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About the interaction of charged spheroidal particles in an electrolyte solution

© S.I. Grashchenkov

Pskov State University,
180000 Pskov, Russia
e-mail: grasi@mail.ru

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Electrostatic interaction of two charged spheroidal macroparticles in an aqueous solution of a symmetric electrolyte is analyzed within the linearized Poisson-Boltzmann model under the condition of a constant charge on their surfaces.It is assumed that the particles have a common axis of symmetry. Interparticle forces are calculated through finite-element method in the regimes of weak and moderate screening in the absence of external field.

Keywords: linearized Poisson-Boltzmann model, two charged microparticles, spheroidal microparticles, colloidal particles, constant charge boundary condition.

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Introduction

When a colloidal particle interacts with an electrolyte solution, a number of processes occur that lead to the occurrence of a charge on its surface [1]. In liquid solutions, a charged particle is surrounded by a diffusive ion layer that screens the electric potential on its surface. Consideration of screening in the interaction of charged particles plays an important role in various technical and biological systems. The distribution of the φ potential in the vicinity of particles can be searched based on the linearized Poisson-Boltzmann equation or the Debye–Hückel equation [3] if the electric field potentials at the considered points of the symmetric electrolyte are sufficiently small [2]:

$$\Delta\varphi - k_{\mathrm{D}}^2\varphi = 0, \tag{1}$$

where φ — potential distribution in the vicinity of particles, k_{D} — screening constant (inverse Debye radius). A typical condition for the applicability of this equation is the calculation of the potential distribution in a colloidal system in which the potentials on the surfaces of particles do not exceed $k_{\mathrm{B}}T/e$, where k_{B} —Boltzmann constant, T — absolute temperature, e — elementary charge (temperature 25°C corresponds to potential 26 mV) [1,2]. Obviously, the potential on the surfaces of particles also increases with the increase of temperature to the value at which the equation (1) becomes applicable. The presence of a charge on the surfaces of particles results in the emergence of electrostatic forces of interaction between them. The forces of interaction between colloidal particles in symmetrical ionic solutions have a significant effect on the properties of biological fluids, pharmaceuticals, food, etc. Therefore, a large number of papers have been devoted to calculating the forces of electrostatic interaction between two macroparticles based on equation (1). A fairly complete overview of such studies is provided in [4]. It should be noted that the distribution of potentials on the surface of particles depends on the distance between them, their sizes, velocities, and the characteristic relaxation time of the surface charge [5], and the search for such a distribution is a separate problem. Therefore, the calculation of interaction forces is often limited to two cases: a constant potential on the surfaces of particles and a constant charge of particles. Let us consider in more detail these conditions for the case of particles in aqueous solutions of a symmetrical electrolyte. In general, the boundary conditions on the surface of each particle have the form

$$\varphi = \varphi_i,$$
$$\left(\nabla\varphi - \frac{\varepsilon_i}{\varepsilon}\nabla\varphi_i\right)\mathbf{n} = \frac{\sigma}{\varepsilon\varepsilon_0}, \tag{2}$$

where $\mathbf{n}$ —the unit vector of the normal to the surface element directed into the particle, ε_0 —the electric constant, ε — the dielectric constant of the medium (aqueous electrolyte solution), ε_i — dielectric constant of the substance ith particle, φ_i — potential distribution inside ith particle, σ — surface density charges. As a general rule, the dielectric constant of an aqueous electrolyte is much greater than the dielectric constant of a particle substance. In this case, the impact of the second term in parentheses in the second condition is usually small and the condition (2) can be replaced by the condition [6]

$$\mathbf{n}\nabla\varphi = \frac{\sigma}{\varepsilon\varepsilon_0}. \tag{3}$$

It can be assumed with low potentials on the surface of a particle that the surface charge density depends only on the surface potential, and this dependence can be represented as [7]

$$\sigma = \sigma_0 + C(\varphi - \varphi_0), \tag{4}$$

where σ_0 — the distribution of the surface charge density obtained for a solitary particle, provided that at all points of its surface the potential value φ_0 is the same, C — a constant depending on the properties of the particle surface. We obtain the following substituting (4) in (3).

$$\nabla\varphi\mathbf{n} = \frac{\sigma_0}{\varepsilon\varepsilon_0} + C\frac{(\varphi - \varphi_0)}{\varepsilon\varepsilon_0}.$$

At $C \to \infty$ on the surface of the particle

$$\varphi = \varphi_0.$$

This condition is called the constant potential condition. In this case, the potential distributions on the surface of the particles do not depend on the distance between them.

At $C \to 0$ on the surface of the particle

$$\nabla\varphi\mathbf{n} = \frac{\sigma_0}{\varepsilon\varepsilon_0}. \tag{5}$$

This condition is called the constant charge condition. In this case, the potential distributions on the surface of the particles depend on the distance between them. When using this condition, it is necessary to know the distribution of σ_0 on the surface of a solitary particle with a homogeneous potential distribution on this surface. The condition of constant charge and the condition of constant potential can be considered as limiting cases that determine the interval in which the values of the electrostatic repulsion force of particles can lie. This abovesaid is well illustrated by the comparison made in [8] of experimental data of the electrostatic interaction forces of spherical submicron particles of silicon dioxide in an aqueous electrolyte NaCl at different salt concentrations with the results of calculation of these forces using constant charge and constant potential conditions. Examples of studies in which these conditions are used as limiting cases are [6,9–12]. Both in the case of the condition of constant potential and in the case of constant charge in the studies devoted to the study of the interaction of two particles based on equation (1), the interaction of spherical particles is considered, as a rule. An exception is the study [13], in which the interaction of spheroidal particles with a common axis of symmetry was considered for given homogeneous potential distributions on their surfaces. The purpose of this work is to modify the method developed in this study for the case of a constant charge, taking into account the boundary condition (5).

1. Calculation procedure

The finite element method is used in this paper to study the electrostatic interaction of macroparticles. In this method the domain, in which the distribution of one or another quantity is determined, is divided into a set of subdomains. As a result, a computational grid is obtained, on the basis of which a set of basis functions is generated that are used to approximate the desired distribution. Therefore, the distribution is sought in the form of expansions into series by these functions with unknown coefficients. At present, there are a number of computer programs that allow to use the finite element method to find a numerical solution of the differential equation by its weak form. The weak form of the equation (1) is known, and it can be represented as [14]

$$\int_{\Omega} \widetilde{\nabla} u \cdot \widetilde{\nabla}\phi d\widetilde{V} + \int_{\Omega} k^2 u\phi d\widetilde{V} + \int_{\Gamma_N} g_N \phi d\widetilde{S} = 0, \tag{6}$$

where

$$u = \frac{\varphi}{\varphi_0},$$

$$k = k_D R_1,$$

$$g_N = \mathbf{n}\widetilde{\nabla} u. \tag{7}$$

Here and below, the use of a tilde over operators and quantities expressed by coordinates indicates that the coordinates are normalized to the characteristic size R_1 of the first particle, which in the case of a spherical particle is equal to its radius, and in the case of a spheroidal particle — to the maximum distance from the general particle symmetry axis to its surface. We assume that the corresponding distance R_2 for the second particle does not exceed R_1. Next φ_0 —the potential of a solitary particle, Ω — the final region in which the potential distribution is sought, V — the volume of this region, Γ_N — sections of the boundaries of the computational domain that coincide with the surfaces of particles, ϕ — test function. Sequential substitution of test functions into equation (6) makes it possible to obtain a system of equations for calculating the above unknown coefficients. In the problem under consideration in the condition (5) σ_0 represents the distribution of the surface charge density of a single particle at a surface potential equal to φ_0. In the case of a spherical particle, this distribution is homogeneous, and g_N is a constant value. However, in the case of a spheroidal particle, this is not the case. To find the distribution g_N, we use the fact that the electric field strength inside the particle is zero at a constant potential on the surface of the particle. [15] shows that this condition results in an unambiguous distribution σ_0 for a given total charge of the particle, coinciding with the distribution on the surface of a conductive spheroid in vacuum [16]. Using the expression for the surface charge density from [15,16], taking into account (5), (7), we obtain that on the surface of the ith particle

$$g_N = \frac{\beta_i}{4\pi}\left(\frac{R_i^2}{R_1^2} + \widetilde{\rho}^2\left(\frac{a_i^2}{R_i^2} - 1\right)\right)^{-\frac{1}{2}}, \tag{8}$$

where

$$\beta_i = \frac{Q_i}{\varepsilon\varepsilon_0\varphi_0 R_i},$$

Q_i — full charge of ith particle, R_i — maximum distance from the axis of symmetry of this particle to its surface, $\widetilde{\rho}$ — normalized value in at the considered point on the surface

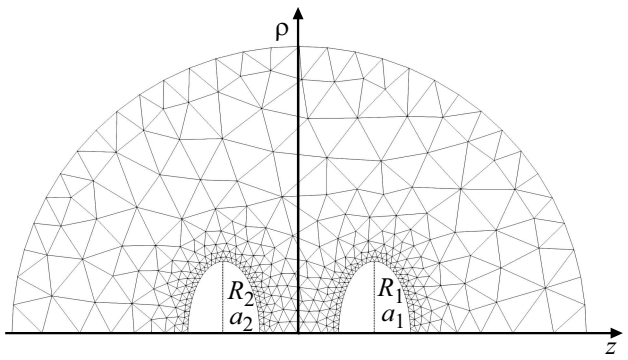

Figure 1. Structure of the initial computational domain.

of a particle of polar radius of a cylindrical coordinate system, the axis z of which coincides with the general axis of symmetry of the particles, a_i — the distance from the center of the particle to its surface along the axis connecting the centers of the particles. If the desired distributions are axisymmetric, like in this case, then the three-dimensional problem can be reduced to a two-dimensional problem by using cylindrical coordinates, in which all distributions depend only on the polar radius ρ and the applicates z of the cylindrical coordinate system. This is the approach used in this paper. An example of the initial computational grid is shown in Fig. 1. The lower boundary of the domain corresponds to the axis of symmetry of the problem. For the convenience of displaying individual elements, the ratio of their sizes differ from those actually used. The radius of the outer boundary was assumed to be $100R_1$ with a distance h_c between the centers of the macroparticles less than $10R_1$, and $100h_c$ in the other case. The information necessary for the transition to a cylindrical coordinate system is given in [17]. The value β_i can be calculated using the finite element method as described in [13]. The values β_i for some values a_i/R_i and k are shown in the table. The values of β_i for the ball are not given, since they can be obtained using the analytical formula

$$\beta_i = 4\pi(1 + k_D R_i),$$

which can be easily deduced from the expressions given in [18]. The same formula was used to estimate the accuracy of the calculation of β_i by the finite element method. It should be noted that the weak form (6) has an unambiguous solution, provided that at least a part of the boundary of the region under consideration has a distribution of u. As such a boundary, the outer boundary of the computational domain is chosen and the potential distribution on it is approximated as a distribution obtained by a superposition of distributions created by single spherical macroparticles [18], whose positions coincide with the centers of the particles under consideration, and the charges coincide with the charges of the particles under consideration. It should be noted that for the values of k considered in this paper, without a noticeable decrease of accuracy, it is possible to simply put the potential at the outer boundary equal to zero.

Values β_i for some values a_i/R_i and $k = k_D R_i$, see (7), (8)

a_i/R_i	$k_D R_i$	β_i
0.5	0.1	11.253
0.5	1	19.0549
2	0.1	18.703
2	1	38.268

The force $\mathbf{F}$ acting on some particle can be found using the expression [6]

$$\mathbf{F} = \oint_S \mathbf{T} \cdot \mathbf{n} dS,$$

where $\mathbf{T}$ — stress tensor

$$\mathbf{T} = \left(\Pi + \frac{1}{2}\varepsilon\varepsilon_0 E^2\right)\mathbf{I} - \varepsilon\varepsilon_0 \mathbf{E} \otimes \mathbf{E},$$

S — body surface area, $\mathbf{E} = -\nabla\varphi$ —electric field strength, $\mathbf{I}$ — unit tensor, Π — hydrostatic pressure due to the difference between local and volumetric osmotic pressures [3]. When using the linearized Poisson-Boltzmann theory [3]

$$\Pi = \frac{1}{2}\varepsilon\varepsilon_0 k_D^2 \varepsilon^2.$$

The difference between this work and [13] lies in the additional term with g_N in a weak form, which takes into account the boundary condition (5) on the particle surface, and in the expression for calculating the force, which in this work takes into account the hydrostatic pressure and the heterogeneity of the potential distribution on the surface particles. Otherwise, the procedure for calculating the normalized potential distribution u based on the finite element method coincides with the one given in [13], and its description is omitted here. Like in [13], the calculation was performed using the NGSolve [19,20] software package. It should be noted that with a homogeneous distribution of potential on the surface of the particles, the contribution to the force due to hydrostatic pressure becomes zero. Therefore, despite the lack of consideration of this contribution in the expression for strength in the work of [13], a comparison of the results of this work with the results of [13] is quite correct.

Since the finite element method is approximate, when using it, it is necessary to carry out test calculations to assess the accuracy of the results obtained. At the same time, since the accuracy of calculations decreases with the increase of the distance between the surfaces of particles [13], it is sufficient to conduct tests for maximum distances at the values k used in this work. The force F of electrostatic interaction of spherical macroparticles tends to the repulsive force F_{DLVO} with an increase of the

distance h between the surfaces of spherical macroparticles as described by the well-known asymptotic expression [1,5] for particles with a constant charge, which in the notation the present work can be written as follows

$$F_{\mathrm{DLVO}} = F_0 4\pi \frac{R_2}{R_1} \frac{1 + \tilde{h}_c k}{\tilde{h}_c^2} \exp(-k\tilde{h}), \qquad (9)$$

where

$$F_0 = \varepsilon\varepsilon_0\varphi_0^2.$$

Here $\tilde{h}$ — normalized to R_1 — minimum distance between particle surfaces. For identical particles at $h = 5R_1$ and $k = 1$, i.e. for the case when the radii of the particles are equal to the Debye radius k_D^{-1}, the difference between the force modules acting on spherical macroparticles from F_{DLVO} was 0.001%. In the case when the radius of the second particle was two times smaller than the first, this difference was 0.03%. For $h = 10R_1$ and $k = 0.1$, i.e. when the particle radii are ten times smaller than Debye radius, these differences were 0.07 and 0.0002%, respectively. To illustrate the above, Fig. 2 shows the dependences of the normalized repulsive forces acting on identical spherical particles from the distance between their surfaces normalized by the Debye radius k_{D}^{-1} at $k = 1$. For comparison, the dependences calculated according to the condition of charge constancy, potential constancy and dependence calculated according to the asymptotic formula (9) are shown. It can be seen from the figure that as the distance between the particles increases, the calculated values of the forces in all three cases tend to each other, and starting from a certain distance, the corresponding curves practically merge. Figure 3 shows similar dependencies for the case $k = 0.1$. A comparison of the dependencies shown in Fig. 2 and 3 shows that for a given distance between particles, an increase of k (or an increase of the radius

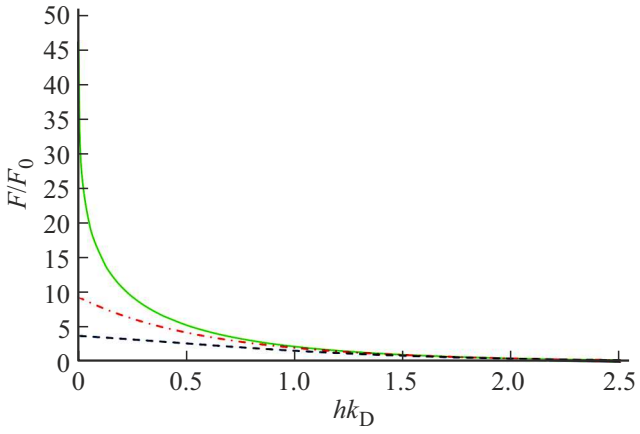

Figure 2. Dependence of the normalized force on the normalized distance between the surfaces of identical spherical particles at $k = 1$: solid line — particles with a constant charge; dash-dotted line — calculation according to the asymptotic formula (5); dashed line — particles with a constant potential on their surfaces.

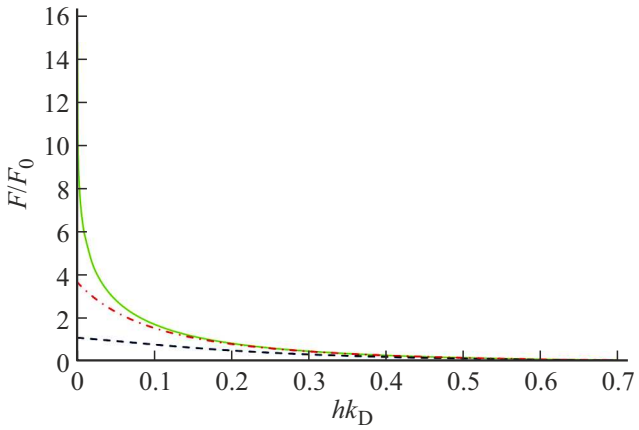

Figure 3. Dependence of the normalized force on the normalized distance between the surfaces of identical spherical particles at $k = 0.1$: solid line — particles with a constant charge; dash-dotted line — calculation according to the asymptotic formula (5); dashed line — particles with a constant potential on their surfaces.

of particles at a given value of the Debye radius) results in an increase of the values of normalized forces, which is easily explained by an increase of normalized charges and a decrease of the distance normalized by the radius of particles $\tilde{h}$.

2. Calculation results

Figure 4 shows the dependences on the distance between particles of the normalized interaction force of a spherical particle with particles of various shapes or sizes at $k = 1$. This figure shows that, with sufficient proximity of the radius of the spherical particle to the Debye radius k_{D}^{-1}, an increase of the longitudinal dimensions of the second particle or a decrease of its transverse dimensions results in a decrease of the forces of electrostatic repulsion of the particles. However, as can be seen from Fig. 5, if the particle sizes are not large enough, then, starting from a certain distance between the surfaces of the particles, an increase of the longitudinal dimensions of the second particle results in an increase of the force of interaction between the particles. The described patterns are also fulfilled for particles of the same shapes, which is well illustrated in Fig. 6. Figure 7 shows in more detail the dependences of forces on the distance between particles of the same shapes at $k = 0.1$ in the range hk_{D} from 0.25 to 0.28. This figure shows that with sufficiently small particle sizes a situation is possible at some distances between them, when both a decrease and an increase of the longitudinal size of the particles results in a decrease of the normalized forces of their interaction. These patterns correspond to the patterns obtained in the work [13] for particles with constant potential on their surfaces. Moreover, a comparison with the results of [13] shows that, as in the case of spherical particles, the normalized forces acting

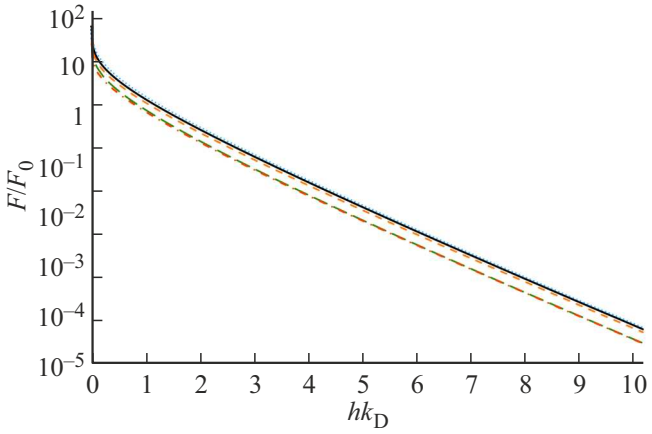

Figure 4. Dependence of the normalized force on the normalized distance between the surfaces of particles with constant charges at $k = 1$ and $R_1 = a_1$: dotted line — $R_2 = R_1$, $a_2 = 0.5R_2$; solid line — $R_2 = R_1$, $R_2 = a_2$; dashed line — $R_2 = R_1$, $a_2 = 2R_2$; long strokes — $R_2 = 0.5R_1$, $a_2 = R_2$; dash-dotted line — $R_2 = 0.5R_1$, $a_2 = 2R_2$.

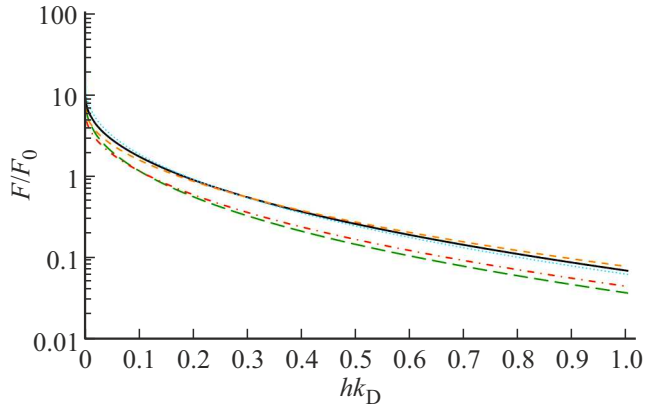

Figure 5. Dependence of the normalized force on the normalized distance between the surfaces of particles with constant charges at $k = 0.1$ and $R_1 = a_1$: dotted line — $R_2 = R_1$, $a_2 = 0.5R_2$; solid line — $R_2 = R_1$, $R_2 = a_2$; dash-dotted line — $R_2 = R_1$, $a_2 = 2R_2$; long strokes — $R_2 = 0.5R_1$, $a_2 = R_2$; dashed line — $R_2 = 0.5R_1$, $a_2 = 2R_2$.

on particles with a constant charge of a spheroidal shape tend to normalize forces acting on particles with a constant potential as the distance between the particles increases. In this case, the forces acting on particles with a constant charge are greater than the forces acting on particles with a constant potential, and differ in order of magnitude at close distances.

Conclusion

The electrostatic interaction of two charged spheroidal macroparticles with a common axis of symmetry and a constant charge on their surfaces under conditions of weak and moderate screening is considered. The calculation

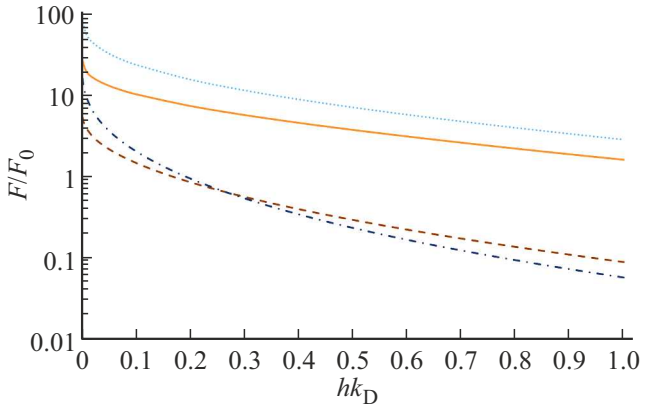

Figure 6. Dependences of the normalized force on the normalized distance between surfaces of identical particles with constant charges: dotted line — $k = 1$, $a_1 = a_2 = 0.5R_1$; solid line line — $k = 1$, $a_1 = a_2 = 2R_1$; dash-dotted line — $k = 0.1$, $a_1 = a_2 = 0.5R_1$; dashed line — $k = 0.1$, $a_1 = a_2 = 2R_1$.

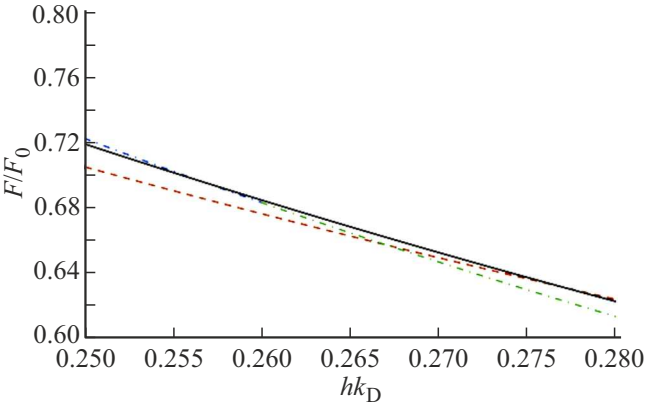

Figure 7. Dependence of the normalized force on the normalized distance between surfaces of identical particles with constant charges at $k = 0.1$: solid line — $a_1 = a_2 = R_1$; dash-dotted line — $a_1 = a_2 = 0.5R_1$; dashed line — $a_1 = a_2 = 2R_1$.

results are applicable for cases when the dielectric constant of the electrolyte is much greater than the dielectric constant of the particle substance, and the electric field potentials on the surface of the particles are quite small compared to the energy of their thermal motion. The normalized forces acting on particles with a constant charge are compared with the forces acting on particles with a constant potential on their surfaces. It is shown that the transition from the condition of constancy of potentials to the condition of constancy of charges results in a multiple increase of the values of forces for closely spaced particles. It follows from the calculation results that, with a sufficiently large degree of particle shielding, an increase of their longitudinal dimensions results in a decrease of the forces of electrostatic interaction between them. However, if the degree of shielding is not small enough, then the dependence of the force on the transverse dimensions of the particles depends on the distance between them. In this case, a situation

is possible when the interaction force between spherical macroparticles will be greater than the interaction forces of particles both in the form of an oblate spheroid and in the form of elongated spheroid.

Conflict of interest

The authors declare that they have no conflict of interest

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