마이크로 채널에서의 정전상호작용과
진한 농도를 갖는 서스펜션에서 구형 콜로이드입자의 구배확산

전 명 석
한국과학기술연구원 복잡유체연구팀

Electrostatic Interaction in a Microchannel and Gradient Diffusion in a Concentrated Suspension of Spherical Colloids

Myung-Suk Chun
Complex Fluids Team, Korea Institute of Sci. and Tech., Seoul 130-650

Introduction

The electrostatic interaction between two charged sphere immersed in an unbounded electrolyte has been studied over the past 50 years[1,2]. Recently, it is found that long-range electrostatic interactions can have a dramatic effect on fluid transports in microchannels. Although the accuracy of the Poisson-Boltzmann(P-B) theory has been examined, the effect of geometrical confinement on the interaction still remains an open problem. The linearized form of the P-B equation has proven useful in evaluating electrostatic interactions when the surface potential of suspended particles is smaller than or comparable to the Boltzmann thermal potential[3].

Another issue related to the electrostatic interaction is the gradient diffusion of particles in a concentrated suspension which is an important behavior in physicochemical micro-hydrodynamics[4]. The calculation of the gradient diffusion coefficient is not a succinct problem because the calculation of multiparticle interactions is basically complicated. In this study, both the thermodynamic coefficient and hydrodynamic coefficient have been evaluated as a function of particle concentration.

Complex Fluids Flow through a Microchannel

When a charged surface is in contact with an electrolyte, the electrostatic charges on the solid surface will influence the distribution of nearby ions in the electrolyte solution. Then an electric field is established, where the charges on the solid surface and the balancing charges in the liquid is called the Debye electric double layer. Electrokinetics refers to those processes in which the boundary layer between one charged phase and another is forced to undergo some sort of shearing process. An understanding of the fundamental behavior of the fluid flow in microchannels is of importance in the research fields of micro- and nanofluidics. Microchannels currently have wide applications in the design and utilization of microfluidic devices, such as diagnostic microdevices, biomedical microchips, microreactors, and other MEMS(micro-electro mechanical system) devices.

The linearized P-B equation governing the electric field is given as

$$\nabla^2 \Psi = \chi^2 \Psi .$$ (1)

Here, the dimensionless potential denotes $Z_i e/kT$ and the inverse Debye double layer thickness is defined by

$$\chi = \left[\frac{2n_{i,b}Z_i^2 e^2}{\varepsilon kT} \right]^{1/2} \qquad (2)$$

where $n_{i,b}$ is the concentration of type i ions in the bulk solution, Z_i the valence of type i ions, e the elementary charge, the dielectric constant, ε the dielectric constant, and kT the Boltzmann thermal energy.

Long-Range Electrostatic Interaction

The electrostatic interaction between dissimilar (bidisperse) particles shown in Fig. 1 can be considered by applying the singularity method previously proposed as a useful scheme for multisphere systems.   In solving Eq. (1), both the constant potential and the constant charge boundary conditions are used.   Here, the boundary condition with a constant charge density σ is taken as

$$\boldsymbol{n} \cdot \nabla \Psi = \sigma \qquad on \ S_A \ . \qquad (3)$$

From the singular solution to Eq. (1) for a point charge at the origin, each of the dimensionless surface charge densities of the particles 1 and 2 are expressed as follows:

$$\sigma_1 = \Psi_{p,w}(1 + \chi a_1) \qquad \text{for } sphere \ 1 \qquad (4a)$$

$$\sigma_2 = \Psi_{p,w}\left(\frac{1 + \chi a_1 m}{m} \right) \qquad \text{for } sphere \ 2 \qquad (4b)$$

where m ($= a_2/a_1$) means the ratio of the radius of two dissimilar particles, and a_1 and a_2 correspond to radii of particle 1 and 2, in respect.   The singular solution for point charge at the origin is easily defined, however, if multisphere interactions are presented we should propose incorporating additional off-center singularities within the spheres[5].   Based on the principle of superposition with both the known contribution of singularities Ψ^c and the corresponding contributions from the off-center singularities Ψ^{oc}, the specified surface potential at a surface point $\mathbf{x}_j$ then yields

$$\sigma(\boldsymbol{x_j}) \equiv \boldsymbol{n} \cdot \nabla \Psi_s(\boldsymbol{x_j}) = \sum_{i=1}^{N} \boldsymbol{n} \cdot \nabla \Psi_i^c(\boldsymbol{x_j}) + \sum_{i=1}^{aN} \boldsymbol{n} \cdot \nabla \Psi_i^{oc}(\boldsymbol{x_j}) \qquad j = 1 \ to \ M \ . \qquad (5)$$

The strengths of the singularities are found by minimizing the deviation from the prescribed boundary conditions at a finite number of points on the surfaces of the solids.   Once the solution for the potential is obtained, the force vector $\boldsymbol{F}$ can be calculated from the surface integration of normal component of Maxwell stress tensor $\boldsymbol{T}$, given by

$$\boldsymbol{F} \equiv \int_{S_A} \boldsymbol{T} \cdot \boldsymbol{n} \, dS_A \ . \qquad (6)$$

Then, the interaction energy profile between pairs of bidisperse particles can be obtained by integrating the force on the sphere as provided in Fig. 2.

Gradient Diffusion of Spherical Colloids

The diffusion coefficient of a particle in the bulk can be obtained from the Stokes-Einstein equation as $D_o = kT/6\pi\mu a$.   Fig. 3 shows that, at finite

concentrations, both colloidal interactions and hydrodynamic interactions modify the dilute limit value. The generalized Stokes-Einstein equation valid over the entire range of particle concentrations is used to evaluate the gradient diffusion coefficient,

$$D(C) = D_o \frac{K(C)}{S(C)} = \frac{kT}{6\pi\eta a} K(C) \left[\frac{\partial \Pi(C)}{\partial C} \frac{4\pi a^3}{3kT} \right] \tag{7}$$

where S(C) is the thermodynamic coefficient determined from the osmotic pressure Π (C), and K(C) is the hydrodynamic coefficient. The osmotic pressure is expressed with osmotic virial coefficients A_2 and A_3. The S(C) coinciding with the structure factor can be derived in power series of the particle concentration as

$$S(C) = 1 - 2A_2C + (2A_2^2 - 3A_3)C^2 + O(C^3) . \tag{8}$$

Here, A_2 is represented by

$$A_2 = \frac{3}{2a^3} \int_0^\infty [1 - g(s)]s^2 ds = \frac{3}{2a^3} \int_0^\infty \left[1 - \exp\left(-\frac{E(s)}{kT}\right) \right]s^2 ds \tag{9}$$

where s is the center-to-center separation distance, g(s) the radial distribution function, and E(s) the pairwise interaction energy mentioned above. The radial distribution function can be determined by integral equations, perturbation methods, and Monte Carlo simulations. Monte Carlo simulations are employed here, since they enable the prediction of suspensions over the wide range of particle concentrations.

The hydrodynamic coefficient K(C) accounts for the fact that the drag force in concentrated suspensions exerted on a single particle deviates from the Stokes law due to the presence of neighboring particles[6]. This coefficient originally describes the sedimentation velocity of an assemblage of spheres, which can be given for ordered suspensions as,

$$K(C) = \left(1 - \frac{3}{2} C^{1/3} + \frac{3}{2} C^{5/3} - C^2 \right) \Big/ \left(1 + \frac{2}{3} C^{5/3} \right) . \tag{10}$$

In Fig. 4, the gradient diffusion coefficient are provided for the particle concentrations ranging from a dilute limit to a high value. The dependence of the solution ionic strength on the diffusion coefficient is weak for the particle concentrations up to about 0.3, however, above 0.3 it shows a rise up behavior for 0.02 and 0.1 mM. The diffusion coefficient increases with the decrease of the solution ionic strength, which implies an enhancement in the particle diffusion.

Acknowledgement

References

[1] Israelachvili, J.N.: "Intermolecular and Surface Forces: With Applications to Colloidal and Biological Systems", Academic Press, New York(1985).
[2] Carnie, S.L. and Chan, D.Y.C.: *J. Colloid Interface Sci.,* **155**, 297(1993).
[3] Russel, W.B., Saville, D.A. and Schowalter, W.R.: "Colloidal Dispersions", Cambridge Univ. Press, New York(1989).
[4] Bowen, W.R., Liang, Y. and Williams, P.M.: *Chem. Eng. Sci.,* **55**, 2359(2000).

[5]   Chun, M.-S., Chung, G.-Y. and Kim, J.-J.: *J. Membrane Sci.*, **193**, 97(2001).
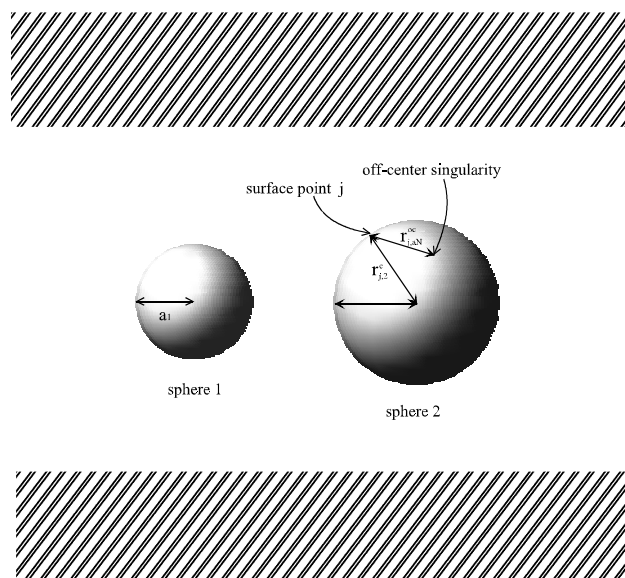[6]   Batchelor, G.K.: *J. Fluid Mech.*, **74**, 1(1976).

Fig. 1. Schematic of dissimilar spherical colloids confined in a microchannel.
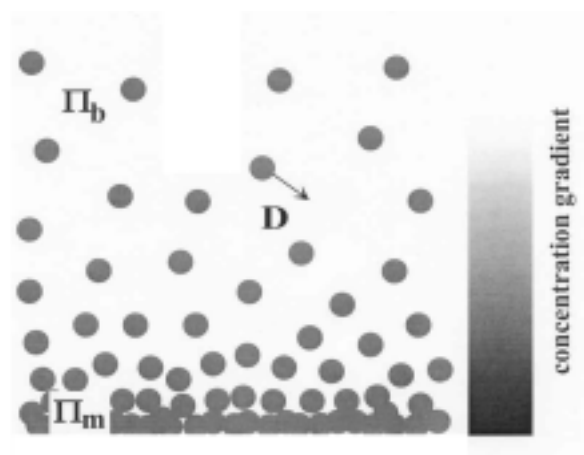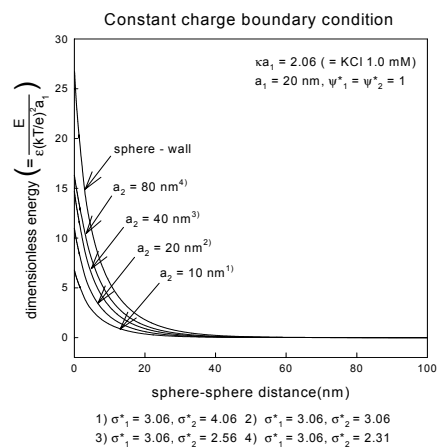

Fig. 2. Dimensionless energy profiles for particle–particle interaction for different sizes with constant charge boundary conditions.

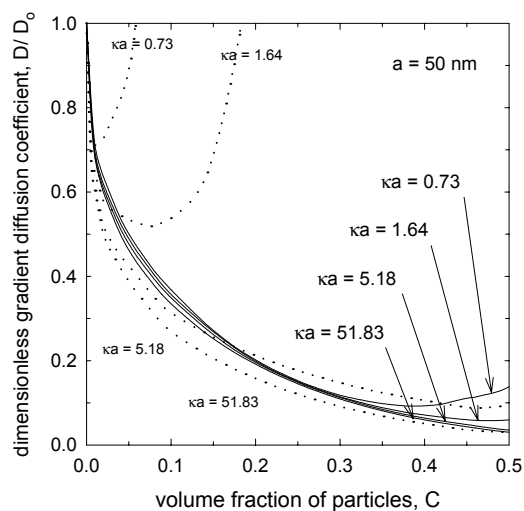Fig. 3. Schematic illustration of gradient diffusion in a concentrated suspension of spherical colloids

Fig 4 The plots of dimensionless gradient diffusion coefficient vs particle concentration with different Debye lengths at pH 6. Dotted curves mean the predictions for dilute limit case