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# Asymptotic formulae for the interaction force and torque between two charged parallel cylinders

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ABSTRACT

The electrostatic interactions between charged particles immersed in an ionic solution play an important role for the stability of colloidal dispersions. The distribution of the electrostatic potential in the continuous phase obeys the nonlinear Poisson–Boltzmann equation. This study aims to calculate the asymptotic expressions for the interaction force and torque between two parallel charged cylinders at large distances between them. The exact formulae obtained are expressed in terms of the modified Bessel function of the second kind. From the general physical principles two theorems about the interaction energy and the stability of the quasi-equilibrium states for multipole–multipole interactions are proved.



## 1. Introduction

The stability of colloidal dispersions is controlled by the so called DLVO (Derjaguin–Landau–Verwey–Overbeek) [1,2] and non-DLVO [3] interaction forces between colloidal particles. The strongest medium range forces have an electrostatic origin [4,5]. Most of the studies consider the electrostatic interactions between spherical particles in the frame of the nonlinear Poisson–Boltzmann equation (PBE). The common application of the cylindrical PBE is to investigate the thermodynamic properties of cylindrical micelles [6,7], polyelectrolytes [8–10], DNA and helical macromolecules [11–14].

For the modeling of the dynamics and statics of many charged rodlike particles immersed in an ionic solution, the electrostatic interaction energy between them should be calculated. Because of the nonlinearity of the PBE the problem for pairwise interaction energy is solved numerically for all distances between them [5]. Usually the practical systems are dilute and the distances between the particles are large. The solution of the PBE for an individual particle decays exponentially with distances (see Section 2) and the electrostatic potential, $\psi$, is small. For small values of $\psi$ the PBE is reduced to the linear PBE. Nevertheless, the linear PBE for two cylinders has not an analytical solution and it is solved numerically in bicylinder coordinates [15].

Our first goal in the present study is to derive general asymptotic formulae for the interaction force and torque between two charged particles at large distances between them (Sections 2 and 3). The application of the obtained results for the 2D case is discussed in Section 4. The exact asymptotic expressions for the interaction force and torque of the all modes of the Fourier expansion are derived in Section 5. Our second goal is to prove the theorems for the interaction energy and for the stability of quasi-equilibrium states for the individual multipole–multipole electrostatic interactions (Section 6).

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## 2. General physical principles

In the classical formulation of $N$-component ionic solutions the electrostatic potential, $\psi$, in a static electric field, $\mathbf{E} = -\nabla\psi$, obeys the Poisson equation [16]:

$$-\varepsilon_0\varepsilon_r\nabla\cdot(\nabla\psi) = \sum_{s=1}^{N} ez_s n_s \tag{2.1}$$

where $\nabla$ denotes the del operator, $\varepsilon_0$ is the vacuum dielectric permittivity, $\varepsilon_r$ is the relative dielectric permittivity of the solution, $e$ is the elementary charge, all ionic-species-number densities are $n_s$ ($s = 1,2,\ldots,N$), and $z_s$ is the charge number of ion species $s$, which is positive for cations and negative for anions. The right-hand side of Eq. (2.1) represents the bulk charge density, $\rho_{el}$. The bulk densities, $n_s$, are altered from their input constant values, $n_{s\infty}$ ($s = 1,2,\ldots,N$), by the corresponding Boltzmann factor and the Boltzmann distribution reads:

$$n_s = n_{s\infty}\exp\left(-\frac{ez_s\psi}{k_B T}\right)(s = 1, 2, \ldots, N) \tag{2.2}$$

where $k_B$ is the Boltzmann constant and $T$ is the temperature. Substituting the Boltzmann distribution, Eq. (2.2), in Eq. (2.1), one calculates the respective PBE [5]:

$$\nabla\cdot(\nabla\psi) = -\frac{e}{\varepsilon_0\varepsilon_r}\sum_{s=1}^{N} z_s n_{s\infty}\exp\left(-\frac{ez_s\psi}{k_B T}\right) \tag{2.3}$$

The electro-neutrality of the solution requires that

$$\sum_{s=1}^{N} ez_s n_{s\infty} = 0 \tag{2.4}$$

The general expression for the pressure tensor, $\mathbf{P}$, reads [16]:

$$\mathbf{P} = \left(p + \frac{\varepsilon_0\varepsilon_r}{2}E^2\right)\mathbf{U} - \varepsilon_0\varepsilon_r\mathbf{E}\mathbf{E} \tag{2.5}$$

where $\mathbf{U}$ is the unit tensor and $p$ is the excess isotropic pressure defined as a difference between the local osmotic pressure and the osmotic pressure at infinity [17]:

$$p \equiv k_B T\sum_{s=1}^{N}(n_s - n_{s\infty}) = k_B T\sum_{s=1}^{N} n_{s\infty}\left[\exp\left(-\frac{ez_s\psi}{k_B T}\right) - 1\right] \tag{2.6}$$

From Eqs. (2.3,2.5) and (2.6) we prove that the pressure tensor obeys the local equilibrium conditions in the static case, that are the conservation of linear and angular momentums (see Appendix A):

$$\nabla\cdot\mathbf{P} = 0 \quad \text{and} \quad \nabla\cdot(\mathbf{P}\times\mathbf{r}) = 0 \tag{2.7}$$

where $\mathbf{r}$ is the radius vector with respect to a given arbitrary point.

The electrostatic force, $\mathbf{F}$, and torque, $\mathbf{T}$, acting on a charged particle with surface $S$ and unit running normal vector $\mathbf{n}$ pointed to the ionic solution (Fig. 1), are calculated from the following integrals [16]:

$$\mathbf{F} = -\oint_S(\mathbf{n}\cdot\mathbf{P})dS \quad \text{and} \quad \mathbf{T} = \oint_S[\mathbf{n}\cdot(\mathbf{P}\times\mathbf{r})]dS \tag{2.8}$$

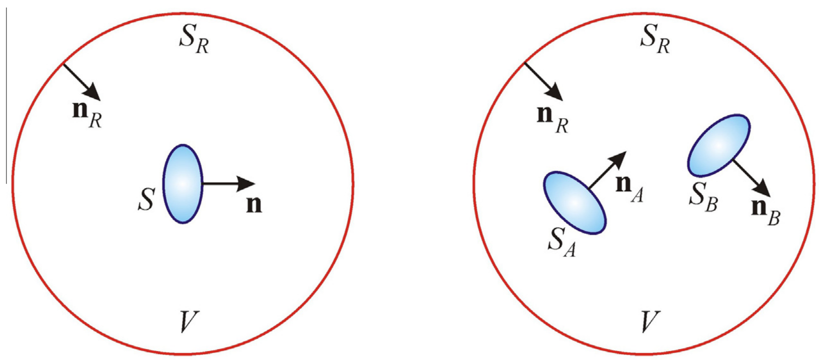


**Fig. 1.** One or two charged particles in an ionic solution. The hypothetical surface, $S_R$, encircles the particles at large distances.

In order to calculate **F** and **T**, we define a hypothetical surface, $S_R$, encircled the particle, with unit running normal vector $\mathbf{n}_R$ pointed to the ionic solution, which occupies the volume, $V$ (Fig. 1). From the divergence theorem, Eqs. (2.7) and (2.8), it follows that:

$$\mathbf{F} = \oint_{S_R} (\mathbf{n}_R \cdot \mathbf{P}) dS_R \quad \text{and} \quad \mathbf{T} = -\oint_{S_R} [\mathbf{n}_R \cdot (\mathbf{P} \times \mathbf{r})] dS_R \tag{2.9}$$

At large distances from the charged particle, the electrostatic potential is small and the PBE, Eq. (2.3), is reduced to its linear form:

$$\nabla \cdot (\nabla \psi) = \kappa^2 \psi \tag{2.10}$$

where the inverse Debye screening length, $\kappa$, is defined as follows [5]:

$$\kappa^2 \equiv \frac{e^2}{\varepsilon_0 \varepsilon_r k_B T} \sum_{s=1}^{N} z_s^2 n_{s\infty} \tag{2.11}$$

Thus, the electrostatic potential decays exponentially at large distances and the integrals in the right-hand sides of Eq. (2.9) vanish. Therefore, $\mathbf{F} = 0$ and $\mathbf{T} = 0$ for an individual charged particle, as can be expected.

In the case of two charged particles ($A$ and $B$, Fig. 1) the sum of forces and the sum of torques are equal to zero:

$$\mathbf{F}_A + \mathbf{F}_B = 0 \quad \text{and} \quad \mathbf{T}_A + \mathbf{T}_B = 0 \tag{2.12}$$

where the forces, $\mathbf{F}_A$ and $\mathbf{F}_B$, and torques, $\mathbf{T}_A$ and $\mathbf{T}_B$, acting on particles $A$ and $B$, respectively, are different than zero. These forces and torques describe the electrostatic interactions between both particles.

## 3. Asymptotic expressions for the electrostatic interaction force and torque at large distances between particles

The derivations of the asymptotic expressions for the interaction force and torque are simpler using the middle plane between particles, which is perpendicular to the line between their mass centers $O_A$ and $O_B$. This plane defines Cartesian coordinate system $Oxyz$, in which the $x$-coordinates of $O_A$ and $O_B$ are $-L/2$ and $L/2$, respectively, where $L$ is the distance between their mass centers (Fig. 2). Using the divergence theorem for the parallelogram around particle $B$ depicted in Fig. 2 and taking the limit for a large extend of the parallelogram, we obtain the following formulae:

$$\mathbf{F}_B = -\oint_{S_B} (\mathbf{n}_B \cdot \mathbf{P}) dS_B = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} (\mathbf{e}_x \cdot \mathbf{P})|_{x=0} dydz \tag{3.1}$$

$$\mathbf{T}_B = \oint_{S_B} [\mathbf{n}_B \cdot (\mathbf{P} \times \mathbf{r})] dS_B = -\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} [\mathbf{e}_x \cdot (\mathbf{P} \times \mathbf{r})]|_{x=0} dydz \tag{3.2}$$

where $\mathbf{e}_x$, $\mathbf{e}_y$, and $\mathbf{e}_z$ are the unit vectors of the Cartesian coordinate system (Fig. 2). For example, in the 2D case the interaction force has $x$- and $y$-components and the interaction torque has only $z$-component, see below. In the general 3D case all components of $\mathbf{F}_B$ and $\mathbf{T}_B$ can be different than zero.

From the physical and computational viewpoints it is important to obtain analytical expressions for the electrostatic interaction force and torque at large distances between them. In this case, the leading order asymptotic solution of the PBE around the plain $x = 0$ is the superposition, $\psi = \psi_A + \psi_B$, of the far field expansions of the solutions of PBE for individual particles $\psi_A$ and $\psi_B$, respectively. Note that $\psi_A$ and $\psi_B$ around the middle plane are solutions of the linear PBE, Eq. (2.10). The respective asymptotic expression for the pressure tensor reads:

$$\mathbf{P} = \left[p + \frac{\varepsilon_0 \varepsilon_r}{2} \nabla(\psi_A + \psi_B) \cdot \nabla(\psi_A + \psi_B)\right] \mathbf{U} - \varepsilon_0 \varepsilon_r \nabla(\psi_A + \psi_B) \nabla(\psi_A + \psi_B) \tag{3.3}$$

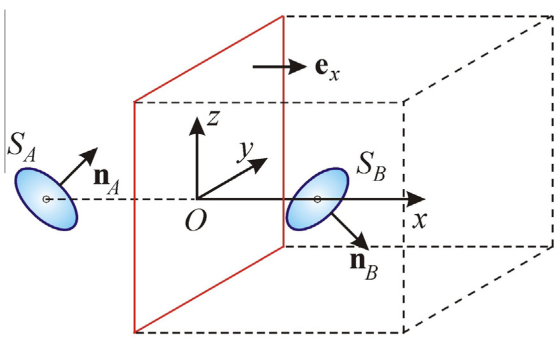


**Fig. 2.** Calculations of the interaction force and torque are simpler using the middle plane between particles perpendicular to the line between their mass centers.

see Eq. (2.5). From Eqs. (2.6) and (2.11) we obtain the asymptotic formula for the isotropic pressure, $p$:

$$p = \frac{e^2}{2k_B T}\sum_{s=1}^{N} z_s^2 n_{s\infty}\psi^2 = \frac{\varepsilon_0\varepsilon_r}{2}\kappa^2(\psi_A+\psi_B)^2 \tag{3.4}$$

The pressure tensor, $\mathbf{P}$, is a superposition of three terms: $\mathbf{P}_A$ – the pressure tensor written for individual particle $A$; $\mathbf{P}_B$ – the pressure tensor written for individual particle $B$; $\mathbf{P}_{AB}$ – the pressure tensor accounting for the interactions between them. These terms are defined as follows:

$$\mathbf{P}_j \equiv \frac{\varepsilon_0\varepsilon_r}{2}\left(\kappa^2\psi_j^2 + \nabla\psi_j\cdot\nabla\psi_j\right)\mathbf{U} - \varepsilon_0\varepsilon_r\nabla\psi_j\nabla\psi_j (j = A, B) \tag{3.5}$$

$$\mathbf{P}_{AB} \equiv \varepsilon_0\varepsilon_r\left(\kappa^2\psi_A\psi_B + \nabla\psi_A\cdot\nabla\psi_B\right)\mathbf{U} - \varepsilon_0\varepsilon_r(\nabla\psi_A\nabla\psi_B + \nabla\psi_B\nabla\psi_A) \tag{3.6}$$

Using the asymptotic expressions, Eq. (3.5), and the linear PBE, Eq. (2.10), one proves that $\nabla\cdot\mathbf{P}_A = 0$, $\nabla\cdot\mathbf{P}_B = 0$, $\nabla\cdot(\mathbf{P}_A\times\mathbf{r}) = 0$, and $\nabla\cdot(\mathbf{P}_B\times\mathbf{r}) = 0$ (see Appendix A). Therefore, $\mathbf{P}_A$ and $\mathbf{P}_B$ do not give contributions to the calculations of the interaction force and torque and the final asymptotic expressions for $\mathbf{F}_B$ and $\mathbf{T}_B$ read:

$$\mathbf{F}_B = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}(\mathbf{e}_x\cdot\mathbf{P}_{AB})|_{x=0}\,dydz \quad\text{and}\quad \mathbf{T}_B = -\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}[\mathbf{e}_x\cdot(\mathbf{P}_{AB}\times\mathbf{r})]|_{x=0}\,dydz \tag{3.7}$$

Eq. (3.7) is the starting point for the calculations of $\mathbf{F}_B$ and $\mathbf{T}_B$ in 2D and 3D cases. From the physical viewpoint, when $\mathbf{T}_B$ is calculated, the radius vector $\mathbf{r}$ is defined with respect to the mass center $O_B$.

## 4. Asymptotic expressions for the 2D case

In the 2D case we assume that all parameters do not depend on $z$, so that the interaction force and torque per unit length $W$ are calculated from Eq. (3.7):

$$\frac{\mathbf{F}_B}{W} = \int_{-\infty}^{\infty}(\mathbf{e}_x\cdot\mathbf{P}_{AB})|_{x=0}\,dy \quad\text{and}\quad \frac{\mathbf{T}_B}{W} = -\int_{-\infty}^{\infty}[\mathbf{e}_x\cdot(\mathbf{P}_{AB}\times\mathbf{r})]|_{x=0}\,dy \tag{4.1}$$

Substituting the Eq. (3.6) in Eq. (4.1), one obtains the following expressions:

$$\frac{\mathbf{F}_B\cdot\mathbf{e}_x}{\varepsilon_0\varepsilon_r W} = \int_{-\infty}^{\infty}\left(\kappa^2\psi_A\psi_B + \frac{\partial\psi_A}{\partial y}\frac{\partial\psi_B}{\partial y} - \frac{\partial\psi_A}{\partial x}\frac{\partial\psi_B}{\partial x}\right)\Bigg|_{x=0} dy \tag{4.2}$$

$$\frac{\mathbf{F}_B\cdot\mathbf{e}_y}{\varepsilon_0\varepsilon_r W} = -\int_{-\infty}^{\infty}\left(\frac{\partial\psi_A}{\partial x}\frac{\partial\psi_B}{\partial y} + \frac{\partial\psi_A}{\partial y}\frac{\partial\psi_B}{\partial x}\right)\Bigg|_{x=0} dy \tag{4.3}$$

$$\frac{\mathbf{T}_B\cdot\mathbf{e}_z}{\varepsilon_0\varepsilon_r W} = -\int_{-\infty}^{\infty}\left(\kappa^2\psi_A\psi_B + \frac{\partial\psi_A}{\partial y}\frac{\partial\psi_B}{\partial y} - \frac{\partial\psi_A}{\partial x}\frac{\partial\psi_B}{\partial x}\right)\Bigg|_{x=0} y\,dy - \frac{L\mathbf{F}_B\cdot\mathbf{e}_y}{2\varepsilon_0\varepsilon_r W} \tag{4.4}$$

For example, in the case of a charged cylinder with radius $a$ and small electrostatic potentials, Eq. (2.10) is presented as follows [5]:

$$\frac{1}{\rho}\frac{\partial}{\partial\rho}\left(\rho\frac{\partial\psi}{\partial\rho}\right) + \frac{1}{\rho^2}\frac{\partial^2\psi}{\partial\phi^2} = \kappa^2\psi \tag{4.5}$$

where $\rho$ is the radial coordinate and $\phi$ is the polar angle of the cylindrical coordinate system with axis of revolution $Oz$. The general solution of Eq. (4.5) is:

$$\psi = \sum_{m=0}^{\infty}\psi_m\frac{K_m(\kappa\rho)}{K_m(\kappa a)}\cos(m\phi - m\phi_m) \tag{4.6}$$

where: $K_m$ is the modified Bessel function of the second kind and order $m$; $\psi_m$ and $\phi_m$ are the amplitude and phase shift for the $m$th mode of the Fourier expansion of the electrostatic potential at the boundary $\rho = a$ [18]. The surface charge density, $\sigma$, is obtained using the Neumann boundary condition [16]:

$$\varepsilon_0\varepsilon_r\frac{\partial\psi}{\partial\rho}\bigg|_{\rho=a} = -\sigma \tag{4.7}$$

From Eqs. (4.6) and (4.7) we obtain the relationship between the $m$th mode of the Fourier expansion of the surface charge density, $\sigma_m$, and the surface electrostatic potential, $\psi_m$:

$$\sigma = \sum_{m=0}^{\infty}\sigma_m\cos(m\phi - m\phi_m) \quad\text{and}\quad \sigma_m = \frac{\varepsilon_0\varepsilon_r\psi_m\kappa}{2K_m(\kappa a)}[K_{m-1}(\kappa a) + K_{m+1}(\kappa a)] \tag{4.8}$$

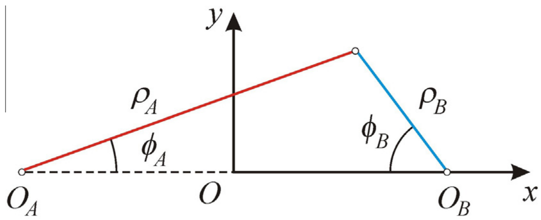


**Fig. 3.** Definitions of the radial distances, $\rho_A$ and $\rho_B$, and the local angles, $\phi_A$ and $\phi_B$.

The terms with subscripts $m = 0, 1, 2, 3, \ldots$ play the role of the rod "charges", "dipoles", "quadrupoles", "hexapoles", etc., respectively [19].

For arbitrary values of the electrostatic potential, $\psi$, the nonlinear PBE is solved numerically for a specific boundary condition at the cylinder surface (Dirichlet – fixed surface potential, Neumann – fixed surface charge, or Robin – fixed electrochemical potential). The asymptotic solution at large distances from the cylinder obeys Eq. (4.6), in which $\psi_m$ represents the $m$th mode of the Fourier expansion of the so-called rescaled surface potential [20].

For two charged cylinders $A$ and $B$ with radiuses $a_A$ and $a_B$, the far field asymptotic expressions for the electrostatic potentials, Eq. (4.6), can be presented as follows:

$$\psi_A = \sum_{m=0}^{\infty} A_m f_{A,m} \quad \text{and} \quad f_{A,m} \equiv K_m(\kappa\rho_A)\cos(m\phi_A - m\phi_{A,m}) \tag{4.9}$$

$$\psi_B = \sum_{n=0}^{\infty} B_n f_{B,n} \quad \text{and} \quad f_{B,n} \equiv K_n(\kappa\rho_B)\cos(n\phi_B - n\phi_{B,n}) \tag{4.10}$$

where: $\psi_{A,m}$ and $\psi_{B,n}$ are the respective Fourier modes of the re-scaled surface potentials of rods $A$ and $B$; $A_m \equiv \psi_{A,m}/K_m(\kappa a_A)$ and $B_n \equiv \psi_{B,n}/K_n(\kappa a_B)$ are constants. The definitions of radial distances $\rho_A$ and $\rho_B$, local polar angles $\phi_A$ and $\phi_B$, and phase shifts $\phi_{A,m}$ and $\phi_{B,n}$ are illustrated in Fig. 3, so that:

$$x = -\frac{L}{2} + \rho_A\cos\phi_A, \quad x = \frac{L}{2} - \rho_B\cos\phi_B, \quad y = \rho_j\sin\phi_j (j = A, B) \tag{4.11}$$

Therefore, the calculations of the interaction force and torque are reduced to the summation of the following series:

$$\frac{\mathbf{F}_B\cdot\mathbf{e}_x}{\varepsilon_0\varepsilon_r\kappa W} = \sum_{m=0}^{\infty}\sum_{n=0}^{\infty} A_m B_n X_{m,n}, \quad \frac{\mathbf{F}_B\cdot\mathbf{e}_y}{\varepsilon_0\varepsilon_r\kappa W} = \sum_{m=0}^{\infty}\sum_{n=0}^{\infty} A_m B_n Y_{m,n}, \quad \frac{\mathbf{T}_B\cdot\mathbf{e}_z}{\varepsilon_0\varepsilon_r W} = \sum_{m=0}^{\infty}\sum_{n=0}^{\infty} A_m B_n T_{m,n} \tag{4.12}$$

where $X_{m,n}$, $Y_{m,n}$, and $T_{m,n}$ are dimensionless coefficients. Using Eqs. (4.2,4.3,4.4,4.9,4.10) and (4.12), one obtains that the values of the dimensionless coefficients are calculated from the following integrals:

$$X_{m,n} \equiv \int_{-\infty}^{\infty}\left(\kappa f_{A,m} f_{B,n} + \frac{1}{\kappa}\frac{\partial f_{A,m}}{\partial y}\frac{\partial f_{B,n}}{\partial y} - \frac{1}{\kappa}\frac{\partial f_{A,m}}{\partial x}\frac{\partial f_{B,n}}{\partial x}\right)\bigg|_{x=0} dy \tag{4.13}$$

$$Y_{m,n} \equiv -\int_{-\infty}^{\infty}\left(\frac{1}{\kappa}\frac{\partial f_{A,m}}{\partial x}\frac{\partial f_{B,n}}{\partial y} + \frac{1}{\kappa}\frac{\partial f_{A,m}}{\partial y}\frac{\partial f_{B,n}}{\partial x}\right)\bigg|_{x=0} dy \tag{4.14}$$

$$T_{m,n} \equiv -\int_{-\infty}^{\infty}(\kappa^2 f_{A,m} f_{B,n} + \frac{\partial f_{A,m}}{\partial y}\frac{\partial f_{B,n}}{\partial y} - \frac{\partial f_{A,m}}{\partial x}\frac{\partial f_{B,n}}{\partial x})\bigg|_{x=0} y dy - \frac{\kappa L}{2}Y_{m,n} \tag{4.15}$$

The integrands in Eqs. (4.13)–(4.15) contain the modified Bessel function of the second kind and decay exponentially at $|y| \to \infty$. Nevertheless, their numerical calculations are time consumable. In Section 5 we will derive the exact formulae for $X_{m,n}$, $Y_{m,n}$, and $T_{m,n}$.

## 5. Exact formulae for the integrals in the asymptotic expressions for the 2D case

To obtain the exact formulae for the integrals in Eqs. (4.13)–(4.15), we transform them in the forms of integrals over the circle. We define a hypothetical cylinder with radius $0 < d < L/2$ and axis of revolution $O_B z$. The projection of the cylinder surface at the plane $z = 0$ is circle $C_d$. The unit running normal vector, $\mathbf{n}_d$, is pointed to the ionic solution (Fig. 4). In Appendix A it is proven that $\nabla\cdot\mathbf{P}_{AB} = 0$ and $\nabla\cdot(\mathbf{P}_{AB}\times\mathbf{r}) = 0$. Using the divergence theorem for the parallelogram around the cylinder (Fig. 4) and taking the limit for a large extend of the parallelogram, we obtain that:

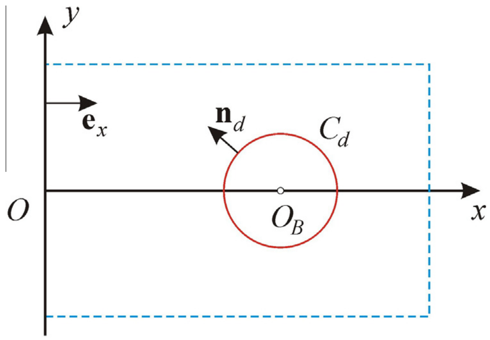


**Fig. 4.** Transformation of integrals to the integrals around a cylinder with radius $d$.

$$\frac{\mathbf{F}_B}{W} = -d\int_0^{2\pi}(\mathbf{n}_d\cdot\mathbf{P}_{AB})|_{\rho_B=d}d\phi_B \quad\text{and}\quad \frac{\mathbf{T}_B}{W} = d\int_0^{2\pi}[\mathbf{n}_d\cdot(\mathbf{P}_{AB}\times\mathbf{r})]|_{\rho_B=d}d\phi_B \tag{5.1}$$

see Eq. (4.1). Note, that Eq. (5.1) is valid for all positive values of $d$ smaller than $L/2$.

From the definition of the pressure tensor accounting for the interactions, Eq. (3.6), and the cylindrical coordinates, Eq. (4.11), after long but trivial calculations, one transforms Eq. (5.11) to the following results:

$$\begin{aligned}\mathbf{F}_B\cdot(\mathbf{e}_x+i\mathbf{e}_y) &= \varepsilon_0\varepsilon_r Wi\int_0^{2\pi}\left(\frac{\partial\psi_A}{\partial\rho_B}\frac{\partial\psi_B}{\partial\phi_B}+\frac{\partial\psi_A}{\partial\phi_B}\frac{\partial\psi_B}{\partial\rho_B}\right)\Bigg|_{\rho_B=d}\exp(-i\phi_B)d\phi_B\\&\quad+\varepsilon_0\varepsilon_r Wd\int_0^{2\pi}\left(\kappa^2\psi_A\psi_B+\frac{1}{d^2}\frac{\partial\psi_A}{\partial\phi_B}\frac{\partial\psi_B}{\partial\phi_B}-\frac{\partial\psi_A}{\partial\rho_B}\frac{\partial\psi_B}{\partial\rho_B}\right)\Bigg|_{\rho_B=d}\exp(-i\phi_B)d\phi_B\end{aligned} \tag{5.2}$$

$$\mathbf{T}_B\cdot\mathbf{e}_z = -\varepsilon_0\varepsilon_r Wd\int_0^{2\pi}\left(\frac{\partial\psi_A}{\partial\rho_B}\frac{\partial\psi_B}{\partial\phi_B}+\frac{\partial\psi_A}{\partial\phi_B}\frac{\partial\psi_B}{\partial\rho_B}\right)\Bigg|_{\rho_B=d}d\phi_B \tag{5.3}$$

where $i$ is the imaginary units. Eqs. (4.9,4.10,4.12,5.2) and (5.3) allow to obtain the following alternative forms of the integrals for the dimensionless coefficients $X_{m,n}$, $Y_{m,n}$, and $T_{m,n}$ appearing in Eqs. (4.13)–(4.15):

$$\begin{aligned}F_{m,n}\equiv X_{m,n}+iY_{m,n} &= i\int_0^{2\pi}\left(\frac{\partial f_{A,m}}{\partial\beta}\frac{\partial f_{B,n}}{\partial\phi_B}+\frac{\partial f_{A,m}}{\partial\phi_B}\frac{\partial f_{B,n}}{\partial\beta}\right)\Bigg|_{\beta=\delta}\exp(-i\phi_B)d\phi_B\\&\quad+\int_0^{2\pi}\left(\beta f_{A,m}f_{B,n}+\frac{1}{\beta}\frac{\partial f_{A,m}}{\partial\phi_B}\frac{\partial f_{B,n}}{\partial\phi_B}-\beta\frac{\partial f_{A,m}}{\partial\beta}\frac{\partial f_{B,n}}{\partial\beta}\right)\Bigg|_{\beta=\delta}\exp(-i\phi_B)d\phi_B\end{aligned} \tag{5.4}$$

$$T_{m,n} = -\int_0^{2\pi}\left(\beta\frac{\partial f_{A,m}}{\partial\beta}\frac{\partial f_{B,n}}{\partial\phi_B}+\beta\frac{\partial f_{A,m}}{\partial\phi_B}\frac{\partial f_{B,n}}{\partial\beta}\right)\Bigg|_{\beta=\delta}d\phi_B \tag{5.5}$$

where $F_{m,n}$ are the complex interaction force coefficients and all distances are scaled with the Debye length, $\alpha\equiv\rho_A\kappa$, $\beta\equiv\rho_B\kappa$, and $\delta\equiv d\kappa$.

After the substitution of the definition for function $f_{B,n}$, Eq. (4.10), in Eqs. (5.4) and (5.5), and subsequent equivalent transformations, we derive the following formulae (see Appendix B):

$$\begin{aligned}F_{m,n} &= \int_0^{2\pi}\frac{\beta}{2}\left[K_{n-1}(\beta)\frac{\partial f_{A,m}}{\partial\beta}-K'_{n-1}(\beta)f_{A,m}\right]\Bigg|_{\beta=\delta}\exp\left[i(n-1)\varphi_B-in\varphi_{B,n}\right]d\varphi_B\\&\quad+\int_0^{2\pi}\frac{\beta}{2}\left[K_{n+1}(\beta)\frac{\partial f_{A,m}}{\partial\beta}-K'_{n+1}(\beta)f_{A,m}\right]\Bigg|_{\beta=\delta}\exp[in\phi_{B,n}-i(n+1)\phi_B]d\phi_B\end{aligned} \tag{5.6}$$

$$T_{m,n} = n\int_0^{2\pi}\beta\left[K_n(\beta)\frac{\partial f_{A,m}}{\partial\beta}-K'_n(\beta)f_{A,m}\right]\Bigg|_{\beta=\delta}\sin(n\phi_B-n\phi_{B,n})d\phi_B \tag{5.7}$$

where $K'_n(\beta)\equiv dK_n(\beta)/d\beta$.

In order to obtain the exact expressions for the coefficients, $F_{m,n}$ and $T_{m,n}$, we will use below Graf's addition theorem [21] written for $f_{A,m}$ in the following form (see Fig. 3):

$$f_{A,m} = K_m(\alpha)\cos(m\phi_A-m\phi_{A,m}) = \sum_{j=-\infty}^{\infty}K_{m+j}(\kappa L)I_j(\beta)\cos(j\phi_B-m\phi_{A,m}) \tag{5.8}$$

where $I_j$ is the modified Bessel function of the first kind and order $j$. For example, as can be expected $T_{m,0} = 0$, see Eq. (5.7). For $n > 0$, if we substitute the Eq. (5.8) in Eq. (5.7), then all integrals are equal to zero except of those for $j = \pm n$. Thus, accounting for the identity $I_n = I_{-n}$, we derive that:

$$T_{m,n} = nK_{m+n}(\kappa L)C_n \int_0^{2\pi} \cos(n\phi_B - m\phi_{A,m}) \sin(n\phi_B - n\phi_{B,n}) d\phi_B \\ + nK_{m-n}(\kappa L)C_n \int_0^{2\pi} \cos(n\phi_B + m\phi_{A,m}) \sin(n\phi_B - n\phi_{B,n}) d\phi_B \tag{5.9}$$

where $C_n$ is defined as follows:

$$C_n \equiv \beta[K_n(\beta)I'_n(\beta) - K'_n(\beta)I_n(\beta)]\big|_{\beta=\delta} \tag{5.10}$$

and $I'_n(\beta) \equiv dI_n(\beta)/d\beta$. The respective Wronskian of the Bessel functions [21] is equal to:

$$K_n(\beta)I'_n(\beta) - I_n(\beta)K'_n(\beta) = \frac{1}{\beta} \tag{5.11}$$

so that $C_n = 1$ and does not depend on $\delta$. Therefore, the final exact expression for the dimensionless torque coefficients reads:

$$T_{m,n} = \pi n[K_{m+n}(\kappa L) \sin(m\phi_{A,m} - n\phi_{B,n}) - K_{m-n}(\kappa L) \sin(m\phi_{A,m} + n\phi_{B,n})] \tag{5.12}$$

In the case of $n > 1$, the substitution of $f_{A,m}$ from Eq. (5.8) in the first integral in the right-hand side of Eq. (5.6) leads to a sum of integrals with respect to $j$. The only different than zero terms in this sum are those for $j = \pm(n - 1)$. Analogous calculations for the second integral in the right-hand side of Eq. (5.6) show that the respective infinite sum is equal to the sum of two terms corresponding to $j = \pm(n + 1)$. Taking into account that $I_{n+1} = I_{-(n+1)}$ and $I_{n-1} = I_{-(n-1)}$, one simplifies Eq. (5.6) to the following result:

$$F_{m,n} = \frac{C_{n-1}}{2} K_{m+n-1}(\kappa L) \int_0^{2\pi} \cos[(n-1)\phi_B - m\phi_{A,m}] \exp[i(n-1)\phi_B - in\phi_{B,n}] d\phi_B \\ + \frac{C_{n-1}}{2} K_{m-n+1}(\kappa L) \int_0^{2\pi} \cos[(n-1)\phi_B + m\phi_{A,m}] \exp[i(n-1)\phi_B - in\phi_{B,n}] d\phi_B \\ + \frac{C_{n+1}}{2} K_{m+n+1}(\kappa L) \int_0^{2\pi} \cos[(n+1)\phi_B - m\phi_{A,m}] \exp[in\phi_{B,n} - i(n+1)\phi_B] d\phi_B \\ + \frac{C_{n+1}}{2} K_{m-n-1}(\kappa L) \int_0^{2\pi} \cos[(n+1)\phi_B + m\phi_{A,m}] \exp[in\phi_{B,n} - i(n+1)\phi_B] d\phi_B \tag{5.13}$$

Finally, calculating the integrals in the right-hand side of Eq. (5.13), accounting for the fact that $C_{n-1} = 1$ and $C_{n+1} = 1$, and separating the real and imaginary parts of the obtained result, we derive the formulae for the force coefficients:

$$X_{m,n} = \frac{\pi}{2}[K_{m+n+1}(\kappa L) \cos(m\phi_{A,m} - n\phi_{B,n}) + K_{m-n-1}(\kappa L) \cos(m\phi_{A,m} + n\phi_{B,n})] \\ + \frac{\pi}{2}[K_{m+n-1}(\kappa L) \cos(m\phi_{A,m} - n\phi_{B,n}) + K_{m-n+1}(\kappa L) \cos(m\phi_{A,m} + n\phi_{B,n})] \tag{5.14}$$

$$Y_{m,n} = -\frac{\pi}{2}[K_{m+n+1}(\kappa L) \sin(m\phi_{A,m} - n\phi_{B,n}) - K_{m-n-1}(\kappa L) \sin(m\phi_{A,m} + n\phi_{B,n})] \\ + \frac{\pi}{2}[K_{m+n-1}(\kappa L) \sin(m\phi_{A,m} - n\phi_{B,n}) - K_{m-n+1}(\kappa L) \sin(m\phi_{A,m} + n\phi_{B,n})] \tag{5.15}$$

In Appendix C we prove that Eqs. (5.14) and (5.15) are valid also for $n = 0$ and $n = 1$.

The obtained formulae for the force and torque coefficients give possibility to derive the respective asymptotic expression for the electrostatic interaction energy.

## 6. Asymptotic expression for the interaction energy and stability of quasi-equilibrium positions

Different approaches for the calculation of the interaction energy between charged particles can be found in the literature [16,19,22,23]. All of them contain integrals over the volume of the solution of the PBE and they are not applicable for the calculation of asymptotic expressions. In our case, the alternative force approach is the most transparent. In the 2D case the function $U$, which describes the interaction energy between two charged cylinders, has the following meaning. If the charged cylinder $A$ is fixed, then the cylinder $B$ has the following degrees of freedom: the position of the mass center $O_B$ can move in the horizontal plane (Fig. 3); the phase shift angles can change. The partial derivatives of $U$ with respect to the degrees of freedom (taken with an opposite sign) must give the respective components of the interaction force and torque.

**Theorem 1.** The asymptotic expression for the interaction energy between two charged cylinders, $U$, in the 2D case reads:

$$\frac{U}{\varepsilon_0\varepsilon_r W} = \sum_{m=0}^{\infty}\sum_{n=0}^{\infty} A_m B_n \pi\left[K_{m+n}(\kappa L)\cos(m\phi_{A,m} - n\phi_{B,n}) + K_{m-n}(\kappa L)\cos(m\phi_{A,m} + n\phi_{B,n})\right] \tag{6.1}$$

where $L$ is the distance between their centers $O_A$ and $O_B$.

**Proof.** We calculate the partial derivative of $-U$ with respect to the degree of freedom, $-\phi_{B,j}$:

$$\frac{\partial}{\partial \phi_{B,j}}\left(\frac{U}{\varepsilon_0\varepsilon_r W}\right) = B_j \sum_{m=0}^{\infty} A_m \pi j\left[K_{m+j}(\kappa L)\sin(m\phi_{A,m} - j\phi_{B,n}) - K_{m-j}(\kappa L)\sin(m\phi_{A,m} + j\phi_{B,n})\right] \tag{6.2}$$

where the sign minus for $\phi_{B,j}$ is taken because of the opposite orientation of the polar angle (see Fig. 3). The comparison between Eqs. (5.12) and (6.2) shows that the respective derivative of the interaction energy gives the components of the torque.

The partial derivative of $-U$ with respect to $x$ reads:

$$-\frac{\partial}{\partial x}\left(\frac{U}{\varepsilon_0\varepsilon_r W}\right) = -\pi\kappa \sum_{m=0}^{\infty}\sum_{n=0}^{\infty} A_m B_n K'_{m+n}(\kappa L)\cos\left(m\phi_{A,m} - n\phi_{B,n}\right) - \pi\kappa \sum_{m=0}^{\infty}\sum_{n=0}^{\infty} A_m B_n K'_{m-n}(\kappa L)\cos(m\phi_{A,m} + n\phi_{B,n}) \tag{6.3}$$

see Fig. 3. Using the formula, $K_{n-1} + K_{n+1} = -2K'$, Eqs. (4.12) and (5.14), we transform Eq. (6.3) to the following result:

$$-\frac{\partial U}{\partial x} = \varepsilon_0\varepsilon_r W\kappa \sum_{m=0}^{\infty}\sum_{n=0}^{\infty} A_m B_n X_{m,n} = \mathbf{F}_B \cdot \mathbf{e}_x \tag{6.4}$$

When the partial derivative of the function $-U$ with respect to $y$ is calculated all other degrees of freedom must be constants. Thus, if the position of center $O_B$ is shifted by $\mathrm{d}y > 0$ along the $y$-axis, then the distance $L + \mathrm{d}L$ increases, the phase shifts $\phi_{A,m} + \mathrm{d}\phi_{A,m}$ decrease, and the phase shifts $\phi_{B,n} + \mathrm{d}\phi_{B,n}$ increase (see Fig. 5). Therefore,

$$-\left.\frac{\partial U}{\partial y}\right|_{y=0} = -\left.\left(\frac{\partial U}{\partial L}\frac{\partial L}{\partial y} + \frac{\partial U}{\partial \phi_{A,m}}\frac{\partial \phi_{A,m}}{\partial y} + \frac{\partial U}{\partial \phi_{B,n}}\frac{\partial \phi_{B,n}}{\partial y}\right)\right|_{y=0} \tag{6.5}$$

From Fig. 5 one calculates that:

$$\left.\frac{\partial L}{\partial y}\right|_{y=0} = 0, \quad \left.\frac{\partial \phi_{A,m}}{\partial y}\right|_{y=0} = -\frac{1}{L}, \quad \left.\frac{\partial \phi_{B,n}}{\partial y}\right|_{y=0} = \frac{1}{L} \tag{6.6}$$

Substituting the Eqs. (6.1) and (6.6) in Eq. (6.5), we obtain the following expression:

$$\begin{aligned}-\left.\frac{\partial U}{\partial y}\right|_{y=0} &= -\varepsilon_0\varepsilon_r W \sum_{m=0}^{\infty}\sum_{n=0}^{\infty} A_m B_n \pi K_{m+n}(\kappa L)\frac{m+n}{L}\sin(m\phi_{A,m} - n\phi_{B,n}) \\ &\quad - \varepsilon_0\varepsilon_r W \sum_{m=0}^{\infty}\sum_{n=0}^{\infty} A_m B_n \pi K_{m-n}(\kappa L)\frac{m-n}{L}\sin(m\phi_{A,m} + n\phi_{B,n})\end{aligned} \tag{6.7}$$

Using the formula, $2nK_n(\kappa L) = \kappa L[K_{n+1}(\kappa L) - K_{n-1}(\kappa L)]$, Eqs. (4.12) and (5.15), one reduces Eq. (6.7) to the following result:

$$-\frac{\partial U}{\partial y} = \varepsilon_0\varepsilon_r W\kappa \sum_{m=0}^{\infty}\sum_{n=0}^{\infty} A_m B_n Y_{m,n} = \mathbf{F}_B \cdot \mathbf{e}_y \tag{6.8}$$

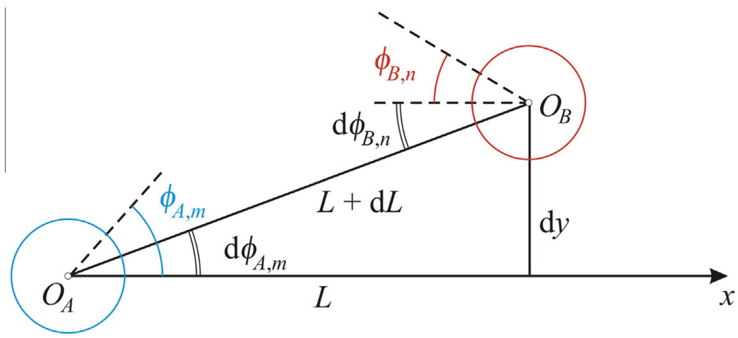


**Fig. 5.** Small variation of the position of center $O_B$ along the $y$-axis by $\mathrm{d}y > 0$. The center to center distance becomes $L + \mathrm{d}L$, the phase shift angles change and they are equal to $\phi_{A,m} + \mathrm{d}\phi_{A,m}$ and $\phi_{B,n} + \mathrm{d}\phi_{B,n}$, respectively.

Thus the partial derivatives of $-U$ with respect to the degree of freedom give the respective components of the interaction force and torque. □

If the cylinders are free to rotate and move, then the quasi-equilibrium state is defined to be the orientation, at which the torque and the $y$-component of the force are equal to zero. In the quasi-equilibrium state only the direct interaction force is different than zero.

*Charge-charge interaction.* For a charge-charge interaction $n = m = 0$ and only the direct force, $\mathbf{F}_B{\cdot}\mathbf{e}_x$, is different than zero [5]:

$$\frac{\mathbf{F}_B\cdot\mathbf{e}_x}{\varepsilon_0\varepsilon_r\kappa W}=2\pi\frac{\psi_{A,0}\psi_{B,0}}{K_0(\kappa a_A)K_0(\kappa a_B)}K_1(\kappa L) \tag{6.9}$$

see Eqs. (4.12,5.12,5.14) and (5.15). Thus, for $\psi_{A,0}\psi_{B,0} > 0$ the interaction force is repulsive and for $\psi_{A,0}\psi_{B,0} < 0$ – it is attractive.

**Theorem 2.** The stable quasi-equilibrium state of the multipole–multipole interaction ($n \neq 0$ or $m \neq 0$) corresponds to the direct attractive force and to the minimum of the interaction energy, $U$.

**Proof.** *Multipole-charge interaction* ($n = 0$ *and* $m > 0$): The interaction torque is equal to zero, see Eq. (5.12). From Eqs. (4.12,5.14) and (5.15) one obtains the following formulae:

$$\frac{\mathbf{F}_B\cdot\mathbf{e}_x}{\varepsilon_0\varepsilon_r\kappa W}=-2\pi\frac{\psi_{A,m}\psi_{B,0}}{K_m(\kappa a_A)K_0(\kappa a_B)}K'_m(\kappa L)\cos(m\phi_{A,m}) \tag{6.10}$$

$$\frac{\mathbf{F}_B\cdot\mathbf{e}_y}{\varepsilon_0\varepsilon_r\kappa W}=-2\pi\frac{\psi_{A,m}\psi_{B,0}}{K_m(\kappa a_A)K_0(\kappa a_B)}\frac{mK_m(\kappa L)}{\kappa L}\sin(m\phi_{A,m}) \tag{6.11}$$

Therefore, for $\psi_{A,m}\psi_{B,0}\cos(m\phi_{A,m}) > 0$ the direct interaction force is repulsive and for $\psi_{A,m}\psi_{B,0}\cos(m\phi_{A,m}) < 0$ – it is attractive.

Two different quasi-equilibrium states are possible: (i) $\phi_{A,m} = 0$; (ii) $m\phi_{A,m} = \pi$. In the case of repulsive direct interactions small perturbations of the “charge” cylinder positions in the $y$-direction lead to the appearance of $\mathbf{F}_B{\cdot}\mathbf{e}_y$, which increases the perturbation magnitude (see for example Fig. 6a). Thus the repulsive quasi-equilibrium state is unstable. In the opposite case of an attraction, the force $\mathbf{F}_B{\cdot}\mathbf{e}_y$ tends to decrease the magnitude of perturbations (see Fig. 6b). Therefore, the attractive direct interactions are stable.

For multipole-charge interactions the energy $U$ is calculated from the following expression:

$$\frac{U}{\varepsilon_0\varepsilon_r W}=2\pi\frac{\psi_{A,m}\psi_{B,0}}{K_m(\kappa a_A)K_0(\kappa a_B)}K_m(\kappa L)\cos(m\phi_{A,m}) \tag{6.12}$$

see Eq. (6.1). Therefore, the stable quasi-equilibrium state corresponds to the minimum of the interaction energy $U$.

*Multipole–multipole interaction* ($m > 0$ *and* $n > 0$): Using the Eqs. (4.12,5.12,5.14) and (5.15) we represent the expression for the interaction force and torque in the following form:

$$\frac{\mathbf{F}_B\cdot\mathbf{e}_x}{\varepsilon_0\varepsilon_r\kappa W}=-\pi\frac{\psi_{A,m}\psi_{B,n}}{K_m(\kappa a_A)K_n(\kappa a_B)}K'_{m+n}(\kappa L)\cos(m\phi_{A,m}-n\phi_{B,n})-\pi\frac{\psi_{A,m}\psi_{B,n}}{K_m(\kappa a_A)K_n(\kappa a_B)}K'_{m-n}(\kappa L)\cos(m\phi_{A,m}+n\phi_{B,n}) \tag{6.13}$$

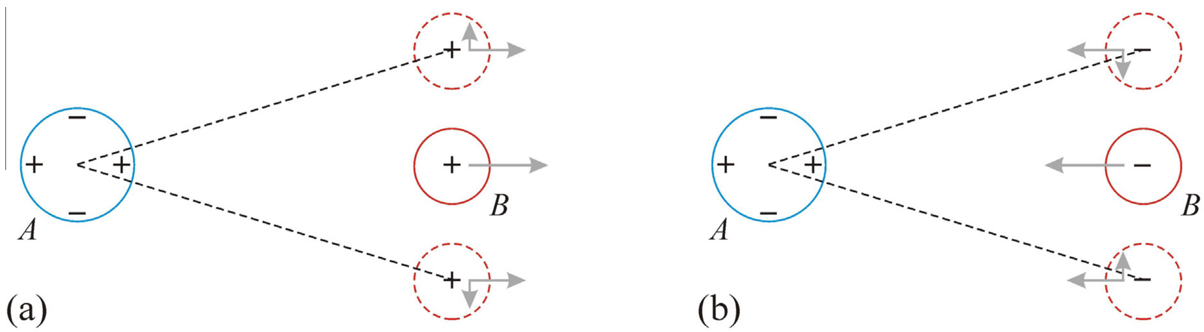


**Fig. 6.** Two different quasi-equilibrium states of quadrupole-charge: (a) unstable repulsive interactions; (b) stable attractive interactions.

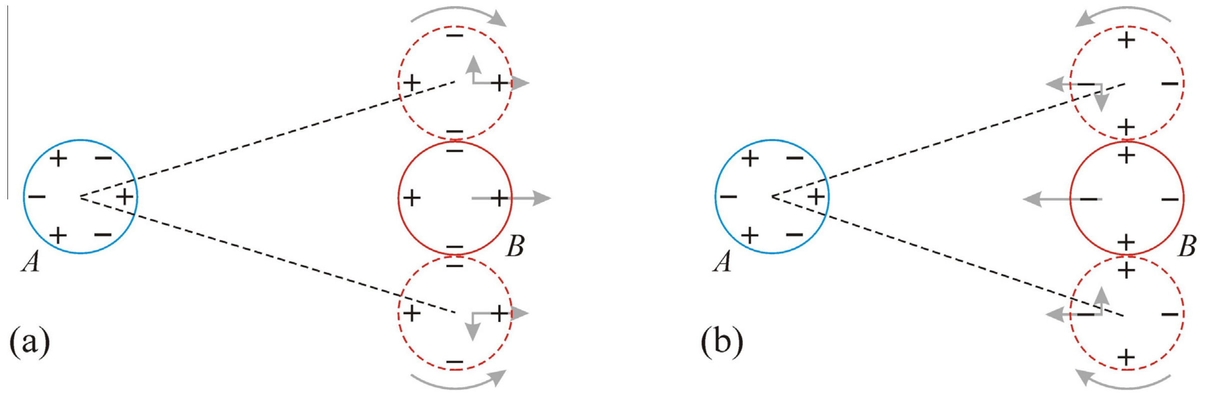


**Fig. 7.** Two different quasi-equilibrium states of hexapole–quadrupole: (a) unstable repulsive interactions; (b) stable attractive interactions.

$$\frac{\mathbf{F}_B \cdot \mathbf{e}_y}{\varepsilon_0\varepsilon_r\kappa W} = -\pi\frac{\psi_{A,m}\psi_{B,n}}{K_m(\kappa a_A)K_n(\kappa a_B)}(m+n)\frac{K_{m+n}(\kappa L)}{\kappa L}\sin(m\phi_{A,m} - n\phi_{B,n}) - \pi\frac{\psi_{A,m}\psi_{B,n}}{K_m(\kappa a_A)K_n(\kappa a_B)}(m-n)\frac{K_{m-n}(\kappa L)}{\kappa L}\sin(m\phi_{A,m} + n\phi_{B,n}) \tag{6.14}$$

$$\frac{\mathbf{T}_B \cdot \mathbf{e}_z}{\varepsilon_0\varepsilon_r W} = \pi\frac{\psi_{A,m}\psi_{B,n}}{K_m(\kappa a_A)K_n(\kappa a_B)}nK_{m+n}(\kappa L)\sin(m\phi_{A,m} - n\phi_{B,n}) - \pi\frac{\psi_{A,m}\psi_{B,n}}{K_m(\kappa a_A)K_n(\kappa a_B)}nK_{m-n}(\kappa L)\sin(m\phi_{A,m} + n\phi_{B,n}) \tag{6.15}$$

For the quasi-equilibrium orientation $\mathbf{F}_B{\cdot}\mathbf{e}_y = 0$ and $\mathbf{T}_B{\cdot}\mathbf{e}_z = 0$, so that using the Eqs. (6.14) and (6.15), one obtains the linear system of equations:

$$\begin{aligned} &(m+n)K_{m+n}(\kappa L)\sin(m\phi_{A,m} - n\phi_{B,n}) + (m-n)K_{m-n}(\kappa L)\sin(m\phi_{A,m} + n\phi_{B,n}) = 0 \\ &nK_{m+n}(\kappa L)\sin(m\phi_{A,m} - n\phi_{B,n}) - nK_{m-n}(\kappa L)\sin(m\phi_{A,m} + n\phi_{B,n}) = 0 \end{aligned} \tag{6.16}$$

This system of equations has only a trivial solution: $\sin(m\phi_{A,m} - n\phi_{B,n}) = 0$ and $\sin(m\phi_{A,m} + n\phi_{B,n}) = 0$. Therefore: $m\phi_{A,m} = 0, \pm\pi, \pm 2\pi, \ldots$; $n\phi_{B,n} = 0, \pm\pi, \pm 2\pi, \ldots$; and $\cos(m\phi_{A,m} - n\phi_{B,n}) = \cos(m\phi_{A,m} + n\phi_{B,n}) = \pm 1$. If the maximums or minimums of both $\psi_A$ and $\psi_B$ around the surfaces of cylinders are faced each other, then the interaction force is positive (repulsion). If the maximum (minimum) of $\psi_A$ is faced to the minimum (maximum) of $\psi_B$, then the respective force is negative (attraction). The magnitude of the interaction force in the quasi-equilibrium is calculated from the simple formula:

$$\frac{|\mathbf{F}_B \cdot \mathbf{e}_x|}{\varepsilon_0\varepsilon_r\kappa W} = \pi\frac{|\psi_{A,m}\psi_{B,n}|}{K_m(\kappa a_A)K_n(\kappa a_B)}|K'_{m+n}(\kappa L) + K'_{m-n}(\kappa L)| \tag{6.17}$$

From Eqs. (6.9) and (6.10) one sees that this formula is general and it is valid for all values of $m$ and $n$.

Fig. 7 illustrates the stability of quasi-equilibrium states. If the interaction force is repulsive, then the small perturbations of the multipole $B$ position along the $y$-direction lead to the appearance of force and torque, which accelerate the instability (Fig. 7a). For an attractive interaction force the respective small perturbations will decrease because of the stabilizing effects of both $\mathbf{F}_B{\cdot}\mathbf{e}_y$ and $\mathbf{T}_B{\cdot}\mathbf{e}_z$ (Fig. 7b). From Eq. (6.1) it follows, that the interaction energy has a minimum (maximum) at the stable (unstable) quasi-equilibrium state.

## 7. Conclusions

In this paper the asymptotic expressions for the interaction force and torque between two parallel charged cylinders immersed in an ionic solution are derived in the case of large distances between them. The ionic solution is modeled using the Poisson–Boltzmann equation. The results are obtained in a close form applying the Graff addition theorem and they are expressed in terms of the modified Bessel function of the second kind.

The proved asymptotic formula for the electrostatic interaction energy between cylinders gives possibility to deduce that the stable quasi-equilibrium state corresponds to the attraction between multipoles and to the minimum of the interaction energy.

This study opens the possibility for calculations of the many charged rodlike particles problem in dilute regime.

## Acknowledgements

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## Appendix A. Conservation of linear and angular momentums

Substituting the Eq. (2.6) in Eq. (2.5), we present the components of the pressure tensor, $P_{ij}$, in Cartesian coordinate system $Ox_1x_2x_3$ in the following form:

$$P_{ij} = \left\{ k_B T \sum_{s=1}^{N} n_{s\infty} \left[ \exp(-\frac{ez_s\psi}{k_B T}) - 1 \right] + \frac{\varepsilon_0 \varepsilon_r}{2} \frac{\partial \psi}{\partial x_k} \frac{\partial \psi}{\partial x_k} \right\} \delta_{ij} - \varepsilon_0 \varepsilon_r \frac{\partial \psi}{\partial x_i} \frac{\partial \psi}{\partial x_j} \tag{A.1}$$

where $\delta_{ij}$ is the Kronecker delta ($i,j,k = 1,2,3$) [18]. Taking the divergence from Eq. (A.1), one obtains:

$$\begin{aligned} \frac{\partial P_{ij}}{\partial x_i} &= \frac{\partial}{\partial x_j} \left\{ k_B T \sum_{s=1}^{N} n_{s\infty} \left[ \exp\left( -\frac{ez_s\psi}{k_B T} \right) - 1 \right] + \frac{\varepsilon_0 \varepsilon_r}{2} \frac{\partial \psi}{\partial x_k} \frac{\partial \psi}{\partial x_k} \right\} - \varepsilon_0 \varepsilon_r \frac{\partial^2 \psi}{\partial x_i \partial x_i} \frac{\partial \psi}{\partial x_j} - \varepsilon_0 \varepsilon_r \frac{\partial \psi}{\partial x_i} \frac{\partial^2 \psi}{\partial x_i \partial x_j} \\ &= -\sum_{s=1}^{N} ez_s n_{s\infty} \exp\left( -\frac{ez_s\psi}{k_B T} \right) \frac{\partial \psi}{\partial x_j} - \varepsilon_0 \varepsilon_r \frac{\partial^2 \psi}{\partial x_i \partial x_i} \frac{\partial \psi}{\partial x_j} \end{aligned} \tag{A.2}$$

where the Einstein summation convention [18] is applied. Finally, from the PBE, Eqs. (2.3) and (A.2) we derive that:

$$\frac{\partial P_{ij}}{\partial x_i} = -\varepsilon_0 \varepsilon_r \frac{\partial \psi}{\partial x_j} \left[ \frac{\partial^2 \psi}{\partial x_i \partial x_i} + \frac{e}{\varepsilon_0 \varepsilon_r} \sum_{s=1}^{N} z_s n_{s\infty} \exp\left( -\frac{ez_s\psi}{k_B T} \right) \right] = 0 \tag{A.3}$$

The cross product $\mathbf{P} \times \mathbf{r}$ is a tensor with components $\varepsilon_{njk} P_{ij} x_k$, where $\varepsilon_{njk}$ is the Levi–Civita symbol [18]. Thus the divergence from $\mathbf{P} \times \mathbf{r}$ is:

$$\frac{\partial}{\partial x_i} (\varepsilon_{njk} P_{ij} x_k) = \varepsilon_{njk} x_k \frac{\partial P_{ij}}{\partial x_i} + \varepsilon_{njk} P_{ij} \delta_{ik} \tag{A.4}$$

Using Eq. (A.3) and the symmetry of the pressure tensor one proves that:

$$\frac{\partial}{\partial x_i} (\varepsilon_{njk} P_{ij} x_k) = \varepsilon_{njk} P_{kj} = (\varepsilon_{njk} + \varepsilon_{nkj}) \frac{P_{kj}}{2} = 0 \tag{A.5}$$

If the components of the pressure tensor, $\mathbf{P}$, are given by the definition:

$$P_{ij} = \frac{\varepsilon_0 \varepsilon_r}{2} \left( \kappa^2 \psi^2 + \frac{\partial \psi}{\partial x_k} \frac{\partial \psi}{\partial x_k} \right) \delta_{ij} - \varepsilon_0 \varepsilon_r \frac{\partial \psi}{\partial x_i} \frac{\partial \psi}{\partial x_j} \tag{A.6}$$

see Eq. (3.5), then the divergence of $\mathbf{P}$ leads to the expression:

$$\frac{\partial P_{ij}}{\partial x_i} = -\varepsilon_0 \varepsilon_r \frac{\partial \psi}{\partial x_j} \left( \frac{\partial^2 \psi}{\partial x_i \partial x_i} - \kappa^2 \psi \right) \tag{A.7}$$

Therefore, $\nabla \cdot \mathbf{P} = 0$ in the frame of the linear PBE, Eq. (2.10), and respectively $\nabla \cdot (\mathbf{P} \times \mathbf{r}) = 0$.

The divergence from the pressure tensor accounting for the interactions, defined by Eq. (3.6) and written in the Cartesian coordinates, reads:

$$\frac{\partial P_{AB,ij}}{\partial x_i} = \varepsilon_0 \varepsilon_r \frac{\partial}{\partial x_j} \left( \kappa^2 \psi_A \psi_B + \frac{\partial \psi_A}{\partial x_k} \frac{\partial \psi_B}{\partial x_k} \right) - \varepsilon_0 \varepsilon_r \left( \frac{\partial^2 \psi_A}{\partial x_i \partial x_i} \frac{\partial \psi_B}{\partial x_j} + \frac{\partial \psi_A}{\partial x_i} \frac{\partial^2 \psi_B}{\partial x_i \partial x_j} + \frac{\partial^2 \psi_A}{\partial x_i \partial x_j} \frac{\partial \psi_B}{\partial x_i} + \frac{\partial \psi_A}{\partial x_j} \frac{\partial^2 \psi_B}{\partial x_i \partial x_i} \right) \tag{A.8}$$

After simple transformations of the right-hand side of Eq. (A.8), one obtains:

$$\frac{\partial P_{AB,ij}}{\partial x_i} = \varepsilon_0 \varepsilon_r \frac{\partial \psi_B}{\partial x_j} \left( \kappa^2 \psi_A - \frac{\partial^2 \psi_A}{\partial x_i \partial x_i} \right) + \varepsilon_0 \varepsilon_r \frac{\partial \psi_A}{\partial x_j} \left( \kappa^2 \psi_B - \frac{\partial^2 \psi_B}{\partial x_i \partial x_i} \right) \tag{A.9}$$

The functions $\psi_A$ and $\psi_B$ obey the linear PBE, Eq. (2.10), so that $\nabla \cdot \mathbf{P}_{AB} = 0$ and respectively $\nabla \cdot (\mathbf{P}_{AB} \times \mathbf{r}) = 0$.

## Appendix B. Simplified expressions for dimensionless coefficients $F_{m,n}$ and $T_{m,n}$

The complex form of function $f_{B,n}$ defined by Eq. (4.10) is:

$$f_{B,n} = \frac{K_n(\beta)}{2} [\exp(in\phi_B - in\phi_{B,n}) + \exp(in\phi_{B,n} - in\phi_B)] \tag{B.1}$$

Substituting the Eq. (B.1) in the integrand of the right-hand side of Eq. (5.5), one obtains

$$\begin{aligned} \beta \frac{\partial f_{A,m}}{\partial \beta} \frac{\partial f_{B,n}}{\partial \phi_B} + \beta \frac{\partial f_{A,m}}{\partial \phi_B} \frac{\partial f_{B,n}}{\partial \beta} = \frac{\beta}{2} \frac{\partial f_{A,m}}{\partial \phi_B} K_n'(\beta) [\exp(in\phi_B - in\phi_{B,n}) + \exp(in\phi_{B,n} - in\phi_B)] + \frac{in\beta}{2} \frac{\partial f_{A,m}}{\partial \beta} K_n(\beta) [\exp(in\phi_B - in\phi_{B,n}) \\ - \exp(in\phi_{B,n} - in\phi_B)] \end{aligned} \tag{B.2}$$

where $K_n'(\beta) \equiv dK_n(\beta)/d\beta$. From Eqs. (B.2) and (5.5) we obtain the following result:

$$T_{m,n} = -\int_0^{2\pi} \frac{\beta}{2}\left[\frac{\partial f_{A,m}}{\partial\phi_B}K_n'(\beta) + in\frac{\partial f_{A,m}}{\partial\beta}K_n(\beta)\right]\Big|_{\beta=\delta} \exp(in\phi_B - in\phi_{B,n})d\phi_B$$
$$- \int_0^{2\pi} \frac{\beta}{2}\left[\frac{\partial f_{A,m}}{\partial\phi_B}K_n'(\beta) - in\frac{\partial f_{A,m}}{\partial\beta}K_n(\beta)\right]\Big|_{\beta=\delta} \exp(in\phi_{B,n} - in\phi_B)d\phi_B \tag{B.3}$$

Integrating by parts the terms containing $\partial f_{A,m}/\partial\phi_B$ in Eq. (B.3), we derive Eq. (5.7).

Substituting the Eq. (B.1) in the integrand of the right-hand side of Eq. (5.4) we derive the following relationship:

$$G \equiv \left(\beta f_{A,m}f_{B,n} + \frac{1}{\beta}\frac{\partial f_{A,m}}{\partial\phi_B}\frac{\partial f_{B,n}}{\partial\phi_B} - \beta\frac{\partial f_{A,m}}{\partial\beta}\frac{\partial f_{B,n}}{\partial\beta} + i\frac{\partial f_{A,m}}{\partial\beta}\frac{\partial f_{B,n}}{\partial\phi_B} + i\frac{\partial f_{A,m}}{\partial\phi_B}\frac{\partial f_{B,n}}{\partial\beta}\right)\exp(-i\phi_B)$$
$$= \beta f_{A,m}\frac{K_n(\beta)}{2}\left[\exp(in\phi_B - in\phi_{B,n}) + \exp(in\phi_{B,n} - in\phi_B)\right]\exp(-i\phi_B)$$
$$+\frac{in}{\beta}\frac{\partial f_{A,m}}{\partial\phi_B}\frac{K_n(\beta)}{2}\left[\exp(in\phi_B - in\phi_{B,n}) - \exp(in\phi_{B,n} - in\phi_B)\right]\exp(-i\phi_B)$$
$$-\beta\frac{\partial f_{A,m}}{\partial\beta}\frac{K_n'(\beta)}{2}\left[\exp(in\phi_B - in\phi_{B,n}) + \exp(in\phi_{B,n} - in\phi_B)\right]\exp(-i\phi_B)$$
$$-n\frac{\partial f_{A,m}}{\partial\beta}\frac{K_n(\beta)}{2}\left[\exp(in\phi_B - in\phi_{B,n}) - \exp(in\phi_{B,n} - in\phi_B)\right]\exp(-i\phi_B)$$
$$+i\frac{\partial f_{A,m}}{\partial\phi_B}\frac{K_n'(\beta)}{2}\left[\exp(in\phi_B - in\phi_{B,n}) + \exp(in\phi_{B,n} - in\phi_B)\right]\exp(-i\phi_B) \tag{B.4}$$

that is

$$G = \frac{1}{2}\left\{\beta f_{A,m}K_n(\beta) + \left(i\frac{\partial f_{A,m}}{\partial\phi_B} - \beta\frac{\partial f_{A,m}}{\partial\beta}\right)[K_n'(\beta) + \frac{n}{\beta}K_n(\beta)]\right\}\exp\left[i(n-1)\phi_B - in\phi_{B,n}\right]$$
$$+\frac{1}{2}\left\{\beta f_{A,m}K_n(\beta) + \left[i\frac{\partial f_{A,m}}{\partial\phi_B} - \beta\frac{\partial f_{A,m}}{\partial\beta}\right]\left[K_n'(\beta) - \frac{n}{\beta}K_n(\beta)\right]\right\}\exp[in\phi_{B,n} - i(n+1)\phi_B] \tag{B.5}$$

Finally, substituting the identities [18]

$$K_n'(\beta) + \frac{n}{\beta}K_n(\beta) = -K_{n-1}(\beta) \quad \text{and} \quad K_n'(\beta) - \frac{n}{\beta}K_n(\beta) = -K_{n+1}(\beta) \tag{B.6}$$

in Eq. (B.5), it results

$$G = \frac{1}{2}\left[\beta f_{A,m}K_n(\beta) + \left(\beta\frac{\partial f_{A,m}}{\partial\beta} - i\frac{\partial f_{A,m}}{\partial\phi_B}\right)K_{n-1}(\beta)\right]\exp\left[i(n-1)\phi_B - in\phi_{B,n})\right]$$
$$+\frac{1}{2}\left[\beta f_{A,m}K_n(\beta) + \left(\beta\frac{\partial f_{A,m}}{\partial\beta} - i\frac{\partial f_{A,m}}{\partial\phi_B}\right)K_{n+1}(\beta)\right]\exp\left[in\phi_{B,n} - i(n+1)\phi_B\right] \tag{B.7}$$

From Eqs. (5.4) and (B.7) one obtains the respective formula for $F_{m,n}$:

$$F_{m,n} = \int_0^{2\pi}\frac{1}{2}\left[\beta f_{A,m}K_n(\beta) + \left(\beta\frac{\partial f_{A,m}}{\partial\beta} - i\frac{\partial f_{A,m}}{\partial\phi_B}\right)K_{n-1}(\beta)\right]\Big|_{\beta=\delta}\exp[i(n-1)\phi_B - in\phi_{B,n}]d\phi_B$$
$$+\int_0^{2\pi}\frac{1}{2}\left[\beta f_{A,m}K_n(\beta) + \left(\beta\frac{\partial f_{A,m}}{\partial\beta} - i\frac{\partial f_{A,m}}{\partial\phi_B}\right)K_{n+1}(\beta)\right]\Big|_{\beta=\delta}\exp\left[in\phi_{B,n} - i(n+1)\phi_B\right]d\phi_B \tag{B.8}$$

Integrating by parts the terms containing $\partial f_{A,m}/\partial\phi_B$ in Eq. (B.8), we derive the following result:

$$F_{m,n} = \int_0^{2\pi}\frac{\beta}{2}\left\{f_{A,m}\left[K_n(\beta) - \frac{n-1}{\beta}K_{n-1}(\beta)\right] + \frac{\partial f_{A,m}}{\partial\beta}K_{n-1}(\beta)\right\}\Big|_{\beta=\delta}\exp\left[i(n-1)\phi_B - in\phi_{B,n}\right]d\phi_B$$
$$+\int_0^{2\pi}\frac{\beta}{2}\left\{f_{A,m}\left[K_n(\beta) + \frac{n+1}{\beta}K_{n+1}(\beta)\right] + \frac{\partial f_{A,m}}{\partial\beta}K_{n+1}(\beta)\right\}\Big|_{\beta=\delta}\exp[in\phi_{B,n} - i(n+1)\phi_B]d\phi_B \tag{B.9}$$

Using the formulae, Eq. (B.6), one represents Eq. (B.9) in the form of Eq. (5.6).

## Appendix C. Formulae for $F_{m,0}$ and $F_{m,1}$

In the case of $n = 0$ Eq. (5.6) is simplified to the following expression

$$F_{m,0} = \int_0^{2\pi}\beta\left[K_1(\beta)\frac{\partial f_{A,m}}{\partial\beta} - K_1'(\beta)f_{A,m}\right]\Big|_{\beta=\delta}\exp(-i\phi_B)d\phi_B \tag{C.1}$$

From the Graff theorem, Eq. (5.8), Eqs. (C.1) and (5.10) one obtains

$$F_{m,0} = K_{m+1}(\kappa L)C_1 \int_0^{2\pi} \cos(\phi_B - m\phi_{A,m}) \exp(-i\phi_B) d\phi_B + K_{m-1}(\kappa L)C_1 \int_0^{2\pi} \cos(\phi_B + m\phi_{A,m}) \exp(-i\phi_B) d\phi_B \tag{C.2}$$

where $C_1 = 1$. The calculation of integrals in the right-hand side of Eq. (C.2) and subsequent separation of the real and imaginary pasts of the complex force coefficients lead to the formulae:

$$X_{m,0} = \pi[K_{m+1}(\kappa L) + K_{m-1}(\kappa L)] \cos(m\phi_{A,m}) \tag{C.3}$$

$$Y_{m,0} = -\pi[K_{m+1}(\kappa L) - K_{m-1}(\kappa L)] \sin(m\phi_{A,m}) \tag{C.4}$$

Therefore, Eqs. (5.14) and (5.15) for $n = 0$ define the values of the force coefficients, see Eqs. (C.3) and (C.4).

In the case of $n = 1$ Eq. (5.6) is reduced to the following result:

$$F_{m,1} = \int_0^{2\pi} \frac{\beta}{2} \left[ K_0(\beta) \frac{\partial f_{A,m}}{\partial \beta} - K_0'(\beta) f_{A,m} \right] \Big|_{\beta=\delta} \exp(-i\phi_{B,n}) d\phi_B + \int_0^{2\pi} \frac{\beta}{2} \left[ K_2(\beta) \frac{\partial f_{A,m}}{\partial \beta} - K_2'(\beta) f_{A,m} \right] \Big|_{\beta=\delta} \exp(i\phi_{B,n} - 2i\phi_B) d\phi_B \tag{C.5}$$

In the first integral in the right-hand side of Eq. (C.5) only the zero term of the Fourier expansion, Eq. (5.8), gives contribution. In the second integral – only the terms corresponding to $j = \pm 2$ are different than zero. Therefore,

$$\begin{aligned} F_{m,1} &= \pi K_m(\kappa L) \cos(m\phi_{A,m}) \exp(-i\phi_{B,n}) C_0 + \frac{K_{m+2}(\kappa L)}{2} C_2 \int_0^{2\pi} \cos(2\phi_B - m\phi_{A,m}) \exp(i\phi_{B,n} - 2i\phi_B) d\phi_B \\ &\quad + \frac{K_{m-2}(\kappa L)}{2} C_2 \int_0^{2\pi} \cos(2\phi_B + m\phi_{A,m}) \exp(i\phi_{B,n} - 2i\phi_B) d\phi_B \end{aligned} \tag{C.6}$$

where $C_0 = 1$ and $C_2 = 1$. After the calculations of the integrals in Eq. (C.6) one obtains:

$$F_{m,1} = \pi K_m(\kappa L) \cos(m\phi_{A,m}) \exp(-i\phi_{B,n}) + \pi \frac{K_{m+2}(\kappa L)}{2} \exp(i\phi_{B,n} - im\phi_{A,m}) + \pi \frac{K_{m-2}(\kappa L)}{2} \exp(i\phi_{B,n} + im\phi_{A,m}) \tag{C.7}$$

Therefore, the real and imaginary parts of $F_{m,1}$ are equal to

$$X_{m,1} = \frac{\pi}{2} K_m(\kappa L) [\cos(m\phi_{A,m} + \phi_{B,n}) + \cos(m\phi_{A,m} - \phi_{B,n})] + \frac{\pi}{2} K_{m-2}(\kappa L) \cos(m\phi_{A,m} + \phi_{B,n}) + \frac{\pi}{2} K_{m+2}(\kappa L) \cos(m\phi_{A,m} - \phi_{B,n}) \tag{C.8}$$

$$Y_{m,1} = \frac{\pi}{2} K_m(\kappa L) [\sin(m\phi_{A,m} - \phi_{B,n}) - \sin(m\phi_{A,m} + \phi_{B,n})] + \frac{\pi}{2} K_{m-2}(\kappa L) \sin(m\phi_{A,m} + \phi_{B,n}) - \frac{\pi}{2} K_{m+2}(\kappa L) \sin(m\phi_{A,m} - \phi_{B,n}) \tag{C.9}$$

One sees that Eqs. (C.8) and (C.9) are identical with Eqs. (5.14) and (5.15) written for $n = 1$.

## References

[1] B.V. Derjaguin, L. Landau, Theory of the stability of strongly charged lyophobic sols and of the adhesion of strongly charged particles in solutions of electrolytes, Acta Phys. Chim. URSS 14 (1941) 633–662.
[2] E.J.W. Verwey, J.Th.G. Overbeek, Theory of the Stability of Lyophobic Colloids, Elsevier, Amsterdam, 1948.
[3] J.N. Israelashvili, Intermolecular and Surface Forces, third ed., Academic Press, Burlington, MA, 2011.
[4] W.B. Russel, D.A. Saville, W.R. Schowalter, Colloidal Dispersions, Cambridge Univ. Press, New York, 1989.
[5] G. Lamm, The Poisson–Boltzmann equation, in: K.B. Lipkowitz, R. Larter, T.R. Cundari (Eds.), Reviews in Computational Chemistry, vol. 19, John Wiley & Sons Inc., Hoboken, NJ, 2003, pp. 147–365.
[6] H. Ohshima, Electrostatic interaction between two parallel cylinders, Colloid Polym. Sci. 274 (1996) 1176–1182.
[7] H. Ohshima, A. Hyono, Electrostatic interaction between two cylindrical soft particles, J. Colloid Interface Sci. 333 (2009) 202–208.
[8] S.L. Brenner, D.A. McQuarrie, Force balances in systems fo cylindrical polyelectrolytes, Biophys. J. 13 (1973) 301–331.
[9] S.L. Brenner, V.A. Parsegian, A physical method for deriving the electrostatic interaction between rod-like polyions at all mutual angles, Biophys. J. 14 (1974) 327–334.
[10] R. Podgornik, V.A. Parsegian, Charge-fluctuation forces between rodlike polyelectrolytes: pairwise summability reexamined, Phys. Rev. Lett. 80 (1998) 1560–1563.
[11] D.C. Rau, B. Lee, V.A. Parsegian, Measurement of the repulsive force between polyelectrolyte molecules in ionic solution: Hydration forces between parallel DNA double helices, Proc. Natl. Acad. Sci. USA 81 (1984) 2621–2625.
[12] A.A. Kornyshev, S. Leikin, Symmetry law for interaction between helical molecules, Biophys. J. 75 (1998) 2513–2519.
[13] A.A. Kornyshev, S. Leikin, Theory of interaction between helical molecules, J. Chem. Phys. 107 (1997) 3656–3674.
[14] A.A. Kornyshev, S. Leikin, Electrostatic interaction between long, rigid helical macromolecules at all interaxial angles, Phys. Rev. E 62 (2000) 2576–2596.
[15] D. Harries, Solving the Poisson–Boltzmann equation for two parallel cylinders, Langmuir 14 (1998) 3149–3152.
[16] L.D. Landau, E.M. Lifshitz, L.P. Pitaevskii, Electrodynamics of Continuous Media, second ed., Pergamon, Oxford, 1984.
[17] P.A. Kralchevsky, K.D. Danov, G. Broze, A. Mehreteab, Thermodynamics of ionic surfactant adsorption with account for the counterion binding: effect of salts of various valency, Langmuir 15 (1999) 2351–2365.

[18] G.A. Korn, T.M. Korn, Mathematical Handbook for Scientists and Engineers: Definitions, Theorems, and Formulas for Reference and Review, second ed., Dover Publications, New York, 2000.
[19] T.B. Jones, Electromechanics of Particles, Cambridge Univ. Press, Cambridge, 2005.
[20] K.D. Danov, E.S. Basheva, P.A. Kralchevsky, P. Ananthapadmanabhan, A. Lips, The metastable states of foam films containing electrically charged micelles or particles: Experiment and quantitative interpretation, Adv. Colloid Interface Sci. 168 (2011) 50–70.
[21] H. Bateman, Higher Transcendental Functions, vol. II, McGraw-Hill Inc., New York, 1953.
[22] J.T.G. Overbeek, The role of energy and entropy in the electrical double layer, Colloids Surf. 51 (1990) 61–75.
[23] A. Ciach, W.T. Góźdź, G. Stell, Mesoscopic theory for size- and charge-asymmetric ionic system: I. the case of extreme asymmetry, J. Phys. Condens. Matter 18 (2006) 1629–1648.