

Elasticity Constants of Clay Minerals Using Molecular Mechanics Simulations

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Abstract The purpose of this paper is to obtain the elasticity constants (including the volume and shear modulus, Young modulus, and Poisson's ratio) of clay minerals, or montmorillonite, kaolinite and illite, using the molecular mechanics simulations. The Lennard-Jones potential function and Ewald summation method were respectively used to compute the Van der Waals' and Coulomb forces. The integrated approach was made to perform the energy optimization of the mineral crystals. The unit and super cells of each mineral were then established to compute the elasticity constants of clay minerals. The substitutions, structural waters and anisotropy were also considered during the simulations. It shows that the montmorillonite easily move laterally while kaolinite is reasonably stable under vertical load; the substitution plays an important role for the elasticity constants of illite; the bulk modulus, shear modulus, Young's modulus decrease if the number of waters increases; the intrinsic anisotropy occurred in the clay minerals; montmorillonite and illite may expand under external load.

1 Introduction

The minerals in clay mainly comprise non-clay minerals and clay minerals. The non-clay minerals mainly include quartz, feldspar, and mica, whereas the clay minerals mainly include kaolinite, montmorillonite, and illite. The features of these minerals in the micro scale may play a significant role on the engineering properties. Therefore, the micro features (i.e., the elasticity constants) of clay minerals are a fundamental aspect in investigating the engineering properties of clays. Nevertheless, the related study goes slowly because of many challenges countered.

In recent years, some progresses were made by the use of molecular dynamics (MD) or molecular mechanics (MM) simulations. Marry and Turq [1] investigated the interlayer spaces of bihydrated Na-montmorillonites containing a small quantity

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of cesium using the Monte Carlo and MD simulations; Chang et al. [2] combined the MD and Monte Carlo (MC) simulations in one-, two-, and three-layer hydrates of K-montmorillonite to obtain the layer spacing, interlayer water potential energy, and counterion mobility; using empirical force field, Yu et al. [3] performed MD simulations to compute the sorption of organic compounds at the surfaces of dioctahedral clay minerals with various water molecules; Zhang et al. [4] constructed a kaolinite cluster model to investigate the intercalation between various water molecular layers; Kuang et al. [5] investigate the montmorillonite features with various water contents and sodium chloride aqueous solutions using MD simulation.

In the current study, the elasticity constants of clay minerals will be computed directly using molecular structural model downloaded from the open source of mineral database. The software Materials Studio and MD simulation will be used to investigate the elasticity constants of clay minerals and their changes with substitutions, water numbers, and directions.

2 Foundation of Molecular Mechanics Simulation

2.1 Foundation of Molecular Mechanics

Molecular mechanics presents the dynamic behaviors of materials in an atomistic scale and is conducted in an ensemble condition. The ensemble is an assembly of the individual systems with various movement states and features. According to the constraint conditions, the ensemble was divided into microcanonical, canonical, grand canonical, isothermal isobaric, and isobaric isenthalpic ones.

Four types of molecular simulation techniques, or MM, MC, MD, and Quantum Mechanics (QM) simulations are generally used. In MM, the deformation of a molecular structure are obtained based on the structural parameters and applied forces; both the changes in bond length, bond angle, and dihedral angle and the potential energy function of non-bonds are used to describe the changes of the internal stresses or energies in the molecular caused by the changes in molecular structures. The MM simulation will be used in the current study to investigate the elasticity features of clay minerals.

The main steps in MM simulation include:

- (1) Establishment of the unit cell based on the space group, lattice parameters, spatial coordinates and charges of each atom, and linkage of the bonded atoms;
- (2) Conduction of the energy optimization to the unit cell;
- (3) Establishment of the super cell based on the optimized unit cells;
- (4) Conduction of the energy optimization to the super cell;
- (5) MM simulation to the optimized unit and super cells; and
- (6) Computation of the micro scale features (i.e., elasticity constants).

2.2 Selection of Force Fields

During MM simulation, the force field was used to conduct the interactions between molecular and described as the potential functions related to the atom coordinates and the distances between atoms. The interactions between atoms include bond actions and non-bond ones. The total potential energy is

$$E = E_1 + E_2 \quad (1)$$

$$E_1 = E_b + E_a + E_t + E_i \quad (2)$$

$$E_2 = E_v + E_c \quad (3)$$

where E_1 is the energy referring to bond action, including E_b (bond's stretching energy), E_a (bending potential energy of bond angles), E_t (retortion potential energy of normal dihedral angle), and E_i (retortion potential energy of abnormal dihedral angle); E_2 is the energy referring to non-bond action, including E_v (potential energy of the Van der Waals action) and E_c (potential energy of the Coulomb action). As for Van der Waals action, the short-range interaction between atoms was computed using the truncation distance; the corresponding energy of the true system was computed by the repetition of the finite boxes; and the Lennard-Jones potential function $4\varepsilon[(r_0/r)^{12} - r_0/r)^6]$ was used during computation. As for Coulomb action, the Ewald summation method was used where the interactions between atoms was considered as the summation of the interactions between an atom and all of the imaginary atoms in the central and periodical lattices.

3 Computations of Elasticity Parameters of Clay Minerals

3.1 Establishment of Unit Cell

Kaolinite is an aluminium silicate mineral with the laminated structure of 1:1, belonging to triclinic system with the space group of P1. The lattice constants of the unit crystal is that $\alpha = 91.93^\circ$, $\beta = 105.04^\circ$, $\gamma = 89.79^\circ$, $a = 5.149 \text{ \AA}$, $b = 8.934 \text{ \AA}$, and $c = 7.384 \text{ \AA}$. The original crystal structure of kaolinite was referred from Gruner [6].

Montmorillonite is an aluminium silicate mineral with the laminated structure of 2:1, or two layers of silicon-oxygen (Si-O) tetrahedron and one layer of aluminium-oxygen (Al-O) octahedral, belonging to monoclinic system with the space group of C2/m. The lattice constants of the unit crystal is that $\alpha = \gamma = 90^\circ$, $\beta = 99^\circ$, $a = 5.23 \text{ \AA}$, $b = 9.06 \text{ \AA}$. The lattice constant c of the unit cell relates to the number of interlayer water. The original crystal structure of montmorillonite was referred from Viani et al. [7].

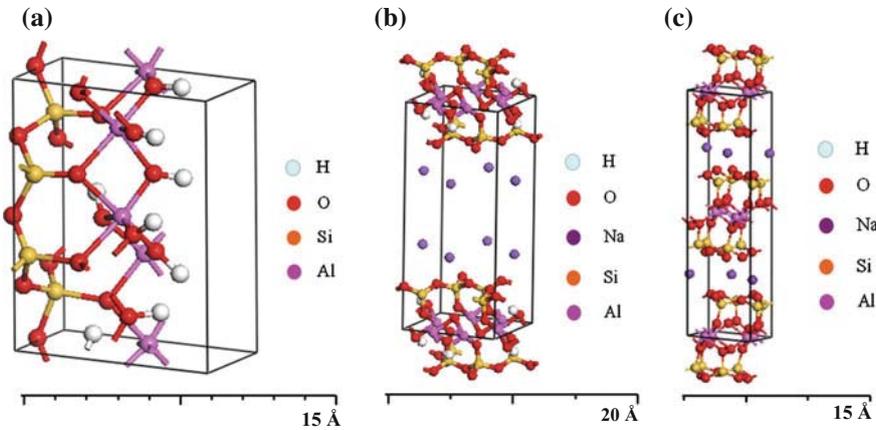


Fig. 1 Initial unit cells of clay minerals, with **a** kaolinite; **b** montmorillonite; and **c** illite

Illite is an aluminium silicate mineral with the laminated structure of 2:1, or two layers of Si-O tetrahedron and one layer of Al-O octahedral, belonging to monoclinic system with the space group of $C2/C$. The lattice constants of the unit crystal is that $\alpha = 90^\circ$, $\beta = 95.18^\circ$, $\gamma = 90^\circ$, $a = 5.194 \text{ \AA}$, $b = 8.996 \text{ \AA}$, and $c = 20.096 \text{ \AA}$. The original crystal structure of illite was referred from Viani et al. [7].

The original crystal structures of kaolinite, montmorillonite and illite were downloaded from the open source <http://www.crystallography.net/>, respectively with Nos. 1011045, 9002779, and 2300189. It should be noted that the substitutions in the montmorillonite and illite crystals were considered: the atoms with the same spatial positions were deleted to establish a crystal; and the deleted atoms were recovered but the original corresponding atoms were deleted to establish a substituted crystal. Figure 1a–c is the initial unit cells of kaolinite, montmorillonite and illite, in which Fig. 1b, c is the substituted cases.

For each original unit cell, the optimizations were then performed. For the purpose of comparison, the commonly-used force field, or universal force field were used during the optimizations.

3.2 Establishment of Super Cell

For each mineral, the super cell is constructed from eight unit cells, arranging with a type of $4A \times 2B \times 1C$. The macro system was considered as the infinite repetition of the three-dimensional periodical boundary condition.

For the constructed super cell, the optimizations were performed again. The force field universal were also used during the optimizations of the super cells.

3.3 Computations of Elasticity Constants

For each of the optimized cells, the tension and shear operations were conducted to compute the internal stress tensor and elasticity matrix, which is used to compute the Reuss's bulk modulus B_R , Voigt's bulk modulus B_V , Reuss's shear modulus G_R , and Voigt's shear modulus G_V . The commonly-used elasticity constants, including the Bulk modulus B , shear modulus G , Young's modulus E , and Poisson's ratio ν were computed using the Voigt–Reuss–Hill method and expressed as [8]

$$B = (B_V + B_R)/2, G = (G_V + G_R)/2, E = 9BG/(3B + G), \nu = (3B - E)/(6B) \quad (4)$$

The computed elasticity constants for the optimized cells of the clay minerals are listed at Table 1.

From Table 1, it can be seen that (1) the great-small sequences of the bulk modulus are montmorillonite, illite-1 (without substitution), and kaolinite; (2) the great-small sequences of the shear modulus are kaolinite, montmorillonite, and illite-1; (3) the great-small sequences of the Young's modulus are montmorillonite, kaolinite, and illite-1; (4) montmorillonite and kaolinite respectively present the greatest and smallest Poisson's ratios in three clay minerals. These results imply that (1) montmorillonite may be isotropic under compression load, and kaolinite may bear more shear force; (2) montmorillonite will easily move laterally while kaolinite are reasonably stable under vertical load.

Table 1 Elasticity constants of unit and super cells for the clay minerals

	Elasticity constants/GPa			
	Bulk modulus/GPa	Shear modulus/GPa	Young's modulus/GPa	Poisson's ratio
Unit cell				
Kaolinite	52.9167	65.3741	138.9159883	0.062469604
Montmorillonite	85.547	58.2601	142.4440593	0.222483821
Illite-1	64.3956	54.6723	127.8383568	0.169132786
Illite-2	107.9736	48.993	127.6690626	0.302931669
Super cell				
Kaolinite	52.20865	44.8468	104.5923975	0.166107699
Montmorillonite	84.7605	57.29565	140.2788089	0.22416631
Illite-1	56.4219	46.24205	108.9593246	0.178141157
Illite-2	106.8931	42.10305	111.6502217	0.325916076

4 Main Factors Influencing Elasticity of Clay Minerals

Three factors, or substitution, structural water and anisotropy, were considered to mainly affect the elasticity constants of clay minerals in the current study.

4.1 Substitution

The substitution was considered by taking illite-1 and illite-2 as examples. The element Al in the former crystal was substituted by the element Si in the later one. The simulated results also presented in Table 1. It can be seen that (1) the bulk modulus and Poisson's ratio of substituted illite reaches to about two times of those without substitution; (2) the shear modulus and Young's modulus of the illites has no obvious change whether the substitution occurred. These simulated results imply that the substitution plays an important role for the elasticity constants of illite.

4.2 Structural Water

The unit cell of montmorillonite was taken as an example to consider the effect of structural waters on the elasticity constants. For the insertion of water Molecular model into montmorillonite, initial water molecular was geometrically optimized. The optimized water was then randomly inserted into the optimized unit cell of montmorillonite with the change in box sizes. For each box size, a stable insertion amounts of water molecular occurred and was considered as the possible number of inserted waters; the optimization were performed again for the montmorillonite with stably-inserted waters; the optimized montmorillonite was used to compute the elasticity constants of montmorillonite with various waters.

The computed results were shown at Table 2. It can be seen that all of the bulk modulus, shear modulus, Young's modulus decrease to about one-third if the number of waters increases from 2 to 11; the Poisson's ratio has no obvious changes with the variation in the number of waters.

Table 2 Elasticity constants of unit cell for montmorillonite with various waters

Number of waters	Elasticity constants			
	Bulk modulus/GPa	Shear modulus/GPa	Young's modulus/GPa	Poisson's ratio
2 (C = 12.450)	84.7605	57.29565	140.2788089	0.22416631
7 (C = 15.000)	73.74825	52.7362	127.7564084	0.211278102
11 (C = 20.000)	57.79805	36.14575	89.7317637	0.241249161

Table 3 Anisotropy of unit cells for clay minerals

Elasticity constants/GPa	Clay minerals		
	Kaolinite	Montmorillonite	Illite
Young's modulus			
In X direction	137.9371	331.6874	1383.4712
In Y direction	143.4928	296.8898	941.6407
In Z direction	15.2942	-4.8042	1356.1799
Poisson's ratio			
In xy	0.3524	0.1747	-0.8557
In xz	0.6926	2.3359	-0.3668
In yx	0.3666	0.1564	-0.5825
In yz	0.3192	1.7190	0.2494
In zx	0.0768	-0.0338	-0.3596
In zy	0.0340	-0.0278	0.3592

4.3 Anisotropy

Because of the non-symmetry of the crystals, the intrinsic anisotropy was the fundamental features of materials. Considering the anisotropy, the Young's modulus and Poisson's Ratio of unit cells for clay minerals were simulated. The results were listed in Table 3.

From Table 3, it can be seen that the Young's modulus of kaolinite and illite in the vertical to horizontal directions are 9.38 ($143.4928/15.2942 = 9.38$) and 1.47 ($1383.4712/941.6407 = 1.47$); the Young's modulus of montmorillonite have a negative value. These results imply that the clay minerals have intrinsic anisotropy; and the montmorillonite may present expansive under external load.

From Table 3, it can also be seen that the Poisson's ratios of three clay minerals change in a great interval in various directions; the Poisson's ratios of montmorillonite and illite have negative values, implying that montmorillonite and illite may expand under external load.

5 Conclusions

In the current study, the molecular mechanics simulation technique was used to establish the molecular models of three clay minerals, or montmorillonite, kaolinite and illite. The elasticity constants of the clay minerals were then obtained. It shows that the montmorillonite will easily move laterally while kaolinite is reasonably stable under vertical load; the substitution plays an important role for the elasticity constants of illite; the bulk modulus, shear modulus, Young's modulus decrease if the number of waters increases; the Poisson's ratio has no obvious changes with the variation in the number of waters; the clay minerals have intrinsic anisotropy; montmorillonite and illite may expand under external load.

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