



# BELBaR

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## Status report on the theoretical understanding of the effect of the Ca on clay gel stability DELIVERABLE D4.3

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## Summary

In the classical Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, the stability of the colloidal solution is determined by the net force resulting from the competition between the van der Waals attraction (vdW) and the diffuse double layer repulsion (DDL). The DLVO theory calculates the double layer interaction based on the Poisson-Boltzmann equation of point-charge electrolytes. As a consequence, this theory neglects entirely the ion-ion correlations and predicts only repulsive forces between electrical double layers for homo-interaction.

The ion-ion correlation effect has been used as one possible argument to interpret the Ca smectite behaviors, which have been observed to be very different from those of the Na smectite. One main effort is to explain, e.g., the formation of quasi-crystals and the limited osmotic swelling of Ca smectite.

It is known that the swelling of bentonite in aqueous system is controlled by different processes, e.g., crystalline swelling, osmotic swelling, breakup and formation of montmorillonite particles (stacks, tactoids or quasi-crystals), demixing of exchangeable cations, co-volume swelling and Brownian swelling.

However, to be not exhaustive here, the main objective of this report is to bring the awareness of the so called “ion-ion correlation” effect to simulate the swelling behavior of a compacted bentonite under water uptake. The scope of the theoretical survey is then limited to the current available methods to calculate the inter-lamellar forces.

In general, this report is devoted to a “first hand” status report of the widely used modern methods of statistic mechanics that have considered the ion-ion correlation effect to quantify the swelling between inter-lamellar layers and to investigate the role of divalent ions such as Ca on the structure of smectite particles. A more extensive report, concerning the “entire process” of bentonite swelling with associated swelling mechanisms and model methods, will be prepared in the future.

## 1 Background

Based on the KBS-3 design, the Swedish repository for spent nuclear fuel is planned to be located at about 500 m depth in granitic rock. The fuel rods containing spent fuel are emplaced in canisters made of an inner steel structure and an outer copper shell. The copper corrodes only if the corrosive agents can be transported to the copper surface. The canisters, which are about 5m long and 1.05 m in diameter, are placed in about 8 m deep vertical boreholes with a diameter of 1.75 m from the floor in the construction tunnels. The canisters are embedded by highly compact bentonite, which swells as the water from the rock fractures intrudes and saturates it. The hydraulic conductivity of the bentonite clay is so low that the water in it is effectively stagnant and the dissolved constituents, including the corrosive agents, transport very slowly through the buffer by molecular diffusion.

A critical issue for the success of such a deep underground repository is to prevent or minimize the release of bentonite clay particles into the water seeping in fractures intersecting the deposition hole. In Sweden, primarily two types of bentonite clays are investigated, i.e., the Na- and Ca-bentonite. This is because the most charge compensating cations residing on the outer surface of the smectite sheets are sodium and calcium, although potassium and magnesium are also found in small amounts in some clay. When clay takes up water, the charge compensating cations stay near to the surface of the sheets. An originally sodium-rich bentonite will exchange the sodium for calcium when exposed to calcium solution. This can impact the evolution of the swelling and other properties of the clay.

Observations suggest that calcium smectite swells nearly as strongly as the sodium smectite at high compaction densities but stops swelling at about 10-20 % volume fraction. By contrast, sodium smectite can swell indefinitely if not restrained by gravity in waters with very low salinity, i.e., under the critical coagulation concentration (CCC). Even in the case of non-saline water, however, calcium smectites do not seem to release colloids in upward expansion tests in a vertical tube. Such calcium gels may not be cohesive but only form larger particles than sodium gels, and consequently calcium gels do not form a distinct diffuse region at the gel/water interface as the sodium smectites do [Neretnieks *et al.*, 2009].

In order to explain the different behaviors of calcium and sodium bentonites, in this report, we discuss and summarize the current status of theoretical understandings of the cation dependence of the swelling of bentonite clays.

## 2 Bentonite properties

There is not a standardized set of terms to describe the properties of bentonite clays. For ease of reference, the following terms and definitions are used for certain entities throughout this report.

*Sheet*: the smallest building of clays, typically a very thin irregular coin-like sheet, sometimes called lamella or platelet.

*Stack*: a number of sheets held together mostly face to face, sometimes called quasi-crystals, tactoids or particles.

*Aggregate*: an agglomeration of stacks or particles held more loosely together than the sheets in the stacks/particles. The number of stacks in an aggregate can range from a few to many.

*Gel*: the stacks are held together and cannot move independently from each other.

*Sol*: the stacks or sheets are so far apart that they can move independently. In a *stable sol*, the repulsive forces are so strong that should particles come near each other by diffusion or gravity, they do not combine to form a new particle.

*Critical coagulation concentration (CCC)*: the CCC, in principle, sets up a borderline for the smectite to form cohesive gels and stable sol at certain conditions.

## 2.1 Bentonite mineral properties

Bentonite is volcanic ash weathering product. It is generally impure aluminum phyllosilicate clay consisting mostly of montmorillonite and typically contains tens of percent of accessory minerals, such as quartz, calcite and gypsum. The main constituent, i.e., montmorillonite, is a member of the smectite family. It is a 2:1 clay built up of a central octahedral layer sandwiched by two tetrahedral layers. The octahedral layer consists mostly of the aluminum oxide and the tetrahedral layer of mostly silicon oxide.

In the octahedral layer the trivalent aluminum is substituted, at some locations, by Mg or other divalent ions. In the tetrahedral layer the tetravalent silicon is occasionally substituted by aluminum. This causes a negative surplus charge in both layers. It is typically in the range between 0.2 and 0.4 eq per formula unit  $(\text{Si,Al})_4\text{O}_{10}$ , and it is compensated by the preferential adsorption of cations on the layer surfaces, intercalated between the unit layers [Olphen, 1997; Lagaly, 2006]. When clay takes up water, the charge compensating cations stay near to the surfaces of the sheets. In addition, the unit layer has at the edges a charge that arises from adsorption or desorption of protons and hence it is pH dependent, positive at acid pH and negative at basic pH. The point of zero charge of the edge sites is located at natural pH, i.e., close to pH 7, according to most literature data. This value has, however, recently been contested and remains under discussion [Lagaly, 2006].

In dry bentonite, the smectite sheets are packed close together with distances between the faces of the sheets of about one nm or less. When wetted with low ionic strength water the sheets form stacks of 5-20 sheets in the case of calcium smectite, but mainly individual sheets for sodium smectite. The sheets are typically hundreds of times larger than they are thick so that these thin sheets must arrange themselves essentially in parallel formation in compact clay. For similar reasons, the thickness of the stacks is increased by sheet-stacking, but still remains negligible in comparison to their major length.

## 2.2 Observations of the gel expansion

One of the experimental series to see the impact of gravity and concentration of mono- and divalent cations was performed by Jansson [2009]. A clay suspension was prepared in a test tube. A net was placed in contact with the suspension, the test tube was filled with solutions of different concentrations and the system was left overnight to settle. The tube was then turned upside down and the behavior was visually observed. Either the clay suspension fell through the net or stayed on top. By using this method, the CCC can be estimated.

The test tube experiments showed that divalent cations (i.e. calcium) are the most important ions for keeping bentonite from dispersing. The critical coagulation concentration obtained by this method was about 1–2 mM for calcium montmorillonite. While the corresponding value for sodium is about 100 times greater.

In short, the compacted bentonite used as buffer material around the copper canisters has a high swelling pressure when wetted. The higher the ionic strength is, the lower is the swelling pressure. The swelling can stop entirely when the ionic strength in the pore water is above the critical coagulation concentration. However, it is noted that below the CCC, sodium clays should expand “forever” if not restrained by gravity. In these situations, sols are formed and the colloidal particles can be transported away by the water seeping the fractures. This causes the buffer erosion.

It is to be noted that the water composition in the deep groundwater at the repository depth is normally above the CCC and no release of the colloids is then expected [Neretnieks *et al.*, 2009].

In the other type of gel expansion experiments, deionized water was added through the top into the vertically standing tubes [Dvinskikh and Furo, 2009]. These experiments showed that sodium as well as calcium rich bentonite swells rapidly and the compact Ca rich bentonite swells to at least 4 times their original volume. The calcium bentonite swells more rapidly than the sodium bentonite at the beginning of the expansion. The NMR imaging suggests that it expands from an average distance between the sheets starting about 1 nm to about 7 to 8 nm average distances between the sheets. By contrast, the purified and Na-exchanged bentonite continues to swell after 8 months. Under such circumstances, the divalent calcium ions seem to cause the smectite to form a denser gel than the monovalent sodium ions. As a consequence, in strongly Ca dominated gels the sheets tend to combine into dense stacks and such stacks will not readily be released even in de-ionized water.

### 3 The impact of bentonite stacks on its gel behavior

It has been found that, when bentonite clays are wetted, the size of Ca stacks is different from that of Na stacks. As a result, the impact on the gel behavior would be different.

When clay is exposed to water, the water molecules must intrude into between the sheets, being absorbed on the surface and hydrate the charge compensating ions. Overlapping diffuse double layers of the ions in the water forms between the sheets. This leads to a very strong swelling pressure of the clay. In low ionic strength waters the repulsive DDL force dominates over the attractive vdW force at all distances and the individual Na-smectite sheets can disengage from the stacks in the gel and form stable colloidal sol.

When sodium is dominating as the compensating ions, the stacks consist of one or at most two sheets on average [Cadene *et al.*, 2005]. If calcium dominates, the stacks or particles consist of 5 to 15 sheets or more. It is to be noted, however, that when sodium dominated clay contains particles with up to 30 to 40% calcium the particles still consist of one to 1.5 sheets on average [Bergaya *et al.*, 2006]. Clay with even up to 90 % Ca and the rest Na has been observed to behave similar to sodium dominated clay at very low ionic strength. Colloidal particles can be released in erosion tests [Birgersson *et al.*, 2009].

The reasons why calcium dominated clays behave so differently are not well understood. The observations that stacks with many sheets are formed in calcium dominated smectite can be explained by ion-ion correlation effects discussed later. This causes very strong attraction between the sheets. If all particles were equally affected by this effect, a total collapse of the gel would be expected and a rigid body with about 50 % porosity should form. This is not the case. One reason for this can be that the sheets have heterogeneous charge densities and charge distribution patterns so that when stacks are formed the outer sheets of a stack does not attract a new sheet. It even repels other sheets by reason(s) unknown. This would explain why calcium dominated clays swell strongly up to a point but no more.

A simple hypothetical model is proposed where the outer sheets of the stack behave as if they are sodium dominated. This would lead to repulsion between the stacks similar or equal to that of the individual sheets in sodium dominated clay. The DDL repulsion force would be the same for the same distance between stacks and sheets. The stacks would swell to the same distance between the outer sheets on the stacks as the distance between the individual sheets in sodium clays, if restrained by the same force e.g. gravity or vdW. The large stacks would be less prone to leave the gel by Brownian movement because of their larger mass. Sol formation would be more difficult.

This hypothetical model does not explain why the stacks are formed with the outer sheets behaving essentially as sodium charged sheets when the inner sheets in the stacks are strongly attracted by ion-ion correlations. However, it would explain why calcium dominated clay stacks have essentially the same swelling pressure at high volume fractions. It also explains why calcium clay expands more rapidly initially as the stacks have smaller surface to volume ratio and thus are less restrained in their movement against the water that intrudes the gel to replace the volume vacated by the stack. The friction force per mass of particle is smaller. It furthermore explains why calcium gel stops expanding at a larger clay volume fraction when the stacks reach the distance when the attractive van der Waals forces balance the repulsive DDL forces. The latter is conditioned on the ionic strength being sufficiently high that it is above the CCC. Below the CCC vdW forces will not be strong enough to balance the DDL forces at any stack/sheet distance. The individual sheets of sodium smectite will be able to release particles by thermal forces- Brownian movement- and form a stable sol. The much more massive stacks will not be released as readily. Gravity has a much stronger effect on the larger stacks and pulls back the stacks more strongly in vertically expanding gels. The above hypothetical model predicts that also calcium gel in de-ionized water should expand “forever”, forming a sol, when allowed to expand horizontally. The gravity then plays no role. The sol formation would be much slower, however, than for sodium clays as the “diffusivity” of the large stacks is much smaller than for individual sheets. We have found no long time experiments described in the literature to support this, however. Hopefully some of the experimental teams in BELBaR can be stimulated to make such experiments.

In order to understand the stack formation and give support to the hypothetical model described above the strong attractive forces between sheets in calcium dominated clays must be better understood and modeled. The ion-ion correlation effect, which retains Ca smectite in stacks of many sheets at close distances, has been postulated to explain why stacks are observed in the calcium system. The attractive forces due to the ion-ion correlations in Ca smectite arrange the individual sheets to form larger particles, i.e., the individual sheet “condensates” to quasi-crystals [Kjellander *et al.*, 1988b]. These are not like the flocculate particles that can form because in the latter case the sheets are loosely attached to each other and can readily be broken up again. By contrast, the quasi-crystals form large flat sheets of up

to 5,000 nm lateral size and several nm thickness [Neretnieks *et al.*, 2009]. The individual sheets in the compound particles (quasi-crystal) are strongly held together by the ion-ion correlations. Such configurations of the Ca exchanged smectite have been observed in the expansion and filtering experiments, where the Ca exchanged bentonite has difficulties in passing 100-200  $\mu\text{m}$  filters while the sodium exchanged smectite readily pass through filters down to 0.5-2  $\mu\text{m}$  [Birgersson *et al.*, 2009].

To be able to understand and simulate the swelling behavior of a compacted bentonite under water uptake, the structure of clay made up of mainly the smectite sheets and how the structure, and charge of counter-ions, could influence the inter-lamellar separations and subsequently the swelling pressure should be investigated.

The following part of this report is devoted to the understanding of the cation dependence of the bentonite swelling and the current methods of statistic mechanics to quantitatively determine the inter-lamellar forces of bentonite clays.

## 4 Cation dependence of inter-lamellar and inter-particle swelling

The basic structural units of smectite clays are negatively charged 0.96 nm thick lamellae, separated by cations and water molecules. However, the description of the structure of macroscopic clay as a simple collection of individual lamellae is far from being satisfactory, except in very dilute aqueous solutions of Na-exchanged montmorillonite. In most situations, at least one or two intermediate or mesoscopic structural features have to be introduced [Jullien *et al.*, 2005].

The swelling process of montmorillonite, which starts from a dry solid sample and expands it all the way to a suspension of individual or aggregated lamellae, is obviously a multi-scale process. In general, the first one is the increase of the distance between the lamellae within each particle. The second one is the increase of the surface-to-surface distance at the mesoscale voids between the particles.

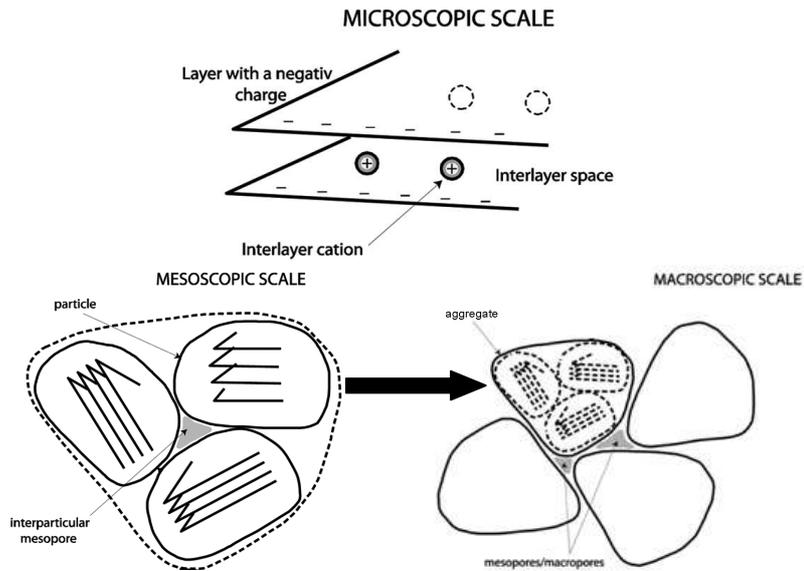


Figure 1. Representation of the multi-scale structure of swelling clays [Jullien *et al.*, 2005]

The expansion of the inter-lamellae space is referred to as crystalline swelling. As suggested by Salles *et al.* [2008], the crystalline swelling is occurring until the inter-lamellar cations have completed their main hydration shells, in a range of relative humidity values from 0.6 to 0.8 depending on the interlayer cation. As soon as the inter-lamellar space is completely filled with three or more layers of water molecules and as the ions and water molecules acquire a larger mobility, electrical double layers develop and a second swelling regime sets in. This swelling regime is often called the osmotic regime because it is ultimately driven by a larger ionic concentration in the lamellar space as compared to the other void spaces.

Still according to Salles *et al.* [2008], in this second process, a well established phenomenon in Na smectites, in which the cations are particularly mobile that it can lead to complete exfoliation that would eventually break up the stack and form individual platelets (sheets). However, in the Ca dominated smectites, the osmotic swelling process is not as complete as that of the Na smectites. The limiting dispersion state is a collection of quasi-crystals (stacks) in which the lamellae remain separated by three or four layers of water molecules. Although there is some understanding of the attractive forces which restrict the osmotic swelling (the so-called ion-ion correlation forces in particular), no theory has been able so far to predict the number of lamellae in a quasi-crystal. It should also be pointed out that, most of the current theoretical studies are based on the primitive model descriptions (as discussed later) for the electrolytes, where the structure effects of water molecules on the lamellar spacing and consequently the swelling pressure have been neglected.

The inter-particles voids normally have a wall-to-wall distance between 2 nm and 50 nm. As one of the current available techniques to measure the inter-particles pore size distribution, a thermoporometry experiment was carried out to verify that the inter-particles mesopores do indeed swell in the case of Na-montmorillonite [Salles *et al.*, 2008]. Those experiments were performed at various relative humidity values on swelling clays saturated with different interlayer cations. This swelling is starting at a relative humidity at the order of 0.54, well before the complete filling of the inter-lamellar voids. The interlayer expansion at the two water layers thickness, corresponding to a interlayer space opening or interlayer distance  $d_{001}$

= 15 Å, is reached at RH = 80% only (figure 2), and therefore the mesopore swelling of Na-bentonite starts when crystalline swelling still dominates.

For the Ca sample, in figure 2, the interlayer expansion to 2 water layer state (around  $d_{001} = 15$  Å) is reached at low RH. By further increasing the RH, the swelling of the mesopores at not very high relative humidity is, however, not observed or strongly limited in the Ca-exchanged montmorillonite [Salles *et al.*, 2010].

A possible interpretation of this difference in the behaviors of Na- and Ca- montmorillonite samples can be related to the capacity of a given ion-exchanged montmorillonite to undergo the osmotic swelling. Osmotic swelling is basically an entropy-driven process [Israelachvili, 1992]. With electrically charged surfaces, it requires a mobile swarm of counter-ions. The osmotic swelling is directly related to the ideal gas behaviors of an ionic cloud. Any deviation from this behavior, due for instance to the ion-ion correlation forces such as in Ca-montmorillonite, restricts the osmotic swelling. From this ideal gas perspective, the privileged osmotic swelling mechanism in Na-montmorillonite is in agreement with the electrical conductivity measurements [Salles *et al.*, 2008] which showed that the Na cations are much more mobile than other larger cations, such as Ca.

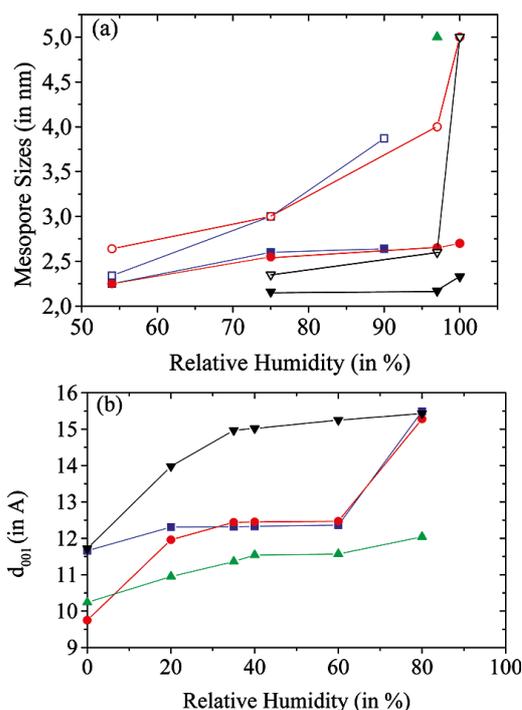


Figure 2. Evolution of the pore sizes as a function of RH for different cations for the principal (closed symbols) and second peak (open symbols) and comparison with XRD data [Ferrage *et al.*, 2005]. In these figures, the Li-, Na-, K-, and Ca-montmorillonites mesopores sizes and  $d_{001}$  are respectively reported by blue squares, red circles, green-up-triangles and black down-triangles [Salles *et al.*, 2010].

It can be concluded from the thermoporometry experiments shown in figure 2 that a swelling acts on the mesopores for Na montmorillonites even at low relative humidity. In contrast, for Ca- montmorillonites, the structure of the mesopores seems not to be influenced when the bentonite is kept unsaturated.

Based on the above discussions, we will proceed in the following to focus on the quantitative understanding of the swelling between inter-lamellar layers, where the calcium acts as dominating cations.

## 5 Ion-ion correlation effect

The ion-ion correlation effect has been considered as one possible argument to explain the Ca smectite behaviors, e.g., the formation of quasi-crystals and the limited osmotic swelling.

The strongly attractive forces were predicted theoretically by Kjellander *et al.* [1988b], when the so called “ion-ion correlation” effect has been included. Such prediction of an attractive region in the inter-lamellar pressure curve was found to be in close agreement with the experimental measurements of attractive forces between mica surfaces in  $\text{CaCl}_2$  solutions. These results present the first quantitative explanation of the marked effect of the calcium ions in arranging the individual sheets to form larger particles and preventing the swelling of the smectite. The short-range ( $<2$  nm) interaction between calcium-clay particles is of fundamental importance to understand the structural behavior of colloidal particles.

In their studies, the validity of the ion-ion correlation effect was tested by direct experimental measurements of the short-range swelling forces between the basal planes of two molecularly smooth muscovite mica surfaces in  $\text{CaCl}_2$  solutions of various concentrations. The surface force measurement technique was developed by Israelachvili and Adams [1978] and has been extensively used to study the liquid structure in very thin films. The forces measured between the negatively charged mica surfaces in a 0.15 M  $\text{CaCl}_2$  solutions are shown in figure 3.

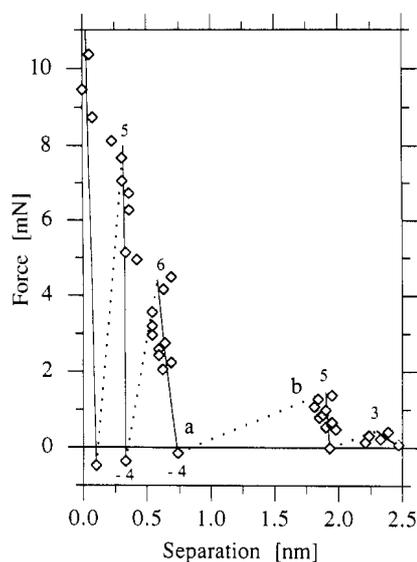


Figure 3. Forces measured between mica crystals in a 0.15 M  $\text{CaCl}_2$  solution [Kjellander *et al.*, 1988b].

In figure 3, the dotted regions of the curve cannot be measured using the spring technique. Instead, the surfaces were observed to jump from the force maxima to the next oscillation (e.g., from b to a). The single figures given on the graph are estimated pressures between mica surfaces at the maxima and minima in units of  $\text{MN}\cdot\text{m}^{-2}$ . It has been observed, at short separations, that the estimated pressures suggest some oscillations with a periodicity of about

0.3 nm, which is close to the diameter of the water molecule. As a result, such “oscillatory” forces were attributed to the ordered water molecular layers.

The measured minimum in pressure is  $-4 \text{ MN}\cdot\text{m}^{-2}$  at the separation of 0.75 nm between the lamellae layers, as indicated in figure 3. These results give strong support to the ion-ion correlation effect, which has been included in their theoretical calculations to predict a relative deep attractive well at separations between 0.65 to 1.8 nm under the same solution and surface conditions. As shown in figure 4, their theory (dots) predicts a pressure of  $-4.7 \text{ MN}\cdot\text{m}^{-2}$  at the separation of 0.85 nm when the surfaces carrying 1 negative unit charge per  $0.9 \text{ nm}^2$  immersed in a 0.15 M  $\text{CaCl}_2$  solution. It may be noted that one  $\text{MN}\cdot\text{m}^{-2}$  is equal to one MPa or about 100 atm. pressure holding the sheets together. For comparison, the tensile strength of concrete is in the same range as that holding the smectite sheets together, i.e., 2-5 MPa.

In figure 4, the theoretical and experimental results are combined to give a semi-schematic picture of the total swelling pressure curve for the Ca-mica platelets (curve). Once the structural effects of the water molecules are included, the inter-lamellar forces should be modified by introducing an oscillatory contribution. Although the three oscillations in the pressure between the positions *b* and *a* could not be measured (cf. figure 3), they have been shown here for clarity. Their theoretical calculations are indicated by dots in figure 4.

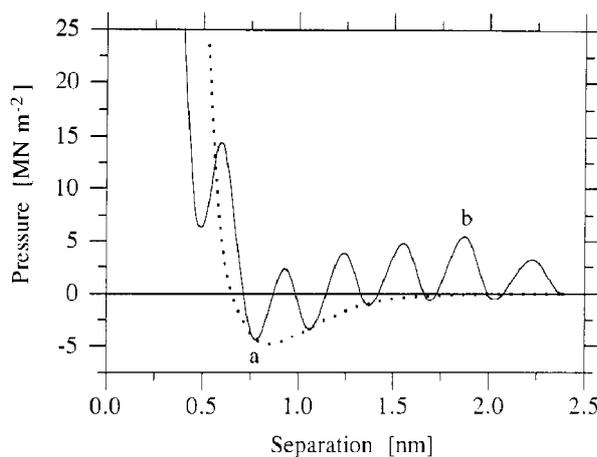


Figure 4. Semi-schematic representation of the interaction law between mica surfaces carrying 1 (negative) elementary charge per  $0.9 \text{ nm}^2$  immersed in a 0.15 M  $\text{CaCl}_2$  solution (curve). The calculated inter-lamellar pressures are shown with dots [Kjellander *et al.*, 1988b].

In addition, their experimental measurements in 0.4 and 2.0 M  $\text{CaCl}_2$  solutions also indicate attractive contributions to the double-layer forces, in rough agreement with the theoretical calculations. The remarkable agreement observed here between a sophisticated theory of the electric double layer and direct experimental measurements supports the conclusion that the limited swelling of the Ca-clays is due to an ion-ion correlation effect, which has been entirely neglected by the classic DLVO theory.

## 6 Forces between inter-lamellar layers

Having discussed the ion-ion correlation effect, the question is, then, how to quantify the forces between inter-lamellar layers. Towards that end, a variety of modern statistic mechanic

methods have been reported to investigate the role of divalent Ca on the swelling behavior of smectite gels.

## 6.1 Model

A simplified model of smectite sheets is to treat them as two planar negatively charged surfaces neutralized by sodium and/or calcium counter-ions. The lamellar structure is assumed to be in equilibrium with an infinite salt reservoir of known concentration.

Such a model system is constructed based on the so-called primitive model, where the smectite sheets are treated as two planar infinitely large walls with uniformly distributed surface charge density  $\sigma$ . As shown in figure 5, the walls are immersed in the primitive model of an electrolyte solution. Water is considered as structure-less dielectric continuum, the ionic species are modeled as charged hard spheres with a diameter  $d$  with the point charges embedded at the center of each sphere. The image charge effects are neglected in this model, since the relative permittivity of the surface wall is assumed to be the same with that of the medium as  $\epsilon_r$ . The dielectric constant of the vacuum is denoted as  $\epsilon_0$ . The walls are separated by a distance  $h$  apart, where the left wall is located at  $z = 0$  and the ions are in contact with the walls with the closest distance of  $d/2$  to the surface.

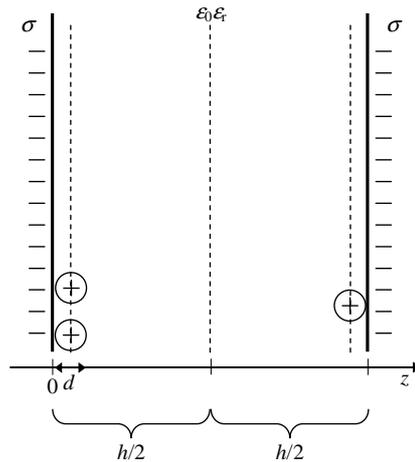


Figure 5. Representation of the model system

## 6.2 Force on a dividing plane

Based on the model system shown above, the force between two walls (or the inter-lamellar layers) can be described by focusing on a single plane in the model system and making a few physically motivated arguments. Regardless of what position of the plane we choose to examine, one would expect the inter-lamellar pressure to take the form [Rodgers, 2008],

$$P_{\text{int}} = k_B T \sum_i \rho_i(z) + \frac{\langle F_{\text{LR}} \rangle}{A} \quad (1)$$

where the inter-lamellar pressure  $P_{\text{int}}$  is evaluated on a dividing plane located at  $z$ .

In Eq. (1),  $\langle F_{LR} \rangle$  is the average force felt by the objects to the right of the plane due to the objects on the left of the plane.  $A$  is the cross-sectional area of the plane.  $k_B$  is the Boltzmann constant and  $T$  is the absolute temperature. The first term on the right-hand side of Eq. (1) is the “ideal gas” part of the pressure [Rodgers, 2008], and the explicit expression of the second term can be derived by counting the net force between the objects to the left and right of the dividing plane.

Obviously, the choice of the dividing plane can be made directly adjacent to one of the confining walls, and this choice gives rise to the commonly known “contact theorem” [Henderson *et al.*, 1979] that has been extensively applied to connect the thermodynamic property of the ionic fluid to its structure at the interface. That is, one can write,

$$P_{\text{int}} = k_B T \sum_i \rho_i \left( \frac{d}{2} \right) + \frac{\langle F_{LR} \rangle}{A} \quad (2)$$

If one assumes the dividing plane is immediately next to the left wall, the total force on the left wall can be written as a sum of the force  $F_{\text{ions-LW}}$  due to all the  $N$  ionic particles in the solution and the force  $F_{\text{RW-LW}}$  due to the right wall [Rodgers, 2008],

$$\frac{\langle F_{LR} \rangle}{A} = \frac{1}{A} (F_{\text{ions-LW}} + F_{\text{RW-LW}}) \quad (3)$$

Since the electric field  $E$  created by an infinitely large and uniformly charged wall is constant pointing out from the surface [Lyklema, 1995],

$$E = \frac{\sigma}{2\epsilon_0\epsilon_r} \quad (4)$$

the forces between the ions and charged wall can be obtained by multiplying the ion charges and the electric field; the force between two walls can be also described in a similar way. As a consequence, Eq. (3) becomes

$$\frac{\langle F_{LR} \rangle}{A} = \frac{1}{A} \left( \sum_{i=1}^N z_i e \frac{\sigma}{2\epsilon_0\epsilon_r} + \sigma A \frac{\sigma}{2\epsilon_0\epsilon_r} \right) \quad (5)$$

By using the overall electro-neutrality condition of the system,

$$\sum_{i=1}^N z_i e = -2\sigma A \quad (6)$$

Eq. (5) can be written as,

$$\frac{\langle F_{LR} \rangle}{A} = -\frac{\sigma^2}{2\epsilon_0\epsilon_r} \quad (7)$$

The combination of Eq. (2) and Eq. (7) results in the exact “contact theorem” as,

$$P_{\text{int}} = k_{\text{B}}T \sum_i \rho_i \left( \frac{d}{2} \right) - \frac{\sigma^2}{2\epsilon_0\epsilon_r} \quad (8)$$

It is, however, to be pointed out that the pressure of a coexisting bulk electrolyte  $P(\infty)$  should be subtracted if one aims to obtain a net pressure  $P_{\text{net}}$  between charged surfaces immersed in an electrolyte solution, i.e., one can write [Tang *et al.*, 1992],

$$P_{\text{net}}(h) = P_{\text{int}}(h) - P(\infty) = k_{\text{B}}T \sum_i \rho_i \left( \frac{d}{2}; h \right) - k_{\text{B}}T \sum_i \rho_i \left( \frac{d}{2}; \infty \right) \quad (9)$$

In Eq. (9), the van der Waals attraction is not included.  $\rho_i(d/2; h)$  denotes the density of ion species  $i$  in contact with the wall when the surfaces separation is  $h$ ;  $\rho_i(d/2; \infty)$  represents the corresponding one when  $h \rightarrow \infty$ .

Provided with the ionic density profile of the system under study, Eq. (8) and/or Eq. (9) is widely applied to evaluate the pressure at planar surfaces. In practice, however, it is numerically demanding to obtain a satisfactory accuracy of the inter-lamellar pressure  $P_{\text{int}}$  via Eq. (8), since the difference of two large quantities on the right-hand side Eq. (8) will probably result in a limited numerical accuracy in  $P_{\text{int}}$  [Gulbrand *et al.*, 1984; Rodgers, 2008]. This is one reason often emphasized for using, instead, a mid-plane as the dividing plane to determine the  $P_{\text{int}}$ . Additionally, the ionic density at mid-plane may be determined to much greater accuracy than the density at contact because the mid-plane density is so much more slowly varying at the center of the simulation cell.

If one uses the mid-plane ( $z = h/2$ ) to divide the system, Eq. (1) becomes,

$$P_{\text{int}} = k_{\text{B}}T \sum_i \rho_i \left( \frac{h}{2} \right) + \frac{\langle F_{\text{LR}} \rangle}{A} \quad (10)$$

or

$$P_{\text{int}} = k_{\text{B}}T \sum_i \rho_i \left( \frac{h}{2} \right) + P_{\text{LR}} \quad (11)$$

The mid-plane substantially divides the system into two subsystems (including two charged walls). It allows interactions between particles to penetrate from one side to the other, i.e., it prevents ions from moving from one half to the other but it is transparent to the electrical interactions [Gulbrand *et al.*, 1984].

In Eq. (11), the first term on the right hand side is the ideal kinetic contribution to the pressure, and it is named as kinetic pressure which is evaluated through the ionic density at the mid-plane of the system. It is to be noted that, the ideal contribution is the only term considered in the classic DLVO theory where the ion-ion correlations are neglected.  $P_{\text{LR}}$  is the average force per unit area across the mid-plane.

In order to evaluate  $P_{\text{LR}}$ , we can separate explicitly the pressure contributions due to the ions and due to the walls, i.e., one can write [Rodgers, 2008],

$$P_{LR} = P_{Li-RW} + P_{RW-LW} + P_{Ri-LW} + P_{Li-Ri} \quad (12)$$

where the subscripts Li denotes ions with  $z < h/2$  while Ri represents ions with  $z > h/2$ ; RW and LW specify the right wall and left wall, respectively.

By also including the ion-ion hard-sphere (hs) correlation,  $P_{LR}$  can be finally written as,

$$P_{LR} = P_{el} + P_{hs} \quad (13)$$

with

$$P_{el} = P_{Li-RW} + P_{RW-LW} + P_{Ri-LW} + (P_{Li-Ri})_{el} \quad (14-1)$$

and

$$P_{hs} = (P_{Li-Ri})_{hs} \quad (14-2)$$

where  $P_{el}$  is the electrostatic correlation pressure, this part gives the direct electrostatic interaction between the two halves of the system on either side of the mid-plane and it originates from the electrostatic correlation between the ions.  $P_{hs}$  is the hard sphere contact pressure arising from the collisions of the ions across the mid-plane.

## 6.3 Integral equation method

To explicitly evaluate the electrostatic correlation pressure  $P_{el}$  and the hard-sphere contact pressure  $P_{hs}$ , Kjellander and Marčelja [1986] formulated expressions for these pressure components based on the integral equation method.

The electrostatic correlation pressure is written as,

$$P_{el} = -\sum_{ij} \int_{h/2}^{h-d/2} dz \rho_i(z) \int_{d/2}^{h/2} dz' \rho_j(z') \times \int dr \frac{\partial u_{ij}(r, z, z')}{\partial z} h_{ij}(r, z, z') \quad (15)$$

where  $u_{ij}$  is the Coulomb pair potential.  $h_{ij}$  is the total correlation function, which depends on three coordinates, i.e., the  $z$ -coordinate of two ionic particles and their separation  $r$  [Kjellander *et al.*, 1988a].

The hard-sphere contact pressure is given by,

$$P_{hs} = k_B T \sum_{ij} 2\pi \int_{h/2}^{h-d/2} dz \rho_i(z) \int_{d/2}^{h/2} dz' \rho_j(z') \times (z - z') g_{ij}([d^2 - (z - z')^2]^{1/2}, z, z') \quad (16)$$

where  $g_{ij}$  is the pair distribution function.

In Eq. (16), the integrals are only to be taken for the values of  $z$  and  $z'$  where the argument of the square root is positive [Kjellander and Marčelja, 1986].

Noticeably, prior to the calculations of these pressures through Eqs. (15) and (16),  $g_{i,j}$  or  $h_{i,j}$ , together with the ionic density distribution  $\rho_i$ , has to be obtained. Towards that end, the formally exact integral Ornstein-Zernike (OZ) equation is given in the planar geometry as [Attard, 2002],

$$h_{i,j}(r, z, z') = c_{i,j}(r, z, z') + \sum_k \int dz'' d\mathbf{r}'' \rho_k(z'') c_{i,k}(|\mathbf{r} - \mathbf{r}''|, z, z'') h_{k,j}(r'', z'', z') \quad (17)$$

where the total correlation function  $h$  between two ions, at  $z$  and  $z'$ , is the sum of the direct correlation  $c$  between them plus the indirect correlation mediated by a third particle at  $\mathbf{r}''$ . This indirect correlation is described by the direct correlation between particle at  $z$  and particle at  $\mathbf{r}''$  times the total correlation between particle at  $\mathbf{r}''$  and particle at  $z'$ , integrated over the space.

Since the OZ equation represents a relation between two unknown correlation functions, i.e.,  $h$  and  $c$ , a second equation is required to close the set,

$$g_{i,j} = h_{i,j} + 1 = \exp[-\beta u_{i,j} + h_{i,j} - c_{i,j} + b_{i,j}] \quad (18)$$

Eq. (18) is called the closure equation.  $\beta = 1/k_B T$  and  $b$  denotes a bridge function. In practice, however, there is no simple expression of the bridge function and it is in fact very difficult to evaluate. For this reason, the anisotropic hyper-netted chain (HNC) integral method developed by Kjellander *et al.* [1992] neglects it entirely.

Eq. (17) and Eq. (18) give a completed system of equations for the case of a homogeneous fluid, where the density is equal everywhere. One usually sets up an iterative procedure to solve these equations numerically. However, for the study of inhomogeneous fluid, the density varies from point to point, Eqs. (17) and (18) have to be supplemented by a equation of the ion density distribution.

For instance, the anisotropic HNC integral method determines the density distribution from the equilibrium condition where the chemical potential  $\mu_i$  of the bulk solution is equal to that of the system under study, i.e.,  $\mu_{i,\text{bulk}} = \mu_i$ , where

$$\mu_i = \mu_i^0 + k_B T \ln \rho_i(z) + \mu_i^{\text{ex}}(z) \quad (19)$$

with

$$\mu_i^0 = k_B T \ln \Lambda_i^3 \quad (20)$$

where  $\Lambda_i$  is the de Broglie thermal wavelength.

In Eq. (19),  $\mu_i^{\text{ex}}$  is the excess (non-ideal) chemical potential that originates from the ionic particle interactions in the system. The last two terms in Eq. (19) are position dependent, but their sum is constant at equilibrium. Based on the anisotropic HNC approximation,  $\mu_i^{\text{ex}}$  can be explicitly determined as,

$$\begin{aligned} \mu_i^{\text{ex}}(z) = & v_i(z) - \frac{1}{2\beta} \left[ h_{i,i}(0, z, z) - c_{i,i}(0, z, z) \right] \\ & + \frac{2\pi}{\beta} \sum_j \int r dr dz' \rho_j(z') \left[ \frac{1}{2} h_{i,j}^2(r, z, z') - c_{i,j}(r, z, z') \right] \end{aligned} \quad (21)$$

where  $v_i$  is the ion-wall interaction potential.

Subsequently, Eq. (21) is used to describe the equilibrium density profile of the ionic particles through,

$$\rho_i(z) = \zeta_i \exp[-\beta\mu_i^{\text{ex}}(z)] \quad (22)$$

with  $\zeta_i$  defined as the activity, and it is given by

$$\zeta_i = \exp(\beta\mu_i) / \Lambda_i^3 \quad (23)$$

For a given chemical potential, the above three equations, i.e., Eqs. (17), (18) and (22), together with the overall electro-neutrality condition of the system, from a closed set of equations for  $h_{i,j}$ ,  $c_{i,j}$  and  $\rho_i$ . The mathematical transformations necessary to solve them are presented by Kjellander *et al.* [1988a].

Within the primitive model of electrolyte solutions, the anisotropic HNC integral method in general gives accurate solution for the surface-surface interaction. The agreement with, e.g., the Monte Carlo simulation is good. In figure 6, the anisotropic HNC calculations from Eqs. (11), (15) and (16) are presented to study the inter-lamellar pressure vs. separation for a system in equilibrium with a 2.0 M 2:1 electrolyte. The surfaces are modeled with uniform surface charge density  $\sigma = -0.267 \text{ C}\cdot\text{m}^{-2}$ .

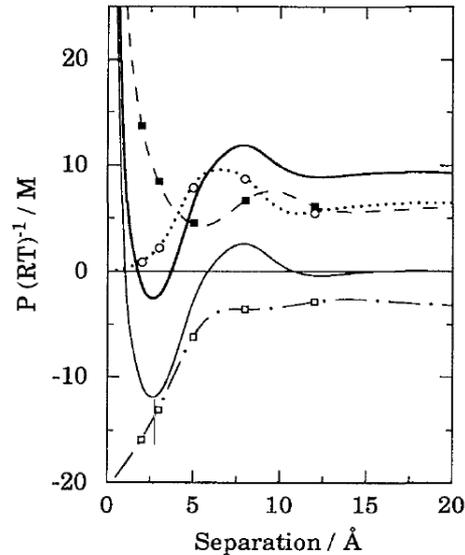


Figure 6. Pressure components for the system in equilibrium with a 2.0 M 2:1 salt solution. (- - -) and (■) kinetic component; (...) and (○) collision (ion-ion core contact) contribution; (-·-·-) and (□) electrostatic correlation component [Kjellander *et al.*, 1992].

In figure 6,  $P_{\text{int}}$  is shown as thick full line while the net pressure  $P_{\text{net}}$  is shown as a thin full line. It should be pointed out that the separation, in this figure and the following figure 7, is defined as the distance between the points of closest approach of the ions to the walls, i.e.,  $h = \text{separation} + d$ , with  $d = 4.25 \text{ \AA}$ . Attractive regions can be observed in both  $P_{\text{int}}$  and  $P_{\text{net}}$  at a separation  $h = \sim 7 \text{ \AA}$ . It is also indicated in figure 6 that the total inter-lamellar pressure is a result of the interplays among different pressure contributions.

## 6.4 Density functional theory method

Although the integral OZ equation method, such as the anisotropic HNC method was proved to be successful in reproducing the Monte Carlo results with respect to the pressures between inter-lamellar layers at different surface separations, the computational efforts to solve the integral OZ equation are formidable. Mainly for this reason, the density functional theory (DFT) that has been intensively developed over the last two decades are also widely used in the study of surface interactions as they involve much less numerical difficulties.

However, the pressure expressions developed by Kjellander *et al.* are formulated in terms of the ion-ion (pair) distribution function, which are the direct result of the integral equation methods but not those of the DFTs.

To tackle this problem, the authors of the present report have developed a novel expression for describing the pressure between charged plates. This expression is similar in structure to that obtained by Kjellander and Marčelja [1986], but it is given as a function of the single-particle direct correlation functions (DCF)  $c_i^{\text{el}}$  and  $c_i^{\text{hs}}$ , which are the byproducts of all the typical DFT approaches. That is, we can write [Wang *et al.*, 2011b],

$$P_{\text{el}} = k_{\text{B}}T \sum_i \int_{h/2}^{h-d/2} \rho_i(z) \left[ dc_i^{\text{el}}(z)/dz \right] dz \quad (24)$$

and

$$P_{\text{hs}} = k_{\text{B}}T \sum_i \int_{h/2}^{h-d/2} \rho_i(z) \left[ dc_i^{\text{hs}}(z)/dz \right] dz \quad (25)$$

Notably, both  $P_{\text{el}}$  and  $P_{\text{hs}}$  are functions of the single-particle DCFs, which are already available from the results of either of the DFT methods that we have proposed, e.g., the fundamental measure theory (FMT)/weighted correlation approach (WCA) method and the FMT/mean spherical approximation (MSA) method [Wang *et al.*, 2011a, 2011b]. This makes Eq. (11) together with Eq. (13) not only convenient to use but also allows us to analyze different contributions to  $P_{\text{int}}$  as done by Kjellander and Marčelja [1986].

As formulated theoretically in our work [Wang *et al.*, 2011a, 2012], the so-called weighted correlation approach (WCA) method was developed to evaluate  $c_i^{\text{el}}$  through,

$$\Delta c_i^{(1)}(z) = \sum_j \int ds \bar{c}_{ij}^{(2)}(z, s) \Delta \rho_j(s) \quad (26)$$

where  $\Delta c_i^{(1)}(z)$  represents the change of single-particle direct correlation function from a reference state to the state under study, i.e.,  $c_i^{(1)}(z)$ .  $\bar{c}_{ij}^{(2)}(z, \mathbf{s})$  is the weighted pair direct correlation function, given by,

$$\bar{c}^{(2)}(z, \mathbf{s}) = \sum_m \alpha_m \frac{\int c^{(2)}(z, \mathbf{s}; f_m) f_m(\mathbf{r}') d\mathbf{r}'}{\int f_m(\mathbf{r}') d\mathbf{r}'} \quad (27)$$

with

$$\sum_m \alpha_m = 1 \quad (28)$$

where  $f_m$  represents a correlation-weight function that may depend spatially on the local densities of the ionic fluid under study.  $c^{(2)}(z, \mathbf{s}; f_m)$  is the pair direct correlation function of the inhomogeneous ionic fluid for a particle at  $z$  and a particle at  $\mathbf{s}$  separated by a distance  $r$ .  $\alpha_m$  denotes a correlation-weight factor that should be specified based on the choice of the  $f_m$ -function.

Based on Eqs. (26) to (28), the ionic density distribution, and consequently the single-particle DCFs, can be obtained via

$$\rho_i(z) = \rho_{i,\text{bulk}} \exp\left[-\beta z_i e \psi(z) + \Delta c_i^{\text{HS}}(z) + \Delta c_i^{\text{EL}}(z)\right] \quad (29)$$

where  $\psi$  is the mean electrostatic potential of the electrolyte, and it is given in the following as,

$$\psi(z) = \frac{1}{\epsilon_0 \epsilon_r} \sum_j \int_z^{h/2} dz' (z - z') \rho_j(z') z_j e + \psi(h/2) \quad (30)$$

In Eq. (30),  $\psi(h/2)$  is the mid-plane potential between the plates and it is an undetermined constant. For each specific separation  $h$ ,  $\psi(h/2)$  has to be computed by solving the ion density distributions from Eq. (29), in combination with the overall electro-neutrality condition.

Having discussed this, in figure 7a, the net pressures between charged plates are calculated from the DFT formulations, and plotted as a function of surface separations for the case of a 2.0 M 2:1 electrolyte solution that has also been studied by the integral equation method in figure 6. The DFT methods, particularly the FMT/WCA method compares well with the MC results that indicate the pressure curve is strongly oscillatory to give not only two attractive minima but also a repulsive maximum.

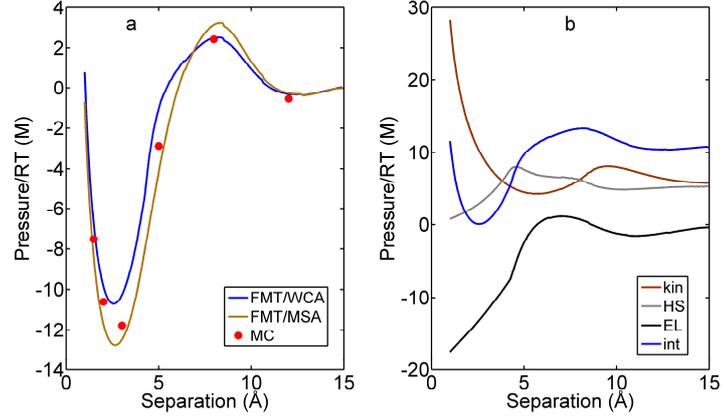


Figure 7. For a system in equilibrium with a 2.0 M 2:1 electrolyte solution: the net pressures calculated by the FMT/WCA and FMT/MSA approaches are shown with Monte Carlo results (MC) in (a); the inter-lamellar pressure (int) with the ideal kinetic (kin) contribution, the hard-sphere (HS) contribution and the electrostatic (EL) contribution calculated by the FMT/WCA approach are plotted in (b).

In order to explore the patterns of the net pressure curve, we present in figure 7b the individual components of the FMT/WCA inter-lamellar pressure for the case shown in figure 7a. Clearly, three distinct regions can be identified on the plot, where the pressure  $P_{\text{int}}$  shows different features. In the first region of  $h < 2d$ ,  $P_{\text{int}}$  first goes down to a minimum and then up. In the second region of  $h$  between  $2d$  and  $3d$ ,  $P_{\text{int}}$  continues to rise until a maximum and then turns down. In the third region of  $h > 3d$ , a secondary minimum can be observed. Since these features are in conformity to those shown in figure 7a and no negative values of  $P_{\text{int}}$  are found, the attractive net pressures can only result from a relatively high bulk pressure  $P_{\text{bulk}}$ , which is on the order of magnitude of  $P_{\text{int}}$  at the end point where  $h = d + 15 \text{ \AA}$ .

## 6.5 Monte Carlo simulation method

The Monte Carlo (MC) simulations [Segad *et al.*, 2010, 2012] also showed that the limited swelling of clay in presence of divalent counter-ions is a consequence of ion-ion correlations. In their study, it has been suggested that when montmorillonite is in contact with a salt reservoir containing both Na and Ca counter-ions, the swelling would be limited unless the Na concentration in the bulk is several orders of magnitude larger than the Ca concentration.

To describe the pressure of the confined solution, Segad *et al.* [2010, 2012] use a very similar expression based on the “force on the dividing plane” to give,

$$P_{\text{int}} = k_B T \sum_i \rho_i \left( \frac{h}{2} \right) + P_{\text{el}} + P_{\text{hs}} \quad (31)$$

In practice, however, they reported an experimentally interesting quantity, i.e., the net pressure between the charged platelets by also including the contribution from van der Waals interaction,

$$P_{\text{net}}^{\text{total}} = P_{\text{net}} - \frac{A_{\text{H}}}{6\pi h^3} \quad (32)$$

where  $A_{\text{H}}$  is the Hamaker constant.

In figure 8, they have initially studied a salt free system with surface charge densities  $-0.16 \text{ C}\cdot\text{m}^{-2}$ , where the monovalent and divalent counter-ions are present. The total pressure, including both  $P_{\text{int}}$  and van der Waals interaction, is drawn as lines without symbols, while the electrostatic component only is drawn as lines with filled circles. Solid lines are for a system with monovalent counter-ions and dashed lines for divalent. It is to be noted that,  $P_{\text{int}}$  obtained from the PB equation are presented by the dashed line with squares for the case of divalent counter-ions.

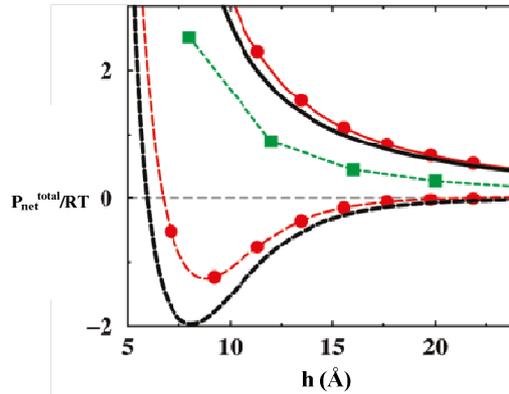


Figure 8. Total net pressure as a function of separation for a surface charge density of  $-0.16 \text{ C}\cdot\text{m}^{-2}$  [Segad *et al.*, 2010].

In addition, they have considered a situation where both mono- and divalent ions are used to neutralize the surface charges; the total net pressure becomes strongly dependent on the counter-ion composition in the double layer.

They simulated a clay system in equilibrium with a salt solution containing a mixture of Na and Ca ions. Even if there will be a competition for the charged surfaces between Na and Ca ions when they are both present in the bulk electrolyte, Ca ions will dominate in the double layer in general, but the detailed outcome will depend mainly on two factors, the surface charge density and the concentration ratio between Na and Ca counter-ions in the bulk [Segad *et al.*, 2010]. Figure 9 shows a system with  $\sigma = -0.14 \text{ C}\cdot\text{m}^{-2}$ . If, however, the surface charge density is low, ion-ion correlation effects becomes less important and consequently the Ca ions will not dominate the double layer interaction.

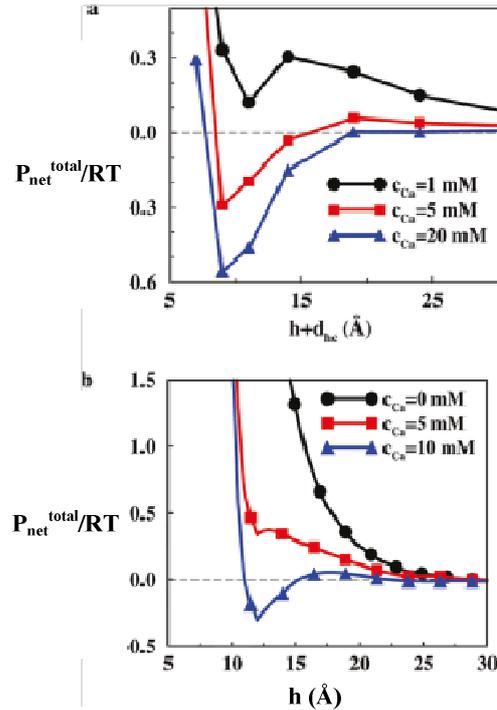


Figure 9. Total net pressure as a function of separation. The bulk contains a mixture of NaCl and CaCl<sub>2</sub> and  $\sigma = -0.14 \text{ C}\cdot\text{m}^{-2}$ . The NaCl concentration is kept constant at (a) 100 and (b) 500mM, while the CaCl<sub>2</sub> concentration is varied as indicated in the graphs [Segad *et al.*, 2010].

The MC simulation has also been performed to investigate the role of divalent Ca on the stable basal spacing of bentonite smectite [Chavez-Paez *et al.*, 2001]. Their study was performed by using the computer simulations in the  $\mu VT$  ensemble (chemical potential, volume and temperature are constant). In this method, the system samples its configuration space through molecular displacements and concentration fluctuation and acceptance probability of finding such a configuration follows the exponential law with respect to the interaction energy in a clay-water system saturated with calcium cation [Bounds, 1985]. It is found that the interlayers developed two or three layers of water in the Ca-montmorillonite of the Wyoming type, which is in agreement with the thermoporometry [Jullien *et al.*, 2005] study shown in figure 2. Whereas the Na montmorillonite has a more open structure than that of the Ca montmorillonite. Ca-clays have a tighter structure, thereby yielding more compact and stable particles at the macroscopic level.

In general, the MC simulation results can be used as the “benchmark” data to quantitatively understand the role of divalent Ca on the swelling between inter-lamellar layers, in the primitive model of the clay-water system that the statistic mechanic approaches, e.g., the integral equation and DFT methods, are always based on. The Monte-Carlo method can be thought of as solving the primitive model “exactly”. The approximate analytical models can be tested against such results.

Recent efforts of the MC studies have been devoted to investigate the effect of surface charge discretization on the ionic structure in contact with the planar surfaces, which would have a direct influence on the inter-lamellar forces of the bentonite clays. For instance, Madurga *et al.* [2007] used the MC simulation to calculate the ionic density distribution near models of discretely charged surfaces. It should be noticed that, dealing with discretized surface charge, the ionic densities should depend on three coordinates, i.e.,  $x$ ,  $y$  and  $z$ . However, their

simulation results were presented in the  $z$ -direction only, and therefore it might be interpreted as a mean value averaged over the directions parallel to the surface. By comparisons with calculations based on the charge smeared out surface, the ion density distributions suggested that significant discrepancies appeared even for 1:1 electrolytes when the surface charges are treated as finite size spheres with a radius of 0.3 nm, whose center are situated at the surface, i.e., DISC2 model in figure 10c. For the model of point charge sites just on the surface (DISC1 in figure 10b), no differences were, however, found in the ionic distribution as compared to those resulting from uniformly charged surface (CONT in figure 10a).

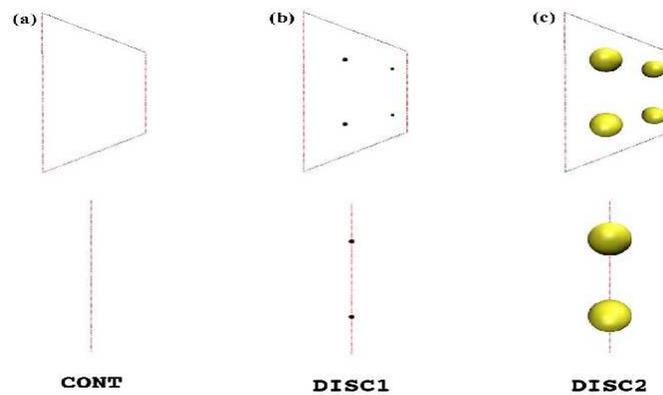


Figure 10. Pictures of the models for surface charge distribution: (a) continuous charge distribution (CONT model), (b) discrete distribution of point charge sites over the surface (DISC1 model), (c) discrete distribution of spherical charge sites of a radius over the surface (DISC2 model) [Madurga *et al.*, 2007].

Additionally, by using a different model of discretely charged surfaces where the point charge sites are located at a distance  $d/2$  behind the surface, the MC simulation carried out by Khan *et al.* [2005] indicated that the attractive force due to the ion-ion correlation effect near a charge smeared out surface was weakened and could even turn to a repulsive force. In any case, the influence of the surface charge configurations should be considered, in a more realistic picture, to study the colloidal stability.

## 7 Remarks

This report is partially based on our main contributions during this period of work [Wang *et al.*, 2011a, 2011b; Liu, 2013]. It aims to bring the awareness of the so called “ion-ion correlation” effect to simulate the swelling behavior of a compacted bentonite under water uptake. In particular, such effect should be well represented in theoretical attempts that try to understand how the structure, and charge of counter-ions, could influence the inter-lamellar separations and subsequently the swelling pressure.

The present report also provides a status report on widely used modern methods of statistic mechanics, by considering the ion-ion correlation effect, to quantify the forces between inter-lamellar layers and to investigate the role of divalent Ca on the swelling behavior of smectite gels.

It should be pointed out that the scope of this report is currently limited to the theoretical understanding of the interactions between inter-lamellar layers of smectite when it has not

swollen as much as it could by given access to more water. However, if one studies the “entire process” of bentonite swelling, there are other swelling stages in addition to the crystalline and/or osmotic interlayer swellings. For instance, Laird [2006] mentions the inter-particle osmotic swelling, breakup and formation of montmorillonite particles (stacks, tactoids or quasi-crystals), demixing of exchangeable cations, co-volume swelling, and Brownian swelling that generally operate in concert to control the swelling of bentonite in aqueous systems. A detailed discussion on these swelling mechanisms can be found in a very recently published paper by one of present authors [Liu, 2013].

It should be also noted that, a variety of methods have been proposed to simulate the swelling pressure of bentonite. Among them, the regression equation methods [Komine and Ogata, 1999], the phenomenological model methods [Alonso *et al.*, 1990; Roscoe and Burland 1968], the thermodynamic methods based on a relationship between swelling pressure and suction [Sposito, 1972; Agus and Schanz, 2008] and the diffuse double-layer model methods [Bolt, 1956; Schanz and Tripathy, 2009] have also been reported in the literatures, in addition to the modern statistic methods that are discussed in this report.

In a different way from the above methods, Liu [2013] has developed a simple mechanistic model method to predict the swelling pressure of fully saturated, bentonite-based materials in distilled water or dilute saline solutions over a large range of final dry densities of bentonite. The model applies in essence the thermodynamic approach of Sposito [1972] to describe crystalline swelling, while using a diffuse double-layer model method to explain the behavior of osmotic swelling. In addition, it accounts for the demixing of exchangeable cations and the disintegration of the montmorillonite particles into small stacks of unit layers upon water uptake.

Readers, who are interested in the detailed formulation of this mechanistic model, are encouraged to refer to the publication [Liu, 2013]. The model performance are, however, summarized here: the model predictions are in excellent agreement with a great number of experimental results of swelling pressures of different types of bentonites and bentonite-aggregate mixtures in both distilled water and saline. It is found that the water chemistry, the montmorillonite content, the type and amount of exchangeable cations in the interlayers are important in determining the extent to which the montmorillonite particles are delaminated and hence the swelling behavior of saturated, bentonite-based materials.

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