RESEARCH ARTICLE

Nanoscale crack propagation in clay with water adsorption through reactive MD modeling

Zhe Zhang  |  Xiaoyu Song

Abstract
The atomic-scale cracking mechanism in clay is vital in discovering the cracking mechanism of clay at the continuum scale in that clay is a nanomaterial. In this article, we investigate mechanisms of modes I and II crack propagations in pyrophyllite and Ca-montmorillonite with water adsorption through reactive molecular dynamics (MD) with a bond-order force field. Clay water adsorption is considered by adding water molecules to the clay surface. During the equilibration stage, water adsorption could cause bending deformation of the predefined edge crack region. The relatively small orientating angle of water molecules indicates the formation of hydrogen bonds in the crack propagation process. The peak number density of adsorbed water decreases with the increasing strains. The atomistic structure evolution of the crack tip under loading is analyzed to interpret the nanoscale crack propagation mechanism. The numerical results show that the crack tip first gets blunted with a significant increase in the radius of the curvature of the crack tip and a slight change in crack length. The crack tip blunting is studied by tracking the crack tip opening distance and O–Si–O angle in the tetrahedral Si–O cell in modes I and II cracks. We compare bond-breaking behaviors between Al–O and Si–O. It is found that Si–O bond breaking is primarily responsible for crack propagation. The critical stress intensity factor and critical energy release rate are determined from MD simulation results.

KEYWORDS
clay, crack propagation, molecular dynamics, reactive force field, water adsorption

1 | INTRODUCTION

Cracking in clay could significantly compromise the integrity of the dam and embankment and trigger failure of soil slopes and foundations on clay (e.g., Refs. [1–10]). Because clay is a nanomaterial by nature, the nanoscale cracking mechanism in clay particles plays a significant role in discovering the cracking mechanism of clay minerals at the continuum and field scales. Water can be strongly attracted to clay mineral surfaces and affect the mechanical and physical properties of clay at multiple scales. The clay–water adsorption can be originated from two primary mechanisms, i.e., short-ranged physicochemical mechanism and capillary condensation at higher relative humidity values. At the nanoscale, physicochemical mechanisms include surface hydration on clay mineral surfaces at low relative humidity, exchangeable cation hydration, and interlayer swelling for expandable clay minerals. The interatomic and interparticle forces could affect physical and chemical bonds such as covalent, ionic, and van der Waals (vdw) bonds in soil with
water. Different structures and properties of adsorbed water are associated with different mechanisms of clay–water interaction. The density and thickness of the adsorbed water layer could be a function of water content and the type of clay. The arrangement/orientation of adsorbed water differs significantly from the bulk water. For example, the formation of strong hydrogen bonds could alter the layout of water molecules. Studies have also clarified the structure of electrical double layers formed on hydrated clay mineral surfaces. Sposito et al. investigated the effect of cation size and charge on the coordination of interlayer cations, interlayer water molecules, and clay mineral surface oxygens. The increasing interlayer cation can enhance the influence of clay mineral structure and hydrophobicity on the configurations of adsorbed water. From the above brief literature review, it may be argued that the clay water adsorption mechanism has been well studied. However, the crack propagation mechanism in clay under water adsorption remains an open question. To help close this knowledge gap, in this study, we hypothesize that water adsorption on clay surfaces could affect the crack propagation mechanism in clay particles under modes I and II cracking at the nanoscale. To test this hypothesis, we conduct reactive molecular dynamics (MD) simulations of two clay minerals (pyrophyllite and Ca-montmorillonite), incorporating water adsorption with a bond-order reactive force field for clay. Next, we briefly review the computational modeling of clay, including clay cracking, at the nanoscale through molecular dynamics. With rapid advances in high-performance computing, MD modeling has become a viable tool to probe the nanoscale mechanics and physics of materials, including clay (e.g., Refs. [21–24]). Indeed, numerous studies on modeling the mechanics and physics of clay using MD have been reported in the literature (e.g., Refs. [25–29] among many others). For instance, Sato et al. and Militzer et al. conducted first-principles studies on the elastic constants of clay minerals based on density functional theory. Zartman et al. studied the tensile moduli, shear moduli, and failure mechanisms for pyrophyllite, montmorillonite, and mica under a wide range of stress conditions through MD simulations. Teich-McGoldrick et al. performed MD simulations of structural and mechanical properties of muscovite under the effect of pressure and temperature. Hantal et al. studied the failure properties of illite with pre-existing cracks within clay layers through MD. However, in the studies mentioned above, dry clay was usually employed without considering water adsorption. A few researchers have investigated the mechanical properties of unsaturated clay with varying hydration by MD simulation. Ebrahimi et al. investigated the anisotropic elastic properties of Na-montmorillonite with water absorption through MD simulations. Carrier et al. calculated elastic properties of swelling montmorillonite as a function of water content. Qomi et al. calculated the nanoscale cohesion, friction angle, and hardness of Na-montmorillonite clay with one water layer. Jia et al. simulated hydraulic fracturing in kaolinite at the nanoscale through MD. Zhe and Song recently investigated the initiation and growth of cracks in dry clay sheets through MD with a general clay force field. However, to the best of our knowledge, no study has been conducted to investigate the mechanism of crack propagation in clay platelets incorporating water adsorption at the atomic scale. Thus, in this article, we conduct MD modeling of crack propagation in clay platelets with water adsorption through reactive MD modeling. In what follows, we review the bond-order reactive force fields for modeling bond breakage during the crack propagation in clay particles using reactive MD with clay–water interaction. We refer to the literature (e.g., Refs. [24, 25, 42, 43]) for a review of general force fields for modeling the mechanics and physics of clay using MD. Bond-order force field is a class of interatomic potentials used in reactive MD simulations, for example, Tersoff, REBO, AIREBO, and ReaxFF. ReaxFF has been utilized to investigate fracture properties of materials such as silicon and graphyne. Zhang et al. examined the stress corrosion process of strained quartz in liquid water and showed the primary role of Si–O bond breakage in crack growth. Buehler et al. investigated the crack limiting speed, crack instabilities, and directional dependence on crystal orientation in a single silicon crystal through MD modeling with ReaxFF. Hou et al. interpreted the disconnecting role of water by studying the tensile failure mechanism of C-S-H gels at different humidity levels. Rimsza et al. investigated the crack propagation in an atomistic amorphous silica model through MD modeling with ReaxFF. Pitman and Van Duin studied the clay–water interaction through the reactive MD simulation. Their proposed ReaxFF parameter set contains a large body of data, including equations of state of metal and metal-oxide phases and a series of chemical reactions involving silicon and aluminum compounds. Therefore, this parameter set is representative of all coordination states occurring during the crack of clays. However, to the best of our knowledge, no work has been done to probe the fundamental crack propagation mechanism in clay sheets using a bond-order force field considering clay–water adsorption. In this article, as a major contribution, the bond-order-based ReaxFF clay force field is utilized to study modes I and II cracking propagation mechanisms in clay particles with water adsorption. The remainder of this article is organized as follows. Section 2 summarizes the clay models and numerical methods, including the model setup, reactive force field parameters, and loading protocols. Section 3 presents the numerical results of the reactive MD modeling of modes I and II crack propagations in the two clay minerals with water adsorption. Section 4
briefly discusses the limitation of ReaxFF for modeling cracking in clay with water adsorption and points out the future research directions, followed by a closure in Section 5.

2 | MATERIAL MODELS AND NUMERICAL METHODS

2.1 | Clay–water model setup

In this study, we adopt two clay minerals to study the water adsorption mechanisms and their potential impact on modes I and II crack propagation in different clay minerals. The clay minerals are pyrophyllite and Ca-montmorillonite, whose chemical formulas are $\text{Al}_2[\text{Si}_4\text{O}_{10}](\text{OH})_2$ and $\text{Ca}\text{Al}_2(\text{Si}_4\text{O}_{11})(\text{OH})$, respectively. The difference between the two types of clay minerals is the isomorphous substitution and cation exchange capacity. Both clay minerals have a 2:1 tetrahedral–octahedral–tetrahedral (T-O-T) structure. The atomic coordinates for the unit cell of the two clay can be found in Ref [54]. Figure 1 shows the initial molecular structure of the clay model. The MD model for pyrophyllite and Ca-montmorillonite consists of 720 unit cells, that is, 36 cells in the $x$ direction, 20 cells in the $y$ direction, and 1 cell in the $z$ direction. The lattice parameters of the pyrophyllite unit cell are $a = 5.16\,\text{Å}$, $b = 8.966\,\text{Å}$, and $c = 9.347\,\text{Å}$. The lattice parameters of the montmorillonite unit cell are $a = 5.19\,\text{Å}$, $b = 9.02\,\text{Å}$, and $c = 10.02\,\text{Å}$. Thus, the two clay particles have dimensions of $185.76\times179.32\,\text{Å}$ and $186.84\times180.40\,\text{Å}$ in the $x$-$y$ plane, respectively. The pre-existing crack is defined through removing atoms in a tapered region along the centerline in the $x$-direction. The length of the pre-existing crack is one half the length of the clay platelet in the $x$-direction, and the angle is $10^\circ$. After introducing the edge crack, a pre-equilibrated water box is placed above the center of clay platelet and the clay-water system is equilibrated using ReaxFF force field at 298 K. The pre-equilibrated rectangular water box contains a total number of 1193 water molecules corresponding to a water mass content of 4.24%. Here mass water content is defined as the ratio of water molecular mass and clay molecular mass. Then the pre-equilibrated water box is placed 10 Å above the center of clay surface to avoid clay–water repulsion during the equilibrium stage. Next, we introduce the ReaxFF force field and input parameters for both clay minerals.

2.2 | ReaxFF force field

In this part, for self-completeness, we briefly introduce the ReaxFF force field and summarize the parameters and their values$^{55}$ for clay minerals adopted in this study. The total potential energy $E_t$ of the ReaxFF force field$^{47,56}$ is written as

$$E_t = E_{\text{bond}} + E_{\text{oc}} + E_{\text{uc}} + E_{\text{lp}} + E_{\text{va}} + E_p + E_\text{ia} + E_\text{conj} + E_{\text{vdw}} + E_{\text{Coul}}, \quad (1)$$

where $E_{\text{bond}}$ is the continuous bond energy function that describes single, double, and triple bonds, $E_{\text{oc}}$ is the over-coordination penalty energy, $E_{\text{uc}}$ is the under-coordination penalty energy, $E_{\text{lp}}$ is the lone-pair energy that handles formation and dissociation of oxygen lone-pairs, $E_{\text{va}}$ is the valence angle energy, $E_p$ denotes the penalty energy, $E_\text{ia}$ is the torsion angle energy, $E_\text{conj}$ is the conjugation energy, $E_{\text{vdw}}$ is vdw energy, and $E_{\text{Coul}}$ is Coulomb energy. These energy terms can be categorized into two groups, bond-order dependent terms (i.e., the first eight terms) and bond-order independent terms (the last two terms). The bond-order dependent energy terms vanish upon bond breakage. Nonbonded interactions are independent of the bond order. Both nonbonded energy terms are calculated between all atom pairs in
TABLE 1  Summary of the parameters for bond order and bond energy terms in the ReaxFF force field.$^{55}$

| Bond  | $D_\sigma^e$ (kcal/mol) | $D_\pi^e$ (kcal/mol) | $p_{bo,1}$ | $p_{bo,2}$ | $p_{bo,3}$ | $p_{bo,4}$ |
|-------|-------------------------|-----------------------|------------|------------|------------|------------|
| Si–O  | 261.907                 | 5.9533                | −0.1083    | 8.5924     | −0.2366    | 29.7817    |
| Al–O  | 228.487                 | 0                     | −0.1750    | 5.2102     | −0.3500    | 25         |

TABLE 2  Summary of parameters for the van der Waals energy.$^{55}$

| Atom i | Atom j | $D_{ij}$ (kcal/mol) | $\alpha_{ij}$ | $r_{vdw}$ (Å) | $\lambda_{vdw}$ | $\gamma_w$ |
|--------|--------|---------------------|---------------|---------------|----------------|-----------|
| Si     | O      | 0.1318              | 10.5055       | 4.2555        | 1.5591         | 8.4893    |
| Al     | O      | 0.1526              | 9.5637        | 4.7628        | 1.5591         | 7.3490    |

the clay–water system. We note that ReaxFF employs the shielded potential to avoid excessive repulsion and un-physical charges between two atoms in close proximity.$^{47,56}$

In ReaxFF, the bond order $BO'_{ij}$ between two atoms $i$ and $j$ is a function of the interatomic distance $r_{ij}$ as

$$BO'_{ij} = BO'^\sigma_{ij} + BO'^\pi_{ij} + BO'^\pi\pi_{ij}$$

$$= \exp \left[p_{bo,1} \left( \frac{r_{ij}}{r_0^\sigma} \right)^{p_{bo,2}} \right] + \exp \left[p_{bo,3} \left( \frac{r_{ij}}{r_0^\pi} \right)^{p_{bo,4}} \right] + \exp \left[p_{bo,5} \left( \frac{r_{ij}}{r_0^{\pi\pi}} \right)^{p_{bo,6}} \right],$$

where $BO'^\sigma_{ij}$, $BO'^\pi_{ij}$, and $BO'^\pi\pi_{ij}$ are bond orders contributed from sigma-bonds, pi-bonds, and double pi-bonds, respectively, $r_0^\sigma$, $r_0^\pi$, and $r_0^{\pi\pi}$ are the reference atomic distance corresponding to sigma-bonds, pi-bonds, and double Pi-bonds, respectively, and $p_{bo,i}$ ($i = 1, \ldots, 6$) is the scaling parameter, which is fitted from quantum mechanics calculations on small representative systems. With Equation (2), the bond energy $E_{bond}$ can be written as

$$E_{bond} = -D_e BO'^\sigma_{ij} \exp \left[p_{bo,1} \left( 1 - \left( BO'^\sigma_{ij} \right)^{p_{bo,2}} \right) \right] - D_e BO'^\pi_{ij} - D_e^{\pi\pi} BO'^\pi\pi_{ij},$$

where $D_e$ is the dissociation energy for each bond type, and $p_{bo,1}$ and $p_{bo,2}$ are atomic parameters fitted from quantum mechanics calculations. The nonbonded vdW interaction between atoms $i$ and $j$ in ReaxFF through a distance-corrected Morse potential is written as

$$E_{vdw} = D_{ij} \left\{ \exp \left[ \alpha_{ij} \left( 1 - \frac{f(r_{ij})}{r_{vdw}} \right)^2 \right] - 2 \exp \left[ \frac{1}{2} \alpha_{ij} \left( 1 - \frac{f(r_{ij})}{r_{vdw}} \right) \right] \right\},$$

where $D_{ij}$, $\alpha_{ij}$, and $r_{vdw}$ are parameters (see Table 2), and $f$ is the shielded interaction term as a function of the atomic distance $r_{ij}$. $f(r_{ij})$ is written as

$$f(r_{ij}) = \left[ r_{vdw}^{\lambda_{vdw}} + \left( \frac{1}{\gamma_w} \right)^{\lambda_{vdw}} \right]^{1/\lambda_{vdw}},$$

where $\lambda_{vdw}$ and $\gamma_w$ are shielding parameters (see Table 2).

The ReaxFF parameter set for clay–water systems was developed in Ref [53]. However, the values of some parameters for the present study are missing in the literature. Table 1 summarizes the values of parameters used to calculate the bond order and bond energy in the ReaxFF force field$^{55}$ in this study. Note that the bond order of Si–O has two components, sigma bond order and pi bond order whereas Al–O only has sigma bond order.

Table 2 summarizes the parameters for the vdw energy in the ReaxFF force field.
In what follows, we briefly show the characteristics (bond order and energy) of the Si–O and Al–O bonds in the ReaxFF force field for clay minerals. In so doing, we plot the bond order and bond and vdw energy curves for the Si–O bond and Al–O bond, respectively. Figure 2 plots the variation of bond order with Si–O and Al–O bond lengths. Two components, the sigma bond order and Pi bond order, give an initial Si–O bond order of 2. The Si–O bond order vanishes as the Si–O bond length increases to 2.6 Å. The maximum bond order of Al–O is 1 due to the only sigma-bond contribution. Bond order of Al–O becomes negligible at the bond length of 3 Å. Figure 3A,B plots the bond energy $E_{\text{bond}}$ and vdw energy $E_{\text{vdw}}$ of the Si–O and Al–O bond as a function of the bond length (the interatomic distance). Note that the energy effects related to under and overcoordination are not taken into account. For both bonds, $E_{\text{bond}}$ remains unchanged when the bond length is less than 1 Å, and then decreases when the bond length exceeds 1 Å. $E_{\text{bond}}$ of Si–O bond reaches zero at the bond length of 2.5 Å. $E_{\text{vdw}}$ of Si–O decreases monotonically with the bond length and vanishes at 2 Å. For Al–O bond, $E_{\text{bond}}$ decreases as the bond length exceeds 1 Å and becomes zero at 3 Å. $E_{\text{vdw}}$ decreases with the bond length and vanishes at the bond length of 2.5 Å. Next, we present the numerical simulations.
2.3 Numerical simulations

We have implemented the ReaxFF force field in LAMMPS, a massively parallel molecular simulator. Thus, all reactive MD simulations are conducted on LAMMPS. Periodic boundary conditions are applied to the clay–water system in the $x$, $y$, and $z$ directions. Simulations are initialized with an energy minimization procedure to avoid unphysical overlap or close contact between atoms. The equilibrium simulations are conducted in the NPT ensemble (constant number of atoms, constant pressure, and constant temperature) at 0 atm and 298 K with a time step of 0.5 fs ($1 \text{ fs} = 10^{-15} \text{ s}$). The temperature remains constant following the Nose–Hoover algorithm. The damping parameters are 50 fs and 100 fs for temperature and pressure, respectively. The equations of motion of atoms are integrated using the Verlet velocity algorithm. Reactive MD simulations feature the flexible atomic charge. In this study, the atomic charge is adjusted at each time step using the charge equilibration method. We note that MD simulations with a reactive force field are computationally more demanding than nonreactive MD. To improve computational efficiency, all simulations are conducted with 128 CPU cores on a supercomputer. The clay–water system could reach an equilibrium after 6 ns.

After the clay–water system reaches equilibrium, the tensile and shear loading are applied through the homogeneous deformation technique for modes I and II cracking propagations, respectively. The strain rate is $10^{-6} \text{ fs}^{-1}$ for computational efficiency and stability. To check the sensitivity of the results to the time step and applied strain rates, Figure 4 presents the stress–strain curves for mode I crack propagation with different values of time steps and strain rates.

Figure 5 presents a schematic of the tensile loading through the homogeneous deformation technique. The deformation is applied by changing the size of the simulation box at a given strain rate. At each time step, the simulation box dimensions are modified based on the strain, and the atomic coordinates are updated based on Newton’s equations of motion and the interatomic potential. It is noted that the uniform stretching of the system avoids the generation of shock waves during simulations. Due to Poisson’s effect, the pressure components in the $x$, $y$, and $z$ directions are controlled independently to allow for transverse deformations. For example, as the simulation box is deformed along the $y$ direction, we apply the free transverse pressure condition by assigning zero pressures in the $x$ and $z$ directions of the clay model. For post-processing, the molecular visualization tool of OVITO is used to visualize and analyze the MD simulation data. In this study, the crack growth is characterized by the bond breakage (e.g., Si–O and Al–O bonds) in clay. The bond breakage is determined by the bond-order number in ReaxFF that is dependent on the bond distance between atoms. In this method, a bond is broken when its bond order is smaller than the critical value. The crack propagates when sufficient bonds are broken at the crack tip. In what follows, we probe modes I and II crack propagation mechanism in clay with water absorption from the reactive MD simulation results.
3 | NUMERICAL RESULTS

We present the numerical results of the MD simulation of cracking propagation in clay with water adsorption. From the results, we interpret the molecular-scale crack propagation mechanism in clay under modes I and II cracks. First, we characterize the water adsorption mechanism and its potential impact on crack propagation. Second, we present the molecular-scale characteristics of the crack propagation, including crack tip blunting and bond breakage along the new crack. Third, we compute the energy release rate and stress intensity factor from our reactive MD simulations and compare our MD results with the data in the literature.

3.1 | Water adsorption mechanism

It is known that pyrophyllite and Ca-montmorillonite have different water adsorption behavior. Figure 6 compares the distribution patterns of water molecules on the two clay surfaces. It can be seen that water molecules on pyrophyllite are dispersed in a discrete and uniform pattern. However, water molecules adsorbed to Ca-montmorillonite are in a clustered and less uniform pattern. Indeed, the locations of adsorbed water clusters on Ca-montmorillonite agree with the locations of surface cations Ca$^{2+}$. Meanwhile, the numerical results show that some water molecules react with the clay crack surface. However, the cluster behavior is not remarkable which may be due to the small dimension in the $z$-direction of the clay sheet (i.e., small crack surface).

Figure 7 shows the orientation of adsorbed water molecule on the clay surface. Water hydrogen atoms move closer to the clay surface than water oxygen atoms due to the hydrogen bond formation between clay surface oxygen and water hydrogen. This is one type of mechanism for clay–water adsorption. The hydrogen bond formation is observed in both
Figure 7: Schematic of the orientation angle $\phi$ of water molecules adsorbed on the clay surface.

Figure 8: Variation of the orientation angle for water adsorbed on (A) pyrophyllite and (B) montmorillonite in mode I crack propagation.

Pyrophyllite and Ca-montmorillonite. The water orientation angle $\phi$ can be used to characterize water adsorption. Here $\phi$ is the angle between the normal to the clay surface ($z$-axis) and the dipole moment of water molecule, as shown in Figure 7. Figure 8 presents the evolution of water orientation angles under the mode I crack. The water molecules within a circle of radius 2 nm at the front of the crack tip are selected for calculating orientation angles. For water orientation angle, we exclude water molecules in the silanol group because the formation of silanol alters water orientation. The circle location is dynamically determined following the location of crack tip during crack propagation. Comparing Figure 8A, B, larger average orientation angles and greater oscillations are found for water adsorbed on montmorillonite than on pyrophyllite. This can be due to the cation hydration on the montmorillonite surface that would alter the structure and orientation of water molecules.

A hydrogen bond (H-bond) with a surface oxygen $O_s$ is defined by the same criterion as the one for bulk water. The distance between the two oxygens $O_sO_w$ is smaller than 3.5 Å. Meanwhile the angle between the vector of $O_wO_s$ and $O_wH_w$ is smaller than 30°. We calculate the number of H-bonds within a cylinder of radius 2 nm centered at the crack tip during crack propagation. The percentage is defined as the ratio of the number of H-bonds and the number of water molecules within the first water layer on the clay surface, which satisfies the criterion that the distance between $O_w$ atoms and the clay surface is less than 4 Å. Figure 9 shows that during crack propagation the percentage of hydrogen
bonds is relatively stable. The mean value of percent of H-bonds is approximately 36.6% and 8.4% for pyrophyllite and montmorillonite, respectively. Comparison of two clay surfaces illustrates the cation hydration on the montmorillonite surface could hinder the formation of hydrogen bonds, thus generating a smaller percentage of H-bonds.

Next, we probe the potential impact of water adsorption on crack propagation through comparing the number density profiles of adsorbed water molecule on both clay minerals before and after the crack propagation. Figures 10 and 11 show the water number density profiles for pyrophyllite and montmorillonite, respectively. The number density profile of water molecules along z-axis is calculated by dividing the simulation box into several bins, that is, 1D slabs and averaging the number density in each bin over time. Thus, we can spatially quantify the distribution and variations of adsorbed water molecules with respect to the distance from the clay surface. The dash vertical line $z = 0$ represents the location of initial clay top surface. The peak density indicates the accumulation of water molecules above clay surface due to water adsorption. The results in Figures 10 and 11 show that the peak water number density decreases after the crack propagation. For montmorillonite, the distance from the clay top surface to the location where the peak density occurs is about 1.8 Å. For pyrophyllite, this distance is 2.3 Å. We find that the number density is not strictly equal to zero at plane $z = 0$ for montmorillonite. The reason could be that the bending occurs near the edge crack region in the clay particle. Then water molecules enter the crack region under the plane $z = 0$. This effect is more remarkable in montmorillonite. The peak number density of water molecules above the montmorillonite surface is smaller than that of pyrophyllite. The reason could be more water molecules absorbed on the crack surface in montmorillonite than in pyrophyllite.

**Figure 9** Percentage of hydrogen bonds in the first water layer near crack tip in mode I crack propagation, (A) pyrophyllite and (B) montmorillonite.

**Figure 10** Number density profile of water molecule adsorbed on the pyrophyllite surface.
Figure 12 plots the variation of number density of water near the crack tip in pyrophyllite and montmorillonite during mode I crack propagation. The number of water molecules is counted within a cylindrical region around the crack tip. The cylinder has a radius of 2 nm and its height is equal to the thickness of the simulation box. Water number density is defined as the ratio of the total number of water molecules in the region and the cylinder volume. Figure 12 shows that for both clay minerals, water number density near the crack tip decreases with tensile strain.

We note that the other type of water adsorption is hydration of surface cations. This adsorption mechanism is unique to Ca-montmorillonite due to the existence of surface cations Ca$^{2+}$. Figure 6B presents cation hydration on the montmorillonite surface. It can be found from Figure 6B that each Ca$^{2+}$ is fully hydrated and surrounded by water molecules. The similar arrangement of water molecules near Ca$^{2+}$ can be also found in Sposito et al.\textsuperscript{19}. We may conclude that the difference of water distribution patterns on the two clay surfaces is attributed to surface cation hydration. In what follows, we further investigate the bending mechanism near the edge crack and silanol formation on the clay surface.

3.1.1 Bending deformation near the edge crack

Our MD simulation results show that the adsorbed water could cause bending deformation near edge crack. Figures 13 and 14 present the deformed edge crack region in pyrophyllite and montmorillonite, respectively. Initially, both clay sheets
remain planar. During the equilibration process, the edge crack region bends upward to some extent, as indicated by the curved dash line. This effect is more remarkable for montmorillonite under the same other conditions, which may explain why the number density of water molecules at \( z = 0 \) is not zero in Figure 11. We note that the bending effect on the clay sample from the water adsorption if water placed on both sides of the clay particle is less obvious than the case with water placed on the clay top surface. Meanwhile, the placement of water molecular on the one-side or both sides of the clay does not affect the crack propagation simulated in this study in that the crack propagation is triggered by mechanical loading (i.e., displacement) and the gravity load is not considered in our MD simulations.

3.1.2 Silanol formation

In the cracking propagation, we observe two distinct behaviors of water molecules. Some water molecules are adsorbed to the clay surface whereas some water molecules react with clay and form new species. For instance, silanol bonds, a functional group in silicon chemistry with the connectivity \( \text{Si–O–H}^{52,63} \), are formed due to the reaction between Si in clay and the hydroxyl groups in water molecules. Clay can react with water molecules and form silanol bonds through two pathways\(^5\) as

\[
O_n\text{Si} - \text{O}^- + \text{H}_2\text{O} \rightarrow O_n\text{Si} - \text{OH} + \text{OH}^-, \tag{6}
\]

\[
O_n\text{Si}^+ + \text{H}_2\text{O} \rightarrow O_n\text{Si} - \text{OH} + \text{H}^+. \tag{7}
\]

Figure 15 illustrates the formed silanol bonds near the crack tip. The two species generated are \((\text{Si–O})_c\text{-H}_w\) and \((\text{Si–OH})_w\). Here, the subscripts \( c \) and \( w \) denote that the atoms or bonds are from clay and water molecules, respectively. For example, \((\text{Si–O})_c\text{-H}_w\) is formed by reactant \( \text{Si–O} \) from clay and \( \text{H} \) from water molecules.

We note that for the data processing of water number density, the water molecules in the form of silanol bonds are considered. For the analysis of water orientation angle and hydrogen bond, water molecules in the form of silanol bonds are not considered since they alter the orientation and structure of water clusters.
3.2 | Mechanism of modes I and II crack propagation

3.2.1 | Crack tip blunting

We investigate the crack tip blunting behaviors by characterizing the shape change of the hexagonal Si–O cell in the tetrahedral layer. A standard hexagonal Si–O cell consists of six silicon atoms and six oxygen atoms connected through Si–O bonds. Figure 16 compares the Si–O cell in pyrophyllite at equilibrium and at the tensile strain of 11.675%. This strain is assumed as the critical strain prior to the first Si–O bond breaking. The crack tip open distance $d$ (i.e., the largest distance between two silicon atoms) and the crack tip opening angle $\alpha$ (i.e., the O–Si–O angle) are adopted to characterize the deformation of the Si–O cell in the crack propagation process. Figures 17 and 18 plot the variations of the Si–O cell open distance and the O–Si–O angle in pyrophyllite and montmorillonite under the mode I crack, respectively. The O–Si–O angles at equilibrium in pyrophyllite and montmorillonite from the MD simulation are about 113° and 108°, respectively. The values are close to the value 109.4° obtained from the X-ray measurement.64 As shown in Figures 17 and 18 both the open distance and the O–Si–O angle increase with fluctuations and reach the maximum values before the Si–O bond breakage.
In this study, the bond breakage is defined based on the critical bond order following the reactive force field. A bond breaks if its bond order is smaller than the critical value. The critical bond order is determined from the bond-order profile as follows. During crack propagation, we monitor the variations of Si–O bond order and Al–O bond order. For instance, Figures 19 and 20 plot the bond order of Si–O bond and Al–O bond in the mode I crack propagation in the pyrophyllite particle, respectively. From the results in Figures 19 and 20 and referring to Figures 2 and 3, in the present study, we assume that the critical bond order is 0.2.

Figure 21 compares the deformation of the Si–O cell in pyrophyllite under the mode II crack. Here the shear strain is defined as the ratio of the displacement in the x-direction and the initial clay length in the y-direction. Figures 22 and 23 plot the variations of the open distance of the Si–O cell and the O–Si–O angle under the mode II crack, respectively. The maximum angle before the Si–O bond breakage is similar in both clays. However, the open distance of the Si–O cell is smaller in pyrophyllite than in montmorillonite at the same strain. For instance, the open distances of the Si–O cell in pyrophyllite and montmorillonite at the same maximum strain are 6.64 and 6.95 Å, respectively.

Considering the O–T–O crystalline structure of pyrophyllite, we present the microstructure evolution of the mixed “O–T (octahedral–tetrahedral) cell” that consists of the central octahedral Al–O cell and the top-layer tetrahedral Si–O cell. The deformation and cracking of the two cells are compared in terms of Al–O and Si–O bond breaking characteristics.
FIGURE 19  Variation of Si–O bond order under the mode I crack propagation.

Figure 20  Variation of Al–O bond order under the mode I crack propagation.

Figure 24 shows the atomic structure of the O–T cell at the crack tip from different view angles when the system is at equilibrium.

Figure 25 plots the snapshots of deformation of the O–T cell under the mode I crack. The dash line between the two atoms indicates the bond breakage. Broken Al–O bonds are in black and broken Si–O bonds are in blue. As the tensile strain reaches 9.1%, the Al–O bond breakage occurs while the Si–O cell still remains intact. The breakage of the Si–O bond in this cell is not observed until $\varepsilon_{yy} = 11.725\%$. The bond breakage in the Si–O cell indicates the occurrence of the crack propagation. Figure 26 presents the deformation of the O–T cell under the mode II crack. The first bond breakages in the octahedral Al–O cell and the tetrahedral Si–O cell occur at the shear strains of 12.97% and 14.44%, respectively. Despite the earlier breakage, the broken Al-O bond does not immediately result in the crack growth in that the Si–O cell can still sustain the external load. Indeed, the bond breakage in the Si–O cell is directly associated with the crack growth. Thus, we may conclude that the tetrahedral Si–O cell is primarily in charge of the crack tip stability.

In what follows, we characterize the crack tip blunting by calculating the radius of the crack tip curvature ($\rho$). Figure 27 presents the schematic of $\rho$ based on a second-order polynomial curve fitting. In this case, the radius of curvature can be
written as

$$\rho = \frac{1}{2a}, \quad (8)$$

where $a$ is the coefficient in the second-order polynomial function.

Figure 28 shows the variations of the radii of the crack tip in both clays under the mode I crack. In Figure 28, the two vertical dash lines denote the critical strains at which the crack starts to propagate. In the crack tip blunting process, the radius of curvature first experiences a stable stage. Then the radius of curvature gradually increases to the maximum value followed by a sharp drop upon the crack propagation. The crack blunting before its propagation is remarkable because about six-time increases in the radius of curvature are observed for both clay models. We note that the critical strain corresponding to the abrupt decrease in $\rho$ is consistent with the abrupt decline in the stress–strain curve. Figures 29 and
FIGURE 23  Variations of O–Si–O angle in pyrophyllite and montmorillonite under the mode II crack.

FIGURE 24  Atomic structure of the O–T cell.

FIGURE 25  Snapshots of the deformation of the O–T cell under the mode I crack.

FIGURE 26  Snapshots of the deformation of the O–T cell under the mode II crack.
plot the stress–strain curves of pyrophyllite and montmorillonite under the modes I and II cracks, respectively. Both pyrophyllite and montmorillonite have a similar peak tensile stress under the mode I crack. However, under the mode II crack, pyrophyllite has a larger peak shear stress than montmorillonite. This can be due to bond breakage, explained in what follows. Figure 31 plots the number of broken Al–O bonds with shear strain under the mode II crack in both clay minerals. The results in Figure 31 show that fewer Al–O bonds are broken in pyrophyllite than in montmorillonite at the shear strain of around 16% (i.e., the shear strain at the peak strength). This may explain why pyrophyllite has a larger peak shear stress than montmorillonite under the mode II crack. Next, we analyze the bond breakage mechanism under both crack modes.

### 3.2.2 Bond breakage characteristics

In this part, we examine the individual bond breakage behavior of Al–O and Si–O bonds, as well as the variations of broken bond number and crack length under both crack modes. Figure 32 plots the mode I crack propagation in the pyrophyllite particle. It can be found that crack propagates forward in a straight way and ultimately breaks into two halves. The process of crack propagation takes about 4.75 ps and the corresponding strain increment is 0.475%, which may imply a brittle fracturing process. Figure 33 plots the mode II crack propagation in pyrophyllite. Different from the mode I crack propagation, the results in Figure 33 show that the clay particle does not fall apart completely under the mode II crack, which may imply a ductile fracturing process. Figures 34 and 35 plot the snapshots of the modes I and II crack propagations, respectively, in montmorillonite. The results in Figures 34 and 35 show that the modes I and II crack
**FIGURE 29** Stress strain curves of pyrophyllite and montmorillonite under the mode I crack.

**FIGURE 30** Stress strain curves of pyrophyllite and montmorillonite under the mode II crack.

**FIGURE 31** Variations of the number of broken Al–O bonds in pyrophyllite and montmorillonite in the mode II crack.
propagation in the montmorillonite particle is brittle. We note that for the model II crack, as edges remain close to each other, atoms could create new bonds through ReaxFF.

Figure 36 plots the bond length variations of the Al–O and Si–O bonds under the modes I and II cracks. Based on our numerical simulations, the equilibrium lengths of the Si–O and Al–O bonds are about 1.6 Å and 1.95 Å, respectively. The numerical results are consistent with the equilibrium bond lengths obtained from the radial distribution function, that is, 1.63 Å and 1.99 Å as shown in Figures 37 and 38. Our numerical results show that the maximum length of Si–O bonds before breakage is increased by 29%, and the length of the Al–O bonds is increased by 16.5%.
The number of broken bonds can be used to characterize the crack propagation process at the atomic scale. Figure 39 plots the variation of the broken Al–O bond number in montmorillonite under the modes I and II cracks. The sudden drop of the curve of the broken bond number after its peak value indicates the crack propagation. Figure 40 plots the variation of the broken Si–O bond number in montmorillonite under the mode I crack. The results show that the Si–O bond breakage differs from that of the Al–O bond. For instance, there is no Si–O bond breakage until the maximum tensile stress is reached.
strains is reached. Figures 41 and 42 plot variations of the broken Al–O and Si–O bonds in pyrophyllite, respectively. The results in Figures 41 and 42 show that the variations of broken bond numbers in pyrophyllite follow the similar trends as in montmorillonite.

Figures 43 and 44 plot the crack length change with respect to the strain under the modes I and II cracks, respectively. It may be implied from Figures 43 and 44 that the modes I and II crack propagation in both clay particles are brittle. For the mode II crack, the results in Figure 44 can be interpreted as frictional resistance between broken edges. Meanwhile, the results in Figures 43 and 44 show that the full propagation of both mode cracks in pyrophyllite may require a larger strain or load under the same other conditions.

Next, the reactive MD simulation results are used to calculate the crack energy release rate and the stress intensity factor.
**Figure 39**  Number of the broken Al–O bonds in montmorillonite under the modes I and II cracks.

**Figure 40**  Number of the broken Si–O bonds in montmorillonite under the mode I crack.

**Figure 41**  Number of the broken Al–O bonds in pyrophyllite under the modes I and II cracks.
**FIGURE 42** Number of the broken Si–O bonds in pyrophyllite under the mode I crack.

**FIGURE 43** Evolution of the crack length in pyrophyllite and montmorillonite under the mode I crack.

**FIGURE 44** Evolution of the crack length in pyrophyllite and montmorillonite under the mode II crack.
3.3 Crack energy release rate

Crack energy release rate $G$ is a fundamental variable in fracture mechanics at the continuum scale. Crack energy release rate is defined as the dissipated energy during fracture per unit crack surface area. In the linear elastic fracture mechanics, the crack propagates when the energy release rate reaches a critical value $G_C$. The J-integral is a method for calculating the energy release rate.\(^\text{65}\) The integration of stress $\sigma_{yy}$ with respect to strain $\varepsilon_{yy}$ provides an estimate of the variation of the free energy per unit volume. At the end of the simulation, the mechanical energy is assumed to be completely released by the creation of new crack surfaces. Under the mode I crack, the critical energy release rate $G_{IC}$ can be written as

$$G_{IC} = \frac{V}{2(L_c - L_0) \times t} \int_{\varepsilon_f}^{\varepsilon_f} \sigma_{yy} d\varepsilon_{yy},$$  \hspace{1cm} (9)

where $V$ is the system volume, $L_c$ is the final crack length, $L_0$ is the initial crack length, $t$ is the crack thickness, $\varepsilon_f$ is the final strain, and the factor 2 denotes the two surfaces of the crack. Figure 45 presents the accumulated strain energy in pyrophyllite and montmorillonite under the mode I crack. From our reactive MD simulations and through Equation (9), the range of critical energy release rate for pyrophyllite is from 3.9 N/m to 4.8 N/m, and for montmorillonite, the range is from 3.7 N/m to 5.1 N/m. Our numerical results are consistent with the experimental results in the literature (e.g., Refs. [66, 67]). Lakshmikantha\(^\text{66}\) conducted compaction tension tests on Barcelona clay at macroscopic scale with different crack lengths and moisture contents resulting to a wide range of numbers for fracture energy. For instance, the critical energy release rate is 3.7 N/m at 5% moisture content. Chandler\(^\text{67}\) performed fracture tests on clay soils with varying water contents. The testing results showed that the energy release rate first increases with crack length and drops after reaching the peak value. The peak energy release rate is 6.0 N/m, 5.5 N/m, and 4.3 N/m for moisture content 31%, 34%, and 42%, respectively. Next, we will present our numerical results of the stress intensity factor.

3.4 Stress intensity factor

In this part, we compute the stress intensity factor from our reactive MD simulation results. For a semi-infinite platelet clay particle with an edge crack, the stress intensity factor for the mode I crack can be written as

$$K_I = 1.12\sigma \sqrt{\pi L_{cp}},$$  \hspace{1cm} (10)

where $\sigma$ is the tensile stress and $L_{cp}$ is the propagated crack length. Similarly, the stress intensity factor for the mode II crack can be obtained by replacing tensile stress $\sigma$ in Equation (10) by the shear stress $\tau$ as

$$K_{II} = 1.12\tau \sqrt{\pi L_{cp}},$$  \hspace{1cm} (11)
FIGURE 46 Variations of the stress intensity factor of pyrophyllite under the modes I and II cracks.

FIGURE 47 Variations of the stress intensity factor of montmorillonite under the modes I and II cracks.

Figures 46 and 47 show the variations of the stress intensity factor in pyrophyllite and montmorillonite, respectively. From Equation (10), the critical fracture toughness $K_{IC}$ for the mode I crack of pyrophyllite is 0.77 MPa-m$^{1/2}$ and the value for montmorillonite is 0.72 MPa-m$^{1/2}$. From Equation (11), the critical mode II stress intensity factors for pyrophyllite and montmorillonite are 0.67 MPa-m$^{1/2}$ and 0.47 MPa-m$^{1/2}$, respectively. We compare the MD simulation results against experimental data in the literature. In what follows, we present some results in the literature to validate our numerical results. The ring tests on CL soils in Ref. [68] showed that the values of $K_{IC}$ ranges from 0.12 MPa-m$^{1/2}$ to 0.2 MPa-m$^{1/2}$. Spray [69] reported that the fracture toughness of phyllosilicates mica is 0.2 MPa-m$^{1/2}$. The results in Refs. [68, 69] are about four times smaller than our data. This discrepancy may be due to the heterogeneity and anisotropy of the tested specimen. Liu [70] measured fracture toughness in clay shale through nanoindentation tests. The values of fracture toughness for Opalinus clay vary between 0.316 MPa-m$^{1/2}$ and 0.698 MPa-m$^{1/2}$ based on the crack length measurement method and the values are ranging from 0.72 MPa-m$^{1/2}$ to 1.62 MPa-m$^{1/2}$ based on an energy method. The discrepancy between our numerical results and the results in Ref. [71] can be due to the effect of different soil mineral types and their internal structures. We note that the impurities and voids in the experimental samples may cause lower fracture toughness at macroscopic scales than our numerical results through MD.
The crack process zone radius $r_p$ at the crack tip can be determined from the stress intensity factor $K_I$ and the yield stress $\sigma_y$ as

$$r_p = \frac{1}{6\pi} \left( \frac{K_I}{\sigma_y} \right)^2.$$  \hspace{1cm} (12)

In this study, the ultimate stress is assumed as the yield stress. Figure 48 plots variations of the crack process zone radius at the crack tip under the mode I crack. The maximum radius of the crack process zone at the crack tip for pyrophyllite is about 24.2 Å and the value for montmorillonite is about 20 Å from our MD simulation results. From the continuum fracture mechanics, the radii of crack process zones represent the size of the crack tip yielding zone. In this study, the ratio between the maximum plastic zone radius and the width of the clay sample is 12.9% and 9.7% for pyrophyllite and montmorillonite, respectively. We note that the sizes of the edge crack and sample can be other factors affecting the crack process zone, which is beyond the scope of the current work. In the next section, we will briefly discuss the phenomenon and reasons of the artificial bond formation and crack healing observed in our reactive MD simulations in this study.

4 | DISCUSSION

Our numerical results show that artificial bond formation and crack healing occur during the equilibrium and crack propagation. In this part, we analyze the artificial bond formation in our reactive MD simulations and interpret the mechanism related to the adopted reactive force field.

4.1 | Artificial bond formation during equilibration

During equilibration, it is found that artificial Al–O bonds form across the crack surfaces. Figure 49 compares the crack region before and after the artificial bond formation near the crack tip. Atoms 1 and 4 are aluminum and they are connected to oxygen atoms 2 and 5, respectively. Thus, the Al–O–Al type bend angles are formed, that is, 1-2-3, and 4-5-6.

Figure 50 describes the bond breakage process of the artificial Al–O bonds formed during equilibration. The first artificial Al–O bond breaks at $\varepsilon_{yy} = 6.4\%$. This artificial bond breakage occurs earlier than the real Al–O bond breakage at the crack tip which occurs at $\varepsilon_{yy} = 8.525\%$. The second artificial Al–O bond breaks at $\varepsilon_{yy} = 7.7\%$. We note that the breakage of the two artificial Al–O bonds does not contribute to the crack propagation.

Figure 51 shows the variation of the open distance $d$ and open angle $\alpha$ of the Al–O cell containing the artificial bonds. Prior to bond breakage, the open distance reaches 6.5 Å and the O–Al–O angle increases to 141° from its equilibrium value of 89°.
4.2 Artificial bond formation under the mode II crack

Unlike the mode I crack propagation in which broken bonds cannot be recovered, the dynamic bond formation at the crack tip is observed in the mode II crack propagation. Figure 52 illustrates the bond breakage and reformation of the Si–O bond under the mode II crack. Atoms 1 and 2 are originally connected within the Si–O bond, and atom 3 is an isolated atom. As the shear deformation proceeds, the original Si–O bond between atoms 1 and 2 breaks. A covalent bond is then formed between atoms 2 and 3, which does not exist initially. Consequently, the artificial bond formation results in the nearly constant number of Si–O bonds in the clay particle under the mode II crack.

The artificial bond formation during the equilibrium and the mode II crack is due to the nature of ReaxFF, a chemical-reaction bond-order force field. Further improvement can be made by developing a deformation-driven bond-order force field for more accurate modeling of crack propagation in clays with water adsorption. For deformation-driven bond order, the criteria of bond breakage is based on the mechanical energy rather than the pure chemical energy and chemically based definition of bond order. To the best of our knowledge, the deformation-driven bond-order force field does not exist. The core of existing bond-order potentials is that the strength of a chemical bond depends on the bonding environment so that they can correctly describe chemical reactions. To prevent artificial bond re-formation, the new force field may need a “memory” of broken bonds and exclude the broken bonds in further deformation because mechanically the bond breakage can be permanent.
5 | CLOSURE

In this article, we have investigated the fundamental mechanisms of modes I and II crack propagations in two clay minerals (pyrophyllite and Ca-montmorillonite) with water adsorption through reactive MD simulations. Clay water adsorption is explicitly considered by adding water molecules to the clay surface. The relatively small orientating angle of the water molecule indicates the formation of hydrogen bonds throughout the crack propagation process. The peak number density of adsorbed water decreases with the increasing strains. Our numerical results show that the crack tip first gets blunted with a significant increase in the radius of the crack tip curvature and a slight change in crack length. The crack tip...
blunting is studied by tracking the evolution of crack tip open distance, and O–Si–O angle in the tetrahedral Si–O cell under modes I and II cracks. The bond breakage behaviors between Al–O and Si–O are compared, which shows that Si–O bond breaking is primarily responsible for crack propagation. The critical stress intensity factor and critical energy release rate are determined from our reactive MD simulation results and are validated against the data in the literature. The range of the critical stress intensity factor is [0.47, 0.77] MPa⋅m$^{1/2}$. The range of the energy release rate is [3.5, 5.1] N/m.

**ACKNOWLEDGMENTS**

This work has been supported by the US National Science Foundation under contract numbers 1659932 and 1944009. The support is greatly acknowledged. The authors are grateful to Professor Adrivan Duin for providing the input parameters of the ReaxFF force field for the two clay minerals in this study. The authors thank the two anonymous reviewers for their expert reviews of the original version of this article.

**DATA AVAILABILITY STATEMENT**

Research data not shared.

**ORCID**

Xiaoyu Song [https://orcid.org/0000-0003-0409-3761](https://orcid.org/0000-0003-0409-3761)

**REFERENCES**

1. Terzaghi K, Peck RB, Mesri G. *Soil Mechanics in Engineering Practice*. John Wiley & Sons; 1996.
2. Lambe TW, Whitman RV. *Soil Mechanics*. Vol 10. John Wiley & Sons; 1991.
3. Mitchell JK, Soga K. *Fundamentals of Soil Behavior*. Vol 3. John Wiley & Sons; 2005.
4. Lu N, Godt JW. *Hillslope Hydrology and Stability*. Cambridge University Press; 2013.
5. Gens A. Soil–environment interactions in geotechnical engineering. *Géotechnique*. 2010;60(1):3-74.
6. Menon S, Song X. Coupled analysis of desiccation cracking in unsaturated soils through a non-local mathematical formulation. *Geosciences*. 2019;9(10):428.
7. Alonso EE. Triggering and motion of landslides. *Géotechnique*. 2021;71(1):3-59.
8. Menon S, Song X. A computational periporomechanics model for localized failure in unsaturated porous media. *Comput Methods Appl Mech Eng*. 2021;384:113932.
9. Menon S, Song X. Computational multiphase periporomechanics for unguided cracking in unsaturated porous media. *Int J Numer Methods Eng*. 2022;123(12):2837-2871.
10. Menon S, Song X. Computational coupled large-deformation periporomechanics for dynamic failure and fracturing in variably saturated porous media. *Int J Numer Methods Eng*. 2023;124(1):80-118.
11. Likos WJ, Song X, Xiao M, Cerato A, Lu N. Fundamental challenges in unsaturated soil mechanics. In: *Geotechnical Fundamentals for Addressing New World Challenges*. Springer; 2019:209-236.
12. Tuller M, Or D, Dudley L.M. Adsorption and capillary condensation in porous media: liquid retention and interfacial configurations in angular pores. *Water Resour Res*. 1999;35(7):1949-1964.
13. Lu N, Khoshidian M. Mechanisms for soil-water retention and hysteresis at high suction range. *J Geotech Geoenvir Eng*. 2015;141(8):04015032.
14. Schoonheydt R, Johnston C. Surface and Interface Chemistry of Clay Minerals. *Developments in Clay Science*. Vol 1. 2006:87-113.
15. Martin RT. Adsorbed water on clay: a review. *Proceedings of the Ninth National Conference on Clays and Clay Minerals*. 1962:28-70.
16. Marry V, Turq P. Microscopic simulations of interlayer structure and dynamics in bihydrated heteroionic montmorillonites. *J Phys Chem B*. 2003;107(8):1832-1839.
17. Tunega D, Gerzabek MH, Lischka H. Ab initio molecular dynamics study of a monomolecular water layer on octahedral and tetrahedral kaolinite surfaces. *J Phys Chem B*. 2004;108(19):5930-5936.
18. Zhang Z, Song X. Nonequilibrium molecular dynamics (NEMD) modeling of nanoscale hydrodynamics of clay-water system at elevated temperature. *Int J Numer Anal Methods Geomech*. 2022;46:889-909.
19. Sposito G, Skipper NT, Sutton R, Park Sh, Soper AK, Greathouse JA. Surface geochemistry of the clay minerals. *Proc Natl Acad Sci*. 1999;96(7):3358-3364.
20. Lu N. Unsaturated soil mechanics: fundamental challenges, breakthroughs, and opportunities. *J Geotech Geoenvir Eng*. 2020;146(5):0252001.
21. Allen MP, Tildesley DJ. *Computer Simulation of Liquids*. Oxford University Press; 2017.
22. Frenkel D, Smit B. *Understanding Molecular Simulation: From Algorithms to Applications*. Vol. 1. Elsevier; 2001.
23. Plimpton S. Fast parallel algorithms for short-range molecular dynamics. *J Comput Phys*. 1995;117(1):1-19.
24. Song X, Wang MC. Molecular dynamics modeling of a partially saturated clay-water system at finite temperature. *Int J Numer Anal Methods Geomech*. 2019;43(13):2129-2146.
25. Cygan RT, Liang JJ, Kalinichev AG. Molecular models of hydroxide, oxyhydroxide, and clay phases and the development of a general force field. J Phys Chem B. 2004;108(4):1255-1266.
26. Song X, Wang MC, Zhang K. Molecular dynamics modeling of unsaturated clay-water systems at elevated temperature. In: Proceedings of the 7th International Conference on Unsaturated Soils 2018 (UNSAT2018). Ng CWW, Leung AK, Chiu ACF, Zhou C, eds. The Hong Kong University of Science and Technology; 2018.
27. Song X, Zhang Z. Determination of clay-water contact angle via molecular dynamics and deep-learning enhanced methods. Acta Geotech. 2021;17:1-15.
28. Zhang Z, Song X. Characterizing the impact of temperature on clay-water contact angle in geomaterials during extreme events by deep learning enhanced method. In: Geo-Extreme 2021. 2021:160-168.
29. Zhang Z, Song X. Nanoscale soil-water retention curve of unsaturated clay via md and machine learning. arXiv preprint arXiv:220104949. 2022.
30. Sato H, Ono K, Johnston CT, Yamagishi A. First-principles studies on the elastic constants of a 1:1 layered kaolinite mineral. Am Mineral. 2005;90(11-12):1824-1826.
31. Militzter B, Wenk HR, Stackhouse S, Stixrude L. First-principles calculation of the elastic moduli of sheet silicates and their application to shale anisotropy. Am Mineral. 2011;96(1):125-137.
32. Zartman GD, Liu H, Akdim B, Pachter R, Heinz H. Nanoscale tensile, shear, and failure properties of layered silicates as a function of cation density and stress. J Phys Chem C. 2010;114(4):1763-1772.
33. Teich-McGoldrick SL, Greathouse JA, Cygan RT. Molecular dynamics simulations of structural and mechanical properties of muscovite: pressure and temperature effects. J Phys Chem C. 2012;116(28):15099-15107.
34. Hantal G, Brochard L, Laubie H, et al. Atomic-scale modelling of elastic and failure properties of clays. Mol Phys. 2014;112(9-10):1294-1305.
35. Schmidt SR, Katti DR, Ghosh P, Katti KS. Evolution of mechanical response of sodium montmorillonite interlayer with increasing hydration by molecular dynamics. Langmuir. 2005;21(17):8069-8076.
36. Katti DR, Schmidt SR, Ghosh P, Katti KS. Molecular modeling of the mechanical behavior and interactions in dry and slightly hydrated sodium montmorillonite interlayer. Can Geotech J. 2007;44(4):425-435.
37. Ebrahimi D, Pellenq RJM, Whittle AJ. Nanoscale elastic properties of montmorillonite upon water adsorption. Langmuir. 2012;28(49):16855-16863.
38. Carrier B, Vandamme M, Pellenq RJM, Van Damme H. Elastic properties of swelling clay particles at finite temperature upon hydration. J Phys Chem C. 2014;118(17):8933-8943.
39. Qomi MA, Ebrahimi D, Bauchy M, Pellenq R, Ulm F. Methodology for estimation of nanoscale hardness via atomistic simulations. J Nanomechanics Micromechanics. 2017;7(4):04017011.
40. Jia X, Hao Y, Li P, Zhang X, Lu D. Nanoscale deformation and crack processes of kaolinite under water impact using molecular dynamics simulations. Appl Clay Sci. 2021;206:106071.
41. Zhang Z, Song X. Molecular dynamics modeling of cracks in dry clay sheets at the nanoscale. Comput Geotech. 2022;152:105037.
42. Brooks BR, Brooks III CL, Mackerell Jr., AD, et al. CHARMM: the biomolecular simulation program. J Comput Chem. 2009;30(10):1545-1614.
43. Pourreau M, Greathouse JA, Cygan RT, Kalinichev AG. Structure of hydrated kaolinite edge surfaces: DFT results and further development of the clayff classical force field with metal—O—H angle bending terms. J Phys Chem C. 2019;123(18):11628-11638.
44. Tersoff J. Empirical interatomic potential for carbon, with applications to amorphous carbon. Phys Rev Lett. 1988;61(25):2879.
45. Brenner DW. Empirical potential for hydrocarbons for use in simulating the chemical vapor deposition of diamond films. Phys Rev B. 1990;42(15):9458.
46. Brenner DW, Shenderova OA, Harrison JA, Stuart SJ, Ni B, Sinnott SB. A second-generation reactive empirical bond order (REBO) potential energy expression for hydrocarbons. J Phys: Condens Matter. 2002;14(4):783-802.
47. Van Duin AC, Dasgupta S, Lorant F, Goddard WA. ReaxFF: a reactive force field for hydrocarbons. J Phys Chem A. 2001;105(41):9396-9409.
48. Buehler MJ, Van Duin AC, Goddard III WA. Multiparadigm modeling of dynamical crack propagation in silicon using a reactive force field. Phys Rev Lett. 2006;96(9):095505.
49. Cranford SW, Buehler MJ. Mechanical properties of graphene. Carbon. 2011;49(13):4111-4121.
50. Zhang YA, Tao J, Chen X, Liu B. Mixed-pattern cracking in silica during stress corrosion: a reactive molecular dynamics simulation. Comput Mater Sci. 2014;82:237-243.
51. Hou D, Ma H, Zhu Y, Li Z. Calcium silicate hydrate from dry to saturated state: structure, dynamics and mechanical properties. Acta Mater. 2014;67:81-94.
52. Rimsza JM, Jones RE, Criscenti LJ. Crack propagation in silica from reactive classical molecular dynamics simulations. J Am Ceram Soc. 2018;101(4):1488-1499.
53. Pitman MC, Van Duin AC. Dynamics of confined reactive water in smectite clay–zeolite composites. J Am Chem Soc. 2012;134(6):3042-3053.
54. Skipper NT, Chang FRC, Sposito G. Monte Carlo simulation of interlayer molecular structure in swelling clay minerals. 1. Methodology. Clays Clay Miner. 1995;43(3):285-293.
55. van Duin A. Personal communications. 2022.
56. Van Duin AC, Strachan A, Stewman S, Zhang Q, Xu X, Goddard WA. ReaxFFSiO reactive force field for silicon and silicon oxide systems. J Phys Chem A. 2003;107(19):3803-3811.
57. Evans DJ, Holian BL. The nose–hoover thermostat. J Chem Phys. 1985;83(8):4069-4074.
58. Rappe AK, Goddard III WA. Charge equilibration for molecular dynamics simulations. J Phys Chem. 1991;95(8):3358-3363.
59. Zhou X, Zimmerman J, Reedy Jr., E, Moody N. Molecular dynamics simulation based cohesive surface representation of mixed mode fracture. Mech Mater. 2008;40(10):832-845.
60. Stukowski A. Visualization and analysis of atomistic simulation data with ovito—the open visualization tool. Modell Simul Mater Sci Eng. 2009;18(1):015012.
61. Marry V, Rotenberg B, Turq P. Structure and dynamics of water at a clay surface from molecular dynamics simulation. PCCP. 2008;10(32):4802-4813.
62. Siever R, Woodford N. Sorption of silica by clay minerals. Geochim Cosmochim Acta. 1973;37(8):1851-1880.
63. He H, Tao Q, Zhu J, Yuan P, Shen W, Yang S. Silylation of clay mineral surfaces. Appl Clay Sci. 2013;71:15-20.
64. Lee JH, Guggenheim S. Single crystal x-ray refinement of pyrophyllite-1Tc. Am Mineral. 1981;66(3-4):350-357.
65. Rice J, Paris P, Merkle J. Some further results of j-integral analysis and estimates. In: Progress in Flaw Growth and Fracture Toughness Testing. ASTM International; 1973.
66. Lakshmikantha MR. Experimental and Theoretical Analysis of Cracking in Drying Soils. 2009.
67. Chandler H. The use of non-linear fracture mechanics to study the fracture properties of soils. J Agric Eng Res. 1984;29(4):321-327.
68. Harison JA, Hardin BO, Mahboub K. Fracture toughness of compacted cohesive soils using ring test. J Geotech Eng. 1994;120(5):872-891.
69. Spray JG. Frictional melting processes in planetary materials: from hypervelocity impact to earthquakes. Annu Rev Earth Planet Sci. 2010;38:221-254.
70. Obreimoff J. The splitting strength of mica. Proc R Soc Lond Ser A, Contain Pap Math Phys Character. 1930;127(805):290-297.
71. Liu Y. Fracture toughness assessment of shales by nanoindentation. 2015.
72. Anderson TL. Fracture Mechanics: Fundamentals and Applications. CRC Press; 2017.

How to cite this article: Zhang Z, Song X. Nanoscale crack propagation in clay with water adsorption through reactive MD modeling. Int J Numer Anal Methods. 2023;47:1103–1133. https://doi.org/10.1002/nag.3507