Molecular simulation study of kaolinite intercalation with realistic layer size

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Abstract

Intercalation phenomena of kaolinite in aqueous potassium acetate and in hexyl-amine solutions are studied by large scale molecular dynamics simulations. The simulated kaolinite particle is constructed from ~6.5×10^6 atoms, producing a particle size of ~100 nm × 100 nm × 10 nm. The simulation with potassium acetate results in a stable kaolinite-potassium acetate complex, with a basal spacing that is in close agreement with experimental data. The simulation with hexyl-amine shows signs of the experimentally observed delamination of kaolinite (the initial phase of the formation of nanoscrolls from the external layers).

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Recently, the investigation of the preparation and application of nanolayers and nanotubes has become a rapidly expanding field of research. Layered inorganic materials are useful precursors of nanomaterials that are promising as catalysts, adsorbents, and composite materials. Exfoliation of layered silicates into nanolayers has received much attention, because silicate nanolayers can be suitable building blocks with designable surfaces for curled layers, nanotubes, and nanoscrolls (scrolled nanolayers forming multiwall nanotubes). The swelling properties and exfoliation behavior of layered silicates are very diverse.[1]

Kaolinite, a 1:1-type clay mineral, exhibits an excellent performance when used as a nanofiller in the production of clay/polymer nanocomposites due to its natural occurrence with a relatively high purity and almost perfect layer structure. A complete exfoliation of kaolinite has been rarely reported, while its delamination (decrease of the stacking number by separating two adjacent layers) has been achieved through multistep intercalation procedures[2]. Various organic and inorganic compounds can be used for direct intercalation of kaolinite, e.g. formamide, dimethyl sulfoxide, urea, or potassium acetate[3-7]. Potassium acetate is the substance by which one of the largest kaolinite basal spacing can be achieved in one-step intercalation, but it generally does not allow for exfoliation or delamination of kaolinite. At the same time, hexyl-amine, e.g., is known to be able to generate delamination of kaolinite. This chemical cannot be intercalated in a direct way, only by displacement reactions using precursors such as dimethyl sulfoxide[2].

Molecular simulation is a suitable tool to study the adsorption and intercalation of molecules in clays, though finite size effects limit the number of observable properties and phenomena. To reduce finite size effects, in our previous studies we conducted simulations with infinite kaolinite layers using periodic boundary conditions[8-11]. In this way, however, the kaolinite platelets cannot be completely brought into direct contact with a surrounding solution, which prevents the

simulation of the intercalation process itself. Also, the real structural changes in the kaolinite sheets remain hidden when a small simulation cell with fully periodic (and thus infinite) crystal is used. In ordinary atomic simulations using 10^3-10^4 atoms, the size of the model system (and/or the time step) basically determines the properties that can be sampled. Today, it is not unusual to consider large systems (10^5-10^{10} atoms) in detailed all-atom MD simulations (e.g. modeling nucleation effects[12-13], complex biological systems[14], or material failures at the nanoscale[15]). Despite the apparent advantage of being able to extend the scope of investigated phenomena, even today, large scale all-atom simulations involve a substantial computational effort and were therefore rarely utilized in the field of clay minerals[16]. In this work, the intercalation phenomenon was studied for realistically sized kaolinite particles.

Molecular simulations were performed with the GROMACS[17-18] program suite. NpT (fixed number of molecules N, constant pressure p and temperature T) Molecular Dynamics (MD) simulations were conducted at ambient conditions ($T = 298$ K and $p = 1.013$ bar).

The composition of the kaolinite unit cell with space group symmetry C1 is $Al_2Si_2O_5(OH)_4$ and the lattice parameters are a = 0.5154 nm, b = 0.8942 nm, c = 0.7391 nm, $\alpha = 91.93°$, $\beta = 105.05°$, $\gamma = 89.80°$ [19]. A nearly life size kaolinite particle was constructed (with a size of 103 nm × 103 nm × 5.7 nm) that consists of eight clay layers built from 192 000 double unit cells that were arranged in a 200×120×8 composition resulting in 81 600 atoms (48 000 Al atoms, 48 000 Si atoms, 21 6000 O atoms, and 96 000 H atoms) per kaolinite layers (this is 1000 or 6000 times larger than that used in our earlier works [8,9,11]. Such multiplication of the unit cell resulted in cutting bonds (according to the unit cell structure) at the finite ends of the layers. The layers were

stacked upon each other forming seven interlayer regions. The initial atomic positions were set according to the experimental crystal structure of kaolinite[19]. The kaolinite particle was surrounded by a nearly saturated aqueous potassium acetate solution or a hexyl-amine solution. The volume of the applied rhombic dodecahedron simulation box was $\sim2\times10^6$ nm^3, which is 71% of the volume of a cube having the same image distance. The aqueous potassium acetate solution surrounding the kaolinite particle contained $\sim5.9\times10^6$ acetate and potassium ions as well as $\sim4.38\times10^7$ water molecules. The hexyl-amine solution was constructed from $\sim5.8\times10^6$ molecules. For the initial configuration, the number of intercalated (interlayer) molecules was specified according to an extrapolation of results for smaller scale equilibrium simulations with a fully periodic (and common size) kaolinite structure (Ref. 11 for potassium acetate, unpublished results for hexyl-amine). The MD time step was set to 1 fs and the leap-frog integrator was used. The linear constraint solver (LINCS) algorithm[20] was employed for constraining the lengths of all bonds involving hydrogen atoms. During the simulation runs the temperature and pressure were fixed. Weak temperature coupling was applied using the modified Berendsen thermostat[21] with a 0.1 ps coupling constant (typically used in MD simulations of condensed-phase systems). The pressure coupling was isotropic using the Berendsen barostat[22] with a 0.5 ps coupling constant, and the compressibility parameter was set to 10^{-6} bar^{-1}. The van der Waals interactions were truncated at 1.2 nm and the periodic electrostatic interactions were calculated by the particle mesh Ewald (PME)[23] algorithm with a 1.2 nm cutoff. Periodic boundary conditions were applied in all three spatial directions. Each simulation ran in parallel on a parallel supercomputer using 768 CPU cores (Intel Xeon E5-2670); the wall clock time for a 100 ps simulation period was ~60 h.

A standard fully flexible all-atom force field was employed: CHARMM[24] and the recently proposed thermodynamically consistent force field INTERFACE[25]. The INTERFACE force field operates as an extension of common harmonic force fields (e.g. CHARMM) for inorganic compounds. The parameters for kaolinite were taken from the available models of the INTERFACE force field that were developed for 2:1 type layered silicates (mica, montmorillonite, pyrophillite). The CHARMM27 force field variant implemented in GROMACS[26] was used for potassium acetate, and the flexible type of the SPC model[27] for water. The acetate model was adapted from the "Combined CHARMM All-Hydrogen Topology File for CHARMM22 Proteins and CHARMM27 Lipids". In these models, the van der Waals nonbonded interactions were described with the standard 12-6 Lennard-Jones potential, using the Lorentz-Berthelot combination rule.

Because of the large number of atoms used in the present simulations, only a few configurations were actually saved (one snapshot per 340 ps, which led to a configuration dump file size of about 10 GB). Therefore, special care was taken during data processing (calculating basal spacing, counting the number of intercalated molecules), which was accomplished with an in-house developed software. The basal spacing distribution was calculated by measuring the distances between all matching Si atoms for each pair of adjacent layers (Si atoms located at the same topological position of adjacent layers were assumed to be matching). Solute/solvent molecules between adjacent layers were identified as intercalated and counted as being between these layers as long as two matching Si atoms and the center of mass of a solute/solvent particle formed an acute-angled triangle with a specific height m (see Fig. 1). m was chosen to be less than a carefully selected atomic size parameter.
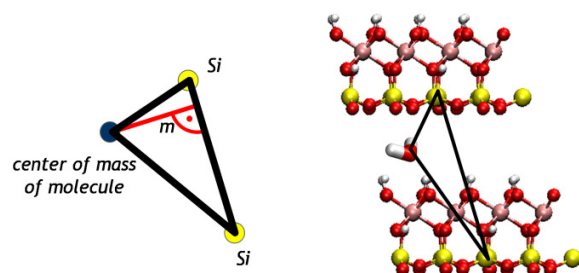
Figure 1. Criteria for identifying solute/solvent molecules as intercalated between adjacent layers.

Basal spacing distributions were sampled (assuming a no-slip condition between adjacent layers) for the obtained kaolinite-potassium acetate and kaolinite-hexyl-amine complexes as well as the number of intercalated molecules. Fig. 2 shows these distributions in the last 0.34 ns period of the simulations. In the case of hexyl-amine solution a fairly broad double-peak is visible, which is in contrast to the sharper and more separate peaks obtained in the aqueous potassium acetate system.
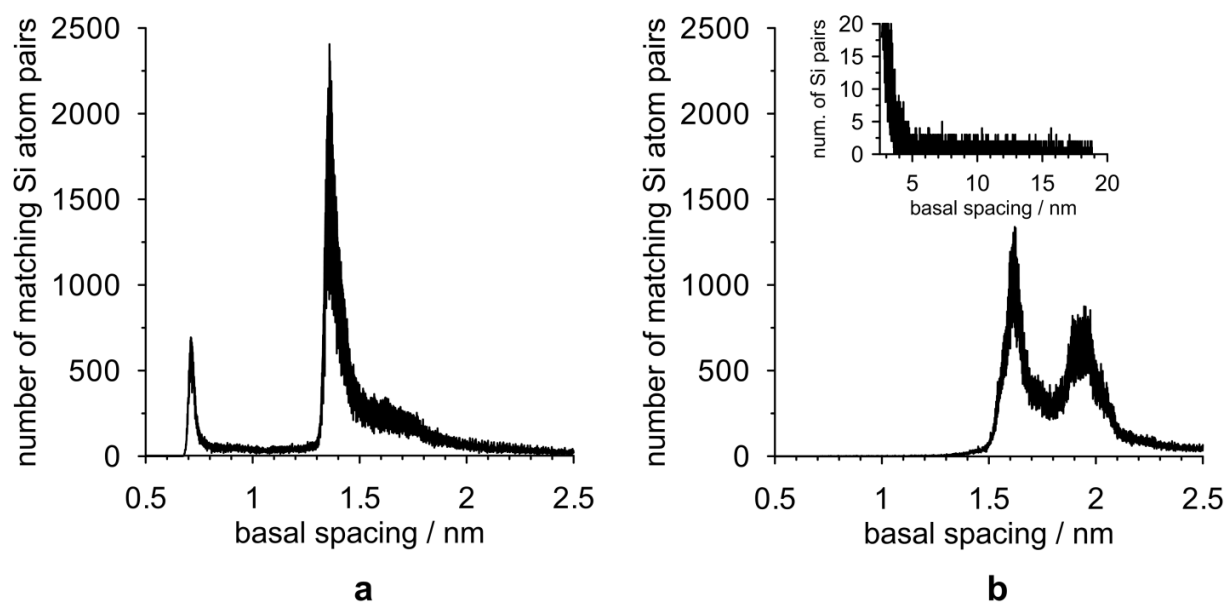
Figure 2. Basal spacing distributions during the last 0.34 ns period of the simulations for aqueous potassium acetate (a) and hexyl-amine solutions (b).

Simulation snapshots were created with VMD (Visual Molecular Dynamics, a molecular visualization program)[28] to illustrate the structure and the dynamic changes in the structure of the kaolinite particle (Fig. 3).
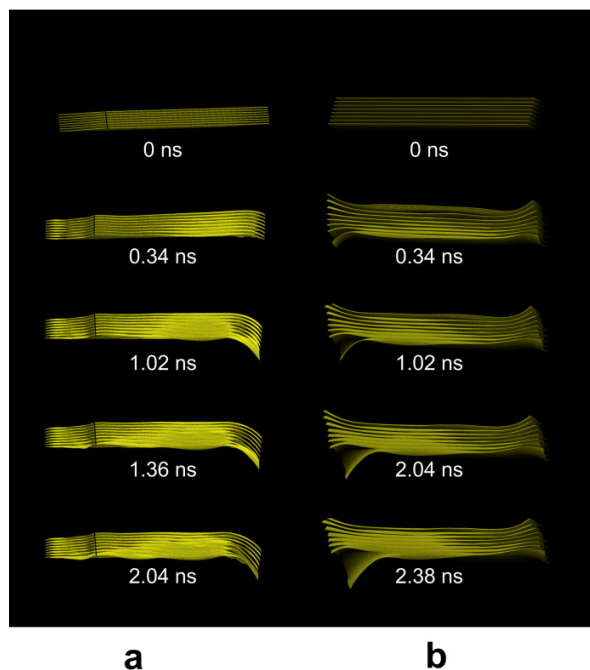
Figure 3. Dynamic changes in the structure of the kaolinite particle from simulation snapshots (left column: aqueous potassium acetate solution, right column: hexyl-amine solution). To achieve a good visibility, only the Si atoms of the kaolinite layers were depicted, while all other molecules were omitted.

Aqueous potassium-acetate solution

The initial basal spacing of the kaolinite particle was set to 1.2 nm, which is below the experimental observations and previous simulation results[11]. The loading of the kaolinite particle was set to 20 000 acetate and potassium ions and 192 000 water molecules per interlayer space to obtain a system composition similar to that of our previous smaller scale simulation results with a fully periodic crystal (~70 wt% of kaolinite, ~11 wt% of potassium acetate and ~19 wt% of water). The particle was surrounded by a nearly saturated aqueous potassium acetate solution

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with a potassium acetate to water molar ratio of ~1:7.3. The experimentally stable complex has a basal spacing of 1.4 nm that was reached in the simulation after ~ 1.5 ns. The change in the slope of the curves in Fig. 4 indicates stability by showing that the number of molecules between layers tends to remain at a constant value.
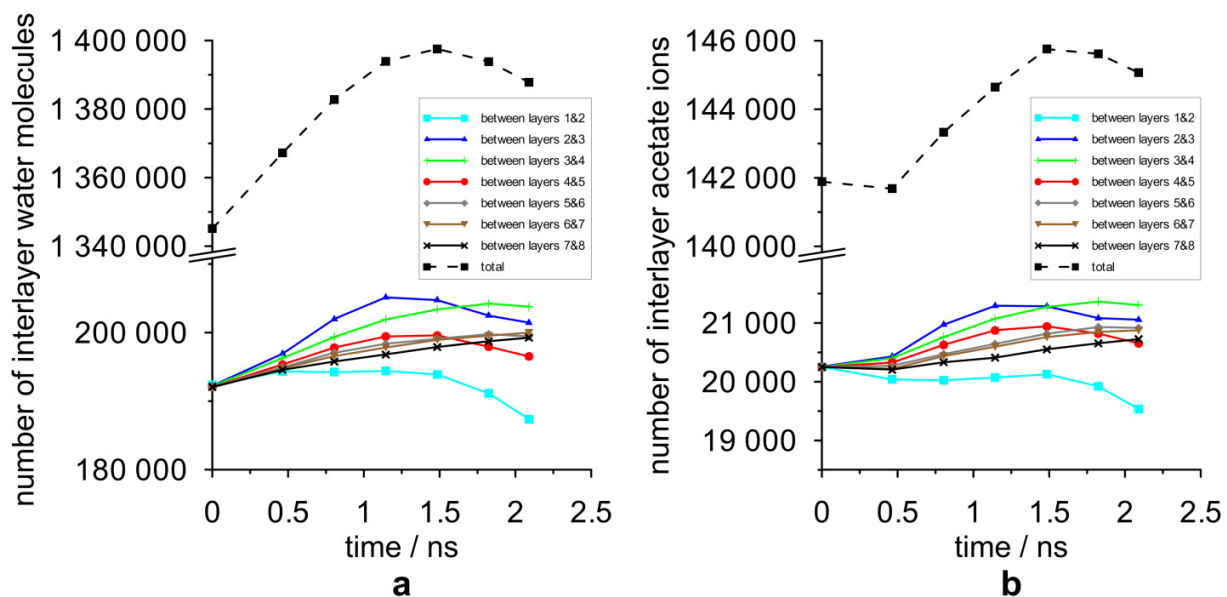

Figure. 4. Distribution of intercalated water molecules (a) and acetate ions (b) in the separate interlayer spaces along with the total number of these molecules. (The curves for the number of intercalated potassium ions are omitted, because of the very close similarity to the curves of acetate ion.)

It is interesting to note that the 0.7 nm peak in Fig. 2a appeared first around 1.5 ns of simulation time, which means that a pair of layers started to collapse to a non-intercalated state releasing the interlayer molecules and forming hydrogen bonds between the layers. Most likely, this corresponds to the decrease in the number of intercalated molecules between layers "1" and "2" (cf. Fig. 4). This is probably due to finite size effects that could not fully be avoided with the specified number of kaolinite layers (eight) and the limited number of solvent molecules in this simulation. (Certainly, as the starting interlayer potassium acetate to water molar ratio was not the same as that of the surrounding solution, this difference in itself can also cause collapse of the layers. However, we believe that in that case all of the layers would show signs of collapse.) The number of molecules between the other six interlayer spaces is considered to be converging to an equilibrium value that is in agreement with that of the experimentally observed complex with a basal spacing of 1.4 nm[11].

Although Singh and Mackinnon[29] reported that hydration of kaolinite by repeated intercalation and deintercalation with potassium acetate might allow for delamination of kaolinite, no signs of any delamination could be observed in the present simulation and the results suggest that the kaolinite particle is in or near a stable state. No such morphologic changes occurred as in the case of hexyl-amine solution (see below). Some bending on one corner of the particle was seen (see Fig. 3a), but all layers bent together (the asymmetric bending of the ends of the stacking layers can be attributed to the small difference originated from the asymmetric cutting of the terminal Si(Al)-O-Si(Al) bonds at the both ends of the layers).

Hexyl-amine solution

The initial basal spacing and loading of kaolinite were set to 2.0 nm (well below the basal spacing of 2.66 nm that was detected by X-ray measurements[2]) and 57 000 molecules per interlayer space (resulting in a composition of ~68 wt% kaolinite and ~32 wt% hexyl-amine). This initial setup was estimated from preliminary equilibrium simulations with a fully periodic kaolinite structure. The variation of the number of intercalated molecules during the simulation is shown in Fig. 5.
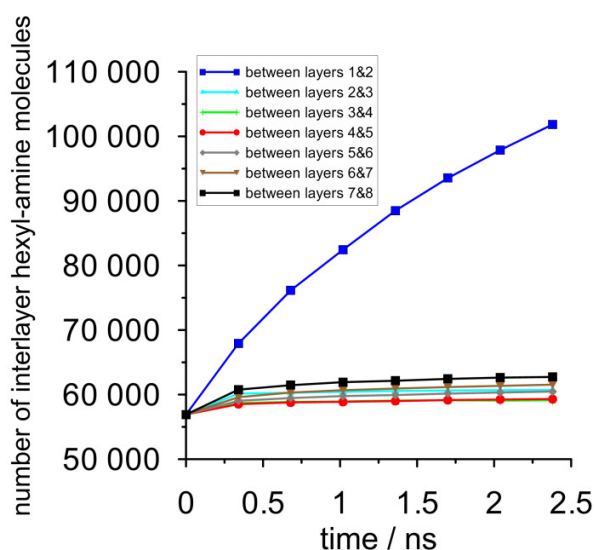

Figure 5. Distribution of intercalated hexyl-amine molecules in interlayer spaces.

With progressing simulation time, a substantial increase in the number of molecules intercalated in one of the terminal interlayer spaces (between layers "1" and "2") was observed, indicating a delamination process. This is in agreement with qualitative observations from the snapshots (Fig.

3b), where apparently the external layers started to roll. This delamination phenomenon also reveals itself qualitatively in the basal spacing distribution (Fig. 2b): the long tail of the curve is clearly observable (see also the inset in Fig. 2b). The basal spacing distribution shows two pronounced peaks, one at 1.6 nm and one at the starting value of 2.0 nm. This suggests the possibility of the formation of some metastable kaolinite-hexyl-amine complexes before the formation of the experimentally observed complex. Even after the total simulation time of 2.38 ns, the kaolinite particle showed a significant and ongoing configurational change in the hexyl-amine solution.

Although our conclusions were drawn with the understanding that these simulations were relatively short (it is obvious that the formation of a nanotube/nanoscroll takes much more time), to our knowledge, this is the first case where results of atomic-resolution simulations (with over 100×10^6 atoms) can be used to make predictions for the initial stage of nanotube/nanoscroll formation from a kaolinite platelet.

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