



Research paper

Molecular dynamic study of capillary forces on clay particles

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ABSTRACT

Capillary forces between discrete colloid particles are of interest in many areas of science and engineering. This study used molecular dynamics (MD) to examine capillary phenomena that develop in a clay–water–air system, which requires an understanding of capillary forces, contact angles, and meniscus curvatures. The capillary formed between two parallel pyrophyllite clay particles and pure water was studied using MD for various system parameters which included particle separation, particle thickness, and strength of the clay–water van der Waals force. For a given set of potential energy parameters, the contact angle was independent of particle separation ($\approx 55^\circ$), the radius of curvature depended on particle separation, and particle thickness had a negligible influence on contact angles and meniscus radii. The van der Waals energy parameters, however, had a profound influence on contact angles and meniscus radii. In all cases, capillary forces on clay particles calculated by MD agreed with values calculated using the classical Young–Laplace equation. When the separation distance is 40 Å, the force was calculated to be 9.87×10^{-10} N by Young–Laplace equation and 8.37×10^{-10} N by MD.

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1. Introduction

Capillary effects are of interest in many fields such as soil science, material science, colloidal science and engineering. For instance, when a dry soil becomes partially saturated, capillary forces develop between particles, resulting in shrinkage in some soils such as clays. Numerous past studies have employed molecular dynamics to further understand the phenomenon of capillarity. Previous studies, which examined capillary flow in narrow pores, used structureless walls or arranged atoms on a lattice to simulate a solid wall (Bitsanis et al., 1987; Heinbuch and Fischer, 1989; Koplik et al., 1989; Martic et al., 2002; Sokołowski, 1991; Thompson and Robbins, 1989; Trozzi and Ciccotti, 1984). De Ruijter et al. (1999) used molecular dynamics to study spreading of liquid droplet on a flat solid surface. The solid surface was modeled using atoms placed on a face-centered cubic lattice. Molecular dynamic technique is proven to be an effective method in studying clay structures and their behaviors. For instance, Nakano et al. (2003) studied adsorption of cesium on clay surfaces. Ichikawa et al. (2004) studied the diffusion of HTO (tritium water) in clay structure using molecular dynamics. The pair-wise interaction between atoms was simulated using the Lennard–Jones (LJ) 12–6 potentials. The contact angle significantly changed as the solid–liquid LJ potential parameters were varied. Martic et al. (2002) showed that contact angle is dependent on the system wetting velocity. There have been numerous attempts to use experiments to understand the surface tension of clay mineral–surfactant interfaces (Cipriano et al., 2005; Docoslis et al., 2000; Lee et al., 2000;

Zhuang et al., 2010). Studies show that the contact angle between water and nanocomposite membranes tends to decrease with increasing clay content (Anadao et al., 2010). A systematic study on the nature of clay–water capillary meniscus has not been done in the past.

The behavior of clays is controlled at the particle level by the van der Waals (Anandarajah and Chen, 1997), double-layer due to electrostatic interactions (Anandarajah and Chen, 1994; Anandarajah and Lu, 1992), and capillary interactions (Amarasinghe and Anandarajah, 2011; Anandarajah and Amarasinghe, 2012). Particle-level studies (Anandarajah, 1994) require quantification of the interparticle forces that arise from these interactions. While classical equations such as the Young–Laplace equation (Laplace, 1806; Young, 1805) may be used to calculate the capillary forces on clay particles, (a) they require knowledge of contact angles and meniscus curvatures and (b) their validity has not been verified for clay–water systems. The present study uses molecular dynamics (MD) to develop the required understanding, and to verify the validity of the Young–Laplace equation. The capillary phenomenon that occurs in the interparticle space (not interlayer space) is of interest.

1.1. The Young–Laplace equation

Capillary meniscus and wetting are primarily characterized by the contact angle θ . Contact angle is the angle at which the liquid–air interface meets the solid surface. The contact angle is a measure of the wettability of the fluid on the solid surface, with $\theta = 0^\circ$ representing perfect wettability and $\theta = 180^\circ$ representing perfect non-wettability. For example, $\theta \approx 0^\circ$ for glass–water–air interface and $\theta \approx 140^\circ$ for glass–mercury–air interface.

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Consider the two-dimensional air–water meniscus between two parallel clay particles as shown in Fig. 1. With the assumption that the meniscus may be approximated by a circular arc of radius r , the Young–Laplace equation for the pressure difference between air and water is

$$p_{air} - p_{water} = \frac{T}{r} \quad (1)$$

where p_{water} is the water pressure inside the meniscus, p_{air} is the air pressure outside the meniscus, T is the air–water surface tension and r is the meniscus radius of the curvature. A positive radius of curvature (Fig. 1) indicates that $p_{water} < p_{air}$. The water pressure is negative when the air pressure is zero. The top clay particle is subjected to the following surface tension force in the z – direction:

$$F_{Tz} = -TL_x \sin\theta \quad (2)$$

where L_x is the length of the clay layer in the x – direction. Assuming that the pressure is uniform in water, it follows that the clay particles are also subjected to a force F_{pz} due to the water pressure acting on its side facing the water. Referring to Fig. 1, F_{pz} is given by

$$F_{pz} = p_{water} L_x L_y \quad (3)$$

where L_y is the length of the clay particle that is in contact with water. Combining Eqs. (1–3), the total force F_z acting on the top clay particle due to capillary water then is

$$F_z = F_{Tz} + F_{pz} = -TL_x \sin\theta + p_{water} L_x L_y = -TL_x \left[\sin\theta + \frac{L_y}{r} \right] \quad (4)$$

Note that the sign of the second term will be opposite if the radius of curvature is negative (as in glass–mercury–air meniscus). When the meniscus can indeed be approximated by a circular arc as done here, the radius is related to (half) the particle separation as $r = d/\cos\theta$. Eq. 4 then may be written as

$$F_z = -TL_x \left[\sin\theta + \frac{L_y}{d} \cos\theta \right] \quad (5)$$

It follows from Eq. 5 that the quantification of capillary forces on clay particles in a partially saturated clay–water system requires knowledge of contact angles and meniscus curvatures.

2. Details of molecular dynamics

2.1. Potential energy functions and simulation software

The fundamentals of molecular dynamics are well established; the details are available in many books (e.g., Allen and Tildesley, 1987).

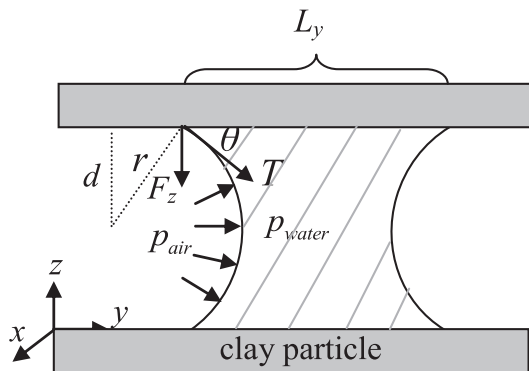


Fig. 1. Schematic of a meniscus between two parallel clay particles.

There are several public domain and commercial computer codes for performing MD, each with specific pre- and post-processing capabilities. The present study is performed using the computer code named NAMD (Kalé et al., 1999), along with the interactive visual molecular dynamics software named VMD (Humphrey et al., 1996). The theoretical details of NAMD may be found in Phillips et al. (2005). One of the force fields supported by NAMD is the CHARMM (Brooks et al., 1983) field. In it, the total potential energy U_{tot} is expressed as a sum of the bonded energy U_b and the non-bonded energy U_{nb} (i.e., $U_{tot} = U_b + U_{nb}$). The present study employs the following expression for U_{nb} :

$$U_{nb} = \sum_{\text{vanderWaals}} \sum_{i \neq j} 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \sum_{\text{electrostatic}} \sum_{i \neq j} \frac{q_i q_j}{r_{ij}} \quad (6)$$

where r_{ij} is the distance between atoms i and j , ϵ_{ij} and σ_{ij} are constants governing the van der Waals energy, and q_i and q_j are the electrostatic charges on atoms i and j respectively. Hence NAMD employs the standard Lennard–Jones 6–12 potential for the van der Waals part. The parameters between two dissimilar atoms i and j are computed as follows

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j} \quad (7a)$$

$$\sigma_{ij} = \frac{1}{2} [\sigma_i + \sigma_j] \quad (7b)$$

where (ϵ_i, σ_i) are parameters associated with atom i and (ϵ_j, σ_j) are parameters associated with atom j . The molecules involved in the present study are treated as rigid, and hence the bonded energy equations are irrelevant.

2.2. Atomic structures of clay and water

The clay used in this study is pyrophyllite, which has the basic structure of smectite type clay mineral. Pyrophyllite has the chemical formula of $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$ (Van Olphen, 1977). Pyrophyllite is a 2:1 clay mineral. The dimension of a unit cell (which consists of 40 atoms) in the x – y – z Cartesian coordinate system is $5.28 \text{ \AA} \times 9.14 \text{ \AA} \times 6.56 \text{ \AA}$. A typical clay layer consists of several unit cells that are repeated both in the x – and y – directions (Fig. 1). In nature several of these layers are stacked up in the z – direction at some basal spacing. To consider the effect of particle thickness, a single-layer particle and a two-layer particle were analyzed in the present study.

2.3. Initial configurations and potential energy parameters

The initial coordinates of the atoms in the pyrophyllite unit cell were obtained from Skipper et al. (1995). The values of the van der Waals parameters (ϵ_{ij} and σ_{ij}) and the electrostatic charges (q_i) used in the study originated from the work of Teppen et al. (1997). These parameters were later cast within the framework of the CHARMM force field, where the functional form of the van der Waals equation is different from those of Teppen et al. (1997) by Katti et al. (2005). These parameters are listed in Table 1. Teppen et al. (1997) have verified the validity of the parameter values by comparing the experimentally measured $d_{(001)}$ spacings with those calculated by molecular dynamics.

Thompson et al. (1993) studied the solid/fluid capillary interaction with the flexibility of the solid atoms modeled using springs. The study indicated that stress build up in the fluid was never large enough to produce substantial deformations of the walls. The focus of the current paper is on the calculation of capillary forces between two parallel particles at fixed separations. This requires that the particles be held at fixed locations. In the current study, it was assumed that the change in the initial coordinates of the atoms of the clay layers during the simulation arising from the clay–water interaction is small. On this basis,

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