Molecular Dynamics Simulation Study of Bubble Attachment at the Coal Surface with Varying Coalfication Degrees

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ABSTRACT: Establishing the dynamics of wetting film thinning and rupture during the bubbles attached on the coal surface is extremely important for flotation. However, studying the dynamics of bubble attachment from the molecular level using molecular dynamics simulation (MDS) has rarely been reported. In this work, the dynamics of bubble attachment at three different coal [low-rank coal (LRC), bituminous coal (BC), and anthracite coal (AC)] surfaces with varying degrees of coalfication were studied using MDS. In the bubble attachment process, the wetting film between the bubble and coal surface gradually become thinner until it ruptures. By comparing the bubble attachment dynamics on three different coal surfaces, the results indicate that the bubble attachment rate on the surface with strong hydrophobicity is faster than that on the surface with weak hydrophobicity. Besides, the number of hydrogen bonds between the molecules of the wetting film is decreased with the attachment of bubbles; however, it is sharply decreased on the BC surface and slowly reduces on the LRC surface before the film rupture. At the same time, the radial distribution functions (RDFs) of hydrogen bonds in the wetting film at the moment of bubble attachment on the coal surface are analyzed, indicating that the peak intensity of the RDF decreases at the time of bubble attachment. The findings in this study may help to better comprehend the dynamics of bubble attachment, which is valuable for future design in practical applications.

1. INTRODUCTION

Froth flotation is an effective separation method that is widely used in mineral processing. The degree of bubble mineralization refers to the liquid film between particles and bubbles from thinning rupture and finally to the three-phase wetting periphery. The process of forming stable mineralized gas flocs is the core function unit in flotation. Therefore, stable mineralized gas flocs are extremely important to determine the separation effect of the flotation process.

It is well-known that the attachment of air bubbles to a hydrophobic surface includes film thinning, film rupture, and the formation of a contact line. During this process, several parameters are important, including the surface chemistry of the minerals, the solution chemistry properties and surfactants, and the surface forces. These factors govern the thinning and rupture of thin liquid films formed between gas bubbles and particles. Experimental techniques have long been used to observe and study the process of bubble attachment to a mineral surface, including atomic force microscopy (AFM) technology, high-speed video, induction time measuring instrument, and so forth. Several measurement techniques and attachment efficiency models have also been proposed, including the Philippoff, Evans, Scheludko, Schulze–Radov, Nguyen, Dobby–Finch, and Yoon–Luttrell models. However, these models cannot be universally applied to all practical bubble attachments. In recent years, benefiting from the rapid development of atomic force microscopy (AFM) technology, direct force measurements between air bubbles and solid particles have been conducted. Xing et al. used AFM and a dynamic wetting film analyzer to test the hydrophobic force between the bubble and the same hydrophobic substrate, respectively; it is found that the liquid film between the hydrophilic substrate and the bubble was stable, and the wetting film between the hydrophobic substrate and the bubble was unstable. In addition, some research work about the use of high-speed video to observe the formation of three-phase contact lines and the stability of the wetting films with bubbles attached to the surface has also been reported. In brief, such research is constantly improving and helping perfect the theory of bubble attachment. However, the dynamics of bubble attachment at the molecular scale is still not clear.

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Owing to the significant improvement in computational capabilities, molecular dynamics simulation (MDS) can be used to explore the interactions between bubbles and minerals and between water and minerals. MDS can also provide molecular-level information regarding the dynamic properties of bubbles or water at the selected mineral surfaces.\textsuperscript{18,19,20} Compared with experimental testing, MDS breaks some objective limits of experimental testing. Numerous studies based on MDS have been reported on the dynamic and wetting characteristics of water or bubbles at mineral surfaces. Li\textsuperscript{21} et al. calculated for the first time the wetting process of water droplets on a smooth mineral surface. Similarly, Zhang\textsuperscript{22} et al. used MDS to calculate the water contact angle of a coal surface with different degrees of coalification and compared the experimental results. They found that the simulated contact angle was consistent with the experimental test results. Furthermore, Jin\textsuperscript{23} et al. examined the MDS bubble attachment and contact angles for a molybdenite face, molybdenite armchair-edge, molybdenite zigzag-edge, and quartz (001) surfaces and compared them with the contact angles obtained from the experiments. This is the first study on the attachment process using MDS. MDS has become an essential research method to study the mineral floatability and wettability, but it still requires further development.

Based on the previous study about water droplet spreading on the coal surface with different degrees of coalification in air,\textsuperscript{24} the dynamics of bubble attachment on different hydrophobic coal surfaces in water were further examined in this work, and the results were compared with the experimental contact angles. During the simulation process, the bubble attachment efficiency of different hydrophobic coal surfaces was considered, and it was verified that the bubble attachment rate was fast on a large hydrophobic coal surface, and it is slow on a weak hydrophobic coal surface. Meanwhile, the stability of the wetting film was also considered when the bubble was attached to the coal surface. Based on the analysis of the number of hydrogen bonds between water molecules in a wetting film, the process of thinning, rupture, and displacement of the wetting film was inferred. The findings in this study may help in comprehending the dynamics of bubble attachment, which will be valuable for future design in practical applications.

2. RESULTS AND DISCUSSION

2.1. Contact Angle Measurement. The test results of the coal contact angle at different times are shown in Figure 1. We found that, with the increase of the coalification degree, the contact angle initially increased and then decreased. The contact angle of low-rank coal (LRC) is the smallest at different test times because numerous hydrophilic oxygen-containing functional groups are present there.\textsuperscript{24,25} Besides, we should note that with the increase of the coalification degree, the hydrophilic functional groups in the coal molecules gradually decreased, and the degree of aromatic condensation increased. Coalification not only reduced the number of hydrophilic functional groups but also that of aliphatic chains in coal. Although few hydrophilic functional groups existed in anthracite coal (AC), no hydrophobic-side chain alkane were present. The hydrophilic functional group and hydrophobic aliphatic chains of bituminous coal (BC) are located between LRC and AC; thus, BC had the highest hydrophobicity.\textsuperscript{26}

2.2. Bubble–Surface Attachment Behavior Analysis. Bubble–surface attachment behavior was observed using the bubble–particle attachment visualization platform, and the results are shown in Figure 2. It is found that the bubble approach the coal surface from the same initial position; however, the bubble–particle attachment time is different. The formation of the three-phase wetting periphery was observed at 100 ms contact time during the attachment process between the bubble and the BC surface, and the formation of the three-phase wetting periphery was observed at 500 ms attachment time during the attachment process between the bubble and the AC surface. However, during the attachment process between the bubble and the LRC surface, the attachment time is 1600 ms. The attachment time between the bubble and the coal surface at different degrees of coalification is different, which indicates that the wetting film between the bubble and coal surface is also different. Relevant research will be discussed in the next section using MDS.

2.3. Simulation Calculation of the Bubble Attachment Dynamics. It is well recognized that the attachment of the air bubble at a hydrophobic surface includes film thinning, film rupture, and the formation of a contact line.\textsuperscript{27} MDS results for the attachment of the nitrogen gas bubble at the coal surface provide molecular-scale information. Figure 3 shows the process of wetting film thinning, rupture, and displacement leading to the equilibrium state of attachment.

During the process of attaching nitrogen gas bubbles to the coal surface, the wetting film between the nitrogen gas bubble and the coal surface first formed, followed by thinning and rupture. The nitrogen gas bubble can diffuse through the wetting film and reach the interface of coal and water. Figure 3 shows that the gas/solid interface was generated and stabilized at 150 ps (Figure 3a), 20 ps (Figure 3b), and 70 ps (Figure 3c), which indicates that the film wetting begins to rupture. When the gas/solid interface is generated, the contact line is formed, and the nitrogen gas bubble can directly touch the coal surface by a molecular bridge of nitrogen between the bubble and the coal surface. Meanwhile, the attachment area expands rapidly. Finally, the attached nitrogen bubble becomes a hemisphere at the coal surface, and the attachment area continues to expand. After a simulation time of 500 ps, a state of equilibrium is achieved, which indicates that a hemispherical shape of the bubble has been established.

The film rupture time can be estimated from MDS. As shown in Figure 3, the film rupture times for the LRC surface (~150 ps) are significantly greater than the rupture time for the BC face surface (~20 ps) and the AC surface (~70 ps). This result is consistent with the previous findings and the law of surface wettability of coal.\textsuperscript{25} The BC surface has a large

![Figure 1. Water contact angles of LRC, BC, and AC.](http://pubs.acs.org/journal/acsodf)
contact angle and strong hydrophobicity, allowing the nitrogen gas bubbles to easily attach to the hydrophobic surface, whereas the attachment rate of the nitrogen gas bubbles is the slowest for the LRC surface owing to the smallest contact area and the poorest hydrophobicity.

2.4. Attachment Area and Number of Hydrogen Bond Analysis. After the rupture of the wetting film, the attachment area sharply increases following a dramatic decrease in the number of hydrogen bonds between the water molecules in the wetting film. Therefore, the change in the attachment area can be evaluated by the number of hydrogen bonds between the water molecules in the wetting film, and the film rupture time can be estimated. Figure 4 shows the evolution of the attachment area and the number of hydrogen bonds between water molecules in the wetting film, and the slope of the curve in Figure 4a indicates the rate of thinning and rupture of the wetting film on different coal surfaces. It can be found that the number of hydrogen bonds is continuously decreased before the wetting film rupture; however, the number of hydrogen bonds decreases fastest on the BC surface and slowest on the LRC surface. Besides, from Figure 4b, it can also be found that the attachment area of the bubble on different coal surfaces is different. From the top view, the attachment area on the BC surface is large, and the

Figure 2. Attachment behavior between the bubble and the particle.

Figure 3. Process of film thinning, rupture, and formation of a contact line for nitrogen bubbles on different coal surfaces. (a) LRC surface, (b) BC surface, and (c) AC surface.
change of bubble attachment area at different times intuitively reflects the dynamic process of attachment of the bubble on different coal surfaces. This result indicates that MDS can properly present the process of wetting film rupture.

2.5. Interfacial Water Analysis. To further analyze the change of the wetting film during the dynamics of bubble attachment, radial distribution functions (RDFs) of hydrogen bonds in the wetting film were carried out, and the results are shown in Figure 5. It can be found that at three different coal surfaces, the peak intensity of the RDF of hydrogen bonds between water molecules in the wetting film was decreased at the time of bubble attachment. Moreover, the peak intensity of the wetting film rupture time on the three different coal surfaces is the lowest, which means that the stability of the wetting film is the weakest at this moment. Based on the analysis of the RDF of the hydrogen bond in interface water, the situation of the wetting film can be better understood in the bubble attachment process. The lowest peak intensity of the RDF implies that the stability of water molecules is also the weakest. By comparing with the RDF of hydrogen bonds at different times, the wetting film rupture time can be evaluated too.

3. CONCLUSIONS
The film thinning, rupture, and formation of a contact line during bubble attachment at the coal surface with three different degrees of coalification were explored using experimental methods and MDS. Experimental results show that the attachment time during the attachment process between the bubble and different coal surfaces is different, and the attachment time of the bubbles and the coal surface is $\text{LRC} > \text{AC} > \text{BC}$. Through simulation, it is found that the film rupture time for a weak hydrophobic coal surface is relatively longer than that for a large hydrophobic coal surface. An MDS
interfacial water analysis showed that the stability of the wetting film decreased sharply at wetting film rupture. Further, by counting the number of hydrogen bonds between water molecules in the wetting film, it was determined that the number of hydrogen bonds is continuously decreased before the wetting film rupture; however, the number of hydrogen bonds decreases fastest on the BC surface and slowest on the LRC surface. The findings in this study may help in comprehending the dynamics of bubble attachment, which will be valuable for future designs applied to practical applications.

4. EXPERIMENTAL SECTION

4.1. Materials. The LRC, BC, and AC samples used in this study were collected from the Shendong mine, Kaifuan coal mine group, and Xuehu coal mine in China, respectively. The raw samples were crushed, dried, and ground to 74 μm for a subsequent contact-angle measurement.

4.2. Contact-Angle Measurements. The contact angles were measured using a contact angle meter (DSA100, KRÜSS, Germany) by applying a sessile drop method. Before the test, the fine particles were pressed on a tabletting machine to form coal pieces with a thickness of approximately 2 mm with the pressure of the tablet press set to 50 MPa. The pressed coal pieces were then placed under a contact angle meter for measurement. Images were recorded using a digital camera as water droplets spread over the coal surface for 2, 4, and 6 s. A subsequent contact-angle measurement.

4.3. Bubble−Surface Attachment Experiment. Bubble−surface attachment behavior was observed using the bubble−surface attachment visualization platform (Figure 6).

The system consists of bubble generation unit, bubble driving unit, high-speed camera, 3D displacement platform, and light source. First, a constant size bubble is generated at the end of the capillary, and the bubble driving unit approximates the coal surface at a constant speed. After reaching the preset stroke, the bubble maintains a certain set contact time with the coal surface. Finally, the bubble driving unit sets the capillary away. The whole dynamic process was observed by a high-speed dynamic camera, and the attachment between the bubble and coal surface was determined by the formation of the capillary bridge away from the process. Keeping other operating parameters unchanged and gradually reducing the contact time until it happens to attach, we define the contact time at this time as the attachment time.

5. MOLECULAR DYNAMICS SIMULATIONS

5.1. Simulation Model. In all simulations, the Wender coal model (Figure 7a), Wiser coal model (Figure 7b), and Wender model (Figure 7c) were used to represent the LRC, BC, and AC molecules, respectively. An extended simple point charge (SPC/E) water model was used in all simulations.

5.2. Initial Configuration of the Bubble Attachment. In a previous study, we constructed a smooth coal surface of three different coal molecules with a size of 75 Å × 75 Å (Figure 8a). Nitrogen gas was chosen for this simulation. A two-point model for nitrogen molecules was used. First, a nitrogen gas bubble (diameter 30 Å) was placed as close as possible to the top of the coal surface (Figure 8c). Then, a 35 Å thick water course was employed around the nitrogen gas (Figure 8b). Finally, a 50 Å thick vacuum slab was employed at the top of each simulation system to eliminate the periodic boundary conditions (Figure 8d).

A nitrogen bubble in water should satisfy the Yang−Laplace equation, which is shown in eq 1:

$$\Delta P = \frac{2\gamma}{R}$$

where $\Delta P$, $\gamma$, and $R$ are the pressure difference across the nitrogen/water interface, the surface tension for water (72.8 mN/m at 298 K), and the radius of the bubble, respectively. According to the Young−Laplace equation, for a nitrogen bubble with a diameter of 30 Å at 298 K, the pressure inside the bubble is 97.07 × 10^−7 dyne/cm².

In addition, at high pressure, the ideal gas law is invalid, and thus, the corrected real gas law at high pressure is applied to the nitrogen bubble, as shown in eq 2:

$$P(V − nb) = nRT$$

where $V$, $P$, and $n$ are the volume, pressure, and moles of nitrogen, and $b$ is a constant, where for nitrogen gas, $b = 4 \times 10^{-5} \text{m}^3/\text{mol}$. In addition, $T$ is 298 K, and $R$ is the molar gas constant (8.314 J·K⁻¹·mol⁻¹).

The number of molecules calculated from both equations is 130 in the nitrogen bubble, which is close to that (158) obtained by MDS. Thus, MDS results are extremely close to the actual situation.

5.3. Simulation Calculation Method. All simulations were conducted in an orthorhombic cell with boundary conditions of 75 Å × 75 Å × 100 Å and $\alpha = \beta = \gamma = 90°$. The molecular structures of the orthorhombic cell were optimized using a smart method with Materials Studio 8.0 software developed by Accelrys, Inc. Subsequently, the condensed-phase optimized molecular potential for atomistic simulation studies II (COMPASS II) was applied for MDS computation.
In this study, we focus on the adsorption of nitrogen gas on different coal surfaces, and the influence of environmental pressure on the entire process was extremely weak. Thus, a constant particle number, volume, and temperature ensemble with a Nose thermostat and a temperature of 298 K were selected, where the number of particles ($N$), the volume of the simulation box volume ($V$), and the temperature ($T$) were kept constant. Considering the actual conditions of the computational resources and the stretching vibration period of C–H in the simulation system, a time step of 1.0 fs was adopted to integrate the equations of motion. The total simulation time was 500 ps. Furthermore, the long-range electrostatic and van der Waals interactions were accounted for using an Ewald summation and an atom-based method, respectively.

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