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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, ψ, is small. For small values of ψ 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, ψ, 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 ∇ denotes the del operator, ε_0 is the vacuum dielectric permittivity, ε_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, ρ_{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]:

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

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]:

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

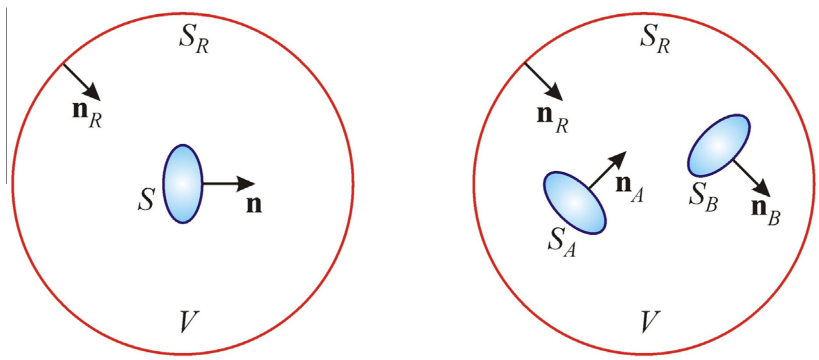

Fig. 1. One or two charged particles in an ionic solution. The hypothetical surface, S_R, encircles the particles at large distances.