Clay micromechanics: Numerical modelling of electrical double-layer interactions to develop particle-based models for clay

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ABSTRACT

Discrete element modelling of clays requires defining the interaction energy between two particles. The Derjaguin, Landau, Verwey and Overbeek (DLVO) theory combining the effect of the van der Waals forces and the Coulombic forces due to the double layer of counterions provides a widely accepted framework to characterise the pair potential energy. Solutions of the Poisson-Boltzmann (PB) equation to quantify the Coulombic forces are only available for the case of infinitely extended and uniformly charged facing plates (1D conditions). However, these assumptions are not representative of a clay particle system. Particles should be represented by platelets of finite size and finite thickness, with different charges between the edge and the basal planes. This paper addresses the problem of deriving the Coulombic interaction forces for plates of finite size and thickness in 3D configuration by solving the Poisson-Boltzmann equation numerically via the Finite Element Method (FEM). It is shown that 2D particles (plates of infinitesimal thickness) provide an adequate representation of Coulombic interaction as long as the particles are uniformly charged. The advantage of 2D particles is to reconcile numerical modelling with analytical solutions available in the literature. The use of 2D particles is questionable when considering different charges between basal planes and edges.

Keywords: clay; micromechanics; Electrical Double Layer; DLVO

1. Introduction

Colloidal-size particles, typically between 10 nm and several microns, develop an electrical surface charge, unlike granular materials (Mitchell and Soga,2005; Sposito 1998). Many physical and chemical properties of clays are directly or indirectly controlled by the nature and the amount of surface charge, as this directly affects interparticle interactions.

Discrete element modelling of clays (Discrete Element Method (DEM) or Coarse-Grained Molecular Dynamics (CGMD) modelling) requires defining the interaction energy or force between two particles. The DLVO theory combining the effect of the van der Waals forces and the Coulombic forces due to the double layer of counterions provides a widely accepted framework to characterise the pair potential energy. However, the analytical solutions usually employed for describing the two competing forces generally considers infinite thickness, infinitely extended and uniformly charged facing parallel plates (one-dimensional condition). This configuration ignores i) the interaction forces arising at the platelet ends that can present an opposite charge with respect to the basal planes, ii) the finite size of the particle, iii) the small thickness of the particle as opposed to the infinite thickness considered in most analytical developments, and iv) the non-parallel configuration.

A realistic description of clay particle systems requires the implementation of a physically-consistent energy/force-separation function that takes into account the 6 degrees of freedom of the particle, the particle geometry and an appropriate spatial description of the non-homogeneous surface charge distribution. To this end, the Coulombic forces arising from the interaction of the Electrical Double Layers (EDL) need to be assessed by solving the Poisson-Boltzmann equation numerically.

This paper focuses on the use of the finite element method (FEM) to characterise the Coulombic interaction between clay particles. The numerical framework is first validated against classical 1D solution for uniformly charged parallel sheets and then used to explore the effect of finite particle thickness and particle size, two of the assumptions that need to be removed from classical DLVO solutions available in the literature. Finally, it addresses the modelling of different charge between faces and edges.

2. Kaolinite electrical charge

The physicochemical properties of clay particle surfaces are determined by the crystal structure. According to Sposito (1998), clay particles develop surface charge from (i) structural isomorphous substitutions and (ii) proton adsorption and desorption reactions. The sum of these two charges is referred to as the ‘intrinsic charge’. The intrinsic charge is counterbalanced by a layer of absorbed ions closely attached to the particle surface (usually denoted 'Stern layer') and by the counterions in the diffuse double layer (Figure 1). Sposito (1998) introduces the concept of total particle charge, hereafter denoted by σ [C/m^2], representing the net surface charge resulting from the intrinsic charge plus the adsorbed ions immobilised in the Stern layer.

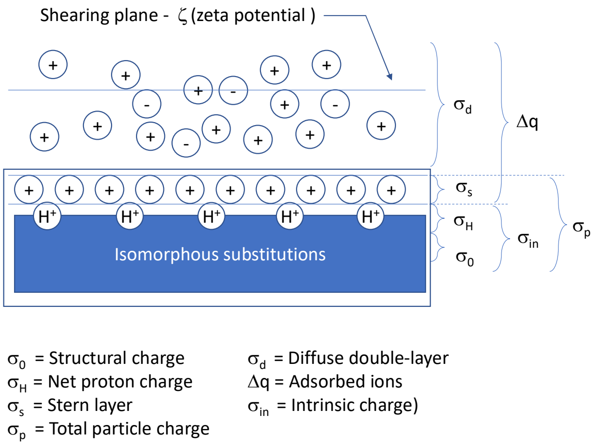

Figure 1. Clay particle electrical charges.

It is possible to measure experimentally the components of the total particle charge through chemical methods. However, data interpretation relies on the assumptions about the distribution of surface charge on basal planes and edges resulting from the layered nature of clay particles.

The structural charge is usually attributed to the basal planes. The surface charge derived from isomorphous substitution only depends on the type and degree of the substitutions. Thus, it is largely independent of the pH and electrolyte composition of the solution. In contrast, the charge on the edge and the alumina (octahedral) face is assumed to be pH-dependent due to the protonation/deprotonation of exposed hydroxyl groups (Wang and Siu 2006).

Traditional methods for measuring the different components of the total particle charge include the Cesium-Adsorption Method and proton titration (Schroth and Sposito 1997). These techniques reveal that the basal planes always carry a homogeneous negative surface charge. On the other hand, in acidic solutions clay edges carry a positive charge, while the edges are negatively charged in alkaline solutions. Measurements of structural and net proton charge carried out by Schroth and Sposito (1997) and Zhou and Gunter (1992) on a reference kaolinite identified as KGa-1 show a negative face surface charge ranging from -40 mC/m^2 to -80 mC/m^2, and a pH-dependent edge surface charge ranging from -60 mC/m^2 to +10 mC/m^2 as pH decreases (Figure 2).

More recently, atomic force microscopy (AFM) measurements of the surface electrical charge have provided an entirely different picture. In kaolinite, these colloidal force measurements reveal that the silica tetrahedral basal plane is negatively charged at pH > 4, whereas the charge on the alumina octahedral changes from negative to positive as pH reduces below 6 (Gupta and Miller, 2010). Overall, surface charge measurements reveal that, in absolute terms, a difference of up to two orders of magnitude in the particle surface charge is observed for KGa-1 kaolinite between the traditional electrical charge measurement techniques (cation exchange and titration) and the AFM measurements. Indeed, all the measurements performed by Gupta and Miller (2010) of the total charge of the basal planes of KGa-1 do not exceed ±10 mC/m^2 (Figure 3).

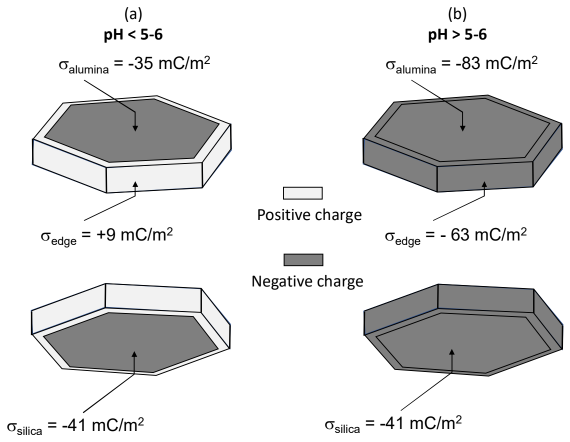

Figure 2. Electrical charge derived from chemical methods for KGa-1 kaolinite (Casarella 2022).

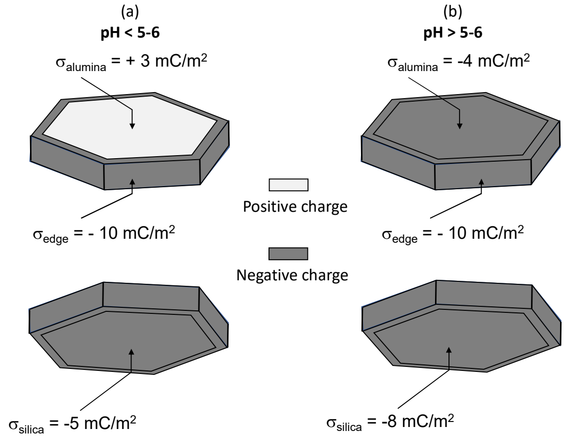

Figure 3. Electrical charge derived from AFM measurements for KGa-1 kaolinite (Casarella 2022).

There is no clear answer on which of the two discussed methods provides the most realistic surface charge determination, as both techniques stand on several assumptions. Regardless of the surface charge model adopted, it appears that Coulombic interactions for kaolinite should be modelled by considering different charges for the alumina (octahedral), silica (tetrahedral) face, and edges.

3. DLVO theory

The DLVO theory assumes that the interaction between two charged particles in an electrolyte depends on the balance of electrostatic Coulombic forces and Van der Waals attractive forces acting between the particles.

Coulombic forces result from the interaction between electric double layers (EDLs). When a charged object is immersed in a polar fluid, it attracts ions of opposite charge and repels ions of like charge. This results in an excess of ions of one sign at the particle surface, referred to as the screening phenomenon (Debye and Huckel 1923), and an excess of ions of the opposite sign in the solution. Hence, a single charged clay particle in a polar fluid is surrounded by an Electrical Double Layer (EDL). The first layer of the EDL is formed by the charged ions firmly attached to the particle surface (Stern layer). The second layer consists of a non-uniform distribution of ions electrically attracted by the particle surface charge and subjected to a progressive thermal motion that drives them away from the particle itself. As a result, the electrostatic potential is exponentially dumped for increasing distance from the charged particle.

On the other hand, at particles distances from hundreds of nanometers down to interatomic spacing (about 0.2 nm), weak attractive van der Waals forces originate from the correlations in the fluctuating polarisations of nearby particles (Israelachvili 2011).

3.1. Coulombic interaction

Within the DLVO framework, the electrostatic energy can be estimated by computing numerically the electric potential distribution around the particle, which satisfies the Poisson-Boltzmann (PB) equation:

$$\nabla^2 \boldsymbol{\psi} = \frac{\delta^2 \boldsymbol{\psi}}{\delta x^2} + \frac{\delta^2 \boldsymbol{\psi}}{\delta y^2} + \frac{\delta^2 \boldsymbol{\psi}}{\delta z^2} = -\frac{n_0 e}{\varepsilon}\left(e^{-\frac{v_i e \psi}{kT}} - e^{\frac{v_i e \psi}{kT}}\right) \quad (1)$$

where $\boldsymbol{\psi}$ [N m C^{-1}] is the electrical potential, n_0 [ion/m^3] is the reference concentration taken at a considerable distance from the surface, ν is the ions valence, $\varepsilon = \varepsilon_0 \cdot \varepsilon_r$ is the dielectric permittivity, ε_0 is the dielectric permittivity in vacuum [ε_0=8.8542·10^{-12} C^{2}J^{-1}m^{-1}], ε_r is the relative dielectric permittivity, and e is the charge of the electron [e=1.602 10^{-19} C],

The boundary conditions to solve Eq. (1) depend on particle geometry and whether constant potential or constant charge is assumed at the particle surface. For the sake of simplicity, all the results proposed in this research are limited to the assumption of constant surface charge.

Resolving Eq. (1) for the electrical potential ψ enables the calculation of the free energy of the EDL in terms of Grand Potential Ω [J] (Gupta et al., 2020). At constant surface charge:

$$\Omega - \Omega_0 = \int_{\mathrm{B}} \sum_j q_j \boldsymbol{\psi}_j dB - \int_{\mathrm{V}} \left[\frac{\varepsilon}{2}|\nabla \boldsymbol{\psi}|^2 + kT\, n_0 \sum_i \left(\frac{n_i}{n_0} - 1\right)\right] dV \quad (2)$$

where Ω_0 [J] is the grand potential in the reservoir, B [m^2] represents all the boundaries indexed by j, V [m^3] is the system volume, ψ_i [V] and q_j [C/m^2] are the electric potential and the charge respectively at the jth surface, k is the Boltzmann constant [k=1.38 10^{-23} J K^{-1}], and T [K] is the absolute temperature.

3.2. Van der Waals interaction

Van der Waals forces are attractive intermolecular forces originating from the correlated motion of electrons in adjacent colloidal particles (Mitchell and Soga, 2005).

The van der Waals interaction energy for pairs of bodies of different geometry can be derived from the van der Waals interaction energy between two atoms. Under the assumption of additive interaction, one may integrate the interaction energy of all the atoms in one body with all the atoms in the other.

In the case of two colloidal square platelets of infinitesimal thickness and size L [m] at separation distance D [m], the van der Waals interaction energy, U_{vdW} [J/m^2], can be calculated as follows:

$$U_{vdW} = -\frac{A_H}{\pi^2 A}\int_0^L dy_2 \int_0^L dy_1 \int_0^L dx_2 \int_0^L \frac{1}{\left(\sqrt{(x_2-x_1)^2+(y_2-y_1)^2+D^2}\right)^6} dx_1 \quad (3)$$

with A_H being the Hamaker constant (Hamaker 1937) and A [m^2] being the particles surface.

According to Hamaker (1937), U_{vdW} is negative and, thus, attractive as the net force between colloidal particles is always attractive.

Eq. (3) can be analytically solved when considering parallel square platelets (De Rocco and Hoover 1960):

$$U_{vdW} = \frac{A_H}{\pi^2 A}\left[\frac{LD^2+2L^2D}{D^4\sqrt{L^2+D^2}}\operatorname{atan}\left(\frac{L}{\sqrt{L^2+D^2}}\right) - \frac{L}{D^3}\operatorname{atan}\left(\frac{L}{D}\right)\right] \quad (4)$$

3.3. DLVO interaction

The total interaction energy, U_t [J/m2], between two colloidal particles is the sum of the van der Waals contribution, U_{vdW}, and Coulomb electrostatic contribution, $U_{Edl} = (\Omega - \Omega_0)/A - U_0$ [J/m^2], with U_0 being the Coulombic free energy at infinite separation distance (Gupta et al., 2020).

$$U_t = U_{vdW} + U_{Edl} \quad (5)$$

where U_{vdW} is analytically computed according to Eq. (4) and U_{Edl} can be numerically derived according to Eq. (1) and Eq. (2).

However, as the van der Waals pair-interaction energy given in Eq. (4) is independent from the particles surface charge, σ, the following study focuses only on the electrostatic component of the total interaction energy, U_{Edl}.

4. Numerical modeling of Columbic interactions

Figure 4 shows the boxlike domain employed for finite element method (FEM) computation in the platform COMSOL to compute the electrostatic potential ψ and hence, the pair-wise electrostatic energy, U_{EDL}. Two charged parallel plates of infinitesimal thickness and finite size L=1000 nm are placed in the central region.

The boundary conditions to solve the PB equation (Eq. (1)) were as follows: (i) a Dirichlet boundary condition (DBC), ψ =0, was imposed on all the six outer surface boundaries of the box domain; (ii) on the platelets surface a Neumann boundary condition (NBC), $\boldsymbol{n} \cdot \nabla\psi = \sigma/\varepsilon$, was considered for the constant surface charge model. The simulation box size depends on the plate size and inter-plate separation. The electric potential, ψ, around the charged plates in electrolyte solutions practically vanishes at a distance of 300 nm outward from the plate surfaces both for constant surface charge and constant surface potential. As a result, the box side was fixed to 1200 nm to ensure that the distance of the particle surface from the outer box boundary was 300nm when the particles were positioned at the maximum interparticle distance of 600nm.

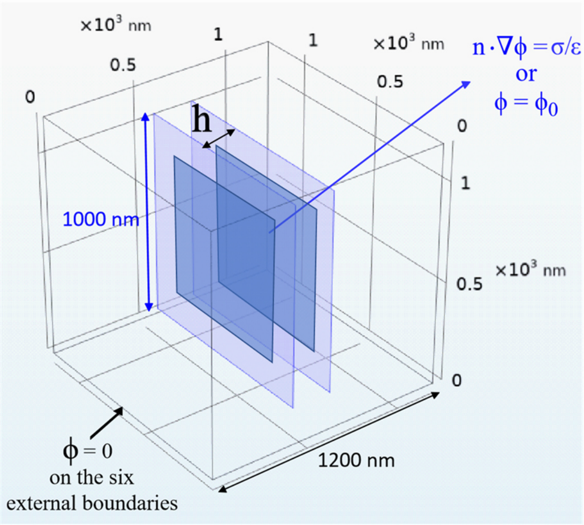

Figure 4. Schematic diagram of the boxlike analysis domain in COMSOL for finite element analysis of face-to-face particle configuration.

To simulate non-homogeneous charge distribution, the particle surface area was divided into two regions: an inner square (dark blue in Figure 4) representing the particle 'face' and an outer region surrounding the inner square (light blue) representing the particle 'edge'. The surface ratio between the face area, S_{face} [m^2], and the edge area, S_{edge} [m^2], is constant for all the performed simulations and equal to S_{face}/S_{edge}=1.77 (meaning that S_{edge} corresponds to 1/3 of the total particle area).

The boxlike domain was divided into two zones to implement the FEM analyses effectively. The squared particles (inner and outer area) were meshed with quadratic elements, having a side of 20 nm. The volume around the particles was meshed with tetrahedral elements, increasing size from the particles' surface to the domain's boundary, with a maximum element growth rate of 1.2.

5. Results and discussion

5.1. Validation of FEM numerical modelling

To assess the accuracy of the potential energy calculated at different interparticle separation distances using FEM in this work, the 1D FEM numerical solution of Eq. (2) was benchmarked against the rigorous solution of the PB equation derived by solving Eq. (1) for two parallel semi-infinite charged plates as proposed by Verwey and Overbeek (1948). The two solutions overlap (Figure 5), and the FEM analysis was used to derive the electrical potential under 3D conditions.

5.2. Effect of finite particle size

The FEM electrostatic energy for infinite parallel plates was compared to the pair-wise electrostatic energy of charged finite parallel plates of infinitesimal thickness.

The different curves presented in Figure 6 nearly overlap. For homogeneous surface charge in face-to-face configuration, the 1D solution can accurately describe clay platelet interaction regardless of particle size (as already proposed by Verwey and Overbeek, 1948). These results confirm that the FEM analysis procedure for solving the non-linear PB equation is successfully carried out also in 3D.

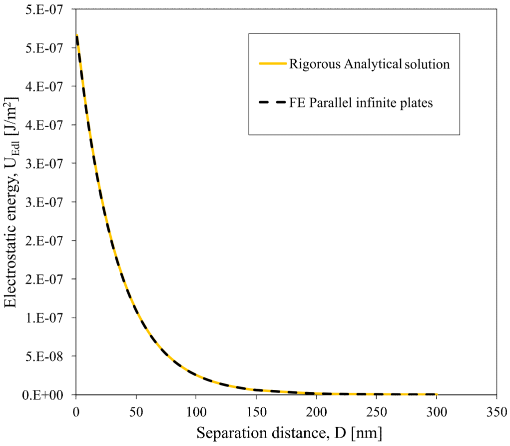

Figure 5. Validation of the finite element analysis for face-to-face infinite charged particles (1D) against the rigorous analytical solution according to Verwey and Overbeek (1948). A homogeneous surface charge equal to 2 mC/m^2.

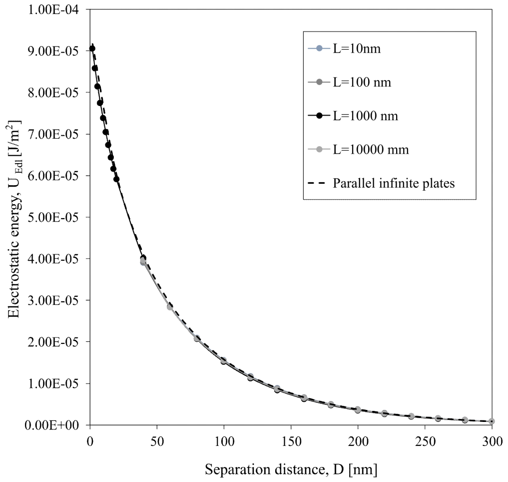

Figure 6. The electrostatic potential energy is computed numerically for facing parallel squared plates of increasing size (constant infinitesimal thickness) and compared with the 1D numerical solution for parallel infinite plates. A constant surface charge equal to 2 mC/m^2 was considered for all the computations.

5.3. Effect of particle thickness

Although real clay particles are plate-like particles with a thickness-to-width ratio varying from 1/10 (kaolinite) to 1/100 (smectite), the FEM domain in Figure 4 assumes infinitesimal particle thickness, as it allows for a consistent reduction in the computational costs of the numerical simulation. To confirm the validity of this assumption, the potential energy of two facing plates of finite thickness, t [m], was compared with the solution for infinitesimal thickness (Figure 7).

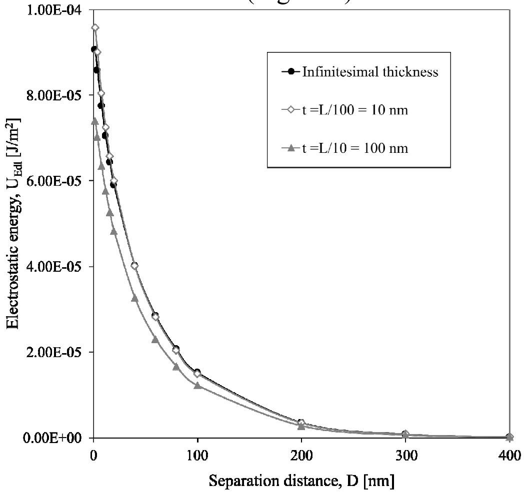

Figure 7. Electrostatic potential energy computed between two facing parallel squared plates of width L=1000 nm for varying plate thickness t. Constant surface charge equal to 2 mC/m^2 was considered for all the computations.

The potential energy for infinitesimally thick particles qualitatively catches the features of the behaviour of platelets characterised with more realistic finite thicknesses (Figure 7). With decreasing plate thickness, the electrostatic energy of the finite plates system approaches the one for infinitesimal thickness. The qualitative agreement between the electrostatic energies computed for particles of finite and infinitesimal thickness legitimises the choice of the model in Figure 4 to explore the influence of the total particle surface charge on the particle-to-particle electrochemical interaction.

5.4. Interaction of particle with homogeneous charge

According to the PB equation, the surface particle charge strongly affects the distribution of ions in the electrolyte solution and, thus, the distribution of electric potential, ψ, in Eq. (1).

Figure 8 shows the dependency of the energy separation function on particle surface charge under the assumption of homogeneous charge ($\sigma_{face} = \sigma_{edge} = \sigma$).

The electrostatic energy increases with increasing particle surface charge (Figure 8a). Moreover, Figure 8b reveals a non-linear dependency between the Coulombic interaction energy and the square of the surface electrical charge, contrary to what happens for purely electrostatic interaction between two charged planar surfaces in a media (capacitors).

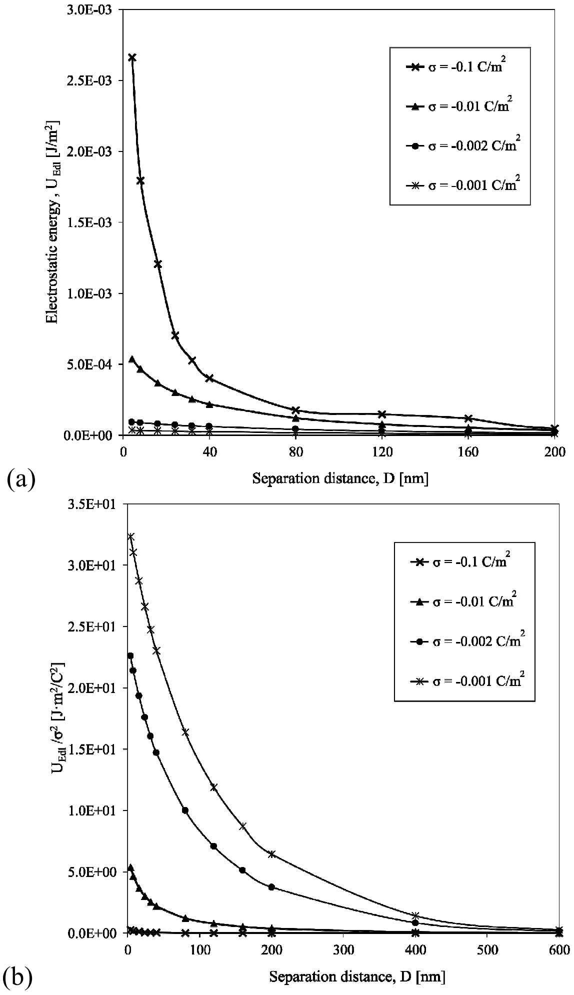

Figure 8. Dependency of the electrostatic potential energy on the homogeneous particle surface charge. A finite particle size equal to 1000 nm was considered for all the computations.

5.5. Interaction of particles with non-homogeneous charge

To investigate the dependency of σ_{edge} on the electrostatic energy between two interacting finite clay platelets, it is convenient to introduce the parameter R as the ratio $\sigma_{face}/\sigma_{edge}$. Considering a constant value of σ_{face}=-2mC/m^2, Fig. 9 explores the effect of positive particle edges (negative values of R) according to the traditional description of particle surface charge.

Figure 9 shows that, for increasing values of edges surface charge, the electrostatic energy does not vary monotonically for varying R. It monotonically decreases for decreasing R when $\sigma_{edge} < |\sigma_{face}|$ (R<0) and monotonically increases for $\sigma_{edge} > |\sigma_{face}|$ (R<-1).

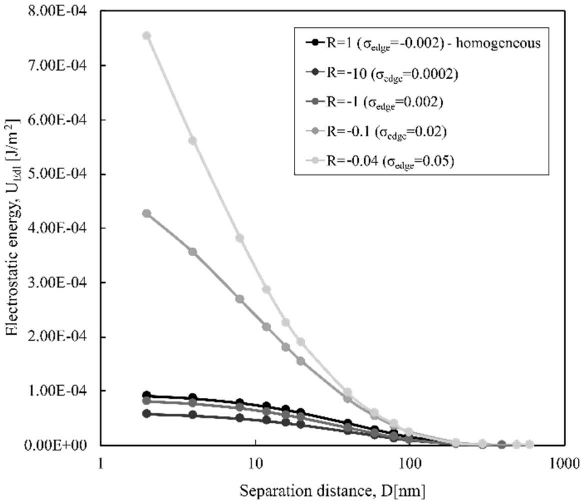

Figure 9. Dependency of the positive edge surface charge on the electrostatic potential energy. Finite particle size equal to 1000 nm and face surface charge σ_{face}=-0.002 mC/m^2 were considered for all the computations.

6. Conclusions

The paper has addressed the problem of deriving the Coulombic interaction forces for plates of finite size and thickness in 3D configuration by solving the Poisson-Boltzmann equation numerically via the Finite Element Method (FEM). It has been shown that 2D particles (plates of infinitesimal thickness) provide an adequate representation of Coulombic interaction as long as the particles are uniformly charged. The advantage of 2D particles is to reconcile numerical modelling with analytical solutions available in the literature. The use of 2D particles is questionable when considering different charges between basal planes and edges. 3D particles (plates with finite thickness) are likely required to model the effect of different charges between basal planes and edges.

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