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Nano-Scale Elastic Properties Due to Montmorillonite Water Adsorption

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Abstract

Smectites are an important group of clay minerals that experiences swelling upon water adsorption. This paper uses molecular dynamics with the CLAYFF force field to simulate isothermal isobaric water adsorption of interlayer Wyoming Na-montmorillonite, a member of the smectite group. Nano-scale elastic properties of the clay-interlayer water system are calculated from the potential energy of the model system. The transverse isotropic symmetry of the elastic constant matrix was assessed by calculating Euclidean and Riemannian distance metrics. Simulated elastic constants of the clay mineral are compared with available results from acoustic and nanoindentation measurements.

Keywords: molecular simulation, clay mineral adsorption, clay swelling, mechanical properties

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1 Introduction

The engineering properties of soils are highly affected by their clay content\(^1,2\). Similarly, the hydration state of the clay mineral plays an important role in physical properties such as the mechanics and transport of ionic substances. This work is motivated by the lack of a universal constitutive model to explain the effect of water adsorption on clay behavior (i.e., from partially saturated clay to fully saturated states). The fundamental understanding of the clay hydration process impacts several application fields from engineering estimates of ground movements caused by seasonal changes in moisture content to swelling pressures exerted by compacted bentonite on nuclear waste canisters.\(^3\) Knowledge of elastic properties is critical in back-analyzing geophysical seismic exploration data and interpreting acoustic scattering measurements.\(^4\) Fundamental mechanical properties of clays are also required to model hydraulic fracturing of oil and gas shale source rocks.\(^5\) Clays are being used to improve mechanical and thermal properties of polymers, via polymer clay nanocomposites (PCNs).\(^6\) These applications also require knowledge of fundamental properties of clay to design properties of the PCN composite materials.

Clay minerals have a layered structure at the nano-scale. Each layer consists of some combinations of two sheet types with silicon tetrahedra and aluminum octahedra as basic units. This work considers montmorillonite, a member of the smectite group that comprises two tetrahedral silicate sheets each with unshared oxygen, O, atoms around a central octahedral hydroxide sheet which has two planes of unshared O atoms and additional hydroxyl groups, OH, to form the base lamellae. Due to isomorphous substitutions of metal ions within the clay sheets, each lamellae has a net negative charge which is compensated by positive exchangeable interlayer cations. Adsorption of water molecules by this system is accompanied by a large increase in the basal layer spacing. This swelling process significantly impacts the structural and mechanical properties of the clay.

It is very challenging to measure the fundamental mechanical properties of clay due to their high affinity for water and their platy geometry.\(^7\) Plan dimensions of each lamellae are typ-
ically one hundred times larger than the 2:1 layer thickness. All of the reported direct 
measurements are for clay minerals that are dry or have a very small amount of water (often 
ill-defined). Most of the available experimental results report only isotropic elastic moduli of 
clay minerals\(^8\text{--}^{12}\). However, clay minerals have inherent anisotropy due to their layered struc-
ture as shown experimentally in the case of muscovite mica, phlogopite and biotite\(^{13}\text{--}^{15}\). For 
example, Vanorio et al.\(^7\) reported isotropic elastic moduli of montmorillonite samples from 
extrapolation of acoustic measurements on cold-pressed samples at different porosities but 
with no control of water content. Similarly, Wang et al.\(^{16}\) presented a method to calculate 
elastic properties of clay from elastic wave velocity measurements on composite samples pre-
pared by mixing the clay with an epoxy resin of known elastic properties. Chen and Evans\(^{17}\) 
argued that this method does not necessarily measure the moduli of individual clay platelets.

To the best of our knowledge, successful direct anisotropic experimental measurements 
on montmorillonite mineral are currently not available in the literature, so theoretical and 
 computational methods can provide useful estimates of these properties. 
Molecular simulation is a computational technique that is used to model behavior of the 
matter at atomic scale. The existing literature on molecular simulation of clay water systems 
has focused on crystalline swelling behavior of the clay and on the interlayer distribution 
of water and ion molecules\(^{18}\text{--}^{27}\). There are very few reported elastic properties for clay 
minerals from numerical simulations. Most of the reported elastic moduli from computer 
simulations are for non-expanding minerals with small interlayer spacing. For example, Sato 
et al.\(^{28}\) reported the first principle calculation of the full elastic stiffness matrix of kaolinite, 
a non expanding clay with small adsorption of water. Recently, Militzer et al.\(^{29}\) reported the 
first principle ab initio calculations of full elastic stiffness constants for dry silicate minerals 
including muscovite, kaolinite, dickite, nacrite as well as a dry illite-smectite mineral. Suter 
et al.\(^{30}\) and Mazo et al.\(^{31}\) calculated in-plane elastic moduli of hydrated Wyoming Na-
montmorillonite clay.
This paper derives the full elastic tensor calculations for Wyoming Na-montmorillonite over a range of hydration conditions using Molecular Dynamics (MD) simulations.

2 Methodology

The crystallography for 2:1 clay mineral has been taken from Refson et al.\textsuperscript{32}. The specific structure of Wyoming Na-montmorillonite includes isomorphous substitutions in both tetrahedral and octahedral sheets with the following experimental formula: \(\text{Na}_{0.75}\text{nH}_{2}\text{O}[\text{Si}_{7.75}\text{Al}_{0.25}]\)[\(\text{Al}_{3.5}\text{Mg}_{0.5}\)]\text{O}_{20}(\text{OH})_{4}\text{. The isomorphous substitutions in Wyoming Na-montmorillonite corresponds to cation exchange capacity of 102 meq/100g. The simulation cell consists of sixteen unit cell (4×2×2 array of clay unit cell) with initial plan dimensions \((X - Y)\) of \(\sim 20.87\ \text{Å} \times \sim 18.15\ \text{Å}\). Sodium ions, Na, were randomly distributed in the interlayer space. Each simulation contains between 0 to 258 water molecules that corresponds to water contents in the range \(M_{\text{H}_{2}\text{O}}/M_{\text{clay}} = 0\) to 0.4 g/g.

The analyses are based on the CLAYFF\textsuperscript{33} force field that has been developed successfully for structural simulation of clay minerals\textsuperscript{30,34}. CLAYFF is a versatile force field built around the flexible version of the simple point charge (SPC) water model\textsuperscript{35}. All parameters and equations are given in the supporting information.

Two simulation packages were used in this work: GROMACS\textsuperscript{36} and GULP\textsuperscript{37}. GROMACS was used for molecular dynamics simulations while GULP was used to create the initial structure of the adsorbed water, to perform static energy minimization and to calculate the elastic stiffness matrix. The visualization of the molecular configurations was carried out using the molecular graphic software VMD\textsuperscript{38}. The initial state of the adsorbed water was generated through Grand Canonical Monte Carlo (GCMC - \(\mu\)-V-T) simulations at 300K. Three-dimensional, periodic boundary conditions were applied along with the min-
imum image convention (a cutoff radius of 8.5 Å was used for short range interactions). The long range electrostatic coulombic interactions were calculated using Particle Mesh Ewald summation\(^{39,40}\).

Isomorphous substitution was carried out randomly by replacing one Si\(^{4+}\) with Al\(^{3+}\) in each tetrahedral sheet, and four Al\(^{3+}\) with Mg\(^{2+}\) in each octahedral sheet. The resulting negative charge was compensated with sodium ions between the clay layers. This type of substitution strategy was also used by Abdolhosseini Qomi et al.\(^ {41}\) to study the effect of elemental substitution on elastic properties of calcium-silicate-hydrate (CSH)—another mineral with layered structure. We carried out two different random isomorphous substitutions in the octahedral layer and created two distinct atomic structures for the computer simulations. Figure 1 shows the radial distribution functions of Mg-Mg defects of the two structures. In simulation(1), the two defects have a separation greater than 7.9 Å, while in simulation(2) they are separated by more than 5.2 Å. Figure 2 shows the typical structure of the simulated clay-water system. Clay swelling was simulated at an isothermal temperature, T=300 K, and isobaric pressure, P=0 GPa, using NPT ensemble over a time period, \(\Delta t=900\) ps (pico second). The Nosé–Hoover thermostat\(^ {42,43}\) is used to control temperature together with the Parrinello–Rahman\(^ {44}\) barostat to control pressure in the system. All properties are calculated from the last 500 ps of the simulations when the system has reached its equilibrium state. An integration time step of 1 fs (femto second) was used in all simulations.

2.1 Calculation of Elastic Properties

The single crystalline elastic stiffness properties were calculated using energy minimization of the structure obtained from MD simulation in GULP program. We use the Voigt notation in representing components of the fourth order elasticity tensor \(C_{ijkl}\) that changes the indices in the following way: \(11\rightarrow 1, 22\rightarrow 2, 33\rightarrow 3, 23\rightarrow 4, 13\rightarrow 5\) and \(12\rightarrow 6\). In this notation, fourth order elasticity tensor can be represented by a symmetrical matrix with components \(C_{ij}\). We
Figure 1: Mg-Mg radial distribution functions of two atomic structures used in simulations.

Figure 2: Typical unit cell in periodic crystal of the simulated clay mineral at $d=12\text{Å}$. 
will use cartesian coordinate system with direction 3 as the one normal to the clay layers (Z) and directions 1 and 2 in the plane of the clay layer (XY) (see Figure 2). The stiffness matrix $C$ is defined as the second derivative of the potential energy with respect to strain:

$$C_{ij} = \frac{1}{\Omega} \frac{\partial^2 U}{\partial \epsilon_i \partial \epsilon_j} \quad i, j = 1, 2, \ldots, 6$$

(1)

where $\Omega$ is the volume of the unit cell, $\epsilon_1$, $\epsilon_2$ and $\epsilon_3$ are the longitudinal strains in the $X$, $Y$ and $Z$ directions and $\epsilon_4$, $\epsilon_5$ and $\epsilon_6$ are the shear strains in the $YZ$, $XZ$ and $XY$ planes, respectively. Energy minimization was accomplished using the BFGS steepest descent algorithm. It should be noted that the minimizer switched to a Rational Function Optimization (RFO) algorithm when the gradient norm fell below $5 \times 10^{-3} \text{eV/Å}$. The RFO approach guarantees to find configurations with positive definite stiffness matrix which corresponds to a stable minimum. A similar procedure has been used to find equilibrium structure at the extrema of the energy surface with positive curvature for other layered minerals.

3 Results and Discussion

3.1 Hydration Mechanism

Cygan et al.\textsuperscript{33} have shown very good agreement between numerical simulation and experimental measurements of swelling reported by Fu et al.\textsuperscript{50} (i.e. basal layer spacing versus water content) for Wyoming Na-montmorillonite as part of the original validation of the CLAYFF\textsuperscript{33} force field. We have performed a similar validation as part of the study (see supporting information). The mechanism of swelling can be explained by considering the average number of hydrogen bonds per water molecule and the density of the interlayer water as a function of the basal layer spacing, $d$, as shown in Figure 3. We have used the common geometric definition of hydrogen bond\textsuperscript{51} in calculating the number of hydrogen bonds that each water molecule creates with surrounding water molecules. A hydrogen bond is assigned
Figure 3: Change in average number of hydrogen bonds per water molecule and density of interlayer water during swelling of Wyoming Na-montmorillonite.

Figure 4: Change in derivative of the density with respect to basal layer spacing during swelling of Wyoming Na-montmorillonite.
when the O-O distance is less than 3.5 Å and simultaneously the H-O-O angle is less than 30°. The average number of hydrogen bonds per water molecule at 300K in bulk water is 3.6 which corresponds to the density of 1 gr cm⁻³. Three regions are identified in Figure 3: In region A, the density of the interlayer water (ρ_w) and number of hydrogen bonds (N_{HB}) increase rapidly to a threshold condition at d≈12.8 Å corresponding to the formation of mono-layer water-clay system. In transition from region A to B, the density of water and number of hydrogen bonds remains constant which indicates that the rate of water adsorption and increase in basal layer spacing are (almost) the same until the system reaches region B. Region B, d≈14.3-15.6 Å, corresponds to the formation of the second water layer. The transition from B to C is identified by the change in slope of both ρ_w and N_{HB}. Figure 4 shows the derivative of water density with respect to the basal layer spacing with maxima at d≈ 12Å and 15Å. We will show that these also correspond to maxima in some of the elastic stiffness constants. The formation of the third water layer (region C) is less visible. Figure 5 shows the density profile of water oxygen(O_w) and water hydrogen(H_w) and sodium(Na) in the direction normal to the clay layers.
5 shows the density profile for interlayer species in the direction normal to the clay layers for three different basal layer spacings (d≈12, 15 and 17.8 Å). These results show clearly the formation of the first, second and third layer of water molecules between clay sheets from the number of peaks in the water oxygen, Ow, distribution. For the two layer system (d≈15Å), the water molecules are distributed evenly between layers while for the three layer system there are more water molecules close to the clay surfaces than in the middle layer. Following Sposito et al. the adsorption of interlayer cations in smectite can be classified as 'inner-sphere' or 'outer-sphere' complexes. Inner-sphere surface adsorption describes the condition where there is no water molecule between the cation and the clay surface, while an outer-sphere surface adsorption has at least one water molecule between the cation and the clay sheet. Formation of these surface complexes depends on both the charge and size of the cations and the location of the charged sites due to substitutions in clay layers. For Wyoming Na-montmorillonite which has isomorphous substitutions in both tetrahedral and octahedral layers and (Na) cations as charge compensating ions, we expect to find formation of both inner and outer sphere complexes. Our simulation results show that upon increasing water content, Na ions become more hydrated and detached from the clay surface. Figure 5, confirms the formation of inner-sphere complexes by having peaks in (Na) cation distributions closer than peaks in (Ow) for all basal layer spacings. For d≈15Å through 17.8Å, there is a high concentration of Na-ions in the middle water layer. This shows an increase in outer-sphere complexes in agreement with Chávez-Páez et al. It should be noted that in our simulations, tetrahedral charge sites represent only 33 percent of the total clay layer charge. This explains the decrease of the number of inner-sphere complexes, as hydration proceeds. One can expect a different situation with a larger number of inner-complexes for a pure tetrahedrally substituted clay (the layer charge being then localized very close to the clay layer surface). The type of substitution (tetrahedral/octahedral layer) and the amount of substitutions define the resulting ion distribution that in turn affects the mechanical properties of the material in terms of the layer-to-layer cohesive pressure as
shown with primitive model simulations\textsuperscript{56}.

3.2 Elasticity

For each hydration state, the full elastic stiffness tensor \((C_{ij})\ i, j = 1, 2, \ldots, 6\) has been calculated. It is usually desirable to approximate the full tensor (with 21 independent parameters) using assumptions of material symmetry. For a stack of clay lamellae, we expect good approximations with an equivalent transversely isotropic tensor composed of five independent engineering elastic constants: \(E_p, E_z, G_{pz}, \nu_p\) and \(\nu_{zp}\). \(E_p\) and \(E_z\) are the Young’s moduli in the plane of the basal layer and in the direction normal to it; \(G_{pz}\) is the shear modulus in planes normal to the isotropic plane; \(\nu_p\) and \(\nu_{zp}\) are the Poisson’s ratios characterizing the lateral strain response in the plane of transverse isotropy to a stress acting parallel and normal to the isotropic plane. Values of the elastic constants of the transversely isotropic plane are calculated by averaging over \(x\) and \(y\) directions and over the two sets of simulations (denoted as \([C_{ij}]\)).

In the following discussion, we will show the variation of elastic stiffness constants \(C_{11}\) (and \(C_{22}\)), \(C_{33}\), \(C_{44}\) (and \(C_{55}\)), \(C_{12}\), \(C_{13}\) (and \(C_{23}\)) as a function of the degree of hydration for two structures with different locations of isomorphous substitutions. These constants can be directly related to the above listed set of engineering elastic constants. The mean and standard deviation between two simulation results will be reported.

Figure 6 shows the variations of \(C_{33}\) upon hydration. There is a sudden decrease in the mean value from \(\overline{C}_{33} = 48.5\pm3.8\ \text{GPa}\) to \(16.8\pm1.2\ \text{GPa}\) from the dry state to the mono layer hydration. The modulus increases upon further water adsorption to a local maximum, \(\overline{C}_{33} = 30.0\pm0.5\ \text{GPa}\) at \(d\approx12\AA\) (middle of region A). As the basal layer expands to accommodate more water molecules, there is a decrease in \(\overline{C}_{33}\) (to \(20.7\pm2.3\ \text{GPa}\) at \(d\approx14\AA\)), until region B. Formation of the second layer of water is associated with another local maximum, \(\overline{C}_{33} = 26.2\pm3.0\ \text{GPa}\) at \(d\approx15\AA\) (middle of region B). Further increase in basal layer spacing has
Figure 6: The $C_{33}$ elastic constant as a function of basal layer spacing. Filled symbols represent data points from simulation (1) and hollow symbols represent data points from simulation (2). Triangular symbols represent equivalent transversely isotropic stiffness constants.
only a small impact on the modulus with $C_{33} = 21.6 \pm 1.08$ GPa for $d \geq 15.6 \text{Å}$.

Ortega et al.\textsuperscript{57} reported values of the elastic stiffness constants of the clay phase of the shale samples by back analyzing Ultrasonic Pulse Velocity (UPV) measurements. The tested samples include higher amounts of illite, smectite and kaolinite and less amounts of other clay minerals like chlorite, glauconite, biotite. They have not reported relative humidity or basal layer spacing for the represented clay packs. The UPV measurements provide elastic properties for macroscopic porous clay-silt inclusion composite (at the μm length scale), referred to as the level II structure, scaling relations are then introduced to estimate the fundamental properties for the individual clay layers (level 0 solid clay denoted by $C_{ij}^s$). Ortega et al.\textsuperscript{57} reported $C_{33} = 11.5-30.4$ GPa (level II) for a wide range of shale mineralogies and estimated $C_{33}^s = 24.2$ GPa. This result is in good agreement with our molecular dynamics simulation for $d \geq 10 \text{ Å}$, but generally underestimates the numerical data for dry clay ($d \leq 9.5 \text{ Å}$).

Figure 7 shows the variations of the computed stiffness components $C_{44}$ and $C_{55}$ upon hydration. These components relate to the shear modulus normal to the basal plane. Shear stiffness decreases rapidly with basal layer spacing from the dry state (with maximum $C_{44} = 7.2 \pm 1.9$ GPa). Water acts as a lubricant to decrease the shear resistance as the system deviates from the dry state. During formation of the first layer of water in region A, there is a slight increase in shear stiffness with maximum $C_{44} = 5.4 \pm 0.1$ GPa. In this region, the clay surface creates strong Coulombic bonding with the adsorbed water, confirming Sayers\textsuperscript{58} argument that water bounded to the clay surface may create an ordered structure with non-zero shear modulus. Between region A and region B, the shear stiffness remains approximately constant. During the formation of the second layer of water shear stiffness decreases slightly and reduces to a constant value $C_{44} = 4.1 \pm 0.3$ GPa for $d \geq 15.6 \text{Å}$. Ortega et al.\textsuperscript{57} reported UPV (level II) measurements for clay shales of $C_{44} = 2.9-8.9$ GPa and interpreted the stiffness for the clay lamellae (level 0), $C_{44}^s = 3.7$ GPa. These values are generally in good
agreement with the current numerical calculations for Wyoming Na-montmorillonite.

Figure 8 shows change in the $C_{13}$ and $C_{23}$ elastic components during hydration. The trend of the $C_{13}$ is similar to $C_{44}$, decreases from a dry state maximum, $C_{13} = 18.0 \pm 1.6 \text{GPa}$ to $4.9 \pm 0.6 \text{GPa}$, at region A, rising to a local maximum $9.7 \pm 0.01 \text{GPa}$ with a constant value $7.7 \pm 0.6 \text{GPa}$ for $d \geq 14.3 \text{Å}$. Ortega et al.\textsuperscript{57} reported a wide range of $C_{13}$ (6.1-24.3 GPa) from UPV tests and interpreted $C_{13}^{s} = 18.1 \text{GPa}$ for the clay lamellae. The $C_{13}$ and $C_{23}$ are related to the lateral Poisson’s ratio connecting deformation between the vertical and horizontal axes. Although the fundamental stiffness component for the solid clay lamellae is consistent with the numerical simulations at small basal layer spacing, the UPV data are generally higher than the computed range for $C_{13}$. This discrepancy may relate to effects of the finite aggregate size on UPV measurements, while the results of the molecular dynamics simulation corresponds to lamellae of infinite length.

The stiffness components $C_{11}$, $C_{22}$ and $C_{12}$ are mainly affected by the strong iono-covalent

Figure 7: The $C_{44}$ and $C_{55}$ elastic constants as a function of basal layer spacing. Legend as in Figure 6.
Figure 8: The $C_{13}$ and $C_{23}$ elastic constants as a function of basal layer spacing. Legend as in Figure 6.

Figure 9: The $C_{11}$ and $C_{22}$ elastic constants as a function of basal layer spacing. Legend as in Figure 6.
bonding inside the clay layers. Figures 9 and 10 show the variations in $C_{11}$, $C_{22}$ and $C_{12}$ elastic constants during hydration. The $C_{11}$ and $C_{22}$ elastic constants represent Young’s moduli in the plane of transverse isotropy. Both $\overline{C}_{11}$ and $\overline{C}_{12}$ continuously decrease by increasing basal layer spacing from $290.5 \pm 3.7\text{GPa}$ at $d \approx 9.3\text{Å}$ to $154.5 \pm 1.6\text{GPa}$ at $d \approx 19.5\text{Å}$. These values are 5 to 8 times larger than corresponding values in the direction normal to the clay layers. The large difference between $C_{11}$ or $C_{22}$ and $C_{33}$ values comes from the difference between iono-covalent bonding inside the clay crystal layer and screened electrostatic bondings between layers. The average values of Young’s moduli at $d \approx 12\text{Å}$ are $E_x = 180\text{GPa}$ and $E_y = 172\text{GPa}$ that are in very good agreement with values from MD simulations by Suter et al.\textsuperscript{30} ($E_x = 182\text{GPa}$ and $E_y = 172\text{GPa}$) and Mazo et al.\textsuperscript{31} ($E_x = 182\text{GPa}$ and $E_y = 180\text{GPa}$). The computed results are much higher than the UPV data\textsuperscript{57} ($C_{11} = 13.8\text{--}46.1\text{GPa}$) and the calculated value for the clay lamellae\textsuperscript{57} ($C_{11}^s = 44.9\text{GPa}$). This discrepancy is almost certainly related to finite length of the clay aggregates affecting experimental measurements at the UPV scale (sliding between layers etc.)

Figure 10 shows the variation of stiffness component $\overline{C}_{12}$ upon hydration. The elastic constant $\overline{C}_{12}$ continuously decreases by increasing basal layer spacing from $140.8 \pm 3\text{GPa}$ at $d \approx 9.3\text{Å}$ to $77.6 \pm 1.5\text{GPa}$ at $d \approx 19.5\text{Å}$. Ortega et al.\textsuperscript{57} reported UPV measurement of $C_{12} = 6.9\text{--}17.8\text{GPa}$ and calculated the stiffness for the clay lamellae $C_{12}^s = 21.7\text{GPa}$\textsuperscript{57} which is less than the values from MD simulation and can also be attributed to finite length effect in the clay aggregation.

Nano-indentation is one of the sub-micron experiments used to measure material stiffness parameters. To the best of our knowledge, there are no nanoindentation measurements on Wyoming Na-montmorillonite. However, Bobko and Ulm\textsuperscript{59} performed a series of nanoindentation tests on the same shale samples analyzed by Ortega et al.\textsuperscript{57}. By doing statistical analysis of the results, they extracted nanoindentation moduli for the clay phase. They
carried out indentation measurements normal and parallel to the bedding plane defining $M_z$ for indentation modulus normal to the bedding plane and $M_p$ for the one parallel to the bedding plane. They reported solid phase nanoindentation moduli extrapolated to zero meso-scale porosity, $M_z^s = 16\text{GPa}$ and $M_p^s = 25\text{GPa}$. Zhang et al.\textsuperscript{60} have also reported a series of nanoindentation results on muscovite and rectorite. The atomic structure of rectorite consists of alternating sequence of fixed and expandable clay layers. They reported a range for the nanoindentation modulus of rectorite $M_z = 19.5 \pm 4.9\text{GPa}$. It should be noted that relative humidity is not controlled or measured during these tests. Indentation moduli can be computed from transversely isotropic stiffness components using the derivation by Delafargue and Ulm\textsuperscript{61}:

$$M_z = 2\sqrt{\frac{C_{11}C_{33} - C_{13}^2}{C_{11}} \left(\frac{1}{C_{44}} + \frac{2}{\sqrt{C_{11}C_{33} + C_{13}}}\right)^{-1}} \quad (2)$$
\[ M_p \approx \sqrt[3]{\frac{C_{11}^2 C_{11}^2 - C_{12}^2}{C_{33} C_{11}}} M_z \] (3)

Figure 11: Indentation modulus in z direction as a function of basal layer spacing. Legend as in Figure 6.

Figures 11 and 12 show the computed nanoindentation moduli of Wyoming Na-montmorillonite from molecular dynamics simulations using an equivalent transversely isotropic elastic stiffness matrix as functions of the basal layer spacing. Figure 11 shows that the variation of \( M_z \) is similar to change in \( C_{33} \) stiffness component (Figure 6). After a sudden decrease from 31.2 ± 7.0 GPa to 13.3 ± 0.1 GPa for \( d \approx 9 \) Å to 11.5 Å, there are local maxima 22.8 ± 1.1 GPa at \( d \approx 12 \) Å and 20.8 ± 1.6 GPa, at \( d \approx 15 \) Å. For \( d \geq 15.6 \) Å, the \( M_z \) value is approximately constant (17 ± 0.3 GPa). Results of the simulations are in very good agreement with the nanoindentation experiments\(^{59,60} \) from region B onward to larger basal layer spacing.

Figure 12 shows the modulus parallel to the basal planes \( M_p \) decreases from 133.5 ± 6.2 GPa (\( d \approx 9.3 \) Å) to 96.5 ± 3.4 GPa (\( d \approx 11.5 \) Å). There is a small increase to 106.0 ± 0.2 GPa at region A which corresponds to the building up of the first water layer which has strong interac-
Figure 12: Indentation modulus in the plane of transverse isotropy as a function of basal layer spacing. Legend as in Figure 6.

Following the methodology of Shahsavari et al.\textsuperscript{62}, the Euclidean and Riemannian distance metrics are used to evaluate the accuracy of the equivalent transversely isotropic parameters ($C_{ij}$) in representing the full elastic stiffness matrix ($C_{ij}$) of the clay-water system. The Euclidean distance metric is one of the most commonly used distance metrics\textsuperscript{63} that relates two square matrices, $A_1$ and $A_2$, as follows:

\[
d_E(A_1, A_2) = \|A_1 - A_2\|_E
\]  

(4)
and the associated norm is defined by:

\[ \|A\|_E = \sqrt{\text{tr} (A^T A)} \]  \hspace{1cm} (5)

where \( \text{tr}(\cdot) \) stands for the trace and the superscript \( T \) denotes the transpose. The classical Euclidean distance metric is fast and easy to compute but lacks certain physically meaningful properties\(^{64}\) and can generate symmetric matrices with null or negative eigenvalues. These problems are avoided using the Riemannian metric. The Riemannian metric is independent of the coordinate system, preserves material symmetries and is invariant under inversion\(^{65}\).

Having two positive definite matrices, \( P_1 \) and \( P_2 \), the Riemannian metric is defined as follows:

\[ d_R(P_1, P_2) = \| \ln \left( P_2^{1/2} P_1^{-1} P_2^{1/2} \right) \|_R = \left[ \sum_{i=1}^{n} \ln^2 \lambda_i \right]^{1/2} \]  \hspace{1cm} (6)

where \( \lambda_i \) are the eigenvalues of \( P_1^{-1} P_2 \).

These metrics are means of measuring similarity between two matrices. For both metrics the smaller value means better approximation in representing full matrix with its equivalent transverse isotropic one.

Figures 13(a) and 13(b), show relative Euclidean and Riemannian distance metrics of full and transversely isotropic elastic stiffness matrices as a function of the basal layer spacing. The results shows that the transversely isotropic approximation is a good representation of elastic stiffness parameters for \( d \geq 12 \text{Å} \), but becomes less reliable for conditions approaching the dry state.

### 4 Conclusion

This paper has presented a complete set of elastic stiffness constants for Wyoming Na-montmorillonite based on computational molecular dynamics simulations. The results show the variation in elastic constants as a function of the hydration state and basal layer spacing.
Figure 13: (a) Relative Euclidean Metric as a function of basal layer spacing. (b) Riemannian Metric as a function of basal layer spacing. Legend as in Figure 6.

Key findings for the individual stiffness components can be summarized as follows:

1. The normal stiffness $C_{33}$ oscillates with hydration level linked to the formation of mono and double layer of inter-lamellae water.

2. The $C_{33}, C_{44}$ (and $C_{55}$) and $M_z$ values are in good agreement with acoustic and nano-indentation experiments for basal layer spacing $d \geq 15.6 \, \text{Å}$ corresponding to a system with two layers of water.

3. The computed in-plane stiffness parameters $C_{11}$ (and $C_{22}$), $C_{12}$ and $M_p$ (and to a less degree $C_{13}$ (and $C_{23}$)) differ from the experimental measurements. However the latter are illustrated by the finite length of clay particles while the current simulations represent conditions for infinitely long plates.

4. Transverse isotropic assumption of mechanical properties for the clay mineral is a good approximation after the formation of the first layer of water but is less reliable for representing the dry state of the clay lamellae.
5 Acknowledgement

This research was supported in part by the National Science Foundation through TeraGrid resources provided by NCSA and TACC under grant number TG-DMR100028. The authors wish to acknowledge the X-Shale Hub at MIT for partial support of this project. The first author has also received support from the Singapore-MIT Alliance for Research and Technology (SMART). We also would like to thank M. J. Abdolhosseini Qomi for the fruitful discussion.

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Figure Captions

Figure 1: Mg-Mg radial distribution functions of two atomic structures used in simulations.

Figure 2: Typical unit cell in periodic crystal of the simulated clay mineral at d=12Å.

Figure 3: Change in average number of hydrogen bonds per water molecule and density of interlayer water during swelling of Wyoming Na-montmorillonite.

Figure 4: Change in derivative of the density with respect to basal layer spacing during swelling of Wyoming Na-montmorillonite.

Figure 5: Density profile of water oxygen (Ow) and water hydrogen (Hw) and sodium (Na) in direction normal to the clay layers.

Figure 6: The $C_{33}$ elastic constant as a function of basal layer spacing. Filled symbols represent data points from simulation (1) and hollow symbols represent data points from simulation (2). Triangular symbols represent equivalent transversely isotropic stiffness constants.

Figure 7: The $C_{44}$ and $C_{55}$ elastic constants as a function of basal layer spacing. Legend as in Figure 6.

Figure 8: The $C_{13}$ and $C_{23}$ elastic constants as a function of basal layer spacing. Legend as in Figure 6.

Figure 9: The $C_{11}$ and $C_{22}$ elastic constants as a function of basal layer spacing. Legend as in Figure 6.

Figure 10: The $C_{12}$ elastic constant as a function of basal layer spacing. Legend as in Figure 6.

Figure 11: Indentation modulus in z direction as a function of basal layer spacing. Legend as in Figure 6.
**Figure 12**: Indentation modulus in the plane of transverse isotropy as a function of basal layer spacing. Legend as in Figure 6.

**Figure 13**: (a) Relative Euclidean Metric as a function of basal layer spacing. (b) Riemannian Metric as a function of basal layer spacing. Legend as in Figure 6.
Figure 1

Radial Distribution Function, $g(r)$

Mg-Mg Spacing, $r[\text{Å}]$
Figure 3

The graph illustrates the relationship between the number of hydrogen bonds per water molecule, $N_{HB}$, and the basal layer spacing, $d$, along with the density of water, $\rho_w$. The data points are marked with three distinct regions labeled A, B, and C, indicating different stages or conditions of the system.

- **Region A**: Indicates an initial phase with fewer hydrogen bonds and density values.
- **Region B**: Represents a transition phase with a significant increase in the number of hydrogen bonds and corresponding density changes.
- **Region C**: Shows a further increase in the number of hydrogen bonds and a gradual rise in density.

The graph helps in understanding the structural and density changes as a function of the basal layer spacing.
Figure 4

\[ \frac{\Delta \rho_w}{\Delta d} \left[ \text{gr/} (\text{cm}^3 \text{Å}) \right] \]

Basal Layer Spacing, \(d[\text{Å}]\)
Figure 5

Density profile

Z direction

d = 12Å  15Å  17.8Å

clay surface

Ow

Hw

Na
Basal Layer Spacing, $d$ [Å]

$C_{33}$ [GPa]

Density, $\rho_w$ [gr/cm$^3$]

UPV Data for Shales

Ortega et al., 2007 [57]

$C_{33}$

$\overline{C}_{33}$

$C_{33}(1)$

$C_{33}(2)$

$\overline{C}_{33}(1)$

$\overline{C}_{33}(2)$

Trendline

$\rho_w$

A

B

Figure 6
Figure 7

UPV Data for Shales
Ortega et al., 2007 [57]

C_{44} or C_{55} [GPa]

C_{44}(1)  C_{55}(1)  \overline{C}_{ii}(1)
C_{44}(2)  C_{55}(2)  \overline{C}_{ii}(2)

Trendline
\rho_w [gr/cm^3]

Basal Layer Spacing, d[Å]

Density, \rho_w [g/cm^3]
Figure 8

UPV Data for Shales
Ortega et al., 2007 [57]

Basal Layer Spacing, \(d[\text{\AA}]\)

Density, \(\rho_w[\text{gr/cm}^3]\)

- Trendline
- \(\rho_w\)

\(C_{ij}(i=13 \text{ or } 23)[\text{GPa}]\)

- \(C_{13}(1)\)
- \(C_{23}(1)\)
- \(\overline{C}_{ij}(1)\)
- \(C_{13}(2)\)
- \(C_{23}(2)\)
- \(\overline{C}_{ij}(2)\)
Figure 9

UPV Data for Shales
Ortega et al., 2007 [57]

Basal Layer Spacing, $d$ [Å]

$C_{11}$ or $C_{22}$ [GPa]

$C_{11}(1)$
$C_{22}(1)$
$C_{ii}(1)$
$C_{11}(2)$
$C_{22}(2)$
$C_{ii}(2)$

Trendline
Figure 10

UPV Data for Shales
Ortega et al., 2007 [57]

Basal Layer Spacing, d[Å]

\[ C_{12}[\text{GPa}] \]

Trendline

- \( C_{12}(1) \)
- \( \overline{C}_{12}(1) \)
- \( C_{12}(2) \)
- \( \overline{C}_{12}(2) \)
Nanoindentation for Shales and Rectorite
Bobko and Ulm, 2008 [59] & Zhang et al., 2009 [60]

Figure 11
Figure 12

Nanoindentation for Shales
Bobko and Ulm, 2008 [59]

M_p [GPa]

ρ_w [gr/cm^3]

Basal Layer Spacing, d[Å]

Trendline

ρ_w

simulation(1)
simulation(2)

A

B