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Interactions between clay portions with various contacts and subjected to specific environmental conditions

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ABSTRACT

So far clays have always been considered, both experimentally and theoretically, as ideally flat and under arbitrary orientations. The goal here is to shed light on the different cases of possible contact between portions of clay, which will be subject to peculiar conditions of temperature and pressure. To this end, molecular dynamics study has been performed to investigate the evolution of nonparallel hydrated Wyoming-type Na-montmorillonite. In the present work, we study two clay structures containing two then three nonparallel portions. The contact manners between each other are considered as point and/or edge. We show that under the effect of environmental constraints, the dihedral angle of the horizontal and inclined portions tend to shrink; at the same time, the clay layers of inclined portions have a tendency to rotate. Due to this rotation, the contact of point can be considered as the evolution of the contact of edge. With the presence of water, the layers of inclined clay portions turn in different ways. The temperature effect is negligible, but the pressure plays an important role on the behaviour of clay layers.

1. Introduction

Swelling clays were used as natural barrier in the repository of radioactive waste. Among these clays, montmorillonite is a typical one, which has been widely used for radioactive waste disposal [1].

A considerable experimental and theoretical research effort has been devoted for investigating the swelling behaviour of the montmorillonite [2–21]. However in all these studies the clay mineral was considered as a system periodically infinite and the neighbouring mineral layers of the clay were always parallel. In the reality, the clay is in fact constituted of several fragments juxtaposed with different orientations and angles of contact.

The finite element numerical technique based on the Gouy–Chapman theory [22,23] has been used to study the repulsion between non-parallel clay particles [24,25]. The Hamaker–De Boer approach [26,27] of general Lifshitz theory [28,29] was used in computing the van der Waals attractive force in systems with macro-bodies of complex shapes. Anandarajah and Chen [30] have proposed a single correction function to compute retarded van der Waals energy and applied to the case of two semi-infinite parallel plates separated by different medium. Discrete element method has been developed for quantifying physico-chemical forces between two arbitrarily oriented platy particles immersed in a fluid of well known properties [24,25,30–32] and studying the role of particle orientation on the behaviour of montmorillonite [33].

With increasing emphasis of environmental concerns, a more deep understanding has become necessary. It is the purpose of this work to shed light on a system constituted of several portions of clay in order to reproduce a more realistic situation of the clay system. Molecular dynamic simulation methods will be performed here to study the behaviour of nonparallel particles under the effect of temperature and pressure in the condition of repository of radioactive waste.

The paper is organized as follows. In Section 2 we give the computational details. In Section 3 we present the results and discussions. Section 4 is the conclusion.

2. Computational details

2.1. Structure model

We have modelled two structures: one contains two portions of clay mineral, the other contains three. In these structures, one portion is placed horizontal, the others are inclined. These portions

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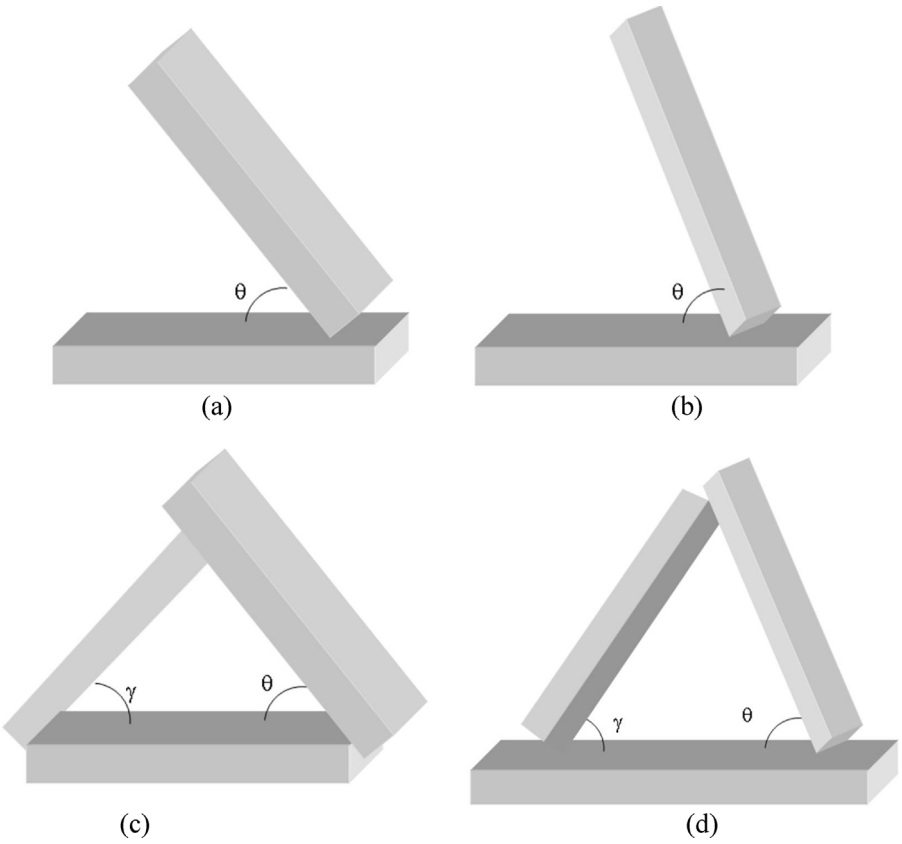

Fig. 1. Clay portions with different orientations: (a) two portions contact with one edge; (b) two portions contact with one point; (c) three portions contact with the edges; and (d) three portions contact with points.

were assembled with two different manners: contact by one edge or by one point, as presented in the sketch of Fig. 1.

The clay mineral model considered here is a Wyoming-type montmorillonite, with the unit cell formula $Na_{0.75}[Si_{7.75}Al_{0.25}](Al_{3.5}Mg_{0.5})O_{20}(OH)_4 \cdot nH_2O$. To well simulate the hydrated clay, we considered that each portion consists of two clay layers and 3-layer hydrate water, like a sandwich. Water molecule is described here by the rigid SPC model [34]. In order to simplify the modelling, the position of the horizontal portion is fixed and considered as infinite in x and y direction (Fig. 1) only the evolution of the inclined clay portion needs to be studied, which have a limited size.

These clay portions are placed in a simulation box of 126 Å × 73 Å× 100 Å. The horizontal clay portion has 126 Å × 73 Å, containing 15,360 atoms in each clay mineral layer and 2304 water molecules in the interlayer space. With the periodic boundary conditions, this clay portion is infinite in x and y direction. The inclined clay portion has 33 Å × 26 Å, totally 676 atoms in each clay layer and 186 water molecules. Since this clay portion has limited size, therefore the effect of edge of clay layer should be considered. On the four edges of the clay layer, the broken bonds were saturated by H or OH groups [35], as illustrated in Fig. 2. The size of horizontal clay portion is chosen large enough to prevent interactions between the neighbouring inclined clay portions.

The interactions between all atoms were modelled using pairwise potentials:

$$U_{ij} = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \quad (1)$$

With the Lorentz-Berthelot combination rules [36], $\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$, $\sigma_{ij} = 1/2(\sigma_i + \sigma_j)$ and q_i the partial charge of atom i.

The interatomic potential parameters in the horizontal clay layer were taken from the CLAYFF force field [37]. The inclined clay layer is more complicated due to the influence of the edge that we have implied another model based on DFT calculations [35] to fit the partial charges of the edge atoms. The L–J parameters were taken from the Smith force field [7]. The charges of atoms not belonging to the edges (i.e., bulk clay atoms) were kept fixed to the ones of the Smith force field [7,10]; while the charges of the edge atoms were taken from DFT fit [35] (see Figs. 3 and 4, and Table 1). No flexibility in the clay lattice was allowed during the simulation.

Table 1
Charges of atoms in the montmorillonite considering the effect of edges.

Atom	Charge (e)	Atom	Charge (e)
Mg	2.00	O6	−1.02
Al1	3.00	O7	−1.00
Al2	2.36	O8	−0.678
Si1	1.20	O9	−0.75
Si2	1.85	O10	−1.424
Si3	1.80705	O11	−1.225
O	−0.80	O12	−1.12
O1	−0.625	H	0.424
O2	−0.942	H1	0.406
O3	−0.614	H2	0.15
O4	−0.956	H3	0.329
O5	−0.99	H4	0.314
		H5	0.307