

Progress of microscopic interaction between fine particles in coal slurry water

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Abstract: The interaction between fine particles is widespread in nature and plays a crucial role in regulating various interfaces for minerals. In coal preparation wastewater treatment, the intricate mechanism of interaction between multi-component fine particles in coal slurry water (denoted as CSW) is a fundamental aspect in addressing the challenges of coal slurry water agglomeration, selective separation, and difficult dewatering. This paper presents a summary of the necessity, current research status, and progress in studying the microscopic interaction between mineral particles in CSW systems. It overviews theoretical calculation formulas for particle-particle interaction, factors that influence such interaction, and modern analysis techniques for studying microscopic particle interaction. These findings enhance and refine relevant theories, establish a theoretical foundation, and offer technical support for stabilizing and optimizing the performance of CSW systems. Additionally, it elucidates the mechanism of particle-particle interaction in CSW, which is of significant importance in achieving efficient separation of CSW.

Keywords: interaction between particles, fine particle, coal slurry water, EDLVO theory, influence factors

1. Introduction

Coal, being the primary energy source in our country, is difficult to change in the foreseeable future. 95% of coal is washed using wet methods (Chen et al., 2016), resulting in more than 100 billion cubic meters of difficult-to-settle CSW each year. This difficult-to-settle CSW is characterized by a high clay mineral content, a significant degree of slurry formation, a high ash content, and a strong chargeability (Lin et al., 2010; Chen et al., 2014; Chen et al., 2014; Min et al., 2018).

Particle interactions are ubiquitous in nature and play a significant role in regulating various interfaces of minerals, such as particle aggregation, flotation separation (Xu et al., 2003; Zhao et al., 2023), organic matter adsorption, polymer adhesion (Kourki and Famili, 2012), and mine wastewater treatment. Particularly, the interactions between mineral particles in CSW are one of the main factors that make it difficult to separate. When two fine mineral particles approach each other, they are influenced by each other, resulting in behaviors such as coagulation, flocculation, aggregation, and dispersion (Zou et al., 2016). Therefore, the coagulation or dispersion of fine mineral particles is directly related to the interaction forces between mineral particles. At the same time, clay minerals have disadvantages such as hydrophilicity, the ease of argillization, which leads to the formation of stable dispersed states (Israelachvili and Mc Guiggan, 1988; Zhang et al., 2022), negatively charged surfaces (Kumar et al., 2016), and impurity defects (Liu et al., 2012; Zhu et al., 2016). This not only causes electrostatic repulsion between particles but also forms a hydration film on the particle surfaces, thereby increasing the hydration repulsion between particles (Yin et al., 2012; Liu, 2013; Peng et al., 2016; Min et al., 2020), greatly increasing the difficulty of separating and sorting single coal or clay minerals in CSW. The study of interactions between fine mineral particles has attracted extensive attention in the academic community (James and Dan, 2003; Cheng et al., 2020), and researchers from the interdisciplinary intersection of mineral processing, interfacial chemistry, quantum chemistry, hydrodynamics, electrochemistry and microbiology, etc., with the help of computational simulation

software and high-end analytical testing means, comprehensively applying multidisciplinary theories and technologies, from different research perspectives, through a variety of advanced means of interactions between the fine mineral particles in the CSW. The interaction force between fine mineral particles in CSW has been investigated by various advanced means from different research perspectives, so that the relevant theories have been enriched and improved. This paper focuses on the calculation of the theoretical formulae for the microscopic interactions between mineral particles in CSW, and reviews the factors affecting the microscopic interactions between mineral particles in coal slurry, such as Hamaker constant, pH value, and the presence of low-valent metal cations, particle size, surface wettability, etc. In addition, this paper introduces methods for calculating the inter-particle micro-interactions, and then explores the influence mechanism of the inter-particle micro-interactions in CSW. Finally, the article looks into the future research directions and challenges of mineral inter-particle micro-interactions with the aim of elucidating the mechanisms behind these interactions in coal slurry as soon as possible. This will provide theoretical support for the efficient separation of CSW.

2. Theory of interaction between particles

Currently, the main theories used to explain inter-particle interactions are the classical DLVO theory and the extended DLVO theory. This theory was proposed by and named after the initials of Derjaguin-Landau and Verwey-Overbeek, respectively. It explains the stability of colloids. The theory is based on mutual attraction and mutual repulsion between colloidal particles, and when particles are in close proximity to each other, these two opposing forces determine the stability of the colloidal system (Li et al., 2022; Wang et al., 2023).

2.1. DLVO theory

The theory suggests that van der Waals gravity and electrostatic repulsion mainly exist between colloidal particles, and the magnitude and direction of the two combined forces determine the stability of the colloidal system. The van der Waals gravitational force is the sum of dispersion force, polarity force and induced dipole force between the particles, and its size and the distance between the particles exist as a function of the distance between the particles, which makes the colloidal particles merged and aggregated sinking (Li et al., 2023). The electrostatic repulsion is generated by the interaction of the double electric layer around the particles when the particles are close to each other, and the repulsion is also functionally related to the spacing index of the particles, which is an important factor to maintain the stability of the colloid (Sun, 2013; Cui et al., 2020).

Mathematically, the classical DLVO theory describes the interparticle interactions as the sum of van der Waals and electrostatic forces:

$$V_T = V_A + V_R \quad (1)$$

where V_T -The total potential energy of the inter-particle interaction, V_A - Van der Waals interaction energy between particles, V_R - Electrostatic interaction energy between particles, J .

Since the shape of the mineral particles is irregular, the way of considering the interaction is uncertain. Zhang et al. (Zhang et al., 2014) gives a formula for the potential energy between particles of different shapes, The specific formula is shown in Table 1.

Table 1. Calculation formula of energy with different particle shape (Sun, 2013)

status	Van der Waals potential energy	electrostatic potential energy	Note
sphere - sphere	$-\frac{A}{12\pi H^2}$	$\frac{6400N_A CkT}{\kappa} \gamma_0^2 \exp(-\kappa H)$	$p = \ln \frac{1 + \exp(-\kappa h)}{1 - \exp(-\kappa h)}$
sphere - surface	$-\frac{AR}{6H}$	$\pi \epsilon R (\varphi_{01}^2 + \varphi_{02}^2) \left[\frac{2\varphi_{01}\varphi_{02}}{\varphi_{01}^2 + \varphi_{02}^2} p + q \right]$	
surface - surface	$-\frac{A}{6H} \cdot \frac{R_1 R_2}{R_1 + R_2}$	$\frac{\pi \epsilon R_1 R_2}{R_1 + R_2} (\varphi_{01}^2 + \varphi_{02}^2) \left[\frac{2\varphi_{01}\varphi_{02}}{\varphi_{01}^2 + \varphi_{02}^2} p + q \right]$	$q = \ln 1 - \exp(-2\kappa h)$

Note: H is the distance between the surfaces of the two particles; A is Hamaker constant; C is the example volume molar concentration; N_A is Avogadro constant; κ is Boltzmann constant; T is the absolute temperature; κ^{-1} is the déby length; R is the radius of the spherical particles; and φ_{01} and φ_{02} are the surface potentials of particles 1 and 2, respectively.

2.2. Extended DLVO theory

With the depth of the study, scholars have found that the interaction between mineral particles not only contains van der Waals action, electrostatic action, there are also some non-DLVO forces, such as hydrophobic action potential (Yao et al., 2016). Hydrophilic particles due to the polarity of the particle surface and other roles, water molecules adsorption, so that the surface of the particles to form a certain thickness of the hydration film. When the spacing between particles is small to the hydration film in contact with each other, the hydration film will certainly produce a hydration repulsion in order to maintain its structural integrity and stability (Chen et al., 2016; Chen et al., 2014; Chen et al., 2014). Similarly, there exists an exceptionally strong, long-distance gravitational force between the surfaces of the hydrophobic coal particles, i.e., hydrophobic gravitational force (Li et al., 2022). The hydrophobic force originates from different mechanisms in different ranges of distances, with the long-range hydrophobic force mainly originating from the anomalous polarization of the water adjacent to the interface and the bridging effect of submicron bubbles. While the short-range hydrophobic force mainly originates from the first change of water molecules near the hydrophobic surface due to the conformational rearrangement (Xing et al., 2019). However, as of today, there is still a big controversy about the mechanism of the origin of hydrophobic forces. In addition, when the surface of mineral particles adsorbed macromolecular agents (e.g., inhibitors or flocculants), there will also be spatial site-blocking repulsive forces between mineral particles (Qian et al., 2018), hydrodynamic forces generated by fluids in the solution system in which the particles are embedded, and so on. The EDLVO theory is a powerful tool for conducting interfacial interaction studies.

The extended DLVO theory suggests that inter-particle coalescence or dispersion is determined by the total potential energy V_T . If $V_T > 0$, particles repel each other and disperse, if $V_T < 0$, particles attract each other and coalesce. Spherical particles with a particle radius of R are usually considered to be below 20 μm . Various interactions between particles can:

$$V_T = V_A + V_R + V_H \quad (2)$$

where V_A - van der Waals interaction energy between particles, V_R - inter-particle electrostatic interaction energy, V_H - interparticle interfacial polar interaction energy, J .

2.2.1. Van der Waals potential energy (Mukherjee and Pisupati, 2015; Cheng et al., 2020)

Assuming that the mineral particles are all spherical in form, the formula is as follows:

$$V_A = -\frac{A_{132}}{6H} \cdot \frac{R_1 R_2}{R_1 + R_2} \quad (3)$$

Calculate the Hamaker constant A_{132} for substances 1, 2 in medium 3.

$$A_{132} = (\sqrt{A_{11}} - \sqrt{A_{33}})(\sqrt{A_{22}} - \sqrt{A_{33}}) \quad (4)$$

where A - Hamaker constant for the interaction of particles in a dispersed medium, J , R - radius of mineral particles, m , H - distance between mineral particles, m .

A_{11} , A_{22} represent the Hamaker constants for the interaction of mineral particles 1 and 2 themselves in vacuum, respectively, and A_{33} represents the Hamaker constant for the interaction of water itself in vacuum, then the Hamaker constant A_{132} for the interaction of mineral particles 1 and 2 in aqueous solution 3 is (Oss et al., 1980; Mukherjee and Pisupati, 2015).

2.2.2. Electrostatic action energy

The electrostatic interaction energy between two mineral particles of radius R , both with a double electric layer overlapping, can be expressed as:

$$V_R = \frac{1}{2} \varepsilon R \varphi_0^2 \ln[1 + \exp(-\kappa H)] \quad (5)$$

where V_R - the energy of double layer repulsion between particles, i.e. the potential energy of electrostatic interaction, J , φ_0 - surface potential of mineral particles, V , κ - inverse of the Debye length (Hu et al., 2019), $\kappa = 9.61 \text{ nm}^{-1}$.

$$\kappa = \left(\frac{8\pi e^2 n_0 Z^2}{\varepsilon kT} \right)^{\frac{1}{2}} \quad (6)$$

where Z - the number of ionic valences in solution, e - electronic charge, ε - the dielectric constant of the medium, F/m.

$$\varepsilon = \varepsilon_0 \times \varepsilon_R \quad (7)$$

where ε_0 - absolute dielectric constant of the medium in vacuum, F/m, ε_R - relative permittivity of the medium.

2.2.3. Interfacial polar interaction energy (Churaev and Derjaguin, 1985; Zhang et al., 2012; Yao et al., 2016)

Minerals are hydrophilic and hydrophobic, and when the surfaces of two mineral particles are hydrophilic and hydrophobic respectively, there is a gravitational interaction between the surfaces of the mineral particles, which is collectively referred to as the interfacial polar interaction force. The interfacial polar interaction energy V_H of two spherical mineral particles with radii R_1 and R_2 respectively, in aqueous solution, is

$$V_H = 2\pi \frac{R_1 R_2}{R_1 + R_2} h_0 V_H^0 \exp\left(\frac{H_0 - H}{h_0}\right) \quad (8)$$

where H_0 - contact spacing between particle interfaces, m, h_0 - decay length, nm or m, V_H^0 - the interfacial polar interaction energy constant between substance 1 and substance 2 in water, J/m².

For colloidal particles in CSW, the interfacial polar interaction energy is calculated using the anljine empirical formula, which is used to determine the constant term and the attenuation length.

$$V_H = -2.51 \times 10^{-3} R k_1 h_0 \exp\left(\frac{H}{h_0}\right) \quad (9)$$

where the hydrophobicity factor k_1 can be expressed as

$$k_1 = \frac{\exp\left(\frac{\theta}{100} - 1\right)}{e - 1} (0 \leq k_1 \leq 1) \quad (10)$$

with θ as contact angle of the particle in the medium, °.

The decay length can be expressed as:

$$h_0 = (12.2 \pm 1.0) k_1 \quad (11)$$

2.2.4. Other non-DLVO forces (spatial site resistance, hydration, etc.) (Yotsumoto and Yoon, 1993; Xing et al., 2017; Kumar et al., 2019)

There are many factors affecting the hydration force, different interpretations of the hydration mechanism and different calculations regarding the hydration force (Marčelja and Radić, 1976; Schiby and Ruckenstein, 1983; Pashley and Israelachvili, 1984; Kwok et al., 1986; Israelachvili and Wennerström, 1996). The article summarises the existing models for the calculation of hydration forces, which are presented in Table 2.

When the distance between two surfaces or particles is less than a few nanometers, the interaction of van der Waals attraction and double layer repulsion between them cannot be described by continuum theory. This may be because one or both of the gravitational and repulsive forces do not satisfy the continuum theory at very small distances, or because the role of other non-DLVO forces becomes significant. These additional forces may be monotone repulsive, monotone attractive, or oscillatory, and at very small intervals they may be stronger than either of the two DLVO forces. At present, there is no accurate calculation formula.

It is worth noting that when calculating the action force, the mineral particles are generally approximated as spherical or other regular shapes, but in reality, the shape of mineral particles is often irregular. Therefore, the calculated result can only represent a theoretical value, which cannot be regarded as the actual force between mineral particles, and there is a certain difference between the two (Zhao et al., 2008).

At present, the theoretical studies of inter-particle forces are mainly carried out around the classical DLVO theory and the extended DLVO theory, although they can explain the flocculation and dispersion of mineral particles in the CSW system in the precise action distance, but the studies on the types and source mechanisms of non-DLVO forces in the extended DLVO theory for the actual CSW system are not yet comprehensive.

Table 2. Calculation of hydration force

Order	Hydration force	Note	
1	$g(z) = g_0 - a\eta^2(z) + c\left[\frac{d\eta(z)}{dz}\right]^2$	g_0 is the energy density of free water in the aqueous system,	
	$V_H(x) = \Delta G(x) = \int_{-\frac{x}{2}}^{\frac{x}{2}} [g(z) - g_0] dz$	a, c are positive parameters, the energy close to free water is greater than the energy close to the hydrophilic surface.	
	$= \frac{a\eta_0^2 x}{\sinh^2(kx/2)}$	$\eta(z)$ is related to the distance to the surface, blocking in the free water system is 0, the closer to the surface its value is larger, the maximum value is η_0 ,	
	$k = \sqrt{a/c}$		
	$F(x) = 2\pi RV(x)$	R is the radius of curvature,	
	$\frac{F_H(x)}{R} = 2\pi a\eta_0^2 \frac{x}{\sinh^2(kx/2)}$	x is the distance to the surface.	
2	$\frac{F_H(x)}{R} = \frac{8\pi^2}{d^5} \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_0 \varepsilon_1 (\varepsilon_1 + \varepsilon_2)}$	Where ε_0 is the vacuum medium constant,	
	$h > 0$	ε_1 is the solution relative medium constant,	
	$[2m_{\perp}^2 (1 - \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \times \exp(-\frac{4\pi h}{d}))^2 + m_{\parallel}^2 (\frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \times \exp(-\frac{4\pi h}{d}))^2] \times \exp(-\frac{4\pi(x-h)}{d})$	ε_2 is the surface relative medium constant,	
	m_{\perp} is the dipole perpendicular to the interface,		
$h < 0$	$\frac{F_H(x)}{R} = \frac{32\pi^2}{d^5} \frac{\varepsilon_1 (\varepsilon_1 - \varepsilon_2)}{\varepsilon_0 (\varepsilon_1 + \varepsilon_2)^3}$	m_{\parallel} is the dipole parallel to the interface, and d is the lattice constant.	
	$(2m_{\perp}^2 + m_{\parallel}^2 \times \exp(-\frac{4\pi(x-h)}{d}))$		
3	$x_{min} \leq x$	$\frac{F_H(x)}{R} = -\frac{4\pi\delta_0\kappa T}{v_w} [\phi_s + \ln(1 - \phi_s) (\frac{2\delta_0}{x} - 1)]$	Where δ_0 is the radius of the hydrated ion,
	$\leq 2\delta_0$		v_w is the volume occupied by water molecules at the surface,
	$x \geq 2\delta_0$	$\frac{F_H(x)}{R} = 0$	ϕ_s is the volume fraction of hydrated ions in the Stern layer.
4	$\frac{F_H(x)}{R} = 2\pi[V_R(x) + V_A(x)]$	Where $V_R(x)$ is the electrostatic potential energy between the surfaces due to molecular polarisation,	
		$V_A(x)$ is the van der Waals potential energy between the surfaces.	
5	$\frac{F_H(x)}{R} = \frac{4\pi d\kappa T}{v_w} \frac{(1+w)(1+2w)}{(1-w)^2 \ln(\frac{3(1+w)}{1-w})} \times \exp(-\frac{x}{d} \ln \frac{3(1+w)}{1-w})$	Where w is the Boltzmann weight, κ is the Debye length, d is the lattice constant.	

3. Factors affecting inter-particle interactions

3.1. Hamaker constant

Van der Waals forces, in molecular physics, are distance-dependent interactions between atoms or molecules and are a kind of important interaction force between macroscopic objects, with different van der Waals potentials between objects of different shapes and sizes (Israelachvili, 2011). Hamaker constant is a parameter characterizing the magnitude of the van der Waals attraction energy between substances and is an important parameter affecting the interaction between particles. Hamaker constant defines the strength of the interaction and is typically 10^{-21} - 10^{-19} J.

Van der Waals interactions are highly dependent on the Hamaker constant, which is closely related to the type, size, morphology and medium of the material. Van der Waals interaction of two identical materials in a medium or vacuum is always attractive (Israelachvili, 2011). If the material/medium are interchanged, the interaction of two identical materials on the medium (vacuum) remains constant, i.e., $A_{LML} = A_{MLM}$. It is worth noting that with respect to van der Waals interactions between different materials in a medium, they may be repulsive ($A < 0$) or attractive ($A > 0$). And for the same material,

the Hamaker constants obtained from different methods using different media usually have considerable differences (Li et al., 2009; Faure et al., 2011; Weber et al., 2021; Weber and Kaufhold, 2021). Table 3 shows the Hamaker constants of different minerals in vacuum and Table 4 shows the Hamaker constants of two minerals in water.

Table 3 Hamaker constant of some minerals in vacuum (Zou et al., 2015; Cheng et al., 2020)

Mineral	Hamaker constant (10^{-20} J)	Mineral	Hamaker constant (10^{-20} J)	Mineral	Hamaker constant (10^{-20} J)	Mineral	Hamaker constant (10^{-20} J)
Water	3.70~4.38	CdS	15.30	Mica	10.00	Quartz	6.30
Air	0.00	MgO	10.60	Fluorite	6.55~7.20	PAM	8.00
Anatase	19.70	CaO	12.40	coal	6.07	Cassiterite	25.60
Rutile	11.00~31.00	Graphite	27.6~59.00	Au	29.60~45.50	Alkane	3.80~5.00
Barytic ore	16.40	Corundum	12.00~15.50	Rhodochrosite	7.05	Heptane	3.80
Hematite	23.20	Kaolinite	31.00	Montmorillonite	22.00	Illite	25.00

Table 4 Hamaker constant of two materials in water (Zou et al., 2015)

Substance 1	Medium 3	Substance 2	Hamaker constant / zj
Coal	Water	Air	-10.50
Coal	Water	Coal	3.00
Coal	Water	Kaolinite	19.90
Kaolinite	Water	Air	-70.10
Kaolinite	Water	Kaolinite	132.80

3.2. pH

pH is one of the most important factors affecting the settling of CSW, which influences the flocculation process and the action of various chemicals by affecting the surface properties of the CSW (Bandini et al., 2001). Changes in solution pH affect the charging state of the mineral particle surface, which in turn causes changes in the zeta potential of the fine particle surface (Yukselen and Kaya, 2003). According to the classical DLVO theory and EDLVO theory, the existence of zeta potential on the surface of clay mineral particles is the main reason for their stable dispersion and difficult to settle, and the stability of the system increases as the absolute value of zeta potential increases.

The surface of clay minerals is negatively charged because of the uneven distribution of electron clouds between interlayer cations and laminar anions in the crystal structure, which leads to the negative charge on the surface. Under different pH conditions, the surface of clay minerals will react with H^+ or OH^- in solution to form different surface states, thus changing the surface charge characteristics. For example, at small pH values, H^+ can neutralize some of the negative ions on the surface of the slurry, reducing the repulsion between the particles and lowering the zeta potential (Liu et al., 2011; Yu et al., 2018). As pH increases, the H^+ decreases, the content of OH^- ions increases, the repulsion between the particles is enhanced, and the zeta potential rises. Therefore, a change in pH will change the electrostatic forces between the two, affecting the dispersion and coalescence of the particles. Fig. 1 (a) shows that the interaction energy between coal and montmorillonite increases with increasing pH. The effect of pH on the approach curves for the coal-kaolinite interaction in DI water is shown in Fig. 1(b). In addition, the surfaces of these minerals contain a large number of hydroxyl groups that can produce protonation and deprotonation in solution (Korolev and Nesterov, 2018; Qiu et al., 2022; Tofighi and Rahnamaie, 2023), and acid treatment promotes hydroxylation of clay mineral surfaces, increasing the hydrophilicity of the surfaces, whereas under alkaline conditions, the negative charge of the clay mineral surfaces is strengthened, which reduces the hydrophilicity of the surfaces.

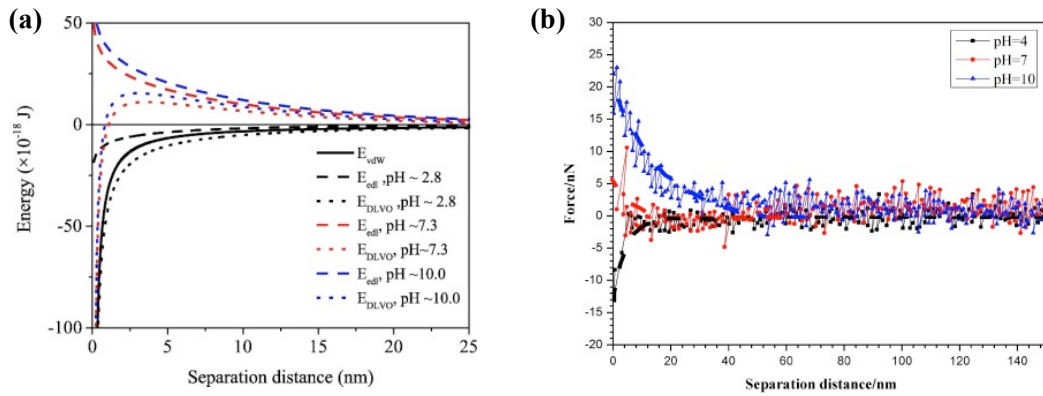


Fig. 1. Effect of pH on mineral interactions (a: montmorillonite and fine coal under different pH, b: The effect of pH on the approach curves for the coal-kaolinite interaction) (Gui et al.,2016; Yu et al., 2018)

3.3. Electrolyte

Electrolytes have an important effect on the interactions between fine mineral particles in solution systems. Firstly, electrolyte ions can interact with ions already present in the bilayer structure of mineral particles, compressing the bilayer on the surface of mineral particles, causing changes in the Zeta potential of the particle surface, and thus altering the electrostatic force between particles (Harvey et al., 2002; Li et al., 2016; Bournival et al., 2017; Bournival and Ata,2021). Liu Jiongtian's team (Zhang et al., 2004; Zhang et al., 2005; Zhang et al., 2008; Feng et al., 2010) found that Ca^{2+} is mainly adsorbed on the surface of clay minerals through electrostatic interactions, which affects the floatability of minerals.

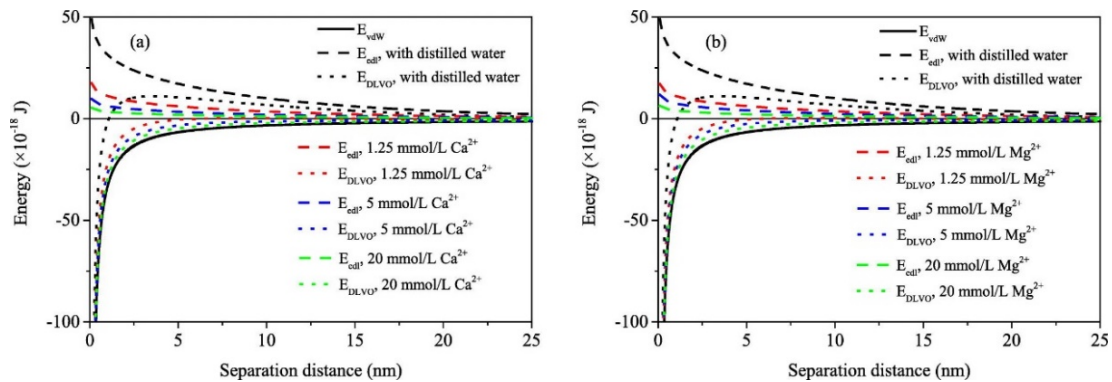


Fig. 2. Montmorillonite and fine coal under different divalent cations (Yu et al., 2018)

Secondly, with the increase of electrolyte concentration, the interaction between electrolyte ions and the particle surface is enhanced, leading to an increase in the interaction force between the particles, which promotes the aggregation of particles. **Fig. 2**, in calculating the interaction energy between montmorillonite and fine coal, it is seen that as the concentration of divalent cations increases, the interaction energy between the particles shifts from positive to negative and the interaction energy increases. However, when the electrolyte concentration is too high, there will be an excess of ions adsorbed on the particle surface, leading to a decrease in the electrostatic repulsive force between particles, or even transformed into an attractive force, so that the particles undergo inverse aggregation. Researchers have found that the addition of electrolytes increases the recovery of mineral impurities (mainly kaolinite, illite, montmorillonite, etc.) and makes flotation less selective (Xing et al., 2016; Chen et al., 2018). In addition, the charge of the ions also affects their interaction with the particle surface. Multivalent metal ions have a stronger charge than monovalent ions and have a more significant effect on the inter-particle interaction.

Furthermore, the surface of mineral particles is usually covered by a hydration film, making them somewhat hydrophobic. The presence of electrolyte ions can thin the hydration film on the surface of coal particles and change their wettability, which in turn affects the inter-particle interaction force

(Zhang et al., 2011; Gui et al., 2016; Yan et al., 2021). For instance, calcium and magnesium ions undergo hydrolysis to create hydroxyl compounds and hydroxides, which are either adsorbed or precipitated on the mineral surface. This alters the hydrophobicity of the particle surface, weakening the mineral particles' hydrophobicity and impacting inter-particle agglomerative behavior. The ions are mainly adsorbed on the clay surface in the form of complexes within the Stern layer of minerals, and there is also electrostatic and sedimentation adsorption. Fig. 3 and Fig. 4 show the variation of interaction forces between illite particles with increasing Ca^{2+} concentration.

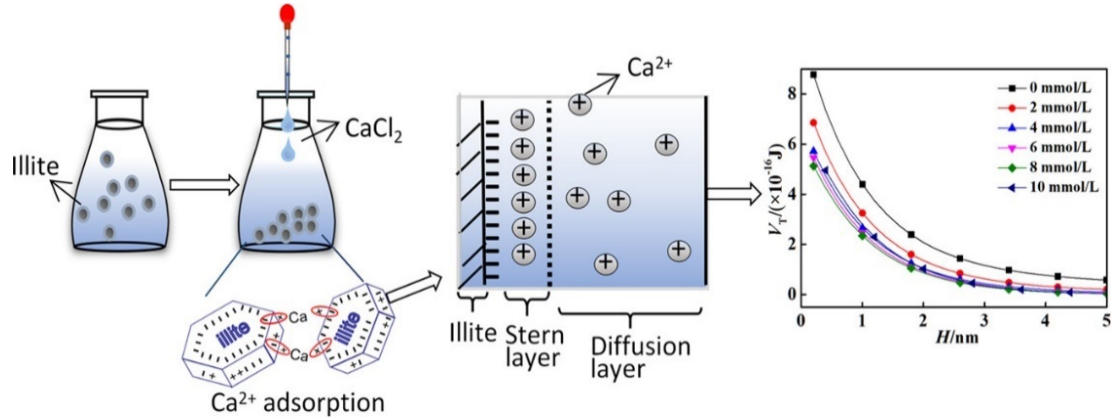


Fig. 3 Mechanism of calcium ion promoting settling of illite particles (Yan et al., 2021)

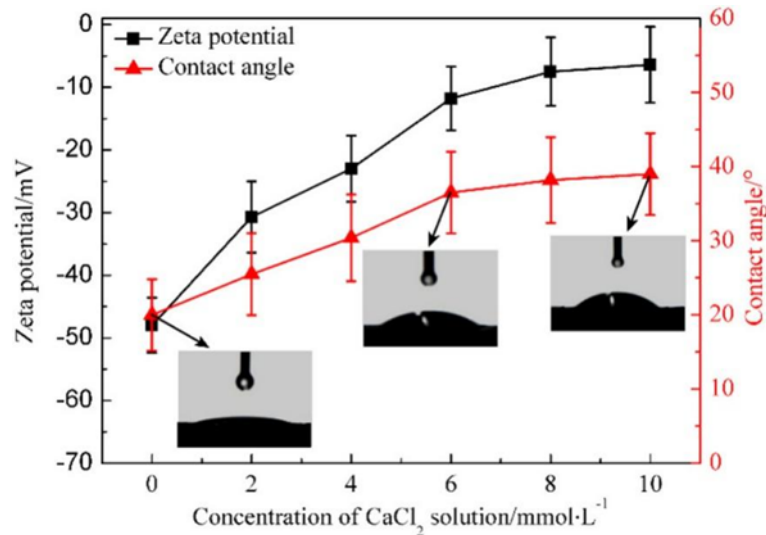


Fig. 4. Effect of different concentration of calcium ions on Zeta potential and contact angle of illite sample (Yan et al., 2021)

3.4. Particle size

For the CSW system, particle size characteristics (including particle size, particle size composition, and homogeneity) are important physical properties of minerals and important factors affecting the sedimentation of CSW. Changes in particle radius will directly affect the aggregation, dispersion, sedimentation and migration behaviour of particles (Li et al., 2016; Zhang et al., 2017; Zhou et al., 2022). Mineral particles are affected by gravity, buoyancy and Brownian motion at the same time, the finer the particle size, the more intense Brownian motion, Brownian motion makes the concentration of CSW tend to be uniform, the electrostatic repulsion between the particles is enhanced, the dispersion of particles is enhanced, and the degree of aggregation of particles is small. With the increase of particle size, the Brownian motion gradually decreases to disappear, and the CSW can be clarified by the free settling of mineral particles (Zhang et al., 2010; Zhang et al., 2022).

Under the condition of free settling, the settling velocity of particles and particle size to meet the Stokes formula, particle settling velocity and particle diameter is proportional to the square of the particle diameter can be seen, the smaller the diameter of the particles, the particles are less likely to settle (Zhu et al., 2008; Zhao et al., 2023). At the same time smaller particles because of its large specific surface area, and the interaction between the water is large, can be effectively adsorbed, has a strong dispersion and adsorption. When the radius of the particles is larger, the free settling speed of the particles is slower and the settling speed of the particles is smaller.

In addition, in CSW, the clay-coal interaction is not only related to the type of clay, but also to the size of coal particles. When the particle size of coal particles is much larger than the clay particles, the clay particles can cover the surface of coal particles.

3.5. Wettability of mineral surface

Wettability is an important surface/interfacial property used to assess the overall hydrophilicity or hydrophobicity of a mineral surface and to make predictions. The wettability - i. e. the degree of hydrophilicity or hydrophobicity - of a mineral surface is usually measured by the contact angle (Alghunaim et al., 2016; Bu et al., 2023). Changes in the wettability of mineral surfaces can be achieved by surface treatment agents, surface modification, nanocoatings and surface roughness modulation (Zhu et al., 2020; Sun et al., 2023). The effect of changes in mineral wettability on the total interaction energy between mineral grains is reflected in changes in the polar interfacial interaction energy V_H .

The addition of surfactants or the adsorption of two hydrophilic polymers can alter the wettability of the mineral surface, which can have a dramatic effect on the interaction properties of the mineral particles, and agents such as flocculants can react with the mineral surface to alter properties such as wettability and zeta potential, leading to different aggregation and dispersion behaviors between mineral particles, and ultimately, different sorting results (Sabah and Erkan, 2006; Zhang et al., 2021).

Secondly, the wettability of mineral surfaces can be changed by modifying them, which has been explored by experts and scholars in experiments and simulations (Kruszelnicki et al., 2024). Chen et al. (Ling et al., 2023) used molecular simulation to dope clay minerals and found that the surface properties could be changed, which in turn changed the mechanism of inter-particle microscopic interaction. In addition, mineral surface roughness affects surface wetting processes and microscopic interactions between mineral particles. Compared with smooth surfaces, the microstructures present on rough surfaces can provide sites for the adsorption of chemicals and promote the adsorption of chemicals, which can improve the flotation rate (Ahmed, 2010; Wang and Zhang, 2020). It has also been found that the contact angle of some mineral surfaces decreases with increasing roughness, thus affecting the sorting effect (Yekeler et al., 2004; Ulusoy and Yekeler, 2005).

4. Research method of inter-particle interactions

4.1. Validation of empirical formulae

The research method of mineral particle interactions is mainly calculated using DLVO/EDLVO theory. To date, extended DLVO has become a very effective tool to help interpret mineral particle interactions and predict favorable or unfavorable conditions in them (Liu and Wang, 2008; Oats et al., 2010; Yu et al., 2017; Hu and Liang, 2020; Chen et al., 2021; Shi et al., 2022;). The empirical formulas are validated with the DLVO theoretical formulas and extended DLVO theoretical formulas calculations, which have been described in Part II - Theory of interaction between particles.

The main conclusions of the study.

4.2. Modern analytical testing

Surface Force Apparatus (SFA) can directly measure the interaction forces (e.g., van der Waals forces, bilayer forces, hydration forces, spatial site resistance, hydrophobicity, etc.) between two surfaces mediated by a liquid or a gas as a function of distance on a nanoscale (Israelachvili et al., 2010), and thus obtain the trend of the inter-particle forces. Chang Qing (Chang, 2020) used SFA to determine the mutual attraction between salinized glass spheres and silica wafer particles when the medium was water and different concentrations of electrolyte solutions, respectively, and found that the electrolyte

had basically no effect on the hydrophobic forces. Israelachvili et al. (Israelachvili et al., 1978) measured the forces between the smooth surfaces of mica molecules in aqueous solution and found an additional repulsive force in addition to the normal van der Waals and bilayer forces. This force is an additional force rather than a modification of the bilayer force, since it is independent of the type and concentration of the electrolyte. And the use of SFA for sample preparation requires that the interacting surfaces be smooth and at least one of them be transparent or translucent. This requirement may impose some limitations on the measurement process.

Atomic force microscopy (AFM) can directly measure the particle-surface forces (e.g., van der Waals, electrostatic and hydrophobic forces, etc.) versus the spacing distance, and establish a direct connection with the surface properties of the particles, geometrical characteristics, environmental conditions, etc., and has been widely used to study the interaction forces between colloidal particles and surfaces in liquid media (Butt, 1991; Ducker et al., 1991; Mayer, 1992; Butt et al., 2005; Luo et al., 2011). In the field of mineral processing, the use of AFM to study the surface properties of minerals in air or liquid, and to study the van der Waals' gravitational force between the sample surfaces, bilayer electrostatic repulsive force, hydration force, and hydrophobic force have achieved very meaningful results (Alvim and Miranda, 2016; Gui et al., 2016; Qi et al., 2016; Babel and Rudolph, 2018; Xing et al., 2018; Shi et al., 2022). It is well known that forces between particles play an important role in bubble-particle interactions, mineral surface wetting, suspension dispersion, and membrane stability. It provides new ideas and methods to study the cohesion and dispersion of mineral particles, flotation interface interactions, and the mechanism of interactions between mineral particles (Mei et al., 2011; Sun et al., 2023). Fig. 5 shows the interaction between quartz and kaolinite probed using EDLVO theory and atomic force microscopy.

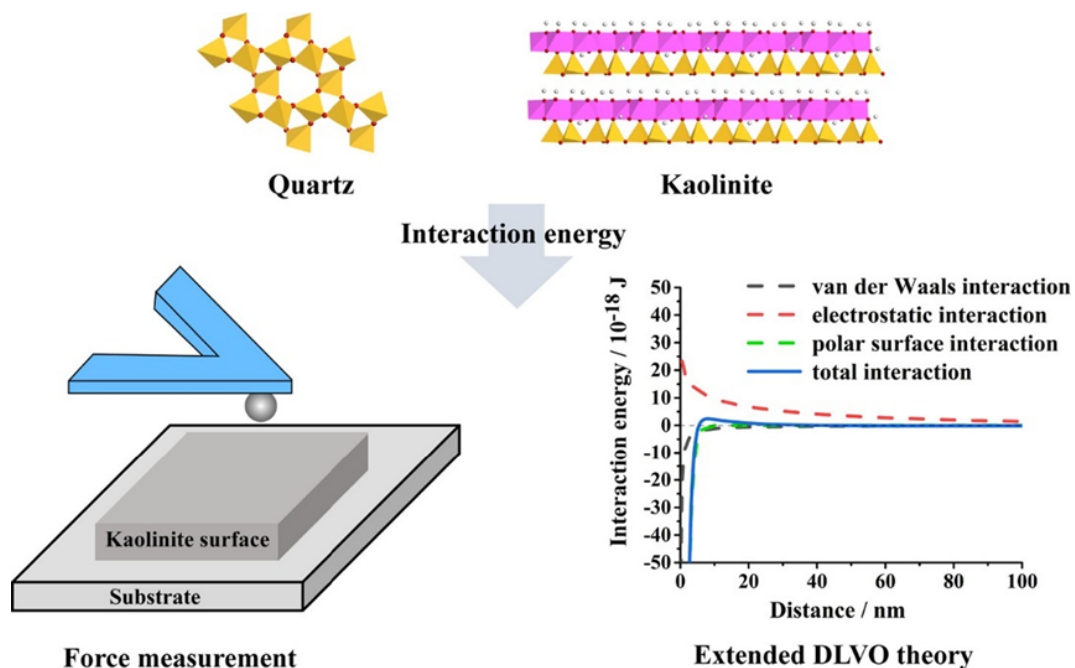


Fig. 5. Determining the interaction energy of a quartz-kaolinite system by atomic force microscopy and extended DLVO theory (Shi et al., 2022)

At present, the measuring instruments for inter-particle interactions are not only limited to SFA and AFM, but also other optical microscopy tests. For example, Zhao et al. (Zhao et al., 2006; You et al., 2008) applied the microscopic high-speed two-phase technique and found that the interaction behaviour of "attraction, circling and repulsion" is common among micron and near-sub-micron particles, and through the force analysis, it is believed that the traditional trailing force, gravity, Coulomb force and Van der Waals force can not explain this kind of inter-particle interactions, the specific test setup is shown in Fig. 6. Liu et al. (Liu et al., 2018) used cryo-scanning electron microscopy to show that bentonite and illite would produce a denser face-to-surface structure in high salinity water, resulting in a higher sedimentation rate.

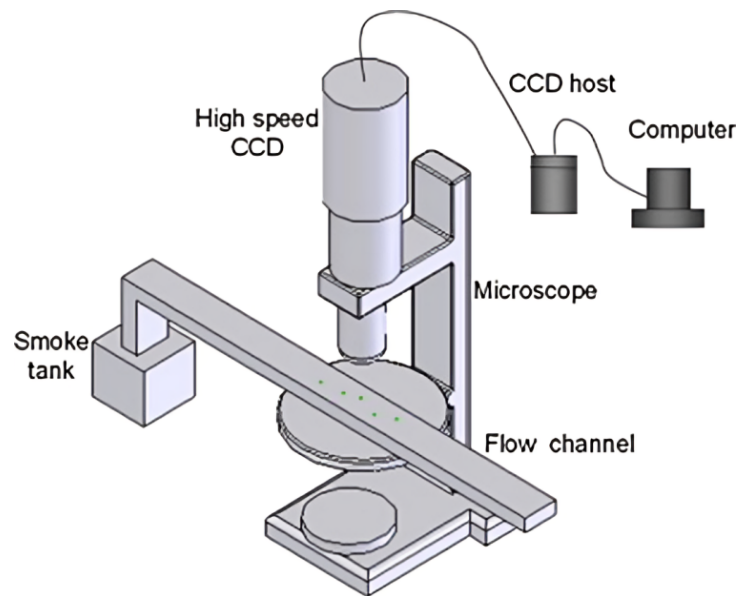


Fig. 6 Experimental setup for observing interactions between tiny burning droplets (You et al., 2008)

4.3. Computer simulation

Molecular simulation is a PC-based computational simulation method. Through the use of some simulation software, experimental data of the original structure are obtained, and these data are imported into the software to build a material model and verify the reasonableness of the determined microstructure of the material. Molecular simulation can not only simulate the structure of substances at the molecular level, but also simulate the changes in molecular motion before and after the reaction of substances, which plays an important role in scientific research (Zhang et al., 2018; Kang et al., 2022). With the development of computer technology, molecular simulation has also gradually become an important tool to study the interactions between mineral particles. Currently, molecular simulation is more often applied to study the interaction of water molecules and agent molecules (or ions) with mineral surfaces in CSW (Chen et al., 2019; Chen et al., 2022; Wei et al., 2023). Molecular simulation methods mainly include quantum mechanics and classical mechanics. Quantum mechanical simulation methods include first-principle calculations based on DFT, semi-empirical (Semi-empirical) and ab initio algorithms (Ab initio). First-principles computational methods based on density functional theory can analyze the mineral-surfactant (Han et al., 2016), and mineral-water (Wang et al., 2015), interaction mechanisms at the molecular/atomic level. Literature (Liu et al., 2015) used quantum chemical methods for DDA, dodecyl-propyl ether amine, and AC1201 as trapping agents and found that their protonated species were readily adsorbed on quartz surfaces by electrostatic attraction. The classical mechanical simulation methods mainly include molecular mechanics method (MM), molecular dynamics simulation method (MD) and Monte Carlo method (MC) (Wen et al., 2003; Akkermans et al., 2013; Thompson et al., 2022). In order to explore the microscopic interaction mechanism between the interfaces of microfine particles in CSW, the molecular dynamics (MD) method was adopted by Chen et al. (Chen et al., 2019). The interaction between microscopic coal and kaolinite particles in aqueous solution was simulated by the MD method, and the results showed that the macromolecules were able to exclude the surrounding water molecules from the kaolinite surface after reaching the adsorption kinetic equilibrium on the surfaces of the kaolinite to undergo a stable adsorption, and the structure of the benzene ring in part of the coal macromolecules. The structure of some benzene rings in the coal macromolecules is roughly parallel to the kaolinite surface. That is, the methods used in the molecular simulation studies of minerals include first-principles calculations, molecular mechanics, molecular dynamics and Monte Carlo methods (Ringl and Urbassek, 2012; Ma et al., 2019; Cheng et al., 2020; Sun et al., 2021; Silva et al., 2021; Shi et al., 2023). Fig. 7 shows the simulation of the microscopic interaction between microfine coal and kaolinite using MD. Fig. 8 shows the characteristics of the microfabric structures of defect-free kaolinite flocs and aggregates probed using large-scale all-atom molecular dynamics simulations.

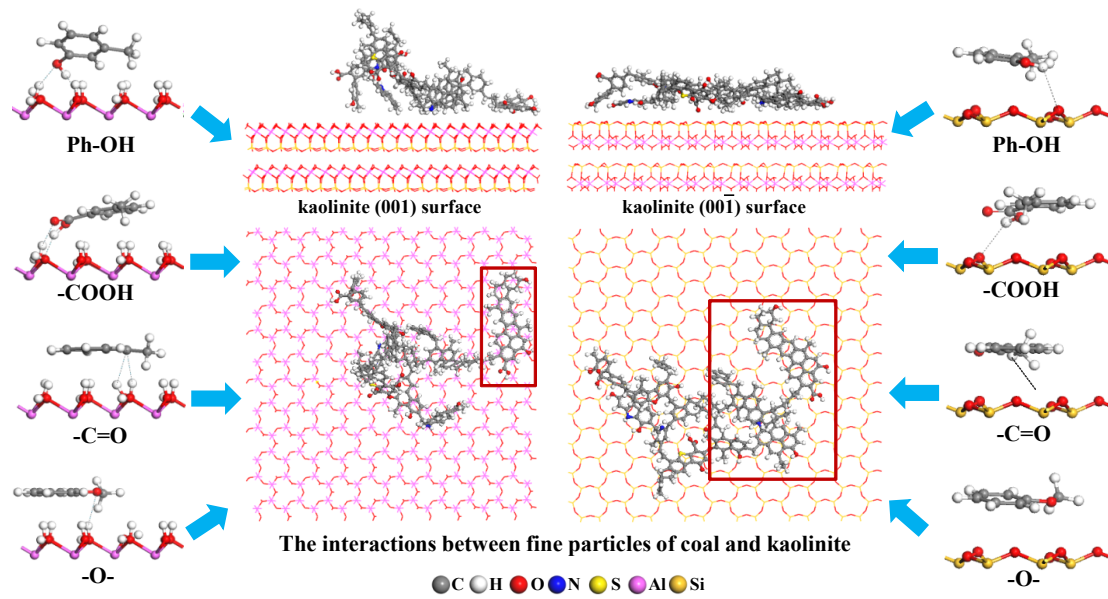


Fig. 7 MD simulation on interactions between fine particles of coal and kaolinite (Chen et al., 2019)

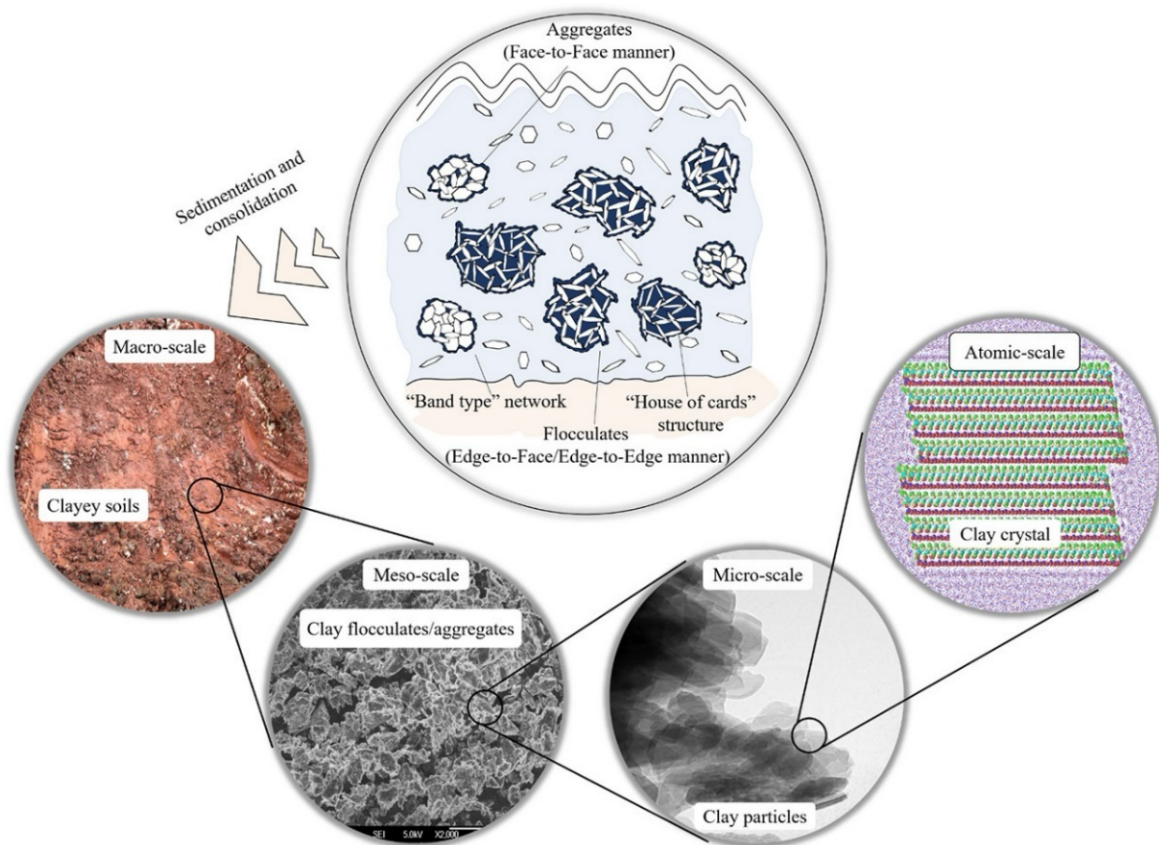


Fig. 8 Characterisation of different microfabric structures of kaolinite studied by large-scale all-atom molecular dynamics simulations (Sun et al., 2021)

Measurement and characterization of inter-particle forces in CSW have received increasing attention, but the modern analytical tests and molecular simulation methods used are idealistic, i.e., they can only determine or characterise the forces between pure minerals, regular shaped particles, or explain the inter-particle interactions in an ideal state by constructing a mineral model simulation, but cannot yet determine and characterise the inter-particle interactions in the complex environment of a real CSW system in a true sense.

5. Summary, conclusion and future research

The paper reviews the microscopic inter-particle interaction in coal-slurry water in terms of theoretical formulas, influencing factors, research methods, etc., and forms the main conclusions and outlook as follows:

(1) Scholars focused on the study of electrostatic forces in CSW, explored the change of the double electric layer on the surface of particles by various factors from a macroscopic point of view, and less research on the hydration repulsion, hydrophobicity and other composite forces on the surface of mineral particles. And the bonding mechanism of the microscopic interaction between the mineral particles is not shown, so more research scholars need to carry out more comprehensive and in-depth research.

(2) In summary, the current research on the microscopic inter-particle interactions in coal-slurry water based on the property of charge of fine particles, but the modern analytical tests and molecular simulation methods used are idealistic, and have not been able to characterise the inter-particle forces under the complex environment of the actual CSW system in a real sense.

(3) At present, computer molecular simulation research methods are more mature and are also used as new tools for the study of interactions between mineral particles in microfine-grained coal-slurry-water systems. The technical means are relatively more available, while the mechanism of inter-particle interactions cannot be elucidated clearly.

(4) In the future, the microscopic interaction between mineral particles in CSW will tend to the study of the complex interaction mechanism in the real environment, and the in-depth excavation of hydrophobic force, hydration repulsion and composite force existing in the CSW is expected to reveal the key microscopic mechanism in the process of CSW treatment. It is expected to reveal the key micro-mechanisms in the process of CSW treatment, provide important theoretical support for the improvement of CSW treatment technology, and also provide new ideas and methods for the treatment and resource utilisation of sludge in the process of CSW treatment, so as to achieve effective recovery and utilisation of valuable minerals in CSW, thus realising the comprehensive utilisation and recycling of resources. Theoretical simulation is used to guide the experiments, and experiments are used to verify the simulation results in a multi-method study. With the continuous development of simulation methods and experimental characterisation techniques, molecular simulation technology will play an important role in the study of mineral-particle interactions in coal-slurry water.

In conclusion, the study of the microscopic role between mineral particles in CSW will provide new ideas and methods for the development of CSW treatment technology and the utilisation of CSW resources, which is expected to promote the development of the coal industry in the direction of cleaner, more efficient and sustainable.

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