Research paper

Effects of adsorptive water on the rupture of nanoscale liquid bridges

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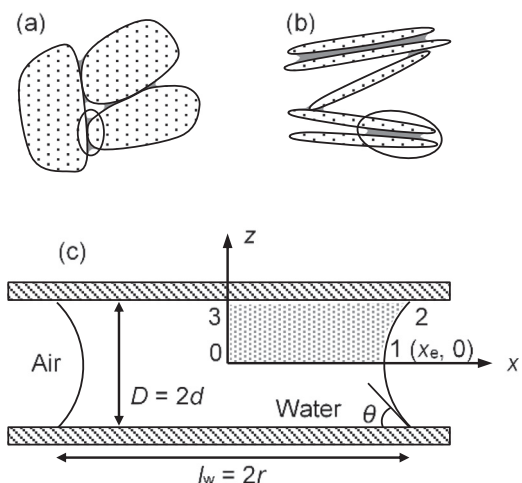
Fig. 1. Schematic of soil-water interaction in the pendular regime for (a) sandy particles, (b) clay particles, and (c) simplified conceptual model of the liquid bridge at contact.

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 θ, 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 θ liquid bridge, in which the plates are infinite, and the boundary condition is the contact angle between the liquid and the plates, θ, 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 θ liquid bridge which is easier to model with the periodic and infinite boundary condition in MD simulation.

The θ 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 $(x_e, 0)$, 2 (r, d), and 3 $(0, d)$. At point 1 $(x_e, 0)$, 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 θ. For the θ 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):

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

where γ_{la}, γ_{sl}, γ_{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:

$$V = 4 \int_0^d [x \cdot (1 + x'^2)^{0.5}] dz \tag{2}$$

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):

$$\gamma_{la} (1 + x'^2)^{-1.5} \left(-x'' + \frac{1 + x'^2}{x} \right) = -\Delta P = P_w - P_a \tag{3}$$

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):

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

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:

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

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

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

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