COMPARATIVE MODELING OF IONS AND SOLVENT

PROPERTIES IN Ca-Na MONTMORILLONITE BY ATOMISTIC SIMULATIONS AND FLUID DENSITY FUNCTIONAL THEORY

GUOMIN YANG^{1,*}, NIKOLAOS PRASIANAKIS¹, AND SERGEY V. CHURAKOV^{1,2}

¹Laboratory for Waste Management, Paul Scherrer Institute, 5232 Villigen-PSI, Switzerland

²Institute of Geological Sciences, University of Bern, Baltzerstrasse 1+3, Room 121, CH-3012 Bern, Switzerland

Running head: Comparative modeling of ions and solvent properties in Ca-Na montmorillonite

*Corresponding author. E-mail: guomin.yang@psi.ch; ygmsysu@gmail.com

ABSTRACT - Molecular dynamics (MD) simulations provide an accurate description of the mineral–fluid interface from the perspective of the atomistic level taking into account all atom interactions. This simulation approach is computationally expensive if applied to large molecular systems. Classical Fluid Density Functional Theory (f-DFT) delivers structural and thermodynamic information at comparatively small computational costs. Numerous applications of f-DFT for electrolytes neglect an explicit consideration of solvent. In this work, an unrestricted three-component model (3CM) of f-DFT was applied, which incorporates Lennard-Jones (LJ) attractions for the description of the short-range interactions of fluid–fluid and fluid–wall rather than the hard sphere repulsions, named DFT/LJ-3CM. The DFT/LJ-3CM model considers ions as charged LJ particles and treats solvent molecules as neutral LJ particles. To validate the performance of the DFT/LJ-3CM, the f-DFT calculations were compared with atomistic simulations for montmorillonite (Mnt) with various hydrated states in electrolyte solutions. This benchmarking was used to assess critically the advantages and limitations of the f-DFT

22 model. The calibrated DFT/LJ-3CM model for Na and Ca Mnt was applied to calculate cation selectivity
23 for the ion exchange equilibrium with effective ion radius and swelling behavior of Mnt. The predictions
24 of the DFT/LJ-3CM model were found to be in good agreement with the atomistic simulations and
25 experimental data under a wide range of conditions. At the same time, the DFT calculations were 3-4
26 orders of magnitude faster than conventional MD simulations. Thus, the DFT/LJ-3CM model can be a
27 computationally effective alternative to atomistic simulation in providing structural and thermodynamic
28 properties of fluid–clay mineral interfaces. The DFT/LJ-3CM model provides a robust approach, which
29 can be used for upscaling in reactive transport simulators and modeling ion migration taking place under
30 more complex thermo-chemo-hydro-mechanical conditions.

31 **Key Words–** ; Clay minerals; Fluid Density Functional Theory; Molecular dynamics; Solvent effects
32 INTRODUCTION

33 Clay minerals are composed of permanently charged platelets with equivalent spherical diameter
34 $<2\ \mu\text{m}$ (Schoonheydt & Johnston 2006). Because of the high surface charge and the large surface area,
35 clay minerals possess high sorption and pH buffering capacity (Bloom 2000). Hydration of charge-
36 compensating interlayer cations in clay minerals leads to swelling and diffusive migration of water
37 molecules and cations. Due to the low hydraulic conductivity and self-sealing properties related to
38 swelling, clays are used as efficient hydraulic barriers to contain migration of hazardous contaminants
39 (Lo et al. 1997; Edil 2003; Rowe 2005). For instance, Opalinus Clay (Switzerland) is proposed as a
40 potential host rock for geological waste disposal (Marschall et al. 2005). Bentonite is used as a sealing
41 material in the Swedish waste disposal concept for high-level radioactive waste (SKB 2006). Clay cap-
42 rocks are used for carbon storage and sequestration (Song & Zhang 2013).

43 The hydraulic permeability of compacted argillaceous rocks is extremely low. Molecular
44 diffusion is the dominant transport mechanism of solute and solvent in these materials. Several
45 experimental observations provide clear evidence that the surface adsorbed cations in compacted clays
46 are not fully immobilized and contribute to the overall diffusive flux (van Schaik et al. 1966; Eriksen et

al 1999; Melkior et al. 2005, 2007; Van Loon & Eikenberg 2005; Gimmi & Kosakowski 2011). The mechanism and the importance of surface diffusion in argillaceous rock is still under debate (Bourg et al. 2003). Effective macroscopic transport in porous media depends on a number of geometrical and electrochemical parameters. The pore network connectivity, tortuosity, and pore size distribution are the geometric constraints controlling mass transport (Tyagi et al. 2013; Churakov et al. 2014; Gimmi & Churakov 2019). The interaction of ions with the charged mineral surfaces leads to the formation of so-called diffuse double layers (DDL). For negatively charged clay minerals, the DDL is enriched in cations and depleted in anions. The mobility of cations within the DDL has been shown to be reduced due to electrokinetic phenomena and the steric interaction of ions with clay mineral surfaces (Rotenberg et al. 2007a,b; Pagonabarraga et al. 2010; Botan et al. 2011; Obliger et al. 2013, 2014; Schaettle et al. 2018). In order to model accurately water and cation diffusion in a reactive transport environment, the effect of DDL (Alt-Epping et al. 2018) and pore network geometry need to be taken into account simultaneously.

Macroscopic reactive transport models (Yang et al. 2019) integrate such complex phenomena in a very simplistic way; for instance, using the Poisson-Boltzmann equation to describe the properties of a mineral–fluid interface. The Poisson-Boltzmann equation is based on the assumption that the ions are point charges embedded in a uniform dielectric continuum and, thus, the molecular nature of solvent and finite ionic size are completely neglected. Consequently, macroscopic models break down, especially when the interlayer space or water content is very small (Rotenberg et al. 2007a, b) or at high surface charge density and high ionic strength.

In contrast to simplified macroscopic models, molecular simulations such as Monte Carlo (MC) (Torrie & Valleau 1980; Boda et al. 2004; Silvestre-Alcantara et al. 2016) and molecular dynamics simulations (MD) (Chang et al. 1998; Marry et al. 2008; Holmboe & Bourg 2014; Yang et al. 2017b) take the finite size of molecular solvent and ions and, most relevant, the interatomic interactions of the system into account (Kosakowski et al. 2008; Churakov & Gimmi 2011; Churakov 2013; Prasianakis et

72 al. 2017). However, they are computationally expensive for the description of mineral–fluid interactions
73 if large systems need to be considered. Classical density functional theory (DFT) (Henderson 1992;
74 Hansen & McDonald 2006; Yang & Liu 2015; Yang et al. 2016, 2017a) at the atomistic level has been
75 widely used to describe the mineral–fluid interfaces because it provides a computationally inexpensive
76 alternative. Numerical modeling based on classical DFT can easily handle molecular systems two to
77 three orders of magnitude larger than one considered in MC and MD simulations. Classical DFT has
78 difficulty taking into account hydrogen bonding between water molecules and the surface of the clay
79 mineral (Sposito 1984) and describing specific orientation-dependent distributions of the interfacial
80 water molecules hydrating the surface and the interlayer ions (Marry et al. 2008). Recently, Borgis and
81 coworkers proposed a DFT for SPC/E water, which has been used to study pyrophyllite (Jeanmairet et
82 al. 2014).

83 Various models have been proposed within the framework of classical DFT to take into account
84 the solvent effects. For example, early work (Tang et al. 1992, Lamperski & Zydor 2007) introduced the
85 solvent primitive model i.e. a three-component model (3CM or the so called DFT/HS-3CM), in which
86 the solvent molecules are represented by neutral hard spheres (HS) on the basis of the simplest restricted
87 primitive model (Yang et al. 2016, 2017a) (RPM or the so called DFT/HS-2CM), where the ions of
88 electrolytes with the same size are modeled by hard spheres with point charges located at their centers,
89 the electrode by a uniformly charged surface, and the solvent by a uniform dielectric continuum.
90 Comparison between the RPM and the 3CM models showed that the solvent plays a significant role in
91 the solid–fluid interfacial properties (Lamperski & Zydor 2007). Later, the 3CM model was validated
92 (Lee et al. 2013) by comparison with the molecular solvent model (Jorgensen et al. 1983; Price &
93 Brooks 2004) in which solvents and ions were explicitly described as distinct atoms, using MD
94 simulations. However, most of the insights into the solvent arrangement could not be provided by the
95 3CM model, notwithstanding the fact that the density distributions and other interfacial properties were
96 qualitatively captured by such a coarse-grained model. Lee et al. (2012), therefore, introduced a

97 modified 3CM which incorporated Lennard-Jones attractions into the fluid–fluid and fluid–wall
98 interactions rather than the hard-sphere and hard-wall repulsions. Other DFT studies of electrolytes in
99 solution also used solvent modes. For instance, Oleksy & Hansen (2010) proposed wetting a solid
100 substrate by a “civilized” model of ionic solutions, in which water is described by dipolar hard spheres.
101 Lian et al (2017) investigated electrostatic energy extraction by few-layer graphene electrodes, where
102 the solvent is described by hard sphere dimers with opposite charges.

103 Many attempts have been made to reproduce the properties of interfacial water layers as revealed
104 by molecular simulations and experimental observations (Fenter et al. 2000; Schlegel et al. 2006) using
105 simplified theories from the perspective of a macroscopic scale (Qiao & Aluru 2003; Tournassat et al.
106 2009; Botan et al. 2013). An advanced Grand Canonical Monte Carlo (GCMC) technique was used
107 (Moucka et al. 2017) to model pyrophyllite and Na-Mnt in equilibrium with a bulk solution having salt
108 concentrations of 3.14 and 6.6 mol kg⁻¹ with pore size ranging from ~7 to 28 Å. This GCMC technique
109 is based on fractional exchanges of dissolved ions and water molecules. The chemical potentials of NaCl
110 and water in the bulk phase were determined using Osmotic Ensemble Monte Carlo simulations. The
111 chemical potential was then used in GCMC to simulate the adsorption of ions and water molecules in
112 the clay pores, and in turn to predict the salt solubility in confined solutions.

113 The present work was motivated by the GCMC and the merits of the modified 3CM model,
114 which can be implemented numerically by classical DFT, to describe the structure and interfacial
115 properties by explicitly taking into account the solvent effects, yet in a simplified form. Atomistic
116 simulations reveal clearly that water molecules play an important role in saturated (Holmboe & Bourg
117 2014) or partially saturated clay systems (Churakov 2013). Therefore, theoretical methods at the atomic
118 level such as classical DFT take into account water molecules for mineral–fluid interfaces. To this end,
119 the objective was to validate the DFT/LJ-3CM of modeling structures of water molecules and ions in
120 Mnt interlayers by atomistic simulations under a wide range of conditions, to compare systematically the
121 new DFT approach with the structural data obtained by MD simulations, and then to test thermodynamic

properties of the model with respect to the swelling behavior of clay systems and ion exchange as a function of water content, ionic strength of electrolyte (1:1, 2:1 salts), and temperature.

METHODS AND MODELS

System Setup for Molecular Simulations

A periodic 3D supercell containing two fully flexible Mnt layers was set up according to the previous modeling studies of hydrated Mnt (Skipper et al. 1995a,b; Tambach et al. 2004; Tournassat et al. 2009; Bourg and Sposito 2011; Holmboe & Bourg 2014; Marry et al. 2008). A single TOT (2:1 tetrahedral-octahedral-tetrahedral) layer in the simulation supercell consisted of $6 \times 6 \times 1$ unit cells of Mnt. The supercell dimensions in the direction perpendicular to the basal plane were adjusted to accommodate the appropriate number of water molecules in the interlayer to simulate the hydration state of Mnt. The Mg-for-Al isomorphic substitutions in the octahedral sheet were distributed randomly, but excluded Mg-Mg pairs to maintain a mean layer surface charge density of -0.116 C/m^2 , consistent with previous MD simulations (Tournassat et al. 2009). A representative snapshot (Fig.1) shows the simulation supercell of Na-Mnt in the 5W hydration state with z dimension $50.8 \text{ \AA}$, containing 52 Na ions, 4 Cl ions, and 1800 H_2O water molecules. In the following discussion, the interlayer size is defined as the distance between the basal planes of the outermost oxygen atoms of Mnt.

Classical MD Simulations

MD simulations were performed using the open source package *GROMACS* (Berendsen et al. 1995; van der Spoel et al. 2005) which uses the *CLAYFF* force field (Cygan et al. 2004) for montmorillonite, the ion-potentials reported by Åqvist (1990) for Ca^{2+} , Joung-Cheatham parameters (Joung & Cheatham III 2008) for monovalent ions (Na^+/Cl^-), and the SPC/E water model (Berendsen et al. 1987) for all interatomic interactions. The Lennard-Jones shift potential was truncated beyond a cutoff value of 1.0 nm. The long-range electrostatic interactions were computed using the Particle-Mesh-Ewald (PME) method (Darden et al. 1993). All atomic simulations were conducted at 298 K using

146 a time step of 1 fs. The integration of the equations of motion was performed using the leap-frog
 147 algorithm. Energy minimization with the steepest descent algorithm was used to prepare the initial
 148 configurations. The equilibration was performed in two steps. First, the system was pre-equilibrated in
 149 the NPT ensemble (pressure P , number of particles N , and temperature T were fixed) for 5 ns using the
 150 Berendsen barostat (Berendsen et al. 1984) at 298 K and 1 bar to relax the Mnt layers and interlayer
 151 electrolytes in all the dimensions. The 5 ns-long NVT (fixed volume V , N , and T) runs were performed
 152 using position restraints of the clay lattices to generate equilibrated systems. The x and y dimensions of
 153 the NVT supercell in all simulated hydration states were kept at $31.0 \text{ \AA} \times 54.2 \text{ \AA}$. The dimensions of the
 154 supercell in the z direction and the composition of the interlayer are given in Table 1. The production
 155 runs were performed for 125 ns in the NVT ensemble at 298 K.

156 *Fluid DFT Calculations*

157 The fluid DFT simulations (f-DFT) were conducted using the open source package *Tramonto*
 158 developed at Sandia National Laboratories (<https://software.sandia.gov/tramonto/>). The f-DFT
 159 simulations were performed in grand canonical ensemble (μVT), where the total volume V , the
 160 temperature T , and the chemical potentials μ of the system were kept constant. Classical MD used in this
 161 study was implemented in the NVT ensemble. Therefore, the assignment of a consistent setup for f-DFT
 162 and MD simulations and μVT and NVT ensembles was not trivial. To match the condition of f-DFT and
 163 MD simulations two different approaches for the system were used at low (<5 water layers) and high
 164 (≥ 5 water layers) degrees of hydration. At low degrees of hydration, the total number of ionic species
 165 and water molecules in the interlayer space were set to be the same in both f-DFT and MD systems. At
 166 high degrees of hydration the chemical potential in f-DFT was set to match the density representing the
 167 regions of homogeneous fluid in the central part of the interlayer space.

168 In f-DFT, the density distributions of molecular species of fluid at equilibrium, $\rho_i(\mathbf{r})$, were
 169 determined by minimization of the grand potential energy at equilibrium described by the Euler-
 170 Lagrange equation. The chemical potential was expressed as a function of the external potential,

171 Coulomb forces, ideal gas components, and excess energy due to hard-sphere repulsions (f_i^{hs}),
 172 Lennard-Jones attractions (f_i^{LJ}), and short-range electrostatic interactions (f_i^{MSA}) were evaluated with
 173 the Mean Spherical Approximation (MSA) (Waisman & Lebowitz 1972):

$$174 \mu_i(\mathbf{r}) = q_i e \psi(\mathbf{r}) + u_i(\mathbf{r}) + kT \ln \rho_i(\mathbf{r}) + f_i^{hs}(\mathbf{r}) + f_i^{LJ}(\mathbf{r}) + f_i^{MSA}(\mathbf{r}) \quad (1)$$

175 in which $\psi(\mathbf{r})$ is the local electrostatic potential resulting from the Coulombic interaction between point
 176 charges and that from the electrostatic part of the external potential, which was obtained by solving
 177 Poisson's equation, q_i is the valence of the ionic species i using the expression

$$178 \nabla^2 \psi(\mathbf{r}) = -\frac{1}{\epsilon_0 \epsilon_r} \sum_i \rho_i(\mathbf{r}) e z_i \quad (2)$$

179 where ϵ_0 is the vacuum permittivity, ϵ_r is the relative permittivity or dielectric constant, z_i is the valence
 180 of the ionic species i , and e is the elementary charge. The external field, $u_i(\mathbf{r})$, is induced by the clay
 181 surface, which is described as a flat wall with surface charge density σ uniformly distributed on the
 182 surface, k is Boltzmann's constant, T is the absolute temperature, and $f_i(\mathbf{r})$ is the Helmholtz free energy
 183 per molecule of the particle i .

184 The one- dimensional external potential due to the wall–fluid interaction was represented by the
 185 Lennard-Jones 9-3 potential:

$$186 \mu_i(z) = \epsilon_{wf}^{LJ} \left[\frac{2}{15} \left(\frac{d}{z} \right)^9 - \left(\frac{d}{z} \right)^3 \right] \quad (3)$$

187 where ϵ_{wf}^{LJ} is the LJ energy interaction parameter for wall–fluid interaction potential, d is the LJ particle
 188 diameter, and z is the position of molecular particle i from the wall in the direction perpendicular to the
 189 wall. The wall-fluid potential cutoff was set at $3.5 d$.

190 The LJ interaction is described in a spirit of perturbation theory as hard-sphere interaction with
 191 an effective hard-sphere parameter d and the correction due to long-range interactions (Tang et al.
 192 1991). The hard-sphere component, $f_i^{hs}(\mathbf{r})$, was calculated using the fundamental measure theory

193 (FMT) developed by Rosenfeld (1989). The short-range interaction cutoff for $f_i^{hs}(\mathbf{r})$ was $1d$. The excess
 194 free energy was based on the following formula,

$$195 \quad f_i^{hs}(\mathbf{r}) = -n_0 \ln(1 - n_3) + \frac{n_1 n_2 - \mathbf{n}_{v1} \cdot \mathbf{n}_{v1}}{1 - n_3} + \frac{1}{24\pi} \frac{n_2^3}{(1 - n_3)^2} - \frac{1}{8\pi} \frac{n_2 (\mathbf{n}_{v2} \cdot \mathbf{n}_{v2})}{(1 - n_3)^2} \quad (4)$$

196 Note that for a complete description including non-local densities, n and $\mathbf{n}_v$, as well as an
 197 analysis of the functionals, the reader is referred to the original references (Rosenfeld 1989).

198 The excess part of free energy due to the LJ attraction with respect to a hard-sphere reference
 199 fluid is defined by a density-weighted integral of a pair potential function over the surrounding fluids,
 200 separately summing the contributions from each species,

$$201 \quad f_i^{LJ}(\mathbf{r}) = \sum_j \int_{1d}^{3.5d} 4\epsilon_{ij}^{LJ} \left[\left(\frac{d}{r} \right)^{12} - \left(\frac{d}{r} \right)^6 \right] \rho_j(\mathbf{r}') d\mathbf{r}' \quad (5)$$

202 where ϵ_{ij}^{LJ} is the LJ energy interaction parameters for fluid-fluid interaction potential, $\mathbf{r} = |\mathbf{s} - \mathbf{r}'|$ refers
 203 to the distance between particles i at position $\mathbf{s}$ and j at $\mathbf{r}'$, and r is the cutoff distance. This contribution
 204 was considered to be within 1 to 3.5 molecular diameters, while it is set to zero outside this region.

205 The contribution to the free energy accounting for the short-range electrostatic interactions is
 206 expressed as

$$207 \quad f_i^{MSA}(\mathbf{r}; \rho_i) = \sum_j \int_0^{1d} c_{ij}^{(2),el}(\mathbf{r}, \mathbf{r}') \rho_j(\mathbf{r}') d\mathbf{r}' \quad (6)$$

208 in which $c_{ij}^{(2),el}(\mathbf{r}, \mathbf{r}')$ is the cross-correlation between the Columbic interaction and the hard-sphere
 209 exclusion, i.e. the electric residual part of the pair direct correlation function defined as the second
 210 functional derivative of the excess part of the free energy functional with respect to the single-particle
 211 density distribution (Hansen & McDonald 2006). It can be modeled with MSA (Waisman & Lebowitz
 212 1972) for homogeneous systems, leading to

$$213 \quad c_{ij,MSA}^{(2),el}(r) = \frac{q_i q_j e^2}{2\pi\epsilon_0\epsilon_r} \left[\frac{B}{d} - \left(\frac{B}{d} \right)^2 \frac{r}{2} - \frac{1}{2r} \right], r < d \quad (7)$$

214 with the B parameter written as $B = \Gamma d / (1 + \Gamma d)$, where $\Gamma = \frac{\sqrt{1+2\kappa d}-d}{2d}$, $\kappa^2 = \frac{e^2}{\epsilon_0 \epsilon_r k_B T} \sum_i q_i^2 \rho_i^b$, ρ_i^b is
 215 the density of species i in bulk reservoir, q_i is the valence of the ionic species i , and e is the elementary
 216 charge. The relative permittivity depends, in general, on the system temperature and composition.

217 RESULTS AND DISCUSSION

218 *Fluid Structure at the Interface*

219 The interaction parameters used in the f-DFT calculations are reported in Table 2. In the
 220 DFT/LJ-3CM results, the structural and thermodynamic properties such as density profiles, cation
 221 selectivity of ion exchange equilibrium, and free energy were fitted to reproduce atomistic simulations
 222 (Marry et al. 2008; Yang et al. 2017b), and the LJ energy parameters for fluid–fluid and wall–fluid were
 223 taken from molecular simulations (Magda et al. 1985; Lee et al. 2012). The uniform surface charge
 224 density in DFT//LJ-3CM was set to be the same as in MD simulations, -0.116 C/m^2 . To test the
 225 performance of the DFT/LJ-3CM in the comparison the DFT/HS-3CM, i.e. the solvent primitive model,
 226 the results for both approaches were compared with MD simulation for Mnt in the 10W hydrate state.
 227 HS radii used in the DFT/HS-3CM were the same as the LJ parameters in Table 2.

228 The DFT/LJ-3CM results taking into account the solvent effects were compared first with the
 229 atomic simulations for the case when Na-Mnt was saturated in a 0.62 M NaCl bulk solutions. Density
 230 distributions were compared among water H_2O (i.e. water oxygen OW in MD simulations), sodium Na^+
 231 and Cl^- in the interlayer obtained with DFT/LJ-3CM, DFT/HS-3CM models, and atomic simulations
 232 (Fig. 2). The structured density profiles of interlayer water and ions from atomic simulations were
 233 predicted accurately by the DFT/LJ-3CM results. DFT/HS-3CM calculations overestimated, by nearly
 234 four times, the contact cation (Na^+) and water concentrations. The excessive cation density at the contact
 235 resulted in overcharging of the surface and too high co-adsorption of anions (e.g. Cl^-) at the interface. In
 236 the DFT/HS-3CM model, the solvent was modeled by neutral spheres instead of a dielectric continuum

as used in DFT/HS-2CM. Therefore, the wall/ion electrostatic interaction would be overestimated in DFT/HS-3CM model and this could explain the overestimation of the densities at contact.

A similar comparison was conducted using the DFT/LJ-3CM model for Mnt saturated in a 0.23 M CaCl_2 bulk solutions for Ca-Mnt in the 10W hydration state. The density distributions of calcium and chloride ions and water molecules as a function of distance from the surface were obtained with the DFT/LJ-3CM model and from atomistic simulations. The DFT/LJ-3CM results agreed well with the atomistic simulations. The DFT/LJ-3CM model successfully captured the damped oscillations of Ca^{2+} and H_2O density distributions in the vicinity of the surface (Fig. 3). These important features were missing from the density profile obtained with the DFT/HS-2CM model. Furthermore, the number of density profiles of ionic and solvent molecules in the vicinity of the charged surface were substantially overestimated by the DFT/HS-3CM model. The mismatch of anion density predicted by the DFT/HS-3CM model in the 2:1 (e.g. CaCl_2) was even larger than in the 1:1 (e.g. NaCl) electrolyte. This can be explained by the stronger electrostatic effect of the Ca^{2+} ion compared to Na^+ . For the same (overestimated) cation atom density, Ca^{2+} resulted in stronger co-adsorption of Cl^- anions at the surface. The comparison demonstrated that the DFT/LJ-3CM model clearly performed better than the DFT/HS-3CM model near the fluid-wall interface, especially for 2:1 electrolytes. Accordingly, further comparison of results from the molecular simulation with the DFT/LJ-3CM model was restricted.

To test further the accuracy of the DFT/LJ-3CM model, the f-DFT results were compared with atomistic simulations of Na-Mnt in NaCl solution with various water contents, i.e. 2W, 3W, 4W, and 5W hydrated states (Holmboe & Bourg 2014; Yang et al. 2017b). The anions were essentially excluded from the nanopore when the distance between Mnt layers was $<10 \text{ \AA}$. The f-DFT results were insensitive to the bulk concentration of NaCl when the nanopore between Mnt layers was $<10 \text{ \AA}$. Accordingly, the concentration of bulk NaCl solutions in DFT calculations was set to be 0.6 M. for Mnt in 2W, 3W, 4W, and 5W hydrated states.

261 The density profiles in a ~ 6.4 Å interlayer pore (Fig. 4) were obtained from the DFT/LJ-3CM
262 model and atomistic simulations corresponding to the 2W hydration state. The DFT/LJ-3CM model
263 predicted two symmetrically peaked, cation-density profiles whereas atomistic simulations predicted
264 single-peaked Na^+ density in the middle of the interlayer (Fig. 4). At such a low hydration state, the
265 observed structuring of the fluid was controlled by the strong orientation-dependent ion-solvent and
266 solvent-surface interactions. The observed difference was clear evidence that important features such as
267 H-bonding and rotation of water molecules were not taken into account by the DFT/LJ-3CM model.

268 Low temperature ion-dipole interaction cannot be captured by the orientation-independent LJ
269 potential. However, the main features of water density distributions were successfully captured by the
270 DFT/LJ-3CM results (Fig. 4). Atomistic simulations also indicated a small fraction of Na^+ forming a
271 small local density maximum at ~ 1.5 Å from the surface. These were inner-sphere complexes entering
272 the hexagonal cavities of the tetrahedral sheet of Mnt. Such complexes were also present at the greater
273 degrees of hydration discussed later. These features cannot be considered in the current DFT/LJ-3CM
274 model which uses a simple planar interface.

275 The density distributions of calcium ions and water molecules in a ~ 9 Å interlayer pore were
276 predicted by the DFT/LJ-3CM model and by atomistic simulations for Mnt in the 3W hydration state
277 (Fig. 5). The DFT/LJ-3CM model captured the features of the density profiles of cations, especially the
278 structure of interlayer water molecules in the 3W hydration state.

279 Again, Na and H_2O density profiles were predicted by the DFT/LJ-3CM model and the atomistic
280 simulations of Mnt in the 4W hydrate state (Fig. 6). Similar Na and H_2O density profiles were predicted
281 by the DFT/LJ-3CM model and the atomistic simulations for the 5W hydration state (Fig. 7). The
282 density profiles of sodium ions predicted by the DFT/LJ-3CM model were more structured than profiles
283 from MD simulations. Both the DFT/LJ-3CM results (blue curves) and the atomistic simulations (black
284 curves) showed that Na^+ ions were enriched at a distance of approximately $0.5d$ from the surface. This is
285 comparable to the typical ion-surface distance of Na-outer-sphere complexes. As for the 3W state,

286 DFT/LJ-3CM slightly over predicted the structuring of the ion and water in the middle of interlayer. The
287 secondary features in the ions and water density distributions related to the non-planar surface
288 topography were not reproduced by the f-DFT model. These secondary density maxima are related to
289 partially hydrated inner-sphere Na ions entering the hexagonal cavities on the Mnt surface. Such a
290 complex solvation behavior cannot be captured by the DFT/LJ-3CM model due to the too simplistic
291 planar representation of the surface and the lack of orientation-dependent ion-dipole interaction.

292 Overall analysis of the data demonstrated that the DFT/LJ-3CM model could capture the primary
293 structural properties of ions and water in the vicinity of a fluid surface interface for very different
294 hydration states of Mnt. The model tended to over predict the structuring at greater distances from the
295 surface in comparison with the MD simulation results. The features related to the non-planar interface
296 and the changes in the hydration state of the ions, because of the changes from outer-sphere to the inner-
297 sphere complexes, cannot be captured within the currently used DFT/LJ-3CM model.

298 *Swelling Behavior*

299 Depending on the chemical potential of water, smectite minerals are known to contain distinct
300 amounts of water molecules in the interlayer, commonly referred to a 1W, 2W, and 3W hydration states
301 (Mooney et al. 1952; Karaborni et al. 1996; Kawamura et al. 1999). The stability of a particular
302 hydration state and the exact interlayer thickness depends on temperature, composition of the electrolyte
303 solution (both concentration and ion speciation in particular), and the distribution of isomorphic
304 substitution in the TOT layer (Boek et al. 1995a,b; Young & Smith 2000; Hensen & Smit 2002; Smith et
305 al. 2006; Tambach et al. 2006). A model-based description of smectite swelling is essential for
306 prediction of a clay's mechanical properties (Hoang & Galliero 2015; Sun et al. 2015). The stable
307 hydration state corresponds to the minimum value of the free energy of the system. The dependence of
308 surface free energy, $\Omega(h)$, on the interlayer separation, h , is calculated by an integration of the solvation
309 force via (Frink & van Swol 1998):

$$\Omega(h) - 2 * \Omega(\infty) = - \int_{\infty}^h dh' f_s(h') \quad (8)$$

The constant $\Omega(\infty)$ is equal to the surface free energy of an isolated wall in equilibrium with bulk fluid. The factor 2 in the left hand side of Eq. 8 accounts for the presence of 2 interfaces in the slit pore. The absolute minimum in $\Omega(h)$ determines the thermodynamically stable equilibrium separation of two walls, separated by h , for an unconstrained swelling condition, where the solvation force f_s is defined as $f_s = p - p_b$, and p is the total normal force per unit area on each wall, whereas p_b is the bulk pressure at the chosen chemical potential and temperature.

The dimensionless free energy of the system for Na- and Ca-Mnt was plotted as a function of slit pore size for various ionic strengths (Fig. 8). The symbol A in the vertical axis represents the surface area. Depending on the ionic strength of the external electrolyte, the stable states of the Ca and Na-Mnt predicted by DFT/LJ-3CM were either a dispersed one at lower ionic strength or a compacted “3W-Layer” state at higher ionic strength. The model for Na-Mnt predicted the dispersion to be stable if the bulk concentration of monovalent ions was <2 M (Fig. 8a). The model for Ca-Mnt predicted the dispersion state to be stable at bulk concentrations of 2:1 electrolyte below 0.01 M (Fig. 8b). The metastable states with 2W and 4W layers were also apparent in the free energy profiles as local minima. The prediction the stable interlayer distances was based on changes in the chemical potential of each ion in the bulk electrolyte. The 2W state can become stable over the 3W state if the chemical potential of solute is further reduced, e.g. partial saturation (Churakov 2013). The behavior of the DFT/LJ-3CM for Mnt agreed qualitatively very well with the behavior of natural systems. The quantitative differences were related to the too simplistic description of solvent and solvent-solute interactions, which were not captured in the model. Contrary to the experimental observations, PB approximations predict repulsive interaction of Mnt platelets in NaCl and CaCl₂ solutions (Segad et al. 2010). The 2-component RPM model improved the predictions, suggesting an attractive force between TOT layers in Ca-Mnt at ~ 10 Å separation. In contrast to the DFT/LJ-3CM, the two-component RPM, did not predict the existence of

other, eventually metastable, hydration states. In this context the DFT/LJ-3CM model used in this study clearly performed better than the widely used DFT based description of swelling in clay minerals.

Thermodynamics of Ion Sorption

In this section, the DFT/LJ-3CM model was applied to evaluate ion exchange equilibrium and to estimate the effect of temperature on cation selectivity. The cation exchange between Ca^{2+} and Na^+ ions in the interlayer of Mnt can be expressed by the following reaction (Appelo & Postma 2005):

where X indicates the clay mineral exchanger. The selectivity coefficient of ion exchange K_{GT} is given by the Gaines-Thomas convention (Gaines & Thomas 1953; Appelo & Postma 2005) as

$$K_{GT} = \frac{[\text{Na}^+][\text{Ca-X}_2]^{0.5}}{[\text{Ca}^{2+}]^{0.5}[\text{Na-X}]} \quad (10)$$

where square brackets denote activities. $[\text{Na}^+]$ and $[\text{Ca}^{2+}]$ represent the activities of ions Na^+ and Ca^{2+} in water, which can be related to the ion concentrations in bulk aqueous solutions. The surface activities $[\text{Na-X}]$ and $[\text{Ca-X}_2]$ are approximated by the equivalent charge fractions of Na^+ and Ca^{2+} ions in the adsorbed phase in the DFT calculations. More detailed discussions on surface activities and ion exchange properties of clay minerals is available elsewhere (Yang et al. 2017a).

The selectivity coefficient K_{GT} as defined with the Gaines-Thomas convention was obtained by the DFT/LJ-3CM and the experimental results (Sposito et al. 1983) of the surface activities $[\text{Na-X}]$ i.e., $\beta_{\text{Na}} = \tau_{\text{Na}}/(\tau_{\text{Na}} + 2\tau_{\text{Ca}})$, where $\tau_i = \int_0^h (\rho_i(x) - \rho_i^b) dx$ (Table 3). The selectivity coefficients K_{GT} obtained previously with the DFT/HS-3CM model (Yang et al. 2017a) are shown for comparison.

To demonstrate the ability of the DFT/LJ-3CM to describe the cation exchange in Ca-Na-Mnt, the corresponding data in Table 3 were plotted (Figs 9 and 10), and revealed (Fig. 9) the equivalent charge fractions of Na ions in the adsorbed phase, i.e. surface activities of Na-X (β_{Na}) from the

experiments and the DFT/LJ-3CM calculations as a function of the mole fraction of Na ions in the mixture of NaCl and CaCl₂ bulk solutions. The calculations were performed at room and higher temperatures taking into account the change in the relative dielectric permittivity of water (Malmberg & Maryott 1956). The dielectric constant in the interlayer and in the bulk solution was assumed to have the same temperature dependence. The model predicted that temperature has a very limited effect on the cation exchange in Na-Ca-Mnt. Na sorption decreased only slightly with increasing temperature. The comparison of f-DFT calculations and experiments showed that the DFT/LJ-3CM model can quantitatively and qualitatively reproduce the measurements of cation exchange for Mnt in the Na and Ca electrolyte solutions.

The selectivity coefficient K_{GT} from the DFT calculations and measurements, represented as a function of the mole fraction of NaCl in the mixture of NaCl and CaCl₂ bulk solutions using the DFT/LJ-3CM (Fig. 10), revealed a distinct advantage over the RPM calculations in comparison with the experimental results (Sposito et al. 1983). The DFT/LJ-3CM results agreed quite well with the experiments when the mole fraction of Na ions in the bulk was >0.4. The interlayer separations in the f-DFT calculations of the selectivity coefficient were set at 30 Å when Na was dominant (i.e. Na mole fraction >0.7), which is commonly used in simulations for pure Na electrolyte solutions because the Mnt layers tend to disperse. However, the Mnt layers collapsed and formed a gel with ~9 Å interlayer separation (the compacted “3W-Layer” state) for Ca salts with bulk ion concentration ≥ 10 mM (Fig. 8). Accordingly, the interlayer separations in the DFT calculations were set to be 9 Å when Ca was dominant in the bulk solutions (i.e. Na mole fraction <0.7). The selectivity coefficient $\log_{10}K_{GT}$ (Fig. 11) was plotted as a function of the Na charge fraction at the surface, i.e. the surface activities in the adsorbed phase. A linear relationship consistent with the experimental observations was recovered between the selectivity coefficient and the surface activities.

SUMMARY AND CONCLUSIONS

380 The accurate description of fluid-solid interface structure and the thermodynamics of the diffuse
381 double layer (e.g. ionic concentration profiles and ionic mobility as a function of distance from the
382 surface) is indispensable for accurate modeling of ion transport and retention in compacted clay systems
383 (van Schaik et al. 1966; Gimmi & Kosakowski 2011). These model parameters can be obtained, in
384 principle, by full-scale atomistic simulations. The direct application of MD simulation to reality-near
385 systems representing complex networks of pores in clays is currently not feasible due to the high
386 computational costs (Churakov & Gimmi 2011; Churakov et al. 2014). Widely used and
387 computationally efficient RPM models of electrolyte on the other hand neglect the molecular nature of
388 the solvent and fail to provide good quantitative description of the ion and solvent profiles close to the
389 solid interface due to the simplistic nature of the underlying interaction potential. Application of three
390 component-f-DFT models for electrolytes, which take into account soft ions and solvent could be a
391 powerful approach to obtain accurate molecular-scale descriptions of mineral electrolyte interfaces at
392 comparatively low computational costs.

393 In the present work, the performance of the three-component DFT/LJ-3CM model was tested
394 against full-scale molecular simulation of Na and Ca Mnt in various hydration states. In good agreement
395 with the atomistic simulation, the DFT/LJ-3CM model accurately reproduced the short-range structuring
396 of the ions and solvent molecules at TOT layer separations >10 Å. In very narrow slit pores of <10 Å,
397 the solvent structure was reasonably reproduced. Under these conditions, the molecular system behavior
398 was controlled by orientation-dependent ion-dipole interaction and hydrogen bonding. Furthermore, the
399 real clay surface has a complex 3-dimensional arrangement of oxygen atoms, allowing ion specific steric
400 interaction, whereas the f-DFT model assumes a planar interface. These coordination-dependent
401 interactions and the molecular nature of the surface were not taken into account properly in the current
402 model.

403 The DFT/LJ-3CM model was further applied to evaluate swelling behavior of Ca and Na Mnt
404 and the Na-Ca exchange equilibrium. The calculations of selectivity coefficients for Na-Ca exchange

405 reactions agreed well with experimental observations. The swelling behavior of DFT/LJ-3CM Mnt was
406 in good qualitative agreement with the experimental observations. Exceptionally, the model predicted
407 local free energy minima of the system for discrete 1W, 2W, and 3W hydration states. The DFT/LJ-
408 3CM model is clearly superior to conventional 3CM and RPM in predicting solvent structure and the
409 thermodynamics of DDL.

410 The DFT/LJ-3CM calculations were at least 3-4 orders of magnitude less demanding in terms of
411 computational resources compared to conventional MD simulations. The DFT/LJ-3CM model applied in
412 this work was able to describe the cation selectivity of ion exchange equilibrium in wide range of
413 solution compositions. Such a model can be used in reactive transport simulators and modeling ion
414 migration taking place under more complex thermo-chemo-hydro-mechanical conditions. The ability of
415 the DFT/LJ-3CM model to capture the water and ion density distributions is of great interest for many
416 practical applications such as upscaling of the results to pore-level for reactive transport simulations in
417 porous media. The f-DFT as one of the most powerful tools provides a more computationally economic
418 way to achieve those goals due to its advantages of its capability of modeling simple fluid systems of
419 increased complexity, for instance 3D systems not restricted to system size. The computational
420 advantage of fluid DFT allows conducting very fast parametric studies (parameters: pore-size/solution
421 concentration) and can bridge between atomistic and pore-level simulations.

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645 **Fig. 1.** Snapshot of a MD simulation cell showing Na-Mnt in the 5W hydration state with z dimension
646 50.8 Å containing Na ions (dark blue), Cl ions (light blue), and water molecules (O and H atoms are in
647 red and white, respectively). The clay layer consists of an octahedral sheet (pink) sandwiched by
648 tetrahedral sheets (gold yellow).

Fig. 2. Density distributions of Na^+ , Cl^- ions, and H_2O from DFT/LJ-3CM calculations as a function of distance from the surface in the 10W hydration state. The DFT/LJ-3CM results compared to atomic simulations (gray curves) and to calculations using the DFT/HS-3CM (blue curves) and the DFT/HS-2CM (dark blue curves) models.

654

655 **Fig. 3.** Density distributions of Ca^{2+} , Cl^- ions, and H_2O from the DFT/LJ-3CM calculations as a function
656 of distance from the surface in the 10W hydration state. The DFT/LJ-3CM results compared to atomic
657 simulations³⁴ (gray curves) and to calculations using the DFT/HS-3CM (blue curves) and the DFT/HS-
658 2CM (dark blue curves) models.

659

660 **Fig. 4.** Comparison of density distributions of Na^+ (dark blue) and water (light blue) predicted by the
661 DFT/LJ-3CM model with atomic simulations (black curves) as a function of distance from the Mnt
662 surface in 2W hydration state. The dashed gray lines represent the position of the outermost oxygen sites
663 on the Mnt surface. The concentration of Cl^- ions was negligibly low and is not shown here for clarity.

664

665 **Fig. 5.** Comparison of density distributions as a function of distance from the surface in the 3W
 666 hydration state from the DFT/LJ-3CM calculations (Na ion density is dark blue and H₂O density is light
 667 blue) with atomic simulations (black curves).

668

669 **Fig. 6.** Comparison of density distributions as a function of interlayer separations in the 4W hydration
 670 state obtained using the DFT/LJ-3CM model (Na ions are dark blue and H₂O is light blue) with atomic
 671 simulations (black curves).

672

673 **Fig. 7.** Comparison of density distributions as a function of interlayer separations in the 5W hydration
 674 state from the DFT/LJ-3CM model (Na ions in dark blue and H₂O in light blue) with atomic simulations
 675 (black curves).

676

677 **Fig. 8.** Free energy per unit surface area as a function of the equilibrium interlayer separation between
678 two smectite TOT layers in (a) NaCl, and (b) CaCl₂ bulk solutions. The ionic concentrations are
679 indicated in the plots.

680
681 **Fig. 9.** Surface activities as a function of the mole fraction of Na⁺ ions in the mixture of NaCl and CaCl₂
682 bulk electrolytes.

683

684 **Fig. 10.** The selectivity coefficient K_{GT} as a function of the mole fraction of Na ions in the mixture of
685 NaCl and CaCl₂ bulk solution. Insert shows the magnified selectivity coefficient varied with the
686 temperature.

687

688 **Fig. 11.** The selectivity coefficient, $\log_{10}K_{GT}$, as a function of the charge fraction of the Na^+ ions in the
689 adsorbed phase. The curve shows the DFT results. The solid dots represent the experimental data from
690 Sposito et al. (1983).

691 **TABLE 1.** Simulation parameters of the supercell for the MD simulations.

Simulation parameter of the supercell	Hydration State				692
	2W	3W	4W	5W	
Dimension in z -direction Å	31.33	38.42	44.46	50.83	
Number of Na ions	50	52	52	52	
Number of Cl ions	2	4	4	4	
Number of water molecules	720	1080	1440	1800	

693 **TABLE 2.** The interaction energy parameters for the DFT/LJ-3CM simulation.

Interaction energy parameter	DFT/LJ-3CM		
	$\text{Ca}^{2+}/\text{Na}^+$	Cl^-	H_2O
fluid-fluid interaction diameter d (Å)	5.3 / 4.848	4.25	2.5

fluid-fluid ε_{ff}^{LJ} (eV)	0.006596	0.006596	0.006596
fluid-fluid cut-off in r (Å)	$3.5d$	$3.5d$	$3.5d$
wall-fluid ε_{wf}^{LJ} (eV)	0.1351	0.1351	0.1351
wall-fluid interaction diameter d (Å)	5.3 /4.848	4.25	2.5
wall-fluid cut-off in z (Å)	$3.5d$	$3.5d$	$3.5d$
relative permittivity ε_r ($T= 298$ K)	--	--	78.3
relative permittivity ε_r ($T= 323$ K)	--	--	69.9
relative permittivity ε_r ($T= 348$ K)	--	--	62.4
relative permittivity ε_r ($T= 373$ K)	--	--	55.7

694 **TABLE 3.** Thermodynamics of Ca-Na exchange in Wyoming Mnt predicted with the DFT/LJ-3CM
695 model (this work), the DFT/HS-3CM model (Yang et al., 2017a), and experimental data of Sposito et al.
696 (1983).

Samples	$C_{Na}/(C_{Na}+C_{Ca})$	C_{Na} (mM)	C_{Ca} (mM)	DFT $K_{GT}(\sqrt{M})$		Experiments ⁶⁹⁷	
				LJ-3CM	HS-2CM	$K_{GT}(\sqrt{M})$	β_{Na}
01	97.9%	47.9	1.03	1.76	2.6	1.4	63.7%
02	96.1%	46.2	1.87	1.74	2.7	1.8	44.0%
03	93.5%	43.9	3.05	1.63	2.7	1.8	34.7%
04	90.4%	41.3	4.39	1.74	2.8	1.8	29.2%
05	85.0%	36.9	6.51	1.79	2.9	2.0	20.7%
06	77.4%	31.6	9.23	1.83	3.0	1.4	21.6%
07	69.7%	26.8	11.7	3.40	3.1	2.9	8.3%
08	61.4%	22.1	13.9	3.90	3.2	3.3	5.6%
09	51.1%	17.1	16.4	3.50	3.3	2.6	5.0%
10	39.4%	12.3	18.9	3.60	3.4	1.1	7.8%
11	22.2%	6.2	21.7	3.70	3.5	1.0	4.0%