Research Paper

Contact angle of soil minerals: A molecular dynamics study

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ABSTRACT

In this paper, molecular dynamics was employed to study the wetting behavior of soil minerals. The basic concepts and methodologies of molecular dynamics were briefly summarized. A specific modeling and simulation procedure was presented to study the contact angles of solids using molecular dynamics. This procedure was employed to simulate the contact angles of three minerals, which are common in sand and silt fractions, i.e. α-quartz, orthoclase and muscovite. The simulated contact angle was 29° for α-quartz; 36° for orthoclase; and 116° for muscovite, which shows good agreement with the reported experimental or numerical results and thus substantiates the feasibility and accuracy of the proposed method. The simulation results also reveal that the contact angles of these minerals are considerably larger than zero and quite different from each other.

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1. Introduction

Wettability of soil minerals is of critical importance in many aspects of geotechnical engineering, petroleum engineering, and soil science. Contact angle is a major indicator for wettability which could be measured experimentally. According to Young [1], the contact angle is a result of interfacial equilibrium and could be expressed as a function of interfacial surface tension. Fig. 1 schematically depicts the contact angle of the soil mineral–water–vapor interface θ where γ_{SL}, γ_{SA} and γ_{LA} denote the surface tension of soil mineral–water, soil mineral–vapor and water–vapor interfaces, respectively. In geotechnical engineering, the wettability of soils is a crucial element in formulating the Soil Water Characteristic Curve (SWCC), which is a fundamental concept in unsaturated soil mechanics [2,3]. Due to the high surface energy of soil minerals, for simplicity's sake, the contact angles of soil minerals are usually assumed to be constant (mostly zero) in unsaturated soil mechanics [4–6]. However, some recent experimental results revealed that these assumptions may be inappropriate for soil minerals [7]. In fact, the contact angle has been identified to be dependent on water potential, roughness, and temperature by soil scientists, agricultural engineers, and physical chemists [8–12]. Despite a few investigations into the effect of the contact angle [13], the effect of contact angles of soil minerals on the unsaturated soil behavior is far from being thoroughly understood.

It is therefore indispensable to understand contact angles of soil minerals and quantify their effects on the unsaturated soil behavior.

The contact angle is measurable at the macroscopic scale while the surface tensions of solid–water and solid–vapor interfaces are difficult to be directly measured via experimental techniques [14]. According to Young's equation [1], the solid surface tensions could be obtained by measuring the contact angle experimentally [14]. In recent years, various experimental methods have been proposed to measure the surface tensions of the soil mineral–water system [15], for example, the capillary rise method [16], the sessile drop method [17] and Wilhelmy plate method [18]. As illustrated before, the contact angle may be affected by various factors, such as, roughness, temperature, heterogeneity, particle size and shape [19], which still needs a long-term further research to investigate. As a result, for one soil mineral, the contact angles measured by different researchers or different experimental methods usually exhibit discrepancies [20,21]. However, a thorough experimental research quantifying these effects on the contact angles of minerals is still absent [19]. The possible reason for this is that, to date, there is no efficient experimental or numerical tool capable of quantifying these factors.

Molecular Dynamics (MD) simulation has been recognized as an efficient tool to investigate the complex physical mechanisms at the molecular scale. The physical nature of the surface energy is dominated by crystallographic orientation of the solid surface [22]. Therefore, molecular dynamics simulation is by nature an efficient approach to study the contact angle of materials. In recent years, molecular dynamics simulations have been implemented to

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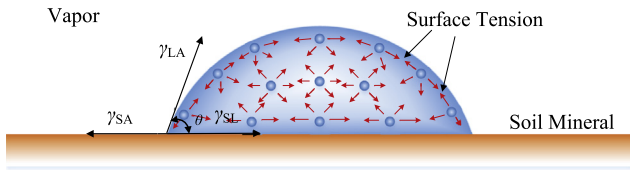E-mail address: zhenl@mtu.edu (Z. Liu).

Fig. 1. Schematic diagram of contact angle of soil mineral–water–vapor system.

study the wetting behavior of some specific materials by materials scientists and chemists. Yuan and Zhao [23,24] studied the dynamic wetting, electrowetting and wetting on flexible hydrophilic pillar-arrays by means of molecular dynamics simulations. Werder et al. [25] studied the contact angles of carbon nanotubes through parallel molecular dynamics simulations. In their model, the simulated system was divided into three parts: water–water interaction, carbon nanotubes, and carbon–water interaction. In particular, the carbon–water interaction was modeled as Lennard–Jones interaction where the parameters need to be calibrated with reference to experimental data. Hong et al. [26] investigated the static and dynamic behavior of contact angles of a solid surface using molecular dynamics simulations. They pointed out that the wetting behavior, i.e. hydrophobic or hydrophilic, of the simulated solid surface could be identified as the changes in water–solid interaction energies. Park et al. [27] studied the effect of the solid surface morphology on the contact angles. The random roughness was created by adjusting the distribution function of the solid surface. Yan et al. [28] introduced a solvent environment to a simulated system of contact angles. They found that the water–solvent interaction was an important factor to the wetting behavior of the solid surface.

In contrast with the wide application of molecular dynamics to the contact angle study of graphite and carbon nanotubes, there is a very limited number of molecular dynamics studies targeting at the contact angles of minerals. Šolc et al. [29] studied the wettability of kaolinite using molecular dynamics simulations. They found that the tetrahedral surface of kaolinite is typically hydrophobic with a simulated contact angle of 105°. Tenney and Cygan [30] investigated the carbon dioxide, brine and kaolinite interactions through molecular dynamics simulations and calculated the corresponding contact angles. Despite these few molecular dynamics studies from Šolc et al. [29] and Tenney and Cygan [30], the contact angles of soil minerals have not been extensively investigated using molecular dynamics simulations.

Other than soil wettability, molecular dynamics has been employed by some geotechnical researchers to study soil behaviors. Ichikawa et al. [31] proposed a unified molecular dynamics and homogenization analysis framework to investigate the seepage behavior of bentonite. This framework was later extended to study a series of the seepage, diffusion and consolidation problems of bentonite [32–35]. Song et al. [36] explored the bridging scales methods for geo-materials from the molecular scale, the particle scale to the continuum scale. Bourg and Sposito have explored the double layer structure and diffusion performance of smectite or smectite-rich porous media [37,38]. Katti et al. have employed molecular dynamics simulations to study the mechanical behaviors of clay minerals under various loading schemes [39–42]. Amarasinghe and Anandarajah have studied the influence of fabric variables on the clay interparticle capillary water and upscaled the simulation results to model the hysteresis of fine-grained soils [43,44].

To promote its application in the geotechnical engineering community, molecular dynamics simulations are adopted in this study to explore the wetting behavior of soil minerals. Some basic concepts and methodologies of molecular dynamics are introduced in Section 2. A specific simulation method is presented in Section 3 particularly for the contact angles of soil minerals. Based on the method, a series of molecular dynamics simulations are conducted to explore the contact angles of soil minerals. Three typical soil minerals that are common in sand and silt fractions are selected for this study. The wetting processes of these soil minerals are simulated and their contact angles are determined from the time-average density profiles of droplets. The underlying physical mechanisms of wetting processes and their implications on unsaturated soil mechanics are discussed further in detail.

2. Basic concepts and methodologies of molecular dynamics

Molecular dynamics has been proven to be an efficient tool for investigating material behavior at the nanoscale. Two main assumptions are typically made in classical molecular dynamics [45,46]: (1) molecules or atoms are described as a system of interacting points, whose motion is described dynamically with a vector of instantaneous positions and velocities, and the interaction between atoms has a strong dependence on the spatial orientation and distances between separate atoms and (2) neither the mass nor number of atoms in the system will be changeless during the simulation process.

2.1. Governing equations

Newton mechanics is the theoretical basis for classical molecular dynamics. The motion of atoms could be represented by Newton's second law [47]:

$$m_i \frac{\partial^2 \mathbf{r}_i}{\partial t^2} = \mathbf{F}_i = \sum_{\substack{j=1 \\ (i \neq j)}}^{N_a} \mathbf{f}_{ij}, \tag{1}$$

where m_i is the mass of atom; $\mathbf{r}_i = (x_i, y_i, z_i)$ is the coordinate of atom i; t is time; $\mathbf{F}_i$ is the total force applied on atom i; $\mathbf{f}_{ij}$ is the interaction force applied on atom i by atom j, and is usually a function of the displacement between atom i and atom j; N_a is the number of atoms in the system.

A complex formulation of classical mechanics is required for complicated simulation systems. The Lagrangian or Hamiltonian formulation of classic mechanics is usually employed for this purpose. For example, the Lagrangian formulation of the molecular dynamics system could be written as [45]:

$$m_i \frac{\partial^2 \mathbf{r}_i}{\partial t^2} = -\frac{\partial U(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_{N_a})}{\partial \mathbf{r}_i} \equiv \mathbf{F}_i, \tag{2}$$

where U represents the total potential energy of the system, which is a function of atomic coordinates.

2.2. Interatomic potentials

From Eqs. (1) and (2), it could be observed that the mechanical properties are mainly dominated by the expression of the interatomic force $\mathbf{f}_{ij}$ or the total potential energy U. In reality, the total potential energy of the system could be very complicated due to the presence of quantum effects. Therefore, in order to simulate the complex system with acceptable computational costs, the interatomic potentials should well consider the complicated quantum effects during the simulated mechanical process. In practice, for simplicity, the interatomic potentials are usually treated as pairwise interatomic potentials by assuming that the interatomic potential between two atoms is a function of the coordinates and physical properties of these two atoms, and independent of other atoms. The interatomic potential usually decays with the distance