of a colloidal dispersion. Ise et al. [11] and Ito et al. [12], for instance, concluded that, if the volume of a colloidal particle is considered, the Coulombic force between two particles having the same electrical property can be attractive. In a study of the attractive interaction between similarly charged colloidal particles, Chu and Wasan [13] found that, if the concentration of colloidal particles is high, and the amount of charges on the surface of a particle is large, the variation of the effective pair interaction energy as a function of the center-to-center distance between two particles can be oscillatory. At an elevated particle concentration, the distribution coefficient of colloidal particles can be estimated by adopting a Virial expansion technique [5,6,9,10,14]. In this approach, the distribution coefficient is expanded in an infinite power series of the bulk concentration of colloidal particles. The coefficients of the series are calculated through integrating the Mayer function associated with the cluster diagrams [9,14]. If some of these diagrams are neglected, the resultant integration leads to either the Percus–Yevick approximation, or the hypernetted chain approximation. In practice, since the coefficients of higher-order terms involve a complicated multiple integration, the corresponding terms are usually dropped for simplicity. One of the possible approaches to avoid this difficulty is to solve simultaneous integral equations based on the hypernetted chain approximation. This approach is often adopted to determine the distribution of ions in an electrical double layer. Lozada-Cassou [15], for example, used the hypernetted chain approximation associated with a mean spherical approximation to calculate the distribution of ions near a cylindrical electrode. It was shown that, if the linear size of an ion is infinitely small, and the radius of the electrode approaches infinity, the result reduces to that predicted by the Gouy–Chapman theory [16]. Zaini et al. [17] used the same approach to evaluate the distribution of ions in a cylindrical pore.

A bridge function was proposed to correct the deviation arises from the negligence of some of the graphs in the cluster diagram. Yeomans et al. [18] discussed the distance of ions within and surrounding a charged cylindrical pore by adopting a hypernetted chain/mean spherical approximation approach. It was concluded that the result obtained differs both quantitatively and qualitatively from that based on the Poisson–Boltzmann theory, especially for small pores. Greathouse and McQuarrie [19,20] discussed the electrical interaction force between two charged planar surfaces. A variational method was adopted to solve the hypernetted chain equations. In a study of the electrical interaction between two charged surfaces, Patey [21] solved a set of three hypernetted chain equations. Lozada-Cassou and co-workers [22–24] suggested using a three-point extension hypernetted chain method to improve the performance of the method proposed by Patey [21].

Reported theoretical analyses in the literature are mainly of one-dimensional nature. While the result derived in this limited domain provides valuable information, a systematic analysis in a higher-dimensional space is highly desirable for practical considerations [1]. This is done in the present work. One of the key problems which needs to be solved in this case is the treatment of the set of equations governing the spatial variation of particle concentration. The analysis is based on a hypernetted chain approximation, and an efficient solution procedure proposed. Three representative examples, namely, particles in a planar slit, a cylindrical pore, and a square duct, are discussed.

2. Modeling

The system under consideration is illustrated in Fig. 1 where monodispersed colloidal particles with scaled radius R , represented by open circles, are dispersed in an electrolyte solution, and the shaded area denotes a rigid object. The concentration of colloidal particles follows some distribution as a response to the presence of the object. The object can be a rigid wall, a closed boundary, or a relatively large particle having a concentration much dilute than that of the colloidal particles. The density distri-

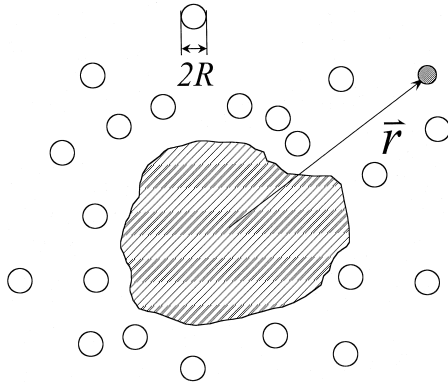


Fig. 1. Schematic representation of the system under consideration where the open circles represent the colloidal particles and the shaded area a relatively large object. R is the radius of a colloidal particle, and $\vec{r}$ the scaled vector from the gravity center of the object to that of a particle.

bution of colloidal particles, $\rho(\vec{r})$, can be expressed as [25]:

$$\rho(\vec{r}) = \rho_{\infty} g_{wc}(\vec{r}), \quad (1)$$

where ρ_{∞} and $g_{wc}(\vec{r})$ are, respectively, the bulk number concentration and the radial distribution of colloidal particles. The subscripts w and c denote the rigid object and the colloidal particle, respectively, and $\vec{r}$ the scaled vector from the gravity center of the former to that of the latter which is scaled by the factor $\rho_{\infty}^{-1/3}$, i.e.,

$$\vec{r} = \vec{r}_{\rho_{\infty}}^{1/3}, \quad (1a)$$

$\vec{r}$ being the center-to-center vector connecting object and colloidal particle. For the system shown in Fig. 1, $g_{wc}(\vec{r})$ can be determined by the Ornstein–Zernicke equations [25]:

$$h_{cc}(\vec{r}) = c_{cc}(\vec{r}) + \int_V h_{cc}(\vec{r}') c_{cc}(\vec{r} - \vec{r}') d\vec{r}', \quad (2a)$$

$$h_{wc}(\vec{r}) = c_{wc}(\vec{r}) + \int_V h_{wc}(\vec{r}') c_{cc}(\vec{r} - \vec{r}') d\vec{r}', \quad (2b)$$

with

$$g_{ij} = 1 + h_{ij}, \quad i, j = w, c. \quad (2c)$$

The integrations in Eqs. (2a) and (2b) are conducted over the space, and $c_{ij}(\vec{r})$ and $h_{ij}(\vec{r})$ are, respectively, the direct and indirect correlation functions

between entities i and j , $i, j = w, c$. The derivations of Eqs. (2a) and (2b) are based on the assumption that the concentration of w is low. Employing the hypernetted-chain approximation [25], we have

$$c_{ij}(\vec{r}) = h_{ij}(\vec{r}) - \ln[1 + h_{ij}(\vec{r})] - u_{ij}(\vec{r}),$$

$$i, j = w, c, \quad (3)$$

where $u_{ij}(\vec{r})$ is the scaled, paired potential energy between entities i and j . Eqs. (2a), (2b) and (3) lead to two independent problems. First, given ρ_{cc} and u_{cc} , we have to solve the following equations for h_{cc} and c_{cc} :

$$h_{cc}(r) = c_{cc}(r) + h_{cc}(r) * c_{cc}(r), \quad (4a)$$

$$c_{cc}(r) = h_{cc}(r) - \ln[1 + h_{cc}(r)] - u_{cc}(r), \quad (4b)$$

where the asterisk symbol denotes the convolution operator. Second, given c_{cc} and u_{wc} , we have to solve the following equations for h_{wc} and c_{wc} :

$$h_{wc}(\vec{r}) = c_{wc}(\vec{r}) + h_{wc}(\vec{r}) * c_{cc}(\vec{r}), \quad (5a)$$

$$c_{wc}(\vec{r}) = h_{wc}(\vec{r}) - \ln[1 + h_{wc}(\vec{r})] - u_{wc}(\vec{r}). \quad (5b)$$

For convenience, we assume that colloidal particles are spherical. In this case, both h_{cc} and c_{cc} are functions of the distance between two particles only, and the vector $\vec{r}$ can be replaced by its magnitude r .

The method proposed by Broyles et al. [26] is adopted to solve Eqs. (4a) and (4b). The first step is to extend the domain of h_{cc} and c_{cc} from $[0, \infty)$ to $(-\infty, \infty)$ by defining

$$h_{cc}(r) = h_{cc}(-r), \quad r \in (-\infty, 0], \quad (6a)$$

$$c_{cc}(r) = c_{cc}(-r), \quad r \in (-\infty, 0]. \quad (6b)$$

Also, we define

$$H_{cc} = r(h_{cc} - c_{cc}), \quad (7a)$$

$$G_{cc} = -rh_{cc}, \quad (7b)$$

$$I_{cc} = -rc_{cc} = H_{cc} - rh_{cc}, \quad (7c)$$

$$J_{cc} = -\int_{-\infty}^r I(s) ds. \quad (7d)$$

Therefore, Eqs. (4a) and (4b) can be rewritten as

$$H_{cc}(r) = 2\pi \left[\int_{-\infty}^{\infty} I_{cc}(r') J_{cc}(r - r') dr' - \int_{-\infty}^{\infty} H_{cc}(r') J_{cc}(r - r') dr' \right], \quad (8a)$$

$$h_{cc} = -1 + \exp(H_{cc}/r - u_{cc}). \quad (8b)$$

For a simpler numerical treatment, these expressions are transformed to the corresponding discrete forms as

$$H_{cc,n} = 2\pi\delta \left[\sum_{n'=-N}^N I_{cc,n'} J_{cc,(n-n')} - \sum_{n'=-N}^N H_{cc,n'} J_{cc,(n-n')} \right], \quad (9a)$$

$$h_{cc,n} = -1 + \exp(H_{cc,n}/n\delta - u_{cc,n}), \quad (9b)$$

where δ is a discretizing interval, N an integer sufficiently large such that $H_{cc,N} \approx 0$ for $|n| > N$, and F_n the corresponding discrete form of $F(r)$ i.e., $F_n = F(n\delta)$. The following iterative procedure is used to solve Eqs. (9a) and (9b):

Step 1. Guess an initial $H_{cc,n}$ and substitute it into Eq. (9b) to evaluate $h_{cc,n}$.

Step 2. Substitute $h_{cc,n}$ into Eq. (7c), and the resultant expression into Eq. (7d) to obtain $I_{cc,n}$ and $J_{cc,n}$.

Step 3. Substitute $I_{cc,n}$ and $J_{cc,n}$ into Eq. (9a), and take a discrete Fourier transform to obtain

$$\hat{H}_{cc,k} = \frac{2\pi \hat{f}_{cc,k} \hat{f}_{cc,k}}{1 + 2\pi \hat{f}_{cc,k}}, \quad -\infty < k < \infty, \quad (10)$$

where $\hat{F}_k$ is the Fourier transform coefficient of F_n .

Step 4. Take the inverse Fourier transform on $\hat{H}_{cc,k}$ to obtain $H_{cc,n}$, and substitute the resultant expression into Eq. (9b) to obtain the corrected $h_{cc,n}$. The procedure is repeated until $H_{cc,n}$ converges.

$F(n)$ can be recovered from F_n by choosing an appropriate interpolation method. A linear interpolation approximation is used in the present study. It can be shown that $H_{cc}(t)$, $I_{cc}(r)$, $J_{cc}(r)$, $G_{cc}(r)$ are negligible for $|r| \geq L$. Typically, L is on the order of six radii of a colloidal particle.

Note that in Eqs. (5a) and (5b), h_{wc} and c_{wc} are functions of vector $\vec{r}$, and not functions of scalar r . For a two-dimensional problem, we expand h_{wc} and c_{wc} as

$$h_{wc}(\vec{r}) = \sum_n h_{wc,n} N_n(\vec{r}, \vec{r}_n), \quad n = 1, 2, \dots, \quad (11)$$

$$c_{wc}(\vec{r}) = \sum_n c_{wc,n} N_n(\vec{r}, \vec{r}_n), \quad n = 1, 2, \dots, \quad (12)$$

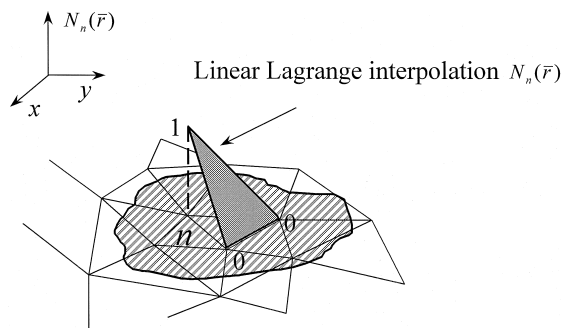


Fig. 2. Meshes used in the linear Lagrange interpolation of $N_n(\vec{r})$.

where n is a mesh node shown in Fig. 2, $h_{wc,n}$ the value of $h_{wc}(\vec{r})$ at n , and $N_n(\vec{r}, \vec{r}_n)$ an interpolation function, $\vec{r}_n$ being the vector pointing to node n . One of the interpolation functions often adopted is the linear Lagrange interpolation function, the property of which is shown in Fig. 2. This approach was used in a finite-element method to solve a variational problem [27]. It was also used by Zaini et al. [17] in the discussion of the double layer profile in a charged cylindrical pore. Substituting Eqs. (11) and (12) into Eqs. (5a) and (5b) and letting the residuals vanish at the nodes, we obtain

$$h_{wc,n} = c_{wc,n} + \sum_{n'} w_{n'} h_{wc,n'} \tilde{c}_{cc}(|\vec{r}_n - \vec{r}_{n'}|), \quad n = 1, 2, \dots, \quad (13a)$$

$$c_{wc,n} = h_{wc,n} - \ln(1 + h_{wc,n}) - u_{wc,n}, \quad n = 1, 2, \dots, \quad (13b)$$

where w_n is a weighting factor, which reflects the integral of interpolation functions over the area occupied by node n by all mesh elements enclosing node n , and $\tilde{c}_{cc}$ is defined as

$$\tilde{c}_{cc}(r) = \int_{-\infty}^{\infty} c_{cc}(\sqrt{r^2 + z^2}) dz. \quad (14)$$

Note that Eq. (13a) is linear and Eq. (13b) nonlinear algebraic equations. The former can be rewritten as

$$\bar{h}_{wc} - \bar{c}_{wc} = \bar{M} \bar{h}_{wc}, \quad (15)$$

where the (i, j) element of matrix $\bar{M}$ is $w_j \tilde{c}_{cc}(|\bar{r}_i - \bar{r}_j|)$, and

$$\bar{h}_{wc} = \begin{bmatrix} h_{wc,1} \\ h_{wc,2} \\ h_{wc,3} \\ \vdots \end{bmatrix}, \quad (15a)$$

$$\bar{c}_{wc} = \begin{bmatrix} c_{wc,1} \\ c_{wc,2} \\ c_{wc,3} \\ \vdots \end{bmatrix}. \quad (15b)$$

Substituting Eq. (15) into Eq. (13b) gives

$$\bar{h}_{wc} = -1 + \text{EXP}(\bar{M}\bar{h}_{wc} - \bar{u}), \quad (16)$$

where

$$\bar{u}_{wc} = \begin{bmatrix} u_{wc,1} \\ u_{wc,2} \\ u_{wc,3} \\ \vdots \end{bmatrix}, \quad (16a)$$

$$\text{EXP}(\bar{x}) = \begin{bmatrix} \exp(x_1) \\ \exp(x_2) \\ \exp(x_3) \\ \vdots \end{bmatrix}. \quad (16b)$$

Eq. (16) is solved by the Newton–Raphson method through using the iterative expression

$$\bar{h}_{wc(k+1)} = \bar{h}_{wc(k)} - \bar{S} \left[-1 + \text{EXP}(\bar{M}\bar{h}_{wc(k)} - \bar{u}_{wc}) - \bar{h}_{wc(k)} \right], \quad (17)$$

where $\bar{h}_{wc(k)}$ is the k th iterative solution with parameter ε , $0 < \varepsilon \leq 1$, and

$$\bar{S} = \left(\bar{M} \otimes \left[\text{EXP}(\varepsilon \bar{M}\bar{h}_{wc(k)} - \bar{u}_{wc}) \times [111 \cdots 1] - \bar{I} \right)^{-1}. \quad (18)$$

The operator $\otimes$ has the property

$$[a_{ij}] \otimes [b_{ij}] = [c_{ij}], \quad c_{ij} = a_{ij}b_{ij}. \quad (18a)$$

The parameter ε is designed to improve the performance of the present numerical scheme, which consists of the following steps:

Step 1. Assign a small value, say 0.1, to ε , and assume the initial guess

$$\bar{h}_{wc(0)}^\varepsilon = \text{EXP}(-\bar{u}_{wc}) - 1. \quad (19)$$

Step 2. Substitute this expression into Eq. (17), and evaluate $\bar{h}_{wc(1)}^\varepsilon$. Repeat this step until a convergent expression, $\bar{h}_{wc(\infty)}^\varepsilon$, is obtained.

Step 3. Increase the value of ε , use $\bar{h}_{wc(\infty)}^\varepsilon$ as the initial guess, and return to step 1. This is repeated until ε reaches unity.

3. Results

Three examples are discussed to illustrate the applicability of the present method. These include colloid particles in a planar slit, a cylindrical pore, and a square duct. The rectangular meshes shown in Fig. 3 are used in all these problems. According to Fig. 3, we have

$$w_n = A/4, \quad (20)$$

where A is the area of the mesh which encloses node n .

The distribution of colloidal particles depends on the energies of colloidal–colloidal and colloidal–object interactions. In the following discussions all the length scales are scaled by the inverse Debye length

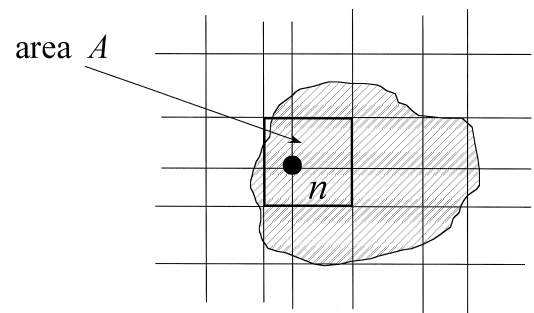


Fig. 3. Rectangular meshes used in the numerical simulation.

κ . A general expression for the colloidal–colloidal interaction energy, $u_{cc}(r)$, is [5,6]

$$u_{cc}(r) = 4\pi\epsilon_r\epsilon_0\kappa^{-1}R_1R_2Y_1Y_2\frac{\exp[-(r-R_1-R_2)]}{r}, \quad (21)$$

where subscripts 1 and 2 denote the properties of particles 1 and 2, respectively, ϵ_r and ϵ_0 are the relative permittivity of the liquid phase and the permittivity of a vacuum, respectively, r is the scaled center-to-center distance between two particles, R_i is the scaled radius of particle i , and Y_i is the scaled surface potential of particle i . Here we assume that the permittivity of the solid phase is much smaller than that of the liquid phase, as is usually the case in practice.

The interaction energy between colloidal particle and wall depends on their shapes and surface conditions. Suppose that it can be estimated through the linear superposition. Then, for the case of constant charge density, the interaction energy can be evaluated by

$$u_{wc}(r) = W\frac{1}{2}\rho_c\int\Psi_w^0 dS + W\frac{1}{2}\rho_w\int\Psi_c^0 dS, \quad (22)$$

where $W = \epsilon_r\epsilon_0k_B T/\kappa e^2$, k_B and T are, respectively, the Boltzmann constant and the absolute temperature, e is the elementary charge, ρ_c and ρ_w are, respectively, the scaled surface charge densities of a particle and the wall, Ψ_w^0 and Ψ_c^0 are the scaled surface potentials of an isolated wall and an isolated particle, respectively.

As an example, we consider porous (ion-penetrable) particles, which simulate a wide class of colloidal particles, such as biological cells and particles covered by an artificial membrane. In this case, Y_i , $i = 1, 2$, in Eq. (21) should be replaced by the scaled potential at particle–liquid interface, and ρ_c in Eq. (22) denotes the scaled volume charge density. It can be shown that for an ion-penetrable particle,

$$\Psi_c^0(r) = \rho_c \exp[-(r-R)][R-1 + \exp(-2R)(R+1)]/2r, \quad r \geq R, \quad (23)$$

where R is the radius of the particle, and the interaction energy between two ion-penetrable spheres is

$$u_{cc}(r) = W\pi\rho_c^2[\exp(R)(R-1) + \exp(-R)(R+1)]^2 \exp(-r)/r. \quad (24)$$

3.1. Planar slit

Consider a planar slit with a scaled width $2L$. Let R be the scaled radius of a particle. The origin of the coordinates (x, y) is located on the center line of the slit. For the case of a planar surface and an ion-penetrable sphere, the energy contributed by the latter is

$$u_c(r) = W\pi\rho_c\rho_w[\exp(R)(R-1) + \exp(-R)(R+1)]\exp(-r), \quad (25a)$$

and that by the former is

$$u_w(r) = \frac{W\pi\rho_c\rho_w}{2}[\exp(R)(R-1) + \exp(-R)(R+1)]\exp(-r). \quad (25b)$$

In this case, the electrical potential energy can be calculated by an image method [28]. We obtain

$$u_{wc}(x) = W\pi\rho_w\rho_c[\exp(R)(R-1) + \exp(-R) \times (R+1)]\frac{3\exp(-L)}{1-\exp(-2L)}[\exp(-x) + \exp(x)] + W\pi\rho_c^2[\exp(R)(R-1) + \exp(-R)(R+1)]^2 \times \left\{ \sum_{k=0}^{\infty} \left[\frac{\exp[-(2L+2x+4kL)]}{2L+2x+4kL} + \frac{\exp[-(2L-2x+4kL)]}{2L-2x+4kL} \right] + \sum_{k=1}^{\infty} \frac{2\exp(-4kL)}{4kL} \right\}. \quad (26)$$

3.2. Cylindrical pore

Let us consider a cylindrical pore with scaled diameter D . Let r be the scaled radial distance. It can be shown that

$$\Psi_w^0(r) = \frac{\rho_w I_0(r)}{I_1(D/2)}, \quad (27)$$

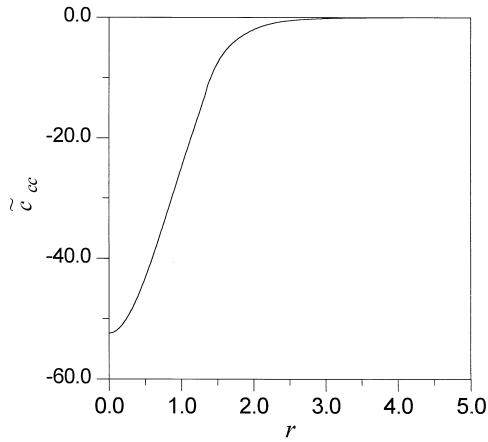


Fig. 4. Variation of $\tilde{c}_{cc}$ as a function of the radial distance r . The interaction energy between two colloidal particles is calculated by Eq. (24). Key: the liquid phase is a 0.01 M 1:1 electrolyte solution, $T = 298$ K, $\epsilon_f = 78$, $\rho_c = 6$, $\rho_w = 2$, $\rho_\infty = 6 \times 10^{23}$ no./m³, and $R = 5 \times 10^{-9}$ m.

where I_0 and I_1 are the modified Bessel functions of first kind of orders zero and one, respectively, r and D are, respectively, the radial distance and the diameter of the pore. $u_{wc}(r)$ can be calculated by substituting Eqs. (23) and (27) into Eq. (22).

3.3. Square duct

Consider a square duct with scaled width $2L$. The origin of the coordinates (x, y) is located at the center of the duct. We assume that the electrical energy between wall and particle, u_{wc} , can be estimated through linear superposition, and the square duct simulated by the combination of two perpendicular planar slits. Therefore, after neglecting some higher-order images, we have

$$\begin{aligned}
 u_{wc}(x, y) = & u_{wc}(x) + u_{wc}(y) \\
 & + u_{cc} \left[2\sqrt{(L - |x|)^2 + (L - |y|)^2} \right] / 2 \\
 & + u_{cc} \left[2\sqrt{(L - |x|)^2 + (L + |y|)^2} \right] / 2 \\
 & + u_{cc} \left[2\sqrt{(L + |x|)^2 + (L - |y|)^2} \right] / 2 \\
 & + u_{cc} \left[2\sqrt{(L + |x|)^2 + (L + |y|)^2} \right] / 2 \\
 & + o[\exp(-2L)/2L]. \quad (28)
 \end{aligned}$$

Here, $u(r)$ is scaled by

$$u(r) = u(r\rho_\infty^{-1/3}\kappa). \quad (29)$$

The simulated variation in the modified direct correlation function $\tilde{c}_{cc}$ defined in Eq. (14) as a function of the distance x for the case of planar slit is shown in Fig. 4. This figure reveals that $\tilde{c}_{cc}$ becomes negligible if x is ≥ 2 . This means that the integration limits in Eq. (14) can be narrowed down, and the computational efficiency improved significantly. The effective range of $\tilde{c}_{cc}$ also has an influence on the computational domain.

By referring to Fig. 5, in the estimation of h_{wc} through Eqs. (13a) and (13b), its value is assumed to be negligible for a point outside the computational domain Ω , which is defined by $|x| \leq (L + E_1)$ and $|y| \leq E_2$. To avoid the deviation caused by this assumption, E_1 and E_2 need to be chosen adequately. Apparently, the effective range of $\tilde{c}_{cc}$ should be taken into account. Fig. 6 shows the variation of h_{wc} as a function of x at y for various E_1 . As can be seen from this figure, the result for $E_1 = 3$ is close to that for $E_1 = 2$, the effective range of $\tilde{c}_{cc}$. In other words, the range of x in Ω should cover at least the effective range of $\tilde{c}_{cc}$. Fig. 7 shows the magnitude of E_2 on the variation of h_{wc} as a function of x in a slit. As can be seen from this figure, an E_2 greater than 6 should be chosen.

Fig. 8 shows the variation of h_{wc} as a function of x at various widths of a planar slit, measured by R/L . For the present case, the average concentration of colloidal particles for $R/L = 0.1, 0.3$, and 0.5 ,

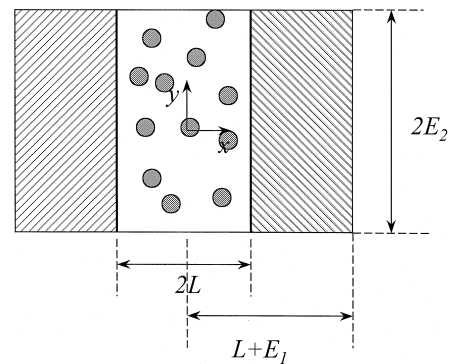


Fig. 5. The computational domain, defined by $|x| \leq (L + E_1)$ and $|y| \leq E_2$, for the case of a planar slit.

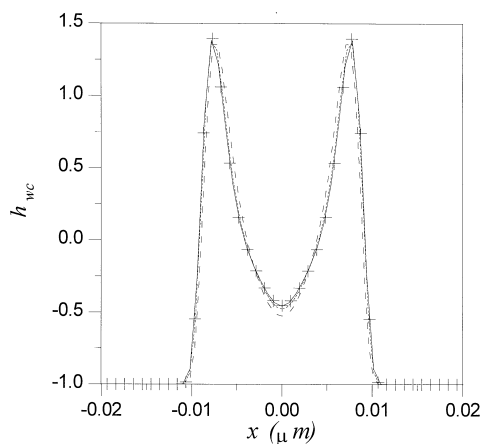


Fig. 6. Variation of h_{wc} as a function of position variable x for the case of a planar slit at various E_1 . Parameters used are: $R/L = 0.3$, and $E_2 = 6$. — — —: $E_1 = 0.5$; - - -: $E_1 = 1$; ———: $E_1 = 2$; + + +: $E_1 = 3$. Key: same as Fig. 4.

are, respectively, 6.09×10^{23} , 6.31×10^{23} , and 6.83×10^{23} no./m³. That is, under the conditions assumed, the narrower the slit, the higher the concentration of colloidal particles. Therefore, narrowing the width of a slit has the effect of increasing the mean concentration of particles inside. The same conclusion can be drawn for the cases examined by Anderson and Brannon [9] and Glandt [10].

The effect of electrical interaction between particle and wall on the distribution of the former in a

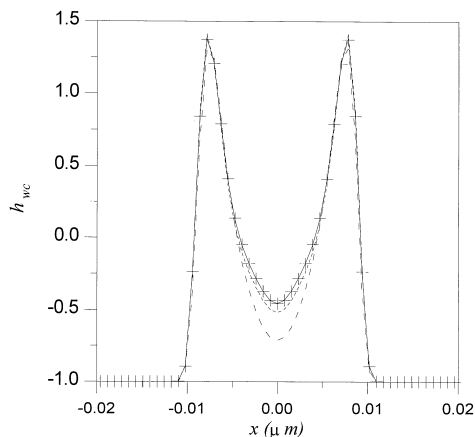


Fig. 7. Variation of h_{wc} as a function of position variable x for the case of a planar slit at various E_2 . Parameters used are $R/L = 0.3$, and $E_1 = 2$. — — —: $E_2 = 1.5$; - - -: $E_2 = 3$; ———: $E_2 = 6$; + + +: $E_2 = 8$. Key: same as Fig. 4.

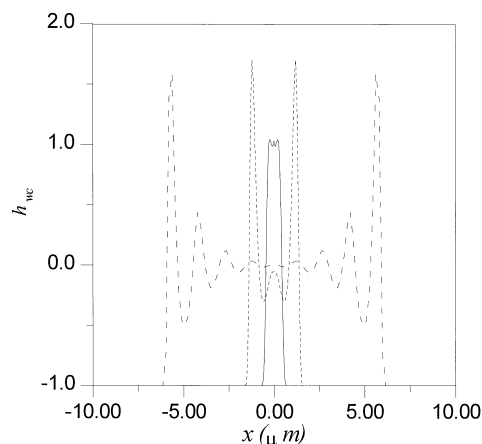


Fig. 8. Variation of h_{wc} as a function of x at various width of a planar slit, measured by R/L . $R/L = 0.1$: — — —; $R/L = 0.3$: - - -:; $R/L = 0.5$: ———. Key: same as Fig. 4.

planar slit is presented in Fig. 9. As can be seen from this figure, increasing the electrical repulsive interaction between particle and wall has the effect of decreasing the mean particle concentration in the slit. This is expected, since the greater the repulsive interaction between particle and wall, the less favorable for particles to enter the slit. The average concentration in the slit for $u_{wc}/u_{wc}^* = 0.5$, 1, and 2 are,

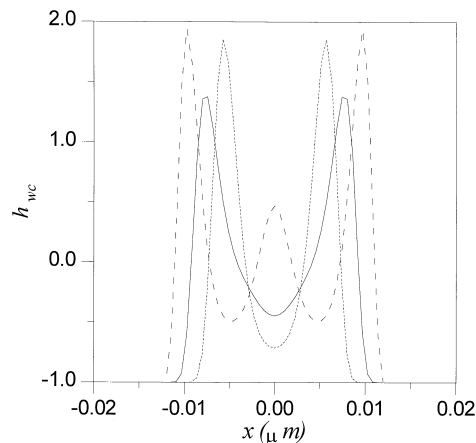


Fig. 9. Variation of h_{wc} as a function of x at various interaction energy between wall and particle u_{wc} for the case where $R/L = 0.3$. The interaction energy u_{wc}^* is calculated by Eq. (26). — — —: $u_{wc}/u_{wc}^* = 0.5$; ———: $u_{wc}/u_{wc}^* = 1$; - - -: $u_{wc}/u_{wc}^* = 2$, u_{wc}^* being the value of u_{wc} evaluated under the conditions of Fig. 7. Key: same as Fig. 4.

respectively, 7.30×10^{23} , 6.31×10^{23} , and 5.34×10^{23} no./m³, where u_{wc}^* is the value of u_{wc} under the conditions of Fig. 4. On the other hand, the greater the electrical repulsive interaction between two particles, the higher the average concentration of particles in a slit, as can be seen from Fig. 10. For example, the average concentration of colloidal particles in the slit for $u_{cc}/u_{cc}^* = 0.5$, 1, and 2, are, respectively, 4.98×10^{23} , 6.31×10^{23} , and 6.78×10^{23} no./m³, where u_{cc}^* is the value of u_{cc} under the conditions of Fig. 4. As can be seen in Fig. 11, the higher the bulk concentration of colloidal particles, the higher the average particle concentration in a slit. The average concentration of colloidal particles in the slit for $\rho_\infty = 6 \times 10^{23}$, 4×10^{23} , and 2×10^{23} no./m³ are, respectively, 6.31×10^{23} , 3.73×10^{23} , and 1.37×10^{23} no./m³. Note that the ratio (average particle concentration in slit/ ρ_∞) decreases nonlinearly with ρ_∞ .

The variation of h_{wc} as a function of the radial distance r at various radius of a cylindrical pore is presented in Fig. 12. The value of u_{cc} is obtained from Eq. (24), and u_{wc} from Eq. (22). This figure suggests that the larger the cylindrical pore, the closer the result to that for a planar slit. This is expected since the larger the pore, the less significant the curvature effect, and the closer the pore to a

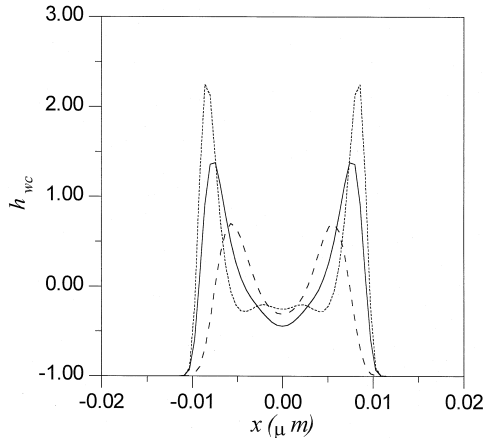


Fig. 10. Variation of h_{wc} as a function of x at various interaction energy between two colloidal particles u_{cc} for the case where $R/L = 0.3$. The interaction energy u_{wc}^* is calculated by Eq. (24). —: $u_{cc}/u_{cc}^* = 0.5$; ---: $u_{cc}/u_{cc}^* = 1$; ...: $u_{cc}/u_{cc}^* = 2$, u_{cc}^* being the value of u_{cc} evaluated under the conditions of Fig. 4. Key: same as Fig. 4.

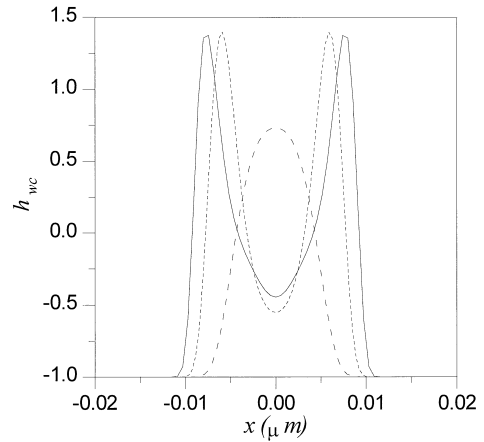


Fig. 11. Variation of h_{wc} as a function of x at various ρ_∞ for the case where $R/L = 0.3$. —: $\rho_\infty = 6 \times 10^{23}$ no./m³; ---: $\rho_\infty = 4 \times 10^{23}$ no./m³; ...: $\rho_\infty = 2 \times 10^{23}$ no./m³. Key same as Fig. 4.

planar surface. The average particle concentration for $2R/D = 0.1$, 0.3, and 0.5, are, respectively, 6.77×10^{23} , 7.64×10^{23} , and 13.3×10^{23} no./m³.

Fig. 13 shows the variation of h_{wc} for the case of a square duct with $R/L = 0.3$. Similar to the case of Fig. 8, the spatial variation of h_{wc} has a maximum at a distance about R from the wall, and decreases oscillatory with the distance away from the wall. This implies that a layer of colloidal particles is

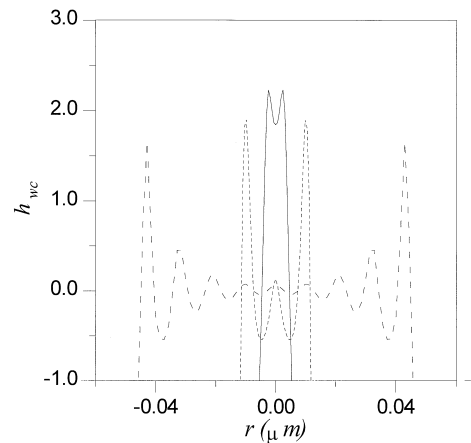


Fig. 12. Variation of h_{wc} as a function of r at various radius of cylindrical pore. —: $2R/D = 0.1$; ---: $2R/D = 0.3$; ...: $2R/D = 0.5$. u_{cc} is calculated by Eq. (24), and u_{wc} obtained by Eq. (22). Key: same as Fig. 4.

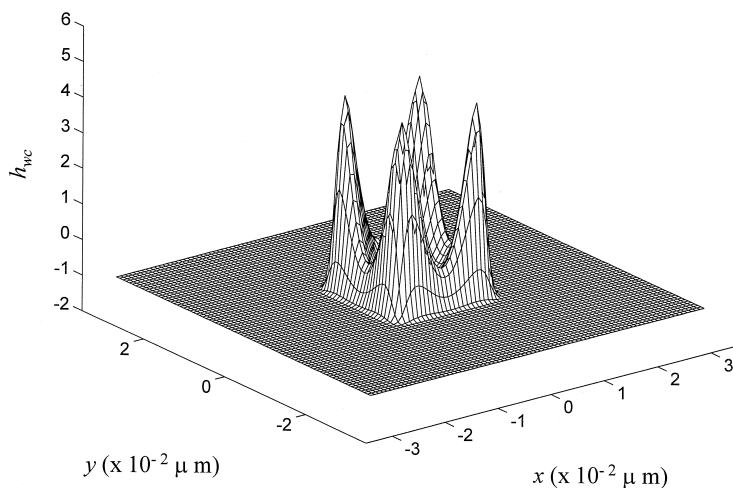


Fig. 13. Variation of h_{wc} as a function of x and y for a square duct with $R/L = 0.3$ and $\rho_{\infty} = 6 \times 10^{23}$ no./m³. Key: same as Fig. 4.

formed near the wall. The qualitative behavior of the spatial variation of the concentration of colloidal particles predicted by the present study is consistent with that observed experimentally [1]. The maximum and the oscillatory behavior of the spatial variation of h_{wc} disappear, however, if the bulk particle concentration ρ_{∞} is low, as can be seen from Fig. 14. This is because that as ρ_{∞} decreases, the available space for particles increases. The average particle concentration for $R/L = 0.1, 0.3$, and 0.5 , are, re-

spectively, 6.15×10^{23} , 6.37×10^{23} , and 6.74×10^{23} no./m³ under the conditions of Fig. 4.

In summary, the hypernetted chain approximation is applied to evaluate the direct correlation functions of particle–particle and particle–object interactions. These functions are readily applicable to the determination of the spatial distribution of colloidal particles in the presence of an energy field. Since the direct correlation functions are described by two independent equations, the present analysis is also applicable

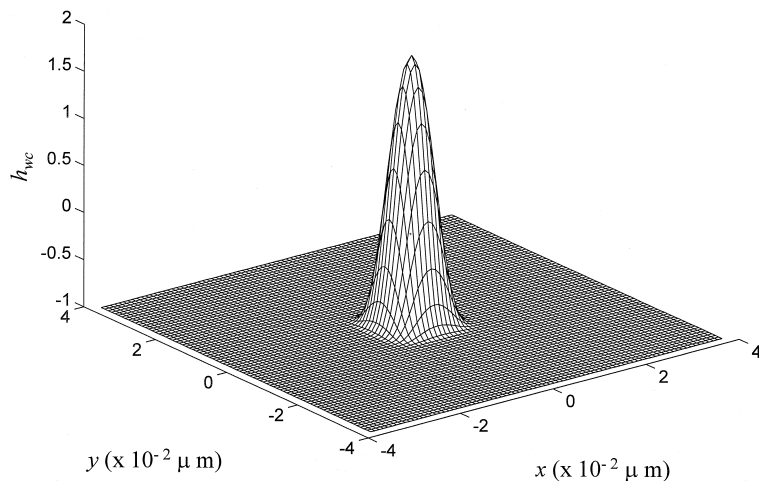


Fig. 14. Variation of h_{wc} as a function of x and y for a square duct with $R/L = 0.3$, and $\rho_{\infty} = 2 \times 10^{23}$ no./m³. Key: same as Fig. 4.

if the hypernetted chain approximation for the direct correlation function of particle–particle interaction is replaced by the mean spherical approximation [2–4], and/or that for the direct correlation function of particle–wall interaction replaced by the Percus–Yevick approximation. Although only three special cases are examined in the numerical simulation, i.e., planar slit, cylindrical pore, and square duct, the present method can be extended directly to an arbitrary two-dimensional problem.

Acknowledgements

This work is supported by the National Science Council of the Republic of China.

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