INTRODUCTION
The physics and mechanics of unsaturated soils are important in geotechnical and geoenvironmental engineering (e.g., Gens, 2010; Fredlund, 2006; Alonso, 2021; Ng & Menzies, 2014). Soil-water retention/characteristic curve is a mathematical relationship between soil water content and matric suction (e.g., Brooks, 1965; Van Genuchten, 1980; Fredlund & Rahardjo, 1993; Fredlund & Xing, 1994; Cao et al., 2018). It is a fundamental constitutive law for modeling the physics and mechanics of unsaturated soils. For instance, soil water retention curve is required in modeling multiphase fluid flow, shear strength, deformation, and stress-strain relationships of unsaturated soils (e.g., Alonso et al., 1990; Gens & Alonso, 1992; Delage et al., 1996, 1998; Wheeler & Sivakumar, 1995; Wheeler et al., 2003; Gallipoli et al., 2003; Wheeler et al., 2002; Delage et al., 2008; Alonso et al., 2010; d’Onza et al., 2011; Niu et al., 2019; Molinero-Guerra et al., 2020).
In unsaturated soil mechanics or continuum-based numerical methods for modeling unsaturated soils, with no osmosis effect matric suction is usually assumed as capillary pressure, i.e., pore air pressure minus pore water pressure (e.g., Fredlund & Rahardjo, 1993; Alonso, 2021; Song et al., 2018a; Song & Menon, 2019; Menon & Song, 2020, 2021b; Song et al., 2017; Wang & Song, 2020; Menon & Song, 2021a), which ignores adsorptive pressure and soil-water interface effect. The adsorptive pressure might be ignored at high degree of saturation. However at low degree of saturation, it should be considered to interpret high matric suction (e.g., in the order of hundred mega pascals (e.g., Fredlund & Rahardjo, 1993; Lu & Likos, 2006). Furthermore, both experimental and theoretical studies have suggested that wetting-nonwetting (water-air) interface should be taken into account to better describe soil water retention curves of unsaturated soils (e.g., Fredlund & Morgenstern, 1977; Hassanizadeh & Gray, 1990; Joekar-Niasar et al., 2008; Lourenço et al., 2012; Lu & Likos, 2006; Likos, 2014; Fredlund, 2006). Fredlund & Morgenstern (1977) firstly incorporated interfaces into stress analysis of unsaturated soils where the air-water interface is treated as an independent phase. Lu & Likos (2006) lumped the interfacial effects into the suction stress in addition to capillary pressure. Nikooee et al. (2013) integrated interfacial energy and air-water specific interfacial area into effective stress tensor based on thermodynamic approach. Interfacial force arises due to the unbalanced force exerted on two sides of interfaces, which may influence the macroscopic soil behavior. Several physicochemical effects contribute to the origin of interface force, such as van der Waals forces, surface tension, and electric double layer forces. These interface forces could produce surface energy change and deformation of soil (Butt et al., 2013).

Over the past decades, computational modeling through physics-based numerical methods has gained success in resolving and quantifying water-air interface in porous media. One common method is the pore-network modeling technology (e.g., Lowry & Miller, 1995; Joekar-Niasar et al., 2008).
Several techniques have been also developed to measure water-air interfacial area in porous media (e.g., Costanza-Robinson & Brusseau, 2002; Chen & Kibbey, 2006; Wildenschild et al., 2002; Brusseau et al., 2007; Lourenço et al., 2012). However, the configuration of pore network is user-defined instead of the actual pore space in nature. However, it remains challenging to quantify the impact of adsorption on SWRC and explain the mechanism of soil-water adsorption at the nanoscale. At the nanoscale adsorptive forces in fine-grained clay become pronounced and could modify the water structure, e.g., adsorptive water film tightly attached to clay surface (Evans et al., 1986; Tuller et al., 1999). It is noted that the laboratory measurement techniques only suffice to account for capillary effects in the water retention mechanism (Likos et al., 2019). Indeed no viable experimental technique exists to quantify adsorption and its impact on SWRC in unsaturated soils at the nanoscale (Lu, 2016).

As a numerical method at the atomic scale, molecular dynamics can naturally consider adsorption at the nanoscale. With advances in high-performance supercomputers, molecular dynamics simulations have been extensively used to gain detailed insights into the physics and mechanics of unsaturated soils at the atomic scale (e.g., Cygan et al., 2004; Katti et al., 2015; Song & Zhang, 2021; Song et al., 2018b; Song & Wang, 2019; Zhang & Song, 2021). MD is a computational simulation technique that numerically solves Newton’s equations of a classical N-body system at equilibrium. It is a viable numerical tool to study the effect of soil-water interactions on the physics and mechanics of unsaturated soils. The strong interaction could cause a divergence from the bulk phase behavior of water. Examples include capillary condensation and solid-water adsorption (Shi & Dhir, 2009; Leroy & Müller-Plathe, 2010; Socchi et al., 2011; Botan et al., 2011). To the best of our knowledge, few studies have used MD simulations to investigate soil-water retention curves accounting for water-air interface and soil-water adsorption. In this article, molecular dynamics is utilized to study the impacts of water-air interface and soil-water adsorption on the nanoscale soil water retention mechanism at low degrees of saturation.

The area of water-air interface also called concave water meniscus is nontrivial to compute from the MD data. In this article, the point cloud method coupled with surface construction as detailed in Section 2 will be used to compute the area of water-air interface at different degrees of saturation (water mass content). Note that the surface reconstruction is a subject in computer graphics that deals with surface/shape properties of a point set, such as surface normal estimation (Boissonnat, 1984; Edelsbrunner & Mücke, 1994). Among various surface reconstruction techniques, alpha shape has been employed to characterize the shape of molecules like proteins (Peters et al., 1996; Liang et al., 1998). Wilson et al. (2009) validated the robustness and effectiveness of alpha shape method in characterizing the shapes of small molecules compared to other shape predictors. Singh et al. (1996) applied alpha shape method in molecular recognition and identified binding sites in proteins. Inspired by the broad applications in molecular biology, in this study the alpha shape method was utilized to calculate water-air interfacial area from the MD results.

Section 2 presents the adopted unsaturated clay model and the technique details of MD simulations, as well as the alpha shape method for the interfacing area calculation. Section 3 concerns the numerical results of water-air interface area, capillary and adsorptive pressures and conducts data analytics regarding adsorptive pressure and capillary pressure curves through machine-learning based curving fitting, followed by a short summary in Section 4.

MATERIAL MODEL AND METHODS

Pyrophyllite, a 2:1 clay mineral composed of silicon tetrahedral and aluminum octahedral layers, was chosen in this study. The aluminum octahedral (O) sheet is bounded by two opposing silicon tetrahedral (T) sheets, which forms a T-O-T structure. The chemical formula of pyrophyllite is $Al_2[Si_2O_5](OH)_2$. The unit cell of pyrophyllite has the dimensions of \(5.28 \times 9.14 \times 6.56\) Å in the x-y-z Cartesian coordinate system (Skipper et al., 1995). Figure 1 shows one unit cell of pyrophyllite made up of six types of atoms. In Figure 1, ao is aluminum in octahedral layer, ocl and hcl are oxygen and hydrogen in the octahedral layer that form the covalent bond, sz is silicon in tetrahedral layer, oss is oxygen in Si-O-Si linkages, and oas is oxygen in Si-O-Al linkages in the tetrahedral layer. Unlike other smectite clay minerals with a strong cation exchange capacity, pyrophyllite has a weak capacity to swell or shrink because of its neutral surface charge. Considering its structural stability, the clay particle is treated as a rigid body and its motion was frozen during simulation. Figure 2 shows the initial configuration of the clay-water model. Each clay layer consists of \(36 \times 21 \times 1\) unit cells in the x-y-z directions, which corresponds to \(190.08 \times 191.94\) Å in the x-y plane. Water is modeled by the TIP3P model (Jorgensen et al., 1983). Water molecule is considered as a rigid body during the simulation. The space between the parallel clay layers is \(d = 50\) Å, which could avoid any possible interlayer interactions between clay plates (Amarasinghe et al., 2014).
CHARMM force field (Brooks et al., 1983) is employed in this study to describe soil-water interaction in that CHARMM force field is compatible with the TIP3P water model (Berendsen et al., 1987). CHARMM force field has been widely utilized to study clay-water systems (Katti et al., 2015; Song & Wang, 2019). The non-bonded potential energy $U$ in CHARMM force field can be defined as

$$U = \sum_{i \neq j} 4\varepsilon_{ij} \left( \frac{R_{ij}}{r_{ij}} \right)^{12} - 2 \left( \frac{R_{ij}}{r_{ij}} \right)^6 + \sum_{i \neq j} \frac{q_i q_j}{4\pi \varepsilon_0 r_{ij}}$$

where $\varepsilon$ is the well-depth of Lennard-Jones (LJ) potential and $R$ is the distance at the minimum LJ interaction energy, $q_i$ and $q_j$ are the charge of atoms $i$ and $j$, respectively, $\varepsilon_0$ is the vacuum permittivity, $r_{ij}$ is the distance between atoms $i$ and $j$. In this study, clay particles are assumed immobilized and only non-bonded interactions between clay and water were simulated (Song et al., 2018b).

Table 1. Nonbonded parameters for CHARMM force field.

| Symbol | $q_i$ (e) | $\varepsilon_i$ (kcal/mol) | $R_i$ (Å) |
|--------|----------|---------------------------|----------|
| hw     | 0.417    | 0.046                     | 0.44     |
| ow     | -0.834   | 0.152                     | 3.53     |
| ocl    | -0.96    | 6                         | 2.8      |
| hcl    | 0.4      | 0.0001                    | 2.4      |
| oas    | -0.91    | 6                         | 2.8      |
| ss     | -0.7     | 1                         | 3        |
| sz     | 1.4      | 0.001                     | 7.4      |
| ao     | 1.68     | 0.15                      | 6.3      |

Fig. 4. Time evolution of potential energy during simulation.

All MD simulations were performed on LAMMPS, a large-scale atomic/molecular massively parallel simulator (Plimpton, 1995), using NVT ensemble at the temperature 298 K. Periodic boundary conditions were assigned in all directions. Water molecules were kept rigid using the SHAKE algorithm (Ryckaert et al., 1977). The velocity Verlet algorithm with a time step of 0.5 fs (1 fs = $1 \times 10^{-15}$ s) was employed to integrate the equations of motion of water. The simulation was first run for 2 ns to bring the system into equilibrium. Then the production simulation was run for 1 ns to output averaged water trajectories. The potential energy profile was monitored to check the equilibrium state. Figure 4 shows the time evolution of potential energy for clay-water system during the equilibration. It can be seen that the system reached a dynamic equilibrium after 0.6 ns.

In this study, mass water content or moisture content ($\theta_w$) was chosen to represent the degree of water saturation. Mass water content is defined as the ratio between the weight of water...
and the weight of solid.

\[ \theta_g = \frac{N_w M_w}{N_x N_y N_z M_p}, \]

where \( N_w \) is the total number of water molecules, \( M_w \approx 18 \) g/mol is the molar mass of water, \( M_p \approx 360 \) g/mol is the molar mass of pyrophyllite, and \( N_x = 36, N_y = 21, \) and \( N_z = 1 \) are the number of unit cells in the \( x, y \) and \( z \) directions, respectively.

The variation of mass water content was realized by adjusting the number of water molecules between the clay particles. The degree of saturation is calculated by

\[ S_r = \frac{\theta_g G_s}{\epsilon}, \]

where \( \epsilon \) is void ratio and \( G_s \) is specific gravity of dry clay. In molecular dynamics, the stress tensor can be expressed through the virial stress tensor (Clausius, 1870) as

\[ \sigma_{ij} = \frac{\sum_i m_i v_i v_j}{V} + \frac{\sum_i r_i f_{ij}}{V}, \]

where \( k \) is the atom index, \( N \) is the number of atoms in the system, \( V \) is the system volume, \( i = j = 1, 2, 3, \) and \( m_i, v_i, r_i \) and \( f_{ij} \) denote the mass, velocity, position and force of atom \( k \), respectively. The pore water pressure can be determined from equation (4) as

\[ p_w = \frac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{33}). \]

Next, the method for determining the water-air interface area will be introduced.

**Procedure of interfacial area calculation via alpha shape**

In this study, the point cloud concept and alpha shape method were adopted to determine the water-air interface area. Point clouds are commonly produced by 3D scanners which collect points on the external surfaces bounding the objects. In this work, the MD simulator functions as a 3-D scanner. Figure 5 illustrates the construction of a water point cloud based on trajectories of water molecule. Once the clay-water system reaches an equilibrium, we can obtain time-averaged trajectories of water molecules and convert the water body into a 3-D point cloud using the center-of-mass method (Song & Zhang, 2021). The coordinate of center-of-mass \( r \) of a water molecule can be expressed as

\[ r_e = \frac{\sum m_0 r_0 + m_h (r_{h1} + r_{h2})}{m_0 + 2m_h}, \]

where \( m \) and \( r = (x, y, z) \) denote the atomic mass and Cartesian coordinate system vector, and subscripts \( o \) and \( h \) stands for oxygen and hydrogen, respectively.

Having obtained the water point cloud, we reconstruct its surface using alpha shape method (Edelsbrunner & Mücke, 1994). The general idea is finding piece-wise triangles, (the so-called alpha shapes) to represent the surface of water point cloud. Figure 6 shows the schematic procedure of interfacial area calculation using the alpha shape method. We could define a point set \( A \) where each point represents the center-of-mass of one water molecule. Let \( B \) be an open ball with radius \( \alpha \). We restrict \( B \) to be empty such that it can occupy its space without enclosing any of the points of \( A \), i.e., \( B \cap A = \emptyset \). Let \( T = \{S_1, S_2, S_3\} \) be a subset of \( A \). Given \( T \), we could define a 2-simplex \( \Delta_T \) (i.e., a triangle) as the convex hull of \( T \). Here, convex hull is the smallest convex set that contains all points in \( T \) (Barber et al., 1996). The 2-simplex is said to be \( \alpha \)-exposed if \( T = \partial B \cap A \). Here \( \partial B \) is the boundary of \( B \).

For implementation, we first perform the Delaunay triangulation of the surface of the water point cloud and then define the alpha complex that associates Delaunay triangulation with the alpha shape (Edelsbrunner & Mücke, 1994). The algorithm adopted is summarized as follows.

a) Compute the Delaunay triangulation of \( A \), knowing that the boundary of \( \alpha \)-shape is contained in Delaunay triangulation.

b) Determine \( \alpha \)-complex by inspecting all simplices \( \Delta_T \) in Delaunay triangulation. If the circumsphere of \( \Delta_T \) is empty and the radius of circumsphere is smaller than \( \alpha \), we accept \( \Delta_T \) as a member of \( \alpha \)-complex.

c) All simplices on the boundary of \( \alpha \)-complex form the \( \alpha \)-shape.

In Figure 6 (2), the gray object is an empty open ball \( B \), the red sphere is the boundary \( \partial B \), and \( T = \partial B \cap A = \{S_1, S_2, S_3\} \). Meanwhile, we must have \( B \cap A = \emptyset \) and \( B \) is exterior to \( A \). The spherical cap is straightened by a 2-simplex/triangle connected by points \( S_1, S_2, \) and \( S_3 \). Thus, the alpha shape
of $A$ is the polytope whose boundary consists of all the 2-simplices/triangles. The interfacial area is the sum of the area of each boundary triangle. The parameter $\alpha$ controls the desired level of shape detail. We note that the critical $\alpha$ calculated by MATLAB is assumed as the value of parameter $\alpha$ in this study. It is the smallest alpha that produces an alpha shape with no inner cavities developed.

Figure 7 compares alpha shapes when $\alpha$ is equal to 2, 5, and 8 Å. Alpha smaller than the critical value produces cavities and unreasonable interfacial area. Figure 8 shows parameter (\(\alpha\)) sensitivity of wetting-nonwetting interfacial area. The results correspond to mass water content 29.1%. The critical alpha for this case is 4.9 Å. It can be found that $\alpha$ has little to no effect on interfacial area when $\alpha$ is greater than 5 Å. Thus, we assume $\alpha = 5$ Å in this study.

### NUMERICAL RESULTS

In this section, we present the numerical results of water-air interface area, capillary and adsorptive pressures and conduct data analytics regarding adsorptive pressure and capillary pressure curves through machine-learning based curve fitting.

Table 2 summarizes 24 MD simulations with corresponding adsorptive values of mass water content and degree of saturation. For each simulation, we computed pore-water pressure (capillary pressure and adsorptive pressure), water number density, interfacial area and interface thickness.

| Simulation number | $\theta_r$ (%) | $S_r$ (%) | Simulation number | $\theta_r$ (%) | $S_r$ (%) |
|-------------------|--------------|----------|-------------------|--------------|----------|
| 1                 | 6.2          | 2.3      | 2                 | 7.3          | 2.8      |
| 3                 | 8.4          | 3.2      | 4                 | 9.7          | 4.0      |
| 5                 | 11.0         | 4.7      | 6                 | 12.4         | 5.4      |
| 7                 | 13.9         | 6.1      | 8                 | 14.7         | 6.3      |
| 9                 | 15.5         | 6.9      | 10                | 17.2         | 7.6      |
| 11                | 18.1         | 8.0      | 12                | 19.0         | 8.5      |
| 13                | 20.8         | 9.5      | 14                | 22.7         | 10.5     |
| 15                | 24.8         | 10.6     | 16                | 26.9         | 12.0     |
| 17                | 27.9         | 12.6     | 18                | 29.1         | 13.6     |
| 19                | 31.3         | 14.7     | 20                | 32.5         | 15.1     |
| 21                | 33.7         | 16.0     | 22                | 34.9         | 16.2     |
| 23                | 36.2         | 17.3     | 24                | 37.4         | 17.4     |

**Adsorptive and capillary pressures at the nanoscale**

The water number density profile from the MD results is utilized to distinguish adsorption and capillarity in pore water. To do this, the nanopore space is evenly divided into a number of parallel layers along the $z$ direction. The number density of each layer is computed as the number of water molecules...
divided by the volume of the layer. We note that water number density is for describing water distribution rather than mass density in that the local mass density of water at the nanoscale deviates substantially with that of bulk water at the macroscale. Figure 9 shows the water number density profiles at various water contents. Despite the different magnitudes of number density, these density curves exhibit a similar mode: the first and second density peaks locate at a distance of 3.75 Å and 6.75 Å from clay surface (i.e., \( z_{\text{clay}} = \pm 25 \) Å), respectively. Further away from clay surface, water number density gradually decreases. At the center of the clay nanopore (i.e., \( z = 0 \)), water number density reaches the minimum value. The maximum number density is 2.36 \( \text{Å}^{-3} \) that is about three times the minimum number density (e.g., 0.73 \( \text{Å}^{-3} \) at \( \theta_g = 17.2\% \)). Large number density fluctuations in the vicinity of clay-water interface could indicate the strong effect of soil-water adsorption. It also results in the layered water structure. Based on number density distribution, the pore space could be partitioned into two regions, e.g., adsorptive region and capillary region. The adsorptive region starts from clay surface and extends to the trough after the second density peak in the number density profile. The pore space outside the adsorptive region is the capillary region where the capillary effect is dominant. The interface between two regions may be located at \( z = \pm 16.75 \) Å based on our MD simulations (see Figure 9).

Figure 10 plots the variation of percentages of adsorptive and capillary water pressures versus mass water content. Table 3 summarizes the percentages of adsorptive and capillary water pressure in the total pore water pressure at different mass water content. At low mass water content, e.g., \( \theta_g = 6.2\% \), the adsorptive water pressure occupies 62.9% of the total pore water pressure. As water content increases, the effect of adsorption is gradually weakened. When the mass water content is around 15%, the effect of adsorption and capillarity are similar. The percentage of adsorptive pressure fluctuates around 45% when mass water content exceeds 20% and capillarity becomes a dominant factor in the total negative pore water pressure (i.e., matric suction). It may be concluded from the MD results that the adsorption play a significant role in the soil water retention mechanism at low degree of saturation in clay.

To evaluate the adsorptive pressure from MD simulations, it was compared to that from an empirical formula (Tuller et al., 1999) that reads

\[
\phi_{\text{ads}} = \phi_{\text{vdw}} = \frac{A_H}{6rt^3} \tag{7}
\]

where \( A_H \) is the Hamaker constant and \( t \) is the thickness of adsorptive water layer. For a soil-water system, \( A_H \) is on the order of \( -10^{-20} \) to \( -10^{-19} \) Joules. In this work the value suggested by Or & Tuller (1999) \( A_H = -6 \times 10^{-20} \) J was adopted. From Figure 9 the thickness of adsorptive water layer \( t = 6.5 \) Å, e.g., the distance between the trough following the second peak density \( z = 16.75 \) Å and the outermost water layer \( z = 23.25 \) Å. From equation (7), we have \( \phi_{\text{ads}} = -11.59 \) MPa, which is close to the average adsorptive pressure \( P_{\text{ads}} = -11.90 \) MPa from our molecular simulations. This consistency may imply that the adsorption potential is dominated by van der Waals force at the nanoscale.
The pairwise energy and interaction force between clay and adsorptive water layer can be used to describe clay-water interactions. Pairwise energy includes van der Waals component and long-range Coulombic component. Since only adsorptive water is included, this energy term specifically refers to sorptive energy. Table 4 summarizes the sorptive energy between clay and adsorptive water at different mass water contents. Figure 11 plots the interaction force and mass water content. As mass water content increases from 9.7% to 34.9%, the magnitude of sorptive energy increases by 170% due to enriched adsorptive interactions.

Table 4. Sorptive energy between clay and adsorptive water at different mass water contents.

| θ_g (%) | Sorptive energy (kcal/mol) |
|---------|---------------------------|
| 9.7     | -263.9                    |
| 11.0    | -297.1                    |
| 12.4    | -328.3                    |
| 13.9    | -355.8                    |
| 14.7    | -371.3                    |
| 17.2    | -388.0                    |
| 18.1    | -424.2                    |
| 20.8    | -460.8                    |
| 27.9    | -597.5                    |
| 31.3    | -671.7                    |
| 34.9    | -721.5                    |

Fig. 11. Plot of adsorptive force versus mass water content.

Area and thickness of water-air interface at various mass water contents

The water-air interface area is computed through the method introduced in the previous section. Figure 12 shows the water point clouds for 6 simulations. Since clay particles were fixed, the height of soil water remains almost unchanged (h_w = 43.5 ± 0.1Å) and the soil water body expands along the radial direction with increasing mass water content. Figure 13 and Figure 14 present the schematic of water-air interface and clay-water interface, respectively. Figure 15 plots the water-air interface area versus water mass content. For comparison, the total interface area (i.e., summation of water-air interface area and water-soil interface area) and the water-soil interface area are also plotted. The total interface area increases from 9350 Å² to 31984 Å² as mass water content varies from 6.2% to 37.4%.

Both the water-air interface area and clay-water interface area show a nearly linear increase with mass water content. It can be found that clay-water interfacial area has a relatively larger growth rate than the water-air interface area with respect to the mass water content. The two curves for water-air and clay-water interface areas intercept at around θ_g = 20%.

The effectiveness of center-of-mass method in surface area calculation was evaluated by comparing the results with the ones from the original (default) water point cloud. The major difference between the two methods is the total number of points in the point cloud. In the default water point cloud, the total number of points is 3N_w and each atom determines the coordinate of the corresponding point. In the center-of-mass
water is defined as the water on the thickness of water change density to that the pore center along the and analyzed to avoid the effect of water clay the number MD simulations, we could determine interface thickness from method. Fig. 16. Comparison of water air interface area and soil-water interface area versus mass water content.

implementation, the total number of points is \(N_w\). Figure 16 compares the water-air interface area calculated from the COM based point cloud and default point cloud. The deviation is less than 0.1% for all mass water contents.

Fig. 16. Comparison of water-air interface area calculated via the center-of-mass (COM) method and the default water point cloud method.

The thickness of water-air interface is an important physical property of water-air interface (Fredlund, 2006). Based on our MD simulations, we could determine interface thickness from number density distribution of water in the middle plane of the clay pore. The water between the planes parallel to the clay surface at \(z = -0.5\) Å and \(z = 0.5\) Å were collected and analyzed to avoid the effect of water-clay interactions. Figure 17 present the number density distribution of water at the pore center along the \(x\) and \(y\) directions. It can be found that the water number density increases sharply from zero to a peak value near the clay surface. The first density peak is marked with a black circle in Figure 17. For example, a density jump up to 0.036 Å⁻² can be seen within a distance of \( \Delta x = 5\) Å at \(\theta_w = 37.4\%\). Since water density shows a significant change across the water-air interface, we assume that the thickness of water-interface is equal to the distance between the outermost water layer and the first density peak. Based on this assumption, the values of interfacial thickness at mass water contents 11.0%, 22.7%, and 37.4% are 5 Å, 5.5 Å, and 5.75 Å, respectively. Previous studies have shown that the thickness of water-air interface is in the order of 1.5-2 water molecular diameters, e.g., approximately 5 Å (Townsend & Rice, 1991; Fredlund & Rahardjo, 1993; Israelachvili, 2015). This consistency could imply that the water number density from our MD simulations is viable in determining the thickness of water-air interface in unsaturated clay.

Fig. 17. Water number density at the pore center along (a) the \(x\) - direction and (b) \(y\) - direction.

Soil-water retention curves incorporating adsorptive pressure through neural network fitting

The results of our MD simulations were analyzed to distinguish adsorption and capillarity in soil-water retention mechanism through neural network curve fitting. Figure 18 plots the apparent interfacial area versus mass water content. Here the apparent water-air interfacial area is defined as the water-air interfacial area per unit water volume. Figure 19 plots the total pore-water pressure versus mass water content. Figure 19 indicates that as mass water content increases from 6.2% to 37.4% (the degree of saturation from 2.3% to 17.4%) the total pore-water pressure decreases from -21.1 MPa to -27.5 MPa. As shown in Figure 18, the apparent interfacial area increases with the decrease of mass water content. For the mass water content in the range of 5% to 20% , the reduction of apparent interfacial area is from 0.147 Å⁻² to 0.070 Å⁻². It is noted that the \(A_w\)-\(\theta_w\) relationship obtained from MD simulation is
The neural network fitting toolbox in MATLAB (Demuth et al., 1992) was utilized in this study. For comparison, we also present the results from the traditional low-order polynomials curve fitting. Given the input and corresponding output, the neural network could predict an unknown model function without any knowledge about the structure of the function. This is the fundamental difference from the traditional curve fitting where a structure of polynomial is first assumed for the unknown model function. Figure 20 presents the architecture of a two-layer feed-forward neural network adopted for this study. With sigmoid hidden neurons and linear output neurons, the neural network allows to fit 2-dimensional mapping problems. The neural network is trained with Levenberg-Marquardt backpropagation algorithm (Moré, 1978). Input of the neural network is the vector of mass water content ($\theta_g$ or degree of saturation) or apparent interfacial area ($A_i$). Once received by the hidden layer and multiplication, they are passed to the neurons of the output layer. In the hidden layer, a neuron first computes the weighted sum of input vectors. Then, a constant bias is added to the weighted sum. Finally, the value is fed into the activation function to obtain the output. The operation in the hidden layer can be expressed as

$$Y = F_{act} \left( \sum (w \ast X) + b \right),$$

where $X$ and $Y$ are the input and output vectors, respectively, $w$ and $b$ are weights and bias, $F_{act}$ is the activation function in the form of a hyperbolic tangent sigmoid (Vogl et al., 1988). The computation in the output layer is similar to that in the previous hidden layer. This only difference is that the hyperbolic tangent sigmoid function is replaced with a linear function. Neurons of this type are commonly used in the output layer of multilayer networks used as function approximators (Demuth et al., 1992). The input vectors (e.g., mass water content or apparent interfacial area) and target vectors (MD data of the total matric suction, adsorptive pressure, or capillary pressure) are randomly divided into three groups. 90% of the input data will be used for training, 5% of the input data will be used to examine if the neural network is generalized to terminate training before overfitting. The remaining 5% input data is used as an independent test of the neural network generalization. Levenberg-Marquardt (L-M) (Moré, 1978) is used as the training algorithm. Training automatically stops when generalization stops improving, as indicated by an increase in the mean square error of the training samples. For example, given mass water content as the input, we train the neural network to map between mass water content (input) and capillary pressure (target output). For traditional curve fitting, the data was fitted to a second degree polynomial, i.e., $P_{\text{cap}} = a(\theta_g)^2 + b\theta_g + c$, and the parameters were obtained through the least squares method.

The results are presented in Figures 21, 22, 23, and 24. In these figures, blue dots represent original output from MD simulations. Red square points are trained output from neural network and used to predict the retention curve. Green dash line is fitted from the second degree polynomial. Figure 21 shows the relationship between adsorptive water pressure and mass water content. We can divide the curve into three parts based on the range of water mass content, i.e., part 1 - $\theta_g < 12\%$, part 2 - $12\% < \theta_g < 18\%$, and part 3 - $\theta_g > 20\%$. The average adsorptive water pressure in part 1 is -13.5 MPa. It is found that the adsorptive pressure reaches the peak value (-10.5 MPa) at the mass water content of 18%. As water content continues to increase, the adsorptive pressure decreases in part 3. The mean square error of neural network fitting is 0.28 that is much smaller than the value of polynomial curving fitting, 0.659. Thus, the curve fitted using neural network could faithfully represent the relationship between adsorptive pressure and mass water content. Furthermore, it can be observed from the results in Figures 21, 22, 23, and 24 that polynomial curve fitting significantly simplifies the local features of the curve.

Figure 22 presents the variation of capillary pressure versus mass water content. It can be found that capillary pressure first experiences a relatively stable stage when mass water content is less than 12%. Capillary pressure keeps decreasing until $\theta_g$
Fig. 20. Architecture of two-layer feed-forward network.

= 22%, followed by a stable stage. Figure 23 and Figure 24 present the variations of adsorptive pressure and capillary pressure with respect to apparent interfacial area, respectively. The results Figure 23 show that the maximum adsorptive pressure occurs at $A_r=0.072 \, \text{Å}^{-1}$. Then the adsorptive pressure decreases with respect to the apparent interfacial area. By contrast, as shown in Figure 24 capillary pressure increases continuously with the increase of apparent interfacial area. A plateau has reached when the apparent interfacial area is larger than 0.11 Å$^{-1}$. Finally, Figure 25 presents the predicted matric suction from the MD results using the neural network fitting technique. The results show that from the MD results the neural network fitting function can be used to predict the total matric suction at given water mass content and apparent interfacial area.

Fig. 21. Variation of adsorptive water pressure versus mass water content.

Fig. 22. Variation of capillary water pressure versus mass water content.

Fig. 23. Variation of adsorptive water pressure versus apparent interfacial area.

Fig. 24. Variation of capillary water pressure versus apparent interfacial area.

Fig. 25. Matric suction at sampled water mass content and apparent interfacial area predicted by the neural network curve fitting function.

SUMMARY
We have conducted MD simulations to investigate soil-water adsorptive and capillary mechanism of clay. The MD model
consists of two parallel clay plates and water confined in the clay nanopore. MD simulations were performed at low mass water content. To analyze the MD results, soil water was represented by a point cloud through the center-of-mass method. Water-air interfacial area was calculated using alpha shape method. Adsorption is considered by distinguishing adsorptive pressure from capillary pressure. The nanoscale soil-water retention curves were plotted in terms of mass water content, apparent interfacial area, and the total matric suction including adsorptive pressure and capillary pressure. Machine learning based curve fitting technique was utilized to plot the adsorptive pressure and capillary pressure curves versus mass water content and apparent interfacial area respectively. The trained neural network generates fitted adsorptive pressure and capillary pressure curves that more faithfully represent MD data than the traditional polynomial curve fitting. The MD results have demonstrated that at low mass water content, adsorption is the dominant mechanism on soil water retention. For instance, the adsorptive water pressure accounts for more than 60% of the total pore-water pressure at low mass water content (or low degree of saturation). The apparent interfacial area (water-air interfacial area per unit water volume) decreases during the imbibition of water. The numerical results also showed that adsorption potential is mainly dominated by van der Waals forces at the nanoscale.

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DATA AVAILABILITY STATEMENT
The data that support the findings of this study are available from the corresponding author, X. S., upon reasonable request.

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