



## Review article

# Role of molecular simulation in understanding the mechanism of low-rank coal flotation: A review

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## ABSTRACT

Flotation is the main method for recovering and reusing fine low-rank coal by taking advantage of the difference in physicochemical properties of the mineral surface, but its efficiency has not yet reached a satisfactory level. Particles, flotation reagents, and air bubbles are highly dispersed and interact with each other in a flotation cell. Therefore, a basic understanding on the fundamental mechanism of the above interactions involved in a low-rank coal flotation system is the prerequisite for improving low-rank coal flotation recovery. In recent years, with the development of theoretical chemistry and computational chemistry, molecular simulation has gradually become a powerful tool for studying low-rank coal flotation, which has shed new light on the molecular structure of low-rank coal and the interfacial interaction in low-rank coal flotation at the molecular or atomic levels. In this paper, we first review the basic theory of molecular simulation, and then we review the recent advances in the molecular structure of low-rank coal. Coal-water, coal-reagent, coal-bubble, and coal-clay interactions are discussed comprehensively from the viewpoint of molecular simulation. This review is closed with a brief conclusion and perspective discussion.

## 1. Introduction

It is well known that coal is the primary fossil fuel and supplies approximately 42% of the electricity to the world [1]; it will still hold a dominant position in the energy supply until 2050 [2,3]. Nearly half of all global coal deposits are low-rank coals including subbituminous coal and lignite, which are very abundant in China, Australia, Turkey, India, and the northern US [3–7]. Because of the advantages of low-rank coals, such as easy access, low mining cost, high reactivity, and low price, it is feasible to use low-rank coals in the energy supply and industrial feedback [8–11]. With the deep mining of coal mine, wide application of gravity separation techniques, and large consumption of high-quality coal, a large amount of fine low-rank coal is continually produced and accumulated [12]. The utilization of low-rank coal has gained widespread attention from various fields. However, it is necessary to clean low-rank coal before its use in industry due to its low calorific value and high ash content, which improve resource utilization efficiency and avoid environmental pollution [3,4].

The froth flotation technique, which is based on the differences in

surface hydrophobicity between organic matter and mineral matter, is an effective separation method for such low-rank coal cleaning and upgrading [13–15]. The target mineral particles can be attached onto the bubble surface and separated with rising bubbles under the premise that the hydrophobicity of the floating particles is higher than that of the sinking particles [16]. The flotation process is accompanied by three sub-processes: particle-bubble collision, attachment, and detachment [17]. During the process of particle-bubble attachment, rupturing of the water film on the particle surface, and the formation and expansion of a gas-liquid-solid three-phase wetting perimeter will be observed [18]. To enhance the hydrophobicity of floating particles, collectors that interact with the mineral surface are usually added in the flotation pulp [19].

However, efficiency flotation of low-rank coal has been difficult to achieve at a satisfactory level. The existence of abundant oxygenated functional groups on low-rank coal's surface, such as carboxyl, hydroxyl, carbonyl and methoxyl groups [8–10], leads to the generation of hydrogen bonds with water molecules and the formation of hydration films that block the adsorption of oily molecules/droplets [20].

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Hydrogen bonds are formed between these oxygen-containing groups and water molecules, preventing collector adsorption and air bubble attachment. During low-rank coal flotation, particles, flotation reagents, and air bubbles are highly dispersed and interact with each other in a flotation cell [21]. A basic understanding of the fundamental mechanism behind the above interactions involved in low-rank coal flotation system is the prerequisite for improving low-rank coal flotation recovery.

Great progress has been made in the flotation intensification of low-rank coal. Many methods, including the use of emulsification oil, novel polar reagent, and a compound/mixed collector have been proposed [22,23]. The oil emulsification technique is an effective method for enhancing oil's interaction capability with the coal surface, which contains mechanical emulsification and surfactant emulsification. To stabilize the emulsions, a surfactant emulsification is favored [24]. It was found that emulsification with the addition of surfactants (anionic and cationic) reduces the droplet size to approximately 1.5–2.0  $\mu\text{m}$  [25]. The increased number of oil droplets assists the flotation kinetics by increasing the probability of coal particle-oil droplet collisions [26]. The addition of surfactants also lowers the energy required to spread the oil collector across the coal surface through adsorption at the coal-water interface and coal-oil interface. The emulsification technique significantly increases the number of operations and the emulsified liquid may be unstable, which makes it difficult in industrial applications. The development and use of novel oxygen-containing oils or polar reagents have been proved to effectively achieve high flotation efficiency and have received widespread attention [19,23]; these include oxidized diesel, amine,  $\alpha$ -furanacrylic acid, tetrahydrofuran ester series, and carboxylic acid [23,27–32]. The polar collectors are prone to spread on the coal surface and have high interfacial interaction free energy with the coal surface. The interaction forces between the coal surface and the polar collector can be classified as follows: hydrophobic interaction,  $\pi$ -bonding, hydrogen bonding, and electrostatic force [23,31,33]. In terms of low-rank and/or oxidized coal, it is expected that the polar head of the collector interacts with its hydrophilic surface [31]. Mixtures of oily materials and non-hydrocarbon reagents, namely compound/mixed collectors, such as vegetable oils, engine oils, biodiesel, and polar/nonpolar mixture, have all been found to be more effective than polar reagent alone in terms of flotability [19,30,34,35]. It was found that some oily products have more complex compositions, such as polar groups, which will improve the flotation performance via the synergistic effect of polar oil molecules and nonpolar oil molecules [36,37]. Although these methods significantly enhance the low-rank and/or oxidized coal flotation yield [38], the underlying mechanism between collector and coal is still not clear.

It is also important to note that clay minerals are mixed in the clean coal with proportions of 10–50%, and these are not expected to float [39]. The clay particles will coat the surface of clean coal during flotation, which makes coal particles equally hydrophilic as clay particles, and hinders the coal particles from floating. However, the driving force for clay coating is still under debate. The interaction behaviors, including the force and configuration between coal and clay, have not been shown intuitively.

In recent years, with the rapid development of theoretical chemistry and computational chemistry, molecular simulation has become an effective means for investigating low-rank coal flotation, which has shed new light on the molecular structure of low-rank coal and the interfacial interaction in low-rank coal flotation at the molecular or atomic levels [40]. In this paper, we first review the basic theory of molecular simulation, and then we review the recent advances in our understanding on the molecular structure of low-rank coal. Coal-water, coal-reagent, coal-bubble, and coal-clay interactions are discussed comprehensively from the viewpoint of molecular simulation. This review is closed with a brief conclusion and perspective discussion.

## 2. Theories in molecular simulation

### 2.1. Density functional theory

In 1926, Austrian physicist Schrödinger established a linear partial differential equation describing the rule of particle motion, such as an electron wave function, called the Schrödinger equation [41]. Solving the Schrödinger equation is the core problem of quantum mechanics.

$$\hat{H}\psi(r, R) = E\psi(r, R) \quad (1)$$

where  $\Psi(r, R)$  is the wave function corresponding to the energy eigenvalue  $E$ ,  $r$  and  $R$  are the coordinates of the electron and the nucleus in the system, respectively, and  $\hat{H}$  is the Hamiltonian operator. In this theory, the wave function is regarded as the basic physical quantity of the system. Due to the large numbers of nuclei and electrons and the interaction between particles, classical electronic structure theories, such as the Hartree-Fock (HF) method and wave function method, were not applicable for the calculation of this complex multi-electron system, which requires some necessary approximations and assumptions to deal with the electronic structure. Density functional theory (DFT) uses the electron density (i.e., the square of wave function modulus) instead of the wave function as the basic quantity. The electron density is only a function of three spatial variables, so the computational complexity is clearly reduced because the multi-electron wave function has  $3N$  variables, where  $N$  is the number of electrons, and each electron contains three spatial variables.

The concept of DFT originates from the Thomas-Fermi model [42,43], which was proposed by Thomas and Fermi by solving the Schrödinger equation using a uniform electron gas model. However, it cannot determine basic chemical facts because the energy functional of the actual molecular system is more complex. Until 1964, Hohenberg and Kohn [44] gave the functional relationship between energy and electron density distribution. By using the variation principle, the multi-body problem can be strictly transformed into a single problem, which provides a solid mathematical basis for the Thomas-Fermi theory. Hohenberg and Kohn's first theorem points out that the ground state energy of the system is only a functional of electron density. Hohenberg and Kohn's second theorem proves that the ground state energy is obtained after minimizing the system energy by taking the ground state density as a variable. The corresponding energy functional expression of the system is given as

$$E[\rho(r)] = T[\rho(r)] + U[\rho(r)] + E_{xc}[\rho(r)] = \int \rho(r)v(r)dr + F_{HK}[\rho(r)] \quad (2)$$

where  $\rho(r)$  is the number density of particles,  $T[\rho(r)]$  is the kinetic energy,  $U[\rho(r)]$  is the potential energy,  $E_{xc}[\rho(r)]$  is the exchange correlation functional, and  $F_{HK}[\rho(r)]$  is the energy functional. The Hohenberg-Kohn theorems prove the feasibility of using electron density as a variable to obtain the ground state properties, but the specific form of  $F_{HK}[\rho(r)]$  cannot be obtained.

On the basis of the Hohenberg-Kohn theorems in 1965, Kohn and Sham [45] used a virtual system without interaction between particles to replace the electron kinetic energy of the real system interaction while supposing that the electron density is constant, and the difference in energy between the two systems was put into the exchange correlation functional. The K-S equation was thus established:

$$\left[ -\frac{1}{2}\nabla^2 + v(r) + \int \frac{\rho(r_2)}{|r_1 - r_2|} dr_2 + E_{xc}[\rho(r)] \right] \varphi_i(r) = \varepsilon_i \varphi_i(r) \quad (3)$$

According to the above equation, the multi-electron system problem is converted to a single-electron system problem. Meanwhile, the computational complexity is transformed to that of the exchange-correlation energy functional, which introduces functional approximation when being solved.

There is no clear mathematical expression for the electronic

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