TOPICAL REVIEW

Theory of electrostatics and electrokinetics of soft particles

Hiroyuki Ohshima

Faculty of Pharmaceutical Sciences and Institute of Colloid and Interface Science, Center for Colloid and Interface Science, Tokyo University of Science, Chiba 278-8510, Japan

E-mail: ohshima@rs.noda.tus.ac.jp

Received 31 August 2009
Accepted for publication 12 November 2009
Published 29 December 2009
Online at stacks.iop.org/STAM/10/063001

Abstract

We investigate theoretically the electrostatics and electrokinetics of a soft particle, i.e. a hard particle covered with an ion-penetrable surface layer of polyelectrolytes. The electric properties of soft particles in an electrolyte solution, which differ from those of hard particles, are essentially determined by the Donnan potential in the surface layer. In particular, the Donnan potential plays an essential role in the electrostatics and electrokinetics of soft particles. Furthermore, the concept of zeta potential, which is important in the electrokinetics of hard particles, loses its physical meaning in the electrokinetics of soft particles. In this review, we discuss the potential distribution around a soft particle, the electrostatic interaction between two soft particles, and the motion of a soft particle in an electric field.

Keywords: soft particle, Donnan potential, electrostatic interaction, electrophoretic mobility

1. Introduction

The potential and charge of colloidal particles play fundamental roles in their interfacial electric phenomena, such as electrostatic interactions between colloidal particles and the motion of colloidal particles in an electric field [1–5]. When a charged colloidal particle is immersed in an electrolyte solution, mobile electrolyte ions, which are charged oppositely to the particle surface and which are called counter ions, tend to approach the particle surface to neutralize the particle surface charges, but the thermal motion of these ions prevents their accumulation so that an ionic cloud is formed around the particle. In the ionic cloud, the concentration of counter ions becomes very high, whereas that of coions (electrolyte ions with charges of the same sign as the particle surface charges) is very low. The ionic cloud, together with the particle surface charge, forms an electrical double layer. Such layer is often called an electrical diffuse double layer, since the distribution of electrolyte ions in the ionic cloud takes a diffusive structure owing to the thermal motion of ions. Here, we focus on the case where the particle core is covered by an ion-penetrable surface layer of polyelectrolytes, which we term a surface charge layer (or, simply, a surface layer). Polyelectrolyte-coated particles are often called soft particles [4]. As seen in figure 1, a soft particle becomes a hard particle in the absence of the surface charge layer, while it tends to form a spherical polyelectrolyte (or a porous sphere) in the absence of the particle core. Soft particles serve as a model for biocolloids, such as cells. In such cases, the electrical double layer is formed not only outside but also inside the surface charge layer. Particles without surface structures or their surfaces, on the other hand, are called hard particles or hard surfaces.

In this article, we start with the potential and charge of a soft particle in an electrolyte solution. We show that the Donnan potential plays an important role in determining the potential distribution across a surface charge layer. Then, we discuss the electrostatic interaction between soft particles. In conventional interaction models, it is assumed that the surface potential or the surface charge density remains constant during interaction. In the electrostatic interaction of soft particles, however, the potential deep inside the surface charge layer, which coats soft particles, remains constant at the
Donnan potential. We thus call this type of interaction the Donnan-potential regulated interaction. Finally, we consider the motion of a soft particle in an external electric field. In the usual electrophoresis of hard particles, the particle zeta potential plays an essential role. In the electrophoresis of a soft particle, however, two parameters are involved, that is, the volume charge density of charged groups in the surface layer and the electrophoretic softness of the surface layer.

2. Charge and potential of a soft particle

2.1. Poisson–Boltzmann equation

Consider the simple case of a charged soft plate, that is, a hard plate covered with an ion-penetrable surface layer of polyelectrolytes. Imagine a surface charge layer of thickness $d$ coating a planar hard surface that is immersed in a general electrolyte solution containing $M$ ionic species with valence $z_i$ and bulk concentration (number density in units of m$^{-3}$) $n_i^\infty (i=1,2,\ldots,M)$. We treat the case where fully ionized groups of valence $Z$ are distributed at a uniform density of $N$ in the surface charge layer, and the particle core is uncharged [4]. We assume that the relative permittivity $\varepsilon_r$ takes the same value in the regions outside and inside the surface layer. See [6] for a detailed discussion on the equality of the relative permittivity outside and inside the surface charge layer. We take an $x$-axis perpendicular to the surface charge layer with its origin $x=0$ at the boundary between the surface charge layer and the surrounding electrolyte solution, so that the surface charge layer corresponds to the region $-d < x < 0$ and the electrolyte solution to $x > 0$, as in figure 2.

The charge density $\rho_d(x)$ resulting from the mobile charged ionic species is related to the electric potential $\psi(x)$ by the Poisson equation,

$$\frac{d^2 \psi}{dx^2} = -\frac{\rho_d(x)}{\varepsilon_r \varepsilon_0}, \quad 0 < x < +\infty,$$

(1)

$$\frac{d^2 \psi}{dx^2} = -\frac{\rho_d(x) + ZeN}{\varepsilon_r \varepsilon_0}, \quad -d < x < 0,$$

(2)

where $\varepsilon_r$ is the relative permittivity of the solution, $\varepsilon_0$ is the permittivity of a vacuum, and $e$ is the elementary electric charge. Note that the right-hand side of equation (2) contains the contribution of the fixed-charges of density $\rho_{fix} = ZeN$ in the polyelectrolyte layer. We also assume that the distribution of the electrolyte ions $n_i(x)$ obeys Boltzmann’s law. Then, we have

$$n_i(x) = n_i^\infty \exp\left(-\frac{z_i e \psi(x)}{kT}\right)$$

(3)

\[\text{Figure 1.} \ A \ soft \ particle \ becomes \ a \ hard \ particle \ in \ the \ absence \ of \ the \ surface \ charge \ layer, \ while \ it \ tends \ to \ form \ a \ spherical \ polyelectrolyte \ (or \ a \ porous \ sphere) \ in \ the \ absence \ of \ the \ particle \ core \ [4].\]

\[\text{Figure 2.} \ Schematic \ representation \ of \ ion \ distribution \ (upper) \ and \ potential \ distribution \ \psi(x) \ (lower) \ across \ an \ ion-penetrable \ surface \ charge \ layer \ [4].\]
and the charge density \( \rho_d(x) \) at \( x \) is given by
\[
\rho_d(x) = \sum_{i=1}^{M} \varepsilon_i \varepsilon_0 \left( e^{\frac{\psi(x)}{kT}} \right)^{z_i} \exp \left( -\frac{z_i e}{kT} \right).
\] (4)

The potential \( \psi(x) \) at position \( x \) in the regions \( x > 0 \) and \(-d < x < 0 \) thus satisfies the following Poisson–Boltzmann equations,
\[
\frac{d^2 \psi}{dx^2} = -\kappa^2 \sum_{i=1}^{M} \varepsilon_i n_i^{\infty} \exp(-z_i \psi) \left( \frac{z_i e}{kT} \right)^{z_i} \exp \left( -\frac{z_i e}{kT} \right), \quad 0 < x < +\infty,
\] (5)
\[
\frac{d^2 \psi}{dx^2} = -\kappa^2 \sum_{i=1}^{M} \varepsilon_i n_i^{\infty} \exp(-z_i \psi) \left( \frac{z_i e}{kT} \right)^{z_i} \exp \left( -\frac{z_i e}{kT} \right) \left( \frac{Z N}{2 \pi n} \right)^2, \quad -d < x < 0,
\] (6)
with
\[
y = \frac{e \psi}{kT},
\] (7)
\[
\kappa = \left( \frac{1}{\varepsilon_0} \right)^{1/2} \sum_{i=1}^{M} \left( \kappa^2 \varepsilon_i^2 n_i^{\infty} \right)^{1/2},
\] (8)
where \( y \) is the scaled potential and \( \kappa \) is the Debye–Hückel parameter of the solution. The boundary conditions are
\[
\left. \frac{d\psi}{dx} \right|_{x=-d^+} = 0,
\] (9)
\[
\psi(-0^-) = \psi(-0^+),
\] (10)
\[
\left. \frac{d\psi}{dx} \right|_{x=-0^-} = \left. \frac{d\psi}{dx} \right|_{x=-0^+},
\] (11)
\[
\psi(x) \to 0 \quad \text{as} \quad x \to \infty,
\] (12)
\[
\left( \frac{d\psi}{dx} \right) \to 0 \quad \text{as} \quad x \to \infty.
\] (13)

Equation (9) corresponds to the situation in which the particle core is uncharged.

For the special case, where the electrolyte is symmetrical and has valence \( z \) and bulk concentration \( n \), we have
\[
\frac{d^2 \psi}{dx^2} = \frac{2zeN}{\varepsilon_0} \left( \frac{z e \psi}{kT} \right) \left( \frac{Z eN}{2\varepsilon_0} \right)^2, \quad x > 0,
\] (14)
\[
\frac{d^2 \psi}{dx^2} = \frac{2zeN}{\varepsilon_0} \left( \frac{z e \psi}{kT} \right) - \frac{Z eN}{\varepsilon_0}, \quad -d < x < 0,
\] (15)
\[
\frac{d^2 \psi}{dx^2} = \kappa^2 \sinh y, \quad x > 0,
\] (16)
\[
\frac{d^2 \psi}{dx^2} = \kappa^2 \left( \sinh y - \frac{Z N}{2\pi n} \right), \quad -d < x < 0,
\] (17)
with
\[
y = \frac{z e \psi}{kT},
\] (18)
where \( y \) and \( \kappa \) are, respectively, the scaled potential and the Debye–Hückel parameter of a symmetrical electrolyte solution. Note that the definition of \( y \) for symmetrical electrolytes contains \( z \).

2.2. Donnan potential

If the thickness of the surface layer \( d \) is much greater than the Debye length \( 1/\kappa \), then the potential deep inside the surface layer becomes the Donnan potential \( \psi_{\text{DON}} \), which is obtained by setting the right-hand side of equation (15) or equation (17) to zero, viz.,
\[
\psi_{\text{DON}} = \left( \frac{kT}{z e} \right) \left\{ \sinh \left( \frac{z e \psi_{\text{DON}}}{kT} \right) - \sinh \left( \frac{z e \psi}{kT} \right) \right\}.
\] (20)

Equation (16) may be rewritten in terms of the Donnan potential \( \psi_{\text{DON}} \) as
\[
\frac{d^2 \psi}{dx^2} = \frac{2zeN}{\varepsilon_0} \left( \frac{z e \psi}{kT} \right) - \frac{Z eN}{\varepsilon_0}, \quad -d < x < 0.
\] (21)

When \( |ZN/zn| \ll 1 \), equation (21) gives the following linearized Donnan potential:
\[
\psi_{\text{DON}} = \frac{Z N kT}{2z^2 ne} = \frac{ZeN}{\varepsilon_0 \varepsilon_0 k^2}.
\] (22)

Moreover, we call \( \psi_o \equiv \psi(0) \), which is the potential at the boundary between the surface layer and the surrounding electrolyte solution, the surface potential of the polyelectrolyte layer.

For the simple case where \( \psi(x) \) is low, equations (14) and (15) can be linearized to
\[
\frac{d^2 \psi}{dx^2} = \kappa^2 \psi, \quad x > 0,
\] (23)
\[
\frac{d^2 \psi}{dx^2} = \kappa^2 \left( \psi - \frac{Z N kT}{2z^2 ne} \right), \quad -d < x < 0.
\] (24)

The solution to equations (23) and (24), subject to equations (9)–(13), is given by
\[
\psi(x) = \frac{Z N kT}{4z^2 ne} \left( 1 - e^{-2x/\kappa} \right) e^{-e x}, \quad x > 0,
\] (25)
\[
\psi(x) = \frac{Z N kT}{2z^2 ne} \left( 1 - \frac{e^{e x} + e^{-e x + 2x/\kappa}}{2} \right), \quad -d < x < 0
\] (26)
and the surface potential \( \psi_o \equiv \psi(0) \) is given by
\[
\psi_o = \frac{Z N kT}{4z^2 ne} \left( 1 - e^{-2x/\kappa} \right) = \frac{Z e N}{2\varepsilon_0 \varepsilon_0 k^2} \left( 1 - e^{-2x/\kappa} \right),
\] (27)
If we take the limit \( d \to 0 \) in equation (27), keeping the product \( Nd \) constant, i.e., keeping constant the total amount of fixed charges \( \sigma = ZeNd \), then equation (27) becomes

\[
\psi_o = \frac{\sigma}{\varepsilon \varepsilon_0 k},
\]

where we have defined \( \sigma \) as

\[
\sigma = Ze \lim_{Nd \to 0} (Nd).
\]

Equation (28) is the surface potential of a hard surface carrying a surface charge density \( \sigma \).

Note that when \( \kappa d \gg 1 \), the potential deep inside the surface layer approaches the linearized Donnan potential (equation (22)), that is,

\[
\psi(x) \approx \psi(-d) \approx \psi_{DON} = \frac{Z N kT}{2 \varepsilon^2 n e} = \frac{Z e N}{2 \varepsilon \varepsilon_0 k},
\]

and that the surface potential \( \psi_o \) (equation (27)) becomes half the Donnan potential

\[
\psi_o = \frac{\psi_{DON}}{2} = \frac{Z N kT}{4 \varepsilon^2 n e} = \frac{Z e N}{2 \varepsilon \varepsilon_0 k^2}.
\]

### 2.3. Arbitrary potential

The solution to the nonlinear differential equations (16) and (17), which is required for the arbitrary potential case, can be obtained as follows. Equation (16) subject to equations (12) and (13) can be integrated to give [4]

\[
\frac{dy}{dx} = -2 \kappa \sinh \left( \frac{y}{2} \right), \quad x > 0,
\]

which is further integrated to give

\[
y = 4 \arctanh \left[ \tanh \left( \frac{y_0}{4} \right) e^{-kx} \right], \quad x > 0,
\]

where \( y_0 \equiv y(0) = \varepsilon \psi(0)/kT \) is the scaled surface potential. Integration of equation (17) subject to equation (9) yields

\[
\frac{dy}{dx} = -\text{sgn}(y_o)k \left[ \cosh y - \cosh y(-d) - \frac{Z N}{zn} \right]
\times \left[ y - y(-d) \right]^{1/2}, \quad -d < x < 0.
\]

Equation (34) can be further integrated to give

\[
\kappa x = \text{sgn}(y_o) \int_y y_0 \frac{dy}{ \left[ 2(\cosh y - \cosh y(-d)) - \frac{Z N}{zn} \right]^{1/2}},
\]

which determines \( y \) as a function of \( x \). Evaluating equation (35) at \( x = -d \), we obtain

\[
\kappa d = -\text{sgn}(y_o) \int_{y(-d)}^{y_0} \frac{dy}{ \left[ 2(\cosh y - \cosh y(-d)) - \frac{Z N}{zn} \right]^{1/2}}
\]

On the other hand, evaluating equations (33) and (35) at \( x = 0 \) and substituting the results into equation (11), we obtain

\[
4 \sinh^2 \left( \frac{y_0}{2} \right) = 2 \left( \cosh y_o - \cosh y(-d) \right) - \frac{Z N}{zn} \left[ y_o - y(-d) \right],
\]

which can be rewritten as

\[
2 \sinh^2 \left( \frac{y_0}{2} \right) = \{ \cosh y_o - \cosh y(-d) \}
- \sinh y_{DON} \{ y_o - y(-d) \}.
\]

Here equation (20) (i.e. \( \sinh y_{DON} = \varepsilon \psi_{DON}/kT \)) has been used and \( y_{DON} \equiv \varepsilon \psi_{DON}/kT \) is the scaled Donnan potential. Equations (36) and (37) (or equation (38)) form coupled transcendental and integral equations for \( y_o \) and \( y(-d) \). By using the obtained values for \( y_o \) and \( y(-d) \), the potential \( y \) at an arbitrary point \( x \) can be calculated from equations (33) and (35).

Consider the case where the thickness of the surface layer \( d \) is much larger than the Debye length \( 1/\kappa \). In this case, the electric field \( (\text{d}y/\text{d}x) \) and its derivative \( (\text{d}^2y/\text{d}x^2) \) deep inside the surface layer become zero so that the potential deep inside the surface layer becomes the Donnan potential \( \psi_{DON} \) given by equation (20). Note that this is valid only for \( d \gg 1/\kappa \). If the condition \( d \gg 1/\kappa \) does not hold, there is no region where the potential reaches the Donnan potential. When \( d \gg 1/\kappa \), by replacing \( y(-d) \) by \( y_{DON} \) in equation (38), we obtain [4]

\[
\psi_o = \psi_{DON} - \frac{kT}{\varepsilon e} \tan \left( \frac{ze \psi_{DON}}{2kT} \right)
\]

\[
= \frac{kT}{\varepsilon e} \left[ \ln \left( \frac{ZN}{2zn} + \left( \frac{ZN}{2zn} \right)^2 + 1 \right)^{1/2} \right]
+ \frac{2zn}{ZN} \left[ 1 - \left( \frac{ZN}{2zn} \right)^2 + 1 \right]^{1/2}
\]

or

\[
y_o = y_{DON} - \tan \left( \frac{\psi_{DON}}{2} \right)
\]

\[
= \ln \left( \frac{ZN}{2zn} + \left( \frac{ZN}{2zn} \right)^2 + 1 \right)^{1/2}
+ \frac{2zn}{ZN} \left[ 1 - \left( \frac{ZN}{2zn} \right)^2 + 1 \right]^{1/2}.
\]

An approximate expression for the potential \( \psi(x) \) at an arbitrary point in the surface layer can be obtained by expanding \( y(x) \) in equation (35) around \( y_{DON} \). Alternatively, it can be obtained in the following way. If we substitute \( \psi = \psi_{DON} + \Delta \psi \) in equation (21) and linearize it with respect to \( \Delta \psi \), we obtain

\[
\frac{d^2\psi}{dx^2} = \kappa_m^2 (\psi - \psi_{DON}),
\]
\[ \kappa_m = \kappa \cosh^{1/2} \psi_{DON} = \kappa \left[ 1 + \left( \frac{ZN}{2ZM} \right)^2 \right]^{1/4}, \]  

(42)

where \( \kappa_m \) may be interpreted as the effective Debye–Hückel parameter of the surface charge layer that involves the contribution of the fixed-charges \( Z \varepsilon N \). Equation (41) is solved to give

\[ \psi(x) = \psi_{DON} + (\psi_0 - \psi_{DON}) e^{-x_0|x|}, \]  

(43)

We thus see that the potential distribution within the surface layer is characterized by \( \psi_{DON} \) and \( \psi_0 \), as schematically shown in figure 2.

When a thick soft plate is immersed in a general electrolyte solution, the Donnan potential \( \psi_{DON} \) is given by setting to zero the right-hand side of equation (6), in which \( -d \) is replaced by \( -\infty \). That is, \( \psi_{DON} \) is given as a root of the following transcendental equation

\[ \sum_{i=1}^{M} z_i n_i^\infty \exp(-z_i \psi_{DON}) + \frac{ZN}{\kappa^2} = 0. \]  

(44)

The relationship between \( \psi_{DON} \) and \( \psi_0 \) is obtained in the following way. Integrating equations (5) and (6) gives

\[ \left( \frac{dy}{dx} \right)^2 = \frac{2\kappa^2 \sum_{i=1}^{M} n_i^\infty (e^{-z_i y} - 1)}{\sum_{i=1}^{M} z_i^2 n_i^\infty}, \quad 0 < x < +\infty, \]  

(45)

\[ \left( \frac{dy}{dx} \right)^2 = \frac{2\kappa^2 \sum_{i=1}^{M} n_i^\infty (e^{-z_i y} - e^{-z_i \psi_{DON}}) - 2ZN(y - \psi_{DON})}{\sum_{i=1}^{M} z_i^2 n_i^\infty}, \quad -\infty < x < 0. \]  

(46)

By evaluating equations (45) and (46) at \( x = 0 \) and equating the results, we obtain

\[ \psi_0 = \psi_{DON} - \frac{\sum_{i=1}^{M} n_i^\infty (1 - e^{-z_i \psi_{DON}})}{\sum_{i=1}^{M} z_i n_i^\infty e^{-z_i \psi_{DON}}}, \]  

(47)

where equation (44) has been used. For a mixed solution of 1:1 electrolyte of bulk concentration \( n_1 \) and 2:1 electrolyte of bulk concentration \( n_2 \), equation (47) becomes

\[ \psi_0 = \psi_{DON} - \frac{(e^{\psi_{DON}} - 1) [(3 - \eta)e^{\psi_{DON}} + \eta]}{(3 - \eta)e^{\psi_{DON}}(e^{\psi_{DON}} + 1) + 2\eta}. \]  

(48)

with

\[ \eta = \frac{3n_2}{n_1 + 3n_2}. \]  

(49)

For the potential distribution around a spherical soft particle or a cylindrical soft particle, refer to [7, 8].

3. Electrostatic interaction between soft particles

3.1. Two parallel semi-infinite soft plates

Consider two parallel dissimilar soft plates 1 and 2 at a separation \( h \) between their surfaces immersed in an electrolyte solution [9]. We assume that each soft plate consists of a core and an ion-penetrable surface charge layer of polyelectrolytes covering the plate core and that there is no electric field within the plate core. We denote by \( d_1 \) and \( d_2 \) the thicknesses of the surface charge layers of plates 1 and 2, respectively. The \( x \)-axis is taken perpendicular to the plates with the origin at the boundary between the surface charge layer of plate 1 and the solution, as shown in figure 3.

![Diagram showing potential distribution](image)

Figure 3. Potential distribution \( y(x) \) across two parallel soft plates 1 and 2 [9].

The Poisson–Boltzmann equations for the present system are then

\[ \frac{d^2 \psi}{dx^2} = -\frac{1}{\varepsilon_0 \varepsilon_r} \sum_{i=1}^{M} z_i e n_i^\infty \exp \left( -\frac{z_i e \psi}{kT} \right) \]  

\[ -\frac{\rho_{fix1}}{\varepsilon_0 \varepsilon_r}, \quad -d_1 < x < 0, \]  

(52)

\[ \frac{d^2 \psi}{dx^2} = -\frac{1}{\varepsilon_0 \varepsilon_r} \sum_{i=1}^{M} z_i e n_i^\infty \exp \left( -\frac{z_i e \psi}{kT} \right), \quad 0 < x < h, \]  

(53)
where $\psi(x)$ is the electric potential at position $x$ relative to that at a point in the bulk solution far from the plates (the plates are actually surrounded by the electrolyte solution). We assume that the relative permittivity $\varepsilon_r$ in the surface layers takes the same value as that in the electrolyte solution.

We consider the case where $N_1$ and $N_2$ are low. The Poisson–Boltzmann equations (52)–(54) can be linearized to give

$$\frac{d^2\psi}{dx^2} = \kappa^2 \psi - \frac{\rho_{\text{fix}1}}{\varepsilon_r \kappa^2_0}, \quad -d_1 < x < 0,$$

$$\frac{d^2\psi}{dx^2} = \kappa^2 \psi, \quad 0 < x < h,$$

$$\frac{d^2\psi}{dx^2} = \kappa^2 \psi - \frac{\rho_{\text{fix}2}}{\varepsilon_r \kappa^2_0}, \quad h < x < h+d_2,$$  \hspace{1cm} (55) \hspace{1cm} (56) \hspace{1cm} (57)

where $\kappa$ is the Debye–Hückel parameter (equation (8)). Integration of equations (55)–(57) with appropriate boundary conditions gives

$$\psi(x) = \frac{1}{\varepsilon_r \kappa^2_0} \left[ \rho_{\text{fix}1} \sinh[\kappa (h+d_2)] \right], \quad -d_1 \leq x \leq 0,$$

$$\psi(x) = \frac{1}{\varepsilon_r \kappa^2_0} \left[ \frac{\rho_{\text{fix}1} \sinh[\kappa (d_1) \cosh[\kappa (h+d_2-x)] + \rho_{\text{fix}2} \sinh[\kappa (x+d_1)]]}{\sinh[\kappa (h+d_1+d_2)]} \right], \quad 0 \leq x \leq h,$$

$$\psi(x) = \frac{1}{\varepsilon_r \kappa^2_0} \left[ \rho_{\text{fix}2} + \frac{-\rho_{\text{fix}1} \sinh[\kappa (h+d_1)] + \rho_{\text{fix}2} \sinh[\kappa (d_1)]}{\sinh[\kappa (h+d_1+d_2)]} \right] \cosh[\kappa (h+d_2-x)], \quad h \leq x \leq h+d_2.$$  \hspace{1cm} (58) \hspace{1cm} (59) \hspace{1cm} (60)

The electrostatic force acting between two plates can be obtained by integrating the osmotic pressure and Maxwell’s stress over an arbitrary surface enclosing one of the plates [4]. We choose the surfaces $x = -\infty$ (in the bulk electrolyte solution phase) and $x = 0$ (at the boundary between plate 1 and the electrolyte solution) as a surface enclosing plate 1. When the potential is low, the electrostatic force $P(h)$ between the two parallel plates 1 and 2 per unit area is then given by [9, 10]

$$P_{pl}(h) = \frac{1}{2} \varepsilon_r \kappa_0^2 \left[ \kappa^2 \psi(0)^2 - \frac{d^2 \psi}{dx^2} \bigg|_{x=0^+} \right]^2.$$  \hspace{1cm} (61)

The first term on the right-hand side of equation (61) corresponds to the osmotic pressure and the second term to Maxwell’s stress, and $P > 0$ means repulsion and $P < 0$ attraction. The values of $\psi(0)$ and $d^2 \psi/dx$ at $x = 0$ can be obtained as functions of plate separation $h$ from equation (59). Substituting the results into equation (61) gives the force $P$ per unit area as a function of $h$. When the potential $\psi(x)$ is low, the electrostatic force $P_{pl}(h)$ between the two parallel plates 1 and 2 at separation $h$ per unit area can be calculated from equation (61) with the result that

$$P_{pl}(h) = \frac{1}{8 \varepsilon_r \kappa^2_0} \left[ \frac{\rho_{\text{fix}1} \sinh[\kappa (d_1)] + \rho_{\text{fix}2} \sinh[\kappa (d_2)]^2}{\sinh^2[\kappa (h+d_1+d_2)/2]} \right] - \frac{\rho_{\text{fix}1} \sinh[\kappa (d_1)] - \rho_{\text{fix}2} \sinh[\kappa (d_2)]^2}{\cosh^2[\kappa (h+d_1+d_2)/2]} \hspace{1cm} (62)$$

Integrating equation (62) with respect to $h$ gives the potential energy $V_{pl}(h)$ of the electrostatic interaction between the plates per unit area as a function of $h$:

$$V_{pl}(h) = \frac{1}{4 \varepsilon_r \kappa^2_0} \left[ \rho_{\text{fix}1} \sinh[\kappa (d_1)] + \rho_{\text{fix}2} \sinh[\kappa (d_2)]^2 \right] \times \left\{ \coth \left( \frac{\kappa (h+d_1+d_2)}{2} \right) - 1 \right\} - \frac{\rho_{\text{fix}1} \sinh[\kappa (d_1)] - \rho_{\text{fix}2} \sinh[\kappa (d_2)]^2}{\cosh^2[\kappa (h+d_1+d_2)/2]} \times \left\{ 1 - \tanh \left( \frac{\kappa (h+d_1+d_2)}{2} \right) \right\}.$$  \hspace{1cm} (63)

For the special case of two similar soft plates carrying $Z_1 = Z_2 = Z, N_1 = N_2 = N$, and $d_1 = d_2 = d$ so that $\rho_{\text{fix}1} = \rho_{\text{fix}2}$, equations (62) and (63) reduce to

$$P_{pl}(h) = \frac{\rho_{\text{fix}}^2}{2 \varepsilon_r \kappa^2_0} \sinh^2[\kappa (d)] \coth \left( \frac{\kappa (h/2 + d)}{2} \right) - 1 \right\}.$$  \hspace{1cm} (64)

When the magnitude of $\psi(x)$ is arbitrary, one must solve the original nonlinear Poisson–Boltzmann equations (52)–(54). Consider the case of two parallel similar plates in a symmetrical electrolyte with valence $z$ and bulk concentration $n$. In this case, we need to consider only the region $-d < x < h/2$ so that the Poisson–Boltzmann equations to be solved are [4, 10]

$$\frac{d^2 y}{dx^2} = \kappa^2 \sinh y, \quad 0 < x < h/2,$$

$$\frac{d^2 y}{dx^2} = \kappa^2 (\sinh y - \sinh y_{\text{DON}}), \quad -d < x < 0.$$  \hspace{1cm} (66) \hspace{1cm} (67)
Here, \( y = ze\psi/kT \), \( \psi_{DON} \) and \( y_{DON} = ze\psi_{DON}/kT \) are, respectively, the scaled potential, Donnan potential given by equation (20) and scaled Donnan potential. The solution to equations (66) and (67), subject to appropriate boundary conditions, takes a complicated form, involving numerical integration. However, for \( \kappa d > 1 \) the value of \( y(h/2) \) can be calculated by solving the following coupled equations:

\[
2 \cosh y_{DON} + \frac{Z N_e}{z n} \left[ y_0 - y_{DON} \right] = 2 \cosh \left( \frac{h}{2} \right), \tag{68}
\]

\[
cosh \left( \frac{y_0}{2} \right) = \cosh \left( \frac{y(h/2)}{2} \right) dc \times \left( \frac{\kappa h}{2} \cosh \left( \frac{y(h/2)}{2} \right) \right)^{1/\cosh \left( \frac{y(h/2)}{2} \right)}.
\tag{69}
\]

Here, \( dc \) is a Jacobian elliptic function with modulus \( 1/cosh(y(h/2)) \), and \( y_0 \equiv y(0) \) is the scaled unperturbed potential at the front edge \( x = 0 \) of the surface layer and is given by equation (40).

The interaction force between two parallel similar plates per unit area \( P_{pl}(h) \) is given by [4]

\[
P_{pl}(h) = 4nkT \sinh^2 \left( \frac{ze\psi(h/2)}{kT} \right), \tag{70}
\]

where \( \psi(h/2) \) is the potential at the midpoint between the plates. A simple approximate analytic expression for \( P_{pl}(h) \) can be obtained using the linear superposition approximation (LSA) [4]: \( \psi(h/2) \) in equation (70) is approximated by the sum of the asymptotic values of the two unperturbed potentials, which is produced by the respective plates in the absence of interaction. For two similar plates,

\[
\psi \left( \frac{h}{2} \right) \approx 2 \psi_s \left( \frac{h}{2} \right). \tag{71}
\]

This approximation is correct in the limit of large \( \kappa h \). From equation (33), the value of the unperturbed potential of a single plate at \( x = h/2 \) is given by

\[
\psi_s \left( \frac{h}{2} \right) = 4 \left( \frac{kT}{ze} \right) \arctanh \left[ \tanh \left( \frac{ze\psi_0}{4kT} \right) e^{-k h/2} \right], \tag{72}
\]

where the unperturbed surface potential \( \psi_0 \) is given by equation (39). For large \( \kappa h \), equation (72) becomes

\[
\psi_s \left( \frac{h}{2} \right) \approx 4 \left( \frac{kT}{ze} \right) \tanh \left( \frac{ze\psi_0}{4kT} \right) e^{-k h/2}. \tag{73}
\]

Hence

\[
\psi \left( \frac{h}{2} \right) = 8 \left( \frac{kT}{ze} \right) \tanh \left( \frac{ze\psi_0}{4kT} \right) e^{-k h/2}. \tag{74}
\]

For large \( \kappa h \), equation (70) asymptotes to

\[
P_{pl}(h) \approx 4nkT \left( \frac{ze\psi(h/2)}{2kT} \right)^2. \tag{75}
\]

Substituting equation (74) into equation (75), we obtain

\[
P_{pl}(h) = 64 \tanh\left( \frac{ze\psi_0}{4kT} \right)^2 \frac{n k T}{kT} \exp(-\kappa h). \tag{76}
\]

The potential energy \( V_{pl}(h) \) can be obtained by integrating equation (76) with the result

\[
V_{pl}(h) = 64 \frac{n k T}{kT} \tan(\frac{ze\psi_0}{4kT})^2 \frac{n k T}{kT} \exp(-\kappa h). \tag{77}
\]

3.2. Interaction between two dissimilar soft spheres

Consider the electrostatic interaction between two dissimilar spherical soft spheres 1 and 2 (figure 4). We denote by \( d_1 \) and \( d_2 \) the thicknesses of the surface charge layers of spheres 1 and 2, respectively. Let the radius of the core of soft sphere 1 be \( a_1 \) and that for sphere 2 be \( a_2 \). We imagine that each surface layer is uniformly charged. Let \( Z_1 \) and \( N_1 \), respectively, be the valence and density of the fixed charge layer of sphere 1 and \( Z_2 \) and \( N_2 \) be those for sphere 2.

With the help of Derjaguin’s approximation [11], viz.,

\[
V_{sp}(H) \equiv \left( \frac{\pi a_1 a_2}{a_1 + a_2} \right) \int_H^{\infty} V_{pl}(h) dh, \tag{78}
\]

one can calculate the interaction energy \( V_{sp}(H) \) between two dissimilar soft spheres 1 and 2, separated by a distance \( H \) between their surfaces, via the corresponding interaction energy \( V_{pl}(h) \) between two parallel dissimilar plates. Substituting equation (77) into equation (78), we obtain [12]

\[
V_{sp}(H) = \frac{1}{\varepsilon \varepsilon_0 k^2 a_1 a_2} \left[ (\rho_{fix1} \sinh(\kappa d_1)) + \rho_{fix2} \sinh(\kappa d_2) \right] \ln \left( \frac{1}{1 - e^{-\kappa (H + d_2)}} \right)
\]

\[
- (\rho_{fix1} \sinh(\kappa d_1) - \rho_{fix2} \sinh(\kappa d_2))^2 \times \ln \left( 1 + e^{-\kappa (H + d_2)} \right) \right]. \tag{79}
\]

For the special case of two similar soft spheres carrying \( Z_1 = Z_2 = Z \), \( N_1 = N_2 = N \), \( d_1 = d_2 = d \) so that \( \rho_{fix1} = \rho_{fix2} = \rho_{fix} \), equation (79) becomes

\[
V_{sp}(H) = \frac{1}{\varepsilon \varepsilon_0 k^2 a_1 a_2} (\rho_{fix} \sinh(\kappa d)) \ln \left( \frac{1}{1 - e^{-\kappa (H + d)}} \right)
\]

\[
- (\rho_{fix} \sinh(\kappa d))^2 \times \ln \left( 1 + e^{-\kappa (H + d)} \right) \right]. \tag{80}
\]
In this case, soft plates and soft spheres become planar hard plates without surface charge layers. In this limit, \( \sigma \) density and that for two hard spheres at constant surface charge two parallel hard plates at a constant surface charge density expression for the electrostatic interaction energy between two interacting surface charge layers, which are, respectively, the amounts of fixed charges contained in the surface layers per unit area on spheres 1 and 2. If we take the limit \( d_1, d_2 \to 0 \) and \( N_1, N_2 \to \infty \), keeping the products \( N_1 d_1 \) and \( N_2 d_2 \) constant, then \( \sigma_1 \) and \( \sigma_2 \) reduce to the surface charge densities of two interacting hard plates without surface charge layers. In this limit, equations (62), (63) and (79), respectively, reduce to

\[
\begin{align*}
P_{pl}(h) &= \frac{1}{8\varepsilon_r \varepsilon_0} \left[ (\sigma_1 + \sigma_2)^2 \csc^2 \left( \frac{kh}{2} \right) - (\sigma_1 - \sigma_2)^2 \coth^2 \left( \frac{kh}{2} \right) \right] \quad \text{for \( \kappa d_1 \gg 1 \) and \( \kappa d_2 \gg 1 \).}
\end{align*}
\]

Equations (84) and (85), respectively, agree with the expression for the electrostatic interaction energy between two parallel hard plates at a constant surface charge density and that for two hard spheres at constant surface charge density [16]. When \( \kappa d_1 \gg 1 \) and \( \kappa d_2 \gg 1 \), which holds for practical cases, the potential deep inside the plates remains constant and equal to the Donnan potential for the respective surface charge layers, which are

\[
\begin{align*}
\psi_{DON1} &= \frac{\rho_{fix1}}{\varepsilon_r \varepsilon_0 k^2}, \\
\psi_{DON2} &= \frac{\rho_{fix2}}{\varepsilon_r \varepsilon_0 k^2}.
\end{align*}
\]

Equations (86) and (87) are, respectively, also obtained by setting the right-hand sides of equations (55) and (57) to zero.

Consider the limiting case of \( \kappa d_1 \gg 1 \) and \( \kappa d_2 \gg 1 \). In this case, soft plates and soft spheres become planar polyelectrolytes and spherical polyelectrolytes, respectively, and equations (83), (84) and (85) reduce, respectively, to

\[
\begin{align*}
P_{pl}(h) &= \frac{1}{4\varepsilon_r \varepsilon_0 k^2} \left[ (\sigma_1 + \sigma_2)^2 \coth \left( \frac{kh}{2} \right) \right. \\
&\quad \left. - (\sigma_1 - \sigma_2)^2 \left( 1 - \tanh \left( \frac{kh}{2} \right) \right) \right] \quad \text{for \( \kappa d_1 \gg 1 \) and \( \kappa d_2 \gg 1 \).}
\end{align*}
\]

\[
\begin{align*}
V_{sp}(H) &= \frac{1}{\varepsilon_r \varepsilon_0 k^2} \left( \frac{\pi a_1 a_2}{d_1 + d_2} \right) \\
&\times \left[ (\sigma_1 + \sigma_2)^2 \ln \left( \frac{1}{1 - e^{-kH}} \right) - (\sigma_1 - \sigma_2)^2 \ln(1 + e^{-kH}) \right].
\end{align*}
\]

4. Electrophoretic mobility of soft particles

In this section, we deal with a general theory of electrophoresis of soft particles and approximate analytic expressions for the mobility of soft particles [4, 15–21]. This theory unites the electrophoresis theories of hard particles and of polyelectrolytes.

Consider a spherical soft particle, i.e., a charged spherical particle covered with an ion-penetrable layer of polyelectrolytes moving with a velocity \( U \) in a liquid containing a general electrolyte in an applied electric field \( E \). We assume that the uncharged particle core of radius \( a \) is coated with an ion-penetrable layer of polyelectrolytes of thickness \( d \) and that ionized groups of valence \( Z \) are distributed within the polyelectrolyte layer at a uniform density \( N \) so that the polyelectrolyte layer is uniformly charged at a constant density \( \rho_{fix} = ZeN \). The polymer-coated particle thus has an inner radius \( a \) and an outer radius \( b \equiv a + d \) (figure 5).
The origin of the spherical polar coordinate system \((r, \theta, \psi)\) is fixed at the center of the particle core and the polar axis \((\theta = 0)\) is set parallel to \(E\). Let the electrolyte be composed of \(N\) ionic mobile species of valence \(z_i\), bulk concentration \((\text{number density}) n_i^\infty\), and drag coefficient \(\lambda_i\) \((i = 1, 2, \ldots, M)\). The drag coefficient \(\lambda_i\) of the \(i\)th ionic species is further related to the limiting conductance \(\Lambda_i^0\) of that ionic species by

\[
\lambda_i = \frac{N_A \varepsilon^2 |z_i|}{\Lambda_i^0},
\]

where \(N_A\) is the Avogadro number. We adopt the model of Debye–Bueche [19], in which the polymer segments are regarded as resistance centers, which are uniformly distributed in the polyelectrolyte layer, exerting frictional forces on the liquid flowing in that layer. We give below the general theory in the polyelectrolyte layer, regarding as resistance centers, which are uniformly distributed.

The fundamental electokinetic equations for the liquid velocity \(\mathbf{u}(r)\) at position \(r\) relative to the particle \((\mathbf{u}(r) \rightarrow -U\) as \(r \rightarrow \infty\)) and the velocity of the \(i\)th species \(v_i\) are the same as those for rigid spheres, except that the Navier–Stokes equations for \(\mathbf{u}(r)\) become different for the regions outside and inside the surface layer [4], viz.,

\[
\eta \nabla \times \nabla \times \mathbf{u} + \gamma \nabla \cdot \mathbf{u} + \rho_\eta \nabla \psi = 0, \quad r > b, \tag{92}
\]

\[
\eta \nabla \times \nabla \times \mathbf{u} + \gamma \mathbf{u} + \nabla p + \rho_\eta \nabla \psi = 0, \quad a < r < b. \tag{93}
\]

Here equation (92) is the usual Navier–Stokes equation. The term \(\gamma \mathbf{u}\) on the left-hand side of equation (93) represents the frictional forces exerted on the liquid flow by the polymer segments in the polyelectrolyte layer, and \(\gamma\) is the frictional coefficient. If it is assumed that each resistance center corresponds to a polymer segment, which in turn is regarded as a sphere of radius \(a\), and the polymer segments are distributed at a uniform volume density of \(N_p\) in the polyelectrolyte layer, then each polymer segment exerts the Stokes resistance \(6\pi \eta a_p \mathbf{u}\) on the liquid flow in the polyelectrolyte layer so that

\[
\gamma = 6\pi \eta a_p N_p. \tag{94}
\]

Similarly, the Poisson equation relating the charge density \(\rho_\eta(r)\) resulting from the mobile charged ionic species and the electric potential \(\psi(r)\) are also different for the different regions,

\[
\Delta \psi(r) = -\frac{\rho_\eta(r)}{\varepsilon_i \varepsilon_0}, \quad r > b, \tag{95}
\]

\[
\Delta \psi(r) = -\frac{\rho_\eta(r) + Z e N}{\varepsilon_i \varepsilon_0}, \quad a < r < b. \tag{96}
\]

For a weak applied field \(E\), the electokinetic equations (92) and (93) are linearized to give

\[
\eta \nabla \times \nabla \times \mathbf{u} = \sum_{i=1}^M \nabla \delta n_i \times \nabla n_i^0, \quad r > b, \tag{97}
\]

\[
\eta \nabla \times \nabla \times \mathbf{u} + \gamma \nabla \cdot \mathbf{u} + \sum_{i=1}^M \nabla \delta n_i \times \nabla n_i^0, \quad a < r < b.
\]

\[\eta \nabla \times \nabla \times \mathbf{u} + \gamma \nabla \cdot \mathbf{u} + \rho_\eta \nabla \psi = 0, \quad a < r < b \tag{98}\]

and

\[
\nabla \cdot \left( n_i^0 \mathbf{u} - \frac{1}{\lambda_i} \nabla n_i^0 \nabla \delta \mu_i \right) = 0, \tag{99}\]

where \(n_i^0(r)\) is the equilibrium concentration \((\text{number density})\) of the \(i\)th ionic species \((n_i^0 \rightarrow n_i^\infty\) as \(r \rightarrow \infty)\), and \(\delta n_i^0(r)\) and \(\delta \mu_i(r)\) are, respectively, the deviation of \(n_i^0(r)\) and that of the electrochemical potential \(\mu_i(r)\) of the \(i\)th ionic species due to the applied field \(E\).

Symmetry considerations permit us to write

\[
\mathbf{u}(r) = \left( -\frac{2}{r} h(r) E \cos \theta, \frac{1}{r} \frac{d}{dr} \left( r h(r) \right) E \sin \theta, 0 \right), \tag{100}\]

\[
\delta \mu_i(r) = -z_i e \phi_i(r) E \cos \theta, \tag{101}\]

where \(E = |E|\). The fundamental electokinetic equations can be transformed into equations for \(h(r)\) and \(\phi_i(r)\) as

\[
L(Lh) = G(r), \quad r > b, \tag{102}\]

\[
L(Lh - \lambda^2 h) = G(r), \quad a < r < b, \tag{103}\]

\[
L\phi_i = \frac{dy}{dr} \left( z_i \frac{d\phi_i}{dr} - \frac{2\lambda_i h}{e r} \right), \tag{104}\]

\[
\lambda = \left( \gamma/\eta \right)^{1/2}, \tag{105}\]

\[
L \equiv \frac{d}{dr} \frac{1}{r^2} \frac{d}{dr} r^2 = \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{2}{r^2}, \tag{106}\]

\[
G(r) = -\frac{e}{\eta r} \frac{dy}{dr} \sum_{i=1}^M z_i^2 n_i^\infty e^{-z_i/e \phi_i}. \tag{107}\]

Here, \(\gamma = e \psi^{(0)}/kT\) is the scaled equilibrium potential outside the particle core and the value \(1/\lambda\) is called the electrokinetic softness.

The boundary conditions for \(\psi(r), u(r)\) and \(v_i(r)\) are as follows.

(i) \(\psi(r)\) and \(-\nabla \psi(r)\) are continuous at \(r = b\),

\[
\psi(b^-, \theta) = \psi(b^+, \theta), \tag{108}\]

\[
\left. \frac{\partial \psi(r, \theta)}{\partial r} \right|_{r=b^-} = \left. \frac{\partial \psi(r, \theta)}{\partial r} \right|_{r=b^+}, \tag{109}\]

\[
\left. \frac{\partial \psi(r, \theta)}{\partial \theta} \right|_{r=b^-} = \left. \frac{\partial \psi(r, \theta)}{\partial \theta} \right|_{r=b^+}, \tag{109}\]

where the continuity of \(-\nabla \psi(r)\) results from the assumption that the relative permittivity \(\varepsilon_i\) takes the same value both inside and outside the polyelectrolyte layer.
The normal and tangential components of \( \mathbf{u} \) are continuous at \( r = b \),

\[
\begin{align*}
    u_r(b^-) & = u_r(b^+), \\
    u_\theta(b^-) & = u_\theta(b^+). 
\end{align*}
\]  

(v) The normal and tangential components of the stress tensor \( \sigma^I \), which is the sum of the hydrodynamic stress \( \sigma^H \) and the Maxwell stress \( \sigma^E \), are continuous at \( r = b \). From the continuity of \( -\nabla \psi(r) \), the normal and tangential components of \( \sigma^E \) are continuous at \( r = b \).

Therefore, the normal and tangential components of \( \sigma^H \) must be continuous at \( r = b \) so that the pressure \( p(r) \) is continuous at \( r = b \).

(vi) The electrolyte ions cannot penetrate the particle core, viz.,

\[
|v_i \cdot n|_{r=\infty} = 0, 
\]

where \( n \) is the unit normal outward from the surface of the particle core.

(vii) In the stationary state, the net force acting on the particle (the particle core plus the polyelectrolyte layer) or an arbitrary volume enclosing the particle must be zero. Consider a large sphere \( S \) of radius \( r \) containing the particle. The radius \( r \) is taken to be sufficiently large so that the net electric charge within \( S \) is zero. There is then no electric force acting on \( S \) and we need to consider only hydrodynamic force \( F^H \), which must be zero, viz.,

\[
F^H = \int_S (\sigma^H \cos \theta - \sigma^H \sin \theta) dS, \quad r \to \infty, 
\]

where the integration is carried out over the surface of the sphere \( S \).

The electrophoretic mobility \( \mu = U/E \) (where \( U = |U| \)) can be calculated from

\[
\mu = 2 \lim_{r \to \infty} \frac{h(r)}{r}, 
\]

with the result \([4, 16]\)

\[
\mu = \frac{b^2}{9} \int_b^\infty \left[ 3 \left( 1 - r^2 \right) - \frac{2L_2}{L_1} \right] \frac{G(r)dr}{b^3} + \frac{2L_3}{3\lambda^2 L_1} \int_a^\infty \left( 1 + \frac{r}{b^2} \right) \frac{G(r)dr}{b^3} 
\]

\[
= \frac{2}{3\lambda^2} \int_a^b \left[ 1 - \frac{3a}{2\lambda^2 b^3 L_1} [(L_3 + L_3) \cos(h(r) - a))] 
\]

\[
= \left[ -(L_4 + L_3) \sinh[h(r) - a)] \right] G(r)dr, 
\]

\]

with

\[
L_1 = \left( \frac{1}{2} \frac{a^3}{2b^3} + \frac{3a}{2\lambda^2 b^3} - \frac{3a^2}{2\lambda^2 b^4} \right) \cosh[\lambda(b - a)] 
\]

\[
- \left( \frac{1}{2} \frac{3a^2}{2b^3} + \frac{a^3}{2b^3} + \frac{3a}{2\lambda^2 b^4} \right) \sinh[\lambda(b - a)], 
\]

\]

\[
L_2 = \left( \frac{1}{2} \frac{a^3}{2b^3} + \frac{3a}{2\lambda^2 b^3} \right) \cosh[\lambda(b - a)] 
\]

\[
+ \frac{3a^2}{2b^3} \sinh[\lambda(b - a)] - \frac{3a}{\lambda b}, 
\]

\]

\[
L_3 = \cosh[\lambda(b - a)] - \frac{\sinh[\lambda(b - a)]}{\lambda b} - \frac{a}{b}, 
\]

\]

\[
L_4 = \sinh[\lambda(b - a)] - \frac{\cosh[\lambda(b - a)]}{\lambda b} - \frac{\lambda a^2}{3b} - \frac{2\lambda b}{3a} + \frac{1}{\lambda b}. 
\]

We derive approximate mobility formulae for the simple but important case where the potential is arbitrary but the double layer potential still remains spherically symmetrical in the presence of the applied electric field (the relaxation effect is neglected). Moreover, we treat the case where the following conditions hold

\[
\kappa a \gg 1, \quad \lambda a \gg 1 \quad \text{and} \quad \kappa b \gg 1, 
\]

\[
\kappa d \gg 1 \quad \text{and} \quad \kappa d \gg 1, 
\]

which are satisfied for most practical cases. When the electrolyte is symmetrical with a valence \( z \) and bulk concentration \( n \), and if \( \kappa d \gg 1 \), then the potential inside the polyelectrolyte layer can be approximated using equation (43). Using this approximation, we obtain \([4, 30]\)

\[
\mu = \frac{\varepsilon \varepsilon_0 \psi_0/\kappa m + \psi_{DON}/\lambda}{1/\kappa m + 1/\lambda} f \left( \frac{d}{a} \right) \frac{ZeN}{\eta \lambda^2}, 
\]

with

\[
f \left( \frac{d}{a} \right) = \frac{2}{3} \left( 1 + \frac{a^3}{2b^3} \right) \frac{2}{3} \left( 1 + \frac{1}{2(1+d/a)^3} \right). 
\]

In the limit of \( d \gg a \), in which case \( f(d/a) \to 2/3 \), equation (123) reduces to

\[
\mu = \frac{2\varepsilon \varepsilon_0 \psi_0/\kappa m + \psi_{DON}/\lambda}{3\eta \lambda^2} \frac{ZeN}{\kappa m + 1/\lambda}. 
\]

For the low-potential case, equation (125) further reduces to

\[
\mu = \frac{ZeN}{\eta \lambda^2} \left[ 1 + \frac{2}{3} \frac{\lambda}{\kappa} \left( \frac{1 + \lambda/2\kappa}{1 + \lambda/\kappa} \right) \right], 
\]

which agrees with Hermans–Fujita’s equation for the electrophoretic mobility of a spherical polyelectrolyte (a soft particle with no particle core) \([23]\).
In the opposite limit of $d \ll a$, in which case $f(d/a) \to 1$, equation (123) reduces to

$$
\mu = \frac{\varepsilon \varepsilon_0}{\eta} \frac{\psi_0}{1/\kappa_m + \psi_{\text{DON}}/\lambda} + \frac{ZeN}{\eta \lambda^2},
$$

which, for low potentials, reduces to

$$
\mu = \frac{ZeN}{\eta \lambda^2} \left[ 1 + \left( \frac{\lambda}{\kappa} \right)^2 \left( \frac{1 + \lambda/2\kappa}{1 + \lambda/\kappa} \right) \right].
$$

Equation (117) covers a plate-like soft particle. Indeed, in the limiting case of $a \to \infty$, the general mobility expression (equation (117)) reduces to

$$
\mu = \frac{\varepsilon \varepsilon_0}{\eta} \frac{1}{\cosh(\lambda d)} \left[ \psi^{(0)}(-d) \right.
+ \lambda \int_{-d}^{0} \psi^{(0)}(x) \sinh \lambda(x + d) dx
+ \left. \frac{ZeN}{\eta \lambda^2} \left( 1 - \frac{1}{\cosh(\lambda d)} \right) \right],
$$

which is the general mobility expression of a plate-like soft particle. For the case of $\kappa d \gg 1$ and $\lambda d \gg 1$, equation (129) becomes equation (127).

Equation (123) consists of two terms: the first term is a weighted average of the Donnan potential $\psi_{\text{DON}}$ and the surface potential $\psi_0$. It should be stressed that only the first term is subject to the shielding effects of electrolytes, approaching zero as the electrolyte concentration $n$ increases, while the second term does not depend on the electrolyte concentration. In the limit of high electrolyte concentrations, all the potentials vanish and only the second term of the mobility expression remains, viz.,

$$
\mu \to \mu^{\infty} = \frac{ZeN}{\eta \lambda^2}.
$$

Equation (130) shows that as $\kappa \to \infty$, $\mu$ approaches a nonzero limiting value $\mu^{\infty}$. This is a characteristic of the electrokinetic behavior of soft particles, in contrast to the case of the electrophoretic mobility of hard particles, which should reduce to zero owing to the shielding effects, since the mobility expressions for rigid particles do not contain $\mu^{\infty}$. The term $\mu^{\infty}$ can be interpreted as resulting from the balance...
between the electric force acting on the fixed-charges \((ZeN)E\) and the frictional force \(\gamma u\), viz.,

\[
(ZeN)E + \gamma u = 0 \tag{131}
\]

from which equation (130) follows.

To see this more clearly, in figures 6(a) and (b) we give a schematic representation of the liquid velocity \(u(x) (= |u(x)|)\) as well as potential distributions \(\psi(x)\) around a soft particle in comparison with those for a hard particle. There, \(x\) is given by \(x = r - a\) across the surface charge layer. Figure 6(c) shows the electrophoretic mobility \(\mu\) as a function of electrolyte concentration \(n\) for a soft particle and a hard particle. It is seen that the liquid velocity \(u(x)\) in the middle region of the surface charge layer (the plateau region in figure 6(b)), where the potential is almost equal to the Donnan potential \(\psi_{\text{DON}}\) (figure 6 (a)), gives \(\mu^\infty\). It is this term that yields the term independent of the electrolyte concentration. We also note that \(1/\lambda\) can be interpreted as the distance between the slipping plane at the core surface at \(r = a(x = 0)\) and the bulk phase of the surface layer (the plateau region in figure 6(b)), where \(u(x)/E\) is given by \(-\mu^\infty\). Figure 6(a) shows that a small shift of the slipping plane has no effect on the mobility value. Therefore, the mobility of soft particles is insensitive to the position of the slipping plane and the zeta potential loses its significance.

The above electrophoresis theory of soft particles has been applied to analyze the electrophoretic mobility data of biological colloids such as cells and their model particles [24–35]. Ohshima [36, 37] proposed a theory of electrophoresis of soft particles in concentrated suspensions. Keh and Liu presented theories of sedimentation [38] and electrical conductivity [39] of a dilute suspension of soft particles, and these theories were extended to the concentrated case [40, 41]. An approximate expression for the dynamic electrophoretic mobility of a spherical soft particle was derived in reference [39]. The electroosmotic velocity in an array of parallel soft cylinders was discussed in [40]. Dukhin et al [44] pointed out the importance of the degree of dissociation of charged groups in the polyelectrolyte layer. Duval and Ohshima [45] presented a new electrophoresis model of diffuse soft particles. In that model, a diffuse soft particle consists of an uncharged impenetrable core and a charged diffuse polyelectrolyte layer. The diffuse character of the polyelectrolyte layer is defined by a gradual distribution of the density of polymer segments in the interstitial region separating the core from the bulk electrolyte solution. Successful application of that model has been reported for humic acids [46], bacteria [47] and red blood cells [48]. For numerical calculations of the electrophoretic mobility based on more rigorous theories, the readers are referred to the studies of Hill et al [49–52] and Lopez-Garcia et al [53–55] as well as that of Duval and Ohshima [45].

5. Summary

In this article, we discussed the electrostatics and electrokinetics of soft particles in comparison with those of hard particles. It has been shown that the Donnan potential in the surface layer, which is related to the density of the fixed charge in the surface layer, plays an essential role in the potential distribution across the surface layer, electrostatic interactions between soft particles and the electrophoretic mobility of soft particle in an external electric field.

References

[1] Israelachvili J N 1992 Interfacial and Surface Forces 2nd edn, (New York: Academic)
[2] Lyklema J 1995 Fundamentals of Interface and Colloid Science, Solid–Liquid Interfaces vol 2 (New York: Academic)
[3] Ohshima H 1998 Electrical Phenomena at Interfaces: Fundamentals, Measurements, and Applications 2nd edn, Revised and expanded ed H Ohshima and K Fujimura (New York: Dekker) chapter 3
[4] Ohshima H 2006 Theory of Colloid and Interfacial Electric Phenomena (New York: Elsevier/Academic)
[5] Tadros T F (ed) 2007 Colloid Stability: The Role of Surface Forces—Part I (Weinheim: Wiley-VCH)
[6] López-García J J, Horno J and Grosse C 2003 J. Colloid Interface Sci. 268 371
[7] Ohshima H 2008 J. Colloid Interface Sci. 323 92
[8] Ohshima H 2008 J. Colloid Interface Sci. 323 313
[9] Ohshima H, Makino K and Kondo T 1987 J. Colloid Interface Sci. 116 196
[10] Ohshima H and Kondo T 1987 J. Theor. Biol. 128 187
[11] Derjaguin B V 1934 Kolloid Z. 69 155
[12] Ohshima H 2008 J. Colloid Interface Sci. 328 3
[13] Wiese G R and Healy T W 1970 Trans. Faraday Soc. 66 490
[14] Ohshima H and Hyono A 2009 J. Colloid Interface Sci. 202 208
[15] Ohshima H 1994 J. Colloid Interface Sci. 163 474
[16] Ohshima H 1995 Colloids Surf. A 103 249
[17] Ohshima H 1995 Adv. Colloid Interface Sci. 62 189
[18] Ohshima H 1995 Electrophoresis 16 1360
[19] Ohshima H 2000 J. Colloid Interface Sci. 228 190
[20] Ohshima H 2006 Electrophoresis 285 1411
[21] Ohshima H 2007 Colloid Polym. Sci. 285 1411
[22] Debye P and Bueche A 1948 J. Chem. Phys. 16 573
[23] Hermans J J and Fujita H 1955 Koninkl. Ned. Akad. Wetenschap. Proc. B 58 182
[24] Ohshima H, Makino K, Kato T, Fujimoto K, Kondo T and Kawaguchi H 1993 J. Colloid Interface Sci. 159 512
[25] Makino K, Yamamoto S, Fujimoto K, Kawaguchi H and Ohshima H 1994 J. Colloid Interface Sci. 166 251
[26] Takashima S and Morisaki H 1997 Colloids Surf. B 9 205
[27] Bos R, van der Mei H C and Busscher H J 1998 Biophys. Chem. 74 251
[28] Larsson A, Rasmussen M and Ohshima H 1999 Carbohydr. Res. 317 223
[29] Morisaki H, Nagai S, Ohshima H, Ikemoto E and Kogure K 1999 Microbiology 145 2797
[30] Rasmussen M, Vincent B and Marston N 2000 Colloid Polym. Sci. 278 253
[31] Hayashi H, Tsuneda S, Hirata A and Sasaki H 2001 Colloids Surf. B 22 149
[32] Garcia-Salinas M I, Romero-Cano M S and de las Nieves F J 2001 Progr. Colloid Polym. Sci. 118 180
[33] Kiers P J M, Bos R, van der Mei H C and Busscher H J 2001 Microbiology 147 757
[34] Molina-Bolivar J A, Galisteo-Gonzalez F and Hidalgo-Alvarez R 2001 Colloids Surf. B 21 125
[35] Hyono A, Mazda T, Okazaki H, Tadokoro K and Ohshima H 2008 Vox Sang. 95 131
[36] Ohshima H 2000 J. Colloid Interface Sci. 225 233
[37] Ohshima H 2001 *Colloids Surf. A* **195** 129
[38] Keh H J and Liu Y C 1994 *J. Colloid Interface Sci.* **163** 474
[39] Liu Y C and Keh H J 1998 *Langmuir* **163** 474
[40] Ohshima H 2000 *J. Colloid Interface Sci.* **229** 140
[41] Ohshima H 2000 *J. Colloid Interface Sci.* **229** 307
[42] Ohshima H 2001 *J. Colloid Interface Sci.* **233** 142
[43] Ohshima H 2001 *Colloids Surf. A* **192** 227
[44] Dukhin S S, Zimmermann R and Werner C 2005 *J. Colloid Interface Sci.* **286** 761
[45] Duval J F L and Ohshima H 2006 *Langmuir* **22** 3533
[46] Duval J F L, Wilkinson K J, van Leeuwen H P and Buffle J 2005 *Environ. Sci. Technol.* **39** 6435
[47] Duval J F L, Busscher H J, van de Belt-Gritter B, van der Mei H C and Norde W 2005 *Langmuir* **21** 11268
[48] Hyono A, Gaboriaud F, Mazda T, Takata Y, Ohshima H and Duval J F L 2009 *Langmuir* **25** 10873
[49] Hill R J, Saville D A and Russel W B *J. Colloid Interface Sci.* **258** 56
[50] Hill R J, Saville D A and Russel W B *J. Colloid Interface Sci.* **263** 478
[51] Hill R J and Saville D A 2005 *Colloids Surf. A* **267** 31
[52] Hill R J 2004 *Phys. Rev. E* **70** 051406
[53] Lopez-Garcia J J, Grosse C and Horno J J 2003 *J. Colloid Interface Sci.* **265** 327
[54] Lopez-Garcia J J, Grosse C and Horno J J 2006 *J. Colloid Interface Sci.* **291** 651