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A. Trokhymchuk, D. Henderson*, E. Sovyak, D.T. Wasan†

The apparent attraction between like charges near a charged surface

*Department of Chemistry and Biochemistry, Brigham Young University, Provo, UT 84602

†Department of Chemical Engineering, Illinois Institute of Technology, Chicago, IL 60616

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“Ефективне” притягання між однойменними зарядами біля зарядженої поверхні

А.Трохимчук, Д.Хендерсон, Є.Сов'як, Д.Т.Васан

Анотація. Аналітичний розв'язок рівняння Пуасона використано для пояснення спостереженого зовсім недавно явища притягання між парою колоїдів поблизу склянної поверхні. Ми знайшли, що не має безпосереднього притягання між однойменними зарядами. Показано, що спостережуване на експерименті явище може бути проінтерпретовано як “ефективне” притягання, яке є наслідком дії додаткової сили на кожен з пари зарядів, що перебувають у електричному полі зарядженої поверхні. Індукована поверхнею сила спрямована до центру поверхні і при певних умовах спрямована проти кулонівського відштовхування.

The apparent attraction between like charges near a charged surface

A.Trokhymchuk, D.Henderson, E.Sovyak, D.T.Wasan

Abstract. Analytic solution of the Poisson's equation for a system of two like charges near a uniformly charged plane is used to explain the phenomenon of an attraction between a pair of colloids bound by a charged glass wall that has been observed recently. We found that there is no attractive interaction between like charges. We have shown that what is observed experimentally could be interpreted as the “apparent attraction” resulting from the extra force experienced by each charge being in the electric field due to the charged surface. This surface-induced force is directed to the center of the surface and under appropriate conditions works against the Coulomb repulsion between like charges. Both the field and force can be revealed naturally within the framework of classical electrodynamics if the effects of the finite size of a charged surface are taken into account.

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The forces acting between like-charged objects are important to both applied and basic science since these forces play a crucial role in determining the physical properties of a variety of systems, ranging from biological DNA solutions to industrial colloidal suspensions. Recently, attention to this subject has arisen because of speculations on the surprising possibility of a change in the sign (repulsion/attraction) of the effective electrostatic interaction between a pair of like-charged objects (colloidal particles, ionic micelles, DNA aggregates, etc.) when they are immersed in a confined electrolyte. Although recent experiments convincingly demonstrate an attraction between like-charged colloids bound by a charged glass wall [1–5], such an apparently illogical interaction has not been recognized as a common phenomenon yet since a satisfactory theoretical explanation has proven elusive and remains an unresolved problem currently [6–11].

Several mechanisms leading to a like charge attraction have been proposed [12–15]. Since attractive forces between colloids have been reported for confined solutions in the presence of counterions and salt ions, all aforementioned theories (as well as some other studies) exploit the idea that the processes carried out in confined electrolytes (charge fluctuations of condensed counterions, strong counterion correlations, colloid overcharging due to counterions etc.) are responsible for this observed phenomenon. Although the attractive forces discussed in previous theoretical approaches could still exist for charged particles in the presence of an electrolyte, the behavior of like-charged metal balls at the air/glass boundary revealed recently by Tata et al. [16] represents a novel experimental evidence that, in our opinion, rules out existing explanations as a general mechanism and highlights the governing role of the confining surfaces itself to control an effective interaction between nearby charged particles.

Partially inspired by this observation, we will show that the phenomenon of attraction between like-charged particles can be easily understood and interpreted within the framework of text-book classical electrodynamics [17] if the effect of the finite longitudinal extension of a charged surface is taken into account. Our approach to the problem is straightforward and is based on the important constraints imposed on theoretical attempts by existing experimental evidence [18]: (i) the observed phenomenon of like-charge attraction is of electrostatic origin; (ii) the attraction takes place next to a charged confining surfaces but is absent in the bulk; (iii) the discrete natures of the solvent or simple ions do not play a role in mediating the attraction, i.e. even continuum models should suffice. Then we suggest that an extra electric field exists next to the surface and that such an electric field is exclusively due to the array of charges spread over the surface. As with any field around an assembly of charges, the field near a charged plane is three-dimensional with three components defined by three gradients of the scalar electric potential. This means, that if there is the electrostatic force parallel to the surface, it requires that the electric potential at the points near the surface should depend not only on the normal distance from the surface but on the tangential position along the surfaces as well.

In general, the determination of the electric potential (and hence the field, by differentiation) due to a given surface distribution of charges is extremely complicated, if not impossible, except for surfaces of simple geometrical shapes (cylindrical, spherical or planar). Even in these cases some assumptions are usually applied. The most common requirement is that the electric potential due to the charged surface possesses reflection symmetry about the midplane of the pair of nearby particles [6–8]. In the case of a charged planar surface, such a requirement is equivalent to assuming that the confining surface is of an infinite longitudinal extension. However, in practice, one always is concerned with charged confining surfaces *of finite size* irrespective of the shape. To our knowledge, the surface size effect has not been accounted for properly when forces next to a charged confinement were analyzed. Recently, Trizac and Raimbault [10] have drawn attention to this issue. These authors studied one special case of a finite surface where the electric potential possesses reflection symmetry with respect to the surface midplane. They found their results were the same as those obtained by Neu [7] and Sader and Chan [8] for the infinite surface: the effective pair interaction between like-charged particles in the vicinity of a charged surface is always repulsive. We would like to mention that Mateescu [11] has recently commented regarding the calculation performed by Trizac and Raimbault [10] concluding that, in general, like-charged particles next to a finite confinement do not always repel.

To shed more light on the role played by the finite size of a confining surface, let us consider the simplest non-trivial electrostatic problem. The domain $\mathcal{V}$ of the finite dimensions $2a \times 2a \times h$ in the XYZ directions contains two like-charged particles. Since we are interested in the effects of electrostatic origin, it will be enough to identify both particles as point charges $q_1 = q_2 \equiv q$ (assumed to be positive for convenience). The charges are constrained to be above the oppositely charged horizontal plane $Z = 0$, and are related with the positions $\mathbf{R}_1$ and $\mathbf{R}_2$, respectively, in the rectangular coordinate system with the origin at the center of a plane $Z = 0$. The plane $Z = 0$ is a perfectly smooth impenetrable square area, $\mathcal{S} = \{-a \le X \le a,\ -a \le Y \le a\}$, and carries a negative charge spread uniformly over the surface with density σ that exactly compensates the total charge of nearby particles. The dielectric permittivities of media behind ($Z < 0$) and above the plane $Z = 0$ are the same and equal unity. Additionally, we require that both charges are situated at any, but always the same, altitude, i.e., $Z_1 = Z_2 = h$, so that vector $\mathbf{R}_{12} \equiv \mathbf{s}_{12}$ is (horizontal) parallel to the surface.

To study the electrostatic force experienced by charge $q_{\rm i}$ (i=1,2) we require the electric potential Φ at this charge in the localized field due to other charge $q_{\rm j}$ (j≠i) plus the field due to the charges distributed over the surface area $\mathcal{S}$. It should be noted that although the charges q_1 and q_2 are constrained to move only in two dimensions (within the horizontal plane $Z = h$), the Coulomb interaction that is acting between them is three-dimensional and requires a full 3D solution of the governing Poisson's equation:

$$\nabla^2 \Phi(\mathbf{R}) = -4\pi\rho(\mathbf{R}), \qquad (1)$$

which relates the electric potential of interest, $\Phi(\mathbf{R})$, to the local charge density, $\rho(\mathbf{R})$. All sources of charges within domain $\mathcal{V}$, including charges spread over the surface $\mathcal{S}$, contribute to $\rho(\mathbf{R})$.

Poisson's equation (1) has been solved subject to the (constant surface charge) electrostatic boundary conditions. The general result for the electric potential Φ at charge $q_{\rm i}$ is as follows:

$$\Phi(\mathbf{R}_{\rm i}) = \phi^{\rm Coul}(\mathbf{R}_{\rm ij}) + \phi^{\rm sur}(\mathbf{R}_{\rm i}) = \frac{q}{|\mathbf{R}_{\rm i} - \mathbf{R}_{\rm j}|} + \int\limits_{\mathcal{S}\{\mathbf{R}_{\rm i}\}} \frac{\sigma\, d\mathbf{s}}{\sqrt{s^2 + h^2}}, \quad \text{for} \quad {\rm i} \ne {\rm j}, \qquad (2)$$

where $s^2 = X^2 + Y^2$ is the horizontal coordinate parallel to the surface $\mathcal{S}$ and $d\mathbf{s}$ is an element of the surface area. The first term, $\phi^{\rm Coul}$, is the electric potential at the charge $q_{\rm i}$ due to the other charge $q_{\rm j}$ (j≠i) (direct Coulomb contribution). The second term, $\phi^{\rm sur}$, is the electric potential at charge $q_{\rm i}$ due to the charges spread over the surface $\mathcal{S}$ (surface-induced contribution).

Qualitatively, result (2) is quite evident and is expected. The feature that makes this result novel are the limits in the surface integral: $\mathcal{S}\{\mathbf{R}_{\rm i}\} \equiv \{-a + X_{\rm i} \le X \le a + X_{\rm i};\ -a + Y_{\rm i} \le Y \le a + Y_{\rm i}\}$. The latter indicates that the surface-induced potential at the charge $q_{\rm i}$ depends not only on the vertical distance h from the surface but also on the horizontal position $(X_{\rm i}\,; Y_{\rm i})$ of the charge $q_{\rm i}$ with respect to the surface.

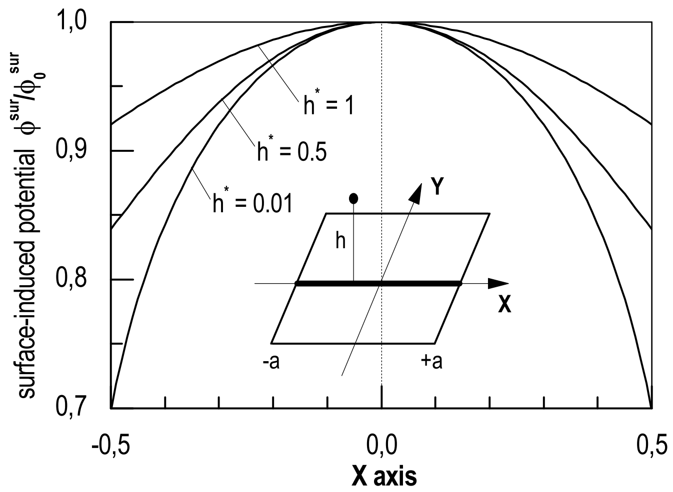

Figure 1. Electric potential due to a uniformly-charged planar surface of finite dimensions at a point charge placed along the X axis at different altitudes h shown on the figure.

This dependence (can be expressed analytically [19] as well) is illustrated on Fig. 1 for the case when charge $q_{\rm i}$, for simplicity, is placed along the X axis ($Y_{\rm i} = 0$). Three curves shown in Fig. 1 represent the potential $\phi^{\rm sur}(\mathbf{R}_{\rm i})$ (normalized with respect to its value $\phi^{\rm sur}(0,0,h) \equiv \phi_0^{\rm sur}(h)$ above the center of the surface $\mathcal{S}$) calculated for three reduced distances above the surface, $h^\star = h/2a$, ranging from 0.01 to 1 (all distances throughout the paper are scaled by the side length of the surface square $2a$). Indeed, we observe that $\phi^{\rm sur}$ varies in the direction along the surface. The graph of $\phi^{\rm sur}$ vs X is symmetric with respect to the surface midplane, exhibiting a non-zero positive slope that increases going from the center of the surface to its boundary. As the normal distance h increases, $\phi^{\rm sur}$ gradually approaches the constant value at the center of the surface; $\phi^{\rm sur}$ roughly is kept constant only in a narrow vicinity of the center of the surface.

From this it follows that the tangential component of the surface-

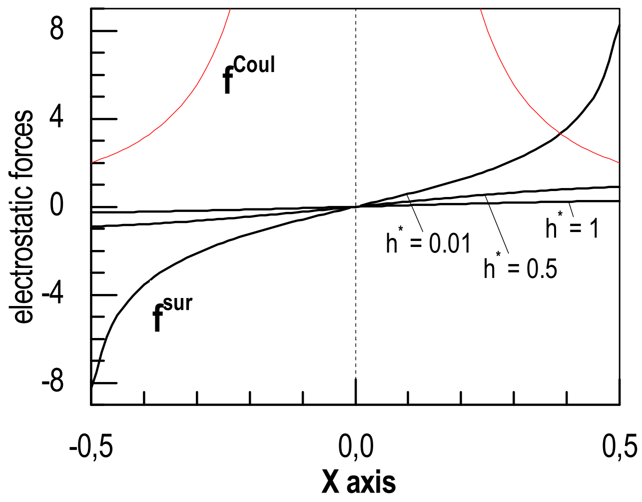

Figure 2. Surface-induced force experienced by point charge in the lateral direction near a uniformly-charged plane for the setup shown in Fig. 1.

induced electric field, $-\nabla_{\mathbf{R}_i}\phi^{\rm sur}$, is non-zero next to a surface, except for a region above the center of the surface. Hence, the finite plane with uniformly charged surface induces the force $\mathbf{f}^{\rm sur} = -q\nabla_{\mathbf{R}_i}\phi^{\rm sur}$ acting on charge $q_{\rm i}$ in all three directions (not just only the constant normal force, $f_\infty^{\rm sur} = 2\pi q\sigma$, as in the case of an infinite plane). This surface-induced force could be evaluated analytically by differentiation of the surface integral in expression (2). In a particular case when charge $q_{\rm i}$ is placed along X axis (i.e., $Y_{\rm i} = 0$, same as in Fig. 1), the result for the horizontal component of the surface-induced force reads:

$$f^{\rm sur}(X_{\rm i}, 0, h) \;=\; 2\pi q\sigma \, \ln \frac{(X_{\rm i}^- + a)(X_{\rm i}^+ - a)}{(X_{\rm i}^- - a)(X_{\rm i}^+ + a)}, \qquad (3)$$

where we used notation: $X_{\rm i}^\pm = \sqrt{a^2 + (X_{\rm i} \pm a)^2 + h^2}$ (the general expression for the lateral force if the charge is not on the X axis only is more complex [19]).

The force calculated according to Eq. (3) is plotted in Fig. 2. For convenience, we also plot the Coulomb force, $4\pi q^2/X_{\rm i}^2$, on charge $q_{\rm i}$ due to another charge $q_{\rm j}$ (j≠i) at the center of the surface, i.e. at $X_{\rm j} = 0$. Both forces are scaled by the constant $f_\infty^{\rm sur}$ that is the force experienced by a point charge near an infinite flat surface of the uniform charge density σ. The surface-induced force, $f^{\rm sur}$, is always directed to the center of the surface area. The magnitude of this force depends on the normal distance from the surface and on the horizontal position with respect to the center of the surface. The attraction to the center is stronger if the charge is placed far from the center; attraction continuously vanishes when the charge approaches the position at the center of the surface. There is a reflection symmetry of the surface-induced force with respect to the surface midplane. The change of sign reflects the change of direction of the surface-induced force crossing the center.

Figure 3 shows a vertical view of the surface area, $\mathcal{S}$, with a charge $q_{\rm i}$ at the horizontal position ($X_{\rm i}, Y_{\rm i}$). One always can construct the (dashed) area around charge $q_{\rm i}$ such that point ($X_{\rm i}, Y_{\rm i}$) will be at the center of this area. Obviously, the force due to the dashed area on charge $q_{\rm i}$ is equal to zero. The resulting force experienced by charge $q_{\rm i}$ due to the charged surface is determined then by the rest of the surface area $\mathcal{S}$, i.e. the white part in Fig. 3. There will be only the dashed area (which is equal to the whole area $\mathcal{S}$) for the charge placed in the center of the surface area: the longitudinal component of the surface-induced force on the charge $q_{\rm i}$ placed at the center of the uniformly-charged planar surface is absent.

So far we analyzed one charge near a charged surface. The total force on each of two charges, q_1 and q_2, comprises the surface-induced force, $\mathbf{f}^{\rm sur}$, that pushes the charges to the center of the surface, plus the Coulomb repulsion between charges, $\mathbf{f}^{\rm Coul}$, in the direction of the line $\mathbf{R}_{12}$ connecting these charges. In general, the directions of both forces, $\mathbf{f}^{\rm sur}$ and $\mathbf{f}^{\rm Coul}$, are different, and the resulting force on each charge could be different and does not necessary coincide with the direction of line $\mathbf{R}_{12}$. When $\mathbf{f}^{\rm sur}$ vanishes, i.e. far from the surface, the resulting force is always dominated by Coulomb repulsion. However, this is not so obvious when the charges are next to the surface. We now consider the case when both charges are placed along the X axis, i.e. we assume that $Y_1 = Y_2 = 0$. In this geometry, all forces presented in the problem lie on one line that coincides with $\mathbf{R}_{12}$. It is quite evident from Fig. 2 that, at an appropriate distance from the surface, the resulting force on each charge will depend on whether the direction to the center (of the surface) for each charge would coincide with that of the Coulomb repulsion or be

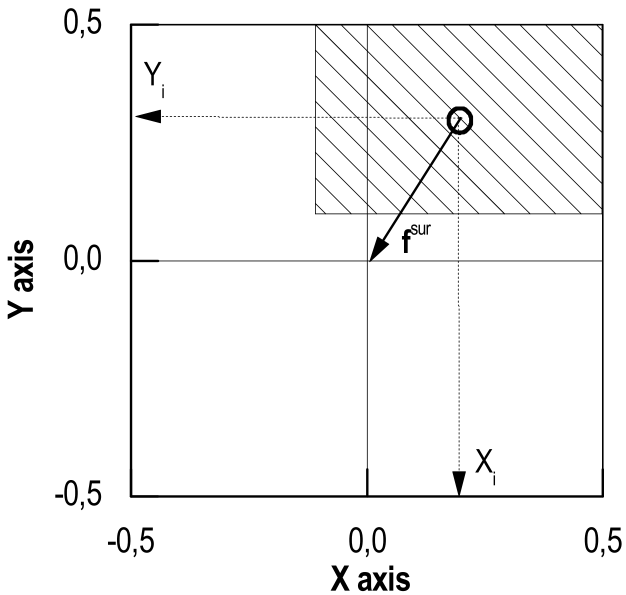

Figure 3. Schematic interpretation of the surface-induced force acting on a point charge due to the finite size of the charged surface

directed against it. The latter could happen when charges are positioned symmetrically with respect to the center of the surface. This discussion is summarized in Fig. (4) where the results for the potential distribution for two charges along the line $Y = 0$ are shown in the form of two contour plots appropriate to the confined and isolated (bulk) systems. There are closed contours when charges are next to the surface indicating the existence of potential depth with an absolute minima at the center of the contours. The potential lines never close when the charges are far from the surface.

We have presented the qualitative and quantitative theoretical proofs that there exist what we call the "apparent attraction" between a pair

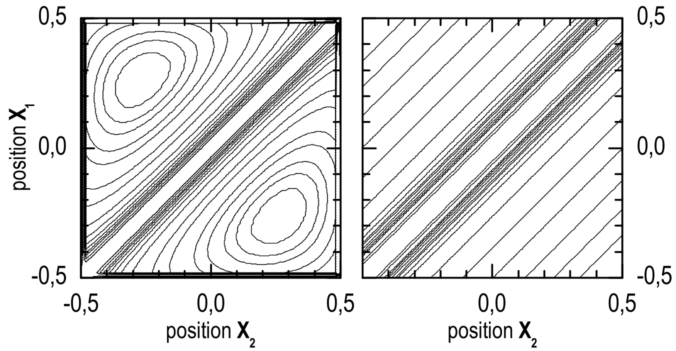

Figure 4. Isopotential lines for the system of two like charges near ($h^\star = 0.01$) an oppositely-charged planar surface of finite extension (left side) and without surface (right side).

of like-charged particles if they are placed next to an oppositely-charged planar surface. The term "apparent attraction" means that there is no attractive interaction between like charges. However, there is the surface-induced force of electrostatic origin that, at appropriate conditions, works against the Coulomb repulsion between charges. Our findings are based on the direct analytic solution of Poisson′s equation for two like charges next to an oppositely-charged planar surface. In a transparent way we have shown that an extra component in the force experienced by each of the two charges is presented in the theory due to an effect of the finite longitudinal extension of a nearby charged plane, which always takes place in reality. The results are obtained in an analytical form and are not contingent upon approximations of an asymptotic or numerical character. We analyzed in detail the simplest case in which the charge on a confined surface is kept constant and distributed uniformly while both particles are considered as point charges; the main conclusions presented here are valid and can be generally applied. We believe that this is the first microscopic explanation of the phenomenon of the net attraction observed between like-charged particles next to a charged surface.

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Андрій Трохимчук
Даглас Хендерсон
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