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Molecular Dynamics Simulations of Systems Including Clay, Water and Organic Matters

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Abstract - Molecular dynamics (MD) simulations of the clay-water system were carried out taking account of an extension to complex and large-scaled systems composed of clay, water, and organic molecules. To simulate such a system, it is important to define appropriate interaction potential models between different materials. In the present study, an estimation of the clay-water interaction was done on the basis of infrared spectra of hydrated clay mineral. The obtained clay-water interaction model was adopted to simulate some complex systems composed of clay (kaolinite, in the present study) and water. The expanding character of kaolinite and states of H_2O adsorption on the surface of kaolinite layer were investigated. This process of estimating the clay-water interaction potential could be applied also to characterize other interaction potentials between different molecules. Such interactions are important factors in the simulation of a complex system which additionally includes organic molecules.

I. Introduction

Molecular dynamics (MD) simulation is now one of popular methods in computational chemistry . Large number of works using MD method have been done on water, organic molecules, minerals, proteins, and so on. In the environmental sciences, we are required to understand the complexes of all such materials. To simulate a complex and large-scaled system composed of many different molecules and clusters is a next step of computer chemistry using MD method. Some attempts dealing with clay minerals and organic matters by means of MD method have been made by previous workers[1, 2, 3]. The systems studied in these works are rather small-scaled and simple. Problems we find in the environmental sciences are containing a number of chemical compounds, both of organic and inorganic. Such themes are to be investigated in future with regard to research method by computational approach.

In the present work, MD calculations of systems containing clay mineral (kaolinite) and water were carried out. Kaolinite is one of dioctahedral 1:1 phyllosilicates with chemical composition of $Si_2Al_2O_5(OH)_4$. The unit layer is composed of one gibbsite sheet and one Si tetrahedral sheet as illustrated in Fig. 1. In interlayer region, hydrogen bonds between the hydrogen atoms on gibbsite sheet and the

oxygen atoms at tetrahedral basal plane are made. The structural features are well investigated[4]. A potential model of kaolinite have been already developed in previous work[5]. This potential model can reproduce crystal structure and give an atomic vibrational state comparable with spectroscopic data[6, 7].

Using this potential model and a previously developed model of water, some clay-water systems were simulated by means of MD calculation to investigate expansion behavior of hydrated kaolinite and water adsorption properties of kaolinite surface. In this process, it is clarified that some problems related to interaction between different molecules are sensitively influenced by intermolecular potentials. Considering this difficulty on simulation method, some discussions were made on how to approach more complex and large-scaled system in environmental sciences.

II. Simulation Method
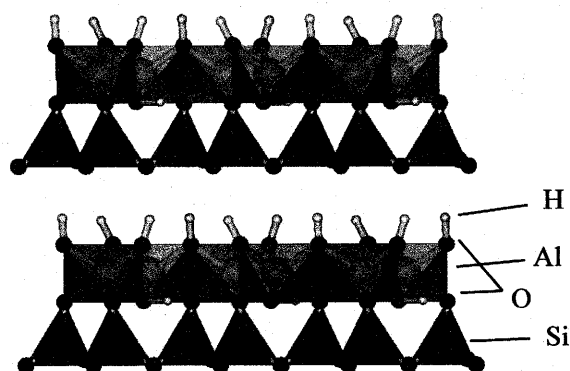
A. Potential model and details of calculation

Fig. 1. Kaolinite structure projected on to (100). Interlayer region is bounded by week hydrogen bonds with c.a. 2.0 Å of bond distance.

TABLE I
Interatomic Potential Parameters used in the Present Study

atom	Z (e)	W (g/mol)	a (Å)	b (Å)	c (kJ/mol)$^{1/2}$/ (Å)^3
O	-1.23889	16.00	1.86	0.148	29.6
Si	2.56966	28.09	0.969	0.090	-
Al	2.23444	26.98	1.02	0.078	-
H	0.38545	1.01	0.128	0.044	-
O_w	-0.72	16.00	1.833	0.138	23.88
H_w	0.36	1.01	0.159	0.041	-

atom pair	D_1 (kJ/mol)	β_1 (Å)	D_2 (kJ/mol)	β_2 (Å)	D_3 (kJ/ mol)	β_3 (Å)	r_3 (Å)
O-Si	12500	4.00	-1250	2.00	-	-	-
O-Al	11000	4.0	-1200	2.00	-	-	-
O-H	4580	5.49	-1020	2.76	13.0	9.2	1.37
O_w-H	4580	5.49	-1020	2.76	13.0	9.2	1.37
O-H_w	-1137	2.72	0	2.20	15.7	9.1	1.16
O_w-H_w	-1137	2.72	0	2.20	15.7	9.1	1.16

	f_a	θ_o (°)	r_m (Å)	g_r
O_w-H_w-O_w	0.000126	99.5	1.41	9.8

The subscript w means that the atom belongs to water molecule.

The first step in the MD method based on the model potential is to obtain appropriate interatomic potential parameters. The systems calculated in the present study includes silicate layers and water molecules interacting each other on layer surfaces. The interatomic potential model treating these system is regarded as consisting of three parts: potential models for silicate layers, for bulk water, and for the interaction between the silicate layer and the water molecule.

The potential functions used in the present study are as follows;

Two-body potential:

$$U_{ij}(r_{ij}) = \frac{Z_iZ_je}{4\pi\varepsilon r_{ij}} + f_o(b_i + b_j)\exp\left(\frac{a_i + a_j - r_{ij}}{b_i + b_j}\right) - \frac{c_ic_j}{r_{ij}^6}$$
$$+ D_{1ij}\exp(-\beta_{1ij}r_{ij}) + D_{2ij}\exp(-\beta_{2ij}r_{ij}) + D_{3ij}[-\beta_{3ij}(r_{ij} - r_{3ij})^2]$$

Three-body potential:

$$U_{ijk}(r_{ij}, r_{ik}) = -f_a[\cos\{2(\theta_{ijk} + \theta_o)\} - 1]\sqrt{k_1k_2}$$

$$k_j = \frac{1}{\exp\{g_r(r_{ij} - r_m)\}}$$

Where, r_{ij} is the interatomic distance, Z is the electronic charge of each atom, and a, b, c are parameters for each atom. The parameters D's, β's, and r_3 are for anion-cation pairs. The f_o (=6.9511×10^{-11}N) is a constant for unit conversion.

The two body potential is called the Born-Mayer-Huggins

potential, which is composed of the Coulombic term, the short range repulsion term, the van der Waals term, and three terms of the modified Morse potential. The three body potential is required to reproduce the H-O-H angle (c.a. 104°) of H_2O molecule.

The interatomic potential parameters used in this study are listed in Table 1. In this table, the parameters (Z, W, a, b, c) for single atoms, O_w and H_w, and those (D's, βs, r_3) for an atom pair, O_w-H_w, describe the potential model of bulk water. Similarly, those for atoms, Si, Al, O, H, and for atom pairs, O-Si, O-Al, O-H, describe the potential model of kaolin minerals. The rests for the atom pairs of Ow-H and O-Hw are required to describe the interaction between the silicate layer and the water molecule.

The parameters describing the potential model of kaolin minerals used in the present study is derived from a previous work [5], in which the potential parameters were optimized referring an experimental crystal structure [4] and I.R. spectra [7, 8, 9, 10]. The modified KKY potential, which was water potential model developed empirically [10], was adopted to water potential model.

Kaolin-H_2O interaction was determined empirically in the present study referring to I.R. spectra of synthesized hydrated phase of kaolinite [11]. This interaction (D's, βs, r_3's for O-H_w and O_w-H) was assumed to be one of simple combinations composed of parameters for kaolinite and for bulk water. Five combinations of (O-H_w, O_w-H) can be listed as candidates for the approximated interaction model, which are (null, null), (O_w-H_w, O_w-H_w), (O-H, O-H), (O_w-H_w, O-H) and (O-H, O_w-H_w) to be placed in (O-H_w, O_w-H). Atomic vibrational spectra were calculated from MD results using these different five interactions. Among them, the combination of (O-H, O_w-H_w) was selected for reasons of concordance with the experimental infra-red spectra.

This potential model gives atomic vibrational spectra illustrated in Fig. 2. The spectra of water hydrogen has a peak at 1600 cm^{-1}, broad band in a range from 3200 cm^{-1} to 3400 cm^{-1}. That of kaolinite hydrogen has several peaks in a range from 3600 cm^{-1} to 3700 cm^{-1}. These peak positions are concordant with experimental infra-red spectra of hydrated
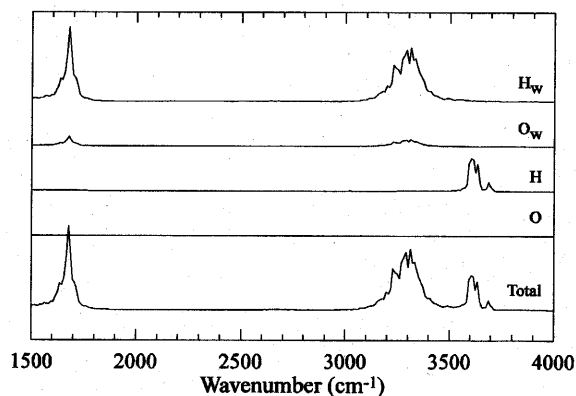

Fig. 2. Atomic vibrational spectra calculated from MD results of the hydrated kaolinite with N=1. The N is a number of water molecule per $Si_2Al_2O_5(OH)_4$.

N=1.00   N=1.50   N=2.00   N=3.00   N=4.00

← H₂O
← kaolinite layer
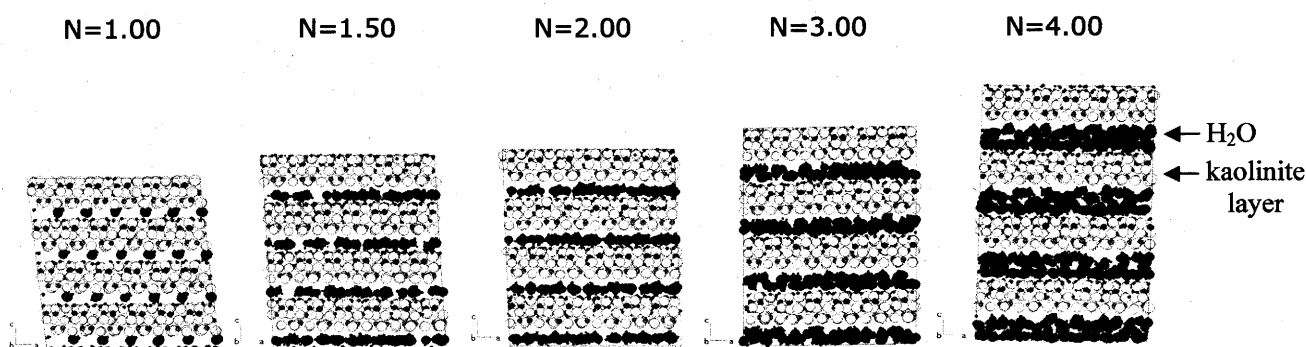
Fig. 3. Selected snapshots of hydrated kaolinite structures with various amount of water. N's are number of water molecules per $Si_2Al_2O_5(OH)_4$. The state with N=1 has regular alignment of water molecules which is constrained by tetrahedral six-membered rings. The state of N=2 corresponding to 10Å-halloysite have one layer of water.

kaolinite[11], in which OH stretchings of kaolinite hydroxyls appear at 3622 cm^{-1}, 3640 cm^{-1}, and 3690 cm^{-1}, those of H_2O at 3522 cm^{-1} and 3572 cm^{-1}, and H-O-H bending at 1650 cm^{-1}. In consequence, the resulted potential model in Table I is able to reproduce dynamical characters of kaolinite-water complex.

On the basis of this potential model, MD simulations were carried out using the program MXDTRICL & MXDORTO [12], in which the electrostatic potential was calculated using the Ewald lattice sum method. The Verlet method with 0.4 fs of time step was used in numerical integrations. Statistical values of some physical quantities were sampled during 20000 steps of run.

B.   Objects of simulation

Using MD method, an expanding behavior of kaolinite resulted from compulsive intercalation of water and adsorption state of water molecules on kaolinite surface were simulated.

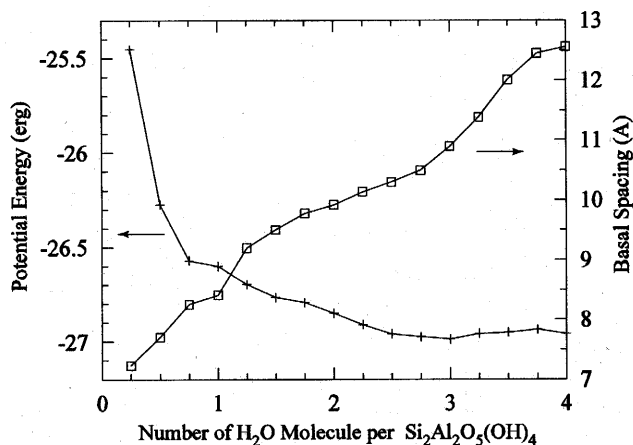Kaolinite is non-expandable species, not like smectite

which is a typical expandable clay mineral. Although smectite expands in wet condition, kaolin minerals have no expandability. 10 Å hydrated phase of kaolinite was synthesized, and its partially dehydrated 8.6 Å phase exists in meta-stable state[11]. 10 Å phase contains two H_2O molecules per the formula $Si_2Al_2O_5(OH)_4$ (N=2), and 8.6 Å phase one H_2O molecule (N=1).

In order to investigate expanding properties of kaolin minerals, different numbers of H_2O molecules were compulsively intercalated into kaolin structural models. Calculations were done each for different contents of H_2O molecule per $Si_2Al_2O_5(OH)_4$, assigned by N, in a range from 0.25 to 4.0 with interval of 0.25. Simulations were carried out with NPT ensemble. Potential energies of interlayer water molecule were averaged for each model with different water content. Structural features of interlayer water were observed in snapshots of relaxed structure.

As kaolin minerals have two different types of surface, hydroxyl surface and oxygen surface, it is expected that H_2O adsorption behavior also different on the two sides of layer.

Fig. 4. Expansion curve of kaolin interlayer and potential energy of intercalated water per molecule as functions of water content.
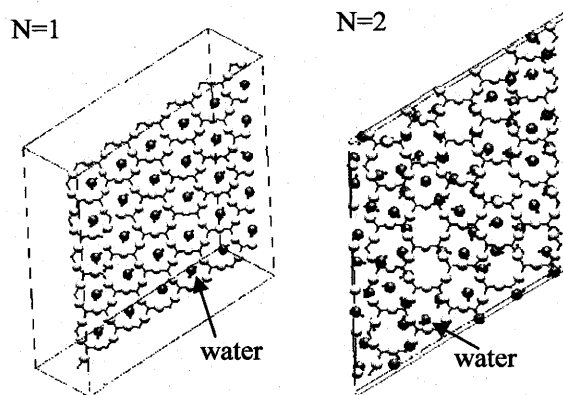
N=1   N=2

water   water

Fig. 5. States of intercalated water in kaolin minerals for different amount of water, illustrated as (001) projection. Tetrahedral six-membered rings also illsutrated to present configurational relationships of water and silicate layer. The N's meaning is similar to that of Fig. 1.

Simulation was carried out using a model of hexagonal kaolin unit layer surrounded by H_2O molecules. NTV ensemble was adopted to keep the surrounding space.

III. Results

A. Expanding behavior of kaolin minerals

Simulations with different amounts of water were carried out. Fig. 3 shows selected snapshots of hydrated kaolinites with different amount of water intercalated compulsively. An expansion curve of basal spacing and potential energies of one water molecule are plotted as functions of water content in Fig. 4. The expansion curve shows irregularly increasing curve. The potential energy curve of interlayer water has minimum at N=3.0, which is concordant to that this mineral is not expandable with water.

In Fig. 5, relaxed states of interlayer water are illustrated for water contents of N=1 and N=2. The snapshot of the state with N=1 in Fig. 5 shows a regular arrangement of H_2O molecules. This corresponds to partially dehydrated 8.6 Å phase. This regular alignment of water molecules coincide to "hole water" [11, 13], which is strongly bound to tetrahedral six-membered rings.

The state of N=2 in Fig. 5 shows structural relationship of H_2O molecules with tetrahedral sheet (10 Å phase). There seems to be no "hole water" neither "associated water" [11, 13]. The "associated water" is less strongly bonded to silicate layer and its dehydration temperature is lower than "hole water". In contrast, the relaxed state in Fig. 5, all water molecules seems to be in a equivalent condition in which all water molecules are making a network of hydrogen bond. This is caused by the stronger water-water interaction than the water-kaolin interaction.

B. Hydrophilicity of kaolin surfaces

Adsorption behaviors of water molecules on kaolin surfaces were simulated. Fig. 6 shows a relaxed state the MD simulation. In i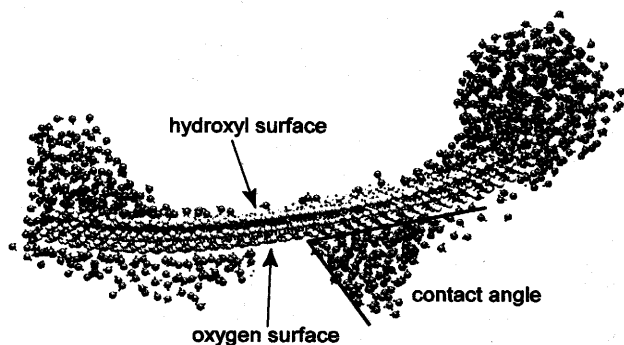nitial state, water molecules are sparsely distributed around a hexagonal kaolin layer with hydroxyl surface upward (with oxygen surface downward). Starting relaxation, the water molecules flocculate into small drops, then were adsorbed on the kaolin layer.

A cross section of adsorbed water on the layer is shown in Fig. 6. Large area of the hydroxyl surface (upside) is covered by one-molecule layer of H_2O. In contrast, the oxygen surface (downside) has significant uncovered part and high contact angles between the layer and the drop surface. These different adsorption characters implies that the hydroxyl surface is hydrophilic and the oxygen surface is hydrophobic.

IV. Discussions

A. Importance of intermolecular potential

In the process to choose an appropriate potential model of the clay-water interaction, we assumed five potential models. These different models result in apparent changes of expanding behavior. This fact implies that the model of intermolecular potential is important as well as that of intramolecular potential in the classical MD method. Obtaining an appropriate intermolecular potential might be quite critical to get correct results in simulation of large and complex system composed of different types of molecule.

B. MD simulation of large complex system related to environmental sciences

Applying the MD method to environmental sciences will require to estimate many kinds of intermolecular potential between different organic and inorganic matters. Until now, large number of simulation works have been done on DNA, proteins, lipid layer, and micelle. But large-scaled complex systems including organic and inorganic matters are still untouched by computational approaches. Continuing improvements of computer power will provide us in near future abilities to try such complex problems. Some objects related to biomineralogy are thought to be such future themes; magnetite in magnetotactic bacteria, ferrihydrite in ferritin, goethite around iron oxidizing bacteria. Applying computational approaches to these themes will result in essential knowledge on mineralization related with biochemical processes.

V. Conclusions

Intermolecular potentials between different kind of molecules are important factors in such a complex system that includes various organic molecules and inorganic clusters, like a cell of bacterium. It is necessary to estimate the intermolecular potential in enough precision to reproduce delicate behaviors of complex system. In the present study, the intermolecular potential between clay-water interface was estimated on the basis of spectroscopic data from synthesized complex sample. In case that any spectroscopic data are available in attempts to

Fig. 6. Cross section of kaolinite unit layer with adsorbed water molecules on the surface.

simulate complex system, it would be possible to use the sane method as the present case to estimate the interaction. But if not, the ab-initio calculation would be required to optimize the parameters of intermolecular potential.

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