Settling of Polydisperse Particles with Thin Double Layer at Small Péclet Number

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The special-function expansion method is used to solve the sedimentation problem of polydisperse colloid particles with thin double layer. The pair-distribution function is expanded into Legendre polynomials. The recurrence formulas for calculating the coefficients of the Legendre polynomials and the expressions for calculating the sedimentation coefficient are deduced analytically. Then, the sedimentation of polydisperse particles with thin double layer at small Péclet number is analyzed numerically by the perturbation method. Results indicate that the sedimentation of potential interacting particles is more complex than that of the hard spheres, and the existence of the thin double layer affects the particles settling heavily. Critical double-layer thickness exists, without which a colloid system may change from a stable one into an unstable one and the hindered settling may change into accelerated settling.

Introduction

Sedimentation of small particles in a suspension is a basic problem in colloid science and has important practical value in many industries. Numerous investigations have been made into the sedimentation in a dilute, stable suspension, yet only two special cases have been concentrated on, namely, the sedimentation of hard spheres (Batchelor, 1972; Reed and Anderson, 1980; Batchelor and Wen, 1982; Kops-Werkhoven et al., 1982; Davis and Birdsell, 1988; Al-naafa and Selim, 1992) and the sedimentation of spheres with interacting potential in a monodisperse system (Batchelor and Wen, 1982; Russel et al., 1989; Petsev and Denkov, 1992; Thies-Weesie et al., 1995; Dhont, 1996; Nägele, 1996). In an earlier article, we showed (Wang and Wen, 1998) that in a monodisperse system with a thin double layer, particles settle more quickly than hard spheres when the attractive interparticle potential exceeds the repulsive potential; whereas, when the repulsive interparticle potential exceeds the attractive potential, the reverse occurs. When the attraction greatly exceeds the repulsion, for example, when the double-layer thickness is less than the critical value, even a stable suspension changes to an unstable one, and the hindered settling turns into an accelerated settling.

On the other hand, although the sedimentation in a polydisperse suspension also should be heavily affected by the interparticle potential, study has been hindered by two key problems. The first is the lack of a reasonable way to deal with the interparticle potential for a stable colloid system; the second is discovering how to solve the pair-distribution equation for a colloid system with interparticle potential. In a monodisperse suspension, the pair-distribution function (PDF) of the potential interacting spheres follows the well-known Boltzmann distribution, so the second problem can be avoided and one can focus on the influence of the interparticle potential. We analyzed this problem in the same article just cited (Wang and Wen, 1998) and established a new potential model for colloid particles with a thin double layer, which could explain the sedimentation experimental data better than before. We now extend these results to the problem of sedimentation in a polydisperse suspension, the PDF is expanded into Legendre polynomials, and then the expressions for calculating the sedimentation coefficient are deduced. Subsequently, the coefficients of the Legendre polynomials representing the radial parts of the PDF are further expanded into a power series of small Péclet number, which is a measure of the ratio of gravitational convection to Brownian diffusion, thereby deriving an approximate solution for the PDF and the sedimentation coefficient for a polydisperse suspension with a thin double layer at a small Péclet number. Also discussed are numerical results for the PDF and the sedimentation coefficient.

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Expansion of the PDF into Legendre Polynomials

The microstructure of a dilute colloid system is described by the PDF, p_{ij}, which is the solution of the pair-distribution equation (Wen, 1996)

$$\frac{\partial \rho_{ij}}{\partial t} = -\nabla\cdot(V_{ij} p_{ij}) + \nabla\cdot\left\{ p_{ij} D_{ij}\cdot\nabla\left(\frac{\Phi_{ij}}{kT}\right)\right\} + \nabla\cdot(D_{ij}\cdot\nabla p_{ij}), \quad (1)$$

where p_{ij} is defined as the probability that the center of sphere j (with radius a_j and density ρ_j) lies with unit volume at position r relative to the center of the test sphere i (with radius a_i and density ρ_i); V_{ij} is the relative gravitational velocity of the two spheres; D_{ij} is the relative Brownian diffusivity tensor of the two spheres; Φ_{ij} is interparticle potential; and kT is the thermal energy of Brownian particles. V_{ij} and D_{ij} can be expressed as (Batchelor, 1982)

$$V_{ij} = V_{ij}^{(0)}\cdot\left\{ L(s)\frac{ss}{s^2} + M(s)\left(I - \frac{ss}{s^2}\right)\right\} \quad (2)$$

and

$$D_{ij} = D_{ij}^{(0)}\cdot\left\{ G(s)\frac{ss}{s^2} + H(s)\left(I - \frac{ss}{s^2}\right)\right\}. \quad (3)$$

Here s is the dimensionless center-to-center separation between two spheres scaled on the average radius $(a_i + a_j)/2$; $V_{ij}^{(0)}$ is the relative velocity; and $D_{ij}^{(0)}$ is the relative Brownian diffusivity when the two spheres are far apart from each other. The four scalar functions L, M, G, and H can be obtained from the low-Reynolds-number hydrodynamics (Jeffrey and Onishi, 1984).

Choosing $V_{ij}^{(0)}$ as the representative magnitude of V_{ij} and $D_{ij}^{(0)}$, the representative magnitude of D_{ij}, for stable systems, Eq. 1 reduces to its dimensionless form:

$$Pe\cdot\nabla\cdot\left(\frac{V_{ij}}{V_{ij}^{(0)}} p_{ij}\right) - \nabla\cdot\left\{ p_{ij}\frac{D_{ij}}{D_{ij}^{(0)}}\cdot\nabla\left(\frac{\Phi_{ij}}{kT}\right)\right\} - \nabla\cdot\left(\frac{D_{ij}}{D_{ij}^{(0)}}\cdot\nabla p_{ij}\right) = 0, \quad (4)$$

in which the Péclet number is defined as

$$Pe = \frac{1}{2}\frac{(a_i + a_j)V_{ij}^{(0)}}{D_{ij}^{(0)}}. \quad (5)$$

The boundary conditions corresponding to Eq. 4 may be written as

$$\begin{cases} s\cdot\left(Pe\dfrac{V_{ij}}{V_{ij}^{(0)}} p_{ij} - \dfrac{D_{ij}}{D_{ij}^{(0)}}\cdot\nabla\left(\dfrac{\Phi_{ij}}{kT}\right) p_{ij} - \dfrac{D_{ij}}{D_{ij}^{(0)}}\cdot\nabla p_{ij}\right) = 0 & (s = s_{15kT}), \\ p_{ij} = 1, & (s\to\infty), \end{cases} \quad (6)$$

where s_{15kT} represents the cutoff position of the interparticle potential presented in the earlier article (Wang and Wen, 1998).

The pair-distribution equation (Eq. 4) cannot be solved analytically. Different methods have been used to solve it approximately for different purposes (Batchelor and Wen, 1982; Wang and Wen, 1990; Zinchenko and Davis, 1994). In this article, investigations begin with the expansion of the PDF into Legendre polynomials in consideration of its axis symmetry around the gravity direction. We express the PDF as

$$p_{ij}(s,\theta) = \sum_{n=0}^{\infty} R_n(s) P_n(\cos\theta), \quad (7)$$

in which $P_n(\cos\theta)$ are the Legendre polynomials, the function $R_n(s)$ denotes the radial parts of the PDF; and θ is the polar angle between s and the polar axis along which the sphere of species j enters. Substituting Eq. 7 into Eq. 4, and using the recurrent properties of the Legendre polynomials, we obtain the recurrence formulas for $R_n(s)$:

$$R_1 = \frac{1}{Pe}\frac{3G}{L}\left(\frac{d(\Phi_{ij}/kT)}{ds} R_0 + \frac{dR_0}{ds}\right), \quad (8)$$

and for $n \geq 2$,

$$\begin{aligned} & Pe\cdot\frac{n}{2n+1}\frac{d}{ds}(s^2 L R_n) + Pe\cdot sM\frac{n(n-1)}{2n+1} R_n \\ & - \left[\frac{d}{ds}\left(s^2 G\frac{d(\Phi_{ij}/kT)}{ds} R_{n-1} + s^2 G\frac{dR_{n-1}}{ds}\right) - n(n-1) H R_{n-1}\right] \\ & + Pe\cdot\frac{n-1}{2n-3}\frac{d}{ds}(s^2 L R_{n-2}) - Pe\cdot sM\frac{n(n-1)}{2n-3} R_{n-2} = 0. \quad (9) \end{aligned}$$

The corresponding boundary conditions for $R_n(s)$ are given by

$$\begin{cases} Pe\cdot\dfrac{n}{2n+1} L R_n - G\left(\dfrac{d(\Phi_{ij}/kT)}{ds} R_{n-1} + \dfrac{dR_{n-1}}{ds}\right) + Pe\cdot\dfrac{n-1}{2n-3} L R_{n-2} = 0 & (s = s_{15kT}), \\ R_{n=0} = 1, \quad R_{n\neq 0} = 0 & (s\to\infty). \end{cases} \quad (10)$$

It should be noticed here that Eq. 8 is a special result of equation

$$Pe\cdot\frac{1}{3} L R_1 - G\left(\frac{d(\Phi_{ij}/kT)}{ds} R_0 + \frac{dR_0}{ds}\right) = \frac{C}{4\pi s^2}, \quad (11)$$

the righthand side of which represents the flux of sphere j across the surface with radius s. The constant C is zero for a stable system, thereby Eq. 11 transforming to Eq. 8; and nonzero for an unstable system.

One specific objective of the study on the sedimentation in a dilute suspension is to calculate the sedimentation coefficient S_{ij} defined by the expression (Batchelor, 1982; Batchelor and Wen, 1982)

$$\langle U_i \rangle = U_i^{(0)} \left(1 + \sum_{j=1}^{m} S_{ij} \phi_j \right) \qquad (i = 1, 2, \ldots, m) \qquad (12)$$

for the mean velocity of spheres of species i correct to the order of the first power of the total particle volume fraction $\phi(=\sum_{j=1}^{m} \phi_j)$. Here $U_i^{(0)}$ is the velocity of an isolated sphere of species i under gravity. The summation is over the m different species of particle in the suspension. The sedimentation coefficient S_{ij} is a function of the ratios of the radii and of the reduced densities of the spheres of species i and j denoted by $\lambda = a_j/a_i$ and $\gamma = (\rho_j - \rho)/(\rho_i - \rho)$, respectively.

According to Batchelor's theory (Batchelor, 1982), the sedimentation coefficient of a dilute suspension can be decomposed into independent direct contributions from gravity, interparticle force, and Brownian thermodynamic force, namely, $S_{ij} = S_{ij}^{(G)} + S_{ij}^{(I)} + S_{ij}^{(B)}$, where $S_{ij}^{(G)}$ denotes the contribution from gravity, and it reads

$$S_{ij}^{(G)} = \left(\frac{1+\lambda}{\lambda} \right)^3 \left(\frac{g \cdot J \cdot g}{g^2} + \gamma \lambda^2 \frac{g \cdot J'' \cdot g}{g^2} \right) - \gamma(\lambda^2 + 3\lambda + 1), \qquad (13)$$

in which

$$J = \frac{3}{4\pi} \int \left[A_{11} \frac{ss}{s^2} + B_{11} \left(I - \frac{ss}{s^2} \right) - I \right] p_{ij}(s)\, ds, \qquad (14)$$

$$J'' = \frac{3}{4\pi} \frac{2\lambda}{1+\lambda} \int \left\{ \left[A_{12} \frac{ss}{s^2} + B_{12} \left(I - \frac{ss}{s^2} \right) \right] p_{ij}(s) - \left[\frac{3}{4s} \left(I + \frac{ss}{s^2} \right) + \frac{1+\lambda^2}{(1+\lambda)^2 s^3} \left(I - \frac{3ss}{s^2} \right) \right] \right\} ds, \qquad (15)$$

and $S_{ij}^{(I)}$ denotes the contribution from the interparticle force. It reads

$$S_{ij}^{(I)} = \frac{3}{8\pi} \frac{\gamma\lambda^2 - 1}{Pe} \frac{(1+\lambda)^2}{4\lambda^2} \cdot \int \left(A_{11} - \frac{2}{1+\lambda} A_{12} \right) \frac{s \cdot V_{ij}^{(0)}}{s V_{ij}^{(0)}} \frac{d(\Phi_{ij}/kT)}{ds} p_{ij}(s)\, ds, \qquad (16)$$

and $S_{ij}^{(B)}$ denotes the contribution from the Brownian thermodynamic force. It reads

$$S_{ij}^{(B)} = \frac{3}{4\pi} \frac{\gamma\lambda^2 - 1}{Pe} \frac{(1+\lambda)^2}{4\lambda^2} \int \left\{ \frac{A_{11} - B_{11}}{s} + \frac{1}{2} \frac{dA_{11}}{ds} - \frac{2(A_{12} - B_{12})}{(1+\lambda)s} - \frac{1}{1+\lambda} \frac{dA_{12}}{ds} \right\} \frac{s \cdot V_{ij}^{(0)}}{s V_{ij}^{(0)}} (1 - p_{ij})\, ds. \qquad (17)$$

In Eqs. 14–17, A_{11}, A_{12}, B_{11}, and B_{12} are four mobility functions given by Jeffrey and Onishi (1984). Substituting Eq. 7 into Eqs. 13, 16, and 17 finally yields the following three expressions:

$$S_{ij}^{(G)} = \frac{2}{5} \left(\frac{1+\lambda}{2\lambda} \right)^3 \int \left[A_{11} - B_{11} + \frac{2\gamma\lambda^3}{1+\lambda} (A_{12} - B_{12}) \right] R_2 s^2\, ds + \left(\frac{1+\lambda}{2\lambda} \right)^3 \int \left\{ \left[A_{11} + 2B_{11} + \frac{2\gamma\lambda^3}{1+\lambda} (A_{12} + 2B_{12}) - 3 \right] R_0 - \frac{6\gamma\lambda^3}{1+\lambda} \frac{1}{s} \right\} s^2\, ds - \gamma(\lambda^2 + 3\lambda + 1), \qquad (18)$$

$$S_{ij}^{(I)} = \frac{\gamma\lambda^2 - 1}{Pe} \frac{(1+\lambda)^2}{8\lambda^2} \cdot \int \left(A_{11} - \frac{2}{1+\lambda} A_{12} \right) \frac{d(\Phi_{ij}/kT)}{ds} R_1 s^2\, ds, \qquad (19)$$

and

$$S_{ij}^{(B)} = -\frac{\gamma\lambda^2 - 1}{Pe} \frac{(1+\lambda)^2}{8\lambda^2} \int \left\{ \frac{A_{11} - B_{11}}{s} + \frac{1}{2} \frac{dA_{11}}{ds} - \frac{2(A_{12} - B_{12})}{(1+\lambda)s} - \frac{1}{1+\lambda} \frac{dA_{12}}{ds} \right\} R_1 s^2\, ds. \qquad (20)$$

Thus, calculation of the sedimentation coefficient for a dilute and stable suspension has been reduced to the calculations of $R_n(s)$ as well as the three sedimentation integrals in Eqs. 18, 19, and 20. It is interesting that, although the full description of the PDF of $R_n(s)$ for each n needs to be known, the sedimentation coefficient concerns only $R_0(s)$, $R_1(s)$, and $R_2(s)$, owing the orthogonal properties of the Legendre polynomials.

PDF for Polydisperse Systems at Small Péclet Number

Equations 8 and 9 are complex recurrence formulas including differentials of $R_n(s)$, and generally speaking $R_n(s)$ cannot be derived analytically. However, if the situation was restricted to the case of small Péclet number ($Pe \ll 1$), we can continue the derivation of the PDF by expanding $R_n(s)$ into a power series of Pe.

Suppose $R_n(s)$ can be expanded into a power series of small Péclet numbers. For the first step, we write $R_0(s)$ as

$$R_0(s) = e^{-\Phi_{ij}/kT} \cdot \left[1 + \int \frac{L}{3G} f(s) \cdot ds \right], \qquad (21)$$

in which $f(s)$ should be a power series of Pe. Substituting Eq. 21 into Eq. 8, one obtains

$$R_1(s)=\frac{1}{Pe}\cdot e^{-\Phi_{ij}/kT}\cdot f(s). \tag{22}$$

It is necessary that the PDF reaches the Boltzmann distribution $e^{-\Phi_{ij}/kT}$ in the limit $Pe\to 0$. It demands that $R_0(s)\to e^{-\Phi_{ij}/kT}$ and $R_n(s)\to 0$ for $n\geq 1$. Thus, $f(s)$ should behave like $Pe^2\cdot Q(s)+o(Pe^2)$. Now we rewrite $R_0(s)$ and $R_1(s)$ as

$$R_0(s)=e^{-\Phi_{ij}/kT}\cdot\left[1+Pe^2\cdot\int\frac{L}{3G}Q(s)\cdot ds+o(Pe^2)\right], \tag{23}$$

$$R_1(s)=e^{-\Phi_{ij}/kT}\cdot[Pe\cdot Q(s)+o(Pe)]. \tag{24}$$

Substituting Eqs. 23 and 24 into Eq. 9 and neglecting the terms of order Pe^2, we are left with

$$\frac{2}{5}\frac{d}{ds}(s^2LR_2)+\frac{2}{5}sMR_2=\frac{d}{ds}(s^2Ge^{-\Phi_{ij}/kT}Q)-2He^{-\Phi_{ij}/kT}Q-\frac{d}{ds}(s^2Le^{-\Phi_{ij}/kT})+2sMe^{-\Phi_{ij}/kT}. \tag{25}$$

Just as with the constraints on $R_0(s)$ and $R_1(s)$ discussed earlier, the sum of the righthand terms of Eqs. 25 should be zero, or a term of order Pe^0 will appear in $R_2(s)$. That is to say, the function $Q(s)$ ought to be the solution of equation

$$\frac{d}{ds}\left(s^2G\frac{dQ}{ds}\right)-\frac{d(\Phi_{ij}/kT)}{ds}s^2G\frac{dQ}{ds}-2HQ=s^2W-\frac{d(\Phi_{ij}/kT)}{ds}s^2L, \tag{26}$$

which is consistent with the result given by Batchelor and Wen (1982). Here the function $W(s)$ has the form (Batchelor, 1982)

$$W(s)=\frac{2(L-M)}{s}+\frac{dL}{ds}. \tag{27}$$

The boundary conditions of $Q(s)$ corresponding to Eq. 26 are

$$\begin{cases} G\cdot\frac{dQ}{ds}-L=0 & (s=s_{15\,kT}),\\ Q\to 0 & (s\to\infty). \end{cases} \tag{28}$$

To summarize, the PDF for a dilute, polydisperse suspension at small Péclet number may be approximately expressed as

$$p_{ij}(s,\theta)=e^{-\Phi_{ij}/kT}[1+Pe\cdot Q(s)\cos\theta]. \tag{29}$$

For monodisperse suspensions, the spherically symmetric Boltzmann distribution is the exact solution of the PDF, whereas now it is only the leading term of the approximate solution (Eq. 29). Substituting $R_0(s)$ into Eq. 18 and $R_1(s)$ into Eqs. 19 and 20, respectively, considering that both $S_{ij}^{(I)}$ and $S_{ij}^{(B)}$ are preceded by a constant inversely proportional to Pe, one obtains the sedimentation coefficient corrected to Pe^0 for polydisperse suspensions at a small Péclet number. The result is more complex than that of the monodisperse case (Wen, 1996).

Interparticle Potential

Typically, the potential interaction between two hydrosol particles consists of the electric repulsive double-layer potential and the van der Waals attractive potential. A practical way to deal with the interparticle potential for the stable suspension of small particles with a thin double-layer presented in the previous article (Wang and Wen, 1998) is employed here. It has the form

$$\Phi=\begin{cases}\infty & (s<s_{15\,kT}),\\ V_A+V_R & (s\geq s_{15\,kT}).\end{cases} \tag{30}$$

Here V_A denotes the van der Waals attractive potential, which can be expressed as (without retardation) (Russel et al., 1989)

$$V_A=-\frac{A}{6}\times\left[\frac{8\lambda}{(s^2-4)(1+\lambda)^2}+\frac{8\lambda}{s^2(1+\lambda)^2-4(1-\lambda)^2}+\ln\frac{(s^2-4)(1+\lambda)^2}{s^2(1+\lambda)^2-4(1-\lambda)^2}\right], \tag{31}$$

where A is the composite Hamaker constant. In Eq. 30, V_R denotes the electrical repulsive double-layer potential, and depending on the thin double layer and low surface potential, it can be expressed as (Russel et al., 1989)

$$V_R=4\pi\epsilon\epsilon_0 a_i\psi_s^2\cdot\frac{\lambda}{(1+\lambda)}\cdot\ln[1+\exp(-\kappa(s-2))], \tag{32}$$

where ϵ is the relative dielectric constant of the medium; ϵ_0 is the dielectric constant of vacuum; ψ_s is the surface potential; and the dimensionless Debye screening parameter, κ, can be expressed as

$$\kappa=\frac{(a_i+a_j)}{2}\frac{1}{\xi_{0,\,D}}. \tag{33}$$

Here the double-layer thickness, $\xi_{0,\,D}$, and the surface potential are two independent parameters of the repulsive potential. The surface potential, which is relevant to the surface charges of a hydrosol sphere, describes the strength of the repulsive potential. The double-layer thickness is determined by the system temperature and the electrolyte, and describes the extension of the repulsive potential. Its crucial influence on the sedimentation phenomena will be revealed in the following section.

Numerical Results and Discussion

We have solved Eq. 26 for $Q(s)$ numerically. As $s\to\infty$, G, H, L, and M approach unity, W is of order s^{-5}, and Φ_{ij} is of order s^{-6}. Consequently, in the far field $Q(s)$ in Eq. 26 behaves like the case of hard spheres described by Batchelor and Wen (1982)

$$Q(s) = \frac{K_2}{s^2} + \sum_{m=3}^{\infty} \frac{K_m}{s^m}, \tag{34}$$

in which, when $s \gg 1$, K_2 is unknown and K_m can be found in terms of K_2 by substituting Eq. 34 into Eq. 26, writing G, H, L, M, W, and Φ_{ij} as power series in s^{-1}, and equating coefficients of s^{-m}. The procedure for solving Eq. 26 is to guess a value of K_2, thereby determining Q numerically in the far field $s \geq 10$, and then to integrate the equation numerically from $s = 10$ to the smaller value of s. The correctness of the assumed value of K_2 is judged by whether the inner boundary condition is found to be satisfied; if it is not, further trials are needed.

The earlier work of Batchelor and Wen (1982) ought to be mentioned before calculating the function Q. In their article, they showed that for hard spheres, when λ was fixed, it was unnecessary to recalculate Q for each value of γ, since one had

$$(\lambda^2\gamma - 1) \cdot Q(s, \gamma, \lambda) = Q'(s, \lambda) + \gamma Q''(s, \lambda), \tag{35}$$

in which Q' and Q'' were independent of γ, and could be expressed as

$$\begin{cases} Q'(s, \lambda) = -Q(s, \gamma, \lambda)|_{\gamma=0}, \\ Q''(s, \lambda) = Q(s, \gamma, \lambda)|_{\gamma=0} + (\lambda^2 - 1) \cdot Q(s, \gamma, \lambda)|_{\gamma=1}. \end{cases} \tag{36}$$

Thus, the function Q for any other values of γ can be easily obtained for the hard spheres system, provided Q' and Q'' are known, as can the sedimentation coefficient. Regretfully, however, when the interparticle potential with a thin double layer is considered, we have to give up this valuable approach. As indicated in Eq. 36, Q' and Q'' are determined by $Q|_{\gamma=0}$ and $Q|_{\gamma=1}$, in which $\gamma = 0$ implies $\rho_j = \rho$ and $\rho_j \neq \rho_i$, while $\gamma = 1$ implies $\rho_j = \rho_i$. In other words, the system of $\gamma = 0$ and the system of $\gamma = 1$ contain different species of sphere i or/and sphere j, and thus a different composite Hamaker constant. Since it is meaningless to follow Batchelor and Wen's approach anymore, the following numerical study only looks at the practically interested suspensions containing spheres of identical density (namely $\gamma = 1$). The bidisperse polystyrene–water suspension, whose typical value of the Hamaker constant is about 7×10^{-12} J (Wang and Wen, 1998), is chosen as the sample system. The radius of sphere i is fixed at 1 μm; thus, the variation of the radius ratio λ results from the different size of sphere j.

First of all, the numerical results of Q for potential interacting spheres with a thin double layer are presented Figure 1a. As we find, since the interparticle potential is also γ-dependent, the curves in Figure 1a are much different from those in Figure 1b, which shows the numerical results for hard spheres, and in which Q diminishes smoothly with the decrease in s and is identical to the case of λ and $1/\lambda$.

Equation 29, indicates that $e^{-\Phi_{ij}/kT}$ is the leading term of the approximate solution of the PDF, and $e^{-\Phi_{ij}/kT}Q(s)$ is the radial part of the $O(Pe^1)$ term. To show how the interparticle potential influences the behavior of the PDF, the $e^{-\Phi_{ij}/kT} \sim \xi_{0,D}$ curves and $e^{-\Phi_{ij}/kT}Q \sim \xi_{0,D}$ curves are presented in Figure 2a and 2b for the fixed surface potential. When the double layer becomes thinner, the secondary minimum of the interparticle potential becomes deeper and closer to the particle surface, leading to the larger corresponding peak values of $e^{-\Phi_{ij}/kT}$ and $e^{-\Phi_{ij}/kT}Q$ (see Figures 2a and 2b). In the actual situation, this predicts the appearance of more spheres in close pairs—which fall more quickly than well-separated pairs—in the suspension; hence, the more accelerated sedi-

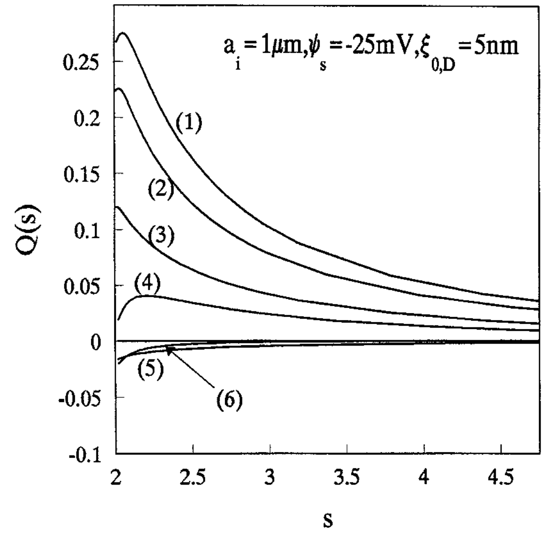

Figure 1a. Calculated values of *Q* vs. dimensionless center-to-center separation *s* for potential interacting spheres with thin double layer.

(1) $\lambda = 2$; (2) $\lambda = 4$; (3) $\lambda = 8$; (4) $\lambda = 1/2$;' (5) $\lambda = 1/4$; (6) $\lambda = 1/8$.

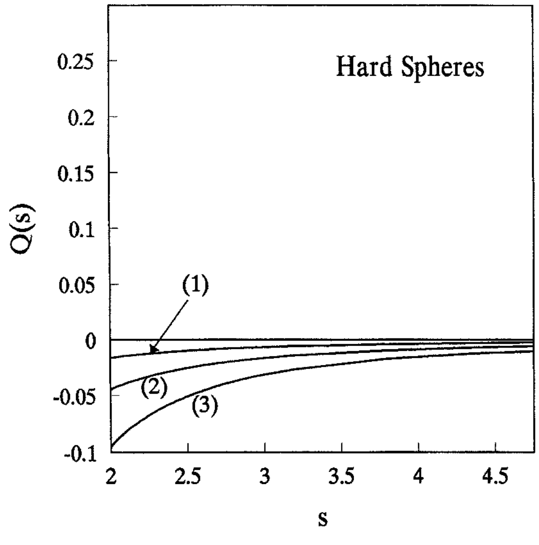

Figure 1b. Calculated values of *Q* vs. dimensionless center-to-center separation *s* for hard spheres.

(1) $\lambda = 1/8$ and 8; (2) $\lambda = 1/4$ and 4; (3) $\lambda = 1/2$ and 2.

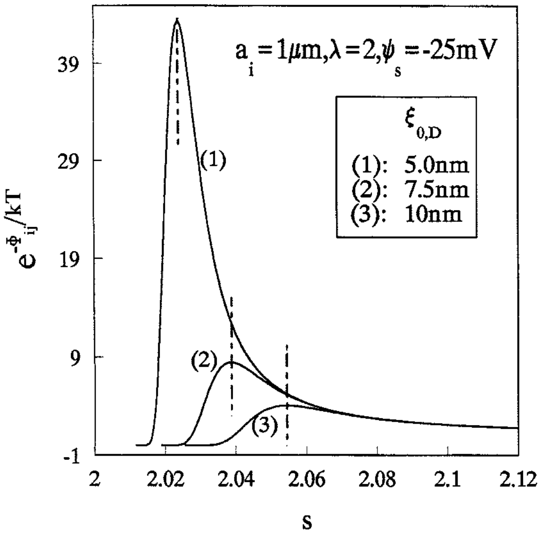

Figure 2a. $e^{-\Phi_{ij}/kT}$ **as a function of** s.

The peaks of the curves correspond to the secondary minimums one by one, whose positions are marked by the dashed lines.

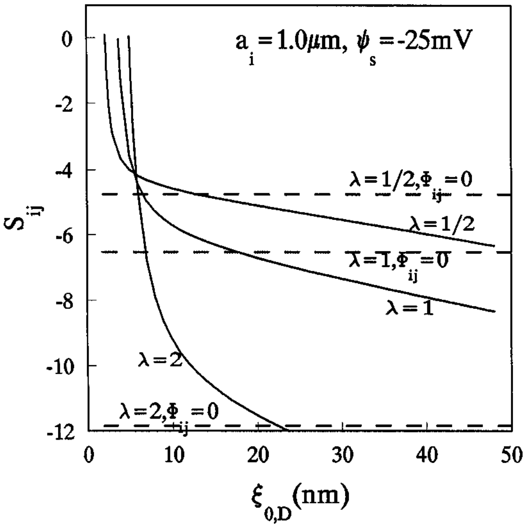

Figure 3. Sedimentation coefficient S_{ij} **as a function of the double-layer thickness** $\xi_{0,D}$.

The sedimentation coefficients of hard spheres (dashed lines) are shown for comparison.

mentation. This phenomenon is indicated in Figure 3 by the increase in the sedimentation coefficient with the decrease in $\xi_{0,D}$. There exists a critical double-layer thickness $\xi_{0,C}$, which may be defined as the value of the double-layer thickness giving $S_{ij} = 0$. On condition that $\xi_{0,D} < \xi_{0,C}$, many close pairs appear in a system that the hindered sedimentation turns into accelerated sedimentation (S_{ij} changes from negative to positive), and a stable suspension turns into an unstable one. For the sample system, when the surface potential is fixed on -25 mV, the values of the critical double-layer thickness are about 2.5 nm for $a_j = 0.5$ μm, 4 nm for $a_j = 1$ μm, and 5 nm for $a_j = 2$ μm (see Figure 3).

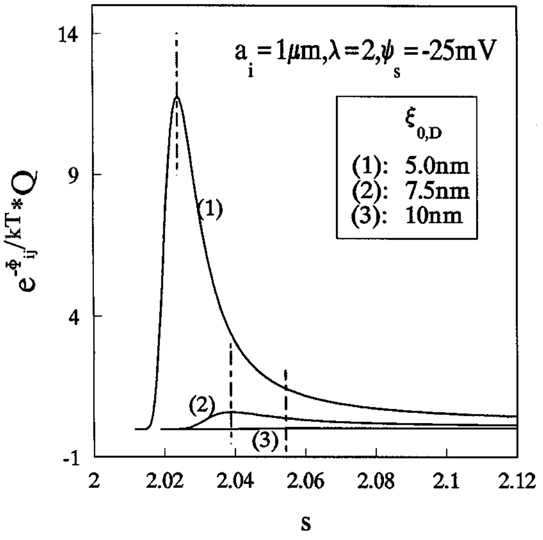

Figure 2b. $e^{-\Phi_{ij}/kT}Q$ **as a function of** s.

The peaks of the curves correspond to the secondary minimums one by one, whose positions are marked by the dashed lines. Parameters of the interparticle potential are identical to those in Figure 2a.

Further calculations have been made to demonstrate the behaviors of the sedimentation coefficient and its three independent direct contributions. Results are given in Tables 1 and 2. The term $-(\lambda^2 + 3\lambda + 1)$ is subtracted from the calculated values of S_{ij} and $S_{ij}^{(G)}$ to reduce the variation in the tabulated numbers over the whole range. It is found in these tables that even for the case of a small Péclet number, $S_{ij}^{(I)}$ and $S_{ij}^{(B)}$ are generally rather small compared with $S_{ij}^{(G)}$. This result seems to conflict with the case where $Pe \ll 1$ implies a strong interparticle force and a Brownian diffusive force, as well as relatively weak gravity, yet it may be explained as follows: the spherically symmetrical leading term of the PDF contributes only to $S_{ij}^{(G)}$ among the three independent direct contributions, whereas the axis symmetrical term of order Pe^1 contributes to $S_{ij}^{(I)}$ and $S_{ij}^{(B)}$. This does not mean that the effects of the interparticle force and the Brownian diffusive force can be ignored in an approximate treatment; the indirect effects of the two forces exerted through their influence on the structure of the system—namely, on the PDF in the case of the dilute system—are significant.

Table 1. Calculated Sedimentation Coefficient for the Sample System in the Case where $\xi_{0D} = 20$ nm, $\psi_s = -25$ mV

λ	$S_{ij}^{(G)} + \lambda^2 + 3\lambda + 1$	$S_{ij}^{(I)}$	$S_{ij}^{(B)}$	$S_{ij} + \lambda^2 + 3\lambda + 1$
0.125	−2.59	−0.21	−0.02	−2.82
0.25	−2.54	−0.16	−0.04	−2.74
0.5	−2.39	−0.10	−0.04	−2.54
1	−1.99	0	0	−1.99
2	−1.18	0.07	0.09	−1.02
4	0.17	0.06	0.17	0.40
8	2.45	0.04	0.22	2.71

Table 2. Calculated Sedimentation Coefficient of the Sample System in the Case where $\xi_{0D}=20$ nm, $\psi_s=-50$ mV

λ	$S_{ij}^{(G)}+\lambda^2+3\lambda+1$	$S_{ij}^{(I)}$	$S_{ij}^{(B)}$	$S_{ij}+\lambda^2+3\lambda+1$
0.125	-2.67	-0.32	-0.02	-3.01
0.25	-2.65	-0.23	-0.04	-2.91
0.5	-2.54	-0.14	-0.04	-2.72
1	-2.23	0	0	-2.23
2	-1.63	0.10	0.10	-1.44
4	-0.71	0.10	0.20	-0.42
8	0.72	0.07	0.27	1.06

Conclusions

In order to solve the sedimentation problem in a polydisperse suspension containing potential interacting particles, we expanded the pair-distribution function (PDF) into Legendre polynomials. Relevant formulas for calculating the PDF and the sedimentation coefficient were obtained. The sedimentation of polydisperse, potential interacting particles with a thin double layer in the case of a small Péclet number was analyzed in detail. Numerical results revealed the significant influence of the interparticle potential on the particle settling as well as the character of the sedimentation.

We end by offering some conclusions relating to the sedimentation in the case of a small Péclet number: (1) the function Q in the approximate solution of the PDF may possess a peak value, due to the existence of the secondary minimum, yet in the case of hard spheres, Q diminishes smoothly with the decrease of s; (2) among the three independent direct contributions to the sedimentation coefficient, the contribution from gravity generally exceeds the contributions from the interparticle force and the Brownian diffusive force, and the latter two forces affect the sedimentation indirectly through its influence on the PDF; (3) a critical double layer for the polydisperse suspensions exists, as it does for the monodisperse suspension. When the double-layer thickness is less than the critical value, the sedimentation may be so strongly accelerated that the hindered settling turns into enhanced settling.

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Notation

A_{11}, A_{12} = longitudinal mobility functions
B_{11}, B_{12} = transverse mobility functions
e = electron charge
k = Boltzmann constant
ξ = dimensionless gap between two spheres
ξ_0 = dimensionless double layer thickness
ξ_{0C} = critical double layer thickness

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