Introduction

Intercalation of layered clay minerals and separation of their layers are the principal methods for producing clay-polymer nanocomposites and inorganic nano-structures with advanced sorption and catalytic properties. Delamination of the platy 1:1 type clay mineral, kaolinite has been found to be one of the most promising ways to obtain curled aluminosilicate layers and aluminosilicate nanoscrolls. For the delamination of kaolinite, a series of interdependent intercalation/deintercalation steps are applied, resulting in free-standing layers.

These layers tend to curl or form nanoscrolls, in order to minimize the misfit of their tetrahedral and octahedral sheets [1]. According to theory [2], a single kaolinite layer rolls up with the octahedral sheet inside; however, there is as yet no ample experimental evidence to support this curling process. Classical molecular simulations using atomistic force fields (ClayFF [3], INTERFACE [4]) were employed to investigate the behavior of a life-sized model [5] of free-standing kaolinite layers.

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Model and Method

The ClayFF force field [3]

- general force field suitable for the simulation of hydrated and multicomponent mineral systems and their interfaces with aqueous solutions
- treats almost all interatomic interactions as being non-bonded
- standard 12-6 Lennard-Jones potential for the van der Waals non-bonded interactions with Lorentz-Berthelot combination rule
- bulk structures, relaxed surface structures, and intercalation processes have been evaluated and compared to experimental and spectroscopic findings for validation

The INTERFACE force field [4]

- extension of common harmonic force fields (same functional form, except for short range interactions)
- flexible models, explicit bonding and angle bending interactions
- standard 12-6 Lennard-Jones potential for the van der Waals non-bonded interactions with Lorentz-Berthelot combination rule
- enables accurate simulations of inorganic-organic interfaces
- validity of the force field parameters has been tested for layered silicates, other aluminosilicates and further inorganic compounds (e.g. hydroxyapatite)

Real structural changes in the kaolinite sheets remain hidden when an ordinary atomistic simulation cell (10^2 – 10^4 atoms) with fully periodic (and thus infinite) crystal is used. Also, artifacts emerge when simulating with such small layers without periodicity (i.e. the crystal is finite). Realistic results can only be obtained by using life-sized kaolinite layers. The colloidal kaolinite particles consist of layers with a usual surface area in the order of > 10^3 nm².

KGO<sub>1</sub> unit cell

space group symmetry: C<sub>1</sub>
composition: Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>

lattice parameters: a = 0.5154 nm, b = 0.8942 nm, c = 0.7391 nm, α = 91.93°, β = 105.05°, γ = 89.80° [6]

Free-standing kaolinite layer

size: 105 nm × 105 nm
number of atoms: 816 000 (96 000 Al atoms, 96 000 Si atoms, 432 000 O atoms, 192 000 H atoms)

NVT MD simulations (T=298 K) with the GROMACS software package [7]

simulation lengths: from some tenths to a few nanoseconds

- treatment of interactions: simple cut-off for the non-bonded interactions
- long range electrostatic correction (Particle Mesh Ewald (PME), Reaction Field)
- non-periodic simulation without cut-off (direct calculation of all interactions)

Results

Type I: kaolinite layer rolls up with the octahedral sheet inside
Type II: kaolinite layer rolls up with the tetrahedral sheet inside

<table>
<thead>
<tr>
<th>ClayFF</th>
<th>INTERFACE</th>
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</thead>
<tbody>
<tr>
<td>Type I (a(b))</td>
<td>simple cut-off at 0.5154 nm</td>
</tr>
<tr>
<td>Type I (b(a))</td>
<td>simple cut-off at 0.8942 nm</td>
</tr>
<tr>
<td>Type I (a(b))</td>
<td>simple cut-off at 1.0308 nm</td>
</tr>
<tr>
<td>Type I (b(a))</td>
<td>simple cut-off at 1.5461 nm</td>
</tr>
<tr>
<td>Type I (a)</td>
<td>simple cut-off at 1.7884 nm</td>
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<tr>
<td>Type I (b)</td>
<td>simple cut-off at 2.0614 nm</td>
</tr>
<tr>
<td>Type II (b(a))</td>
<td>simple cut-off at 2.6826 nm</td>
</tr>
<tr>
<td>Type II (b)</td>
<td>simple cut-off at 30 nm*</td>
</tr>
<tr>
<td>Type I (b(a))</td>
<td>PME, direct space cut-off at 1.6 nm</td>
</tr>
<tr>
<td>Type I (b)</td>
<td>Reaction Field, cut-off at 1.2 nm**</td>
</tr>
<tr>
<td>Type I (b(a))</td>
<td>non-periodic, without cut-off**</td>
</tr>
</tbody>
</table>

* prediction for the effective range of non-bonded interatomic interactions (personal communication [9])
** literature Si-O bond lengths are increased by < 3%