Molecular Dynamics Simulation of the Mechanical Behavior of Mixed-Layer Clay upon Hydration

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Abstract. A proper understanding of the mechanical behavior of clay minerals is of crucial importance in earth sciences, soil mechanics, and geotechnical engineering. Although more than seventy percent of all clays are of mixed layer types, the vast majority of the previous studies are devoted to pure clays, which make the hydraulic and mechanical properties of the widespread mixed-layer clay (MLC) and its role in soils are little understood, especially the most common illite-montmorillonite (I-M) mixed-layer clay (MLC). This research reports on a molecular dynamics (MD) study of the differences in mechanical behavior between I-M MLC containing mixed K⁺ and Na⁺ and Na⁺-montmorillonite (Na-MMT). The variations of key components in stiffness matrix with hydration have been analyzed. It is found that the stiffness tensor of two types of clay could be split into two groups: the in-plane coefficients (C11, C12, C22, and C66) and the out-of-plane coefficients (C13, C23, C33, C44, and C55). Due to the different forms of the support force of the clay layered structure in the two directions, they exhibit significantly different hydration mechanisms. Moreover, the I-M MLC is more difficult to hydrate and swell due to the asymmetric I-M interlayer and the existence of K⁺, and its ability to resist deformation is stronger than Na-MMT. This work offers insight into the molecular mechanism for initial swelling and mechanical behavior in widespread MLC. This will help to decipher its specific role in soils and controlling clay swelling.

1. Introduction

A proper understanding of the mechanical behavior of clay minerals is of crucial importance in earth sciences, soil mechanics, and geotechnical engineering, etc[1]. It is required not only for rock physics modeling, but also for geomechanics applications such as excavation stability analysis, hydraulic fracture design, and geophysical monitoring, etc. These layered clay minerals are rich in nature and are the main components of clay stone and many soils. Even a tiny amount in the soil could cause significant swelling. The main reason is that these expansive clays have the ability to adsorb water and expand upon hydration. This process significantly impacts the structural and mechanical properties of the clay. Many studies have been attempted to understand the swelling process and identify the evolution of hydraulic and mechanical properties.

However, most of the past studies, whether experiment or computation, have focused on pure clays of one type or another. In reality, there is a wide variety of mixed-layer (ML) clays that contain an intermixed stacking sequence of two or more types of different layers within a single crystal[2]. For instance, a study indicated that more than 70% of sedimentary rocks in America include some form of mixed-layer clays (MLCs). Hence, they are more likely to be found than pure clays in geological formations, and the most interesting and abundant mixed layer type is illite-montmorillonite (I-M) clay.
[3]. They may exist in soils more widely, but the relevant studies are very limited. Actually, MLCs have different layer types, layer charge positions, and cation types, so the mechanical properties of the clay and their interactions with water are also distinct.

Traditional researches on clay mechanical behavior mainly include theoretical and experimental methods. Although they can obtain some macroscopic mechanical properties, the available data are also very limited. It is very challenging to measure the essential mechanical properties of clays because of their small grain size, high affinity for water, and layer geometry. In addition, although these properties are very sensitive to water content at the scale of the clay layer, in these measurements, the water content is not controlled. Whereas regarding the assemblage of anisotropic clay minerals and the mixed layer clays, we know very little. This is mainly because it is difficult to prepare the samples of these types of clays, which have the complications such as stacking disorder, poor crystallinity, and mixed charges. However, MD method offers the possibility of solving these problems.

MD simulation based upon classical statistical mechanics is the computational technique used to understand the molecular-scale behavior. Its application in some micro-scale geotechnical problems has become a hotspot[4]. As the main component of soils, the clay minerals have been widely studied, including the micro-mechanisms of surface wettability, matter adsorption, clay swelling and shrinking, and, most importantly, mechanical properties. However, in spite of the numerous studies on clays, few of them were focused on the hydration mechanical properties, especially the widespread MLCs.

In this work, the molecular modeling of I-M MLCs during swelling processes has been carried out to understand the hydration mechanical behavior and the same phenomenon in Na-MMT was reported to grasp their differences. The incremental insertion of water molecules into the clay interlayer has been conducted by writing the script, which simulates the initial phase of water sorption to the greatest extent. Sufficient MD simulations have been run to obtain the hydrated clay model after swelling. Next, a script based on static method has been used to compute the key coefficients of stiffness tensor for each swollen model. The evolutions of key elastic constants have been analyzed, and their different compression and shear mechanisms have been identified. And the mechanical behavior of the two types of clays has been compared and explained from the MD perspective.

2. Theoretical Calculations

One major factor for the abundance of MLCs is that, under a solid-state conversion, pure clay is transformed into MLC under the influence of earth temperature and pressure. Fig. 1 shows the most typical MLC model with 50% Na+ and 50% K+ in the form of I-M-M-I, where the bottom and top layers are illite, and MMT builds the two central ones. The details have been shown in the figure.

Among them, the structure units of illite and MMT are both obtained from the latest American Mineralogist Crystal Structure Database, of which the type of illite is RM30, and the MMT type is Arizona-MMT. They are organized as 4 × 2 unit cells and the three dimensions of the entire MLC model are 20.85 Å × 18.01 Å × 39 Å. All the initial structures are established on Materials Studio 8.0 software, for the subsequent adsorption of H2O molecules, which are flexible simple point charge (SPC) water models. The recently developed CLAYFF[5] force field is employed to describe the interatomic interactions, and charges are assigned to each atom.

In the simulation process, the constructed clay structures were first geometrically optimized to obtain a low-energy configuration. Next, the script was executed to realize the incremental insertion of H2O molecules into the clay interlayer, followed by an equilibrium step before the subsequent insertion. In the equilibrium process, the MD simulation in the NPT ensemble (constant number of particles, pressure, and temperature) was conducted to perform a full swelling using the LAMMPS package. Because the swelling entered a stable state after a certain time, and the MD simulations of 1 ns and 5 ns were proved to yield very similar results; hence, the time of MD equilibrium and MD production were both 1 ns, and the time step was 1fs (1 ns = 10^9 ps = 10^6 fs). After the swelling simulation, a script based on static method has been used to compute the key coefficients of stiffness tensor for each swollen clay model, which is achieved by minimizing the energy of the system and allowing the atomic coordinates and cell parameters to relax.
Figure 1. Snapshot of the molecular model of the hydrated mixed layer clay with 50% Na\(^+\) and 50% K\(^-\).

3. Results and discussions

3.1. In-plane elastic constant

The evolution of hydration mechanics of different types of clay can be further obtained by analyzing the key components in the stiffness matrix. In this work, we reported all relevant stiffness tensor values for the two types of clays we studied. The results indicated that these stiffness tensor coefficients could be split into two groups: the in-plane coefficients (C11, C12, C22, and C66) and the out-of-plane coefficients (C13, C23, C33, C44, and C55). Due to the different forms of the support force of the structure in the two directions, they exhibited significantly different hydration mechanisms.

Figure 2 shows the in-plane elastic constants of two types of clay as a function of water content, obtained through the MD calculations, including C11, C12, C22, and C66. It can be found that these in-plane elastic constants have the same trend as a whole: They obviously decrease more or less stepwise with increasing hydration. Among them, the in-plane elastic constant C22 is the largest under the same water content, followed by C11, C12, and finally C66. Compared with other in-plane elastic constants, C11 and C22 have a larger range of variation, which is closely related to the Young's modulus in the X and Y directions. What is interesting is that they both have three approximately flattened segments when the water content is about 40, 120, and 240, which correspond to the one-layer, two-layer, and three-layer hydration state (the 1W, 2W, and 3W states).

However, it can be found that the in-plane elastic constants of MLC are higher than that of MMT under the same water content. And when about two hydration layers were formed, the in-plane elastic constants of MMT began to decrease significantly at the water content of 120, while MLC was postponed to a higher water content of about 150. In addition, the mechanical properties of MLC at this time also declined more slowly than that of MMT. This was because MLC had stronger...
Figure 2. Evolution of in-plane elastic constants with increasing water content for two types of clay; (a) I-M MLC with 50% Na⁺ and 50% K⁺; (b) MMT-MMT with Na⁺ only. The results for C11 are represented by blue, C12 by gray, C22 by red, and C66 by yellow; negative values of interaction energies indicate attractive interactions.

intermolecular interactions, so it was more difficult to swell into the next hydration stage. The trend of in-plane elastic constants for pure MMT was consistent with the study by Ebrahimi et al. [6], which further increased the credibility of these simulated data.

By observing the structure of the hydrated clay and its interlayer, it can be concluded that the difference of the C11, C22, and C12 elastic constants derived from the ion-covalent bonding strength within clay layers, the isomorphic substitution positions, and the change in geometric conformation for clay-water system. It is obvious that the geometric effects of swelling of the interlayer space caused the reduction of the elastic constants. Moreover, these in-plane coefficients did not exhibit strong hydration characteristics and fluctuating changes like the out-of-plane coefficients described later. This was due to the forces needed to apply a given strain in a direction parallel to the clay sheet were mostly supported by the clay crystalline structure and not by the interlayer water. The shear stiffness tensor C66 was mainly controlled by the relative torsional of the bonding atoms. The primary reason for its decrease was that the contribution of interlayer water in the weak shear part increased.

It can also be found that during the hydration process, water molecules were preferentially adsorbed on the clay surface. But with the increase of water content, more outer-sphere surface complexes (OSSCs) were formed around the interlayer Na⁺ to promote swelling. Meanwhile, the geometric effects of the interlayer spacing change were also more obvious, and the elastic constants were greatly reduced. Compared with MMT, MLC containing asymmetric I-M interlayer and K⁺ formed fewer OSSCs. Therefore, its interlayer space was more difficult to swell and its ability to resist deformation was stronger. In addition, the crystalline structure of illite was inherently stiffer than MMT. These factors caused the elastic stiffness of MLC to always be greater than Na-MMT.

3.2. Out-of-plane elastic constant
Figure 3 shows the variations in out-of-plane elastic constants of two types of clay during hydration, including C33, C13, C23, C44, and C55. It can be found the varying trend of these five stiffness parameters fluctuate stepwise determined by the hydrated state. They rapidly decrease in the initial hydration stage and reach a local minimum at the water content of 40. Then they gradually increase and reach a local maximum when about two hydration layers are formed (at the water content of 120). As hydration continues, these out-of-plane stiffnesses begin to decline rapidly again, but their descending rate slows down when the water content is 240. On the whole, they stabilize after reaching the 3W state and are significantly lower than that of dry state. Among them, the out-of-plane elastic constant C33 is the largest under the same water content and C44 is the smallest. The variation curves of C13, C23, and C55 are relatively close, and their values are between C33 and C44. They also step into a relatively flat evolution period when different numbers of hydration layers are formed. It can be
Figure 3. Evolution of out-of-plane elastic constants with increasing water content for two types of clay; (a) I-M MLC with 50% Na⁺ and 50% K⁺; (b) MMT with Na⁺ only. The results for C33 are represented by red, C13 by gray, C23 by blue, C44 by yellow, and C55 by green.

found that these elastic constants are sensitive to water content because water impacts strongly the interaction between the clay layers (i.e., from partially saturated states to fully saturated clay).

By observing the structure of hydrated clay and its interlayer, it can be found that at the beginning of hydration, the interlayer was propped up by water molecules, resulting in the decrease in out-of-plane elastic constants. In the subsequent filling stage, the interlayer spacing was not significantly changed and the water molecules were adsorbed on the clay surface to form the strongly bound-water ordered structure with strong attraction and hydrogen-bond interactions. Therefore, the mechanical stiffness of clay was enhanced at this stage. But when the two hydration layers were formed, the clay began to be excessively stretched and the bound-water film became thicker. The attraction and hydrogen bonding interactions of some water molecules on clay surface were weakened, and its existence as weakly bound-water caused a rapid decline in mechanical properties. Finally, as hydration approached osmotic swelling, hydrogen bonds were continuously formed only between water molecules, and the interlayer atomic pores and these elastic constants were also close to stability.

Among these out-of-plane coefficients of the stiffness tensor, C33 was the most concerned, that was, the ability to resist deformation in the direction perpendicular to the mineral surface. It can be found that the normal stiffness C33 oscillated with interlayer hydration linked to the formation of different numbers of hydration layers. In addition, the in-plane elastic constants C11 and C22 were approximately 3 times that of C33, which indicated that the tensile and compressive strength in the direction perpendicular to the mineral plane was significantly lower than the strength within the clay layers. This anisotropy is due to the difference between ionic-covalent bonding inside the crystal structure and screened electrostatic bondings between clay layers.

As for the clay shear, the shear resistance of water in the clay confinement layer was the most concerned, that was, the shear stiffness components C44 and C55 along the mineral plane. They oscillated with hydration like the stiffness tensor C33. This showed that the shear strength of the interlayer water was closely related to the formation of hydrogen bonds and the size of atomic pores in clay interlayer. It can be found that the interlayer ions and water molecules were free to move in the interlayer and the clay layers could move with respect to each other. The elastic constants were very sensitive to water content because there is no covalent bonding in this direction. However, these water molecules did not exhibit the shear-free strength characteristics of free water but increased with hydration at a certain stage. For example, when the interlayer reached a stable 2W hydration state, the shear strength was increased to a local maximum. In this region, the clay surface created strong Coulombic bonding with the adsorbed water, which may create an ordered structure with nonzero shear modulus. This is consistent with the study by Sayers et al. On the whole, the shear resistance between dry clays was much greater than that of the 3W hydration state. Thus, the addition of water had a lubricating effect on shear friction between layers, resulting in a sharp decrease of C44 and C55.
It can be concluded that the different hydration mechanisms between the in-plane and the out-of-plane elastic constants are due to the clay layered structure. The mechanical behaviors in the plane of the layer and in the orthogonal direction are governed by different interactions. And mechanisms in the direction of compression and shear are controlled by the formation of hydrogen bonds and the size of atomic pores in clay interlayer. These elastic coefficients of the stiffness tensor can be directly related to the engineering elastic modulus, and related research will be reported in the future.

4. Conclusions
The MD study of clay with increasing hydration was carried out to compare I-M MLC’s mechanical behavior containing K⁺ and Na⁺ with Na-MMT. The variations of key components in the stiffness matrix of two types of clays have been analyzed, and their different compression and shear mechanisms have been identified at the molecular level. It is found that the stiffness tensor of two types of clay could be split into two groups: the in-plane coefficients (C11, C12, C22, and C66) and the out-of-plane coefficients (C13, C23, C33, C44, and C55). Because of the different forms of support force of the clay layered structure in the two directions, they exhibit different hydration mechanisms.

Among them, the in-plane elastic constants are not very sensitive to the hydration state. Their decrease with hydration can be explained by the geometric effect of interlayer swelling. In contrast, the out-of-plane elastic constants are very sensitive to the water content and oscillate significantly with interlayer hydration linked to the formation of different numbers of hydration layers. Due to the asymmetric I-M interlayer and the existence of K⁺, the mechanical behavior of MLC is different from that of pure MMT. It is found that the I-M MLC is more difficult to hydrate and swell, and its ability to resist deformation and elastic constants are significantly stronger than Na-MMT. In addition, the most concerned coefficients of the stiffness tensor C33, C44, and C55 in geotechnical engineering have been discussed. The mechanical behavior and micro-mechanism of the two types of clays have been compared and explained from the MD perspective.

This study provides the perception of the molecular mechanism for initial swelling and mechanical behavior in the widespread MLCs. From this study, it will help in disclosing underlying changes in stiffness tensor for MLC and identifying its specific role in practical engineering.

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