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SHORT COMMUNICATION

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Electrostatic interaction between two parallel cylinders

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Abstract Explicit exact analytic expressions are obtained for the electric potential distribution and for the electrostatic interaction energy for the system of two parallel dissimilar cylinders in an electrolyte solution on the basis of the linearized Poisson–Boltzmann equation.

Key words Electrostatic interaction – Poisson–Boltzmann equation – cylinder

Introduction

So far we have demonstrated [1–6] that the linearized Poisson–Boltzmann equation can exactly be solved for various systems of two interacting charged spherical colloidal particles in an electrolyte solution, i.e., two ion-penetrable spheres (which we call "soft" spheres) [1], a soft sphere interacting with an ion-impenetrable hard sphere, and two interacting hard spheres at constant surface potential and at constant surface charge density. On the basis of the obtained analytic expressions for the potential distribution, we have derived *explicit* exact expressions for the interaction energy for these systems [1–6] without recourse to Derjaguin's approximation [7].

In the present paper, we apply the above method to the system of two parallel cylinders of various types, i.e., ion-penetrable (soft) cylinders and hard cylinders, the latter of which may have either constant surface potential or constant surface charge density.

Linearized Poisson–Boltzmann equation

Consider two parallel charged cylinders 1 and 2 of radii a_1 and a_2, respectively, separated by a distance R between their axes O_1 and O_2, immersed in an electrolyte solution, as shown in Fig. 1, where $H \equiv R - a_1 - a_2$ is the closest distance between the surfaces of the two cylinders. We employ a cylindrical coordinate system. Let r_1 and r_2, respectively, be the distances measured from any point P to the axis O_1 of cylinder 1 and the axis O_2 of cylinder 2, and θ_1 and θ_2, respectively, be the angles between PO_1 and O_1O_2 and that between PO_2 and O_1O_2. As a result of symmetry of the system, the potential ψ is a function of r_1 (or r_2) and θ_1 (or θ_2) only. We use two cylindrical coordinate systems (r_1, θ_1) and (r_2, θ_2). Let the cylinders be either ion-penetrable cylinders (soft cylinders) or ion-impenetrable cylinders (hard cylinders). For the case of soft cylinders, we imagine that the particle-fixed charges are distributed with a constant density ρ and that the relative permittivity of the internal region of the soft cylinder takes the same value as that of the bulk solution. We assume that the electric potential ψ at any point in the system, measured relative to the bulk solution phase (where ψ is set equal to zero), is low enough to obey the following linearized Poisson–Boltzmann equations, viz.,

$$\Delta\psi = \kappa^2\psi, \quad \text{outside cylinders 1 and 2} \qquad (1)$$

where κ is the Debye–Hückel parameter of the electrolyte solution. For the internal region of each of the interacting cylinders, the equation for the electric potential ψ depends on the type of the cylinders. If cylinder i ($i = 1$ or 2) is soft (i.e., permeable to electrolyte ions), then the linearized

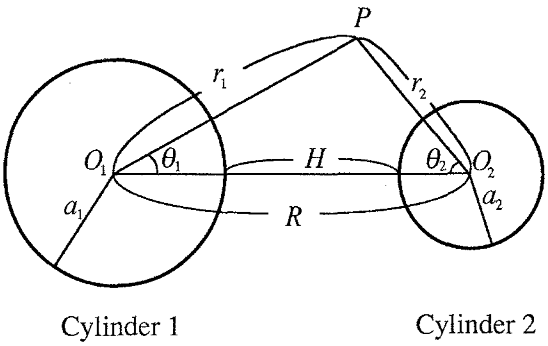

Fig. 1 Interaction between two charged hard cylinders 1 and 2 of radii a_1 and a_2 at a separation R between their centers. H $(=R-a_1-a_2)$ is the closest distance between their surfaces

Poisson–Boltzmann equation for ψ is given by

$$\Delta\psi = \kappa^2\psi - \frac{\rho_i}{\varepsilon\varepsilon_0}, \quad \text{inside cylinder } i\,, \tag{2}$$

where ε and ε_0 are, respectively, the relative permittivity of the solution and the permittivity of a vacuum. If cylinder i ($i = 1$ or 2) is hard, on the other hand, the potential inside it obeys the Laplace equation, viz.,

$$\Delta\psi = 0, \quad \text{inside cylinder } i\,. \tag{3}$$

The boundary conditions are given below. If cylinder i ($i = 1$ or 2) is soft, then the boundary condition for ψ on the surface of cylinder i is given as follows.

ψ and $\dfrac{\partial\psi}{\partial n}$ are, respectively, continuous across the surface of cylinder i, (4)

the derivative of ψ being taken along the outward normal to the surface of cylinder i. The boundary condition at the surface of a hard cylinder, on the other hand, depends on the type of the cylinder. If the surface potential of cylinder i ($i = 1$ or 2) remains constant at ψ_{oi} during interaction, then the boundary condition is given by

$$\psi = \psi_{oi} \quad \text{at } r = a_i\,. \tag{5}$$

If the surface charge density σ_i (instead of the surface potential ψ_{oi}) of cylinder i remains constant during interaction, then the boundary conditions become

ψ is continuous at $r = a_i$, and

$$\varepsilon_i \left.\frac{\partial\psi}{\partial r}\right|_{r=a_i^-} - \varepsilon \left.\frac{\partial\psi}{\partial r}\right|_{r=a_i^+} = \frac{\sigma_i}{\varepsilon_o}\,, \tag{6}$$

where ε_i is the relative permittivity of cylinder i.

Potential distribution for a single cylinder

The potential distribution in and around a single cylinder, that is, an undisturbed potential distribution, is derived by solving the corresponding linearized Poisson–Boltzmann equation for a single cylinder. If cylinder i ($i = 1$ and 2) is a soft cylinder, then the unperturbed potential outside and inside the cylinder $\psi_i^{(0)}(r_i)$ can be expressed in terms of the modified Bessel functions of the first and second kinds $I_n(z)$ and $K_n(z)$ as

$$\psi_i^{(0)}(r_i) = \begin{cases} \psi_{oi}\dfrac{K_0(\kappa r_i)}{K_0(\kappa a_i)}, & r_i \geq a_i \\ -\psi_{oi}\dfrac{K_1(\kappa a_i)I_0(\kappa r_i)}{K_0(\kappa a_i)I_1(\kappa a_i)} + \dfrac{\rho_i}{\varepsilon\varepsilon_o\kappa^2}, & r_i \leq a_i \end{cases} \tag{7}$$

where ψ_{oi} is the unperturbed surface potential of cylinder i and is related to the density ρ_i of the fixed charges within cylinder i by

$$\psi_{oi} = \frac{\rho_i}{\varepsilon\varepsilon_o\kappa} a_i K_0(\kappa a_i) I_1(\kappa a_i)\,. \tag{8}$$

If cylinder i is a hard cylinder, then the unperturbed potential inside and outside the cylinder $\psi_i^{(0)}(r_i)$ ($i = 1$ and 2) are given by

$$\psi_i^{(0)}(r_i) = \begin{cases} \psi_{oi}\dfrac{K_{oi}(\kappa r_i)}{K_{oi}(\kappa a_i)}, & r_i \geq a_i \\ \psi_{oi}, & r_i \leq a_i \end{cases}. \tag{9}$$

Here the unperturbed surface potential ψ_{oi} of the cylinder is related to the surface charge density σ_i of cylinder i by

$$\psi_{oi} = \frac{\sigma_i}{\varepsilon\varepsilon_o}\frac{K_o(\kappa a_i)}{K_1(\kappa a_i)}\,. \tag{10}$$

Potential distribution for two interacting parallel cylinders

Two soft cylinders

Consider first the case where cylinders 1 and 2 are both soft. Let the fixed-charge densities of cylinders 1 and 2 be ρ_1 and ρ_2, respectively. The linearized Poisson–Boltzmann equations for the electric potential ψ for the present system are given by Eqs. (1) and (2), which are subject to the boundary condition (4). It can readily be shown that the solution to Eqs. (1) and (2) can be expressed as the sum $\psi = \psi_1^{(0)} + \psi_2^{(0)}$, where $\psi_i^{(0)}$ ($i = 1$ and 2) is given by Eq. (7). The potential distribution for two interacting soft cylinders are thus simply given by the superposition of the unperturbed potentials produced by the respective cylinders.

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Soft cylinder and hard cylinder

Consider next the case where cylinder 1 is soft and cylinder 2 is hard. Imagine that fixed charges are distributed within the soft cylinder 1 at a uniform density ρ_1. Let ψ_{o1} and ψ_{o2} be the unperturbed surface potentials of cylinders 1 and 2, which are given by Eqs. (7) and (9), respectively. The electric potential ψ satisfies Eq. (1) for the outside of both cylinders, Eq. (2) for the inside of cylinder 1 and Eq. (3) for inside cylinder 2.

Further, we treat the case where the surface potential of the hard cylinder 2 remains constant at ψ_{o2} during interaction. The boundary conditions on the cylinder surfaces are given by Eq. (4) (with $i = 1$) for cylinder 1 and Eq. (5) (with $i = 2$) for cylinder 2. The sum of the unperturbed potentials, $\psi = \psi_1^{(0)}(r_1) + \psi_2^{(0)}(r_2)$, where, $\psi_1^{(0)}(r_1)$ and $\psi_2^{(0)}(r_2)$, respectively, are given by Eqs. (7) (with $i = 1$) and (9) (with $i = 2$), satisfies the boundary conditions (4) at the surface of the soft cylinder 1 but does not satisfy the boundary condition (5) at the surface of the hard cylinder 2. The reason is that the unperturbed potential $\psi_1^{(0)}$ gives rise to a non-zero value at the surface of cylinder 2, which breaks the boundary condition Eq. (5) (with $i = 2$) at the surface of cylinder 2. One thus needs an additional potential $\psi_1^{(1)}(r_2, \theta_2)$ so as to cancel $\psi_1^{(0)}(a_2, \theta_2)$ at the surface of cylinder 2 and the potential can then be expressed as the sum

$$\psi = \psi_1^{(0)}(r_1) + \psi_2^{(0)}(r_2) + \psi_1^{(1)}(r_2, \theta_2) . \tag{11}$$

Note that the boundary condition (4) (with $i = 1$) on the soft cylinder 1 is automatically fulfilled.

In order to find the form of $\psi_1^{(1)}(r_2, \theta_2)$, let us rewrite the potential $\psi_1^{(0)}(r_1)$ for the external region of cylinder 1 (see Eq. (7)), viz.,

$$\psi_1^{(0)}(r_1) = \psi_{o1} \frac{K_{o1}(\kappa r_1)}{K_{o1}(\kappa a_1)} . \tag{12}$$

on the basis of the (r_2, θ_2) coordinate system. We employ the following relation [8]:

$$K_m(\kappa r_i)\cos(m\theta_i) = \sum_{n=-\infty}^{\infty} K_{m+n}(\kappa R) I_n(\kappa r_j)\cos(n\theta_j),$$
$$(i, j = 1, 2;\ i \neq j), \quad r_j < R . \tag{13}$$

The corresponding expression for the region $r_j > R$ is not needed for the calculation of the interaction energy between two parallel cylinders. Using Eq. (13) with $m = 0$, Eq. (12) can be rewritten as

$$\psi_1^{(0)}(r_2, \theta_2) = \psi_{o1} \frac{1}{K_0(\kappa a_1)} \sum_{n=-\infty}^{\infty} K_n(\kappa R) I_n(\kappa r_2)\cos(n\theta_2) . \tag{14}$$

The additional term $\psi_1^{(1)}(r_2, \theta_2)$ must thus take the following form:

$$\psi_1^{(1)}(r_2, \theta_2) = \frac{\psi_{o1}}{K_0(\kappa a_1)} \sum_{n=-\infty}^{\infty} K_n(\kappa R) G_n(2) K_n(\kappa r_2)\cos(n\theta_2) , \tag{15}$$

where $G_n(i)$ ($i = 1$ and 2) is defined by

$$G_n(i) = -\frac{I_n(\kappa a_i)}{K_n(\kappa a_i)} . \tag{16}$$

Equation (15) indeed cancels $\psi_1^{(0)}$ at the surface of cylinder 2, i.e., $\psi_1^{(0)}(a_2, \theta_2) + \psi_1^{(1)}(a_2, \theta_2) = 0$. Note that $\psi_1^{(1)}$ can be regarded as an image potential of $\psi_1^{(0)}$ with respect to sphere 2.

We thus find that the potential distribution outside both cylinders is given by

$$\psi = \psi_{o1} \frac{K_0(\kappa r_1)}{K_0(\kappa a_1)} + \psi_{o2} \frac{K_0(\kappa r_2)}{K_0(\kappa a_2)} + \frac{\psi_{o1}}{K_0(\kappa a_1)} \sum_{n=-\infty}^{\infty} K_n(\kappa R) G_n(2) K_n(\kappa r_2)\cos(n\theta_2) , \tag{17}$$

and the potential inside the soft cylinder 1 is given by

$$\psi = -\psi_{o1} \frac{K_1(\kappa a_1) I_0(\kappa r_1)}{K_o(\kappa a_1) I_1(\kappa a_1)} + \frac{\rho_1}{\varepsilon\varepsilon_o \kappa^2} + \psi_{o2} \frac{K_0(\kappa r_2)}{K_0(\kappa a_2)} + \frac{\psi_{o1}}{K_0(\kappa a_1)} \sum_{n=-\infty}^{\infty} K_n(\kappa R) G_n(2) K_n(\kappa r_2)\cos(n\theta_2) . \tag{18}$$

The potential inside the hard cylinder 2, on the other hand, is always equal to ψ_{o2}.

Similarly, when the surface charge density of the hard cylinder 2 remains constant at σ_2 during interaction, the potential outside both cylinders and that inside cylinder 2 are given by Eqs. (17) and (18) with $G_n(2)$ replaced with $H_n(2)$, where $H_n(i)$ ($i = 1$ and 2) is defined by

$$H_n(i) = -\frac{I_n'(\kappa a_i) - (\varepsilon_i |n|/\varepsilon\kappa a_i) I_n(\kappa a_i)}{K_n'(\kappa a_i) - (\varepsilon_i |n|/\varepsilon\kappa a_i) K_n(\kappa a_i)} . \tag{19}$$

The potential inside the hard cylinder 2 is given by

$$\psi_{in2}(r_2, \theta_2) = \psi_{o2} + \frac{\psi_{o1}}{K_0(\kappa a_1)} \sum_{n=-\infty}^{\infty} \left(\frac{r_2}{a_2}\right)^{|n|} K_n(\kappa R)[I_n(\kappa a_2) + H_n(2) K_n(\kappa a_2)]\cos(m\theta_2) . \tag{20}$$

Two hard cylinders

Finally, consider the case cylinders 1 and 2 are both hard. We first treat the case where the surface potentials of cylinders 1 and 2 both remain constant at ψ_{o1} and ψ_{o2}, respectively, during interaction independent of R. The boundary conditions are given by Eq. (5) with $i = 1$ and 2. In this case we need, other than $\psi_1^{(1)}$ and $\psi_2^{(1)}$, image potentials of higher orders: $\psi_1^{(2)}, \psi_1^{(3)}, \dots, \psi_2^{(2)}, \psi_2^{(3)}, \dots$. Thus we can write the external solution to Eq. (1) subject to the boundary conditions (5) with $i = 1$ and 2 in the following form:

$$\psi = \psi_1^{(0)} + \psi_2^{(0)} + (\psi_1^{(1)} + \psi_1^{(2)} + \psi_1^{(3)} + \cdots + \psi_1^{(2\nu)} + \psi_1^{(2\nu+1)} + \cdots) + (\psi_2^{(1)} + \psi_2^{(2)} + \psi_2^{(3)} + \cdots + \psi_2^{(2\nu)} + \psi_2^{(2\nu+1)} + \cdots), \quad (21)$$

where $\psi_1^{(0)}$ and $\psi_1^{(1)}$ are given by Eqs. (12) and (15), and

$$\psi_1^{(2\nu-1)}(r_2, \theta_2) = \frac{\psi_{o1}}{K_0(\kappa a_1)} \sum_{n_1=-\infty}^{\infty} \sum_{n_2=-\infty}^{\infty} \cdots \sum_{n_{2\nu-1}=-\infty}^{\infty} L_{21}(n_1, n_2, \dots, n_{2\nu-2}) \times K_{n_1}(\kappa R) K_{n_{2\nu-2}+n_{2\nu-1}}(\kappa R) G_{n_{2\nu-1}}(2) K_{n_{2\nu-1}}(\kappa r_2) \times \cos(n_{2\nu-1}\theta_2), \quad (\nu = 2, 3, \dots), \quad (22)$$

$$\psi_1^{(2\nu)}(r_1, \theta_1) = \frac{\psi_{o1}}{K_0(\kappa a_1)} \sum_{n_1=-\infty}^{\infty} \sum_{n_2=-\infty}^{\infty} \cdots \sum_{n_{2\nu}=-\infty}^{\infty} L_{21}(n_1, n_2 \cdots n_{2\nu}) \times K_{n_1}(\kappa R) K_{n_{2\nu}}(\kappa r_1) \cos(n_{2\nu}\theta_1), \quad (\nu = 1, 2, \dots), \quad (23)$$

with

$$L_{21}(n_1, n_2, \dots, n_{2\nu}) = K_{n_1+n_2}(\kappa R) K_{n_2+n_3}(\kappa R) \times \cdots \times K_{n_{2\nu-2}+n_{2\nu-1}}(\kappa R) K_{n_{2\nu-1}+n_{2\nu}}(\kappa R) \times G_{n_1}(2) G_{n_2}(1) \times \cdots \times G_{n_{2\nu-1}}(2) G_{n_{2\nu}}(1), \quad (24)$$

Expressions for $\psi_2^{(1)}$, $\psi_2^{(2\nu-1)}$, and $\psi_2^{(2\nu)}$ can be derived by the interchange $r_1 \leftrightarrow r_2$, $\theta_1 \leftrightarrow \theta_2$, $a_1 \leftrightarrow a_2$, $\psi_{o1} \leftrightarrow \psi_{o2}$, and $G_n(1) \leftrightarrow G_n(2)$ in Eqs. (15) and (22)–(24). The potentials inside cylinders 1 and 2 are always constant at ψ_{o1} and ψ_{o2}, respectively.

If, on the other hand, the surface charge densities of cylinders 1 and 2 maintain constant at σ_1 and σ_2, respectively, then the potential distribution is given by replacing L_{21} by M_{21} and $G_n(i)$ by $H_n(i)$ in that for the constant surface potential case, where M_{21} is defined below.

$$M_{21}(n_1, n_2, \dots, n_{2\nu}) = K_{n_1+n_2}(\kappa R) K_{n_2+n_3}(\kappa R) \times \cdots \times K_{n_{2\nu-2}+n_{2\nu-1}}(\kappa R) K_{n_{2\nu-1}+n_{2\nu}}(\kappa R) \times H_{n_1}(2) H_{n_2}(1) \times \cdots \times H_{n_{2\nu-1}}(2) H_{n_{2\nu}}(1). \quad (25)$$

As for the potential inside the cylinders, we find

$$\psi_{in1}^{(1)}(r_1, \theta_1) = \frac{\psi_{o2}}{K_0(\kappa a_2)} \sum_{n=-\infty}^{\infty} \left(\frac{r_1}{a_1}\right)^{|n|} K_n(\kappa R)[I_n(\kappa a_1) + H_n(1) K_n(\kappa a_1)] \cos(m\theta_1), \quad (26)$$

$$\psi_{in1}^{(2)}(r_1, \theta_1) = \frac{\psi_{o1}}{K_0(\kappa a_1)} \sum_{n=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} \left(\frac{r_1}{a_1}\right)^{|m|} \times K_n(\kappa R) K_{n+m}(\kappa R) H_n(2) \times [I_m(\kappa a_1) + H_m(1) K_m(\kappa a_1)] \cos(m\theta_1), \quad (27)$$

$$\psi_{in1}^{(2\nu-1)}(r_1, \theta_1) = \frac{\psi_{o2}}{K_0(\kappa a_2)} \sum_{n_1=-\infty}^{\infty} \sum_{n_2=-\infty}^{\infty} \cdots \sum_{n_{2\nu-1}=-\infty}^{\infty} \left(\frac{r_1}{a_1}\right)^{|n_{2\nu-1}|} \times M_{12}(n_1, n_2, \dots, n_{2\nu-1}) K_{n_1}(\kappa R) K_{n_{2\nu-2}+n_{2\nu-1}}(\kappa R) \times [I_{n_{2\nu-1}}(\kappa a_1) + H_{n_{2\nu-1}}(1) K_{n_{2\nu-1}}(\kappa a_1)] \cos(n_{2\nu-1}\theta_1), \quad (\nu = 2, 3, \dots), \quad (28)$$

$$\psi_{in1}^{(2\nu)}(r_1, \theta_1) = \frac{\psi_{o1}}{K_0(\kappa a_1)} \sum_{n_1=-\infty}^{\infty} \sum_{n_2=-\infty}^{\infty} \cdots \sum_{n_{2\nu}=-\infty}^{\infty} \left(\frac{r_1}{a_1}\right)^{|n_{2\nu}|} \times M_{21}(n_1, n_2, \dots, n_{2\nu-2}) K_{n_1}(\kappa R) K_{n_{2\nu-2}+n_{2\nu-1}}(\kappa R) \times K_{n_{2\nu-1}+n_{2\nu}}(\kappa R) H_{n_{2\nu-1}}(2) [I_{n_{2\nu}}(\kappa a_1) + H_{n_{2\nu}}(1) K_{n_{2\nu}}(\kappa a_1)] \cos(n_{2\nu}\theta_1), \quad (\nu = 2, 3, \dots). \quad (29)$$

Expressions for $\psi_{in2}^{(1)}(r_2, \theta_2)$, $\psi_{in2}^{(2)}(r_2, \theta_2)$, $\psi_{in2}^{(2\nu-1)}(r_2, \theta_2)$ and $\psi_{in2}^{(2\nu)}(r_2, \theta_2)$ can be derived by the interchange $r_1 \leftrightarrow r_2$, $\theta_1 \leftrightarrow \theta_2$, $a_1 \leftrightarrow a_2$, $\psi_{o1} \leftrightarrow \psi_{o2}$ and $H_n(1) \leftrightarrow H_n(2)$ in Eqs. (26)–(29). Note that one can change the coordinate system from (r_1, θ_1) to (r_2, θ_2) and vice versa using Eq. (13).

Interaction energy between two parallel cylinders

The free energy of the present system can be obtained by applying a method of Verwey and Overbeek [9]. The free energy of the system of two interacting cylinders is expressed as the sum of the free energies of the respective cylinders, the form F of which depends on the type of the cylinders. If cylinder i ($i = 1$ or 2) is a soft cylinder with a fixed-charge density ρ_i, then the free energy of cylinder i per unit length is given by

$$F_i = +\frac{1}{2} \int_{V_i} \rho_i \psi \, dV, \quad (30)$$

where the integration of the product of the potential ψ and ρ_i is carried out over the volume V_i of cylinder i per unit length. If cylinder i ($i = 1$ or 2) is a hard cylinder with a constant surface potential ψ_{oi}, then the free energy of

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cylinder i per unit length is given by

$$F_i = -\frac{1}{2}\int_{S_i} \sigma_i \psi_{oi}\, dS \ , \tag{31}$$

where σ_i is the surface charge density of cylinder i, which is not a constant but depends on the cylinder separation R. Finally, if cylinder i ($i = 1$ or 2) is a hard cylinder with a constant surface charge density σ_i, then the free energy of cylinder i per unit length is given by

$$F_i = +\frac{1}{2}\int_{S_i} \sigma_i \psi\, dS \ . \tag{32}$$

Here the integration in Eqs. (31) and (32) is carried out over the surface S of the cylinder per unit length. Note that Eqs. (30)–(32), which correspond to the linearized form of the free energy expressions for the respective cases, are consistent with the linearized Poisson–Boltzmann Eqs. (1) and (2). The total free energy per unit length is the sum of the free energies F_1 and F_2 for the respective cylinders. The electrostatic interaction energy $V(R)$ per unit length can thus be expressed as the free energy of the system of two cylinders 1 and 2 at separation R minus that at infinite separation, viz., $V(R) = \{F_1(R) + F_2(R)\} - \{F_1(\infty) + F_2(\infty)\}$.

Consider the case where both cylinders are hard. We first treat the case where the surface potentials of cylinders 1 and 2 both remain constant at ψ_{o1} and ψ_{o2}, respectively, during interaction independent of R. On the basis of the above obtained results and the free energy expression (31), we finally obtain the required result for the interaction energy per unit length between two parallel hard cylinders with constant surface potentials ψ_{o1} and ψ_{o2}, viz.,

$$\begin{aligned} V(R) &= 2\pi\varepsilon\varepsilon_o \psi_{o1}\psi_{o2} \frac{K_0(\kappa R)}{K_0(\kappa a_1)K_0(\kappa a_2)} \\ &+ \pi\varepsilon\varepsilon_o \psi_{o1}^2 \frac{1}{K_0^2(\kappa a_1)} \sum_{n=-\infty}^{\infty} G_n(2) K_n^2(\kappa R) \\ &+ \pi\varepsilon\varepsilon_o \psi_{o2}^2 \frac{1}{K_0^2(\kappa a_2)} \sum_{n=-\infty}^{\infty} G_n(1) K_n^2(\kappa R) \\ &+ 2\pi\varepsilon\varepsilon_o \psi_{o1}\psi_{o2} \frac{1}{K_0(\kappa a_1)K_0(\kappa a_2)} \\ &\times \sum_{n=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} G_n(2) G_m(1) K_n(\kappa R) K_{n+m}(\kappa R) K_m(\kappa R) \\ &+ \cdots + \pi\varepsilon\varepsilon_o \psi_{o1}\psi_{o2} \frac{1}{K_0(\kappa a_1)K_0(\kappa a_2)} \\ &\times \sum_{n_1=-\infty}^{\infty} \sum_{n_2=-\infty}^{\infty} \cdots \sum_{n_{2\nu}=-\infty}^{\infty} \{L_{21}(n_1, n_2, \ldots, n_{2\nu}) \\ &+ L_{12}(n_1, n_2, \ldots, n_{2\nu})\} K_{n_1}(\kappa R) K_{n_{2\nu}}(\kappa R) \\ &+ \pi\varepsilon\varepsilon_o \sum_{n_1=-\infty}^{\infty} \sum_{n_2=-\infty}^{\infty} \cdots \sum_{n_{2\nu-1}=-\infty}^{\infty} \left[\frac{\psi_{01}^2}{K_0^2(\kappa a_1)} \right. \\ &\times L_{21}(n_1, n_2, \ldots, n_{2\nu-2}) G_{2\nu-1}(2) \\ &\left. + \frac{\psi_{02}^2}{K_0^2(\kappa a_2)} L_{12}(n_1, n_2, \ldots, n_{2\nu-2}) G_{2\nu-1}(1) \right] \\ &\times K_{n_1}(\kappa R) K_{n_{2\nu-2}+n_{2\nu-1}}(\kappa R) K_{n_{2\nu-1}}(\kappa R) + \cdots \ , \end{aligned} \tag{33}$$

where L_{12} is obtained from L_{21} by the interchange $G_n(1) \leftrightarrow G_n(2)$ in Eq. (24).

The interaction energy per unit length between hard cylinders 1 and 2 with constant surface charge densities σ_1 and σ_2 is obtained by replacing $G_n(i)$ by $H_n(i)$, L_{21} by M_{21} and L_{12} by M_{12} in Eq. (33). Here M_{12} is obtained from M_{21} by the interchange $H_n(1) \leftrightarrow H_n(2)$ in Eq. (25). Note that in this case the unperturbed surface potentials ψ_{oi} ($i = 1$ and 2) are related to σ_i by Eq. (10).

Results and discussion

Equation (33) is an explicit exact expression for the interaction energy between two dissimilar *hard* cylinders at constant surface potential. It can be shown that the leading term of the interaction energy, i.e., the first term on the right-hand side of Eq. (33), denoted by $V^{(0)}(R)$, coincides with that obtained by the linear superposition of the unperturbed potentials $\psi_1^{(0)}(r_1)$ and $\psi_2^{(0)}(r_2)$ [11]. It is also of interest to note that if cylinders 1 and 2 were both *soft* cylinders, the interaction energy (calculated via Eq. (30)) would be given by only this term. If cylinder i ($i = 1, 2$) were not hard but a soft cylinder (with cylinder j kept hard ($j = 1, 2$; $j \neq i$)), then the interaction energy would be equal to the sum of only $V^{(0)}(R)$ and $V_i^{(1)}(R)$, where the second and third terms on the right-hand side of Eq. (33) are, denoted by $V_1^{(1)}(R)$ and $V_2^{(1)}(R)$, respectively. The interaction $V_i^{(1)}(R)$ depends only on the surface potential ψ_{oi} of cylinder i ($i = 1, 2$) and can be interpreted as the interaction between cylinder i and its "image" with respect to cylinder j ($j = 1, 2$; $j \neq i$). Note that this image interaction is always attractive. If, on the other hand, the charge density on the cylinder surface (instead of the surface potential) remains constant during interaction, the image interaction may be either repulsive or attractive in contrast to the case where the surface potential remains constant.

The expressions for the potential distribution and the interaction energy at constant *surface* charge density derived in the present paper correspond to the case of two *surface*-charged hard cylinders. It can readily be proven that the same expressions can be applied also for the case of two *space*-charged hard cylinders, i.e., to the case of two hard cylinders with constant *space* charge density except for expressions for the unperturbed potential distribution inside the cylinders, $\psi_i^{(0)}(r_i)$ and for the relation between the particle charge density ρ_i and the unperturbed surface potential ψ_{oi}. These expressions are derived as follows. If cylinder i $(i = 1, 2)$ is charged at constant space charge density ρ_i, then the potential inside cylinder i must satisfy

$$\Delta\psi = -\frac{\rho_i}{\varepsilon_i \varepsilon_o} \tag{34}$$

ψ is continuous across the surface of cylinder i (35)

$$\varepsilon_i \left.\frac{\partial\psi}{\partial r}\right|_{r=a_i^-} = \varepsilon \left.\frac{\partial\psi}{\partial r}\right|_{r=a_i^+} \tag{36}$$

instead of Eqs. (3) and (4). On the basis of these equations, we obtain the following expressions for the relationship between ρ_i, and ψ_{oi}:

$$\psi_{oi} = \frac{\rho_i a_i}{2\varepsilon_i \varepsilon_o \kappa} \frac{K_o(\kappa a_i)}{K_1(\kappa a_i)} \tag{37}$$

and for $\psi_i^{(0)}(r_i)$:

$$\psi_i^{(0)}(r_i) = \psi_{oi} + \frac{\rho_i}{4\varepsilon_i \varepsilon_o}(a_i^2 - r_i^2), \quad r_i \le a_i . \tag{38}$$

Finally, we give below approximate expressions for the interaction energy for the case where $\kappa a_1 \gg 1$ and $\kappa a_2 \gg 1$. In this case, on the basis of Eqs. (A2) and (A3), it can be shown that Eq. (33) tends to

$$V(R) \approx 2\sqrt{2\pi}\,\varepsilon\varepsilon_o \psi_{o1}\psi_{o2}\sqrt{\kappa a_1 a_2}\,\frac{\exp(-\kappa H)}{\sqrt{R}} - \sqrt{\pi}\,\varepsilon\varepsilon_o \frac{\exp(-2\kappa H)}{R}\left[\psi_{o1}^2 a_1 \sqrt{\frac{\kappa a_2 R}{R - a_2}} + \psi_{o2}^2 a_2 \sqrt{\frac{\kappa a_1 R}{R - a_1}}\right] \tag{39}$$

for the constant surface potential case and to

$$V(R) \approx 2\sqrt{2\pi}\,\varepsilon\varepsilon_o \psi_{o1}\psi_{o2}\sqrt{\kappa a_1 a_2}\,\frac{\exp(-\kappa H)}{\sqrt{R}} + \sqrt{\pi}\,\varepsilon\varepsilon_o \frac{\exp(-2\kappa H)}{R}\left[\psi_{o1}^2 a_1 \sqrt{\frac{\kappa a_2 R}{R - a_2}} \times \left\{1 - \frac{2\varepsilon_2}{\varepsilon}\sqrt{\frac{R}{\pi\kappa a_2 (R - a_2)}}\right\} + \psi_{o2}^2 a_2 \sqrt{\frac{\kappa a_1 R}{R - a_1}}\left\{1 - \frac{2\varepsilon_1}{\varepsilon}\sqrt{\frac{R}{\pi\kappa a_1 (R - a_1)}}\right\}\right] \tag{40}$$

for the constant surface charge density case. Further, at small particle separations $H \ll a_1$ and $H \ll a_2$, Eq. (39) reduces to

$$V(R) \approx 2\sqrt{2\pi}\,\varepsilon\varepsilon_o \psi_{o1}\psi_{o2}\sqrt{\frac{\kappa a_1 a_2}{a_1 + a_2}}\exp(-\kappa H) - \sqrt{\pi}\,\varepsilon\varepsilon_o \sqrt{\frac{\kappa a_1 a_2}{a_1 + a_2}}\exp(-2\kappa H)(\psi_{o1}^2 + \psi_{o2}^2), \tag{41}$$

and Eq. (35) to

$$V(R) \approx 2\sqrt{2\pi}\,\varepsilon\varepsilon_o \psi_{o1}\psi_{o2}\sqrt{\frac{\kappa a_1 a_2}{a_1 + a_2}}\exp(-\kappa H) + \sqrt{\pi}\,\varepsilon\varepsilon_o \sqrt{\frac{\kappa a_1 a_2}{a_1 + a_2}}\exp(-2\kappa H) \times \left[\psi_{o1}^2\left(1 - \frac{2}{\sqrt{\pi}}\frac{\varepsilon_2}{\varepsilon}\sqrt{\frac{1}{\kappa a_2} + \frac{1}{\kappa a_2}}\right) + \psi_{o2}^2\left(1 - \frac{2}{\sqrt{\pi}}\frac{\varepsilon_1}{\varepsilon}\sqrt{\frac{1}{\kappa a_2} + \frac{1}{\kappa a_2}}\right)\right]. \tag{42}$$

Equations (41) and (42) agree with results obtained via Derjaguin's approximation (see ref. [13] for the case of identical cylinders at constant surface potential). Equation (37) shows that the next-order curvature correction to Derjaguin's approximation is of the order of $1/\sqrt{\kappa a_i}$ $(i = 1, 2)$ (not of $1/\kappa a_i$), as in the case of sphere–sphere interactions [4] (For the constant potential case, the next-order curvature correction is of the order of $1/\kappa a_i$).

Appendix

For large values of κa_i, $I_n(\kappa a_i)$ and $K_n(\kappa a_i)$ $(i = 1, 2)$ are approximated as [12]

$$I_n(\kappa a_i) \approx \frac{\exp(\kappa a_i)}{\sqrt{2\pi\kappa a_i}}\left(1 - \frac{1}{\kappa a_i}\right)^{n^2/2 - 1/8},$$

$$K_n(\kappa a_i) \approx \sqrt{\frac{\pi}{2\kappa a_i}}\exp(-\kappa a_i)\left(1 + \frac{1}{\kappa a_i}\right)^{n^2/2 - 1/8}. \tag{A1}$$

On the basis of these approximate expressions, when $\kappa a_i \gg 1$ $(i = 1, 2)$, we obtain

$$\sum_{n=-\infty}^{\infty} G_n(i) K_n^2(\kappa R) \approx -\sum_{n=-\infty}^{\infty} \frac{\exp[-2\kappa(R - a_i)]}{2\kappa R} \times \left[\left(1 + \frac{1}{\kappa R}\right)^2 \left(\frac{1 - 1/\kappa a_i}{1 + 1/\kappa a_i}\right)\right]^{n^2/2 - 1/8}$$

$$\approx -\frac{\exp[-2\kappa(R-a_i)]}{2\kappa R}\sum_{n=-\infty}^{\infty}\left[1-\frac{2(R-a_i)}{\kappa a_i R}\right]^{n^2/2-1/8}$$

$$\approx -\frac{\exp[-2\kappa(R-a_i)]}{2\kappa R}\int_{-\infty}^{\infty}\exp\left(-\frac{R-a_i}{\kappa a_i R}x^2\right)dx$$

$$= -\frac{\exp[-2\kappa(R-a_i)]}{2\kappa R}\sqrt{\frac{\pi\kappa a_i R}{R-a_i}}\,, \quad (i=1,2)\,. \qquad \text{(A2)}$$

Similarly, we obtain

$$\sum_{n=-\infty}^{\infty} H_n(i)K_n^2(\kappa R) \approx \frac{\exp[-2\kappa(R-a_i)]}{2\kappa R} \times\left(\sqrt{\frac{\pi\kappa a_i R}{R-a_i}}-\frac{2\varepsilon_i}{\varepsilon}\frac{R}{R-a_i}\right), \quad (i=1,2)\,. \qquad \text{(A3)}$$

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