Electrostatic pair-interaction force between semi-permeable membranes

Electrostatic pair-interaction force between semi-permeable membranes

Armik V M Khachatourian and Anders O Wistrom

Department of Chemical and Environmental Engineering, University of California, Riverside, CA 92521, USA

Abstract
Membrane fusion, protein folding and macromolecular assembly are a few of the many processes in which the interaction of near-neutral and semi-permeable fluid surfaces plays an important role. The electrostatic force between membranes is solved from Coulomb's law by first casting the expression for charge by way of the Fredholm integral equation, and then integrating the effect of the charge distribution to obtain the expression for force. The surface charge density is conveniently described by a Langevin type expression which suggests a saturation type behaviour describing a transition from 'soft' to 'hard' sphere where increasing electrolyte strength and particle size modify the pair-interaction force.

PACS numbers: 41.20.Cv, 05.70.-a, 71.10.Li, 82.70.Dd

1. Introduction

Amphiphilic molecules, such as surfactants, lipids and proteins form a variety of extended, noncovalent structures that include micelles, vesicles and the fundamental bilayers of the membranes of cells [1, 2]. One of the natural consequences of the self-assembled structures made out of amphiphilic molecules is the construction of a semipermeable barrier that exhibits many of the attributes of a cell membrane. While membranes are often considered stable, noninteracting structures, the dynamics of cellular processes require that membranes interact with each other to facilitate transport and exchange of intra-cellular material. Central to these transformations of membrane structure is the process of membrane fusion. The pathway leading to membrane fusion has been suggested to include the following events [3]: (i) close approach of the two membrane surfaces, (ii) destabilization of membrane bilayers and (iii) mixing of components of bilayers and formation of new membrane structures. It is the interaction in this first event, bringing two membranes into close proximity, that is the topic of this contribution.

Since we seek to describe the interaction from a mean-field perspective we must first discuss some properties of self-assembled structures made out of amphiphilic molecules relevant to the electrostatic force. In the context of this contribution, only a limited overview can be given of those aspects of membrane structure and composition that have bearing on the selection of boundary conditions for the interaction force model. Amphiphilic molecules have a hydrophobic portion (the hydrocarbon chain) and a hydrophilic portion (the polar headgroup), which determines what charge the amphiphile as a whole may carry. Bilayers with exposed headgroups thus exhibit a positive, negative or overall neutral charge depending on the chemical structure of the headgroup and pH. Charge may also be modified by electrolyte composition and strength and thus regulates the magnitude of the interaction forces between membranes [4–7].

Membrane integrity also plays an important role modifying the electrical properties. As the membranes become more stressed with increasing temperature more of the hydrocarbon interiors are exposed to the aqueous phase, resulting in a characteristic increase in range and magnitude of the attractive force [8]. Passive diffusion is believed to occur via molecular scale discontinuities (kinks that hydrocarbon chains form under the influence of thermal motion) in the bilayer [3]. Even though it is energetically unfavourable for polar solutes to inhabit the hydrophobic interior of the membrane due to the hydrophobic effect passive transport of charged ions is still observed [9]. For example, measured permeability rates for transport of monovalent ions across unilamellar vesicles range between 2×10^{-5} and 3×10^{-6} s^{-1} [10]. The important consequence of thermally induced local discontinuities is that membranes are more or less permeable to both polar and non-polar solutes despite barriers to transport.

Recent vibrational studies of water at the hydrophobic surface suggest that dipolar interactions between interfacial molecules and the polarizable organic phase play an important role in the interfacial region, resulting in strong orientation effects [11]. The orientation of these water molecules that interact with the hydrocarbon phase is due to weakly bonded water molecules that straddle the interface and make up the majority of the water molecules in the interfacial region and not to a strengthening of the hydrogen-bonding network between water molecules in the bulk [11]. These observations are consistent with molecular simulation studies [12]. Importantly, the orientation of these water molecules that interact with the organic phase creates an icelike structure at the hydrocarbon interface, which suggests that proton conductivity and mobility is higher in the hydrophobic zone than in bulk water [13]. From a molecular point of view important implications include mechanisms for charge transport across the hydrophobic barrier as well as charge transport tangentially along the polarizable hydrocarbon interface.

Given the experimental and theoretical evidence for water and solute penetration, water structure and polarizability in the interfacial region of hydrophobic surfaces it appears possible to cast an expression for the interaction between membrane surfaces in terms of the screened Coulomb force and appropriate boundary conditions. It should be noted, however, that in doing so we neglect the molecular-scale complexity with all its heterogeneities to obtain a mean-field approximation of the interaction force.

2. Model development

The model surfaces considered here are self-assembled structures of amphiphilic molecules that form semi-permeable membranes [3, 14]. Typical examples of such structures are micelles and vesicles, which usually are spheres or spherelike particles, and self-assembled amphiphilic molecules that have been deposited onto a substrate for the purpose of experimental investigation of the interaction force [5, 7, 15]. Many amphiphiles are non-ionic or zwitterionic

and often display only weak surface potentials; either due to screening by the hydrocarbon chains and/or because of selective ion-binding effects [2, 16, 17]. Hence, the linearized form of the Poisson–Boltzmann equation is applicable for the near electro-neutral membrane surfaces under investigation.

The linearized Poisson–Boltzmann equation governing the distribution of potential ψ both inside and outside the semi-permeable membrane assumes the form

$$\nabla^2 \psi = \kappa^2 \psi \qquad \text{(inside and outside)} \tag{1}$$

(which mathematically speaking is valid only for non-constant or zero surface potentials), where the electrolyte is defined by its bulk screening constant κ. Experimentally, the exponential form of the screening can be justified from the asymptotic behaviour of measured interaction forces [18].

To complete the boundary value problem expressed in equation (1), one must specify the boundary conditions at all interfaces involved. The field potential at any point is obtained from Gauss's definition of potential [19]:

$$\psi(\vec{x}) = K\left[\int dQ_1(\vec{x}_1)\frac{e^{-\kappa|\vec{x}-\vec{x}_1|}}{|\vec{x}-\vec{x}_1|} + \int dQ_2(\vec{x}_2)\frac{e^{-\kappa|\vec{x}-\vec{x}_2|}}{|\vec{x}-\vec{x}_2|}\right] \tag{2}$$

where the potential at $\vec{x} \equiv (x, y, z)$ is the sum of the contributions from the charged particles, and K is $1/4\pi\epsilon$, where ϵ is the dielectric permittivity of the solvent. Equation (2) is valid at all points except when $|\vec{x}-\vec{x}_i| \equiv 0$, $i = 1$ for P_1 and $i = 2$ for P_2, where the endpoints of the two vectors coincide on the particle surfaces.

Suppose membrane surfaces are raised to a constant potential, V_1 and V_2 volts, taken as relative to ground the surface potentials for P_1 and P_2 are

$$V_1 = K\left[\int dQ_1\frac{e^{-\kappa R_1}}{R_1} + \int dQ_2\frac{e^{-\kappa R_2}}{R_2}\right]$$
$$V_2 = K\left[\int dQ_1\frac{e^{-\kappa R_1'}}{R_1'} + \int dQ_2\frac{e^{-\kappa R_2'}}{R_2'}\right] \tag{3}$$

where Q_i are point charges and R_i and R_i' are directional vector quantities (figure 1). We note that for a given surface potential and surface-to-surface separation distance the magnitude and location of surface charges are uniquely determined by equation (3). The magnitude and location of charges are obtained self-consistently by way of the Fredholm integral equation [20], where the details of the derivation are found in appendix A.

The effect of the known charge distribution is then integrated to obtain the electrostatic force. Coulomb's law [21] for point charges is readily generalized to account for the screened electrostatic force due to an ensemble of charges residing on two macroscopic surfaces. Recent calibration experiments designed to evaluate Coulomb's law for macroscopic particles held at constant potential revealed an exact (within experimental error) agreement between theory and force measurements [22]. We consider the electrostatic force between two spherical membrane surfaces P_1 and P_2 with radii a_1 and a_2, respectively, immersed in a solvent E. Accordingly, the screened Coulomb force [21] on particle P_1 is then solely due to particle P_2, and is given by

$$\vec{F} = K\int dQ_1(\vec{X}_1)(-\vec{\nabla}_{\vec{X}_1})\int dQ_2(\vec{x}_2)\frac{e^{-\kappa|\vec{X}_1-\vec{x}_2|}}{|\vec{X}_1-\vec{x}_2|} \tag{4}$$

where $\vec{X}_1 \equiv (X_1, Y_1, Z_1)$ and $\vec{x}_2 \equiv (x_2, y_2, z_2)$ are points on P_1 and P_2, respectively. The first integral accounts for all charges residing on P_1 by summing over all charges Q_1 located at $\vec{X}_1$. The potential is obtained by summing over all charges residing on P_2, Q_2, located at $\vec{x}_2$
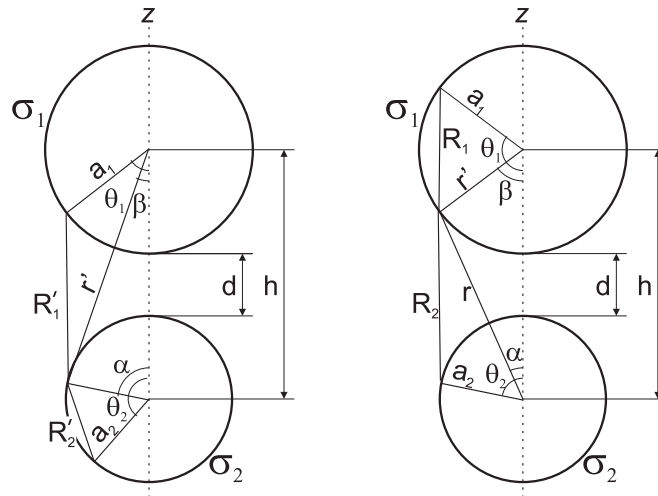
Figure 1. Schematic representation of two semi-permeable particles each having a uniform distribution of potential immersed in a screening solvent E. Potentials, charge densities and the radii on the top and bottom spheres are denoted V_1, σ_1, a_1 and V_2, σ_2, a_2, respectively.

and scaled by the inverse of the separation distance, $|\vec{X}_1 - \vec{x}_2|$, multiplied by an exponential 'screening' factor $e^{-\kappa|\vec{X}_1 - \vec{x}_2|}$.

For a spherical coordinate system equation (4) can be written in terms of Legendre polynomials, $P_\ell(x)$ and modified Bessel functions

$$\vec{F} = \hat{z} K a_1^2 a_2^2 (2\pi)^2 \kappa^2 \sum_{m=0}^{\infty} \frac{I_{m+1/2}(\kappa a_2)}{\sqrt{\kappa a_2}} \int_0^\pi \sin\theta_2 \, d\theta_2 \, \sigma_2(\theta_2) P_m(\cos\theta_2)$$

$$\times \int_0^\pi d\beta \sin\beta \sigma_1(\beta) \left[(m+1) P_{m+1}(\cos\alpha) \frac{K_{m+3/2}(\kappa r)}{\sqrt{\kappa r}} \right.$$

$$\left. + m P_{m-1}(\cos\alpha) \frac{K_{m-1/2}(\kappa r)}{\sqrt{\kappa r}} \right] \tag{5}$$

where contact is avoided by stipulating that $h > a_1 + a_2$ and h is defined as the centre-to-centre separation distance between two particles of radii a_1 and a_2. In light of the constant potential boundary condition, equations (5), (A.1) can be written as

$$\vec{F} = -\hat{z} K a_2^2 (2\pi)^2 \int_{-1}^1 dx \, x \left[\frac{\kappa V_2}{4\pi K} \left(\coth \kappa a_2 - \frac{1}{\kappa a_2} \right) - \sigma_2(x) \right]^2$$

$$= -\hat{z} K a_2^2 (2\pi)^2 \int_{-1}^1 dx \, x [\Sigma_2(x)]^2 \tag{6}$$

which is the sought after expression for the screened Coulomb force. We note that equation (6) can be viewed as a Maxwell–Lorentz type force:

$$\vec{F} = \frac{1}{2}\epsilon \int d\vec{S} \, (\vec{E} \cdot \hat{S})^2$$

when the electric field, $\vec{E}$, on the particle surface is identified as $\vec{E}_i = -\vec{\nabla}\psi_i$. As a check on the validity of the above expression we note that asymptotically, for $h \gg a_1 + a_2$, σ_1 and

σ_2 reduce to a uniform charge distribution on P_1 and P_2, respectively, such that equation (5) reduces to

$$\vec{F} = \hat{z} K Q_1 Q_2 \left(\frac{\sinh \kappa a_1}{\kappa a_1} \right) \left(\frac{\sinh \kappa a_2}{\kappa a_2} \right) \left(\frac{e^{-\kappa h}}{h} \right) \left(\kappa + \frac{1}{h} \right). \tag{7}$$

Equation (7) can also be viewed as the screened electrostatic force between two charged particles with constant surface charge densities σ_1 and σ_2, which in the limit $\kappa \to 0$ reduces to

$$\vec{F} = \hat{z} K \frac{Q_1 Q_2}{h^2}. \tag{8}$$

In classical colloid theory the surface potential is related through the thermodynamic relationships governing the concentration and adsorbability of ions dissolved in the solvent [23]. In the following, only the interaction between particles at the constant potential limit will be discussed, leaving the constant charge limit, which represents the other extreme of a particle system's behaviour, for subsequent analysis [24, 25].

3. Discussion

Experimentally, the composition inside and outside the membrane surface can be assumed to be the same. This is often the case for model membrane systems such as liposomes, vesicles and deposited membranes used for transport studies and fusion experiments [3]. The boundary conditions that correspond to a semi-permeable and polarizable surface yield an expression for surface charge that differs from the classical result [24–27]. The surface charge densities are obtained self-consistently from equation (3), where the details of the evaluation are found in appendix B.

The surface charges on P_1 and P_2 are

$$\Sigma_1(\beta) = -\frac{1}{4\pi K} \frac{\partial \psi}{\partial r_1}\bigg|_{r_1=a_1} = \sigma_1(\beta) - \frac{\kappa V_1}{4\pi K} \left(\coth(\kappa a_1) - \frac{1}{\kappa a_1} \right) \tag{9}$$

and

$$\Sigma_2(\alpha) = -\frac{1}{4\pi K} \frac{\partial \psi}{\partial r_2}\bigg|_{r_2=a_2} = \sigma_2(\alpha) - \frac{\kappa V_2}{4\pi K} \left(\coth(\kappa a_2) - \frac{1}{\kappa a_2} \right). \tag{10}$$

Charge saturation is conveniently described by a Langevin type expression obtained from equation (9) or (10):

$$-\frac{\Sigma_1}{\epsilon \kappa V_1} = \coth(\kappa a_1) - \frac{1}{\kappa a_1} \tag{11}$$

where the Langevin function measures the ratio of the actual charge to its maximum value. Notably, the magnitude and distribution of surface charge are regulated by particle size, a, and by the solvent through the Debye length, κ^{-1}. One deduces that the charge decreases with increasing κ, a phenomenon also noted for a charged particle in isolation [28]. In figure 2 the surface charge is plotted as a function of polar angle θ for the case of two particles of equal size and constant potential in close proximity. The surface charge distribution is obtained self-consistently from equations (A.8) and (A.9) (appendix A) using matrix inversion. For the case of a polarizable surface held at constant potential a charge density depletion is observed at the point of closest approach (small θ), which gives rise to a nonlinear behaviour of the surface charge distribution. Surface elements further away from the point of contact (large θ) are not affected by the presence of the second particle and remain 'hard'. The transition between 'soft' and 'hard' moves closer to the point of contact with increasing κ, which suggests that a saturation effect comes into play. According to equation (9) the cross-over from 'soft' to 'hard' is gradual and finally saturates when $\kappa a \to \infty$. At infinite separation
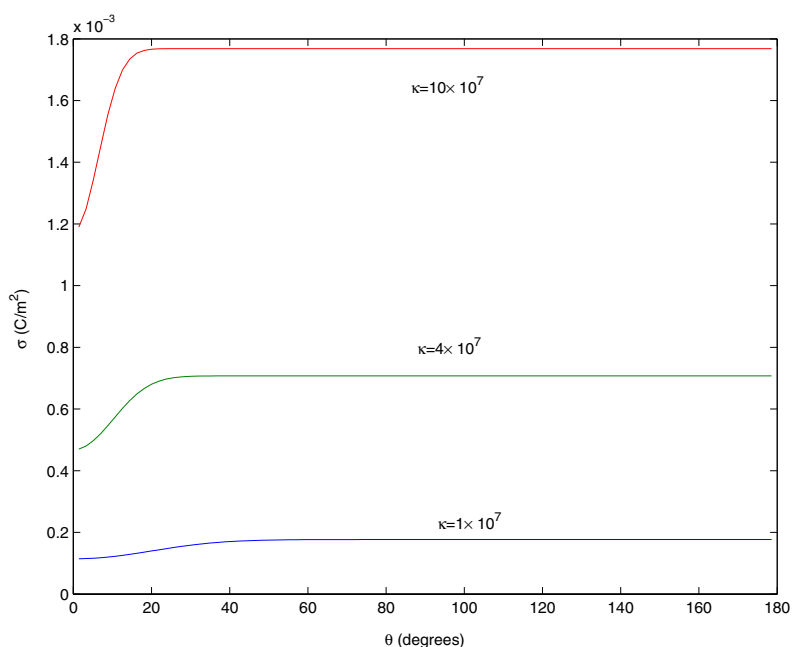
Figure 2. Charge density distribution for a charged particle held at constant potential as a function of the bulk screening constant, κ. The evaluation is carried out for equal sized particles with radii a equal to 1×10^{-6} m. The surface-to-surface separation is chosen to be 1×10^{-11} m for the purpose of demonstrating numerical stability.

(This figure is in colour only in the electronic version)

distance the electric field is due only to the potential carried by the single particle. The surface potential for P_i in isolation is $V_i = (\sigma_i/\epsilon\kappa)\left(1/(\coth\kappa a_i + 1)\right)$ with the electric field given by $[\partial\psi(r, \cos\beta)/\partial r]|_{r=a_1} = -V_1\left(\kappa + 1/a_1\right)$, where surface charge is linearly proportional to κ, an effect opposite to that of a uniform dielectric with relative permittivity ϵ [29]. In the absence of a screening solvent equation (7) reduces to the expected $Q_{1\infty} = 4\pi a_1\epsilon V_1$ when the total charge is defined as $Q_{1\infty} = \int \sigma_1\,\mathrm{d}S_1$.

In a second calculation we integrate the effect of the known charge distribution using equation (5) to obtain the screened Coulomb force. In figure 3 the screened Coulomb force between particles carrying surface potentials $-1 \leqslant V_1/V_2 \leqslant 1/2$ is plotted as a function of separation distance, d. The most important feature is that the screened Coulomb between dissimilar particles of the same sign is everywhere repulsive and monotonic with respect to separation distance but not with respect to potential difference, $V_1/V_2 \neq 1$. The effect of curvature on charge distribution is regulated by particle size, a, and by the solvent through the screening constant, κ. These results demonstrate the importance of the electrical properties of both the surface and solvent, especially in the near-field.

From a mathematical standpoint, the most important feature of equation (6) is that the problem of large values of κa in the exponential term, large differences between particle radii and surface potentials are overcome by first casting the expression for charge by way of the Fredholm integral equation, and then integrating the effect of the charge distribution to obtain the electrostatic force. Specifically, the problem of evaluating the coefficients in the expression for potential, when expanded in terms of the modified Bessel functions, has been bypassed by this method [30, 31].
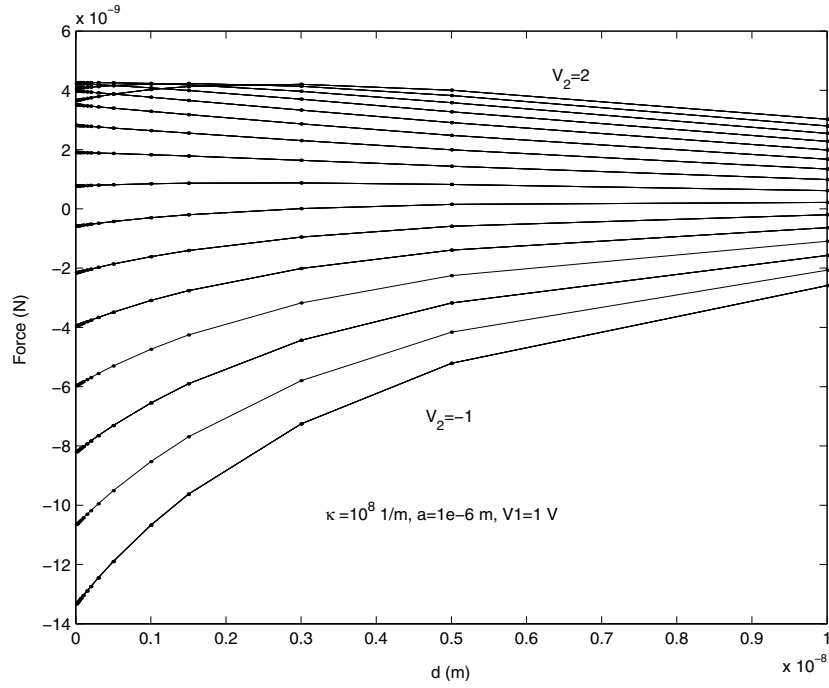
Figure 3. Screened Coulomb force between two charged particles as a function of the surface potential ratio, V_1/V_2, and surface-to-surface separation distance. The evaluation is carried out for equal sized particles with radii a equal to 1×10^{-6} m, bulk screening constant $\kappa = 1 \times 10^8$ m^{-1} and surface potential ratios in the range $-1 \leqslant V_1/V_2 \leqslant 1/2$ for $V_1 = 1$ V in steps of 0.2 V.

4. Conclusions

We report on a mean-field model for the interaction between near electro-neutral and semi-permeable membranes mediated by a screening solvent. The solution is obtained by casting the expression for the charge density distribution in the form of the Fredholm integral equation that is rapidly convergent. From an analytical standpoint most important is that the expression for pair-interaction force can be used for particles of arbitrary size, surface potential and bulk screening constant, thus advancing the analytical capability to include pair-interactions between very dissimilar particles.

Appendix A

Let V_1 and V_2 be the surface potentials (V) for P_1 and P_2 taken as relative to ground:

$$
\begin{aligned}
V_1 &= K \int dQ_1 \frac{e^{-\kappa R_1}}{R_1} + K \int dQ_2 \frac{e^{-\kappa R_2}}{R_2} \\
V_2 &= K \int dQ_1 \frac{e^{-\kappa R_1'}}{R_1'} + K \int dQ_2 \frac{e^{-\kappa R_2'}}{R_2'}
\end{aligned}
\tag{A.1}
$$

where the length quantities R_1, R_1', R_2 and R_2' are shown in figure 1. Transformation into the spherical coordinate system then yields

$$V_1 = K \int_0^\pi \int_0^{2\pi} a_1^2 \sin\theta_1 \, d\theta_1 \, d\phi_1 \, \sigma_1(\theta_1) \frac{e^{-\kappa\sqrt{2a_1^2 - 2a_1^2[\cos\beta\cos\theta_1 + \sin\beta\sin\theta_1\cos(\phi'-\phi_1)]}}}{\sqrt{2a_1^2 - 2a_1^2[\cos\beta\cos\theta_1 + \sin\beta\sin\theta_1\cos(\phi'-\phi_1)]}}$$

$$+ K \int_0^\pi \int_0^{2\pi} a_2^2 \sin\theta_2 \, d\theta_2 \, d\phi_2 \, \sigma_2(\theta_2)$$

$$\times \frac{e^{-\kappa\sqrt{r^2 + a_2^2 - 2a_2 r[\cos\alpha\cos\theta_2 + \sin\alpha\sin\theta_2\cos(\phi-\phi_2)]}}}{\sqrt{r^2 + a_2^2 - 2a_2 r[\cos\alpha\cos\theta_2 + \sin\alpha\sin\theta_2\cos(\phi-\phi_2)]}} \quad \text{(A.2)}$$

where $r = \sqrt{a_1^2 + h^2 - 2a_1 h \cos\beta}$, $\cos\alpha = (h - a_1\cos\beta)/\sqrt{a_1^2 + h^2 - 2a_1 h \cos\beta}$, which must hold for all values of β when $0 < \beta < \pi$, and

$$V_2 = K \int_0^\pi \int_0^{2\pi} a_1^2 \sin\theta_1 \, d\theta_1 \, d\phi_1 \, \sigma_1(\theta_1)$$

$$\times \frac{e^{-\kappa\sqrt{r'^2 + a_1^2 - 2a_1 r'[\cos\beta\cos\theta_1 + \sin\beta\sin\theta_1\cos(\phi'-\phi_1)]}}}{\sqrt{r'^2 + a_1^2 - 2a_1 r'[\cos\beta\cos\theta_1 + \sin\beta\sin\theta_1\cos(\phi'-\phi_1)]}}$$

$$+ K \int_0^\pi \int_0^{2\pi} a_2^2 \sin\theta_2 \, d\theta_2 \, d\phi_2 \, \sigma_2(\theta_2)$$

$$\times \frac{e^{-\kappa\sqrt{2a_2^2 - 2a_2^2[\cos\alpha\cos\theta_2 + \sin\alpha\sin\theta_2\cos(\phi-\phi_2)]}}}{\sqrt{2a_2^2 - 2a_2^2[\cos\alpha\cos\theta_2 + \sin\alpha\sin\theta_2\cos(\phi-\phi_2)]}} \quad \text{(A.3)}$$

where $r' = \sqrt{a_2^2 + h^2 - 2a_2 h \cos\alpha}$, and $\cos\beta = (h - a_2\cos\alpha)/\sqrt{a_2^2 + h^2 - 2a_2 h \cos\alpha}$, which must hold for all values of α when $0 < \alpha < \pi$. Equations (A.2) and (A.3) couple the applied voltages, V_1 and V_2, to the charge densities, σ_1 and σ_2, respectively. For a given surface potential and particle separation distance we note that the magnitude of the surface charge density is uniquely determined.

The magnitude and location of charges are evaluated by first rewriting equations (A.2) and (A.3) in a form convenient for numerical evaluation using Gaussian quadrature [32]. From $r = \sqrt{a_1^2 + h^2 - 2a_1 h \cos\beta}$ and $\cos\alpha = (h - a_1\cos\beta)/\sqrt{a_1^2 + h^2 - 2a_1 h \cos\beta}$ we obtain

$$\frac{1}{\kappa} \int_0^{2\pi} d\phi_2 \frac{e^{-\kappa\sqrt{r^2 + a_2^2 - 2a_2 r[\cos\alpha\cos\theta_2 + \sin\alpha\sin\theta_2\cos(\phi-\phi_2)]}}}{\sqrt{r^2 + a_2^2 - 2a_2 r[\cos\alpha\cos\theta_2 + \sin\alpha\sin\theta_2\cos(\phi-\phi_2)]}}$$

$$= \frac{1}{\kappa} \int_0^{2\pi} d\phi_2 \frac{e^{-\kappa\sqrt{h^2 + a_1^2 + a_2^2 - a_1 h \cos\beta - a_2 h \cos\theta_2 + 2a_2 a_1[\cos\beta\cos\theta_2 + \sin\beta\sin\theta_2\cos(\phi-\phi_2)]}}}{\sqrt{h^2 + a_1^2 + a_2^2 - a_1 h \cos\beta - a_2 h \cos\theta_2 + 2a_2 a_1[\cos\beta\cos\theta_2 + \sin\beta\sin\theta_2\cos(\phi-\phi_2)]}}$$

$$= 2\pi \sum_{m=0}^\infty (2m+1) \frac{I_{m+1/2}(\kappa a_2)}{\sqrt{\kappa a_2}} P_m(\cos\theta_2) \frac{K_{m+1/2}\left(\kappa\sqrt{a_1^2 + h^2 - 2a_1 h \cos\beta}\right)}{\sqrt{\kappa\sqrt{a_1^2 + h^2 - 2a_1 h \cos\beta}}}$$

$$\times P_m\left(\frac{h - a_1\cos\beta}{\sqrt{a_1^2 + h^2 - 2a_1 h \cos\beta}}\right)$$

$$= 2\pi \sum_{m=0}^\infty (2m+1) \frac{I_{m+1/2}(\kappa a_1)}{\sqrt{\kappa a_1}} P_m(\cos\beta) \frac{K_{m+1/2}\left(\kappa\sqrt{a_2^2 + h^2 - 2a_2 h \cos\theta_2}\right)}{\sqrt{\kappa\sqrt{a_2^2 + h^2 - 2a_2 h \cos\theta_2}}}$$

$$\times P_m\left(\frac{h - a_2\cos\theta_2}{\sqrt{a_2^2 + h^2 - 2a_2 h \cos\theta_2}}\right).$$

Charge densities for P_1 are

$$\frac{V_1}{2\pi\kappa K} = \sum_{m=0}^{\infty}(2m+1)\frac{I_{m+1/2}(\kappa a_1)}{\sqrt{\kappa a_1}}P_m(\cos\beta)\left[\frac{K_{m+1/2}(\kappa a_1)}{\sqrt{\kappa a_1}}a_1^2\int_0^{\pi}\sin\theta\,d\theta\,\sigma_1(\theta)P_m(\cos\theta)\right.$$

$$+a_2^2\int_0^{\pi}\sin\theta\,d\theta\,\sigma_2(\theta)\frac{K_{m+1/2}\left(\kappa\sqrt{a_2^2+h^2-2a_2h\cos\theta}\right)}{\sqrt{\kappa\sqrt{a_2^2+h^2-2a_2h\cos\theta}}}$$

$$\left.\times P_m\left(\frac{h-a_2\cos\theta}{\sqrt{a_2^2+h^2-2a_2h\cos\theta}}\right)\right] \tag{A.4}$$

and for P_2

$$\frac{V_2}{2\pi\kappa K} = \sum_{m=0}^{\infty}(2m+1)\frac{I_{m+1/2}(\kappa a_2)}{\sqrt{\kappa a_2}}P_m(\cos\beta)\left[\frac{K_{m+1/2}(\kappa a_2)}{\sqrt{\kappa a_2}}a_2^2\int_0^{\pi}\sin\theta\,d\theta\,\sigma_2(\theta)P_m(\cos\theta)\right.$$

$$+a_1^2\int_0^{\pi}\sin\theta\,d\theta\,\sigma_1(\theta)\frac{K_{m+1/2}\left(\kappa\sqrt{a_1^2+h^2-2a_1h\cos\theta}\right)}{\sqrt{\kappa\sqrt{a_1^2+h^2-2a_1h\cos\theta}}}$$

$$\left.\times P_m\left(\frac{h-a_1\cos\theta}{\sqrt{a_1^2+h^2-2a_1h\cos\theta}}\right)\right]. \tag{A.5}$$

The above relations further imply that

$$\delta_{m,0}\frac{V_1}{2\pi\kappa K} = \frac{I_{m+1/2}(\kappa a_1)}{\sqrt{\kappa a_1}}\left[\frac{K_{m+1/2}(\kappa a_1)}{\sqrt{\kappa a_1}}a_1^2\int_0^{\pi}\sin\theta\,d\theta\,\sigma_1(\theta)P_m(\cos\theta)\right.$$

$$+a_2^2\int_0^{\pi}\sin\theta\,d\theta\,\sigma_2(\theta)\frac{K_{m+1/2}\left(\kappa\sqrt{a_2^2+h^2-2a_2h\cos\theta}\right)}{\sqrt{\kappa\sqrt{a_2^2+h^2-2a_2h\cos\theta}}}$$

$$\left.\times P_m\left(\frac{h-a_2\cos\theta}{\sqrt{a_2^2+h^2-2a_2h\cos\theta}}\right)\right] \tag{A.6}$$

and

$$\delta_{m,0}\frac{V_2}{2\pi\kappa K} = \frac{I_{m+1/2}(\kappa a_2)}{\sqrt{\kappa a_2}}\left[\frac{K_{m+1/2}(\kappa a_2)}{\sqrt{\kappa a_2}}a_2^2\int_0^{\pi}\sin\theta\,d\theta\,\sigma_2(\theta)P_m(\cos\theta)\right.$$

$$+a_1^2\int_0^{\pi}\sin\theta\,d\theta\,\sigma_1(\theta)\frac{K_{m+1/2}\left(\kappa\sqrt{a_1^2+h^2-2a_1h\cos\theta}\right)}{\sqrt{\kappa\sqrt{a_1^2+h^2-2a_1h\cos\theta}}}$$

$$\left.\times P_m\left(\frac{h-a_1\cos\theta}{\sqrt{a_1^2+h^2-1a_1h\cos\theta}}\right)\right]. \tag{A.7}$$

Using the method of Gaussian quadratures where $\int_{-1}^{1} f(x)\,\mathrm{d}x = \sum_{i=1}^{N} w_i f(x_i)$ and $x_i = \cos\theta_i$ we can rewrite equations (A.6) and (A.7) to read

$$\delta_{m,0}\frac{V_1}{2\pi\kappa K} = \sum_{i=1}^{N} w_i \frac{I_{m+1/2}(\kappa a_1)}{\sqrt{\kappa a_1}}\left[\frac{K_{m+1/2}(\kappa a_1)}{\sqrt{\kappa a_1}} a_1^2 \sigma_1(x_i) P_m(x_i)\right.$$

$$\left. + a_2^2 \sigma_2(x_i) \frac{K_{m+1/2}\big(\kappa\sqrt{a_2^2 + h^2 - 2a_2 h x_i}\big)}{\sqrt{\kappa\sqrt{a_2^2 + h^2 - 2a_2 h x_i}}} P_m\left(\frac{h - a_2 x_i}{\sqrt{a_2^2 + h^2 - 2a_2 h x_i}} \right)\right] \quad \text{(A.8)}$$

$$\delta_{m,0}\frac{V_2}{2\pi\kappa K} = \sum_{i=1}^{N} w_i \frac{I_{m+1/2}(\kappa a_2)}{\sqrt{\kappa a_2}}\left[\frac{K_{m+1/2}(\kappa a_2)}{\sqrt{\kappa a_2}} a_2^2 \sin\theta_i \sigma_2(x_i) P_m(x_i)\right.$$

$$\left. + a_1^2 \sigma_1(x_i) \frac{K_{m+1/2}\big(\kappa\sqrt{a_1^2 + h^2 - 2a_1 h x_i}\big)}{\sqrt{\kappa\sqrt{a_1^2 + h^2 - 2a_1 h x_i}}} P_m\left(\frac{h - a_1 x_i}{\sqrt{a_1^2 + h^2 - 2a_1 h x_i}} \right)\right]. \quad \text{(A.9)}$$

The surface charge densities are obtained from equations (A.8) and (A.9) using matrix inversion.

Appendix B

The electric potential just above a particle of radius $r \equiv a_1^+$ is

$$\frac{\psi(r, \cos\beta)}{2\pi\kappa K} = \sum_{m=0}^{\infty} (2m+1) P_m(\cos\beta)\left[\frac{I_{m+1/2}(\kappa a_1)}{\sqrt{\kappa a_1}} \frac{K_{m+1/2}(\kappa r)}{\sqrt{\kappa r}} a_1^2 \int_0^{\pi} \sin\theta\,\mathrm{d}\theta\,\sigma_1(\theta) P_m(\cos\theta)\right.$$

$$\left. + \frac{I_{m+1/2}(\kappa r)}{\sqrt{\kappa r}} a_2^2 \int_0^{\pi} \sin\theta\,\mathrm{d}\theta\,\sigma_2(\theta) \frac{K_{m+1/2}\big(\kappa\sqrt{a_2^2 + h^2 - 2a_2 h\cos\theta}\big)}{\sqrt{\kappa\sqrt{a_2^2 + h^2 - 2a_2 h\cos\theta}}}\right.$$

$$\left. \times P_m\left(\frac{h - a_2\cos\theta}{\sqrt{a_2^2 + h^2 - 2a_2 h\cos\theta}} \right)\right]$$

from which $\left((f)' = \frac{\partial f}{\partial r}\right)$

$$\frac{\frac{\partial\psi(r,\cos\beta)}{\partial r}}{2\pi\kappa K} = \sum_{m=0}^{\infty} (2m+1) P_m(\cos\beta)\left[\frac{I_{m+1/2}(\kappa a_1)}{\sqrt{\kappa a_1}}\left(\frac{K_{m+1/2}(\kappa r)}{\sqrt{\kappa r}} \right)' a_1^2 \int_0^{\pi} \sin\theta\,\mathrm{d}\theta\,\sigma_1(\theta) P_m(\cos\theta)\right.$$

$$\left. + \left(\frac{I_{m+1/2}(\kappa r)}{\sqrt{\kappa r}} \right)' a_2^2 \int_0^{\pi} \sin\theta\,\mathrm{d}\theta\,\sigma_2(\theta) \frac{K_{m+1/2}\big(\kappa\sqrt{a_2^2 + h^2 - 2a_2 h\cos\theta}\big)}{\sqrt{\kappa\sqrt{a_2^2 + h^2 - 2a_2 h\cos\theta}}}\right.$$

$$\left. \times P_m\left(\frac{h - a_2\cos\theta}{\sqrt{a_2^2 + h^2 - 2a_2 h\cos\theta}} \right)\right].$$

Rewrite the above two equations on the surface of the particle of radius a_1 (let $r = a_1$),

$$
\frac{\psi(a_1, \cos\beta)}{2\pi\kappa K} = \sum_{m=0}^{\infty} (2m+1) P_m(\cos\beta) \Bigg[\frac{I_{m+1/2}(\kappa a_1)}{\sqrt{\kappa a_1}} \frac{K_{m+1/2}(\kappa a_1)}{\sqrt{\kappa a_1}} a_1^2 \int_0^\pi \sin\theta \, d\theta \, \sigma_1(\theta) P_m(\cos\theta)
$$

$$
+ \frac{I_{m+1/2}(\kappa a_1)}{\sqrt{\kappa a_1}} a_2^2 \int_0^\pi \sin\theta \, d\theta \, \sigma_2(\theta) \frac{K_{m+1/2}\!\left(\kappa\sqrt{a_2^2+h^2-2a_2 h\cos\theta}\right)}{\sqrt{\kappa\sqrt{a_2^2+h^2-2a_2 h\cos\theta}}}
$$

$$
\times P_m\!\left(\frac{h - a_2\cos\theta}{\sqrt{a_2^2+h^2-2a_2 h\cos\theta}}\right) \Bigg] \tag{B.1}
$$

$$
\frac{\left.\frac{\partial \psi(r,\cos\beta)}{\partial r}\right|_{r=a_1}}{2\pi\kappa K} = \sum_{m=0}^{\infty} (2m+1) P_m(\cos\beta) \Bigg[\frac{I_{m+1/2}(\kappa a_1)}{\sqrt{\kappa a_1}} \left(\frac{K_{m+1/2}(\kappa a_1)}{\sqrt{\kappa a_1}}\right)' a_1^2
$$

$$
\times \int_0^\pi \sin\theta \, d\theta \, \sigma_1(\theta) P_m(\cos\theta) + \left(\frac{I_{m+1/2}(\kappa a_1)}{\sqrt{\kappa a_1}}\right)' a_2^2
$$

$$
\times \int_0^\pi \sin\theta \, d\theta \, \sigma_2(\theta) \frac{K_{m+1/2}\!\left(\kappa\sqrt{a_2^2+h^2-2a_2 h\cos\theta}\right)}{\sqrt{\kappa\sqrt{a_2^2+h^2-2a_2 h\cos\theta}}}
$$

$$
\times P_m\!\left(\frac{h - a_2\cos\theta}{\sqrt{a_2^2+h^2-2a_2 h\cos\theta}}\right) \Bigg]. \tag{B.2}
$$

Next, multiply equation (B.1) by $\left\{ \left(I_{k+1/2}(\kappa a_1)/\sqrt{\kappa a_1}\right)' \right\} \Big/ \left\{ I_{k+1/2}(\kappa a_1)/\sqrt{\kappa a_1} \right\}^{-1}$ $P_k(\cos\beta)$ and integrate from -1 to 1 using the orthonormality relation $\int_{-1}^1 P_m(x) P_k(x) \, dx = [2/(2k+1)]\delta_{m,k}$ to obtain

$$
\frac{\left(\frac{I_{m+1/2}(\kappa a_1)}{\sqrt{\kappa a_1}}\right)' \frac{\int_0^\pi \sin\theta \, d\theta \, P_m(\cos\theta)\psi(a_1,\cos\theta)}{2\pi\kappa K}}{\frac{I_{m+1/2}(\kappa a_1)}{\sqrt{\kappa a_1}}} = 2 \Bigg[\left(\frac{I_{m+1/2}(\kappa a_1)}{\sqrt{\kappa a_1}}\right)' \frac{K_{m+1/2}(\kappa a_1)}{\sqrt{\kappa a_1}} a_1^2
$$

$$
\times \int_0^\pi \sin\theta \, d\theta \, \sigma_1(\theta) P_m(\cos\theta) + \left(\frac{I_{m+1/2}(\kappa a_1)}{\sqrt{\kappa a_1}}\right)' a_2^2
$$

$$
\times \int_0^\pi \sin\theta \, d\theta \, \sigma_2(\theta) \frac{K_{m+1/2}\!\left(\kappa\sqrt{a_2^2+h^2-2a_2 h\cos\theta}\right)}{\sqrt{\kappa\sqrt{a_2^2+h^2-2a_2 h\cos\theta}}}
$$

$$
\times P_m\!\left(\frac{h - a_2\cos\theta}{\sqrt{a_2^2+h^2-2a_2 h\cos\theta}}\right) \Bigg]
$$

and multiply the above equation by $[(2m+1)/2]P_m(\cos\beta)$ and sum over the index to obtain

$$
\sum_{m=0}^{\infty} \frac{2m+1}{2} P_m(\cos\beta) \frac{\left(\frac{I_{m+1/2}(\kappa a_1)}{\sqrt{\kappa a_1}}\right)' \frac{\int_0^\pi \sin\theta \, d\theta \, P_m(\cos\theta)\psi(r,\cos\theta)}{2\pi\kappa K}}{\frac{I_{m+1/2}(\kappa a_1)}{\sqrt{\kappa a_1}}}
$$

$$
= \sum_{m=0}^{\infty} (2m+1) P_m(\cos\beta) \Bigg[\left(\frac{I_{m+1/2}(\kappa a_1)}{\sqrt{\kappa a_1}}\right)' \frac{K_{m+1/2}(\kappa a_1)}{\sqrt{\kappa a_1}} a_1^2
$$

$$\times \int_0^\pi \sin\theta \, \mathrm{d}\theta \, \sigma_1(\theta) \, P_m(\cos\theta) + \left(\frac{I_{m+1/2}(\kappa a_1)}{\sqrt{\kappa a_1}}\right)' a_2^2$$

$$\times \int_0^\pi \sin\theta \, \mathrm{d}\theta \, \sigma_2(\theta) \frac{K_{m+1/2}\left(\kappa\sqrt{a_2^2 + h^2 - 2a_2 h \cos\theta}\right)}{\sqrt{\kappa\sqrt{a_2^2 + h^2 - 2a_2 h \cos\theta}}}$$

$$\times P_m\left(\frac{h - a_2 \cos\theta}{\sqrt{a_2^2 + h^2 - 2a_2 h \cos\theta}}\right)\Bigg]. \tag{B.3}$$

Note that the second terms in equations (B.2) and (B.3) are identical; subtract equation (B.2) from (B.3) to obtain

$$\sum_{m=0}^\infty \frac{2m+1}{2} P_m(\cos\beta) \frac{\left(\frac{I_{m+1/2}(\kappa a_1)}{\sqrt{\kappa a_1}}\right)'}{\frac{I_{m+1/2}(\kappa a_1)}{\sqrt{\kappa a_1}}} \int_0^\pi \sin\theta \, \mathrm{d}\theta \, P_m(\cos\theta) \psi(a_1, \cos\theta) - \frac{\partial\psi(r, \cos\beta)}{\partial r}\Bigg|_{r=a_1}$$

$$= \sum_{m=0}^\infty (2m+1) P_m(\cos\beta) a_1^2 \int_0^\pi \sin\theta \, \mathrm{d}\theta \, \sigma_1(\theta) \, P_m(\cos\theta)$$

$$\times \left\{\left(\frac{I_{m+1/2}(\kappa a_1)}{\sqrt{\kappa a_1}}\right)' \frac{K_{m+1/2}(\kappa a_1)}{\sqrt{\kappa a_1}} - \frac{I_{m+1/2}(\kappa a_1)}{\sqrt{\kappa a_1}} \left(\frac{K_{m+1/2}(\kappa a_1)}{\sqrt{\kappa a_1}}\right)'\right\}.$$

Then, use the Wronskian identity $\left(I_{m+1/2}(\kappa a_1)/\sqrt{\kappa a_1}\right)' K_{m+1/2}(\kappa a_1)/\sqrt{\kappa a_1} - [I_{m+1/2}(\kappa a_1)/\sqrt{\kappa a_1}]\left(K_{m+1/2}(\kappa a_1)/\sqrt{\kappa a_1}\right)' = 1/\kappa a_1^2$ to rewrite the above equation

$$\sum_{m=0}^\infty \frac{2m+1}{2} P_m(\cos\beta) \frac{\left(\frac{I_{m+1/2}(\kappa a_1)}{\sqrt{\kappa a_1}}\right)'}{\frac{I_{m+1/2}(\kappa a_1)}{\sqrt{\kappa a_1}}} \int_0^\pi \sin\theta \, \mathrm{d}\theta \, P_m(\cos\theta) \psi(a_1, \cos\theta)$$

$$- \frac{\partial\psi(r, \cos\beta)}{\partial r}\Bigg|_{r=a_1} = 4\pi K \sigma_1(\beta)$$

with ψ constant on the surface $\psi(a_1, \cos\beta) = V_1$:

$$\frac{\left(\frac{I_{0+1/2}(\kappa a_1)}{\sqrt{\kappa a_1}}\right)'}{\frac{I_{0+1/2}(\kappa a_1)}{\sqrt{\kappa a_1}}} V_1 - \frac{\partial\psi(r, \cos\beta)}{\partial r}\Bigg|_{r=a_1} = 4\pi K \sigma_1(\beta)$$

or

$$\frac{\partial\psi(r, \cos\beta)}{\partial r}\Bigg|_{r=a_1} = \kappa V_1 \left(\coth(\kappa a_1) - \frac{1}{\kappa a_1}\right) - 4\pi K \sigma_1(\beta).$$

A similar procedure will yield the result

$$\frac{\partial\psi(r, \cos\beta)}{\partial r}\Bigg|_{r=a_2} = \kappa V_2 \left(\coth(\kappa a_2) - \frac{1}{\kappa a_2}\right) - 4\pi K \sigma_2(\beta).$$

At infinite separation

$$V_1 = 2\pi K \kappa \frac{I_{0+1/2}(\kappa a_1)}{\sqrt{\kappa a_1}} \frac{K_{0+1/2}(\kappa a_1)}{\sqrt{\kappa a_1}} a_1^2 2\sigma_1 = 4\pi K\sigma_1 \frac{\sinh\kappa a_1 \mathrm{e}^{-\kappa a_1}}{\kappa} = 4\pi K\sigma_1 \frac{1}{\kappa\coth\kappa a_1 + \kappa}$$

$$\frac{\partial\psi(r, \cos\beta)}{\partial r}\Bigg|_{r=a_1} = -V_1\left(\kappa + \frac{1}{a_1}\right)$$

and

$$-4\pi K\sigma_1 = -V_1\left(\kappa + \kappa\coth\kappa a_1\right).$$

References

[1] Fox C F and Kieth A D 1972 *Membrane Molecular Biology* (Stamford, CT: Sinauer)
[2] Israelachvili J N 1992 *Intermolecular and Surface Forces* 2nd edn (New York: Academic)
[3] Yeagle P L 1993 *The Membranes of Cells* 2nd edn (New York: Academic)
[4] Wilschut J, Duzgunes N and Papahadjopoulos D 1981 *Biochem.* **20** 3126
[5] Marra J and Israelachvili J N 1985 *Biochem.* **24** 4608
[6] Marra J 1986 *J. Phys. Chem.* **90** 2145
[7] Claesson P, Carmona-Ribeiro A M and Kurihara K 1989 *J. Phys. Chem.* **93** 917
[8] Claesson P M, Kjellander R, Stenius P and Christenson H K 1986 *J. Chem. Soc. Faraday Trans.* I **82** 2735
[9] Ohki S and Spangler R A 1992 Passive and facilitated transport *The Structure of Biological Membranes* ed
      P L Yeagle (Boca Raton, FL: Chemical Rubber Company)
[10] Mimms L T, Zampighi G, Nozaki Y, Tanford C and Reynolds J A 1981 *Biochem.* **20** 833
[11] Scatena L F, Brown M G and Richmond G L 2001 *Science* **292** 908
[12] Chang T and Dang L X 1996 *J. Chem. Phys.* **104** 6772
[13] Hasted J B 1973 *Aqueous Dielectrics* (London: Chapman and Hall)
[14] Tanford C 1980 *The Hydrophobic Effect* (New York: Wiley)
[15] Kekicheff P and Spalla O 1995 *Phys. Rev. Lett.* **75** 1851–4
[16] McLaughlin S, Mulrine N, Gresalfi T, Yaio G and McLaughlin A 1981 *J. Gen. Physiol.* **77** 445
[17] McLaughlin S 1989 *Annu. Rev. Biophys. Chem.* **18** 113
[18] Larson I and Milling A J 1999 Measurement of ion-mediated and van der Waals forces using atomic force
      microscopy *Surface Characterization Methods: Principles, Techniques, and Applications (Surfactant Science
      Series Vol. 87)* ed A J Milling (New York: Dekker)
[19] Jackson J D 1975 *Classical Electrodynamics* (New York: Wiley)
[20] Sneddon I N 1972 *The Use of Integral Transforms* (New York: McGraw-Hill)
[21] Coulomb A-C 1884 Collection de memoires relatifs a la physique *Publies par La Societe Francaise de Physique,
      Memoires de Coulomb* vol I (Paris: Gauthier-Villars)
[22] Wistrom A O and Khachatourian A V 1999 *Meas. Sci. Technol.* **10** 1296–9
[23] Hiemenz P C and Rajagopalan R 1977 *Principles of Colloid and Surface Chemistry* 3rd edn (New York: Dekker)
[24] Verwey E J W and Overbeek J Th G 1948 *The Theory of Stability of Lyophobic Colloids* (New York: Elsevier)
[25] Derjaguin B V and Landau L 1941 *Acta Physiochem.* **14** 633
[26] Glendinning A B and Russel W B 1983 *J. Colloid Interface Sci.* **93** 95
[27] Carnie S L and Chan D Y C 1993 *J. Colloid Interface Sci.* **155** 297–312
[28] Ramanathan C V 1988 *J. Chem. Phys.* **23** 3887
[29] Jeans J H 1951 *The Mathematical Theory of Electricity and Magnetism* 5th edn (Cambridge: Cambridge
      University Press)
[30] Flammer C 1957 *Spheroidal Wave Functions* (Stanford, CA: Stanford University Press)
[31] Hsu J-P and Liu B-T 1996 *J. Colloid Interface Sci.* **183** 214–22
[32] Abramowitz M and Stegun I A 1972 *Handbook of Mathematical Functions* (New York: Dover)