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# Effects of adsorptive water on the rupture of nanoscale liquid bridges

Chao Zhang<sup>a</sup>, Zhen Liu<sup>b,\*</sup>, Yi Dong<sup>c</sup>

<sup>a</sup> Department of Civil and Environmental Engineering, Michigan Technological University, Houghton, MI 49931, USA

<sup>b</sup> Department of Civil and Environmental Engineering, Michigan Technological University, Houghton, MI 49931, USA

<sup>c</sup> State Key Laboratory of Geomechanics and Geotechnical Engineering, Institute of Rock and Soil Mechanics, Chinese Academy of Sciences, Wuhan, 430071, China

### A R T I C L E I N F O

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## ABSTRACT

The mechanical behavior of liquid bridges has not been thoroughly understood especially at the nanoscale, and the macroscopic solution may not apply to nanoscale liquid bridges. Among possible analysis approaches, molecular dynamics simulation enables investigations of complex physicochemical processes at an atomistic resolution, which is directly built on the fundamental inter- and intra-molecular forces. In this study, molecular dynamics simulation is employed to investigate the mechanical behavior of the liquid bridge between two soil mineral disk particles under tensile loadings. To reveal the dominant physical mechanisms, a series of parametric studies was conducted considering different mineral types, initial inter-particle distances, and water volumes. It was found that the interplay of adsorption and capillarity, which is overlooked in the macroscopic solution, is substantial at the nanoscale.

#### 1. Introduction

Liquid bridges are ubiquitous in granular materials with low degrees of water saturation, e.g., between sand particles and plate clay particles, as shown in Fig. 1a and b. The liquid-air interfaces recede with decreasing degree of saturation until the liquid phase becomes isolated or discontinuous, and then capillarity becomes dominant in the particlewater interactions. The capillary forces exerted by liquid bridges are a primary source of cohesion of granular materials (Mitarai and Nori, 2006), substantially altering their mechanical properties. Therefore, the capillary forces from liquid bridges are common and important in many engineering and science areas, e.g. geotechnical engineering (Lu and Likos, 2004), food process engineering (Peleg, 1977), and medicine (Alencar et al., 2001).

In geotechnical engineering, capillary forces exerted by liquid bridges are among the major physical mechanisms contributing to the tensile strength of soils (Lu and Likos, 2006; Lu et al., 2007). An exact force-inter-particle distance relationship for the liquid bridges between soil particles is required to understand and predict the mechanical behavior of granular soils. For instances, various constitutive models have been proposed for liquid bridges to implement with the discrete element methods (El Shamy and Gröger, 2008; Scholtès et al., 2009; Soulié et al., 2006) with the emerging of the particle level simulation techniques (Cundall and Strack, 1979). From the macroscopic viewpoint, liquid bridges are regarded as a continuum and based on that, a theoretical solution (referred as "macroscopic solution" in the rest of this paper) has been formulated to quantify the capillary forces from liquid bridges (Rowlinson and Widom, 2013). The capillary forces from liquid bridges are composed of two components, i.e. the negative water pressure and the surface tension (Fortes, 1982). The Young-Laplace equation (Laplace, 1806; Young, 1805) is frequently used to relate the negative water pressure to the surface tension. However, it still remains obscure whether the macroscopic solution applies to nanoscale liquid bridges which are prevalent in silty and clayey soils. At the nanoscale, adsorption becomes manifest, and water tends to behave as discrete layers (or even particles) rather than a continuum. Therefore, the macroscopic solution may not be able to fully capture the mechanical behavior of liquid bridges.

Molecular Dynamics (MD) simulation makes it possible to model complex physicochemical processes at an atomistic scale resolution. In recent years, some researchers in soil-related communities have explored complex soil behaviors using MD (Bourg and Sposito, 2010; Bourg and Sposito, 2011; Ichikawa et al., 1999; Katti et al., 2005a; Katti et al., 2005b, 2007; Katti et al., 2015; Zhang et al., 2016a; Zhang et al., 2016b). Most of these studies focused on the clay behaviors under various external conditions. As for the liquid bridge, the meniscus of the capillary water between soil particles have already been investigated via MD simulations. For instance, Amarasinghe and Anandarajah (2011; Anandarajah and Amarasinghe, 2011) employed MD simulations to study the effects of fabric variables on the capillary water meniscus and utilized the simulation results to interpret the hysteresis of fine-grained soils. Amarasinghe et al. (2014) used MD simulations to

\* Corresponding author. E-mail addresses: chao@mtu.edu (C. Zhang), zhenl@mtu.edu (Z. Liu), ydong@mines.edu (Y. Dong).

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**Fig. 1.** Schematic of soil-water interaction in the pendular regime for (a) sandy particles, (b) clay particles, and (c) simplified conceptual model of the liquid bridge at contact.

investigate the capillary forces between pyrophyllite particles. However, to date, no MD studies has been directed to the understanding of the mechanical properties of liquid bridges between soil particles under tensile loadings.

In this study, nanoscale liquid bridges between soil disk particles were investigated via molecular dynamics to investigate the possible limitations and deviations of the macroscopic solution. At first, the capillary force of a liquid bridge between two disk particles was formulated using the macroscopic solution. Then, MD simulation is explored for its use in understanding the mechanical performance of such liquid bridges at the nanoscale. A series of parametric studies was conducted to investigate the effects of the mineral type, initial interparticle distance and liquid water volume on the mechanical behavior of liquid bridges. At last, MD simulation results were compared with the results calculated with the macroscopic solution to highlight possible limitations and deviations of the macroscopic solution.

#### 2. Macroscopic solution

In this section, the liquid bridge between soil particles was formulated using continuum theories to prepare for the later comparisons between MD simulations and the macroscopic solution. The geometry of the liquid bridge of interest was simplified into a physical model illustrated in Fig. 1c. Water is retained between two parallel solid plates with a contact angle of  $\theta$ , a distance between plates of D, and a spreading length of  $l_w$ . The configuration in Fig. 1c can represent two types of liquid bridges (Fortes, 1982): (1) the axisymmetric liquid bridge or  $\theta$  liquid bridge, in which the plates are infinite, and the boundary condition is the contact angle between the liquid and the plates,  $\theta$ , and the spread length,  $l_w = 2r$ ; and (2) cylindrical symmetric liquid bridge or r liquid bridge, in which the plates are circular with a radius of r and the liquid touches the plates. This study focuses on the  $\theta$ liquid bridge which is easier to model with the periodic and infinite boundary condition in MD simulation.

The  $\theta$  liquid bridge can be further divided into four symmetric regions in a 2D *x*–*z* Cartesian coordinate system by placing the origin at the center of the liquid bridge. This allows considering the region of "0123" to evaluate the capillary force, where *x*(*z*) is a function to describe the profile of liquid-air interface. The coordinates of the other three corner points can be identified as 1 (*x*<sub>e</sub>, 0), 2 (*r*, *d*), and 3 (0, *d*). At point 1 (*x*<sub>e</sub>, 0), the slope of *x*(*z*) is a known boundary condition equal to zero (i.e., *x*(0) = 0). For any given liquid bridge profile, the volume of the water can be determined by any combinations of two parameters out of *r*, *d*, and  $\theta$ . For the  $\theta$  liquid bridge, the volume of water (*V*) is defined as the unit volume per length of the plate.

With the assumption of negligible gravitational distortion, the equilibrium shape of the liquid bridge can be determined by minimizing the Helmholtz free energy in a closed solid-liquid-air system (De Bisschop and Rigole, 1982; Fortes, 1982; Truong et al., 2011). In a 2D x-z Cartesian coordination system with an interface profile of liquid bridge x(z), the total Helmholtz free energy (H) of this system in unit length can be expressed as (De Bisschop and Rigole, 1982):

$$H = 4 \int_0^d \left[ \gamma_{\rm la} \cdot (1 + x'^2)^{0.5} + P_{\rm a} \cdot x (1 + x'^2)^{0.5} \right] dz + (\gamma_{\rm sl} - \gamma_{\rm sa}) r \tag{1}$$

where  $\gamma_{la}$ ,  $\gamma_{sl}$ ,  $\gamma_{sa}$ , are the surface tensions of liquid-air, solid-liquid, and solid-air interfaces respectively; and  $P_a$  is the air pressure. Eq. (1) consists of three components: surface free energy on the liquid-air interface, surface free energy on the solid-liquid interface, and the free energy of the liquid body. The liquid profile x(z) meets the requirement of minimizing the total free energy (*H*) under the constraint condition of a constant volume of the liquid bridge (*V*) as:

$$V = 4 \int_0^d \left[ x \cdot (1 + x'^2)^{0.5} \right] dz$$
<sup>(2)</sup>

The minimization of the total free energy is essentially a problem of conditional variation with movable boundaries and can be solved by introducing an additional constraint of Young-Laplace equation (Adamson and Gast, 1997):

$$\gamma_{\rm la} \left(1 + x'^2\right)^{-1.5} \left(-x'' + \frac{1 + x'^2}{x}\right) = -\Delta P = P_{\rm w} - P_{\rm a}$$
(3)

where  $P_a$  and  $P_w$  are the pressures of air and water, respectively. Eqs. (1), (2) and (3) formed a governing equation set which can be solved numerically to determine the liquid bridge profile. Following Lian et al. (1993), the modified Euler method was selected to numerically solve Eqs. (1), (2) and (3).

An attractive or repulsive force is needed to sustain the liquid bridge between parallel plates at a given separation D = 2d in equilibrium, depending on the surface wettability or contact angle. Given the exact liquid bridge profile, the applied force (*F*) can be calculated as (Fortes, 1982):

$$F = \Delta P \cdot \pi r^2 + \gamma_{\rm la} \cdot \sin \theta \cdot 2\pi r \tag{4}$$

In Eq. (4), the force consists of two components: one due to the pressure difference across the curved liquid-air interface and the other term resulting from the surface tension exerted by the liquid-air interface. To better interpret the results from this macroscopic solution and its comparisons with MD simulations, the key quantities such as liquid volume, separation distance, and forces were normalized into relative variables:

$$V^* = \frac{V}{\pi r^3} \tag{5}$$

$$d^* = \frac{d}{V^{1/3}} \tag{6}$$

$$F^* = \frac{F}{\pi \gamma_{\rm la} V^{1/3}}$$
(7)

where  $V^*$ ,  $d^*$ , and  $F^*$  are normalized volume, distance, and capillary force, respectively. A numerical solution of the governing equations for x(z) may not exist for a given contact angle and liquid volume when the distance of plate increases beyond a critical point. This critical point was considered as the rupture of the liquid bridge.

#### 3. Molecular dynamics simulation

#### 3.1. Atomistic structures and force field

In sands and silts, the most common minerals are quartz, feldspar, and mica (Mitchell and Soga, 2005). The wettability of these minerals

#### Table 1

Lattice parameters and contact angles of the selected soil minerals.

Mineral type	Chemical formula	Lattice parameters <sup>d</sup>						Contact angle <sup>e</sup> [°]
		a [Å]	b [Å]	c [Å]	α [°]	β [°]	γ [°]	
α-quartz <sup>a</sup> Orthoclase <sup>b</sup> Muscovite <sup>c</sup>	SiO <sub>2</sub> KSi <sub>3</sub> Al <sub>3</sub> O <sub>12</sub> H <sub>12</sub> KSi <sub>3</sub> AlO <sub>8</sub>	4.916 8.544 5.199	4.916 13.03 9.027	5.405 7.195 20.106	90 90 90	90 115.68 95.782	120 90 90	29 36 116

<sup>a</sup> Levien et al. (1980).

<sup>b</sup> Tseng et al. (1995).

<sup>c</sup> Richardson and Richardson (1982).

<sup>d</sup> Lengths of the unit cell edges (*a*, *b* and *c*) and the angles between them ( $\alpha$ ,  $\beta$ , and  $\gamma$ ).

<sup>e</sup> MD simulation results from Zhang et al. (2016b).

was studied in a recent study of the authors (Zhang et al., 2016b), revealing that their wettability was quite different from each other. As a result, the liquid bridge profile is expected to vary with the soil mineral types. Accordingly, the liquid bridge force varies with the soil mineral types. Due to this consideration, it is important to account for the properties of local soil particles when one performs microscale simulations such as those with discrete element methods. Herein, the effects of the soil mineral types on the capillary force were investigated via MD simulations on the three common minerals, i.e.,  $\alpha$ -quartz, orthoclase and muscovite. The lattice parameters and contact angles of these three soil minerals have been well determined (Levien et al., 1980; Richardson and Richardson, 1982; Tseng et al., 1995; Zhang et al., 2016b), which are summarized in Table 1.

A force field is a fundamental relationship for molecular systems. Such a force field is usually expressed as a set of functions and parameters to describe interatomic potentials mathematically. The current study focused on the liquid bridge between soil mineral disk particles which is composed of soil minerals and water. In such a simulation system, three groups of interatomic interactions need to be taken into consideration: the mineral-mineral interaction, the mineral-water interaction, and the water-water interaction. Herein, the first two groups of interactions were formulated using non-bonded interaction potentials ( $U_{\rm nb}$ ), and the last group of interaction was formulated using conventional water models ( $U_{\rm w}$ ) [32]. Therefore, the total potential energy ( $U_{\rm total}$ ) can be expressed as:

$$U_{\text{total}} = U_{\text{nb}} + U_{\text{w}} \tag{8}$$

#### 3.1.1. Interaction among mineral and water

In terms of the non-bonded interaction, the interatomic potential energy is expressed as a combination of the Coulombic interaction energy ( $U_{\text{coul}}$ ) and the van der Waals interaction energy ( $U_{\text{vdW}}$ ):

$$U_{nb} = U_{\text{Coul}} + U_{\text{vdw}} = \frac{e^2}{4\pi\varepsilon_0} \sum_{i\neq j} \frac{q_i q_j}{r_{ij}} + \sum_{i\neq j} 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right) - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right]$$
(9)

where  $q_i$  and  $q_j$  are partial charges of atom *i* and *j*, respectively;  $\varepsilon_0$  is the dielectric permittivity of vacuum, i.e. 8.85419 × 10<sup>-12</sup>; *e* is the charge of the electron;  $r_{ij}$  is the distance between atom *i* and *j*;  $\varepsilon_{ij}$  is the characteristic energy; and  $\sigma_{ij}$  is the distance corresponding to the minimal interaction energy. As for the interactions between different atomic species *i* and *j*, the values of  $\varepsilon_{ij}$  and  $\sigma_{ij}$  were calculated according to the Lorentz-Bertholet mixing rule as (Allen and Tildesley, 1989):

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}, \, \sigma_{ij} = \frac{1}{2} (\sigma_i + \sigma_j) \tag{10}$$

In Eq. (9), the non-bonded interaction is determined by the parameters  $q_i$  and  $q_j$ ,  $\varepsilon_{ij}$  and  $\sigma_{ij}$ . In general, the partial charges  $q_i$  and  $q_j$  are derived from quantum calculations while the parameters  $\varepsilon_{ij}$  and  $\sigma_{ij}$  are determined by empirically fitting to physical and structural properties (Cygan et al., 2004). A number of values were reported for these parameters in different models (Cygan et al., 2004; Lopes et al., 2006). Among these models, the ClayFF force field model has been successfully employed to simulate quartz (Skelton and Fenter, 2011) and muscovite (Teich-McGoldrick et al., 2012). Therefore, the values of  $q_i$  and  $q_j$ ,  $e_{ij}$ and  $\sigma_{ij}$  were adopted from the ClayFF force field (Cygan et al., 2004) for simulating  $\alpha$ -quartz and muscovite. For orthoclase, the ClayFF force field cannot make the simulation system charge neutral and consequently will result in simulation errors. Hence, the ClayFF force field is not applicable for modeling orthoclase in MD simulations. Kerisit et al. (2008) modified these parameters in the ClayFF force field to enable the simulation of orthoclase. These modified parameters were adopted in the simulations of orthoclase in this study.

#### 3.1.2. Interaction among water molecules

Various water models have been proposed for the water-water interaction (e.g., Simple Point Charge model (Berendsen et al., 1981), Extended Simple Point Charge (SPC/E) model (Berendsen et al., 1987), 3-Point Transferable Intermolecular Potential model, and 4-Point Transferable Intermolecular Potential model (Jorgensen et al., 1983)). Šolc et al. (2011) investigated the contact angle of kaolinite with different water models and found that the simulated contact angle was insensitive to the selection of water models. Therefore, the SPC/E model was adopted to be consistent with the ClayFF force field. The interaction potential for the SPC/E water model can be expressed as (Cygan et al., 2004):

$$U_{\rm w} = U_{\rm Coul} + U_{\rm vdW} + U_{\rm bond\ stretch} + U_{\rm angle\ bend} = U_{\rm Coul} + U_{\rm vdW}$$
$$+ k_1 (r_{ij} - r_0)^2 + k_2 (\theta_{ijk} - \theta_0)^2$$
(11)

where the expressions of  $U_{\text{Coul}}$  and  $U_{\text{vdW}}$  are identical to those in Eq. (9);  $U_{\text{bond stretch}}$  is the bond stretch energy;  $U_{\text{angle bend}}$  is the angle bend energy;  $k_1$  and  $k_2$  are force constants;  $r_0$  is the equilibrium bond length;  $\theta_{ijk}$  is the bond angle for the hydrogen-oxygen-hydrogen; and  $\theta_0$  is the equilibrium bond angle.

#### 3.2. Initial configuration

As illustrated in Fig. 2, the initial liquid bridge system includes two parallel soil mineral substrates and a rectangular bulk water body between them. The dimensions of the simulation box were set as  $200 \times 20 \times (160 + D)$  Å<sup>3</sup> and adjusted to ensure the integrity of



Fig. 2. Initial configuration of the liquid bridge system.

crystal cells of the soil mineral. The dimensions of mineral substrates were selected as  $200 \times 20 \times 20$  Å<sup>3</sup> while those of the bulk water body were  $l_w \times (20-3.1) \times (D - 3.1)$  Å<sup>3</sup>. The dimensions of the liquid bridge system in the *x*- and *y*- directions were identical to those of the simulation box while its dimension of in the *z*- direction was 120 Å smaller than that of the simulation box. The liquid bridge system was placed at the center of the simulation box in the *z*- direction. The extra space in the *z*- direction of the simulation box was reserved for the increase in the distance between plates.

The soil mineral substrates were modeled through stacking soil mineral crystal unit cells, which are summarized in Table 1, to match the dimensions of  $200 \times 20 \times 20$  Å<sup>3</sup>. Then, the two soil mineral substrates were placed in parallel with each other with an inter-particle distance of *D*. The isomorphous substitution in orthoclase and muscovite makes this process more complicated. Herein, the isomorphous substitution was tackled by assuming that it is uniformly distributed in the soil mineral substrates (Zhang et al., 2016b).

A molecular system involving water molecules is usually very sensitive to the initial configuration of the water. A bad initial configuration of the water molecules may cause simulation errors or convergence problems. This issue was tackled with a numerical tool called Packing Optimization for Molecular Dynamics Simulations (PACKMOL) (Martínez et al., 2009) which could generate configurations of water molecules suitable for MD simulations. The dimensions of the water body in the *y*- and *z*- directions are 3.1 Å shorter than those of the initial inter-particle distance ( $D_{initial}$ ) and the simulation box, respectively, to avoid an excessively short distance between water molecules and mineral atoms. The number of water molecules was determined by ensuring that the water body exhibits a density identical to that of bulk liquid water.

In addition to the mineral type, the influences of the initial interparticle distance and the water volume were analyzed through a series of MD simulations. The parametric settings for all the simulation cases were summarized in Table 2. In Simulations No. 1–3, the mineral type varied from  $\alpha$ -quartz, orthoclase to muscovite with  $D_{\text{initial}} = 30$  Å and  $D_{\text{initial}} \times l_{\text{w}} = 1800$  Å<sup>2</sup> to analyze the influence of mineral type. In Simulations No. 1 and 4–6,  $D_{\text{initial}}$  varied from 20 Å, 30 Å, 40 Å to 50 Å with  $\alpha$ -quartz and  $D_{\text{initial}} \times l_{\text{w}} = 1800$  Å<sup>2</sup> to analyze the influence of the initial inter-particle distance. In Simulations No. 1 and 7–9,  $D_{\text{initial}} \times l_{\text{w}}$  varied from 1500 Å<sup>2</sup>, 1800 Å<sup>2</sup> to 2400 Å<sup>2</sup> with  $\alpha$ -quartz and  $D_{\text{initial}} = 30$  Å to analyze the influence of the water volume.

#### 3.3. Simulation details

In order to prepare a stable initial liquid bridge system, the liquid bridge system was first equilibrated for 1.0 ns under an *NVT* ensemble (i.e., constant number, volume, and temperature) with a temperature of 300 K. Then, the liquid bridge systems were subjected to tensile

#### Table 2

Parametric settings for molecular dynamics simulations and corresponding meniscus contact angles.

Simulation No.	Mineral type	Initial Conf	figuration	Equilibrium state	
		D <sub>initial</sub> [Å]	<i>l</i> w [Å]	Contact angle [°]	
1	α-quartz	30	60	29	
2	Orthoclase	30	60	34	
3	Muscovite	30	60	86	
4	α-quartz	20	90	28	
1	α-quartz	30	60	29	
5	α-quartz	40	45	52	
6	α-quartz	50	36	66	
7	α-quartz	30	50	34	
1	α-quartz	30	60	29	
8	α-quartz	30	70	29	
9	$\alpha$ -quartz	30	80	29	

loadings with a step by step displacement-controlled loading scheme in the z-direction. Every step consists of two subsequent stages: loading stage and equilibrium stage. During the loading stage, the upper (upwards) and lower (downwards) soil mineral slabs were moved simultaneously. The velocity of movement was set as  $1.0 \times 10^{-5}$  Å/fs. The loading process was run for 0.1 ns. Thus, the inter-particle distance increased by 2 Å in every step. Then, the liquid bridge system was equilibrated for 2 ns during the equilibrium stage. The capillary force between the water and the soil mineral particles was recorded during the last 1 ns of the equilibrium stage. This process was repeated until the rupture of the liquid bridge. The inter-particle distance in the last step is regarded as the rupture distance of the liquid bridge system.

MD simulations were conducted with the Large-scale Atomic/ Molecular Massively Parallel Simulator (LAMMPS) (Plimpton, 1995; Plimpton et al., 2007) and visualized with the Open Visualization Tool (OVITO) (Stukowski, 2010). The van der Waals interactions were truncated to 12 Å, while the long-range Coulombic forces were calculated using the Particle-Particle Particle-Mesh (PPPM) method (Hockney and Eastwood, 1988) with an accuracy of 99.99%. Water molecules were kept rigid by using the SHAKE algorithm (Ryckaert et al., 1977) to reduce computational costs. The movements of soil mineral atoms were fixed to reduce the computational cost as suggested in Amarasinghe and Anandarajah (2011). Newton's equations of motion were integrated with a time step of 1.0 fs.

#### 4. Density profiles and contact angles

According to the ergodic hypothesis, the MD simulation system will visit all the states in the phase space with sufficient running time. The statistical weights of these states are consistent with the macroscopic variables imposed through ensembles (Tadmor and Miller, 2011). Therefore, it is feasible to compute the macroscopic variables using time average profiles over a time,  $\Delta t$ , that is long enough. The fact that the total potential energy of the simulated systems kept fluctuating around a particular value after 1.0 ns suggests a calibrated time of 1.0 ns. The clear and smooth liquid-air interfaces observed in Figs. 3–5 further proved that  $\Delta t = 1.0$  ns is sufficient to compute the macroscopic variables. The trajectories of water atoms in the last 1.0 ns were recorded to compute time average density profiles.

Fig. 3 presents the snapshots of the liquid bridge systems for different soil minerals (Simulations No. 1, 2 and 3 for  $\alpha$ -quartz, orthoclase, and muscovite, respectively). As a result of free energy minimization, the artificial rectangular water bodies in the initial configuration evolved and formed curved liquid-air interfaces connecting the two mineral substrates. The corresponding time average density profiles for Simulations No. 1, 2 and 3 were obtained following Zhang et al. (2016b). This helped determine the contact point precisely and consequently an accurate contact angle for each mineral. The light color on the liquid-air interface suggests the dynamic balance between the evaporation and condensation of the water molecules across the phase boundary. A thin layer of dark color attached to the mineral surface indicated that the strong interaction between the mineral atoms and adjacent water molecules pulls the molecules tightly together, resulting in a water density of larger than 2.0 g/cm<sup>3</sup>.

Contact angles can be determined by fitting physically-based equations to the time average density profiles [28]. The calculated contact angles are 29° for  $\alpha$ -quartz, 34° for orthoclase, and 86° for muscovite, indicating that  $\alpha$ -quartz and orthoclase are hydrophilic, and muscovite is more or less between hydrophilic and hydrophobic. These contact angles are different from the contact angles measured through placing water droplets on solid substrates (as listed in Table 1). For clarity, the contact angle in these two conditions were differentiated as (a) meniscus contact angle (Table 2) and (b) sessile-droplet contact angles are smaller than the corresponding sessile-droplet contact angles. This decrease is attributed to the change of soil fabrics (Amarasinghe and



Fig. 3. Snapshots of the equilibrated liquid bridge systems (left) and time average density profiles of the liquid bridges (right) between plates of different soil minerals: (a) α-quartz, (b) orthoclase, and (c) muscovite.

Anandarajah, 2011). The values of the meniscus contact angles and sessile-droplet contact angles are very close for  $\alpha$ -quartz and orthoclase. This indicates that soil fabrics have limited effects on the contact angles of these minerals, which agrees with the observation of Amarasinghe and Anandarajah (2011) on pyrophyllite. The contact angle of pyr-ophyllite is around 50°, suggesting that pyrophyllite is also hydrophilic. On the contrary, the values of the meniscus contact angle were found significantly differ from the sessile-droplet contact angle for muscovite. The meniscus contact angle of muscovite is 30° smaller than the sessile-droplet contact angle. Therefore, the observations on pyrophyllite in Amarasinghe and Anandarajah (2011) may not apply to muscovite. It is thus postulated that the contact angles of muscovite are more sensitive to changes in soil fabrics.

The time average density profiles of the liquid bridge systems with different initial inter-particle distances (Simulations No. 4, 5 and 6) were presented in Fig. 4. The liquid bridges formed stable and smooth menisci with these initial distances. Meanwhile, a clear thin layer of water molecules with a dark color extended beyond the contact point of the meniscus with the substrates. This layer of water is an adsorptive water film resulting from the strong attractive interactions of the mineral substrates. The meniscus contact angles were determined as 28° for  $D_{\text{initial}} = 20$  Å, 52° for  $D_{\text{initial}} = 40$  Å, and 66° for  $D_{\text{initial}} = 50$  Å. The meniscus contact angles increase with increasing initial inter-particle distances. This trend can be explained by that, with an increasing  $D_{\text{initial}}$ , the influence of the mineral interaction on the capillary water

turns weaker, leading to a greater meniscus contact angle.

The effects of the water volume on the time average density profiles (Simulations No. 7, 8 and 9) were shown in Fig. 5. No significant differences were observed among the meniscus shapes. The meniscus contact angles were determined as 34° for  $l_w = 50$  Å, 29° for  $l_w = 70$  Å, and 29° for  $l_w = 80$  Å. Despite Simulation No. 7 ( $l_w = 50$  Å), the differences between these meniscus contact angles were negligible. These results clearly indicated that the meniscus contact angle is insensitive to the water volume.

#### 5. Capillary forces and rupture distances

Fig. 6a presents the normalized capillary force of the liquid bridge systems with different mineral types under tensile loadings. As can be seen, the MD results of the normalized capillary force do not change smoothly with inter-particle distance, but instead, demonstrate significant oscillations. This is because the water molecules behave as discrete molecular layers rather than a continuum at the nanoscale. This behavior results in the rapid fluctuations in the disjoining pressure and free energy with the normalized capillary forces before applying tensile loadings (referred as 'initial normalized capillary force' in the rest of the paper) of  $\alpha$ -quartz and orthoclase were close due to their similarity in the wettability. However, the initial normalized capillary force. The initial



Fig. 4. Time average density profiles of the liquid bridges between  $\alpha$ -quartz mineral plates before tensile loadings with different initial inter-particle distances: (a) *D*initial = 20 Å; (b) *D*initial = 40 Å; and (c) *D*initial = 50 Å.



Fig. 5. Time average density profiles of the liquid bridges between *a*-quartz plates with different water volumes in terms of (a) lw = 50 Å; (b) lw = 70 Å; and (c) lw = 80 Å.



Fig. 7. Comparisons of results obtained by molecular dynamic simulations (scatter) and macroscopic solution (lines) for the liquid bridges between  $\alpha$ -quartz substrates with different initial inter-particle distances: (a) normalized capillary force vs. normalized distance, and (b) normalized rupture distance vs. contact angle.

Fig. 8. Comparisons of snapshots for the liquid bridges between  $\alpha$ -quartz substrates at D = 30 Å with different initial inter-particle distances: (a) Dinitial = 20 Å; and (b) Dinitial = 30 Å

normalized capillary forces of these three soil minerals were all positive, indicating that the capillary forces tend to pull the two mineral substrates together. Fig. 6b illustrates the normalized rupture distance with different mineral types. The rupture distance of muscovite is much larger than those of  $\alpha$ -quartz and orthoclase.

Fig. 7a presents the normalized capillary force results of the liquid bridge systems obtained with different initial inter-particle distances under tensile loadings. In general, the initial normalized capillary force decreases with the normalized distance, and large oscillations of the normalized capillary force were observed. Fig. 7b shows that the normalized rupture distance significantly increases with the initial interparticle distance. The trend is very likely to be caused by the interplay

of adsorption and capillarity. Supposing that there is only capillary water between soil particles, all the water molecules should tend to move towards the center of the liquid bridge. However, in fact, adsorptive water molecules remain at their adsorption sites under tensile loadings. To further illustrate this mechanism, the snapshots of the liquid bridge systems at D = 30 Å with different initial inter-particle distance, i.e.,  $D_{\text{initial}} = 20 \text{ Å}$  (Simulation No. 1) and  $D_{\text{initial}} = 30 \text{ Å}$  (Simulation No. 4), were compared in Fig. 8. Although the water volume and current substrate distance are identical in Simulations No. 1 and 4, the distributions of water molecules are quite different. Evidently, more water molecules belong to the adsorptive water in the Simulation No. 4  $(D_{\text{initial}} = 20 \text{ Å})$  while more water molecules belong to the capillary



**Fig. 9.** Comparisons of results obtained by molecular dynamic simulations (scatter) and macroscopic solution (lines) for the liquid bridges between  $\alpha$ -quartz substrates with different water volumes: (a) normalized capillary force vs. normalized distance, and (b) normalized rupture distance vs. contact angle.

**Fig. 10.** Comparisons of snapshots for the liquid bridges between  $\alpha$ -quartz substrates at D = 40 Å with different water volumes: (a) lw = 50 Å; and (b) lw = 80 Å.

water in the Simulation No. 1 ( $D_{initial} = 30$  Å). As a result of such interplay of adsorption and capillarity, the initial inter-particle distance may impact the tensile behavior of the liquid bridges. In other words, such a liquid bridge system has memories in that its historical evolutions affect the current state.

Fig. 9a presents the effects of the water volume on the mechanical response of the liquid bridge systems under tensile loadings. The oscillatory behaviors of the normalized capillary forces were also observed in these cases. The initial normalized capillary force increases with the water volume. Fig. 9b shows that the normalized rupture distance increases with the water volume. This phenomenon can be interpreted through the interplay of adsorption and capillarity as well. The snapshots of the liquid bridge systems at D = 40 Å with different water volumes, i.e.,  $l_w = 50$  Å (Simulation No. 1) and  $l_w = 80$  Å (Simulation No. 4), were compared in Fig. 10. Evidently, the ratio of the adsorptive water to the capillary water decreases with the increasing water volume, albeit the amounts of the adsorptive water are close in both simulation cases. That is, the portion of the capillary water increases with the water volume. As a result, the normalized rupture distance increases with the water volume.

The macroscopic solution was also shown in Figs. 6, 7 and 9 to compare with the MD simulation results. In general, the macroscopic solution is comparable to the MD simulation results in terms of the initial capillary force and rupture distance for  $\alpha$ -quartz and orthoclase. However, as for muscovite, the macroscopic solution differ remarkably from the MD simulation results. Therefore, the macroscopic solution may not apply to the liquid bridges between muscovite substrates. Besides, the oscillatory behavior of the capillary force of the liquid bridges at the nanoscale cannot be captured by the macroscopic solution which is based on the continuum theory. The effect of adsorption on the capillary force becomes manifest at the nanoscale, which is confirmed by the results shown in Figs. 7 and 9. Therefore, the interplay of adsorption and capillarity is not negligible in understanding the mechanic behavior of the liquid bridges at the nanoscale. In summary, the effect of the adsorptive water cannot be captured by the macroscopic solution.

#### 6. Summary and conclusions

The liquid bridge between particles is a primary mechanism explaining the tensile strength of granular materials. Traditional micromechanical theory based on the capillary theory and an assumption of continuous material may fail to predict the mechanical behavior of this structure at the nanoscale. This is because the atomic forces and particles may deviate the behavior of materials from continua and particles. In addition, phenomena such as adsorption are excluded in the continuum theory. This study introduces molecular dynamics simulation as an innovative computational approach to answering the above scientific questions for deepening the understanding of the mechanical behavior of the liquid bridges at the nanoscale. Molecular dynamics simulation was implemented for quantifying the effects of mineral type, initial inter-particle distance and water volume on the mechanical behavior of the liquid bridge, whose results were compared to the macroscopic solution. This study led to several significant findings that have never been reported. The major findings are summarized in the followings.

- 1. As for  $\alpha$ -quartz and orthoclase, the meniscus contact angles are close to the sessile-droplet contact angles. However, the effect of soil fabrics may significantly change the contact angle of muscovite.
- 2. There exist significant oscillations in the capillary force with interparticle distance, caused by the fact that water molecules tend to behave as discrete molecular layers rather than a continuum at the nanoscale. This observation cannot be predicted by the macroscopic solution.
- 3. The nanoscale liquid bridge has memories. That is, the current mechanical behavior is dependent on its historical evolutions.
- 4. The normalized rupture distance increases with the initial interparticle distance and water volume, which is attributed to the interplay of adsorption and capillarity. The effect of adsorption is substantial for the capillary force at the nanoscale. Nonetheless, this effect cannot be captured by the macroscopic solution.

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#### References

- Adamson, A.W., Gast, A.P., 1997. Physical Chemistry of Surfaces. Wiley.
- Alencar, A.M., Buldyrev, S.V., Majumdar, A., Stanley, H.E., Suki, B., 2001. Avalanche dynamics of crackle sound in the lung. Phys. Rev. Lett. 87, 088101.
- Allen, P., Tildesley, D.J., 1989. Computer Simulation of Liquids. Clarendon Press.
- Amarasinghe, P.M., Anandarajah, A., 2011. Influence of fabric variables on clay-water-air capillary meniscus. Can. Geotech. J. 48, 987–995.
- Amarasinghe, P.M., Anandarajah, A., Ghosh, P., 2014. Molecular dynamic study of capillary forces on clay particles. Appl. Clay Sci. 88-89, 170–177.
- Anandarajah, A., Amarasinghe, P.M., 2011. Microstructural investigation of soil suction and hysteresis of fine-grained soils. J. Geotech. Geoenviron. 138, 38–46.
- Berendsen, H.J., Postma, J.P., van Gunsteren, W.F., Hermans, J., 1981. Interaction models for water in relation to protein hydration. In: Intermolecular Forces. Springer, pp. 331–342.
- Berendsen, H.J.C., Grigera, J.R., Straatsma, T.P., 1987. The missing term in effective pair potentials. J. Phys. Chem. 91, 6269–6271.
- Bourg, I.C., Sposito, G., 2010. Connecting the molecular scale to the continuum scale for diffusion processes in smectite-rich porous media. Environ. Sci. Technol. 44, 2085–2091.
- Bourg, I.C., Sposito, G., 2011. Molecular dynamics simulations of the electrical double layer on smectite surfaces contacting concentrated mixed electrolyte (NaCl-CaCl<sub>2</sub>) solutions. J. Colloid Interface Sci. 360, 701–715.
- Cheng, S.F., Robbins, M.O., 2014. Capillary adhesion at the nanometer scale. Phys. Rev. E 89, 62402.
- Cundall, P.A., Strack, O.D.L., 1979. A discrete numerical model for granular assemblies. Geotechnique 29, 47–65.
- Cygan, R.T., Liang, J.J., Kalinichev, A.G., 2004. Molecular models of hydroxide, oxyhydroxide, and clay phases and the development of a general force field. J. Phys. Chem. B 108, 1255–1266.
- De Bisschop, F.R., Rigole, W.J., 1982. A physical model for liquid capillary bridges between adsorptive solid spheres: the nodoid of plateau. J. Colloid Interface Sci. 88, 117–128.
- El Shamy, U., Gröger, T., 2008. Micromechanical aspects of the shear strength of wet granular soils. Int. J. Numer. Anal. Methods 32, 1763–1790.
- Fortes, M., 1982. Axisymmetric liquid bridges between parallel plates. J. Colloid Interface Sci. 88, 338–352.

Hockney, R.W., Eastwood, J.W., 1988. Computer Simulation Using Particles. CRC Press.

Ichikawa, Y., Kawamura, K., Nakano, M., Kitayama, K., Kawamura, H., 1999. Unified molecular dynamics and homogenization analysis for bentonite behavior: current results and future possibilities. Eng. Geol. 54, 21–31.

- Jorgensen, W.L., Chandrasekhar, J., Madura, J.D., Impey, R.W., Klein, M.L., 1983. Comparison of simple potential functions for simulating liquid water. J. Chem. Phys. 79, 926–935.
- Katti, D.R., Ghosh, P., Schmidt, S., Katti, K.S., 2005a. Mechanical properties of the sodium montmorillonite interlayer intercalated with amino acids. Biomacromolecules 6, 3276–3282.
- Katti, D.R., Schmidt, S.R., Ghosh, P., Katti, K.S., 2005b. Modeling the response of pyrophyllite interlayer to applied stress using steered molecular dynamics. Clay Clay Miner. 53, 171–178.
- Katti, D.R., Schmidt, S.R., Ghosh, P., Katti, K.S., 2007. Molecular modeling of the mechanical behavior and interactions in dry and slightly hydrated sodium montmorillonite interlayer. Can. Geotech. J. 44, 425–435.
- Katti, D.R., Srinivasamurthy, L., Katti, K.S., 2015. Molecular modeling of initiation of interlayer swelling in Na-montmorillonite expansive clay. Can Geotech. J. 52, 1385–1395.

- Kerisit, S., Liu, C.X., Ilton, E.S., 2008. Molecular dynamics simulations of the orthoclase (001)- and (010)-water interfaces. Geochim. Cosmochim. Acta 72, 1481–1497.
- Laplace, P.S., 1806. Supplement to book 10 of Mecanique Celeste. Crapelet, Courcier. Bachelier, Paris.
- Levien, L., Prewitt, C.T., Weidner, D.J., 1980. Structure and elastic properties of quartz at pressure. Am. Mineral. 65, 920–930.
- Lian, G., Thornton, C., Adams, M.J., 1993. A theoretical study of the liquid bridge forces between two rigid spherical bodies. J. Colloid Interface Sci. 161, 138–147.
- Lopes, P.E., Murashov, V., Tazi, M., Demchuk, E., Mackerell Jr., A.D., 2006. Development of an empirical force field for silica. Application to the quartz-water interface. J. Phys. Chem. B 110, 2782–2792.
- Lu, N., Likos, W.J., 2004. Unsaturated Soil Mechanics. J. Wiley.
- Lu, N., Likos, W.J., 2006. Suction stress characteristic curve for unsaturated soil. J. Geotech. Geoenviron. 132, 131–142.
- Lu, N., Wu, B.L., Tan, C.P., 2007. Tensile strength characteristics of unsaturated sands. J. Geotech. Geoenviron. 133, 144–154.
- Martínez, L., Andrade, R., Birgin, E.G., Martínez, J.M., 2009. PACKMOL: a package for building initial configurations for molecular dynamics simulations. J. Comput. Chem. 30, 2157–2164.
- Mitarai, N., Nori, F., 2006. Wet granular materials. Adv. Phys. 55, 1-45.
- Mitchell, J.K., Soga, K., 2005. Fundamentals of Soil Behavior. John Wiley & Sons.
- Peleg, M., 1977. Flowability of food powders and methods for its evaluation—a review. J. Food Process Eng. 1, 303–328.
- Plimpton, S., 1995. Fast parallel algorithms for short-range molecular-dynamics. J. Comput. Phys. 117, 1–19.
- Plimpton, S., Crozier, P., Thompson, A., 2007. LAMMPS-Large-Scale Atomic/Molecular Massively Parallel Simulator. Sandia National Laboratories.
- Richardson, S.M., Richardson, J.W., 1982. Crystal structure of a pink muscovite from Archer's Post, Kenya; implications for reverse pleochroism in dioctahedral micas. Am. Mineral. 67, 69–75.
- Rowlinson, J.S., Widom, B., 2013. Molecular Theory of Capillarity. Courier Corporation. Ryckaert, J.-P., Ciccotti, G., Berendsen, H.J., 1977. Numerical integration of the cartesian

equations of motion of a system with constraints: molecular dynamics of n-alkanes. J. Comput. Phys. 23, 327–341.

- Scholtès, L., Chareyre, B., Nicot, F., Darve, F., 2009. Micromechanics of granular materials with capillary effects. Int. J. Eng. Sci. 47, 64–75.
- Skelton, A.A., Fenter, P., 2011. Simulations of the quartz (1011)/water interface: a comparison of classical force fields, ab initio molecular dynamics, and X-ray reflectivity experiments. J. Phys. Chem. C 115, 2076–2088.
- Šolc, R., Gerzabek, M.H., Lischka, H., Tunega, D., 2011. Wettability of kaolinite (001) surfaces — molecular dynamic study. Geoderma 169, 47–54.
- Soulié, F., Cherblanc, F., El Youssoufi, M.S., Saix, C., 2006. Influence of liquid bridges on the mechanical behaviour of polydisperse granular materials. Int. J. Numer. Anal. Methods 30, 213–228.
- Stukowski, A., 2010. Visualization and analysis of atomistic simulation data with OVITO-the Open Visualization Tool. Model. Simul. Mater. Sci. Eng. 18, 015012.
- Tadmor, E.B., Miller, R.E., 2011. Modeling Materials: Continuum, Atomistic and Multiscale Techniques.
- Teich-McGoldrick, S.L., Greathouse, J.A., Cygan, R.T., 2012. Molecular dynamics simulations of structural and mechanical properties of muscovite: pressure and temperature effects. J. Phys. Chem. C 116, 15099–15107.
- Truong, Q.H., Lee, J.S., Dong, Y., Yun, T.S., 2011. Capillary induced small-strain stiffness for hydrophilic and hydrophobic granular materials: experimental and numerical studies. Soils Found. 51, 713–721.
- Tseng, H.Y., Heaney, P.J., Onstott, T.C., 1995. Characterization of lattice strain-induced by neutron-irradiation. Phys. Chem. Miner. 22, 399–405.
- Young, T., 1805. An essay on the cohesion of fluids. Philos. Trans. R. Soc. Lond. 65–87. Zhang, C., Liu, Z., Deng, P., 2016a. Atomistic-scale investigation of effective stress principle of saturated porous materials by molecular dynamics. Geophys. Res. Lett. 43, 10,257–210,265.
- Zhang, C., Liu, Z., Deng, P., 2016b. Contact angle of soil minerals: a molecular dynamics study. Comput. Geotech. 75, 48–56.