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球形帶電軟質粒子懸浮液中之電泳可動度及導電度

Electrophoretic Mobility and Effective Electric Conductivity of Concentrated Suspensions of Charged Soft Spheres

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本論文係劉軒僑君（R03524088）在國立臺灣大學化學工程學系所完成之碩士學位論文，於民國 105 年 6 月 17 日承下列考試委員審查通過及口試及格，特此證明

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摘要

本論文使用單元小室模型複合粒子是由帶有固定表面電荷密度σ，半徑為r_0之球形固體核心以及其表面吸附一帶有固定空間電荷密度Q，厚度為$a-r_0$之溶液可穿透多孔層所構成。藉由探討處理此懸浮系統中之靜電力和電動力方程式，可以獲得複合粒子電泳可動度和懸浮液導電度之解析解，並在任意的r_0/a， λa， κa和粒子於懸複液中之體積分率值的情況下，以σ和Q的線性關係式表示，其中λ為多孔層布林克曼滲透長度之倒數，κ為電雙層德拜屏蔽長度之倒數，這些粒子表面吸附層的特性及粒子間的交互作用等參數對於粒子電泳可動度和懸浮液導電度有著顯著且複雜的影響。本研究除了獲得複合粒子懸浮液中之電泳可動度和導電度結果外，也可在$r_0=a$和$r_0=0$的極限下，分別簡化成為球形硬質粒子和多孔粒子之特例結果，這些結果對於分析相關實驗數據資料有所幫助。

關鍵字：電泳，有效導電度，軟質粒子，濃懸浮液，單元小室模型

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Abstract

A thorough analytical study of the electrophoresis and electric conduction in a suspension of charged soft particles in an arbitrary electrolyte solution is presented through the use of a unit cell model. Each soft particle is a spherical hard core of radius r_0 and constant surface charge density σ covered with a permeable porous layer of constant thickness $a - r_0$ and uniform fixed charge density Q. Solving the relevant electrostatic and electrokinetic differential equations, we obtain closed-form formulas for the electrophoretic mobility of the soft particles and effective electric conductivity of the suspension. These results are expressed as linear functions of σ and Q for arbitrary values of r_0 / a, λa, κa, and the particle volume fraction of the suspension, where λ is the reciprocal of the Brinkman permeation length of the surface layer of each particle, and κ is the reciprocal of the Debye screening length. The effects of the surface layer characteristics and particle interactions on the electrophoretic mobility and effective conductivity are interesting, significant, and complicated. The general results for a suspension of charged soft spheres, which reduce to those of hard spheres and porous spheres in the limits $r_0 = a$ and $r_0 = 0$, respectively, provide valuable information for interpreting experimental data.

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Keywords: Electrophoresis, Effective electric conductivity, Soft sphere, Concentrated suspension, Unit cell model

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Chapter 1
Introduction

When an electric field is exerted on colloidal particles suspended in an electrolyte solution, the charged particles and neighboring counterions will move by electrophoresis and electric migration, respectively. As a result, the ambient fluid is dragged to flow, attended with an electric current. Some analytical expressions for the mean electrophoretic mobility of the particles and effective electric conductivity of the suspension have been obtained in the past for dilute suspensions of charged hard spheres (impermeable to the electrolyte solution) [1-4], porous spheres (permeable) [5, 6], and soft spheres (each is a hard spherical core of radius r_0 covered with a porous surface layer of thickness $a - r_0$) [7, 8]. In the limiting cases of $r_0 = a$ and $r_0 = 0$, the results for the suspension of charged soft spheres reduce to those of hard spheres and porous spheres, respectively, of radius a.

In real situations of electrophoresis and electric conduction, relatively concentrated suspensions of charged particles are often involved, and a unit cell model may be used to estimate the effect of particle interactions. This model allows a homogeneous dispersion of particles to be divided into numerous identical cells, with one particle inhabiting at the center of each cell, and thus the multiple-particle problem is reduced to a single-particle

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one for a cell. Adopting the cell model, many researchers investigated the electrophoresis and electric conduction in suspensions of hard spheres [9-16] and porous spheres [17, 18]. Experimental data for the electrophoretic mobility and effective electric conductivity of suspensions of charged particles [19-21] are in agreement with the predictions from the cell model in broad ranges of the volume fraction of the particles and the relative thickness of the electric double layers.

The electrophoresis in a concentrated suspension of soft spheres was also examined numerically or semi-analytically via the unit cell model to some extent [22-24], but the electrophoretic mobility and effective electric conductivity of concentrated suspensions of charged soft particles have not been thoroughly analyzed yet. In this thesis, the cell model is adopted to analytically study the electrophoresis and electric conduction in a suspension of generally charged soft particles. The linearized Poisson-Boltzmann/Laplace equations, continuity equation of ionic species, and Stokes/Brinkman equation modified with an electric force term are solved for the electric potential, ionic electrochemical potential energy, and fluid velocity fields, respectively, without any restrictions on the values of r_0/a, λa, κa, and the volume fraction of the particles, where λ is the Brinkman shielding coefficient in the surface porous layer of each particle and κ is the Debye screening parameter. Closed-form formulas for the electrophoretic mobility and effective electric conductivity of the suspension in terms of

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the fixed charge densities of the particles are derived as Eqs. (35) and (38), respectively.

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Chapter 2

Solution for the Potential and Flow Fields

We consider a suspension of soft spherical particles of radius a in a fluid solution of M ionic species. Each soft sphere is a charged hard core of radius r_0 covered with a homogeneous, solvent-permeable, ion-penetrable, and charged porous layer of thickness $a-r_0$. When the suspension is subjected to an applied electric field $E_\infty \mathbf{e}_z$, where $\mathbf{e}_z$ is the unit vector along the z axis, the particles undergo electrophoresis with a velocity $U\mathbf{e}_z$ and an electric current passes through the suspension in the same direction. As shown in Fig. 1, we adopt a unit cell model in which each particle is located at the center of a spherical cell of radius b and $\varphi = (a/b)^3$ equals the particle volume fraction of the whole suspension. The origin of the spherical coordinates (r, θ, ϕ) is placed at the center of the cell and $z = r\cos\theta$. Thus, the problem in the cell is axially symmetric without ϕ dependency.

To determine the electrophoretic velocity of the particles and the effective electric conductivity of the suspension at the steady state, we first need to find the distributions of the electric potential, electrochemical potential energy (or concentration) of each ionic species, and fluid flow field in the electrolyte solution within a cell in this chapter.

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2.1. Electric potential field

The electric potential distribution $\psi(r,\theta)$ in the fluid region between the rigid core of the soft particle and the outer (virtual) boundary of the cell ($r_0 \le r \le b$) can be expressed as the equilibrium potential distribution $\psi_{\mathrm{eq}}(r)$ induced by the fixed charges of the particle and mobile ions in the surrounding electric double layer added with the perturbed potential distribution $\psi_{\mathrm{a}}(r,\theta)$ caused by the external electric field $E_\infty \mathbf{e}_z$ [25, 26],

$$\psi = \psi_{\mathrm{eq}} + \psi_{\mathrm{a}}\,, \tag{1}$$

With employing the Debye-Hückel approximation at equilibrium, the electric potential ψ_{eq} is governed by the linearized Poisson-Boltzmann equation,

$$\nabla^2 \psi_{\mathrm{eq}} = \kappa^2 \psi_{\mathrm{eq}} - \frac{Q}{\varepsilon} h(r)\,, \tag{2}$$

In this equation, ε is the dielectric permittivity of the fluid, Q is the fixed-charge density in the porous shell of the soft particle, $h(r)$ is a step function equal to unity if $r_0 \le r < a$ (within the porous shell) and zero if $a < r \le b$, and $\kappa = e(\sum_{m=1}^{M} z_m^2 n_m^\infty / \varepsilon kT)^{1/2}$ is the Debye screening parameter, where n_m^∞ and z_m are the bulk concentration (number density) and valence, respectively, of the species m , e is the elementary electric charge, k is the Boltzmann constant, and T is the absolute temperature.

The boundary conditions for the equilibrium potential are

$$r = r_0: \qquad \frac{\mathrm{d}\psi_{\mathrm{eq}}}{\mathrm{d}r} = -\frac{\sigma}{\varepsilon}\,, \tag{3}$$

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$$r = a: \qquad \psi_{\text{eq}} \text{ and } \frac{\mathrm{d}\psi_{\text{eq}}}{\mathrm{d}r} \text{ are continuous,} \tag{4}$$

$$r = b: \qquad \frac{\mathrm{d}\psi_{\text{eq}}}{\mathrm{d}r} = 0\,, \tag{5}$$

where σ is the constant surface charge density of the dielectric hard core of the soft particle, which is related to the local equilibrium potential via the Gauss condition in Eq. (3). Note that Eq. (5) for the unit cell allows the overlap of the electric double layers of adjacent particles.

The solution to Eqs. (2)-(5) can be obtained as

$$\psi_{\text{eq}} = \frac{1}{\varepsilon\kappa^2}[\psi_1(r)\kappa\sigma + \psi_2(r)Q] \tag{6}$$

where

$$\psi_1(r) = 2(\kappa r_0)^2 \frac{\mathrm{e}^{\kappa(r_0+b)}}{B\kappa r}\{\kappa b\cosh[\kappa(b-r)] - \sinh[\kappa(b-r)]\}\,, \tag{7}$$

$$\psi_2(r) = \frac{\mathrm{e}^{-\kappa r}}{2B\kappa r}\{[\mathrm{e}^{\kappa a}(\kappa r_0+1)(\kappa a-1) - \mathrm{e}^{\kappa(2r_0-a)}(\kappa r_0-1)(\kappa a+1)][\mathrm{e}^{2\kappa b}(\kappa b-1) + \mathrm{e}^{2\kappa r}(\kappa b+1)]\} \quad \text{for } a \le r \le b\,, \tag{8a}$$

$$\psi_2(r) = \frac{\mathrm{e}^{\kappa(2b-a+2r_0-r)}}{2B\kappa r}\{\frac{1}{B} - (\kappa b-1)[\kappa a(\kappa r_0-1)+\kappa r_0] + \kappa b + \mathrm{e}^{\kappa(a-2b)}(\kappa r_0-1)(\kappa b+1) \times[\mathrm{e}^{\kappa a}(\kappa a-1) - 2\mathrm{e}^{\kappa r}\kappa r] + \mathrm{e}^{\kappa(r-2r_0)}(\kappa r_0+1)(\kappa b-1)[2\mathrm{e}^{\kappa a}\kappa r - \mathrm{e}^{\kappa r}(\kappa a+1)] + \mathrm{e}^{2\kappa(a-b-r_0+r)}(\kappa r_0+1)(\kappa a-1)(\kappa b+1)\} \quad \text{for } r_0 \le r \le a\,, \tag{8b}$$

and

$$B = \mathrm{e}^{2\kappa b}(\kappa r_0+1)(\kappa b-1) - \mathrm{e}^{2\kappa r_0}(\kappa r_0-1)(\kappa b+1) \tag{9}$$

The potential ψ_{a} caused by the external electric field $E_\infty \mathbf{e}_z$ satisfies the governing equation

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$$\nabla^2\psi_\mathrm{a} = 0 \tag{10}$$

and boundary conditions

$$r = r_0: \qquad \frac{\partial \psi_\mathrm{a}}{\partial r} = 0, \tag{11}$$

$$r = b: \qquad \psi_\mathrm{a} = -E_\infty r\cos\theta \quad \text{(for the Dirichlet approach [10, 16])}, \tag{12a}$$

$$\frac{\partial \psi_\mathrm{a}}{\partial r} = -E_\infty \cos\theta \quad \text{(for the Neumann approach [9, 11])}. \tag{12b}$$

Because the tangential component of the potential gradient at $r = b$ is not specified in Eq. (12b), the Dirichlet approach in Eq. (12a) may be more logical than the Neumann approach.

The solution to Eqs. (10)-(12) is

$$\psi_\mathrm{a} = -\frac{E_\infty}{2\nu}\left(2 + \frac{r_0^3}{r^3}\right) r\cos\theta \tag{13}$$

where $\nu = 1 + r_0^3/2b^3$ if Eq. (12a) is used and $\nu = 1 - r_0^3/b^3$ if Eq. (12b) is employed. In the limiting case of $r_0/b = 0$ ($r_0 = 0$ or $\varphi = 0$), Eqs. (12a) and (12b) lead to identical result (with $\nu = 1$) as expected.

2.2. Electrochemical potential energy field

The electrochemical potential energy distribution $\mu_m(r,\theta)$ of the species m (a linear combination of the ionic concentration n_m and perturbed potential ψ_a) satisfies the continuity equation of the species [8]

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$$\nabla^2 \mu_m = -\frac{z_m^2 e^2 E_\infty}{kT\nu}(1-\frac{r_0^3}{r^3})\frac{\mathrm{d}\psi_{\mathrm{eq}}}{\mathrm{d}r}\cos\theta \quad (14)$$

and boundary conditions

$$r = r_0: \qquad \frac{\mathrm{d}\mu_m}{\mathrm{d}r} = 0, \quad (15)$$

$$r = a: \qquad \mu_m \text{ and } \frac{\mathrm{d}\mu_m}{\mathrm{d}r} \text{ are continuous,} \quad (16)$$

$$r = b: \qquad \mu_m = -z_m e E_\infty r\cos\theta \text{ (if Eq. (12a) is used),} \quad (17a)$$

$$\frac{\mathrm{d}\mu_m}{\mathrm{d}r} = -z_m e E_\infty \cos\theta \text{ (if Eq. (12b) is used).} \quad (17b)$$

Using Eq. (6) for ψ_{eq} correct to the first orders of the fixed charge densities σ and Q, we obtain the solution to Eqs. (14)-(17) as

$$\mu_m = -\frac{E_\infty}{\nu}\{z_m e(1+\frac{r_0^3}{2r^3})r + \frac{z_m^2 e^2 b}{\varepsilon\kappa^2 kT}[F_1(r)\kappa\sigma + F_2(r)Q]\}\cos\theta, \quad (18)$$

where

$$F_i(r) = \frac{-1}{6br^2}\{[2r_0^3 I_{3i}(a,b) + b^3 I_{0i}(a,b)]\frac{2r^3+r_0^3}{\nu b^3} + [2I_{3i}(r_0,a) + I_{0i}(r_0,a)]\frac{2(1-\nu)r^3+r_0^3}{\nu}$$

$$+2r_0^3 I_{3i}(a,r) - 2r^3 I_{0i}(a,r)\} \qquad \text{for } a \le r \le b \quad (19a)$$

$$F_i(r) = \frac{-1}{6br^2}\{[2r_0^3 I_{3i}(r_0,b) + b^3 I_{0i}(r_0,b)]\frac{2r^3+r_0^3}{\nu b^3} + 2r_0^3 I_{3i}(r_0,r) - 2r^3 I_{0i}(r_0,r)\}$$

$$\text{for } r_0 \le r \le a, \quad (19b)$$

and

$$I_{ni}(r_1,r_2) = \int_{r_1}^{r_2}(1-\frac{r_0^3}{r^3})(\frac{r}{r_0})^n \frac{\mathrm{d}\psi_i}{\mathrm{d}r}\mathrm{d}r. \quad (20)$$

This result will be used in the next chapter to determine the effective electric conductivity

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of the suspension of charged soft spheres.

2.3. Fluid flow field

The velocity field $\mathbf{v}(r,\theta)$ and dynamic pressure distribution $p(r,\theta)$ of the incompressible Newtonian fluid are governed by the following equation of continuity and Stokes/Brinkman equation with an electric force term:

$$\nabla \cdot \mathbf{v} = 0, \tag{21}$$

$$\nabla^2 \mathbf{v} - \lambda^2 h(r)\mathbf{v} = \frac{1}{\eta}(\nabla p - \varepsilon\kappa^2 \psi_{\mathrm{eq}} \nabla \psi_{\mathrm{a}}), \tag{22}$$

where λ is the Brinkman shielding coefficient, which is the reciprocal of a characteristic length for the flow penetration inside the porous shell of the soft particle, and η is the fluid viscosity.

We take the reference frame to travel with the particle in the cell and the boundary conditions for the fluid flow field as

$$r = r_0: \qquad v_r = v_\theta = 0, \tag{23}$$

$$r = a: \qquad v_r,\ v_\theta,\ \tau_{rr} - p, \text{ and } \tau_{r\theta} \text{ are continuous,} \tag{24}$$

$$r = b: \qquad v_r = -U\cos\theta, \tag{25a}$$

$$\frac{\tau_{r\theta}}{\eta} = r\frac{\partial}{\partial r}\left(\frac{v_\theta}{r}\right) + \frac{1}{r}\frac{\partial v_r}{\partial \theta} = 0 \quad \text{(for the Happel model [27]),} \tag{25b}$$

$$[\nabla \times \mathbf{v}]_\phi = \frac{1}{r}\frac{\partial}{\partial r}(r v_\theta) - \frac{1}{r}\frac{\partial v_r}{\partial \theta} = 0 \quad \text{(for the Kuwabara model [28]),} \tag{25c}$$

where v_r and v_θ are the nontrivial components of the fluid velocity, τ_{rr} and $\tau_{r\theta}$ are the nontrivial components of the viscous stress, and U is the electrophoretic velocity of

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the particle to be determined. Because the Happel model does not require an exchange of mechanical energy between the cell and its environment, it might be a more reasonable approach than the Kuwabara model.

The solutions to Eqs. (21)-(25) together with Eqs. (6) and (13) correct to the first orders of the fixed charge densities σ and Q are

$$p = \frac{E_\infty}{\nu\kappa^2 a}[p_1(r)\kappa\sigma + p_2(r)Q]\cos\theta\,, \tag{26}$$

$$v_r = \frac{E_\infty}{\nu\eta\kappa^2}[v_{r1}(r)\kappa\sigma + v_{r2}(r)Q]\cos\theta\,, \tag{27}$$

$$v_\theta = -\frac{\partial(r^2 v_r)}{2r\partial r}\tan\theta\,, \tag{28}$$

where

$$p_i(r) = [C_{2i} + J_{3i}(r)](\frac{a}{r})^2 + 2[5C_{4i} + J_{0i}(r)]\frac{r}{a} - \kappa^2 ar(1+\frac{r_0^3}{2r^3})\psi_i(r)\,, \tag{29a}$$

$$v_{ri}(r) = C_{1i} - J_{2i}(r) + [C_{2i} + J_{3i}(r)]\frac{a}{r} + [C_{3i} - \frac{1}{5}J_{5i}(r)](\frac{a}{r})^3 + [C_{4i} + \frac{1}{5}J_{0i}(r)](\frac{r}{a})^2$$

$$\text{for } a \le r \le b\,, \tag{29b}$$

$$p_i(r) = \lambda^2 ar[-C_{5i} + \frac{C_{6i}}{2}(\frac{a}{r})^3] + J_{3i}(r)(\frac{a}{r})^2 + 2J_{0i}(r)\frac{r}{a} - \kappa^2 ar(1+\frac{r_0^3}{2r^3})\psi_i(r)\,, \tag{30a}$$

$$v_{ri}(r) = C_{5i} + [C_{6i} + C_{7i}\alpha(\lambda r) + C_{8i}\beta(\lambda r)](\frac{a}{r})^3 - \frac{2}{(\lambda a)^2}[J_{0i}(r) - J_{3i}(r)(\frac{a}{r})^3$$

$$- 3J_{\alpha i}(r)\frac{\beta(\lambda r)}{(\lambda r)^3} + 3J_{\beta i}(r)\frac{\alpha(\lambda r)}{(\lambda r)^3}] \quad \text{for } r_0 \le r \le a\,, \tag{30b}$$

$$J_{\alpha i}(r) = \frac{1}{6}(\kappa a)^2 \int_a^r (2 + \frac{r_0^3}{r^3})\alpha(\lambda r)\frac{\mathrm{d}\psi_i}{\mathrm{d}r}\mathrm{d}r\,, \tag{31a}$$

$$J_{\beta i}(r) = \frac{1}{6}(\kappa a)^2 \int_a^r (2 + \frac{r_0^3}{r^3})\beta(\lambda r)\frac{\mathrm{d}\psi_i}{\mathrm{d}r}\mathrm{d}r\,, \tag{31b}$$

$$J_{ni}(r) = \frac{1}{6}(\kappa a)^2 \int_a^r (2 + \frac{r_0^3}{r^3})(\frac{r}{a})^n \frac{\mathrm{d}\psi_i}{\mathrm{d}r}\mathrm{d}r\,, \tag{31c}$$

$$\alpha(x) = x\cosh x - \sinh x\,, \tag{32a}$$

$$\beta(x) = x\sinh x - \cosh x\,, \tag{32b}$$

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$i = 1$ and 2, and the dimensionless constants C_{ni} (independent of σ, Q, and ν) for both the Happel and Kuwabara cell models are given by Eqs. (A1)-(A8) in the Appendix.

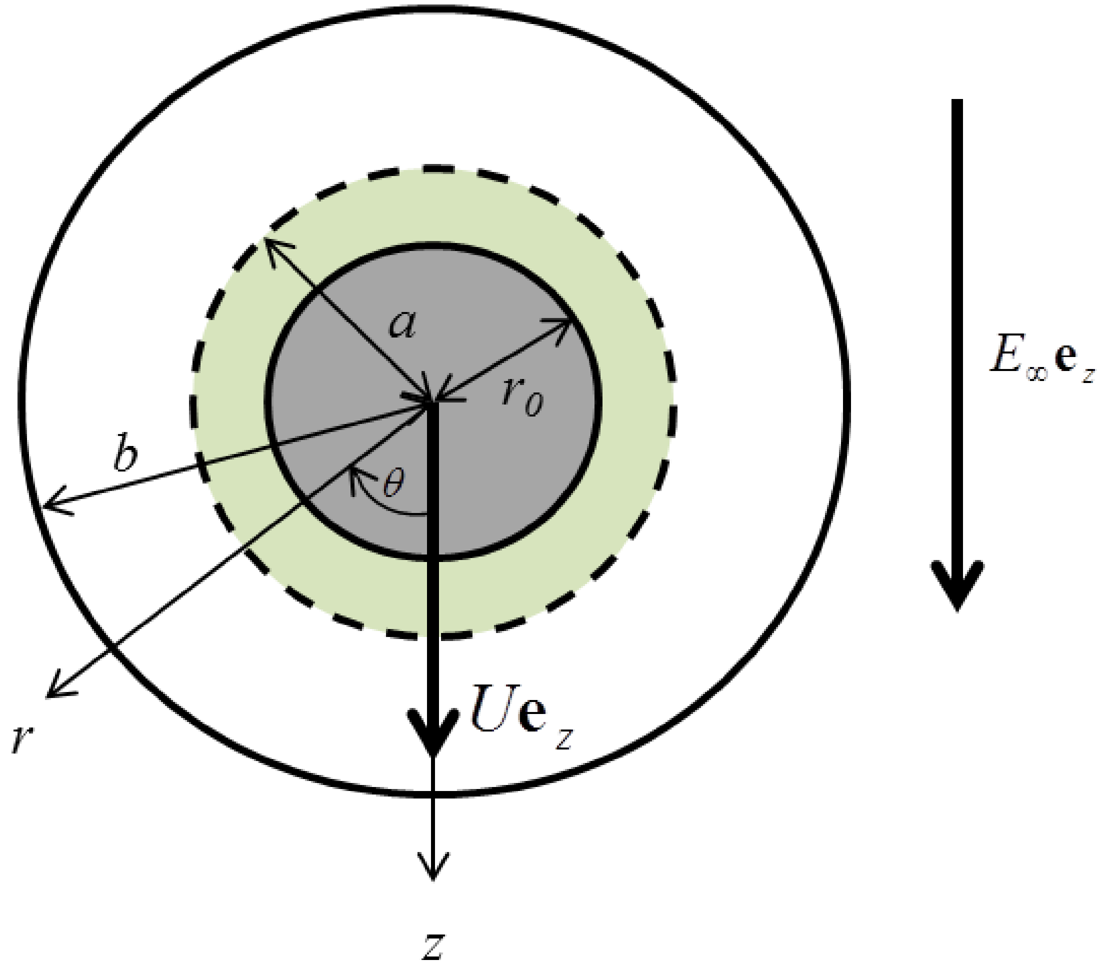

Figure 1. Geometric sketch for a charged soft sphere in a unit cell under an imposed electric field.

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Chapter 3

Solution for the Electrophoretic Velocity and Electric Conductivity

3.1 Electrophoretic velocity

The net force exerted on the soft sphere is composed of the hydrodynamic force

$$\mathbf{F}_{\mathrm{h}} = 2\pi a^2 \int_0^\pi \{(\tau_{rr} - p)\mathbf{e}_r + \tau_{r\theta}\mathbf{e}_\theta\} \sin\theta \, \mathrm{d}\theta \tag{33}$$

and electrostatic force

$$\mathbf{F}_{\mathrm{e}} = 2\pi a^2 \varepsilon \int_0^\pi \nabla\psi_{\mathrm{eq}} \nabla\psi_{\mathrm{a}} \cdot \mathbf{e}_r \sin\theta \mathrm{d}\theta \,, \tag{34}$$

where $\mathbf{e}_r$ and $\mathbf{e}_\theta$ are the unit vectors in the r and θ directions. This net force vanishes at the steady state. The application of this constraint after the substitution of Eqs. (6), (13), and (26)-(30) into Eqs. (33) and (34) results in the electrophoretic velocity of the particle as

$$U = \frac{E_\infty a}{\nu\eta}(U_1\sigma + U_2 aQ)\,, \tag{35}$$

where

$$U_i = \frac{J_{2i}(b)}{(\kappa a)^i} + \frac{1}{(\kappa a)^i A_0}\{\frac{A_1}{6}[(\kappa a)^2(2+\frac{r_0^3}{a^3})\psi_i(a) - 6a\frac{\mathrm{d}\psi_i}{\mathrm{d}r}(a)] + A_2 J_{0i}(b) + A_3 J_{3i}(b)$$

$$+ A_4 J_{5i}(b) + A_5 J_{0i}(r_0) + A_6 J_{3i}(r_0) + A_7 J_{\alpha i}(r_0) + A_8 J_{\beta i}(r_0)\}\,, \tag{36}$$

and the dimensionless constants A_n (independent of σ, Q, and ν) for the Happel and Kuwabara models are given by Eqs. (A9)-(A17) and (A56)-(A64) , respectively, in the Appendix. Equations (35) and (36) show that the electrophoretic velocity U obtained

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from using the Neumann condition in Eq. (12b) is always greater than its corresponding result obtained from using the Dirichlet condition in Eq. (12a) by a factor $(1+\varphi r_0^3/2a^3)/(1-\varphi r_0^3/a^3)$ (which increases monotonically with $\varphi r_0^3/a^3$ from unity at $\varphi = 0$ or $r_0 = 0$) under otherwise the same circumstances.

Evidently, U_1 and U_2 in Eq. (35), which are positive, can be deemed as the normalized electrophoretic mobilities of the soft sphere composed of a charged hard core and an uncharged porous shell ($Q = 0$) and of the soft sphere composed of an uncharged hard core ($\sigma = 0$) and a charged porous shell, respectively. Both normalized electrophoretic mobilities are functions of the radius ratio r_0/a, electrokinetic radius κa, and shielding parameter λa of the soft sphere as well as the particle volume fraction $\varphi = (a/b)^3$ of the suspension. Because of the system's linearity, the effects of the fixed charge densities of the soft sphere on the particle mobility can be simply superimposed. Note that, in the earlier calculations for the electrophoretic mobility of concentrated suspensions of charged soft spheres using the Kuwabara cell model [22, 23], $\sigma = 0$ was assumed and the contribution from U_1 was missing.

3.2 Electric conductivity

The effective electric conductivity for a suspension of charged soft spheres can be obtained from a volume-average current density, with the expression [17]

$$\Lambda = \Lambda^{\infty} - \frac{3e}{2bkTE_{\infty}} \sum_{m=1}^{M} z_m D_m n_m^{\infty} \int_0^{\pi} \left(r\frac{\partial \mu_m}{\partial r} - \mu_m \right)_{r=b} \sin\theta \cos\theta \, \mathrm{d}\theta , \tag{37}$$

where D_m is the diffusion coefficient of the ionic species m and $\Lambda^{\infty} = e^2 \sum_{m=1}^{M} z_m^2 D_m n_m^{\infty} / kT$ is the electric conductivity of the fluid solution with no

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particles. The substitution of Eqs. (18)-(20) for the ionic electrochemical potential energy μ_m together with Eqs. (7) and (8) into Eq. (37) results in the effective conductivity of the suspension correct to the first orders of the fixed charge densities as a linear superposition,

$$\Lambda = \Lambda^{\infty}[1 - \frac{3r_0^3}{2\nu b^3} - \frac{\gamma ea}{\nu\varepsilon kT}(X_1\sigma + X_2 aQ)], \tag{38}$$

where

$$\gamma = \frac{\sum_{m=1}^{M} z_m^3 D_m n_m^{\infty}}{\sum_{m=1}^{M} z_m^2 D_m n_m^{\infty}}, \tag{39}$$

$$X_i = \frac{F_i(b)}{(\kappa a)^i}, \tag{40}$$

which is independent of the reciprocal permeation length λ and the hydrodynamic boundary conditions (Happel and Kuwabara models) at the virtual boundary of the unit cell. The parameters X_1 and X_2 are both positive (and independent of σ and Q), thus the presence of the particle charges reduces the magnitude of the effective conductivity for any volume fraction of particles in the suspension if the product of γ and σ (and Q) is positive and increases this magnitude if $\gamma\sigma < 0$ (and $\gamma Q < 0$). Evidently, $X_1 = X_2 = 0$ and $\Lambda = \Lambda^{\infty}$ as $\varphi = (a/b)^3 = 0$. Equations (38)-(40) also result in a greater effect of particle charges on the effective conductivity for the Neumann condition in Eq. (12b) than for the Dirichlet condition in Eq. (12a).

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Chapter 4
Results and Discussion

The mean electrophoretic mobility and effective electric conductivity for a given suspension of generally charged soft spheres can be readily calculated via Eqs. (35) and (38), respectively. In this chapter, we first consider the mobility and conductivity for the two particular cases of the soft spheres: hard (impermeable) spheres and porous (permeable) spheres. Results for the general case of soft spheres will then be presented.

4.1. Suspension of hard spheres

When there is no permeable layer on the surface of the hard core of the soft sphere, the particle reduces to an impermeable sphere of radius $a = r_0$ and constant surface charge density σ, the terms $U_2 aQ$ in Eq. (35) and $X_2 aQ$ in Eq. (38) are trivial, and the dimensionless mobility parameter U_1 calculated from Eq. (36) and conductivity parameter X_1 calculated from Eq. (40) are functions of the electrokinetic particle radius κa and the particle volume fraction φ $(= a^3/b^3)$. The substitution of Eqs. (7), (19a), and (20) into Eq. (40) leads to

$$X_1 = \frac{e^{\kappa(b+r_0)} {r_0}^2}{8B\kappa^2 ab^3 \nu}\{\cosh(\kappa b - \kappa r_0)[(48 + 6\kappa^2 r_0^2 + \kappa^4 r_0^4)\{\kappa b - \tanh(\kappa b - \kappa r_0)\}$$

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$$+\kappa r_0(48-2\kappa^2 r_0^2-\kappa^4 r_0^4)\{\kappa b\tanh(\kappa b-\kappa r_0)-1\}]$$

$$+\frac{1}{2}\kappa^6 r_0^{\ 6}\cosh(\kappa b)[(1+\kappa b)\{\tanh(\kappa b)-1\}\{E_1(-\kappa b)-E_1(-\kappa r_0)\}$$

$$+(1-\kappa b)\{\tanh(\kappa b)+1\}\{E_1(\kappa b)-E_1(\kappa r_0)\}]-16\kappa^3 b^3+8\kappa^3 r_0^{\ 3}-2\kappa^5 b^{-1} r_0^{\ 6}\}, \quad (41)$$

where

$$E_n(x)=\int_1^\infty t^{-n}\mathrm{e}^{-xt}\mathrm{d}t, \quad (42)$$

which is valid for suspensions of both hard spheres and general soft spheres but depends on the boundary condition for ψ_a at the outer surface of the unit cell given by Eq. (12a) or (12b).

For a suspension of hard spheres with thin electric double layers ($\kappa a >> 1$), Eqs. (36) and (41) have the asymptotic forms

$$U_1 \to \frac{3}{\kappa a}\left(\frac{1-\varphi^{5/3}}{3+2\varphi^{5/3}}-\frac{1}{\kappa a}\right) \quad (43a)$$

for the Happel model in Eq. (25b),

$$U_1 \to \frac{1}{\kappa a}[1-\varphi-\frac{1}{\kappa a}(3+\varphi^{1/3}-\varphi^{4/3})] \quad (43b)$$

for the Kuwabara model in Eq. (25c), and

$$X_1 \to \frac{9\varphi}{2(\kappa a)^2\nu}\left(1-\frac{1+\varphi^{1/3}}{\kappa a}\right) \quad (44)$$

for both models. Note that Eqs. (43) and (44) predict a vanishing particle velocity and no contribution of the particle charges to the effective conductivity in the limit $\kappa a \to \infty$ for a constant surface charge density.

For a suspension of hard spheres with thick double layers ($\kappa a << 1$), Eqs. (36) and

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(41) become

$$U_1 \to \frac{(1-\varphi^{1/3})^2(2+\varphi)(1+\varphi^{1/3})(2+\varphi^{1/3}+2\varphi^{2/3})}{2(1+\varphi^{1/3}+\varphi^{2/3})(3+2\varphi^{5/3})} \tag{45a}$$

for the Happel model,

$$U_1 \to \frac{(1-\varphi^{1/3})^2(2+\varphi)(5+6\varphi^{1/3}+3\varphi^{2/3}+\varphi)}{15(1+\varphi^{1/3}+\varphi^{2/3})} \tag{45b}$$

for the Kuwabara model, and

$$X_1 \to 3\frac{\varphi^{1/3}(4-15\varphi^{2/3}+10\varphi+6\varphi^{5/3}-5\varphi^2)}{40(1-\varphi)\nu} \tag{46}$$

for both models. Equations (45) and (46) lead to a finite particle velocity and finite contribution of particle charge to the effective conductivity in the limit $\kappa a = 0$.

In the limit $\varphi \to 0$ (the suspension is infinitely dilute and $\nu = 1$), Eqs. (36) and (41) reduce to

$$U_1 \to \frac{1}{\kappa a+1}\{1-\mathrm{e}^{\kappa a}[5E_7(\kappa a)-2E_5(\kappa a)]\}, \tag{47}$$

$$X_1 \to \frac{\varphi}{16(\kappa a+1)}[48(\kappa a)^{-2}+48(\kappa a)^{-1}+6-2\kappa a+(\kappa a)^2-(\kappa a)^3+E_1(\kappa a)\mathrm{e}^{\kappa a}(\kappa a)^4]. \tag{48}$$

As expected, Eq. (48) indicates that the effect of the particle charges on the electric conductivity of the suspension vanishes in this limit. It can be shown that Eqs. (41)-(48) for the case of constant σ are consistent with the results obtained for the electrophoretic migration and electric conduction of a suspension of hard spheres of constant zeta potential [12].

The normalized electrophoretic mobility U_1 for a suspension of hard spheres with constant surface charge density σ, as calculated from Eq. (36) for both the Happel and

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Kuwabara cell models, is plotted versus the parameters κa and φ in Fig. 2. The results are presented up to $\varphi = 0.74$, the limit for an assemblage of identical spheres [9]. For a specified value of φ, the value of U_1 decreases monotonically with an increase in κa (a decrease in the overlap of the adjacent electric double layers) from a constant (equal to 2/3 if $\varphi = 0$) at $\kappa a = 0$ (as predicted from Eq. (45)) to zero as $\kappa a \to \infty$ (asymptotically proportional to $(\kappa a)^{-1}$ as predicted from Eq. (43)). For a fixed value of κa, U_1 is a monotonic decreasing function of φ and in general the effect of particle interactions on the electrophoretic mobility is significant. For an arbitrary combination of κa and φ, the Kuwabara model predicts a smaller value (a stronger particle concentration effect) for the electrophoretic mobility than the Happel model does, but the difference is insubstantial. It can be found that the experimental data of electrophoretic mobility for suspensions of human erythrocytes with large κa and various values of φ [20] agree well with U_1 predicted from the Happel model with the Dirichlet approach in Eq. (12a) for the suspension of hard spheres.

The parameter X_1 (effect of the particle surface charges) for the effective electric conductivity of a suspension of hard spheres, as calculated from Eq. (41), is plotted versus the parameters κa and φ in Fig. 3. For a given value of φ, the value of X_1 decreases monotonically with an increase in κa from a constant at $\kappa a = 0$ (as predicted from Eq. (46)) to zero as $\kappa a \to \infty$ (asymptotically proportional to $(\kappa a)^{-2}$ as

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predicted from Eq. (44)). For a constant value of κa, however, X_1 increases with an increase in φ from zero at $\varphi = 0$ (as predicted from Eq. (48)), attains a maximum at some value of φ, and then decreases with a further increase in φ. The location of this maximum shifts to greater φ as κa increases, and the effect of φ on the effective conductivity can be significant. For specified values of κa and φ, the value of X_1 obtained from using the Neumann condition in Eq. (12b) is greater than that from using the Dirichlet condition in Eq. (12a). The experimental data of electric conductivity for suspensions of polystyrene latex spheres in aqueous solutions of 0.1 mM $HClO_4$ with $\kappa a \approx 1$ and φ of the order 0.01 [19] are in reasonable agreement with X_1 predicted from the Dirichlet approach for the suspension of hard spheres.

4.2. Suspension of porous spheres

When the hard core of the soft sphere disappears ($r_0 = 0$), the particle becomes a permeable sphere (such as a polymer coil or colloidal floc) of radius a and fixed charge density Q, the terms $U_1\sigma$ in Eq. (35) and $X_1\sigma$ in Eq. (38) are trivial, and the mobility parameter U_2 calculated from Eq. (36) and conductivity parameter X_2 calculated from Eq. (40) are functions of the electrokinetic radius κa, shielding parameter λa, and particle volume fraction φ and are independent of the boundary condition for ψ_a at the outer surface of a unit cell given by Eq. (12a) or (12b) ($\nu = 1$). Substitution of Eqs.

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(8), (19a), and (20) into Eq. (40) leads to

$$X_2 = \frac{1}{(\kappa a)^2}[\varphi - \frac{\alpha(\kappa a)}{\alpha(\kappa a \varphi^{-1/3})}]. \quad (49)$$

For a suspension of porous spheres with thin electric double layers ($\kappa a >> 1$), Eqs. (36) and (49) have the forms

$$U_2 \to \frac{1}{(\lambda a)^2}, \quad (50)$$

$$X_2 \to \frac{\varphi}{(\kappa a)^2}, \quad (51)$$

for both models. Equations (50) and (51) predict no contribution of particle charges to the effective conductivity but a finite particle velocity in the limit $\kappa a \to \infty$.

For a suspension of porous spheres with thick double layers ($\kappa a << 1$), Eqs. (36) and (49) become

$$U_2 \to \frac{1}{(\lambda a)^2}\{\lambda a[30\varphi^{5/3} + (1+14\varphi^{5/3} - 10\varphi^2)(\lambda a)^2 + \frac{1}{3}(2 - 3\varphi^{1/3} + 3\varphi^{5/3} - 2\varphi^2)(\lambda a)^4]$$

$$-[30\varphi^{5/3} + (1+24\varphi^{5/3} - 10\varphi^2)(\lambda a)^2 - (\varphi^{1/3} - 5\varphi^{5/3} + 4\varphi^2)(\lambda a)^4]\tanh(\lambda a)\}$$

$$\times\{\lambda a[30\varphi^{5/3} + (3+2\varphi^{5/3})(\lambda a)^2] - 3[10\varphi^{5/3} + (1+4\varphi^{5/3})(\lambda a)^2]\tanh(\lambda a)\}^{-1} \quad (52a)$$

for the Happel model,

$$U_2 \to \frac{1}{45}\{\frac{15}{(\lambda a)^2} + [1 + 2\varphi(2-\varphi)] - 6[3\varphi^{1/3} - \varphi(5-2\varphi)] + \frac{10(1-\varphi)^2 \lambda a}{\lambda a - \tanh(\lambda a)}\} \quad (52b)$$

for the Kuwabara model, and

$$X_2 \to \frac{1}{10}(\varphi^{1/3} - \varphi) \quad (53)$$

for both models. Equations (52) and (53) lead to a finite particle velocity and a finite

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contribution of the particle charges to the effective conductivity in the limit $\kappa a = 0$.

In the limit $\varphi \to 0$, Eqs. (36) and (49) result in

$$U_2 \to (\frac{1}{\lambda a})^2 + \frac{1-e^{-2\kappa a}}{3(\kappa a)^3}\{\kappa a \coth(\kappa a) - 1 + \frac{\kappa a + 1}{\lambda^2 - \kappa^2}[\lambda^2 \frac{\kappa a \coth(\kappa a) - 1}{\lambda a \coth(\lambda a) - 1} - \kappa^2]\}, \quad (54)$$

$$X_2 \to \frac{\varphi}{(\kappa a)^2}. \quad (55)$$

Again, Eq. (55) predicts no contribution of the particle charges to the effective conductivity in this limit. Equations (49)-(55) are consistent with the results obtained for a suspension of charged porous spheres [17].

In Fig. 4, the normalized electrophoretic mobility U_2 for a suspension of porous spheres, as calculated from Eq. (36) for the Happel cell model (which differs little from that calculated for the Kuwabara model), is plotted as a function of the parameters κa, λa, and φ. For fixed values of λa and φ, the value of U_2 is a finite monotonic decreasing function of κa from a constant at $\kappa a = 0$ (as predicted from Eq. (52)) to another constant as $\kappa a \to \infty$ (as predicted from Eq. (50)). For constant values of κa and φ, U_2 is a monotonic decreasing function of λa (the relative resistance to the fluid flow within the porous particle). For given values of κa and λa, U_2 decreases monotonically with an increase in φ; when κa is smaller or λa is greater, the effect of φ on U_2 becomes more conspicuous.

In Fig. 5, the parameter X_2 for the effective electric conductivity of a suspension of porous spheres, as calculated from Eq. (49), is plotted versus the parameters κa and φ. Analogous to the parameter X_1 for a suspension of hard spheres, the value of X_2 decreases monotonically with an increase in κa from a constant at $\kappa a = 0$ (as predicted

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from Eq. (53)) to zero as $\kappa a \to \infty$ (asymptotically proportional to $(\kappa a)^{-2}$ as predicted from Eq. (51)) for a specified value of φ. For a given value of κa, X_2 increases with an increase in φ from zero at $\varphi = 0$ (as predicted from Eq. (55)), reaches a maximum at some value of φ (whose location shifts to greater φ as κa increases), and then decreases with a further increase in φ. The effect of φ on X_2 can also be significant.

4.3. Suspension of soft spheres

For a suspension of soft spheres, the electrophoretic mobility parameters U_1 (contribution from the surface charge density σ of the hard core) and U_2 (contribution from the fixed charge density Q of the porous surface layer) calculated from Eq. (36) are plotted in Figs. 6 and 7, respectively, for various values of the particle volume fraction φ, radius ratio r_0/a, electrokinetic radius κa, and shielding parameter λa. Analogous to the outcomes of the particular cases with $r_0/a = 1$ (where λa is trivial) and $r_0/a = 0$ discussed in the previous subsections, both mobility parameters in general decrease with an increase in κa (with some exceptions for U_2), decrease with an increase in λa (from constants at $\lambda a = 0$ to smaller constants as $\lambda a \to \infty$), decrease with an increase in φ, and are smaller as predicted by the Kuwabara model than the Happel model (but the difference is insubstantial).

Figure 6b illustrates that, for specified values of κa, λa, and φ, the mobility

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parameter U_1 increases with an increase in the radius ratio r_0/a (or relative surface area of the hard core of the soft particle) from zero at $r_0/a=0$, but may attain a maximum and then decrease with a further increase in r_0/a (or hydrodynamic resistance to the electrophoretic motion of the particle caused by the hard core). On the contrary, as indicated in Fig. 7b, the mobility parameter U_2 is a monotonic decreasing function of r_0/a (increasing function of $1-r_0/a$ or the relative volume of the porous surface layer of the soft particle), vanishing at $r_0/a=1$ as expected. For cases with a medium value of r_0/a (ca. 1/2), the contributions to the electrophoretic mobility of the soft particle from U_1 and U_2 (or σ and Q) are comparable. Our results of U_2 are consistent with the earlier calculations for the electrophoretic mobility of concentrated suspensions of soft spheres with constant Q and vanishing σ performed by using the Kuwabara cell model [22, 23].

For the effective electric conductivity of a suspension of soft spheres, the parameters X_1 (contribution from the surface charge density σ) and X_2 (contribution from the fixed charge density Q) as calculated from Eq. (40) together with Eq. (19a) (or X_1 as calculated from Eq. (41)) are plotted in Figs. 8 and 9, respectively, for various values of the parameters κa, r_0/a, and φ. Similar to the results of the particular cases with $r_0/a=1$ and $r_0/a=0$ discussed in the previous subsections, for constant values of κa and r_0/a, both X_1 and X_2 increase with an increase in φ from zero at $\varphi=0$

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but may not be monotonic functions (have maxima at some intermediate values of φ), and the effect of φ on these parameters can be significant. For given values of r_0 / a and φ, both X_1 and X_2 decrease with an increase in κa from constants at $\kappa a = 0$ to zero as $\kappa a \to \infty$. For any combination of κa, r_0 / a, and φ, the values of X_1 and X_2 obtained from using the Neumann condition in Eq. (12b) are greater than those from using the Dirichlet condition in Eq. (12a).

For fixed values of κa and φ, Fig. 8b indicates that the parameter X_1 increases with an increase in the radius ratio r_0 / a from zero at $r_0 / a = 0$, but may reach a maximum and then decrease with a further increase in r_0 / a. On the contrary, as illustrated in Fig. 9b, the parameter X_2 is a monotonic decreasing function of r_0 / a from a constant at $r_0 / a = 0$ to zero at $r_0 / a = 1$. For cases with a medium value of r_0 / a, the contributions to the electric conductivity of the suspension from the fixed charge densities σ and Q of the soft particle are comparable.

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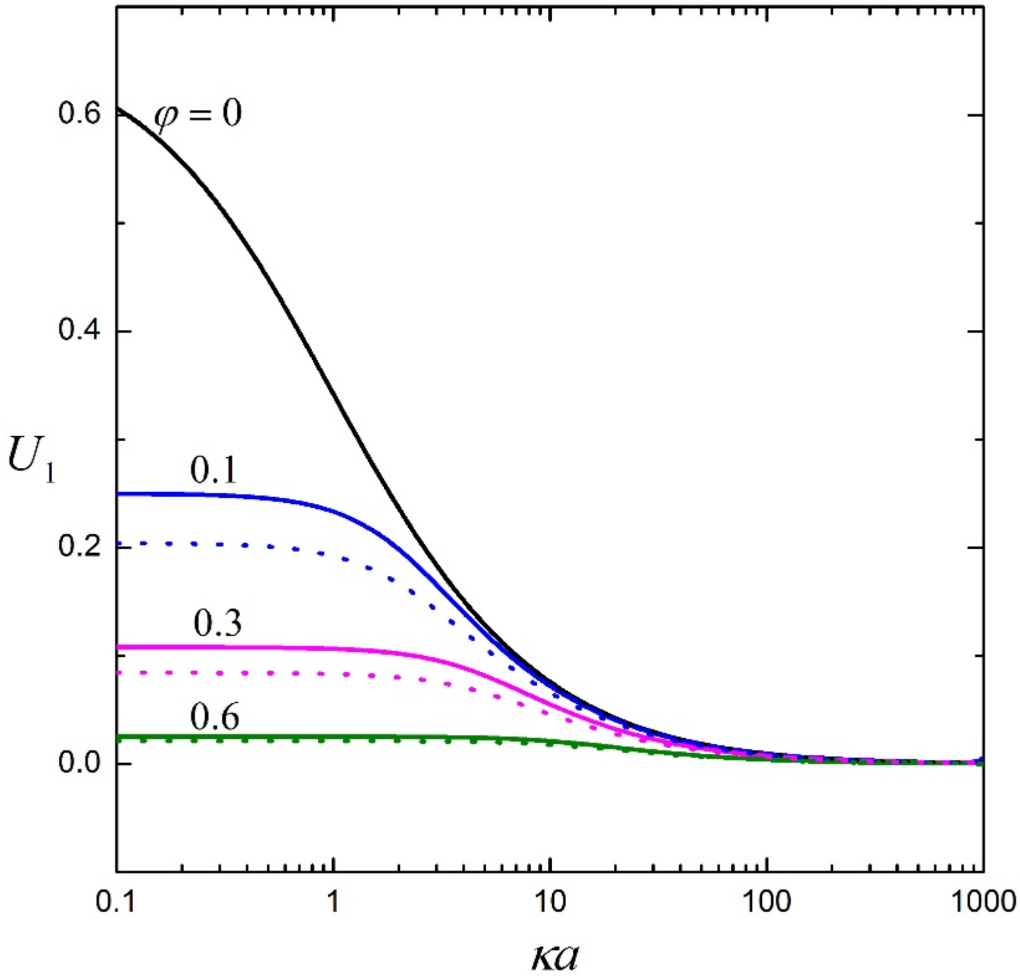

Figure 2(a). Plots of the normalized electrophoretic mobility U_1 for a suspension of hard spheres as calculated from Eq. (36) versus the parameter κa. The solid and dashed curves represent the calculations for the Happel and Kuwabara models, respectively.

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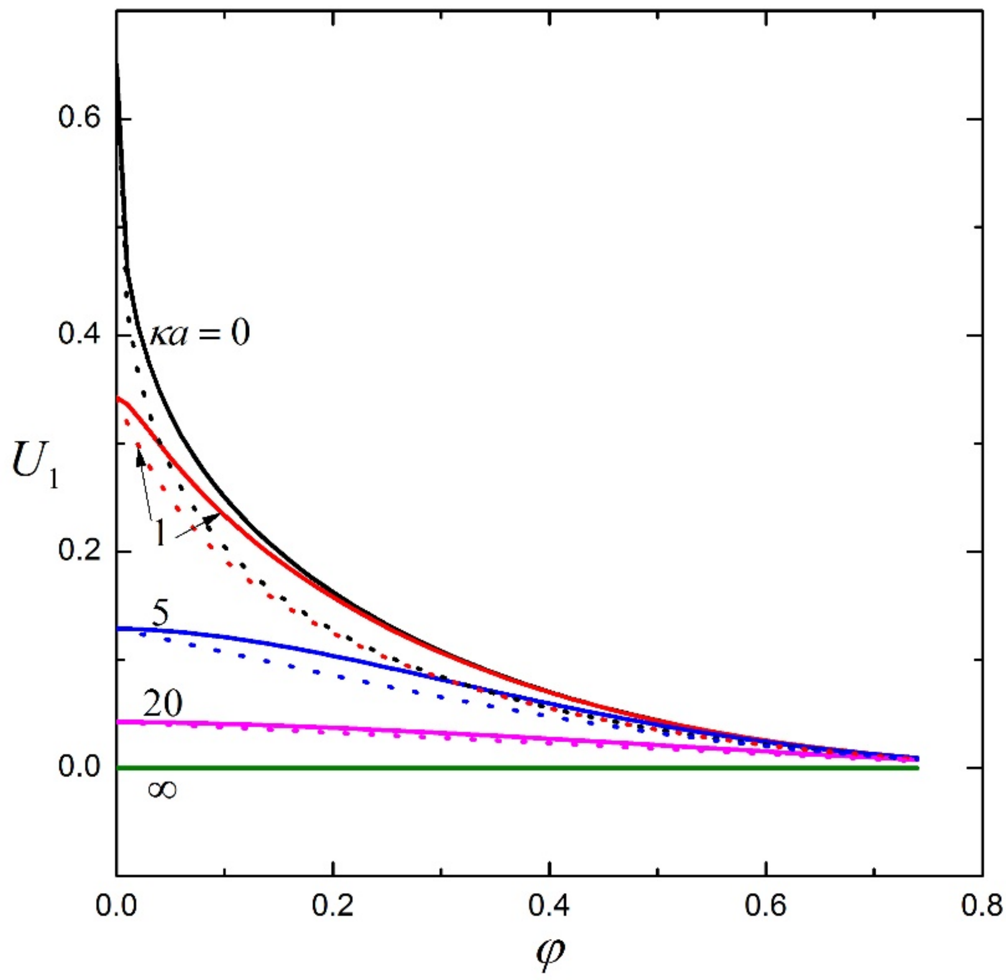

Figure 2(b). Plots of the normalized electrophoretic mobility U_1 for a suspension of hard spheres as calculated from Eq. (36) versus the parameter φ. The solid and dashed curves represent the calculations for the Happel and Kuwabara models, respectively.

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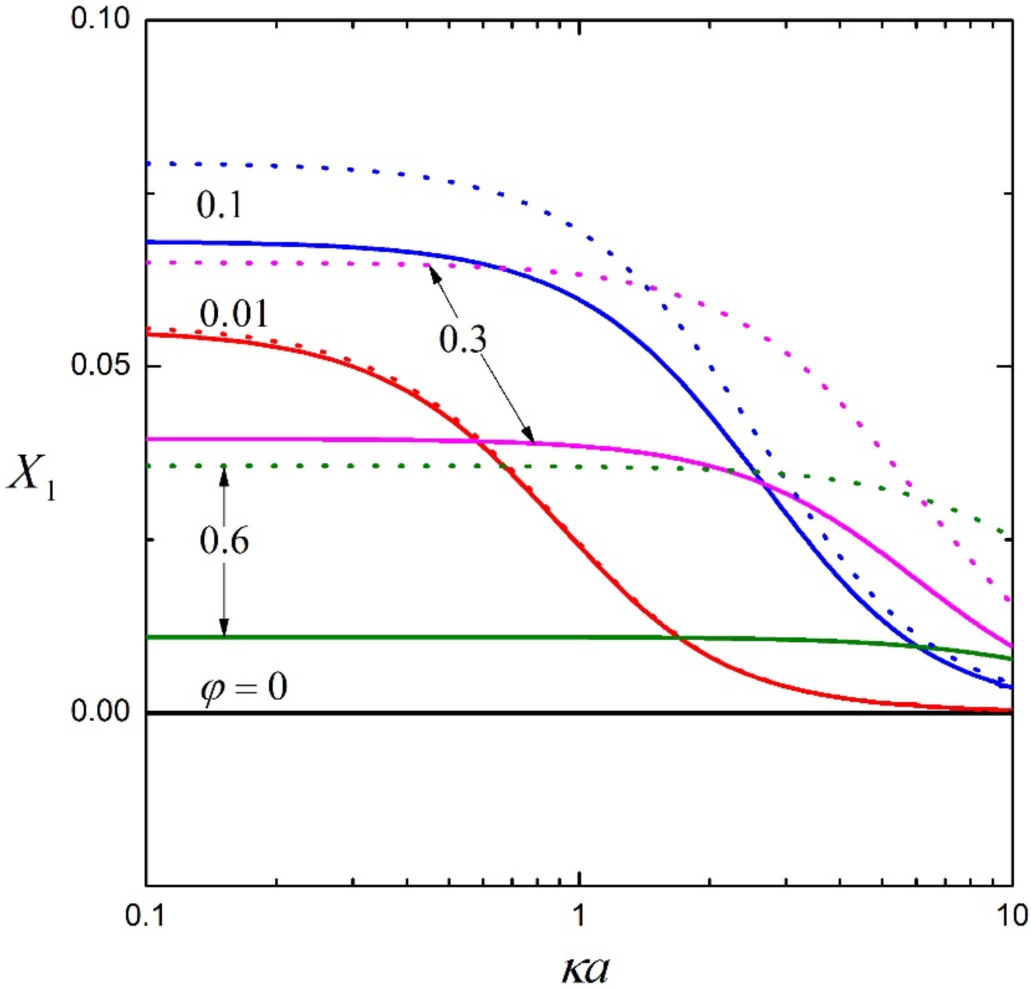

Figure 3(a). Plots of the electric conductivity parameter X_1 for a suspension of hard spheres as calculated from Eq. (41) versus the parameter κa. The solid and dashed curves represent the calculations from using the Dirichlet condition in Eq. (12a) and Neumann condition in Eq. (12b), respectively.

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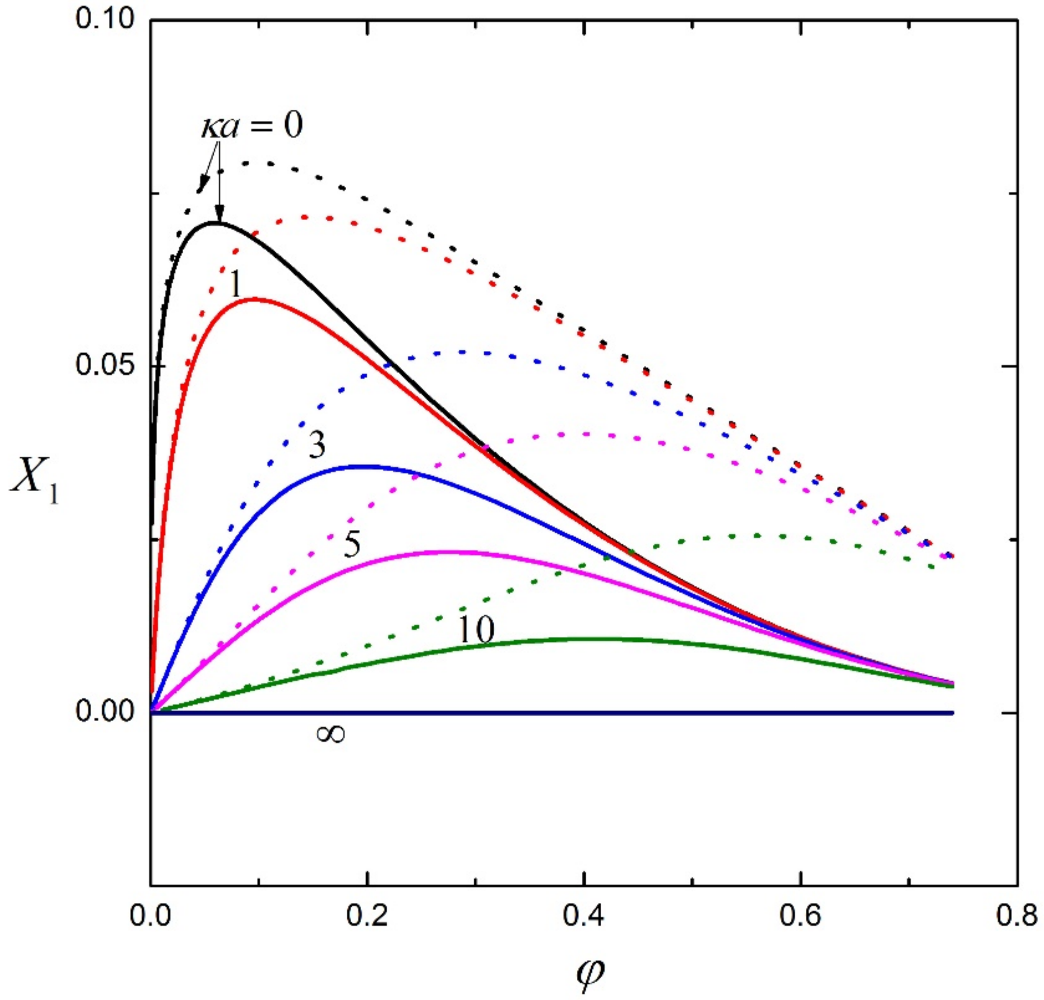

Figure 3(b). Plots of the electric conductivity parameter X_1 for a suspension of hard spheres as calculated from Eq. (41) versus the parameter φ. The solid and dashed curves represent the calculations from using the Dirichlet condition in Eq. (12a) and Neumann condition in Eq. (12b), respectively.

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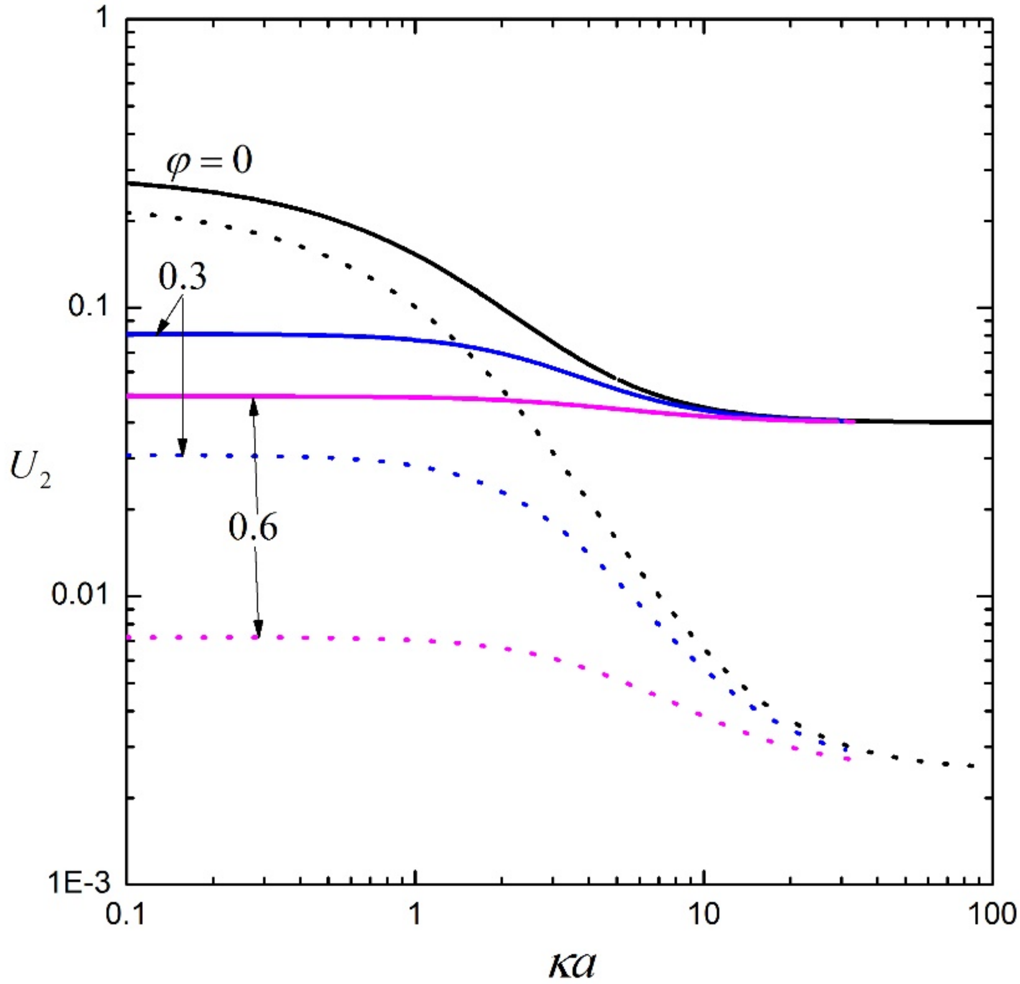

Figure 4(a). Plots of the normalized electrophoretic mobility U_2 for a suspension of porous spheres as calculated from Eq. (36) versus the parameter κa for the Happel model. The solid and dashed curves represent the calculations with $\lambda a = 5$ and $\lambda a = 20$, respectively.

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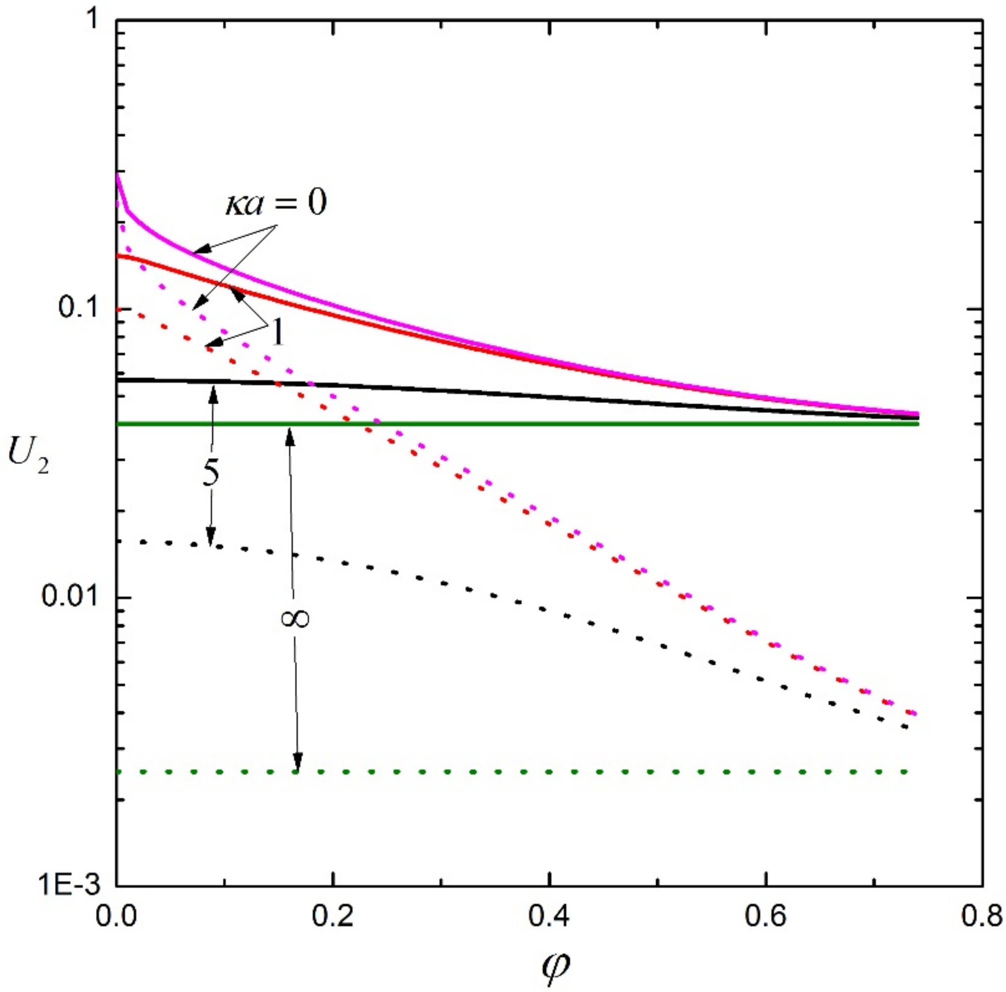

Figure 4(b). Plots of the normalized electrophoretic mobility U_2 for a suspension of porous spheres as calculated from Eq. (36) versus the parameter φ for the Happel model. The solid and dashed curves represent the calculations with $\lambda a = 5$ and $\lambda a = 20$, respectively.

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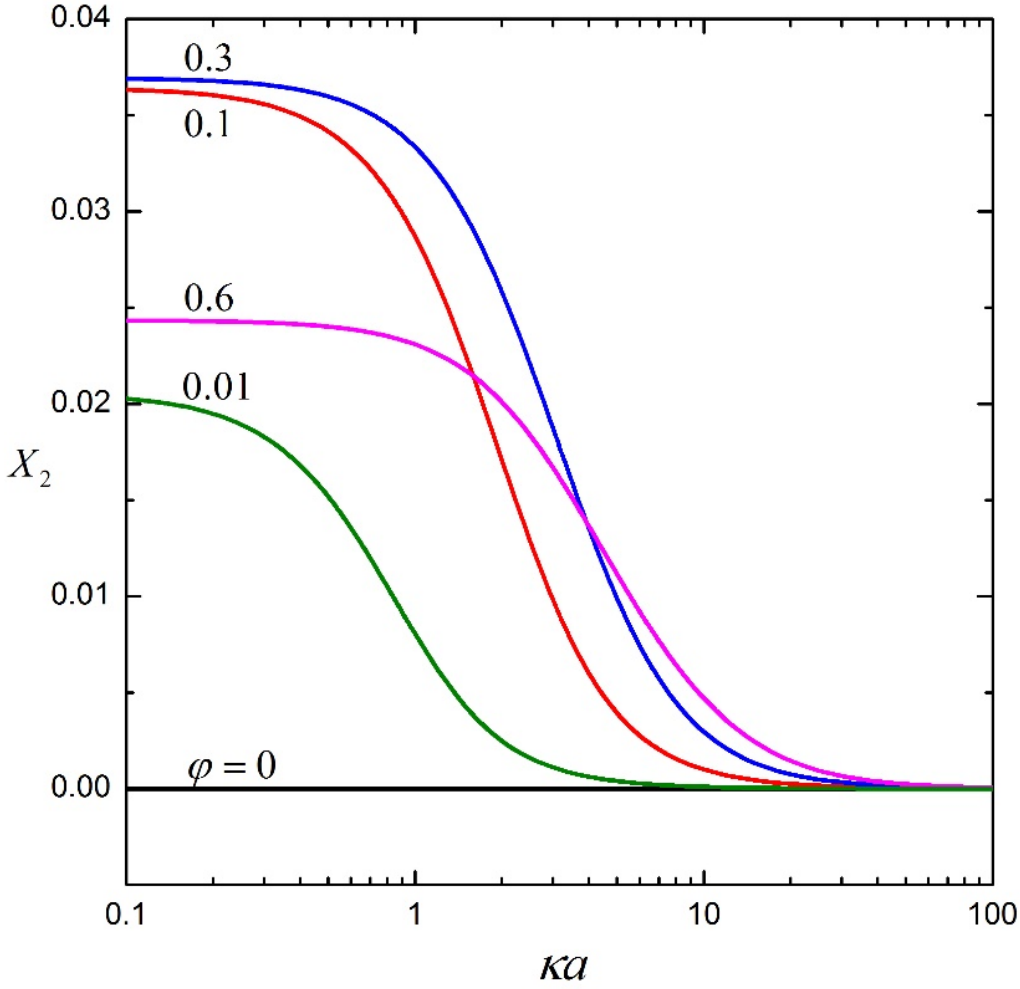

Figure 5(a). Plots of the electric conductivity parameter X_2 for a suspension of porous spheres as calculated from Eq. (49) versus the parameter κa .

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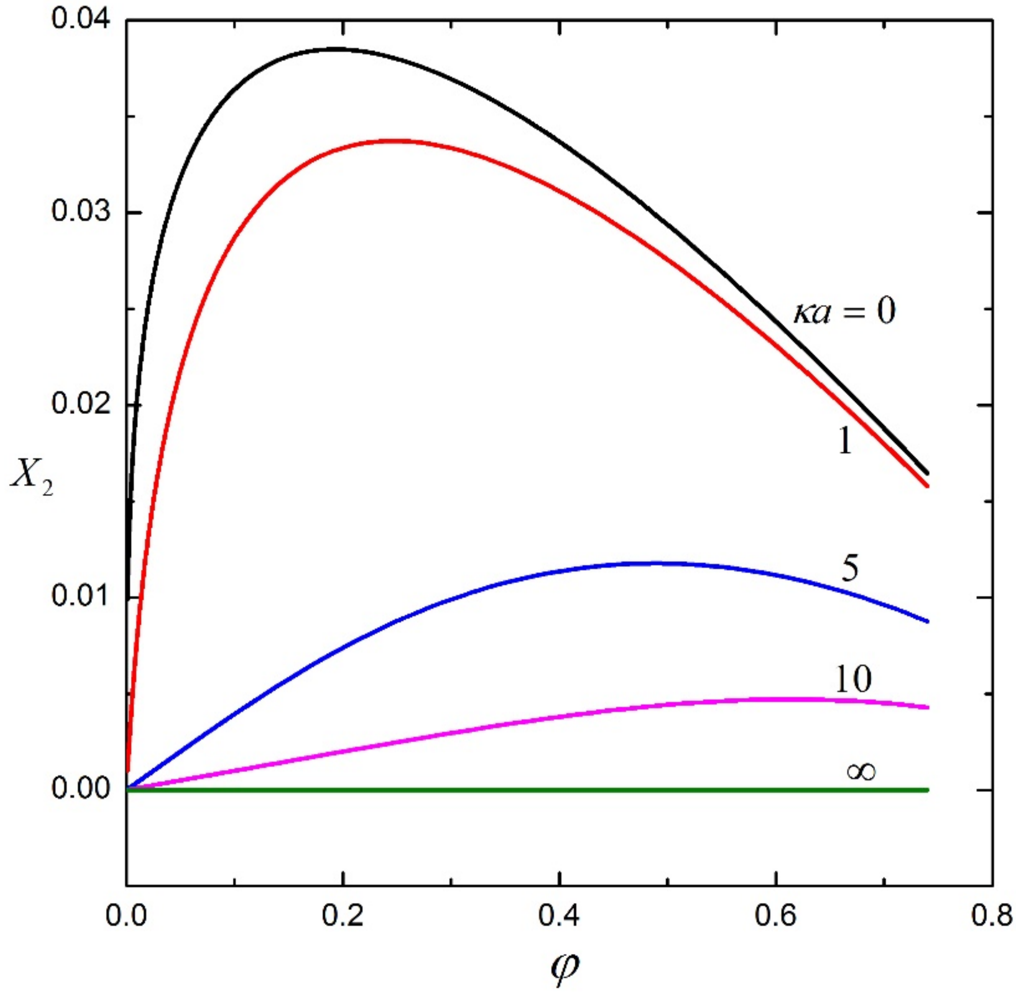

Figure 5(b). Plots of the electric conductivity parameter X_2 for a suspension of porous spheres as calculated from Eq. (49) versus the parameter φ.

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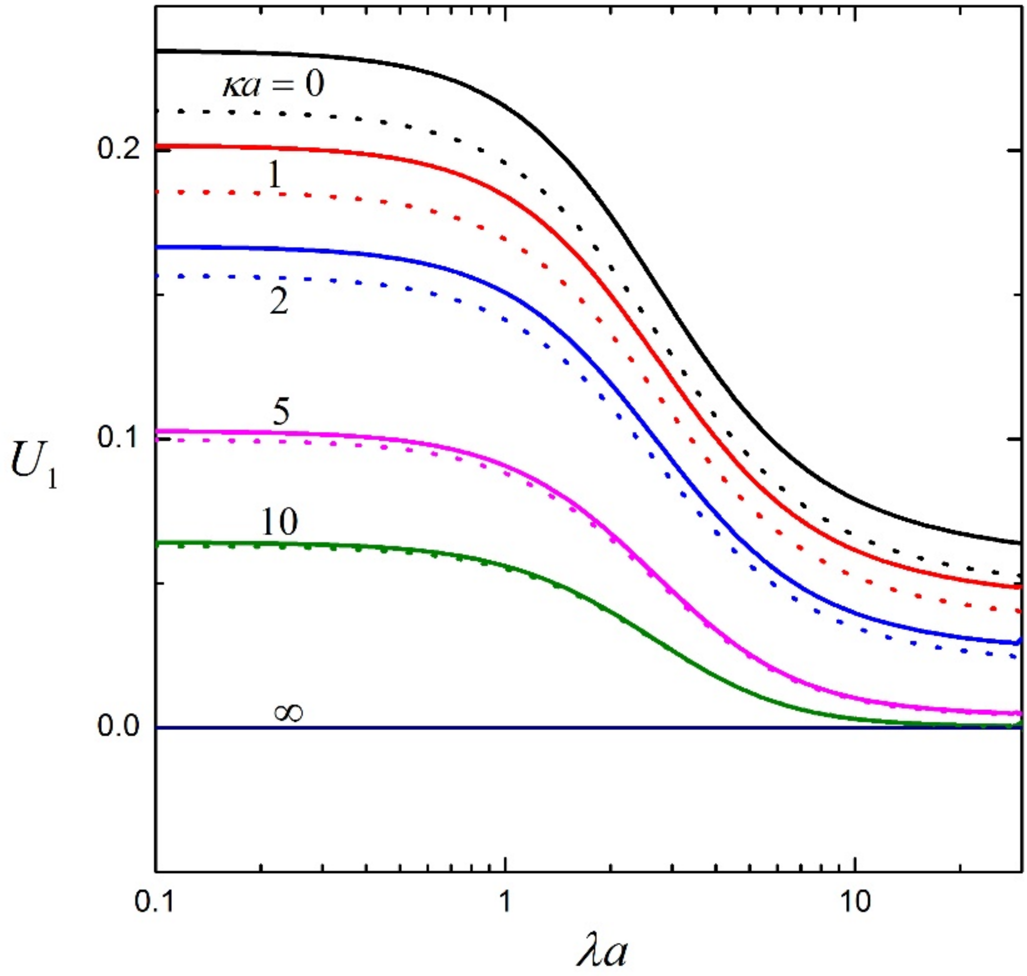

Figure 6(a). Plots of the electrophoretic mobility parameter U_1 for a suspension of soft spheres as calculated from Eq. (36) versus the parameter λa for various values of κa at $\varphi = 0.1$ and $r_0 / a = 0.5$. The solid and dashed curves represent the calculations for the Happel and Kuwabara models, respectively.

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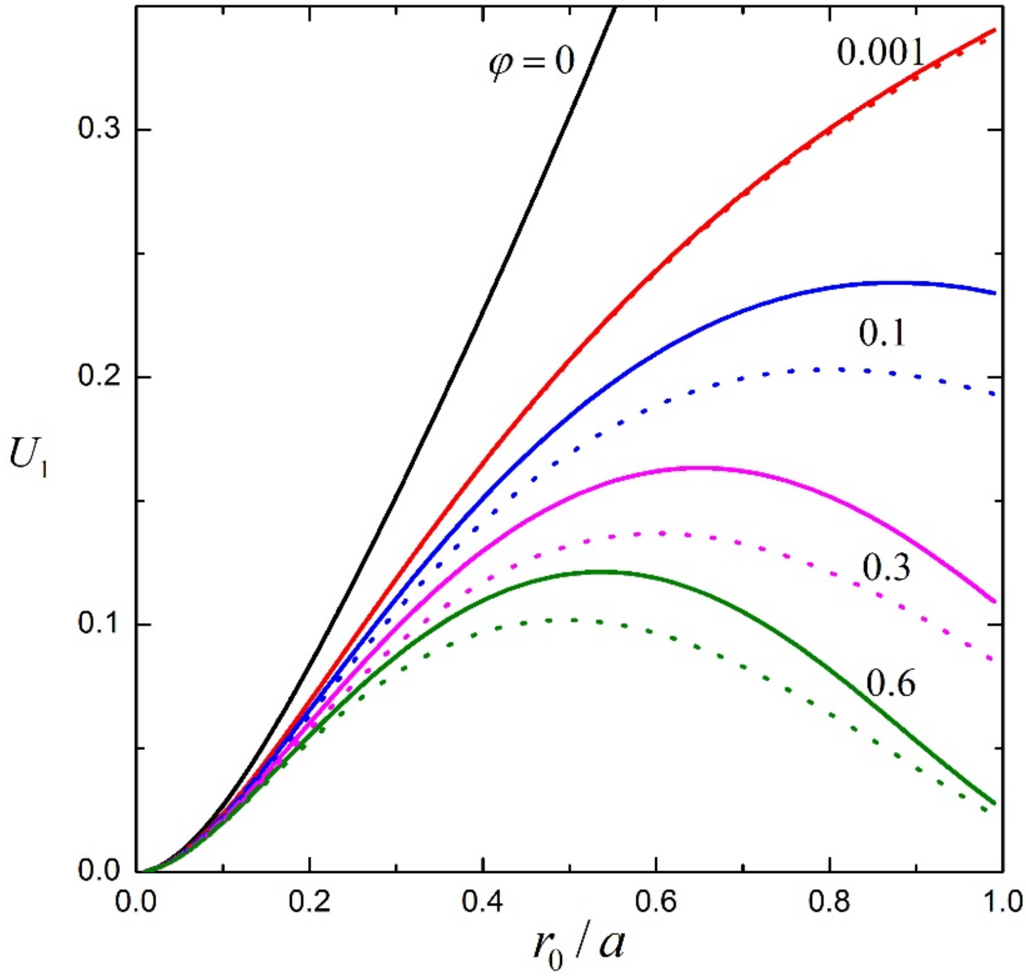

Figure 6(b). Plots of the electrophoretic mobility parameter U_1 for a suspension of soft spheres as calculated from Eq. (36) versus the parameter r_0 / a for various values of φ at $\kappa a = 1$ and $\lambda a = 1$. The solid and dashed curves represent the calculations for the Happel and Kuwabara models, respectively.

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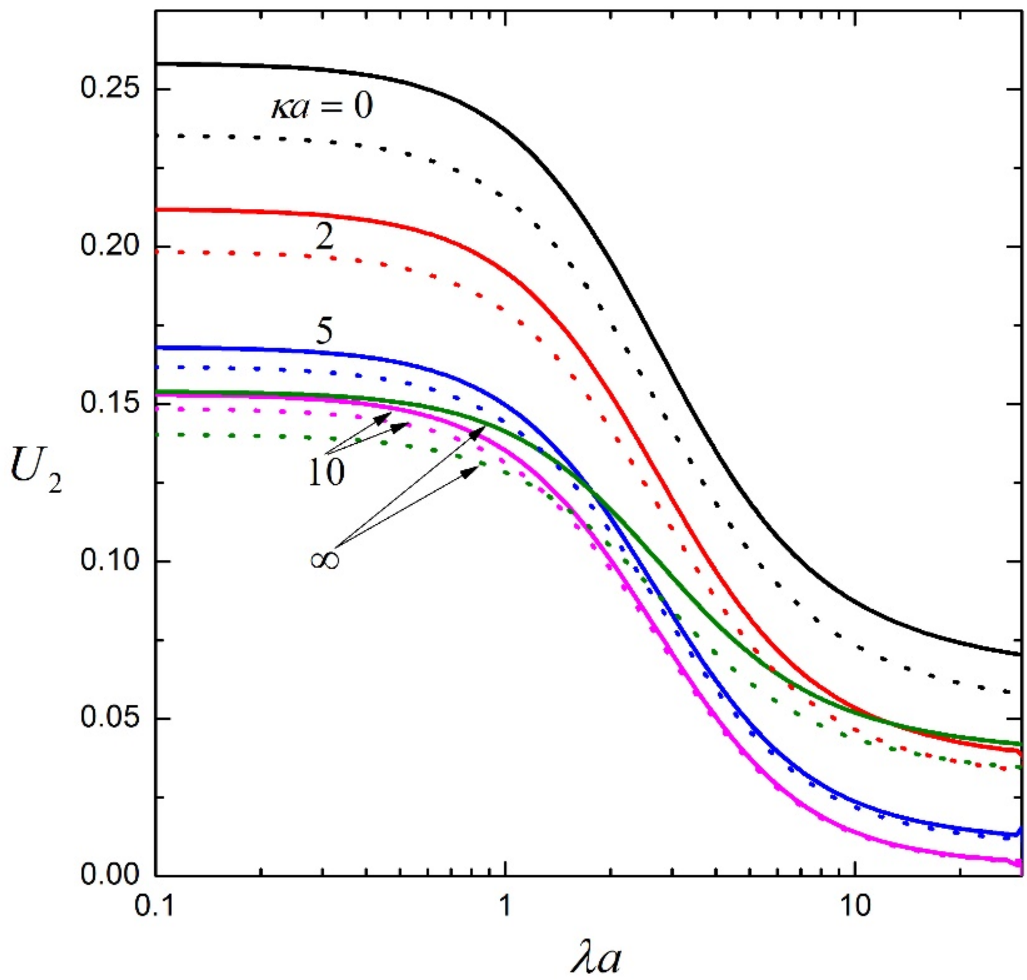

Figure 7(a). Plots of the electrophoretic mobility parameter U_2 for a suspension of soft spheres as calculated from Eq (36) versus the parameter λa for various values of κa at $\varphi = 0.1$ and $r_0 / a = 0.5$. The solid and dashed curves represent the calculations for the Happel and Kuwabara models, respectively.

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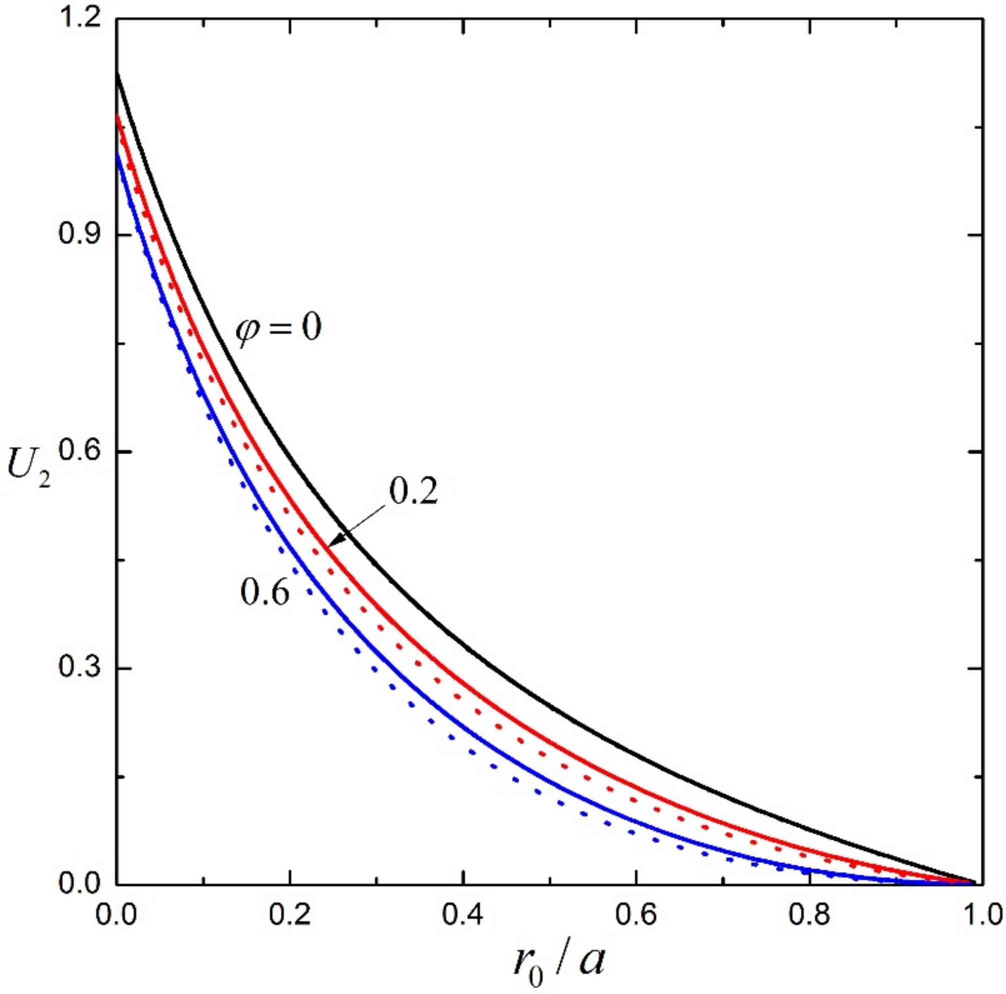

Figure 7(b). Plots of the electrophoretic mobility parameter U_2 for a suspension of soft spheres as calculated from Eq (36) versus the parameter r_0 / a for various values of φ at $\kappa a = 1$ and $\lambda a = 1$. The solid and dashed curves represent the calculations for the Happel and Kuwabara models, respectively.

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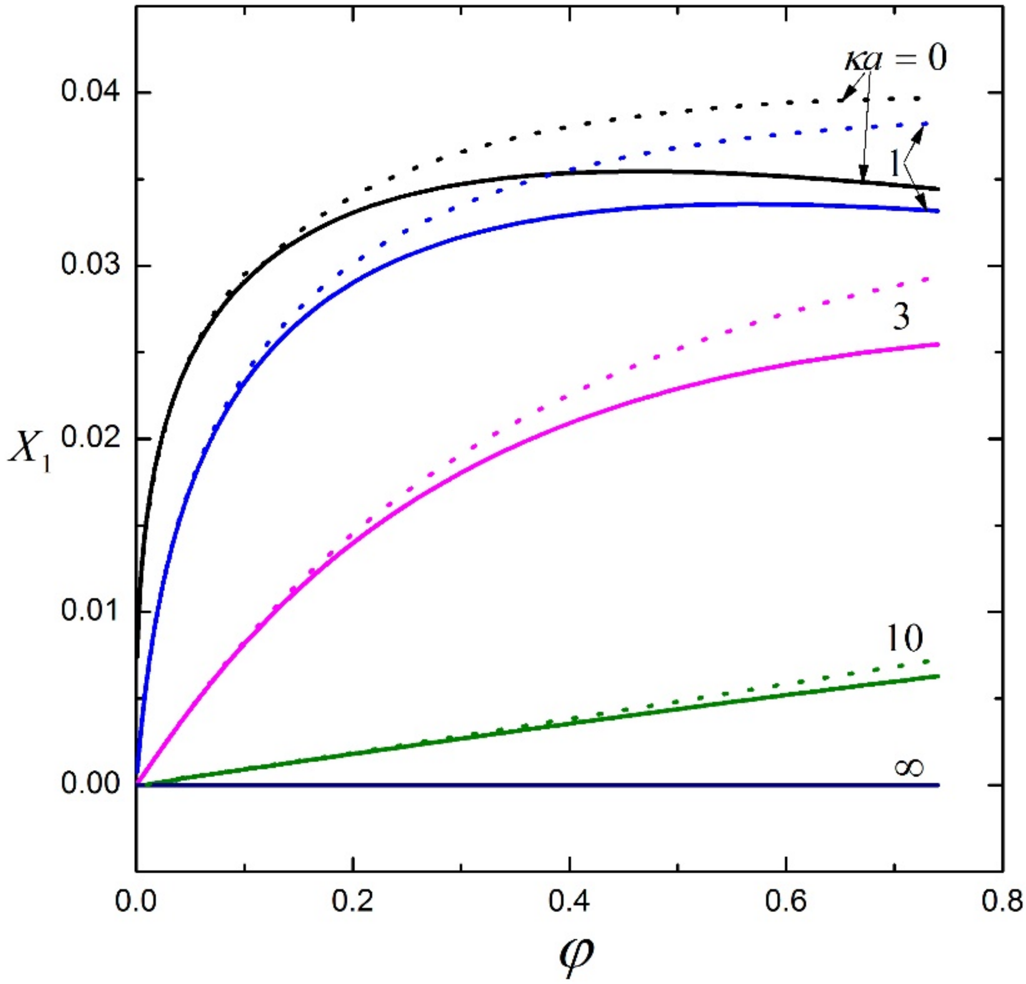

Figure 8(a). Plots of the electric conductivity parameter X_1 for a suspension of soft spheres as calculated from Eq. (40) or (41) versus the parameter φ for various values of κa at $r_0 / a = 0.5$. The solid and dashed curves represent the calculations from using the Dirichlet condition in Eq. (12a) and Neumann condition in Eq. (12b), respectively.

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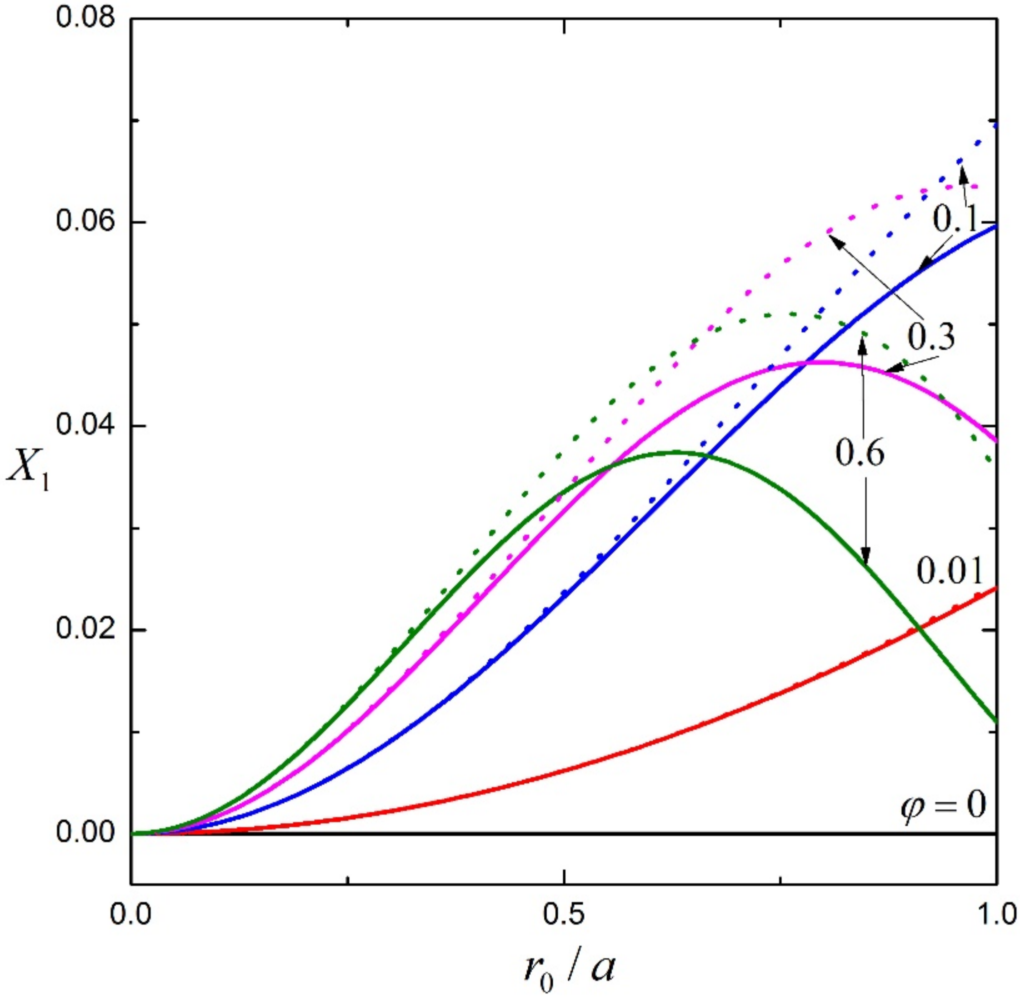

Figure 8(b). Plots of the electric conductivity parameter X_1 for a suspension of soft spheres as calculated from Eq. (40) or (41) versus the parameter r_0 / a for various values of φ at $\kappa a = 1$. The solid and dashed curves represent the calculations from using the Dirichlet condition in Eq. (12a) and Neumann condition in Eq. (12b), respectively.

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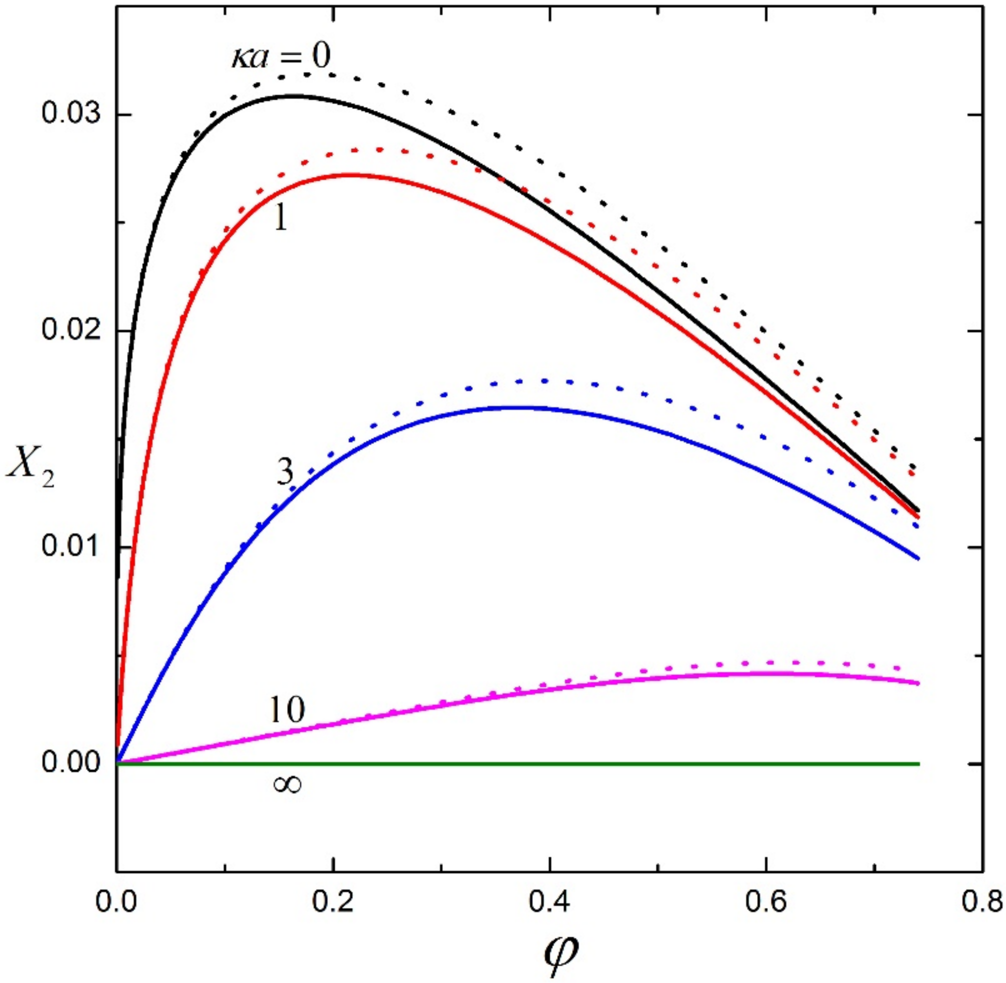

Figure 9(a). Plots of the electric conductivity parameter X_2 for a suspension of soft spheres as calculated from Eq. (40) versus the parameter φ for various values of κa at $r_0/a = 0.5$. The solid and dashed curves represent the calculations from using the Dirichlet condition in Eq. (12a) and Neumann condition in Eq. (12b), respectively.

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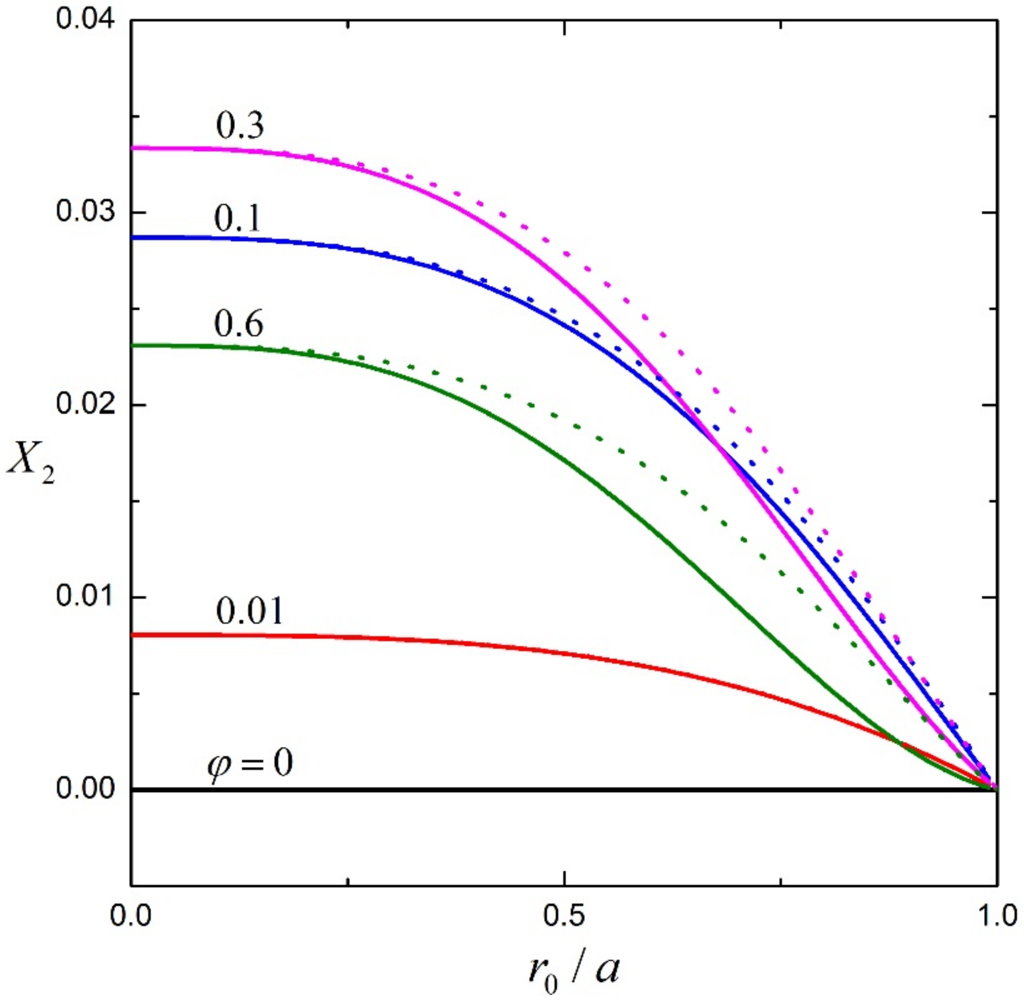

Figure 9(b). Plots of the electric conductivity parameter X_2 for a suspension of soft spheres as calculated from Eq. (40) versus the parameter r_0 / a for various values of φ at $\kappa a = 1$. The solid and dashed curves represent the calculations from using the Dirichlet condition in Eq. (12a) and Neumann condition in Eq. (12b), respectively.

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Chapter 5
Concluding Remarks

Using a unit cell model, we analyze the electrophoresis and electric conduction in a suspension of charged soft particles thoroughly in this thesis. Each soft sphere is a hard core of radius r_0 and surface charge density σ covered with a permeable porous layer of thickness $a-r_0$ in which frictional segments with fixed charge density Q distribute uniformly. The equilibrium electric potential profile outside the hard core in a unit cell and its perturbation caused by the applied electric field are obtained from solving the linearized Poisson-Boltzmann and Laplace equations, respectively. The ionic electrochemical potential energy and fluid flow fields are then obtained by solving the ionic continuity equation and modified Stokes/Brinkman equation, respectively. Through the use of a force balance and a volume-average current density, explicit formulas for the electrophoretic mobility of the soft spheres and effective electric conductivity of the suspension as linear functions of the fixed charge densities σ and Q are obtained in Eqs. (35) and (38) for arbitrary values of the radius ratio r_0/a, electrokinetic radius κa, and shielding parameter λa of the soft spheres as well as the particle volume fraction φ of the suspension. In the limits $r_0 = a$ and $r_0 = 0$, these formulas for a suspension of charged soft spheres reduce to the corresponding formulas of charged hard spheres and

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charged porous spheres, respectively.

Our results indicate that the electrophoretic mobility parameters U_1 and U_2 in Eq. (35) in general decrease with increases in κa, in λa, and in φ. When κa is smaller or λa is greater, the effect of φ on the mobility parameters becomes more substantial. On the other hand, the effects of particle charges on the effective electric conductivity or the parameters X_1 and X_2 in Eq. (38) decrease with an increase in κa from constants at $\kappa a = 0$ to zero as $\kappa a \to \infty$ and increase with an increase in φ from zero at $\varphi = 0$ but may not be monotonic functions (have maxima at some intermediate values of φ). When κa is smaller, the effect of φ on X_1 and X_2 is also more conspicuous. In general, the effects of r_0 / a, κa, λa, and φ on the electrophoretic mobility and effective electric conductivity are interesting, significant, and complicated. These results provide valuable information for interpreting experimental data.

Equations (35) and (38) show that the effects of particle charges on the electrophoretic mobility of the soft particles and effective electric conductivity of the suspension obtained from the unit cell model using the Neumann condition in Eq. (12b) is always greater than their corresponding results obtained from using the Dirichlet condition in Eq. (12a) under otherwise the same circumstances. Also, the Kuwabara cell model predicts a smaller value (a stronger particle concentration effect) for the electrophoretic mobility than the Happel model does, but the difference is insubstantial.

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Lists of Symbols

a	the radius of the soft sphere, m
b	the radius of the unit cell, m
B	defined by Eq. (9)
D_m	diffusion coefficient of the species m, $m^2 \cdot s^{-1}$
e	the elementary electric charge, C
$\mathbf{e}_r$	the unit normal vector outward from the composite sphere surface
$\mathbf{e}_z$	the unit vector in the z-direction
$E_n(x)$	defined by Eq. (42)
E_∞	the magnitude of applied electric field, $V \cdot m^{-1}$
$F_i(r)$	the dimensionless functions of r given by Eq. (19)
$\mathbf{F}_e$	the electric force acting on the soft sphere, N
$\mathbf{F}_h$	the hydrodynamic drag force acting on the soft sphere, N
$h(r)$	unit step function
$I_{ni}(r_1, r_2)$	defined by Eq. (20)
$J_{\alpha i}(r)$	defined by Eq. (31a)
$J_{\beta i}(r)$	defined by Eq. (31b)
$J_{ni}(r)$	defined by Eq. (31c)

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k	Boltzmann's constant, $\mathrm{J \cdot K^{-1}}$
n_m^{∞}	the bulk concentration of species m, $\mathrm{m^{-3}}$
p	the pressure distribution, $\mathrm{N \cdot m^{-2}}$
Q	the volumetric fixed-charge density of the porous layer, $\mathrm{C \cdot m^{-3}}$
r_0	the radius of the rigid core, m
r, θ, ϕ	spherical coordinates
T	the absolute temperature, K
$\mathbf{u}$	the fluid velocity distribution, $\mathrm{m \cdot s^{-1}}$
u_r, u_θ	r and θ components, respectively, of $\mathbf{u}$, $\mathrm{m \cdot s^{-1}}$
U	the electrophoretic velocity of the particle, $\mathrm{m \cdot s^{-1}}$
U_i	the electrophoretic mobility parameters defined by Eq. (35)
X_i	defined by Eq. (40)
z_m	the valence of species m

Greeks

ρ	the space charge density in the fluid phase, $\mathrm{C \cdot m^{-3}}$
ε	the dielectric permittivity of the electrolyte solution, $\mathrm{C^2 \cdot J^{-1} \cdot m^{-1}}$
φ	the particle volume fraction
$\alpha(x)$	defined by Eq. (32a)

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$\beta(x)$	defined by Eq. (32b)
η	the viscosity of the fluid, $\mathrm{kg \cdot m^{-1} \cdot s^{-1}}$
κ	reciprocal of the Debye screening length, $\mathrm{m^{-1}}$
λ	the reciprocal of a constant shielding length featuring the extent of flow penetration inside the porous layer, $\mathrm{m^{-1}}$
μ_m	the electrochemical potential energy distribution of species m, J
ψ	the electric potential distribution, V
ψ_{eq}	the equilibrium electric potential distribution, V
ψ_a	the small perturbation to the equilibrium state of electric potential distribution, V
$\tau_{rr}, \tau_{r\theta}$	the non-vanishing components of the viscous stress of the fluid, $\mathrm{N \cdot m^{-2}}$
γ	defined by Eq. (39)
Λ	the effective electric conductivity of the suspension, $\mathrm{C^2 \cdot m^{-1} \cdot s^{-1} \cdot J^{-1}}$

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Appendix

The constants C_{ni} in Eqs. (29) and (30)

The dimensionless constants C_{ni} in Eqs. (29) and (30) for the fluid flow field are given as follows:

$$C_{1i} = \frac{1}{A_1}\{[U_i - J_{2i}(b)]B_2 - J_{0i}(b)B_1 - J_{3i}(b)B_3 - J_{5i}(b)B_4 - J_{0i}(r_0)B_5 - J_{3i}(r_0)B_6$$

$$- J_{\alpha i}(r_0)B_7 - J_{\beta i}(r_0)B_8\}, \tag{A1}$$

$$C_{2i} = \frac{1}{A_1}\{[U_i - J_{2i}(b)]A_0 - J_{0i}(b)A_2 - J_{3i}(b)A_3 - J_{5i}(b)A_4 - J_{0i}(r_0)A_5 - J_{3i}(r_0)A_6$$

$$- J_{\alpha i}(r_0)A_7 - J_{\beta i}(r_0)A_8\}, \tag{A2}$$

$$C_{3i} = \frac{1}{A_1}\{[U_i - J_{2i}(b)]A_2 - J_{0i}(b)B_9 - J_{3i}(b)B_1 - J_{5i}(b)B_{10} - J_{0i}(r_0)B_{11} - J_{3i}(r_0)B_{12}$$

$$- J_{\alpha i}(r_0)B_{13} - J_{\beta i}(r_0)B_{14}\}, \tag{A3}$$

$$C_{4i} = \frac{1}{A_1}\{[U_i - J_{2i}(b)]A_4 - J_{0i}(b)B_{15} - J_{3i}(b)B_4 - J_{5i}(b)B_{16} - J_{0i}(r_0)B_{17} + J_{3i}(r_0)B_{18}$$

$$- J_{\alpha i}(r_0)B_{19} - J_{\beta i}(r_0)B_{20}\}, \tag{A4}$$

$$C_{5i} = \frac{1}{A_1}\{-[U_i - J_{2i}(b)]A_6 + J_{0i}(b)B_{12} + J_{3i}(b)B_6 - J_{5i}(b)B_{18} - J_{0i}(r_0)B_{21}$$

$$- J_{3i}(r_0)B_{22} - J_{\alpha i}(r_0)B_{23} - J_{\beta i}(r_0)B_{24}\}, \tag{A5}$$

$$C_{6i} = \frac{1}{A_1}\{-[U_i - J_{2i}(b)]A_5 + J_{0i}(b)B_{11} + J_{3i}(b)B_5 + J_{5i}(b)B_{17} - J_{0i}(r_0)B_{25}$$

$$- J_{3i}(r_0)B_{26} - J_{\alpha i}(r_0)B_{27} - J_{\beta i}(r_0)B_{28}\}, \tag{A6}$$

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$$C_{7i}=\frac{1}{A_1}\{-[U_i-J_{2i}(b)]A_7+J_{0i}(b)B_{13}+J_{3i}(b)B_7-J_{5i}(b)B_{29}-J_{0i}(r_0)B_{30}$$

$$-J_{3i}(r_0)B_{31}-J_{\alpha i}(r_0)B_{32}-J_{\beta i}(r_0)B_{33}\}, \quad \text{(A7)}$$

$$C_{8i}=\frac{1}{A_1}\{-[U_i-J_{2i}(b)]A_8+J_{0i}(b)B_{14}+J_{3i}(b)B_8-J_{5i}(b)B_{34}-J_{0i}(r_0)B_{35}$$

$$-J_{3i}(r_0)B_{36}-J_{\alpha i}(r_0)B_{37}-J_{\beta i}(r_0)B_{38}\}, \quad \text{(A8)}$$

where

$$A_0=\frac{1}{a^4}\{-120a^6r_0\lambda^3+\lambda[270a^3r_0(a-r_0)+a\lambda^4(2a^5+3b^5)(2a^3+r_0^3)+3\lambda^2(20a^7$$

$$+r_0(2a^6+3ab^5-3(4a^5+b^5)r_0+30a^4r_0^2))]\cosh(\lambda(a-r_0))-3[90a^3r_0$$

$$+\lambda^4(2a^3(4a^5+b^5)+r_0^2(-2a^6-3ab^5+r_0(4a^5+b^5)))+\lambda^2(20a^6$$

$$+3r_0(4a^5+b^5+10a^3r_0(r_0-3a)))]\sinh(\lambda a-\lambda r_0)\} \quad \text{(A9)}$$

$$A_1=\frac{1}{a^3b}\{-12r_0\lambda(30a^3b-10a^6\lambda^2+9a^5b\lambda^2+b^6\lambda^2)-\lambda[\lambda^4(a-b)^3(a+b)(2a^2$$

$$+ab+2b^2)(2a^3+r_0^3)-90a^3(2ab+r_0(-3a+2b+3r_0))+3\lambda^2(20a^7-28a^6b-2ab^6+r_0(2a^6$$

$$-3a^5b+3ab^5-2b^6-3(4a^5-5a^4b+b^5)r_0+10a^3(3a-2b)r_0^2))]\cosh(\lambda a-\lambda r_0)$$

$$+3[30a^3(3r_0-2b)+\lambda^4(2a^3(4a^5-5a^4b+b^5)+r_0^2(-2a^6+3a^5b-3ab^5$$

$$+2b^6+r_0(4a^5-5a^4b+b^5)))+\lambda^2(20a^6-48a^5b-2b^6+3r_0(4a^5-5a^4b+b^5$$

$$+10a^3r_0(-3a+2b+r_0)))]\sinh(\lambda a-\lambda r_0))\} \quad \text{(A10)}$$

$$A_2=\frac{b^5\lambda^2}{a^4}\{6ar_0\lambda-\lambda[3(4a-3r_0)(a+r_0)+a\lambda^2(2a^3+r_0^3)]\cosh(\lambda a-\lambda r_0)+3[4a+3r_0$$

$$+\lambda^2(2a^3-ar_0^2+r_0^3)]\sinh(\lambda a-\lambda r_0)\} \quad \text{(A11)}$$

$$A_3=\frac{1}{a^3b}\{120a^6r_0\lambda^3-\lambda[270a^3r_0(a-r_0)+a\lambda^4(2a^5+3b^5)(2a^3+r_0^3)+3\lambda^2(20a^7$$

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$$+r_0(2a^6+3ab^5-3(4a^5+b^5)r_0+30a^4r_0^2))]\cosh(\lambda a-\lambda r_0)+3[90a^3r_0+\lambda^4(2a^3(4a^5$$

$$+b^5)-r_0^2(2a^6+3ab^5-r_0(4a^5+b^5)))+\lambda^2(20a^6+3r_0(4a^5+b^5-10a^3r_0(3a$$

$$-r_0)))]\sinh(\lambda a-\lambda r_0)\} \quad \text{(A12)}$$

$$A_4=\lambda^2 a\{-6ar_0\lambda+\lambda[3(4a-3r_0)(a+r_0)+a\lambda^2(2a^3+r_0^3)]\cosh(\lambda a-\lambda r_0)-3[4a+3r_0+\lambda^2(2a^3$$

$$-ar_0^2+r_0^3)]\sinh(\lambda a-\lambda r_0)\} \quad \text{(A13)}$$

$$A_5=\frac{6r_0}{a^6\lambda^2}\{2a^3\lambda^5(a^5-b^5)-\lambda[90a^3(a-r_0)+ar_0^2\lambda^4(4a^5+b^5)+3\lambda^2(a-r_0)(4a^5+b^5$$

$$-10a^4r_0)]\cosh(\lambda a-\lambda r_0)+[90a^3+r_0\lambda^4(-3a(4a^5+b^5)+r_0(14a^5+b^5))+3\lambda^2(14a^5$$

$$+b^5+10a^3r_0(r_0-3a))]\sinh(\lambda a-\lambda r_0)\} \quad \text{(A14)}$$

$$A_6=\frac{6}{a^3r_0}\{[(a^5-b^5)\lambda^3-30a^3\lambda]+[30a^4\lambda+(4a^5+b^5)a\lambda^3]\cosh(\lambda a-\lambda r_0)-[30a^3+(14a^5$$

$$+b^5)\lambda^2]\sinh(\lambda a-\lambda r_0)\} \quad \text{(A15)}$$

$$A_7=\frac{1}{a^6\lambda^2}\{[-18r_0(30a^3+\lambda^2(14a^5+b^5))]\cosh(\lambda a)+[12a^3(b^5-a^5)\lambda^4+6r_0(30a^3-(a^5$$

$$-b^5)\lambda^2)(3+\lambda^2r_0^2)]\cosh(\lambda r_0)+18ar_0\lambda[(30a^3+(4a^5+b^5)\lambda^2)]\sinh(\lambda a)+18r_0^2\lambda[-30a^3$$

$$+(a^5-b^5)\lambda^2]\sinh(\lambda r_0)\} \quad \text{(A16)}$$

$$A_8=\frac{6}{a^6\lambda^2}\{[3r_0^2\lambda(30a^3-\lambda^2(a^5-b^5))]\cosh(\lambda r_0)-3ar_0\lambda[(30a^3+(4a^5+b^5)\lambda^2)]\cosh(\lambda a)$$

$$+[2a^3(a^5-b^5)\lambda^4+(r_0\lambda^2(a^5-b^5)-30a^3)(3+\lambda^2r_0^2)]\sinh(\lambda r_0)+3r_0[30a^3+(14a^5$$

$$+b^5)\lambda^2]\sinh(\lambda a)\} \quad \text{(A17)}$$

$$B_1=\frac{b^4\lambda^2}{a^3}\{-6ar_0\lambda+\lambda[3(4a-3r_0)(a+r_0)+a(2a^3+r_0^{\,3})\lambda^2]\cosh(\lambda a-\lambda r_0)-[3(4a+3r_0$$

$$+(2a^3-ar_0^{\,2}+r_0^{\,3})\lambda^2)]\sinh(\lambda a-\lambda r_0)\} \quad \text{(A18)}$$

$$B_2=\frac{1}{a^3}\{12r_0\lambda[30a^3+(9a^5+b^5)\lambda^2]-\lambda[180a^3(a+r_0)+3(28a^6+2ab^5+3a^5r_0+2b^5r_0$$

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$$-15a^4r_0{}^2+20a^3r_0{}^3)\lambda^2+(3a^5+2b^5)(2a^3+r_0{}^3)\lambda^4]\cosh(\lambda a-\lambda r_0)+3[60a^3+(48a^5$$

$$+2b^5+15a^4r_0-60a^3r_0{}^2)\lambda^2+(10a^7-(3a^5+2b^5)r_0{}^2+5a^4r_0{}^3)\lambda^4]\sinh(\lambda a-\lambda r_0)\} \quad \text{(A19)}$$

$$B_3=\frac{1}{a^2b}\{-12r_0\lambda(30a^3+(9a^5+b^5)\lambda^2)+\lambda[180a^3(a+r_0)+3(28a^6+2ab^5+3a^5r_0+2b^5r_0-15a^4r_0{}^2$$

$$+20a^3r_0{}^3)\ \lambda^2+(3a^5+2b^5)(2a^3+r_0{}^3)\lambda^4]\cosh(\lambda a-\lambda r_0)-3[60a^3+\lambda^2(48a^5+2b^5$$

$$+15a^4r_0-60a^3r_0{}^2)+\lambda^4(10a^7-(3a^5+2b^5)r_0{}^2+5a^4r_0{}^3)]\sinh(\lambda a-\lambda r_0)\} \quad \text{(A20)}$$

$$B_4=\frac{a^2\lambda^2}{b}\{6ar_0\lambda-\lambda[3(4a-3r_0)(a+r_0)+a\lambda^2(2a^3+r_0{}^3)]\cosh(\lambda a-\lambda r_0)+3[4a+3r_0+\lambda^2(2a^3$$

$$-ar_0{}^2+r_0{}^3)]\sinh(\lambda a-\lambda r_0)\} \quad \text{(A21)}$$

$$B_5=\frac{6r_0}{a^5b\lambda^2}\{2a^3\lambda^5(b^5-a^5)+\lambda[90a^3(a-r_0)+3\lambda^2(a-r_0)(4a^5+b^5-10a^4r_0)+ar_0{}^2\lambda^4(4a^5$$

$$+b^5)]\cosh(\lambda a-\lambda r_0)-[90a^3+3\lambda^2(b^5+2a^3(7a^2-15ar_0+5r_0{}^2))+r_0\lambda^4(3a(b^5-4a^5)$$

$$+r_0(14a^5+b^5))]\sinh(\lambda a-\lambda r_0)\} \quad \text{(A22)}$$

$$B_6=\frac{6}{a^2b}\{r_0\lambda(30a^3-a^5\lambda^2+b^5\lambda^2)-a\lambda[30a^3+(4a^5+b^5)\lambda^2]\cosh(\lambda a-\lambda r_0)+[30a^3+\lambda^2(14a^5$$

$$+b^5)]\sinh(\lambda a-\lambda r_0)\} \quad \text{(A23)}$$

$$B_7=\frac{6}{a^5b\lambda^2}\{3r_0[30a^3+\lambda^2(14a^5+b^5)]\cosh(\lambda a)-[90a^3r_0+3r_0\lambda^2(10a^3r_0{}^2-a^5+b^5)-(a^5-b^5)(2a^3$$

$$+r_0{}^3)\lambda^4]\cosh(\lambda r_0)+[-3ar_0\lambda(30a^3+(4a^5+b^5)\lambda^2]\sinh(\lambda a)+3r_0{}^2\lambda[30a^3-a^5\lambda^2$$

$$+b^5\lambda^2]\sinh(\lambda r_0))\} \quad \text{(A24)}$$

$$B_8=\frac{1}{a^5b\lambda^2}\{[18ar_0\lambda(30a^3+(4a^5+b^5)\lambda^2)]\cosh(\lambda a)+18r_0{}^2\lambda[(a^5-b^5)\lambda^2$$

$$-30a^3]\cosh(\lambda r_0)-18r_0[30a^3+(14a^5+b^5)\lambda^2]\sinh(\lambda a)-6[-90a^3r_0-3r_0(10a^3r_0{}^2-a^5+b^5)\lambda^2$$

$$+\lambda^4(a^5-b^5)(2a^3+r_0{}^3)]\sinh(\lambda r_0)\} \quad \text{(A25)}$$

$$B_9=\frac{-b^4}{5a^5}\{12\lambda(30b+a^2r_0\lambda^2(-10a+9b))+\lambda[-90(2ab-3ar_0+2br_0+3r_0^2)+a^2\lambda^4(2a-3b)(2a^3$$

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$$+r_0^3)+3\lambda^2(20a^4-20br_0^3+2a^3(r_0-14b)+15ar_0^2(b+2r_0)-3a^2r_0(b+4r_0))]\cosh(\lambda a-\lambda r_0)$$

$$+3[60b-90r_0+a\lambda^4(2a^3(5b-4a)+ar_0^2(2a-3b)+r_0^3(5b-4a))+\lambda^2(12a^2(4b-r_0)-30r_0^2(2b+r_0)$$

$$+15ar_0(b+6r_0)-20a^3)]\sinh(\lambda a-\lambda r_0)\} \quad \text{(A26)}$$

$$B_{10}=\frac{-1}{5b}\{12\lambda(-30b+a^2r_0(10a-9b)\lambda^2)+\lambda[90(2ab-3ar_0+2br_0+3r_0^2)-a^2\lambda^4(2a$$

$$-3b)(2a^3+r_0^3)+3\lambda^2(a^3(28b-2r_0)-20a^4+20br_0^3-15ar_0^2(b+2r_0)+3a^2r_0(b+4r_0))]\cosh(\lambda a-\lambda r_0)$$

$$+3[90r_0-60b+a\lambda^4(2a^3(4a-5b)+ar_0^2(3b-2a)+r_0^3(4a-5b))+\lambda^2(20a^3+12a^2(r_0-4b)+30r_0^2(2b+r_0)$$

$$-15ar_0(b+6r_0))]\sinh(\lambda a-\lambda r_0)\} \quad \text{(A27)}$$

$$B_{11}=\frac{-6b^4r_0}{a^6}\{2a^3\lambda^3(a-b)-6ab\lambda+\lambda[a(b-2a)\lambda^2r_0^2+3(br_0-2a^2+a(b$$

$$+2r_0))]\cosh(\lambda a-\lambda r_0)+[6a+3b+r_0\lambda^2(3ab+2ar_0+br_0-6a^2)]\sinh(\lambda a-\lambda r_0)\} \quad \text{(A28)}$$

$$B_{12}=\frac{6b^4\lambda^2}{a^3}\{r_0\lambda(b-a)+a\lambda(b-2a)\cosh(\lambda a-\lambda r_0)+(2a+b)\sinh(\lambda a-\lambda r_0)\} \quad \text{(A29)}$$

$$B_{13}=\frac{6b^4}{a^6}\{[3ar_0-6ab-3br_0+\lambda^2(a-b)(2a^3+r_0^3)]\cosh(\lambda r_0)+[3r_0(2a+b)]\cosh(\lambda a)$$

$$+[3r_0{}^2\lambda(b-a)]\sinh(\lambda r_0)+[3ar_0\lambda(b-2a)]\sinh(\lambda a)\} \quad \text{(A30)}$$

$$B_{14}=\frac{-6b^4}{a^6}\{[3r_0{}^2\lambda(b-a)]\cosh(\lambda r_0)+[3ar_0\lambda(b-2a)]\cosh(\lambda a)+[3a(-2b+r_0)-3br_0$$

$$+(a-b)\ \lambda^2(2a^3+r_0^3)]\sinh(\lambda r_0)+[3r_0(2a+b)]\sinh(\lambda a) \quad \text{(A31)}$$

$$B_{15}=\frac{-\lambda^2}{5a^3b}\{12b^6r_0\lambda+\lambda[9ar_0-6ab-6br_0-9r_0^2+(3a-2b)\lambda^2(2a^3+r_0^3)]\cosh(\lambda a-\lambda r_0)$$

$$-3b^5[3r_0-2b+\lambda^2(2a^3-3ar_0^2+2br_0^2+r_0^3)]\sinh(\lambda a-\lambda r_0)\} \quad \text{(A32)}$$

$$B_{16}=\frac{-a^2\lambda^2}{5b}\{-12br_0\lambda+\lambda[6ab-9ar_0+6br_0+9r_0^2-(3a-2b)\lambda^2(2a^3+r_0^3)]\cosh(\lambda a-\lambda r_0)$$

$$+3[3r_0-2b+\lambda^2(2a^3-3ar_0^2+2br_0^2+r_0^3)]\sinh(\lambda a-\lambda r_0)\} \quad \text{(A33)}$$

$$B_{17}=\frac{6r_0}{ab}\{2a^3(a-b)\lambda^3-6ab\lambda+\lambda[ar_0^2\lambda^2(b-2a)+3(br_0-2a^2+a(b$$

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$$+2r_0))]\cosh(\lambda a-\lambda r_0)+[6a+3b+r_0\lambda^2(3ab-6a^2+2ar_0+br_0)]\sinh(\lambda a-\lambda r_0)\} \quad \text{(A34)}$$

$$B_{18}=\frac{6a^2\lambda^2}{b}\{r_0\lambda(a-b)+[a\lambda(2a-b)]\cosh(\lambda a-\lambda r_0)-(2a+b)\sinh(\lambda a-\lambda r_0)\} \quad \text{(A35)}$$

$$B_{19}=\frac{-6}{ab}\{[3ar_0-6ab-3br_0+\lambda^2(a-b)(2a^3+r_0^3)]\cosh(\lambda r_0)+[3r_0(2a+b)]\cosh(\lambda a)$$

$$+3\lambda r_0^{\ 2}(b-a)\sinh(\lambda r_0)+3ar_0\lambda(b-2a)\sinh(\lambda a)\} \quad \text{(A36)}$$

$$B_{20}=\frac{6}{ab}\{3r_0^{\ 2}\lambda(b-a)\cosh(\lambda r_0)+[3ar_0\lambda(b-2a)]\cosh(\lambda a)+[3a(r_0-2b)-3br_0$$

$$+\lambda^2(a-b)(2a^3+r_0^3)]\sinh(\lambda r_0)+[3r_0(2a+b)]\sinh(\lambda a)\} \quad \text{(A37)}$$

$$B_{21}=\frac{2r_0}{a^5b\lambda^2}\{180a^3b\lambda+6\lambda^3(9a^5b-10a^6+b^6)+\lambda[90a^3(3a-2b-3r_0)+(2a^6-3a^5b+3ab^5$$

$$-2b^6)\lambda^4r_0^2+3\lambda^2(2a^6+3ab^5-20a^3br_0^2+15a^4r_0(b+2r_0)-b^5(2b+3r_0)-3a^5(b$$

$$+4r_0))]\cosh(\lambda a-\lambda r_0)-3[90a^3+r_0\lambda^4(-2a^6-3ab^5-5a^4br_0+b^5(2b+r_0)+a^5(3b+4r_0))+3\lambda^2(4a^5$$

$$+b^5+10a^3r_0(2b+r_0)-5a^4(b+6r_0))]\sinh(\lambda a-\lambda r_0)\} \quad \text{(A38)}$$

$$B_{22}=\frac{-2}{a^2b}\{\lambda[30a^3(3a-2b)+(2a^6-3a^5b+3ab^5-2b^6)\lambda^2]\cosh(\lambda a-\lambda r_0)$$

$$-3[30a^3+4a^5\lambda^2-5a^4b\lambda^2+b^5\lambda^2]\sinh(\lambda a-\lambda r_0)\} \quad \text{(A39)}$$

$$B_{23}=\frac{-6}{a^5b\lambda^2}\{2[30a^3b-10a^6\lambda^2+9a^5b\lambda^2+b^6\lambda^2]\cosh(\lambda r_0)-3r_0[30a^3+4a^5\lambda^2-5a^4b\lambda^2$$

$$+b^5\lambda^2]\cosh(\lambda a)+r_0\lambda[30a^3(3a-2b)+(2a^6-3a^5b+3ab^5-2b^6)\lambda^2]\sinh(\lambda a)\} \quad \text{(A40)}$$

$$B_{24}=\frac{6}{a^5b\lambda^2}\{(r_0\lambda(30a^3(3a-2b)+(2a^6-3a^5b+3ab^5-2b^6)\ \lambda^2)\cosh(\lambda a)$$

$$-3r_0(30a^3+4a^5\lambda^2-5a^4b\lambda^2+b^5\lambda^2)\sinh(\lambda a)+2(30a^3b-10a^6\lambda^2+9a^5b\lambda^2$$

$$+b^6\lambda^2)\sinh(\lambda r_0)\} \quad \text{(A41)}$$

$$B_{25}=\frac{-4r_0}{a^8b\lambda^4}[\lambda(270a^3b(a-r_0)-9(a-r_0)(10a^6-14a^5b-b^6+10a^4br_0)\lambda^2+3a(-2a^8-3a^3b^5$$

$$+14a^5br_0^{\ 2}+b^6r_0^{\ 2}-5a^6r_0(3b+2r_0)+a^2b^5(2b+3r_0)+3a^7(b+4r_0))\lambda^4+a^3(-2a^6+3a^5b-3ab^5$$

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$$+2b^6)r_0^{\,2}\lambda^6)\cosh(\lambda a-\lambda r_0)-3(90a^3b+3(-10a^6+24a^5b+b^6-30a^4br_0+10a^3br_0^{\,2})\lambda^2+(-12a^8-3a^3b^5$$

$$-3ab^6r_0+24a^5br_0^{\,2}+b^6r_0^{\,2}+15a^7(b+2r_0)-2a^6r_0(21b+5r_0))\lambda^4+a^3r_0(2a^6+3ab^5+5a^4br_0$$

$$-b^5(2b+r_0)-a^5(3b+4r_0))\lambda^6)\sinh(\lambda a-\lambda r_0)] \qquad \text{(A42)}$$

$$B_{26}=\frac{-4}{a^5b\lambda^2}[90a^3br_0\lambda+3(-10a^6+9a^5b+b^6)r_0\lambda^3+a\lambda(-90a^3b+3(10a^6-14a^5b-b^6)\lambda^2$$

$$+a^2(2a^6-3a^5b+3ab^5-2b^6)\lambda^4)\cosh(\lambda a-\lambda r_0)+3(-10a^6\lambda^2+24a^5b\lambda^2+b^6\lambda^2-4a^8\lambda^4$$

$$+5a^7b\lambda^4+a^3b(30-b^4\lambda^4))\sinh(\lambda a-\lambda r_0)] \qquad \text{(A43)}$$

$$B_{27}=\frac{12\,r_0}{a^8b\lambda^4}\{3\,[10\,a^6\lambda^2-24\,a^5b\lambda^2-b^6\lambda^2+4a^8\lambda^4-5a^7b\lambda^4+a^3b(b^4\lambda^4-30)]\cosh(\lambda a)$$

$$+\lambda a[90a^3b-3\lambda^2(10a^6-14a^5b-b^6)-\lambda^4a^2(2a^6-3a^5b+3ab^5-2b^6)]\sinh(\lambda a)$$

$$+[30a^3b-\lambda^2(10a^6-9a^5b-b^6)][(3+\lambda^2r_0^{\,2})\cosh(\lambda r_0)-3\lambda r_0\sinh(\lambda r_0)]\} \qquad \text{(A44)}$$

$$B_{28}=\frac{-12\,r_0}{a^8b\lambda^4}\{[90\,a^4b\lambda-3\lambda^3a(10\,a^6-14\,a^5b-b^6)-\lambda^5a^3(2a^6-3a^5b+3ab^5-2b^6)]\cosh(\lambda a)$$

$$+3\,[10a^6\lambda^2-24\,a^5b\lambda^2-b^6\lambda^2+4a^8\lambda^4-5a^7b\lambda^4-a^3b(30-b^4\lambda^4)]\sinh(\lambda a)+[30a^3b$$

$$-(10a^6-9a^5b-b^6)\lambda^2]\,[-3\lambda r_0\cosh(\lambda r_0)+(3+r_0^{\,2}\lambda^2)\sinh(\lambda r_0)]\} \qquad \text{(A45)}$$

$$B_{29}=\frac{6}{ab}\{3(2a+b)r_0\cosh(\lambda a)-[6ab-3ar_0+3br_0-(a-b)(2a^3+r_0^{\,3})\lambda^2]\cosh(\lambda r_0)$$

$$-3\,r_0\lambda[a(2a-b)\sinh(\lambda a)+(a-b)r_0\sinh(\lambda r_0)]\} \qquad \text{(A46)}$$

$$B_{30}=\frac{12\,r_0}{a^8b\lambda^4}\{3[10a^6\lambda^2-24a^5b\lambda^2-b^6\lambda^2+4a^8\lambda^4-5a^7b\lambda^4+a^3b(-30+b^4\lambda^4)]\cosh(\lambda a)$$

$$+\lambda a[90a^3b-3(10a^6-14a^5b-b^6)\lambda^2-a^2(2a^6-3a^5b+3ab^5-2b^6)\lambda^4]\sinh(\lambda a)$$

$$+[30a^3b-(10a^6-9a^5b-b^6)\lambda^2]\,[(3+r_0^{\,2}\lambda^2)\cosh(\lambda r_0)-3r_0\lambda\sinh(\lambda r_0)]\} \qquad \text{(A47)}$$

$$B_{31}=\frac{-6}{a^5b\lambda^2}\{-3r_0(30a^3+4a^5\lambda^2-5a^4b\lambda^2+b^5\lambda^2)\cosh(\lambda a)+2(30a^3b-10a^6\lambda^2+9a^5b\lambda^2$$

$$+b^6\lambda^2)\cosh(\lambda r_0)+r_0\lambda[30a^3(3a-2b)+(2a^6-3a^5b+3ab^5-2b^6)\lambda^2]\sinh(\lambda a)\} \qquad \text{(A48)}$$

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$$B_{32}=\frac{-6}{a^8b\lambda^5}\{\cosh(\lambda r_0)[3(30a^3(-2b+3r_0)+(20a^6-15a^4br_0+30a^3r_0{}^3-12a^5(4b-r_0)$$

$$-b^5(2b-3\,r_0))\lambda^2+(a-b)^2(4a^3+3a^2b+2ab^2+b^3)(2a^3+r_0{}^3)\lambda^4)\cosh(\lambda a)$$

$$+\lambda(90a^3(2ab-3ar_0+2br_0)+3\,(-20a^7+ab^5(2b-3r_0)+2a^6(14b-r_0)+3a^5br_0+2b^6r_0$$

$$-30a^4r_0{}^3+20a^3br_0{}^3)\lambda^2-(a-b)^3(a+b)(2a^2+ab+2b^2)(2a^3+\,r_0{}^3)\lambda^4)\sinh(\lambda a)]$$

$$+3r_0{}^2\lambda[-3(30a^3+4a^5\lambda^2-5a^4b\lambda^2+b^5\lambda^2)\cosh(\lambda a)+\lambda(30a^3(3a-2b)+(2a^6-3a^5b$$

$$+3ab^5-2b^6)\lambda^2)\sinh(\lambda a)]\sinh(\lambda r_0)\} \qquad \text{(A49)}$$

$$B_{33}=\frac{-6}{a^8b\lambda^5}\{6\,r_0\lambda[-30a^3b+(10a^6-9a^5b-b^6)\lambda^2]\;+\;3r_0{}^2\lambda\cosh(\lambda r_0)[3(30a^3+4a^5\lambda^2-5a^4b\lambda^2$$

$$+b^5\lambda^2)\cosh(\lambda a)+\lambda(-90a^4+60a^3b-2a^6\lambda^2+3a^5b\lambda^2-3ab^5\lambda^2+2b^6\lambda^2)\sinh(\lambda a)]$$

$$+[-3(30a^3(-2b+3r_0)+(20a^6-15a^4br_0+30a^3r_0{}^3+12a^5(-4b+r_0)+b^5(-2b+3r_0))\lambda^2$$

$$+(a-b)^2(4a^3+3a^2b+2ab^2+b^3)\;(2a^3+r_0{}^3)\lambda^4)\cosh(\lambda a)+\lambda(-90a^3(2ab-3ar_0+2br_0)$$

$$+3(20a^7-3a^5br_0-2b^6r_0+30a^4r_0{}^3-20\,a^3br_0{}^3+2a^6(-14\,b+r_0)+ab^5(-2b+3r_0))\lambda^2$$

$$+(a-b)^3(a+b)(2a^2+ab+2b^2)(2a^3+r_0{}^3)\lambda^4)\sinh(\lambda a)]\sinh(\lambda r_0)\} \qquad \text{(A50)}$$

$$B_{34}=\frac{-6}{ab}\{3r_0[a(-2a+b)\lambda\cosh(\lambda a)-(a-b)r_0\lambda\cosh(\lambda r_0)+(2a+b)\sinh(\lambda a)]$$

$$+[-3br_0-3a(2b-r_0)+(a-b)(2a^3+r_0{}^3)\lambda^2]\sinh(\lambda r_0)\} \qquad \text{(A51)}$$

$$B_{35}=\frac{-12\,r_0}{a^8b\lambda^4}\;\{[90a^4b\lambda-3a(10a^6-14a^5b-b^6)\lambda^3-a^3(2a^6-3a^5b+3ab^5-2b^6)\lambda^5]\cosh(\lambda a)$$

$$+3\,[10a^6\lambda^2-24a^5b\lambda^2-b^6\lambda^2+4\,a^8\lambda^4-5\,a^7b\lambda^4+a^3b(-30+b^4\lambda^4)]\sinh(\lambda a)+[30a^3b$$

$$-(10a^6-9a^5b-b^6)\lambda^2]\,[-3r_0\lambda\cosh(\lambda r_0)+(3+r_0{}^2\lambda^2)\sinh(\lambda r_0)]\} \qquad \text{(A52)}$$

$$B_{36}=\frac{6}{a^5b\lambda^2}\{r_0\lambda[30a^3(3a-2b)+(2a^6-3a^5b+3ab^5-2b^6)\lambda^2]\cosh(\lambda a)-3\,r_0(30a^3\;+4a^5\lambda^2$$

$$-5a^4b\lambda^2+b^5\lambda^2)\sinh(\lambda a)+2(30a^3b-10a^6\lambda^2+9a^5b\lambda^2+b^6\lambda^2)\sinh(\lambda r_0)\} \qquad \text{(A53)}$$

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$$B_{37}=\frac{-6}{a^8b\lambda^5}\{-3[30a^3(-2b+3r_0)+(20a^6-15a^4br_0+30a^3r_0{}^3-12a^5(4b-r_0)-b^5(2b-3r_0))\lambda^2$$

$$+(a-b)^2(4a^3+3a^2b+2ab^2+b^3)(2a^3+r_0{}^3)\lambda^4]\cosh(\lambda r_0)\sinh(\lambda a)+\lambda\cosh(\lambda a)[(-90a^3(2ab$$

$$-3ar_0+2br_0)+3(20a^7-3a^5br_0-2b^6r_0+30a^4r_0{}^3-20a^3br_0{}^3-2a^6(14b-r_0)-ab^5(2b-3r_0))\lambda^2$$

$$+(a-b)^3(a+b)(2a^2+ab+2b^2)(2a^3+r_0{}^3)\lambda^4)\cosh(\lambda r_0)+3r_0{}^2\lambda(-90a^4+60a^3b-2a^6\lambda^2$$

$$+3a^5b\lambda^2-3ab^5\lambda^2+2b^6\lambda^2)\sinh(\lambda r_0)]+3r_0\lambda[60a^3b+2(-10a^6+9a^5b+b^6)\lambda^2+3r_0(30a^3$$

$$+4a^5\lambda^2-5a^4b\lambda^2+b^5\lambda^2)\sinh(\lambda a)\sinh(\lambda r_0)]\} \qquad \text{(A54)}$$

$$B_{38}=\frac{-6}{a^8b\lambda^5}\{3r_0{}^2\lambda\cosh(\lambda r_0)[\lambda(30a^3(3a-2b)+(2a^6-3a^5b+3ab^5-2b^6)\lambda^2)\cosh(\lambda a)$$

$$-3(30a^3+4a^5\lambda^2-5a^4b\lambda^2+b^5\lambda^2)\sinh(\lambda a)]+[\lambda(90a^3(2ab-3ar_0+2br_0)+3(-20a^7$$

$$+ab^5(2b-3r_0)+a^6(28b-2r_0)+3a^5br_0+2b^6r_0-30a^4r_0{}^3+20a^3br_0{}^3)\lambda^2-(a-b)^3(a$$

$$+b)(2a^2+ab+2b^2)(2a^3+r_0{}^3)\lambda^4)\cosh(\lambda a)+3(30a^3(-2b+3r_0)+(20a^6-15a^4br_0$$

$$+30a^3r_0{}^3-12a^5(4b-r_0)-b^5(2b-3r_0))\lambda^2+(a-b)^2(4a^3+3a^2b+2ab^2+b^3)(2a^3$$

$$+r_0{}^3)\lambda^4)\sinh(\lambda a)]\sinh(\lambda r_0)\} \qquad \text{(A55)}$$

for the Happel model;

$$A_0=\frac{1}{a}\{\lambda[3(a-r_0)r_0+a(2a^3+r_0{}^3)\lambda^2]\cosh(\lambda a-\lambda r_0)-[3r_0+(2a^3-3ar_0{}^2$$

$$+r_0{}^3)\lambda^2]\sinh(\lambda a-\lambda r_0)\} \qquad \text{(A56)}$$

$$A_1=\frac{-2}{15b^6\lambda^2}\{30(-2a^6+a^3b^3+b^6)r_0\lambda^3+\lambda[135a^3(a-r_0)r_0+3(10a^7+a^6r_0-5a^3b^3r_0-6a^5r_0{}^2$$

$$+15a^2b^3r_0{}^2-ab^5(5b-9r_0)-b^5r_0(5b+9r_0)+5a^4(-4b^3+3r_0{}^3))\lambda^2+(a-b)^3(a^3+3a^2b$$

$$+6ab^2+5b^3)(2a^3+r_0{}^3)\lambda^4]\cosh(\lambda a-\lambda r_0)-3[45a^3r_0+(10a^6+6a^5r_0-15a^2b^3r_0-45a^4r_0{}^2$$

$$-b^5(5b-9r_0)-5a^3(4b^3-3r_0{}^3))\lambda^2+(4a^8-a^6r_0{}^2-9ab^5r_0{}^2-5a^2b^3r_0{}^3+b^5r_0{}^2(5b+3r_0)+a^3(6b^5+5b^3r_0{}^2)$$

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$$+2a^5(-5b^3+r_0^{\ 3}))\lambda^4]\sinh(\lambda a-\lambda r_0)\} \qquad \text{(A57)}$$

$$A_2=\frac{1}{15ab^3\lambda^2}\{30a(-4a^3+b^3)r_0\lambda^3+\lambda[270a(a-r_0)r_0+3(20a^5+2a^4r_0-5ab^3r_0-12a^3r_0^{\ 2}$$

$$+15b^3r_0^{\ 2}-a^2(20b^3-30r_0^{\ 3}))\lambda^2a(2a^3-5b^3)(2a^3+r_0^{\ 3})\lambda^4]\cosh(\lambda a-\lambda r_0)-3[90ar_0+(20a^4$$

$$-20ab^3+12a^3r_0-15b^3r_0-90a^2r_0^{\ 2}+30ar_0^{\ 3})\lambda^2+(8a^6-2a^4r_0^{\ 2}+5ab^3r_0^{\ 2}-5b^3r_0^{\ 3}$$

$$+a^3(-10b^3+4r_0^{\ 3}))\lambda^4]\sinh(\lambda a-\lambda r_0)\} \qquad \text{(A58)}$$

$$A_3=\frac{1}{15\,b^6\lambda^2}\{30a^3(4a^3-b^3)\,r_0\lambda^3-\lambda(270\,a^3(a-r_0)r_0+3(20\,a^4(a^3-b^3)+a(2a^5-5a^2b^3$$

$$+18b^5)r_0-3(4a^5-5a^2b^3+6b^5)r_0^{\ 2}+30a^4r_0^{\ 3})\lambda^2+a(2a^5-5a^2b^3+18b^5)(2a^3$$

$$+r_0^{\ 3})\lambda^4)\cosh(\lambda a-\lambda r_0)+3\,(90a^3r_0+(20a^3(a^3-b^3)+3(4a^5-5a^2b^3+6b^5)r_0-90a^4r_0^{\ 2}$$

$$+30a^3r_0^{\ 3})\lambda^2+(2a^3(4a^5-5a^2b^3+6b^5)+a(-2a^5+5\,a^2b^3-18b^5)\,r_0^{\ 2}+(4a^5-5a^2b^3$$

$$+6b^5)r_0^{\ 3})\lambda^4)\sinh(\lambda a-\lambda r_0)\} \qquad \text{(A59)}$$

$$A_4=\frac{a^2}{5\,b^3}\{\lambda[3(a-r_0)r_0+a(2a^3+r_0^{\ 3})\lambda^2]\cosh(\lambda a-\lambda r_0)-[3r_0+(2a^3-3ar_0^{\ 2}$$

$$+r_0^{\ 3})\lambda^2]\sinh(\lambda a-\lambda r_0)\} \qquad \text{(A60)}$$

$$A_5=\frac{2\,r_0}{a^3b^3\lambda^2}\{2a^3(a^3-b^3)\lambda^3+(2a^3+b^3)[-\lambda(-3r_0+a(3+r_0^{\ 2}\lambda^2))\cosh(\lambda a-\lambda r_0)+(3$$

$$+r_0(-3a+r_0)\lambda^2)\sinh(\lambda a-\lambda r_0)]\} \qquad \text{(A61)}$$

$$A_6=\frac{2}{b^3}\{(a^3-b^3)r_0\lambda+(2a^3+b^3)[\lambda a\cosh(\lambda a-\lambda r_0)-\sinh(\lambda a-\lambda r_0)]\} \qquad \text{(A62)}$$

$$A_7=\frac{2}{a^3b^3\lambda^2}\{(-a^3+b^3)(3\,r_0+(2a^3+r_0^{\ 3})\lambda^2)\cosh(\lambda r_0)+3(2a^3+b^3)r_0(-\cosh(\lambda a)$$

$$+\lambda a\sinh(\lambda a))+3(a^3-b^3)r_0^{\ 2}\lambda\sinh(\lambda r_0)\} \qquad \text{(A63)}$$

$$A_8=\frac{2}{a^3b^3\lambda^2}\{-3a(2a^3+b^3)r_0\lambda\cosh(\lambda a)+3(2a^3+b^3)r_0\sinh(\lambda a)+(a^3-b^3)[-3r_0^{\ 2}\lambda\cosh(\lambda r_0)$$

$$+(3r_0+(2a^3+r_0^{\ 3})\lambda^2)\sinh(\lambda r_0)]\} \qquad \text{(A64)}$$

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$$B_1 = \frac{-1}{5\,b^3\lambda^2}\{12ar_0\lambda(-10+(-3a^2+b^2)\lambda^2)+\lambda(60a(a+r_0)+(28a^4+3a^3r_0+18b^2r_0{}^2$$

$$-3a^2(8b^2+5r_0{}^2)+a(-6b^2r_0+20r_0{}^3))\lambda^2+a(a^2-2b^2)(2a^3+r_0{}^3)\lambda^4)\cosh(\lambda a-\lambda r_0)+(-60a$$

$$+3(-16a^3+8ab^2-5a^2r_0+6b^2r_0+20ar_0{}^2)\lambda^2+(-10a^5-6ab^2r_0{}^2-5a^2r_0{}^3+6b^2r_0{}^3$$

$$+3a^3(4b^2+r_0{}^2))\lambda^4)\sinh(\lambda a-\lambda r_0)\} \quad \text{(A65)}$$

$$B_2 = \frac{1}{3\,b^3}\{6\,(a^3+2b^3)r_0\lambda-\lambda(3(a+r_0)(4a^3+2b^3-3a^2r_0)+(a^3+2b^3)(2a^3+r_0{}^3)\lambda^2)\cosh(\lambda a-\lambda r_0)$$

$$+3(4a^3+2b^3+3a^2r_0+(2a^5-(a^3+2b^3)\,r_0{}^2+a^2r_0{}^3)\lambda^2)\sinh(\lambda a-\lambda r_0)\} \quad \text{(A66)}$$

$$B_3 = \frac{-a}{5\,b^6\lambda^2}\;\{12r_0\lambda(10a^3+(3a^5+2b^5)\lambda^2)-\lambda(60\,a^3(a+r_0)+(28a^6+12ab^5+3a^5r_0$$

$$+12b^5r_0-15a^4r_0{}^2+20a^3r_0{}^3)\lambda^2+(a^5+4b^5)(2a^3+r_0{}^3)\lambda^4)\cosh(\lambda a-\lambda r_0)+(60a^3+3(16a^5$$

$$+4b^5+5a^4r_0-20a^3r_0{}^2)\lambda^2+(10a^7-3(a^5+4b^5)r_0{}^2+5a^4r_0{}^3)\lambda^4)\;\sinh(\lambda a-\lambda r_0)\} \quad \text{(A67)}$$

$$B_4 = \frac{-a^3}{15b^6}(-6(a^3+2b^3)\,r_0\lambda\;+\lambda(3(a+r_0)(4a^3+2b^3-3a^2r_0)+(a^3+2b^3)(2a^3+r_0{}^3)\lambda^2)\cosh(\lambda a-\lambda r_0)$$

$$-3(4a^3+2b^3+3a^2r_0+(2a^5-(a^3+2b^3)r_0{}^2+a^2r_0{}^3)\lambda^2)\sinh(\lambda a-\lambda r_0)\} \quad \text{(A68)}$$

$$B_5 = \frac{-2\,r_0}{5\,a^2b^6\lambda^4}\{2a^3\lambda^3(15b^3+(a^5+5a^2b^3-6b^5)\lambda^2)-\lambda(90a^3(a-r_0)+3(4a^6+5a^3b^3$$

$$+6ab^5-14a^5r_0+5a^2b^3r_0-6b^5r_0+10a^4r_0{}^2)\lambda^2+a(4a^5+5a^2b^3+6b^5)r_0{}^2\lambda^4)\cosh(\lambda a-\lambda r_0)$$

$$+(90a^3+3(14a^5-5a^2b^3+6b^5-30a^4r_0+10a^3r_0{}^2)\lambda^2+r_0(-3a(4a^5+5a^2b^3+6b^5)$$

$$+(14a^5-5a^2b^3+6b^5)r_0)\lambda^4)\sinh(\lambda a-\lambda r_0)\} \quad \text{(A69)}$$

$$B_6 = \frac{-2\,a}{5b^6\lambda^2}\{-30a^3r_0\lambda+(a^5+5a^2b^3-6b^5)r_0\lambda^3+a\lambda(30a^3+(4a^5+5a^2b^3$$

$$+6b^5)\lambda^2)\cosh(\lambda a-\lambda r_0)-(30a^3+(14a^5-5a^2b^3+6b^5)\lambda^2)\sinh(\lambda a-\lambda r_0)\} \quad \text{(A70)}$$

$$B_7 = \frac{-1}{5a^2b^6\lambda^4}\{-6r_0(30a^3+(14a^5-5a^2b^3+6b^5)\lambda^2)\cosh(\lambda a)-2(-90a^3r_0+3(a^5r_0$$

$$+5a^2b^3r_0-6b^5r_0+10a^3(b^3-r_0{}^3))\lambda^2+(a^5+5a^2b^3-6b^5)(2a^3+r_0{}^3)\lambda^4)\cosh(\lambda r_0)+6\,r_0\lambda(a(30a^3$$

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$$+(4a^5+5\,a^2b^3+6b^5)\lambda^2)\sinh(\lambda a)+r_0(-30a^3+(a^5+5a^2b^3-6b^5)\lambda^2)\sinh(\lambda r_0)\} \qquad \text{(A71)}$$

$$B_8=\frac{1}{5a^2b^6\lambda^4}\{6\,r_0(a\lambda(30a^3+(4a^5+5a^2b^3+6b^5)\lambda^2)\cosh(\lambda a)+\lambda r_0(-30a^3+(a^5+5a^2b^3$$

$$-6b^5)\lambda^2)\cosh(\lambda r_0)-(30a^3+(14a^5-5a^2b^3+6b^5)\lambda^2)\sinh(\lambda a)-2(-90a^3r_0+3(a^5r_0+5a^2b^3r_0$$

$$-6b^5r_0+10a^3(b^3-r_0{}^3))\lambda^2+(a^5+5a^2b^3-6b^5)(2a^3+r_0{}^3)\lambda^4)\sinh(\lambda r_0)\} \qquad \text{(A72)}$$

$$B_9=\frac{1}{25a^2b\lambda^2}\{60\,r_0\lambda(-10b+a^2(4a-3b)\lambda^2)+\lambda(60(5ab-9ar_0+5br_0+9r_0{}^2)+(20a^3(-6a$$

$$+7b)+3a^2(-4a+5b)r_0+3a(24a-25b)r_0{}^2+20(-9a+5b)r_0{}^3)\lambda^2-a^2(4a-5b)(2a^3$$

$$+r_0{}^3)\lambda^4)\cosh(\lambda a-\lambda r_0)+(60(-5b+9r_0)+3(40a^2(a-2b)+a(24a-25b)r_0+20(-9a+5b)r_0{}^2$$

$$+60r_0{}^3)\lambda^2+a(2a^3(24a-25b)+3a(-4a+5b)r_0{}^2+(24a-25b)r_0{}^3)\lambda^4)\sinh(\lambda a-\lambda r_0)\} \qquad \text{(A73)}$$

$$B_{10}=\frac{-a^2}{75b^6\lambda^2}\{30a(4a^3-b^3)r_0\lambda^3+\lambda(270ar_0(-a+r_0)-3(20a^5+2a^4r_0-5ab^3r_0-12a^3r_0{}^2$$

$$+15b^3r_0{}^2+a^2(-20b^3+30r_0{}^3))\lambda^2-a(2a^3-5b^3)(2a^3+r_0{}^3)\lambda^4)\cosh(\lambda a-\lambda r_0)+3(90ar_0+(20a^4$$

$$-20ab^3+12a^3r_0-15b^3r_0-90a^2r_0{}^2+30ar_0{}^3)\lambda^2+(8a^6-2a^4r_0{}^2+5ab^3r_0{}^2-5b^3r_0{}^3$$

$$+a^3(-10b^3+4r_0{}^3))\lambda^4)\sinh(\lambda a-\lambda r_0)\} \qquad \text{(A74)}$$

$$B_{11}=\frac{2r_0}{5a^3b^3\lambda^4}\{30ab^3\lambda^3+2a^3(a^3-6ab^2+5\,b^3)\lambda^5-\lambda(90a(a-r_0)+3(4a^4-14a^3r_0$$

$$+5b^3r_0+ab^2(5b+12r_0)+2a^2(-6b^2+5r_0{}^2))\lambda^2+a(4a^3-12ab^2+5b^3)r_0{}^2\lambda^4)\cosh(\lambda a-\lambda r_0)-(-90a$$

$$+3(-14a^3+5b^3+30a^2r_0+2a(6b^2-5r_0{}^2))\lambda^2+r_0(12a^4-36a^2b^2-14a^3r_0+5b^3r_0$$

$$+3ab^2(5b+4r_0))\lambda^4)\sinh(\lambda a-\lambda r_0)\} \qquad \text{(A75)}$$

$$B_{12}=\frac{2}{5b^3\lambda^2}\{-30ar_0\lambda+(a^3-6ab^2+5b^3)r_0\lambda^3+a\lambda(30a+(4a^3-12ab^2$$

$$+5b^3)\lambda^2)\cosh(\lambda a-\lambda r_0)+(-30a+(-14a^3+12ab^2+5b^3)\lambda^2)\sinh(\lambda a-\lambda r_0)\} \qquad \text{(A76)}$$

$$B_{13}=\frac{1}{5a^3b^3\lambda^4}\{6r_0(-30a+(-14a^3+12ab^2+5b^3)\lambda^2)\cosh(\lambda a)-2(-90ar_0+3(10ab^3$$

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$$+(a^3-6ab^2+5b^3)r_0-10ar_0^{\ 3})\lambda^2+(a^3-6ab^2+5b^3)(2a^3+r_0^{\ 3})\lambda^4)\cosh(\lambda r_0)+6r_0\lambda(a(30a$$

$$+(4a^3-12ab^2+5b^3)\lambda^2)\ \sinh(\lambda a)+r_0(-30a+(a^3-6ab^2+5b^3)\lambda^2)\sinh(\lambda r_0))\} \quad (A77)$$

$$B_{14}=\frac{-1}{5a^3b^3\lambda^4}\{6\ r_0(a\lambda(30a+(4a^3-12ab^2+5b^3)\lambda^2)\cosh(\lambda a)+r_0\lambda(-30a+(a^3$$

$$-6ab^2+5b^3)\lambda^2)\cosh(\lambda r_0)+(-30a+(-14a^3+12ab^2+5b^3)\lambda^2)\sinh(\lambda a))-2(-90ar_0+3(a^3r_0$$

$$+5b^3r_0+2a(5b^3-3b^2r_0-5r_0^{\ 3}))\lambda^2+(a^3-6ab^2+5b^3)(2a^3+r_0^{\ 3})\lambda^4)\sinh(\lambda r_0)\} \quad (A78)$$

$$B_{15}=\frac{1}{75b^3}\{-30\ (a^3+2b^3)r_0\lambda+\lambda(60a^4+6ab^2(5b-9r_0)+15a^3r_0-45a^2r_0^{\ 2}+6b^2r_0(5b+9r_0)$$

$$+(5a^3-18ab^2+10b^3)(2a^3+r_0^{\ 3})\lambda^2)\cosh(\lambda a-\lambda r_0)-3(20a^3+10b^3+15a^2r_0-18b^2r_0$$

$$+(2a^3(5a^2-6b^2)+(-5a^3+18ab^2-10b^3)r_0^{\ 2}+(5a^2-6b^2)r_0^{\ 3})\lambda^2)\sinh(\lambda a-\lambda r_0)\} \quad (A79)$$

$$B_{16}=\frac{a^5}{25b^6}\{\lambda(3(a-r_0)r_0+a(2a^3+r_0^{\ 3})\lambda^2)\cosh(\lambda a-\lambda r_0)-(3r_0+(2a^3-3ar_0^{\ 2}$$

$$+r_0^{\ 3})\lambda^2)\sinh(\lambda a-\lambda r_0)\} \quad (A80)$$

$$B_{17}=\frac{2r_0}{5b^6\lambda^2}\{2a^3(a^3-b^3)\lambda^3+(2a^3+b^3)(-\lambda(-3r_0+a(3+r_0^{\ 2}\lambda^2))\cosh(\lambda a-\lambda r_0)$$

$$+(3+r_0(-3a+r_0)\lambda^2)\sinh(\lambda a-\lambda r_0))\} \quad (A81)$$

$$B_{18}=\frac{2a^3}{5b^6}\{(a^3-b^3)r_0\lambda+(2a^3+b^3)(a\lambda\cosh(\lambda a-\lambda r_0)-\sinh(\lambda a-\lambda r_0))\} \quad (A82)$$

$$B_{19}=\frac{-2}{5b^6\lambda^2}\{(a^3-b^3)(3r_0+(2a^3+r_0^{\ 3})\lambda^2)\cosh(\lambda r_0)-3(2a^3+b^3)r_0(-\cosh(\lambda a)$$

$$+a\lambda\sinh(\lambda a))+3(-a^3+b^3)r_0^{\ 2}\lambda\sinh(\lambda r_0)\} \quad (A83)$$

$$B_{20}=\frac{1}{5b^6\lambda^2}\{-6\ a(2a^3+b^3)r_0\lambda\cosh(\lambda a)+6(2a^3+b^3)r_0\sinh(\lambda a)+2(a^3$$

$$-b^3)(-3\ r_0^{\ 2}\lambda\cosh(r_0\lambda)+(3r_0+(2a^3+r_0^{\ 3})\lambda^2)\sinh(\lambda r_0))\} \quad (A84)$$

$$B_{21}=\frac{4r_0}{15a^2b^6\lambda^4}\{15\ (-2a^6+a^3b^3+b^6)\lambda^3+\lambda(135a^3(a-r_0)+3(a^6-5a^3b^3+9ab^5$$

$$-6a^5r_0+15a^2b^3r_0+15a^4r_0^{\ 2}-b^5(5b+9r_0))\lambda^2+(a^6-5a^3b^3+9ab^5-5b^6)r_0^{\ 2}\lambda^4)\cosh(\lambda a-\lambda r_0)$$

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$$+3(-45a^3 - 3(2a^5 - 5a^2b^3 + 3b^5 - 15a^4r_0 + 5a^3r_0^2)\lambda^2 + r_0(a^6 - 5a^3b^3 + 9ab^5 - 5b^6 - 2a^5r_0$$

$$+5a^2b^3r_0 - 3b^5r_0)\lambda^4)\sinh(\lambda a - \lambda r_0)\} \qquad \text{(A85)}$$

$$B_{22} = \frac{-4a}{15b^6\lambda^2}\{\lambda(45a^4 + (a^6 - 5a^3b^3 + 9ab^5 - 5b^6)\lambda^2)\cosh(\lambda a - \lambda r_0) - 3(15a^3 + 2a^5\lambda^2$$

$$-5a^2b^3\lambda^2 + 3b^5\lambda^2)\sinh(\lambda a - \lambda r_0)\} \qquad \text{(A86)}$$

$$B_{23} = \frac{-4}{5a^2b^6\lambda^4}\{-3r_0(15a^3 + 2a^5\lambda^2 - 5a^2b^3\lambda^2 + 3b^5\lambda^2)\cosh(\lambda a) + \lambda(5(-2a^6 + a^3b^3$$

$$+b^6)\lambda\cosh(\lambda r_0) + r_0(45a^4 + (a^6 - 5a^3b^3 + 9ab^5 - 5b^6)\lambda^2)\sinh(\lambda a))\} \qquad \text{(A87)}$$

$$B_{24} = \frac{4}{5a^2b^6\lambda^4}\{r_0\lambda(45a^4 + (a^6 - 5a^3b^3 + 9ab^5 - 5b^6)\lambda^2)\cosh(\lambda a) - 3r_0(15a^3 + 2a^5\lambda^2$$

$$-5a^2b^3\lambda^2 + 3b^5\lambda^2)\sinh(\lambda a) + 5(-2a^6 + a^3b^3 + b^6)\lambda^2\sinh(\lambda r_0)\} \qquad \text{(A88)}$$

$$B_{25} = \frac{4r_0}{15a^5b^6\lambda^4}\{\lambda(45(2a^6 - 4a^3b^3 - b^6)(a - r_0) + 3a(2a^8 - 10a^5b^3 - 12a^7r_0 + 30a^4b^3r_0$$

$$+10a^6r_0^2 - 5b^6r_0^2 - 2a^2b^5(5b + 9r_0) + 2a^3(9b^5 - 10b^3r_0^2))\lambda^2 + 2a^3(a^6 - 5a^3b^3 + 9ab^5$$

$$-5b^6)r_0^2\lambda^4)\cosh(\lambda a - \lambda r_0) + 3(15(-2a^6 + 4a^3b^3 + b^6) + (-12a^8 + 30a^5b^3 + 30a^7r_0 - 60a^4b^3r_0$$

$$-15ab^6r_0 - 10a^6r_0^2 + 5b^6r_0^2 + a^3(-18b^5 + 20b^3r_0^2))\lambda^2 + 2a^3r_0(a^6 - 5a^3b^3 + 9ab^5 - 2a^5r_0 + 5a^2b^3r_0$$

$$-b^5(5b + 3r_0))\lambda^4)\sinh(\lambda a - \lambda r_0)\} \qquad \text{(A89)}$$

$$B_{26} = \frac{-1}{15a^2b^6\lambda^2}\{60(-2a^6 + a^3b^3 + b^6)r_0\lambda + 4a\lambda(15\ (2a^6 - 4a^3b^3 - b^6) + 2a^2(a^6$$

$$-5a^3b^3 + 9ab^5 - 5b^6)\lambda^2)\cosh(\lambda a - \lambda r_0) - 12(10a^6 - 5b^6 + 4a^8\lambda^2 - 10a^5b^3\lambda^2 + a^3(-20b^3$$

$$+6b^5\lambda^2))\sinh(\lambda a - \lambda r_0)\} \qquad \text{(A90)}$$

$$B_{27} = \frac{4r_0}{5a^5b^6\lambda^4}\{3[10a^6 - 5b^6 + 4a^8\lambda^2 - 10a^5b^3\lambda^2 + a^3(-20b^3 + 6b^5\lambda^2)]\cosh(\lambda a)$$

$$+a\lambda(15(-2a^6 + 4a^3b^3 + b^6) - 2a^2(a^6 - 5a^3b^3 + 9ab^5 - 5b^6)\lambda^2)\sinh(\lambda a)$$

$$-5(2a^6 - a^3b^3 - b^6)[(3 + r_0^2\lambda^2)\cosh(\lambda r_0) - 3r_0\lambda\sinh(\lambda r_0)]\} \qquad \text{(A91)}$$

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$$B_{28}=\frac{-4r_0}{5a^5b^6\lambda^4})\{a\lambda[15(-2a^6+4a^3b^3+b^6)-2a^2(a^6-5a^3b^3+9ab^5-5b^6)\lambda^2]\cosh(\lambda a)$$

$$+3[10a^6-5b^6+4a^8\lambda^2-10a^5b^3\lambda^2+a^3(-20b^3+6b^5\lambda^2)]\sinh(\lambda a)-5(2a^6-a^3b^3$$

$$-b^6)[-3r_0\lambda\cosh(\lambda r_0)+(3+r_0{}^2\lambda^2)\sinh(\lambda r_0)]\} \quad \text{(A92)}$$

$$B_{29}=\frac{1}{5b^6\lambda^2}\{2(a^3-b^3)[3r_0+(2a^3+r_0{}^3)\lambda^2]\cosh(\lambda r_0)-6(2a^3+b^3)r_0[-\cosh(\lambda a)$$

$$+a\lambda\sinh(\lambda a)]+6(-a^3+b^3)r_0{}^2\lambda\sinh(\lambda r_0)\} \quad \text{(A93)}$$

$$B_{30}=\frac{4r_0}{5a^5b^6\lambda^4}\{3[10a^6-5b^6+4a^8\lambda^2-10a^5b^3\lambda^2+a^3(-20b^3+6b^5\lambda^2)]\cosh(\lambda a)$$

$$+a\lambda(15(-2a^6+4a^3b^3+b^6)-2a^2(a^6-5a^3b^3+9ab^5-5b^6)\lambda^2)\sinh(\lambda a)-5(2a^6-a^3b^3$$

$$-b^6)[(3+r_0{}^2\lambda^2)\cosh(\lambda r_0)-3r_0\lambda\sinh(\lambda r_0)]\} \quad \text{(A94)}$$

$$B_{31}=\frac{-4}{5a^2b^6\lambda^4}\{-3r_0(15a^3+2a^5\lambda^2-5a^2b^3\lambda^2+3b^5\lambda^2)\cosh(\lambda a)+\lambda[5(-2a^6+a^3b^3$$

$$+b^6)\lambda\cosh(\lambda r_0)+r_0(45a^4+(a^6-5a^3b^3+9ab^5-5b^6)\lambda^2)\sinh(\lambda a)]\} \quad \text{(A95)}$$

$$B_{32}=\frac{-4}{5a^5b^6\lambda^7}\{\cosh(\lambda r_0)(3(45a^3r_0+(10a^6+6a^5r_0-15a^2b^3r_0+b^5(-5b+9r_0)$$

$$+5a^3(-4b^3+3r_0{}^3))\lambda^2+(a-b)^2(2a^3+4a^2b+6ab^2+3b^3)(2a^3+r_0{}^3)\lambda^4)\cosh(\lambda a)$$

$$-\lambda(135a^4r_0+3(10a^7+a^6r_0-5a^3b^3r_0-5b^6r_0+ab^5(-5b+9r_0)+5a^4(-4b^3+3r_0{}^3))\lambda^2+(a-b)^3(a^3$$

$$+3a^2b+6ab^2+5b^3)(2a^3+r_0{}^3)\lambda^4)\sinh(\lambda a))+3r_0{}^2\lambda(-3(15a^3+2a^5\lambda^2-5a^2b^3\lambda^2$$

$$+3b^5\lambda^2)\cosh(\lambda a)+\lambda(45a^4+(a^6-5a^3b^3+9ab^5-5b^6)\lambda^2)\sinh(\lambda a))\sinh(\lambda r_0)\} \quad \text{(A96)}$$

$$B_{33}=\frac{-4}{5a^5b^6\lambda^7}\{15\ (2a^6-a^3b^3-b^6)r_0\lambda^3+3r_0{}^2\lambda\cosh(\lambda r_0)(3(15a^3+2a^5\lambda^2-5a^2b^3\lambda^2$$

$$+3b^5\lambda^2)\cosh(\lambda a)-\lambda(45a^4+(a^6-5a^3b^3+9ab^5-5b^6)\lambda^2)\sinh(\lambda a))+(-3(45a^3r_0+(10a^6$$

$$+6a^5r_0-15\ a^2b^3r_0+b^5(-5b+9r_0)+5a^3(-4b^3+3r_0{}^3))\lambda^2+(a-b)^2(2a^3+4a^2b+6ab^2$$

$$+3b^3)(2a^3+r_0{}^3)\lambda^4)\cosh(\lambda a)+\lambda(135a^4r_0+3(10a^7+a^6r_0-5a^3b^3r_0-5b^6r_0+ab^5(-5b+9r_0)$$

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$$+5a^4(-4b^3+3r_0^3))\lambda^2+(a-b)^3(a^3+3a^2b+6ab^2+5b^3)(2a^3+r_0^3)\lambda^4)\sinh(\lambda a))\sinh(\lambda r_0)\} \quad \text{(A97)}$$

$$B_{34}=\frac{-2}{5b^6\lambda^2}\{-3a(2a^3+b^3)r_0\lambda\cosh(\lambda a)+3(2a^3+b^3)r_0\sinh(\lambda a)$$

$$+(a^3-b^3)(-3r_0^2\lambda\cosh(\lambda r_0)+(3r_0+(2a^3+r_0^3)\lambda^2)\sinh(\lambda r_0))\} \quad \text{(A98)}$$

$$B_{35}=\frac{-4r_0}{5a^5b^6\lambda^4}\{a\lambda(15(-2a^6+4a^3b^3+b^6)-2a^2(a^6-5a^3b^3+9ab^5-5b^6)\lambda^2)\cosh(\lambda a)$$

$$+3(10a^6-5b^6+4a^8\lambda^2-10a^5b^3\lambda^2+a^3(-20b^3+6b^5\lambda^2))\sinh(\lambda a) \quad \text{(A99)}$$

$$B_{36}=\frac{4}{5a^2b^6\lambda^4}\{r_0\lambda(45a^4+(a^6-5a^3b^3+9ab^5-5b^6)\lambda^2)\cosh(\lambda a)-3r_0(15a^3+2a^5\lambda^2$$

$$-5a^2b^3\lambda^2+3b^5\lambda^2)\sinh(\lambda a)+5(-2a^6+a^3b^3+b^6)\lambda^2\sinh(\lambda r_0)\} \quad \text{(A100)}$$

$$B_{37}=\frac{-1}{5a^5b^6\lambda^7}\{60(-2a^6+a^3b^3+b^6)r_0\lambda^3+4\cosh(\lambda r_0)(\lambda(135a^4r_0+3(10a^7+a^6r_0$$

$$-5a^3b^3r_0-5b^6r_0+ab^5(-5b+9r_0)+5a^4(-4b^3+3r_0^3))\lambda^2+(a-b)^3(a^3+3a^2b+6ab^2+5b^3)(2a^3$$

$$+r_0^3)\lambda^4)\cosh(\lambda a)-3(45a^3r_0+(10a^6+6a^5r_0-15a^2b^3r_0+b^5(-5b+9r_0)+5a^3(-4b^3$$

$$+3r_0^3))\lambda^2+(a-b)^2(2a^3+4a^2b+6ab^2+3b^3)(2a^3+r_0^3)\lambda^4)\sinh(\lambda a))$$

$$+12r_0^2\lambda(-\lambda(45a^4+(a^6-5a^3b^3+9ab^5-5b^6)\lambda^2)\cosh(\lambda a)+3(15a^3+2a^5\lambda^2$$

$$-5a^2b^3\lambda^2+3b^5\lambda^2)\sinh(\lambda a))\sinh(\lambda r_0)\} \quad \text{(A101)}$$

$$B_{38}=\frac{-4}{5a^5b^6\lambda^7}\{3r_0^2\lambda\cosh(\lambda r_0)(\lambda(45a^4+(a^6-5a^3b^3+9ab^5-5b^6)\lambda^2)\cosh(\lambda a)$$

$$-3(15a^3+2a^5\lambda^2-5a^2b^3\lambda^2+3b^5\lambda^2)\sinh(\lambda a))+(-\lambda(135a^4r_0+3(10a^7+a^6r_0-5a^3b^3r_0$$

$$-5b^6r_0+ab^5(-5b+9r_0)+5a^4(-4b^3+3r_0^3))\lambda^2+(a-b)^3(a^3+3a^2b+6ab^2$$

$$+5b^3)(2a^3+r_0^3)\lambda^4)\cosh(\lambda a)+3(45a^3r_0+(10a^6+6a^5r_0-15a^2b^3r_0+b^5(-5b+9r_0)+5a^3(-4b^3$$

$$+3r_0^3))\lambda^2+(a-b)^2(2a^3+4a^2b+6ab^2+3b^3)(2a^3+r_0^3)\lambda^4)\sinh(\lambda a))\sinh(\lambda r_0)\} \quad \text{(A102)}$$

for the Kuwabara model.

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Biographical Sketch

Hsuan-Chiao Liu was born in Nantou on October 11, 1990. He graduated from Rangitoto College in New Zealand in the summer of 2009, and then entered the Department of Chemical and Material Engineering of Chang Gung University in the next year. After earning his Bachelor's Degree in 2014, he continued his advanced study in the graduate school at the Department of Chemical Engineering of National Taiwan University for a Master Degree up to the present.

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