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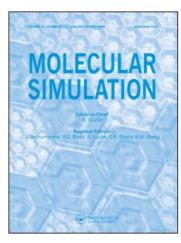
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Computer Simulations of a Monolayer of Like-charged Particles Condensed on an Oppositely-charged Flat Area

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A non-traditional approach to the computer simulation study of a class of quasi-two-dimensional Coulomb systems (charged particles confined to a layer near a charged planar surface) is presented. The essence of the approach lies in exploiting the fact that the charged confinement is of finite dimensions. The main consequence of such a finiteness is a non-zero potential gradient along the finite charged area that includes a nonzero tangential component of the electric field. A system of like-charged spherical particles confined by the planar surface that includes an oppositely charged squared area is considered as an example. We find that the likecharged particles, independent of their concentration, all become confined on the oppositely charged area, if the surface charge balances the total charge carried by the particles, and if the electrostatic coupling is sufficiently large. The local density of the particles above the charged area is not homogeneous; near the boundaries of the charged square a clear tendency of layer formation along the square sides is observed.

INTRODUCTION

The properties of a monolayer of like-charged particles, spread out on a charged substrate plane, represent a challenge in many different areas of both basic and applied science. Systems in which the distribution of like-charged particles on a surface play a central role ranging from protein and DNA solutions in biology to colloidal suspensions in industrial products. Attention to this topic increased recently because of speculations on the possibility of like-charge attraction that has been raised by direct measurements [1–6] of the pair interaction between

identical charged particles (latex or silica macrospheres) confined to a plane by charged glass walls. If this occurs, such an attraction may be responsible for a variety of otherwise unexplained anomalies that include observations of large stable voids in colloidal fluids and crystals [7], phase separation between colloidal suspensions of different densities [8] and metastable colloidal crystallites in dilute suspensions [9]. A common feature in the examples quoted is that the charged particles are immersed in an electrolyte solution and the Coulomb forces acting between them are mediated by a surrounding electrolyte. As a result, all approaches [10–16] that have been proposed so far to explain the interaction between identically charged particles exploit the idea that processes carried out in a confined cloud of electrolyte ions are responsible for this observed phenomenon.

Quite recently, we have turned our attention [17] towards a different class of measurements, which are known as analog simulations, where attraction is observed between like-charged macroscopic stainless steel balls at the air/glass interface [18–20], i.e. with no electrolyte involved. In the particular experiment of Tata *et al.* [18], several hundred or thousand steel balls are placed on a polymer surface. Through shaking, the steel balls are charged. A charge balance is obtained via the supporting surface. With this setup, stable structures form above the rectangular area, which, depending on the density of charged balls, vary from gas-like over liquid-like to 2D solids. In all these structures,

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the short-range repulsion between the like charges is balanced by long-range attraction.

In the above mentioned study [17] we have analyzed Poisson's equation for a single charge next to an oppositely charged plane and have shown that the extra contribution to the long-range interaction has its origin in the finiteness of the charged surface area. In particular, the uniformly charged planar surface, when finite, induces a nonzero tangential electric force on the nearby countercharge that points towards the center of the rectangular area. Thus, a single charge always tends to be placed at the center of the oppositely charged area. When a pair of identical charges is located on the surface, each one will compete for the central position, simulating what we call an apparent attraction between them and finally occupying the positions symmetrical with respect to the area midplane.

In the present work, we have implemented this pair potential energy to probe by means of molecular dynamics (MD) simulations the behavior of a system of a larger number of identical charges. We show that the Coulomb interactions indeed lead to confinement of similarly charged spherical particles on an oppositely charged surface area. It is conjectured that the origin of some apparently attractive interactions between like-charged entities originates from the finite size of the charged plane surface.

MODELS AND SIMULATIONS

Setup of the Simulation Cell

The simulation cell mimics a real system that contains a number N of identically charged particles (assumed to be similar to a potassium cation for convenience) of charge +e, with e, the proton charge. These particles can move above a horizontal surface Z = 0 and are located with the positions \mathbf{R}_i (i = 1, ..., N) in the rectangular coordinate system with the origin at the center of the planar surface Z = 0. In the center of this surface there is a quadratic region $S = \{ -a \le X \le a; -a \le Y \le a \}$ of area $4a^2$. This quadratic region carries a homogeneously distributed negative charge of a magnitude -Ne, corresponding to a surface charge density $\sigma =$ $-Ne/4a^2$. It is assumed that the dielectric constant is equal to 1 everywhere. In order to keep the model as simple as possible, no assumptions are made concerning the short-range interactions between particles and surface. Although the charged particles are moving only in two dimensions changing X_i and Y_i coordinates, the Coulomb interaction acting between them is fully three-dimensional. The particles are simply constrained to move at a fixed height h above the charged surface, i.e. $Z_i = h$.

Configurational Potential Energy

In order to perform computer simulations of this system, one needs to calculate the configurational potential energy for N particles and the corresponding forces on each particle for an arbitrary configuration. In general, for the system of charged particles near a charged confinement, the total potential energy due to all the forces acting on them to a good extent is found to be:

$$W(\{\mathbf{R}_i\}) = \Phi_1(\{\mathbf{R}_i\}) + \Phi_2(\{\mathbf{R}_i\}), \tag{1}$$

where Φ_2 is the pair-wise additive interactions between charged particles that consist of a super-position of the direct Coulomb repulsion and the short-range Lennard–Jones (LJ) interaction:

$$\Phi_2(\{\mathbf{R}_i\}) = \sum_{i=1}^N \sum_{j < i} \left[\frac{q^2}{|\mathbf{R}_i - \mathbf{R}_j|} + 4\epsilon_{\mathrm{LJ}} \left[\left(\frac{\sigma_{\mathrm{LJ}}}{|\mathbf{R}_i - \mathbf{R}_j|} \right)^{12} \right] \right]$$

$$-\left(\frac{\sigma_{\mathrm{LJ}}}{|\mathbf{R}_{i}-\mathbf{R}_{i}|}\right)^{6}\right].$$
 (2)

In the simulations reported below, the Lennard–Jones parameters are chosen to be $\epsilon_{\rm LJ} = 107.93 \times 10^{-23} \, {\rm J}$ (or 78 K), and $\sigma_{\rm LJ} = 0.3 \, {\rm nm}$. The contribution Φ_1 is a sum of one-body terms:

$$\Phi_1(\{\mathbf{R}_i\}) = \sum_{i=1}^N \phi^{\text{sur}}(\mathbf{R}_i), \tag{3}$$

where ϕ^{sur} , in general, must depend on all three cartesian coordinates and not only on the distance from the surface [14].

Electric Potential due to the Charged Flat Area

To obtain the electric potential $\phi^{\rm sur}$ we explore the solution to Poisson's equation for a point charge next to the finite charged area $\mathcal S$ on a horizontal plane Z=0. For a uniform charge density σ , over the region $\mathcal S$, the general result for the electric potential $\phi^{\rm sur}$ becomes:

$$\phi^{\text{sur}}(\mathbf{R}_i) = \int_{S\{\mathbf{R}_i\}} \frac{\sigma \, \mathrm{d}\mathbf{s}}{\sqrt{s^2 + h^2}},\tag{4}$$

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. Reduction of the problem to point charges should be considered as a simplification but not as a limitation. Equation (4) can be extended for the charged Lennard–Jones particles by making the reasonable approximation that their charge is embedded at the center of the Lennard–Jones sphere. If necessary, the height at which ions move above the charged surface can be related with their diameter, e.g. $h = \sigma_{\rm LI}/2$ etc.

Qualitatively, result (4) is quite evident and is expected. However, since the charged surface has the shape of a finite square, the limits in the surface integral are: $S\{\mathbf{R}_i\} \equiv \{-a + X_i \le X \le a + X_i; -a + X_i \le X \le a + X_i\}$ $Y_i \le Y \le a + Y_i$. The latter indicates that the surfaceinduced potential, ϕ^{sur} , at the charged particle on position \mathbf{R}_i depends not only on the vertical distance $h = Z_i$ from the surface but also on the horizontal position $(X_i; Y_i)$ of the charged particle on the surface. The surface integral (4) can be easily evaluated numerically and it has been shown [17] that the electric potential $\phi^{\text{sur}}(\mathbf{R}_i)$ has a parabolic shape with the equilibrium potentials value at the center of the charged area, i.e. $X_i = Y_i = 0$. For the simple geometries of the charged area S, the surface integral (4) can be evaluated analytically, which is convenient for practical applications such as computer simulations. Particularly, for the present case of a charged square area, $\phi^{\text{sur}}(\mathbf{R}_i)$ can be presented in the form of equation:

$$\phi^{\text{sur}}(X_{i}, Y_{i}; h) = q\sigma \int_{-a}^{a} \int_{-a}^{a} \frac{dX dY}{\sqrt{(X_{i} - X)^{2} + (Y_{i} - Y)^{2} + h^{2}}}$$

$$= q\sigma \left[I_{1}(X_{i}, Y_{i}) - I_{2}(X_{i}, Y_{i}) - I_{3}(X_{i}, Y_{i}) + I_{4}(X_{i}, Y_{i}) \right], \tag{5}$$

with

$$I_{n}(X_{i}, Y_{i}) = C_{n} \ln \left[B_{n} + \sqrt{C_{n}^{2} + A_{n}^{2}} \right] - C_{n}$$

$$+ B_{n} \ln \left[C_{n} + \sqrt{C_{n}^{2} + A_{n}^{2}} \right] + \sqrt{A_{n}^{2} - B_{n}^{2}}$$

$$\times \sin^{-1} \left[\frac{B_{n}^{2} - A_{n}^{2}}{A_{n}} \cdot \frac{1}{\sqrt{C_{n}^{2} + A_{n}^{2}} + B_{n}} - \frac{B_{n}}{A_{n}} \right],$$
(6)

where n = 1, ..., 4 and $A_1^2 = A_2^2 = Y_{i,-}^2 + h^2$; $A_3^2 = A_4^2 = Y_{i,+}^2 + h^2$; $B_1 = B_2 = Y_{i,-}$; $B_3 = B_4 = -Y_{i,+}$; $C_1 = C_3 = X_{i,-}$; $C_2 = C_4 = -X_{i,+}$. Here we introduced the notations $Y_{i,\pm} = a \pm Y_i$ and $X_{i,\pm} = a \pm X_i$. Equations (5) and (6) explicitly express the dependence of the one-body term, $\phi^{\text{sur}}(\mathbf{R}_i)$, on all three cartesian coordinates.

The Force due to the Charged Flat Area of Finite Size

From the results in the previous subsection as well as from the analysis performed in Ref. [17], it follows that the tangential component of the surface-induced electric field, $-\nabla_{\mathbf{R}_i}\phi^{\mathrm{sur}}$, will no longer be zero when considered next to a charged surface, except for a region exactly above the center of the charged area. Hence, the finite and uniformly charged planar

surface induces the force $f^{\rm sur} = -q \nabla_{{\bf R}_i} \phi^{\rm sur}$ acting on charge q_i in all three directions (not just only the constant normal force, $f^{\rm sur}_{\infty} = 2\pi q\sigma$, as in the case of an infinite plane). This surface-induced force can be evaluated by differentiation of the surface integral in expression (4). The lateral force acting on charged particle at ${\bf R}_i$ can be obtained by calculating the change in the total electrostatic energy of the system under small virtual displacements. The result is as follows:

$$\frac{1}{q\sigma} \mathbf{f}^{\text{sur}}(X_{i}, Y_{i}; h)
= -\left(\mathbf{i}_{x} \frac{d}{dX_{i}} + \mathbf{i}_{y} \frac{d}{dY_{i}}\right) \phi^{\text{sur}}(X_{i}, Y_{i}; h)
= -i_{x} \left[\ln \left(\frac{Y_{i,-} + \sqrt{X_{i,-}^{2} + Y_{i,-}^{2} + h^{2}}}{-Y_{i,+} + \sqrt{X_{i,-}^{2} + Y_{i,+}^{2} + h^{2}}} \right) \right]
- \ln \left(\frac{Y_{i,-} + \sqrt{X_{i,+}^{2} + Y_{i,-}^{2} + h^{2}}}{-Y_{i,+} + \sqrt{X_{i,+}^{2} + Y_{i,+}^{2} + h^{2}}} \right) \right]
- i_{y} \left[\ln \left(\frac{X_{i,-} + \sqrt{X_{i,-}^{2} + Y_{i,-}^{2} + h^{2}}}{-X_{i,+} + \sqrt{X_{i,+}^{2} + Y_{i,-}^{2} + h^{2}}} \right) \right]
- \ln \left(\frac{X_{i,-} + \sqrt{X_{i,+}^{2} + Y_{i,-}^{2} + h^{2}}}{-X_{i,+} + \sqrt{X_{i,+}^{2} + Y_{i,+}^{2} + h^{2}}} \right) \right] .$$
(7

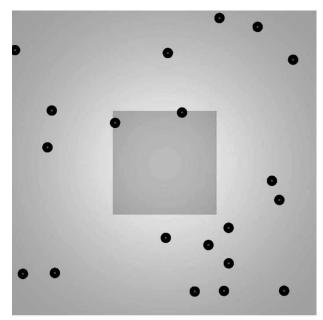
The surface-induced force, f^{sur}, is always directed towards the center of the charged area on the planar surface. The magnitude of this force varies depending on the horizontal position. The attraction to the center is stronger if the particle is placed far from the center; the attraction vanishes continuously when the charged particle approaches the position at the center of the surface.

Molecular Dynamics Simulations

We have performed MD simulations with the simulation box that is periodic with length $L=300\,\mathrm{nm}$ in the x and y dimensions in order not to "lose" particles in the course of the simulation. The size of a side length of the charged square area at the center of the cell was fixed at $2a=25\,\mathrm{nm}$. Several values of the number of charged particles N=50, 486, 972, 1458 and 1944 have been used that correspond to area packing fraction, $\eta=N\sigma_{\mathrm{LJ}}^2/4a^2$ in the range 0.05-0.28.

The simulations were started from initial configurations, where the identical charged particles

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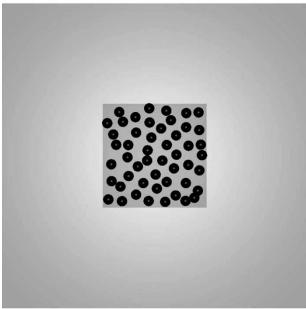


FIGURE 1 Snapshots of the initial configuration (top) and an equilibrated configuration after 500 ps (bottom) of a simulation run with N=50 charged particles. For better visibility, the particles are displayed with a radius $r=10\sigma_{\rm LJ}$.

were randomly placed at $h=0.3\,\mathrm{nm}$ above the entire cell base area. During an equilibration period the particles condense due to the long-range surface-induced attractive interactions and become confined above the charged area \mathcal{S} . The velocity Verlet algorithm with a timestep of 2.5 fs was employed. Simulations lasted 200,000 steps or 500 ps, after an equilibration period of the same length during which confinement of particles on the charged surface took place. A Berendsen [22] thermostat with a time constant of 40 ps was used to keep the temperature constant. The temperature in all runs reported here was 720 K, which

corresponds to a Coulomb coupling parameter $e^2/(4\pi\epsilon_0\sigma_{\rm LJ}kT)=78.5$, with e the elementary charge, ϵ_0 the vacuum permittivity, k Boltzmann's constant and T the absolute temperature; other temperatures in the range $100-1500\,\rm K$ were also studied but are not reported here. Unmodified "naked" Coulomb interactions were used throughout. Since after equilibration the particles do not notice the periodic boundaries due to their confinement to the charged area, the system can, for the calculation of electrostatic forces, effectively be regarded as infinite. Hence, no lattice summations like the Ewald method need to be used, thus simplifying the simulation.

RESULTS AND DISCUSSION

Figure 1 shows the initial configuration (top) and a configuration after 500 ps (bottom) for a simulation run with a small number of particles, N=50. The charged area is shown as the dark gray square in the center. Starting from the random initial configuration, all 50 identically charged particles become confined after a 500 ps equilibration phase in which excess kinetic energy is continuously removed, overcoming the strong Coulomb repulsion between them. This behavior clearly demonstrates the confining effect of the homogeneously charged planar area of finite size. The spacing between the particles is rather large, compared to their real size. Note, that the radii of the particles are exaggerated by a factor of 10 in Fig. 1.

The confinement of the particles on the quadratic charged area is already apparent from the snapshots in Fig. 1. A quantitative characteristic of such confinement is presented in Fig. 2 where the particle local density distribution along the x axis, $\rho(x)$, is displayed. This has been calculated by averaging the number of particles over the y coordinate according to $\rho(x) = \int_{-\infty}^{\infty} dy \tilde{\rho}(x, y)$, with $\tilde{\rho}(x, y)$ the

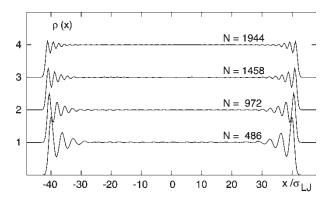


FIGURE 2 Particle local density, $\rho(x)$, for simulations with different number, N, of particles as indicated. The x axis is given in units of σ_{LJ} . Curves are shifted by one unit for better visibility.

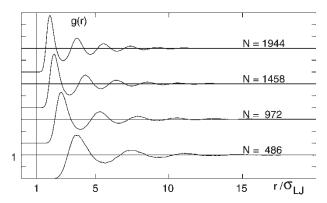


FIGURE 3 Radial distribution function, g(r), for simulations with different number, N, of particles as indicated. The r axis is given in units of $\sigma_{\rm LJ}$ and the vertical line at $r/\sigma_{\rm LJ}=1$ indicates the close-packing distance. Curves are shifted by 1.5 units for better visibility. g(r) is calculated only around those particles located in the central circle of radius 3 nm of the area \mathcal{S} . The reduced area packing fractions, η , of the central circle are 0.07, 0.14, 0.21 and 0.28, practically the same as the total area densities of the entire charged area.

total density distribution above the charged area. In the center of the charged area, the particle density is constant (set to 1 in the figure). Close to the boundary of the charged square, density oscillations appear, which are reminiscent of those appearing in a simple liquid in contact with a solid. With increasing number of particles, both the amplitude and the period of the density oscillations decrease. Due to the symmetry between x and y axes in the system, the densities $\rho(y)$ are identical and therefore not shown here. The oscillations of density that we see in Fig. 2 are very similar to the those observed in Ref. [21].

From the local density distribution of the particles over the charged area one observes a homogeneous density region in the central part of the area. Radial distribution functions (RDFs) can be computed for the particles from the center of this homogeneous region only. Figure 3 shows the like-charged particle RDFs in two dimensions for four different number of particles as indicated. The particle RDFs were calculated only around those particles which were located in a central circular area of radius 3 nm, i.e. around ten particle LJ diameters. Around any of these particles, several shells of other particles are visible. With increasing number of particles in the system, the number of discernible shells increases and the distance between consecutive shells decreases, i.e. the arrangement becomes, necessarily, more compact. In all cases, however, the first maximum of the RDF is well beyond the distance $r/\sigma_{LI} = 1$ that corresponds to close packing of the charged LJ spheres. This indicates that the direct repulsive Coulomb forces dominate at short distances, whereas at long distances, the surface-induced forces derived from $\phi^{\rm sur}$ contribute.

CONCLUDING REMARKS

The main result of the present study is that confinement of like-charged particles on an oppositely charged surface happens as a consequence of the finiteness of the distribution of the surface charge. The finite nature of the charged area on the surface leads to a non-zero electric potential gradient along the confining plane. The equilibrium position for a single charge is above the center of the charged area. If more than one charge is present near the surface, these charges compete for this equilibrium position, and at the same time, repel each other due to Coulomb interactions between them, effectively leading, as the simulations have shown, to a rather stable equilibrium between particle-particle Coulomb repulsion and surface-induced Coulomb attraction due to the surface finiteness. For the particle densities studied here, the short-range Lennard-Jones interactions between particles are not important.

If the confining surface has a simple geometry, as in the case considered, analytic solution for the forces acting on particles due to the charged surface area can be obtained, and the simulations are straightforward. The fact that the interacting system has a finite dimension, makes the simulations even more simple, since the treatment of long-range Coulomb forces via lattice summation methods, such as the Ewald method, is not necessary.

As an example, the system of like-charged spherical particles in contact with a planar surface carrying an opposite charge has been studied. For reasons of convenience, we have approximated the particles as being similar in size to potassium ions, assuming the most simple charge distribution, a point charge in the center of ions. The important size parameter for this system is the ratio of the particle hard-core diameter to the side length of the charged area on the planar surface, which was chosen to be roughly 1:100. The important interaction parameter is the Coulomb coupling $e^2/(4\pi\epsilon_0\sigma_{LJ}kT)$, which is equal to 78.5 for the systems studied here and whose properties are displayed in Figs. 1-3. The value is similar to the one in the steel ball experiment of Ref. [18]. The number of particles explored in the MD simulations was varied from 50 to almost 2000. For the coupling constant 78.5 we have observed complete confinement of ions. The density of ions is more or less homogeneous in the center of the charged area; near the edges of this area, density oscillations occur, which are similar in nature to those near liquid/solid interfaces. Confinement is only partial, when the coupling constant is significantly lower and when the charged area does not completely balance the charge of the particles. In particular, we find for example, that for a coupling constant of 0.5 still 60% of the ions are confined on

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the surface, or, in another simulation with coupling constant 78.5, we observe that 72% of the ions are confined on the surface, even if the charged area carries only 50% of the charge necessary to balance the ion charge.

In summary, we have studied a system of very simple geometry that shows the effect of confinement of like-charged species on a finite charged surface, even if the Coulomb repulsion (i.e. the Coulomb coupling constant) is very large. We have made the most simplifying assumptions concerning short-range interactions and charge distribution of the particles. Specifically, it should be noted that no polarizability effects are included. Other geometries, shapes and parameters should be studied in order to be able to generalize the conclusions. These efforts are currently undertaken in our laboratories.

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