

Theoretical Study of Kaolinite Structure; Energy Minimization and Crystal Properties

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Abstract

Computational energy minimization techniques have been used to study the structure and crystal properties of kaolinite. The full elastic tensors of the sheet silicates of clay have been derived with first-principles calculations based on density functional theory. All calculations were performed using GULP program.

Keywords: Kaolinite, GULP, Energy, Crystal Properties, Calculation, Elasticity

1. Introduction

Molecular modeling methods have been increasingly used in the past decade to simulate a wide range of materials and to evaluate their microscopic structure, physical, and thermodynamic properties. Clays and related layered minerals are fine grained and poorly crystalline materials. Large single crystals of clay minerals suitable for X-ray refinement studies are lacking and therefore only a few detailed structural characterizations exist [1-4]. Clay minerals also possess low crystal symmetry and have a unique chemistry that is characterized by a variety of multicomponent substitutions in the tetrahedral and octahedral sheets. Depending upon the type of structural substitution and net charge, the clay may become expandable and provide a suitable host for a variety of intercalates.

Molecular computer simulations have become extremely helpful in providing an atomistic perspective on the structure and behavior of clay minerals.

In other hand elastic properties of clay minerals are almost unknown, mainly because of the difficulty presented by the intrinsic properties. Their small grain size makes it impossible to isolate an individual crystal of clay large enough to measure acoustic properties [5]. So far the effective elastic properties of clays have been derived either by theoretical computation [6-8], by a combination of theoretical and experimental investigations on clay-epoxy mixture [9] or by empirical extrapolations from measurements on shales [10-12]. These derived values of clay moduli show little agreement.

Kaolinite is a 1:1 layer clay composed of a repeating layer of an aluminum octahedral (O) sheet and a silicon tetrahedral (T) sheet. Interlayer hydroxyl groups extend from the octahedral sheet into the interlayer region where they form hydrogen bonds to basal oxygens of the opposing tetrahedral silicate sheet [13] (**Figure 1**).

In this paper a tentative of junction between energetic and crystal properties of kaolinite is presented.

2. Methods

2.1. Energy Calculation

Energy minimizations were carried out using the program GULP [15]. This utilizes interatomic potentials for describing the interactions within the layered silicate structure. The interatomic potentials used are given in **Table 1**. A shell model [16] is used to describe the polarization of the O^{2-} ions. All atoms have integral charges except for the OH groups, whose component atoms have partial charges [17] so as to reproduce the dipole moment of the OH group [18]. Atom based cut-offs to 12 Å are used for describing the two body short range interactions and a Ewald summation technique is used for the dispersion and electrostatic interactions [19].

2.2. Simulation Principle

The potential model describing the effective forces acting between the atoms in the structure has the following



Figure 1. Stacking polytypism in kaolinite; Only the Si^{4+} ions (dark) and the Al^{3+} (light) are shown for simplicity. The view direction is perpendicular to the sheets and a shading has been added to the lower Si^{4+} layer. The thin lines denote the unit cell [14].

components [18].

A two-body short-range term describes repulsions from electron cloud overlap and attractions due to dispersion and covalence. In this study we describe cation-O and the O-O interactions using a Buckingham function: $U_{sr} = A\exp(-r/\rho) - C/r^6$, where the exponential

term describes the repulsive energy and the r^6 term the longer range attraction. The intramolecular OH interaction is represented by a Morse function: $U_{sr} = D\{1 - \exp[-\beta(r - r_e)]\}^2$, where r and r_e are the observed and equilibrium interatomic distances, respectively. Coulomb forces are not included between atoms coupled by a Morse potential, as it is assumed that this potential describes all components of the interactions between the two atoms. As in many previous simulation studies on silicates, the short range cation-cation interactions are not significant and were therefore neglected.

A three-body short-range term describes angular dependent covalent forces. A simple approach is to include bond-bending terms about the tetrahedral cation of the type: $U_{thb} = 1/2K_{thb}(\theta - \theta_0)^2$, where K_{thb} is the harmonic three-body force constant, and θ and θ_0 are the observed and ideal tetrahedral O-T-O bond angles, respectively.

A term to describe electronic polarizability is required if dielectric and dynamic properties are to be modeled accurately. In this study the shell model was used, which provides a simple mechanical model of electronic polarizability. The coreshell self energy is given by $U_s = 1/2K_s r^2$ where K_s is the harmonic spring constant and r is the core-shell separation.

In **Table 1** are represented all the potential used during

Table 1. Potential used in simulation.

<i>Two body short range interaction^a</i>						
Atom 1	Atom 2	Potential	A/eV	$\rho/\text{\AA}$	$C/\text{eV}\text{\AA}^6$	References
Al1 c	O1 s	Buckingham	1460	0.299	0.00	[17]
O2 c	Al1 c	Buckingham	1140	0.299	0.00	[17]
Si1 c	O1 s	Buckingham	1280	0.321	10.7	[17]
O2 c	Si1 c	Buckingham	984	0.321	10.7	[17]
O1 s	O1 s	Buckingham	22800	0.149	27.9	[17]
O2 c	O1 s	Buckingham	22800	0.149	27.9	[17]
O2 c	O2 c	Buckingham	22800	0.149	27.9	[17]
H1 c	O1 s	Buckingham	312	0.250	0.00	[17]
<i>Morse potential</i>						
Atom 1	Atom 2	Potential	D_e/eV	$\beta/\text{\AA}^{-1}$	$r_e/\text{\AA}$	References
H1 c	O2 c	Morse-Coulomb	7.05	2.20	0.949	[17]
<i>Shell model interaction</i>						
Atom 1	Atom 2	Potential	$K_s/\text{eV}\text{\AA}^{-2}$			References
O1 c	O1 s	Spring	74.90			[17]
<i>Three body interaction</i>						
Atom 1	Atom 2	Atom3	$K_{thb}/\text{eV rad}^{-2}$	θ°	References	
Si1 c	O1 s	O1 s	2.097	109.470	[17]	
Al1 c	O2 c	O1 s	2.097	109.470	[17]	

this work.

2.3. Elastic Constant

The calculation of elastic constants is potentially very useful, since the full tensor has only been measured experimentally for a very small percentage of all known solids. This is primarily because the practical determination typically requires single crystals with a size of a few micrometers at least.

The elastic constant tensor C , is calculated analytically using standard procedures, which require the prior calculation of the second derivatives of the total lattice energy with respect to the six bulk strain components and with respect to atomic coordinates.

The elastic constants were calculated using GULP program.

3. Results and Discussion

In **Table 2**, energetic simulation of structural properties of kaolinite is presented.

The value of kaolinite total lattice energy obtained is equal to -827.41650215 eV, primitive cell volume is 321.304389\AA^3 . This result is near to energy values found in previous works [20]. The lowest total energy structure obtained from these calculations was that which started from the experimental structures reported by Neder *et al.* [20] and by Bish [2], *i.e.*, both initial structures yield essentially identical final structures with the same total energy, the same internal bond lengths, and unit cell volumes that differ by only 0.025% (**Table 2**), this difference is due to hydroxyl (OH) orientation in interlayer region of kaolinite structure.

Lattice parameters a and b from Sato *et al.* (2005) [21] are shorter and agree better with experiment than those of the present work, while the opposite is true for the c parameter. This means that our calculations predict a smaller sheet separation, but larger lattice parameters in the planes.

Elastic constant was calculated using structural parameter listed in **Table 2**, the results are summarized on **Table 3**, and are compared to many works.

The qualitative study of the table shows:

- C11~ C22 >> C33.
- C12 differs significantly from bibliographic value.
- C23 ~ C13
- C15 and C46 is different to zero.

These values of elastic constant reflect the hexagonally symmetric structure.

Differences in other elastic constants are either related to this or the difference of the density value, concentration and arrangement of defects ([14] and [22]).

Table 2. Structural properties derived from simulations of kaolinite.

Cell structure	Kaolinite			
	Calculated (this work)	Observed (Bish) [2]	Observed (Neder) [21]	Observed (Sato) [22]
a axis (\AA)	5.149	5.153	5.154	5.144
b axis (\AA)	8.934	8.941	8.942	8.924
c axis (\AA)	7.384	7.390	7.401	7.587
α angle (deg)	91.93	91.92	91.69	91.08
β angle (deg)	105.0420	105.046	104.61	104.60
γ angle (deg)	89.9710	89.79	89.82	89.86
ρ (g/cm^3)	2.668652	-	2.599	2.544

Table 3. Calculated elastic constant.

Elastic constant	Sato [22]	Militizer [14]	This work
C11	178.5 ± 8.8	169.1	209.0343
C22	200.9 ± 12.8	179.7	209.6761
C33	32.1 ± 2.0	81.1	68.4720
C44	11.2 ± 5.6	17.0	12.4953
C55	22.2 ± 1.4	26.6	6.7199
C66	60.1 ± 3.2	57.6	50.1239
C12	71.5 ± 7.1	66.1	126.0545
C13	2.0 ± 5.3	15.4	16.8481
C14	-0.4 ± 2.1	-0.4	2.9326
C15	-41.7 ± 1.4	-34.0	-0.9305
C16	-2.3 ± 1.7	-7.8	-3.6306
C23	-2.9 ± 5.7	10.2	19.1547
C24	-2.8 ± 2.7	-3.4	1.6428
C25	-19.8 ± 0.6	-16.1	0.0802
C26	1.9 ± 1.5	-0.1	9.0795
C34	-0.2 ± 1.4	-2.9	-2.3010
C35	1.7 ± 1.8	6.7	-2.9557
C36	3.4 ± 2.2	-0.1	-0.7526
C45	-1.2 ± 1.2	-0.7	-0.0226
C46	-12.9 ± 2.4	-12.4	2.2793
C56	0.8 ± 0.7	1.1	3.6822

The calculated elastic constant tensors indicate that the a direction is slightly more flexible than the b direction. The calculated elastic constant tensor along c is much

lower than the constants calculated along a and b consistent with the crystal structure of kaolinite [22].

4. Conclusions

In summary, these calculations have shown that the computational techniques are a useful tool for investigating clay structures and mechanical properties. Predicting the mechanical properties of minerals that are difficult to obtain experimentally because of their small particle size (typically <2 micrometers).

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6. References

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