Reciprocal relation of charged particle with thin electric double layer

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薄い電気２重層を持った球状粒子の電気泳動、沈降電位などの相反定理について考察した。

1 Introduction

The Onsager's reciprocal relation about the charged particle with thin electric double layer is discussed in this study. The boundary condition of the velocity $\boldsymbol{v}^s$ and electric current $\boldsymbol{j}^s$ on the particle surface is denoted as functions of the shear force $\boldsymbol{f}^t$ and tangential component of the electric field $\boldsymbol{E}^t$. This boundary condition is consistent with Onsager's reciprocal relation. Using this boundary condition, the reciprocal relation of the spherical charged particle is shown. The velocity $\boldsymbol{V}$ and the current dipole $\boldsymbol{P}$ of the particle is expressed as a linear relation of the force $\boldsymbol{F}$ and the external electric field $\boldsymbol{E}$. The relation is denoted as the symmetric matrix which shows electrophoretic mobility, sedimentation potential and reduction of sedimentation mobility.

2 Boundary condition

In this study, the charged particle with radius a dispersed in ionic solution which has viscosity η, permittivity ϵ and bulk conductivity σ_b is considered. We assumed that the electric double layer length κ^{-1} on the particle surface is thin. Using Navier, Smolchowski, Ohm and Brunet-Ajdari's[1)] discussions, the Onsager's reciprocal relation on the charged surface is expressed as

$$\begin{pmatrix} \boldsymbol{v}^s \\ \boldsymbol{j}^s \end{pmatrix} = \begin{pmatrix} \frac{\xi}{\eta} & -\frac{\epsilon\zeta}{\eta} \\ -\frac{\epsilon\zeta}{\eta} & \sigma^s \end{pmatrix} \begin{pmatrix} \boldsymbol{f}^t \\ \boldsymbol{E}^t \end{pmatrix} \tag{1}$$

where ξ is Navier's slip length, ζ is surface potential and σ^s is surface conduction. The condition of the positive definite matrix is

$$\gamma_h \gamma_e > \gamma_c^2 \tag{2}$$

where

$$\gamma_e = \frac{\sigma_s}{a\sigma_b}, \quad \gamma_h = \frac{\xi}{a}, \quad \gamma_c = \frac{\epsilon\zeta}{a\sqrt{\sigma_b \eta}}. \tag{3}$$

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γ_e is called Dukhin number[2].

Using the reciprocal relation on the surface, the slip velocity $\boldsymbol{v}^s$ and the current continuity

$$\sigma_b \boldsymbol{E}(\boldsymbol{r}) \cdot \boldsymbol{n}(\boldsymbol{r}) + \nabla^s \cdot \boldsymbol{j}^s(\boldsymbol{r}) = 0 \tag{4}$$

, where $\boldsymbol{n}$ is unit normal to bulk region on the sruface and $\nabla^s = (\boldsymbol{I} - \boldsymbol{nn}) \cdot \nabla$, are applied and the velocity and electric fields are solved.

3 Reciprocal relation of spherical particle

The velocity $\boldsymbol{V}$ and the current dipole $\boldsymbol{P}$ of the spherical particle under external force $\boldsymbol{F}$ and electric field $\boldsymbol{E}$ are expressed as

$$\begin{pmatrix} \boldsymbol{V} \\ \boldsymbol{P} \end{pmatrix} = \begin{pmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{pmatrix} \begin{pmatrix} \boldsymbol{F} \\ \boldsymbol{E} \end{pmatrix} \tag{5}$$

where

$$L_{11} = \frac{1}{6\pi\eta a} \frac{(1+\gamma_e)(1+3\gamma_h) - 3\gamma_c^2}{(1+\gamma_e)(1+2\gamma_h) - 2\gamma_c^2}, \quad L_{12} = L_{21} = \frac{\epsilon\zeta}{\eta} \frac{1}{(1+\gamma_e)(1+2\gamma_h) - 2\gamma_c^2}$$

and

$$L_{22} = \frac{-2\pi\sigma_b a^3}{(1+\gamma_e)(1+3\gamma_h) - 3\gamma_c^2} \left[(1-2\gamma_e)(1+3\gamma_h) + 6\gamma_c^2 - \frac{3\gamma_c^2}{(1+\gamma_e)(1+2\gamma_h) - 2\gamma_c^2} \right]. \tag{6}$$

The current $\boldsymbol{J}$ of the system with volume V is denoted as

$$\boldsymbol{J} = \sigma_b \boldsymbol{E}' + \frac{1}{V} \sum_{particles} \boldsymbol{P}. \tag{7}$$

When $\boldsymbol{J} = 0$, the sedimentation potential $\boldsymbol{E}'$ is calculated as

$$\boldsymbol{E}' = -\frac{1}{\sigma_b V} \sum_{particles} \boldsymbol{P} = -\frac{\epsilon\zeta\Delta\rho g\phi}{\eta\sigma_b} \frac{1}{(1+\gamma_e)(1+2\gamma_h) - 2\gamma_c^2} \tag{8}$$

where $\Delta\rho$ is the density difference between the particle and the solvent, g is gravity and ϕ is the volume fraction of the particle.

References

1) E. Brunet and A. Ajdari, Phys. Rev. E **73**, 056306 (2006)

2) S.S. Dukhin, Adv. Colloid and Interface Sci. **44**, 1 (1993)