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# Investigation of the microscopic mechanism of H<sub>2</sub>O adsorption by low-rank coal slit pores through GCMC and MD simulations



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| ARTICLE INFO   | A B S T R A C T  |  |  |
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| A R T I C L E I N F O<br>Keywords:<br>LRC slit-pore model<br>Slit pore diameter<br>Adsorption active site<br>Energy distribution<br>Kinetic properties | This study investigates the influence of pore structure on H <sub>2</sub> O adsorption in low-rank coal (LRC) models at a molecular level, employing variously sized LRC slit-pore models H <sub>2</sub> O adsorption behavior is analyzed across different pore sizes ranging from 0.001 to 100 kPa fugacity, by employing the Grand canonical Monte Carlo (GCMC) method and molecular dynamics (MD) simulations to explore saturated adsorption kinetics. The findings indicate a positive correlation between H <sub>2</sub> O adsorption levels and both fugacity and pore diameter. Furthermore, at constant pore diameter, the adsorption heat increases exponentially with increasing adsorption levels. Notably, H <sub>2</sub> O adsorption in LRC slit pores exhibits multilayer adsorption characteristics. First, adsorption occurs as monomolecular layers on the LRC surface, transitioning to secondary adsorption sites formed by previously adsorbed H <sub>2</sub> O molecules with increasing fugacity, ultimately saturating the pores. This adsorption process exhibits a correlation with a shift in potential energy distribution from high to low potential energy directions. Moreover, the ordering of H <sub>2</sub> O molecule arrangements between hydrogen atoms, oxygen atoms, and H <sub>2</sub> O molecules decreases with increasing pore diameters. Larger pore diameters correspond to increased H <sub>2</sub> O molecule diffusion, the stronger interaction between the LRC slit pores and H <sub>2</sub> O molecules but reduced interaction |  |  |

#### 1. Introduction

Coal serves as a pivotal fossil fuel across various domains and stands as one of the primary sources globally for electricity generation and a foundational material for numerous chemical products (Zhu et al., 2019; Xie, 2019; Xie, 2017). Despite its multifaceted utility, the utilization of coal entails environmental, climatic, and geological challenges, including notable risks such as coal and gas hazards arising from mining activities (Zhao and Liu, 2022). Within coal seams, water is inherently present in various forms: intrinsic, extrinsic, and chemosynthetic (Jin et al., 2017). Moisture assumes a critical role in both the extraction and application of coal. Its presence mitigates coal dust generation and dispersion, thereby reducing the risk of dust explosions in mines, as well as curbing greenhouse gas emissions (Qin et al., 2022; Zou et al., 2021; Shekarian et al., 2021). Injection of water into coal seams is a common practice aimed at averting disasters such as spontaneous combustion, coal and gas outbursts, explosions, and surface subsidence (Lun et al., 2022; Yue et al., 2022; Jiang et al., 2022; Gao et al., 2023). However,

moisture compromises the calorific value of coal, elevates transportation expenses, and undermines coal storage stability. In coal flotation, the pronounced hydrophilicity of the LRC surfaces engenders poor floatability of fine coal particles and necessitates increased use of flotation agents (Zhao and Liu, 2022; Zhao and Liu, 2023; Bao et al., 2022; Li et al., 2021; Niu et al., 2022). Given the prevalence of water molecules in these processes, examining the interaction between coal and water molecules, as well as the wettability of coal surfaces, emerges as imperative for the safe extraction and efficient utilization of coal.

with individual H<sub>2</sub>O molecules. Overall, this study establishes a theoretical foundation for further studies on coal pore wetting and offer valuable insights for studies aimed at reducing dust and preventing gas outbursts.

Coal surface wettability correlates with coal rank, oxygen-containing functional groups (OFGs), particle size, surface morphology, pore structure, and the degree of defects (You et al., 2018; Horikawa et al., 2021; Li et al., 2013; Wang et al., 2020). Molecular simulation is extensively applied across various domains such as materials science, biochemistry, drug design, and nanotechnology. This method effectively predicts the properties, behaviors, and interactions of substances, simulating their atomic and molecular dynamics across different temporal and spatial scales (Hao et al., 2022; Bai et al., 2021; Li et al., 2019;

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Wang et al., 2020; Long et al., 2021; Ge et al., 2023; Swenson and Stadie, 2019). Zhang et al. conducted a study on the wettability of coal seam surfaces in the Pingdingshan mining area, employing experiments such as contact angle measurements and scanning electron microscopy tests. Their findings indicated the significant influence of moisture content, ash composition, mass fraction of inorganic mineral constituents, and OFG content on coal seam wettability. Notably, Group E coal seams exhibited the highest content of inorganic mineral SiO2, characterized by rough and loose surface morphology, indicative of pronounced wettability (Zhang et al., 2021). Additionally, Zhang et al. investigated the relationship between coal rank and water wettability through experimental analysis and molecular simulation. They deduced that low-rank coals exhibited the highest hydrophilicity, while bituminous coals exhibited lower wettability. The number of hydrogen bonds emerged as a pivotal criterion for assessing wettability strength (Zhang et al., 2020). Furthermore, Zhao et al. analyzed the bonding mechanism between OFGs in coal molecules and H<sub>2</sub>O molecules using density functional theory (DFT). Their analysis revealed that H 1 s and O 2p orbitals interacted to form hydrogen bonds, with carboxylate groups exhibiting the strongest affinity for H<sub>2</sub>O molecules (Zhao and Liu, 2022). Zhao et al. employed electrostatic potentials and frontier orbital analyses in DFT to predict the relative strength of wettability across various OFG surfaces. Their findings were consistent with the calculated interaction energies between functional groups and H<sub>2</sub>O molecules (Zhao et al., 2023). In another study, Xu et al. utilized first-principle molecular dynamics to simulate the ordered arrangement of H<sub>2</sub>O molecules on lignite surfaces. They determined that the distance between the carboxyl group and H<sub>2</sub>O molecules required for hydrogen bond formation ranged from 0.151 to 0.186 nm. Additionally, a stable hydrogen bonding network formed among H<sub>2</sub>O molecules proximal to the carboxyl group. Conversely, ether bonds did not engage in hydrogen bonding with H<sub>2</sub>O molecules; instead, hydrogen bonding was exclusively observed between H<sub>2</sub>O molecules (Xu et al., 2022). Jiang et al. conducted macroscopic experiments and MD simulations to examine the interaction between different functional groups and water molecules. Both sedimentation experiments and contact angle tests indicated that an increase in OFGs promoted enhanced hydrophilicity on coal surfaces. Moreover, the interfacial hydrophilicity was notably stronger in polar group simulation systems compared to nonpolar ones, corroborating experimental findings (Jiang et al., 2023). In a related investigation, Jin et al. explored H<sub>2</sub>O adsorption behavior on Tashan bituminous coal by constructing a coal macromolecule model and employing GCMC simulations. Their analysis revealed that the quantity of adsorbed H<sub>2</sub>O molecules was contingent upon temperature and pressure. Notably, a significant increase in adsorption occurred, leading to the formation of water clusters at 298.15 K and 20 kPa, indicating possible capillary coalescence (Jxxin et al., 2017). Zhang et al. delved into the impact of pore structure on the wettability of LRC using the GCMC method and MD simulations. They observed that H<sub>2</sub>O adsorption in LRC pores conformed to Langmuir isothermal adsorption, with adsorption quantity escalating with porosity. Additionally, H2O predominantly existed in clustered form within larger pores (Zhang et al., 2022). While studies have predominantly investigated the influence of OFGs on the interaction between coal and H<sub>2</sub>O molecules, the significance of targeting coal pore structure on H<sub>2</sub>O adsorption has been scarcely explored. Analysis of multilayer adsorption of H<sub>2</sub>O molecules from various perspectives, particularly concerning the LRC slit-pore model and energy distribution during H<sub>2</sub>O adsorption, remains an underexplored area requiring further study.

LRC is distinguished by its abundant reserves and cost-effective extraction processes worldwide, making it a viable energy resource. The implementation of coal bed water injection serves a multitude of purposes, including enhancing coalbed methane recovery rates, mitigating gas outbursts, reducing coal dust suspension concentrations to enhance mine safety, and modifying coal bed mechanical properties to improve stability. Given the inherent connection between LRC and H<sub>2</sub>O

molecules in practical applications, employing molecular simulation to scrutinize  $H_2O$  adsorption characteristics in LRC assumes paramount importance. In this study, we investigate the impact of coal pore structure on  $H_2O$  adsorption and diffusion at a molecular level. To accomplish this, we developed LRC slit-pore models with varying pore diameters. Utilizing GCMC simulation, we examined the adsorption quantity, isosteric heat of adsorption, energy distribution, and probability density field distribution of  $H_2O$  molecules across nanoporous, microporous, and mesoporous LRC models to elucidate the adsorption mechanism. Additionally, MD simulations were employed to analyze the kinetic properties of  $H_2O$  in distinct LRC slit-pore models. The findings of this research provide theoretical foundations for further exploration into coal pore wetting and offer valuable insights for studies aimed at reducing dust and preventing gas outbursts.

# 2. Methods

#### 2.1. Model building and optimization

The coal molecule comprises a continuous polycyclic aromatic hydrocarbon structure composed of carbon atoms and containing various heteroatoms. In this study, the Wender coal model, illustrated in Fig. 1 (a), was selected to represent the LRC molecule (Xia et al., 2019). The molecular formula of the Wender coal model is C43H46O12, with a molecular weight of 754 and elemental content of 25.46 % O, 6.10 % H, and 68.44 % C. The abundant OFGs and fewer branched chains of the Wender coal model are consistent with the structural features of the LRC. Extensive research has demonstrated the congruence of the Wender coal model with LRC properties (Zhao and Liu, 2023; Zhang et al., 2020), confirming its suitability for investigating the adsorptiondiffusion characteristics of H<sub>2</sub>O in LRC slit pores. Geometry Optimization tasks were conducted using the Materials Studio software to optimize the structural energy of individual coal molecules. Periodic boundary conditions were applied to these molecules to simulate realistic coal behavior. Subsequently, the single coal molecules were arranged within a crystal cell measuring  $10.15 \times 10.15 \times 10.15$  Å using the Amorphous Cell module. The cell model was simulated with geometry optimization and annealing kinetics at temperatures ranging from 298 K to 1498 K. Upon simulation, the density stabilized at 1.12 g/ cm<sup>3</sup>, the energy was minimized and stabilized, and the optimal configuration was achieved, as depicted in Fig. 1(b). Geometry optimization and annealing were performed with medium accuracy, employing the COMPASS II force field to assign corresponding force field parameters to the atoms in the model. Details of the force field parameters are provided in the Appendix, along with the use of Forcefield assigned to assign charges (Meng et al., 2021; Xia et al., 2019). The COMPASS II force field was selected for its broader applicability and higher accuracy compared to the Dreiding force field. Numerous scholars have employed the COMPASS II force field to investigate coal adsorption characteristics with various gas molecules, yielding results consistent with experimental findings (Tan et al., 2022; Wang et al., 2020). Long-range electrostatic interactions were analyzed using Ewald summation with an accuracy of  $1.0 \times 10^{-3}$  kcal/mol, while van der Waals interactions were examined via Atom-based analysis with a truncation radius of 12.5 Å (You et al., 2019). Detailed parameter settings are outlined in Table 1. Finally, the single-cell model underwent cell expansion to construct the slit-pore model, as illustrated in Fig. 1(c). The structure of the  $H_2O$ molecule is presented in Fig. 1(d), with an optimized bond length of 0.93 Å and a bond angle of 104.55°.

Coal possesses a natural porous structure characterized by complexity. According to the International Union of Pure and Applied Chemistry (IUPAC), pores are categorized into macropores, mesopores, and micropores, with size boundaries set at 50 nm and 2 nm, while micropores smaller than 1 nm are referred to as nanopores (Sharon et al., 2015). Microporous pores constitute the majority of coal pores, whereas macroporous pores are less prevalent. In this study, we investigate the



Fig. 1. Structure of coal and H<sub>2</sub>O molecules: (a) Wender coal molecule, (b) single-coal cell model, (c) slit pore model, and (d) H<sub>2</sub>O molecule.

 Table 1

 Geometric optimization and annealing kinetics simulation details.

| Geometry<br>Optimization | Algorithm           | Smart                                    | Max.<br>iterations          | $5 \times 10^3$ (Zhao and Liu, 2022)      |
|--------------------------|---------------------|--|-----------------------------|---|
|                          | Energy              | $\frac{1\times10^{-3}}{\text{kcal/mol}}$ | Force                       | 0.5 kcal/mol/Å<br>(Zhao and Liu,<br>2023) |
| Anneal                   | Annealing<br>cycles | 5  | Total<br>number of<br>steps | $6 	imes 10^5$                            |
|                          | Ensemble            | NPT (Zhao<br>and Liu,<br>2022)           | Time step                   | 1.0 fs                                    |
|                          | Thermostat          | Andersen                                 | Barostat                    | Berendsen                                 |

H<sub>2</sub>O adsorption mechanism in coal by establishing models of LRC with nanopores of 0.5 and 1 nm, micropores of 1.5 and 2 nm, and mesopores of 2.5 and 3 nm. First, the single-cell model was expanded to 3  $\times$  3  $\times$  2 cells. Subsequently, slit-shaped pore structures with varying pore diameters were constructed by introducing vacuum layers with different thicknesses between the two layers of expanded cell models using the Build Lavers tool. Fig. 2 illustrates the different slit hole models and cell parameters. The model conforms to the orthorhombic crystal system with interprong angles  $\alpha$ ,  $\beta$ , and  $\gamma$  set at 90°, prong lengths a and b measuring 3.12 nm, and prong lengths c measuring 5.39/5.89/6.39/ 6.89/7.39/7.89 nm, respectively. To ensure comparability with the LRC slit-pore model (b)(c)(d)(e)(f) depicted in Fig. 2, model (a) does not impose restrictions such as rotations on the H<sub>2</sub>O molecular configuration. Additionally, the empty space above the LRC model contains H<sub>2</sub>O molecules during the simulation. However, the impact of these molecules on H<sub>2</sub>O adsorption in the slit pores is minimal and can be

#### disregarded.

2.2. Simulation and calculation methods

#### 2.2.1. GCMC simulations

Before adsorption simulations, the structural optimization of the LRC slit-pore model was performed. The Materials Studio software facilitated the calculation of isothermal adsorption and kinetic properties of H<sub>2</sub>O molecules within various LRC slit pores. Isothermal adsorption of LRC slit-pore model was performed using the Sorption module based on the GCMC method. The Adsorption isotherm task term was employed, with the computational method selected as Metropolis (Mosher et al., 2013), and the adsorbate designated as the geometry-optimized H<sub>2</sub>O molecule. The simulation encompassed a fugacity range of 0.001–100 kPa, with 10 fugacity steps, conducted at a temperature of 298 K. A total of  $2 \times 10^6$ Monte Carlo steps were executed during the isothermal adsorption simulation, with 10<sup>6</sup> equilibration steps followed by 10<sup>6</sup> production steps for statistical averaging. The parameter settings for the force field and non-covalent interaction forces mirrored those used in the geometry optimization task item. Upon completion of the isothermal adsorption, data on isothermal adsorption quantity, isosteric heat of adsorption, probability density field distribution, and energy distribution were obtained.

#### 2.2.2. MD simulations

The kinetic properties of H<sub>2</sub>O within LRC slit pores of varying diameters were investigated through simulations conducted using the Locate task item within the Sorption module, with the loading amount set to the saturated adsorption level achieved during isothermal adsorption. The maximum loading steps were set at  $1 \times 10^6$ , with  $1 \times$  $10^6$  production steps and temperature controlled at 298 K over four



Fig. 2. LRC molecular slit pore model illustrating free volume (blue areas) and volume occupied by the atomic skeleton (gray areas) at various pore sizes: (a) 0.5 nm, (b) 1 nm, (c) 1.5 nm, (d) 2 nm, (e) 2.5 nm, and (f) 3 nm.

temperature cycles. Subsequently, geometry optimization and MD simulations were executed using the Forcite module for different LRC slitpore models/H<sub>2</sub>O molecular systems. Canonical ensemble NVT was employed for MD simulations (Nie et al., 2023), with the Nose thermostat selected to maintain a constant temperature of 298 K (Song et al., 2017). The initial rate followed a Boltzmann random distribution. Each simulation comprised  $1 \times 10^6$  steps, with a total simulation time of 1000 ps and a time step of 1 fs. Equilibration of the system was allowed for the first 500 ps, with data from the subsequent 500 ps utilized for characterizing the kinetic behavior of H<sub>2</sub>O molecules within the LRC slit-pore model, including H<sub>2</sub>O diffusion and the interaction strength between H<sub>2</sub>O and the LRC slit-pore model.

#### 3. Results and discussion

#### 3.1. Adsorption isotherms

The adsorption isotherms of H<sub>2</sub>O molecules within the LRC slit-pore model, featuring various pore sizes, are illustrated in Fig. 3(a). Additionally, the Freundlich isothermal adsorption model was employed for fitting, vielding satisfactory results as depicted in Fig. 3(b). Analysis of Fig. 3 reveals that, at the same fugacity, larger apertures of the slit pores corresponded to higher H<sub>2</sub>O adsorption amounts. For instance, at a fugacity of 100 kPa, the adsorption amounts of H<sub>2</sub>O by 0.5, 1, 1.5, 2, 2.5, and 3 nm LRC slit pores were 16.55, 22.05, 27.74, 33.51, 38.43, and 44.23 mmol/g, respectively. Compared with the 0.5 nm nanopore slit model, the other five LRC slit-pore models exhibited increased adsorption by 33.19 %, 67.56 %, 102.44 %, 132.15 %, and 167.20 %, respectively. This phenomenon can be attributed to the dependency of H<sub>2</sub>O adsorption in the LRC model on both the kinetic diameter of the H<sub>2</sub>O molecule itself and the aperture of the slit pore. The kinetic diameter of the H<sub>2</sub>O molecule was 0.28 nm, with pore diameters greater than 0.28 nm serving as effective adsorption pore diameters within the determined LRC model. Hence, the pore diameters of the slit pores primarily dictate the adsorption amount. Below a fugacity of 10 kPa, the adsorption of H<sub>2</sub>O in the LRC slit pores of varying sizes exhibited gradual increases, indicating monomolecular layer adsorption. Beyond 10 kPa, a sharp increase in H<sub>2</sub>O molecule adsorption was observed, signifying the formation of multilayer adsorption and the appearance of numerous water clusters until the slit pores of low-rank coal reached saturation. An increase in fugacity leads to adsorption saturation, reaching adsorption equilibrium at a specific fugacity point where the adsorption rate stabilizes. Notably, the fugacity point of adsorption equilibrium varied across the LRC slit-pore models of different pore sizes. For instance, adsorption equilibrium occurred at approximately 50 kPa for a pore

diameter of 0.5 nm, at 60 kPa for pore diameters of 1 and 1.5 nm, and at approximately 80 kPa for a pore diameter of 2 nm. Moreover, no equilibrium was observed even at fugacities exceeding 80 kPa for pore diameters of 2.5 and 3 nm. The greater the pore size of the LRC slit-pore model, the higher the fugacity point of adsorption equilibrium, making adsorption saturation more challenging. The existence of multilayer adsorption of H<sub>2</sub>O molecules on the LRC slit-pore model was indicated by the energy distribution (Fig. 6) and the interaction energy of  $H_2O$ molecules with the LRC slit-pore model in Fig. 10. Notably, the formation of potential energy bimodal peaks at low fugacities and the increasing interaction energy of individual H<sub>2</sub>O molecules with the LRC pore model with increasing pore diameter confirmed the occurrence of multilayer adsorption of H<sub>2</sub>O molecules. Yang et al. analyzed the adsorption behavior of low-rank coal and high-rank coal using water vapor isothermal adsorption tests and analyzed them using the Freundlich model (Yang et al., 2021). Their findings revealed a transition from monolayer adsorption of H<sub>2</sub>O molecules to multilayer adsorption with increasing water content, eventually leading to capillary condensation. They concluded that the difference in coal water absorption was primarily related to the degree of pore development, aligning with the conclusions drawn from the adsorption of H<sub>2</sub>O molecules in different LRC slit-pore models in this paper.

#### 3.2. Isosteric heat of adsorption

H<sub>2</sub>O adsorption by the LRC slit-pore model was assessed from an energy perspective by analyzing the isosteric adsorption heat. Fig. 4 illustrates the relationship between the adsorbed H<sub>2</sub>O amount and the corresponding isosteric adsorption heat across different pore diameters. As depicted in Fig. 4, within the same LRC slit-pore model, the adsorption heat exhibited an exponential increase with rising H<sub>2</sub>O molecular adsorption capacity, exhibiting an average growth rate of approximately 160.56 %. When the adsorption amount remained below 0.56 mmol/g, the isosteric adsorption heat measured less than 42 kJ/mol, indicating physical adsorption where H<sub>2</sub>O primarily adsorbed onto LRC molecules at the main adsorption site (Zhao and Liu, 2022; Wang et al., 2020). However, upon surpassing the 0.56 mmol/g threshold, the isosteric adsorption heat increased sharply before stabilizing, consistently exceeding 42 kJ/mol. For example, a 3 nm slit pore adsorption of 44.23 mmol/g, the isosteric adsorption heat peaked at 70.40 kJ/mol, surpassing the range of physical adsorption. This notable increase suggests a shift in the adsorption site, where the H<sub>2</sub>O adsorbed on the LRC acts as the active site for adsorption (the second adsorption site) and thus adsorbs the H<sub>2</sub>O molecules. As the isosteric adsorption heat stabilized, it indicated saturation of the second adsorption site, with an accumulation



Fig. 3. Adsorption amounts of H<sub>2</sub>O molecules at various pore diameters. (a) adsorption isotherm (b) Freundlich fit.



Fig. 4. Correlation between adsorption amount and isosteric adsorption heat.

of  $H_2O$  molecules forming water clusters within the LRC slit pores. At this stage, the  $H_2O$ - $H_2O$  interaction outweighed the interaction between LRC and  $H_2O$ . Notably, there was no direct correlation between adsorption heat and LRC slit pore diameter. In summary, the adsorption mechanism of  $H_2O$  by the LRC slit-pore model differs from that of other gases, characterized by multilayer adsorption, changing active adsorption sites, and a sharp increase in isosteric adsorption heat.

#### 3.3. Probability density field distribution

Visualizing the adsorption of  $H_2O$  within the LRC slit pores is facilitated by the probability density field distribution (Wu et al., 2019). Fig. 5 illustrates the fluctuation in  $H_2O$  adsorption density within 0.5 nm LRC slit pores across eight fugacities: 1, 5, 10, 20, 30, 50, 70, and 100

kPa. The closer to the blue area in the figure, the higher the density of H<sub>2</sub>O molecules. At a fugacity of 1 kPa, H<sub>2</sub>O predominantly occupied the adsorption sites on the LRC surface, particularly the OFGs, which are inclined to form hydrogen bonds with H<sub>2</sub>O, while the presence of H<sub>2</sub>O within the slit pores was minimal. With an increase in fugacity to 5 kPa, albeit with the adsorbed H<sub>2</sub>O on the LRC escalated, a lower density within the slit pores, where the interaction between LRC and H<sub>2</sub>O prevailed. Subsequently, at 10 kPa fugacity, the density of H<sub>2</sub>O within both the LRC and the slit pores experienced a moderate increase, accompanied by a slight aggregation of H<sub>2</sub>O within the pores. By the time the fugacity reached 20 kPa,  $H_2O$  concentration within the slit pores increased substantially, forming denser water clusters. When the fugacity increased to 50 kPa, the LRC slit pores approached saturation with H<sub>2</sub>O, exhibiting a very high density, signifying saturation of adsorption where H<sub>2</sub>O molecules occupied the second adsorption site. However, due to the aperture limitation of the slit pores, there was no substantial increase in H<sub>2</sub>O density when the fugacity was further increased to 100 kPa, akin to the degree of H<sub>2</sub>O aggregation observed at 50 kPa. This study comprehensively analyzed the probability density field of H<sub>2</sub>O within 0.5 nm slit pores across different fugacities, with the distribution of the probability density field of H<sub>2</sub>O in slit pores of other aperture sizes demonstrating similar patterns.

# 3.4. Energy distribution

The number of adsorption sites and the strength of adsorption were determined based on the energy distribution of H<sub>2</sub>O during adsorption within the LRC slit-pore model. Fig. 6 depicts the energy distribution of H<sub>2</sub>O adsorption within 0.5 nm LRC slit pores at varying fugacities. The number of peaks indicated the number of adsorption sites, with lower energies suggesting stronger adsorption. At a fugacity of 1 kPa, a distinct potential energy peak around -27 kJ/mol, corresponding to the preferred adsorption site of H<sub>2</sub>O, was observed, indicating that all H<sub>2</sub>O molecules were adsorbed on the LRC. With increasing fugacity, the energy of H<sub>2</sub>O adsorption within the LRC slit pores exhibited a bimodal



Fig. 5. Probability density field distribution of H<sub>2</sub>O at different fugacities: (a) 1 kPa, (b) 5 kPa, (c) 10 kPa, (d) 20 kPa, (e) 30 kPa, (f) 50 kPa, (g) 70 kPa, and (h) 100 kPa.



Fig. 6. Energy distribution of H<sub>2</sub>O in the LRC slit-pore model.

distribution, signifying the presence of two adsorption sites for H<sub>2</sub>O, each with different interaction regions. When the fugacity increased to 5 kPa, the potential energy peak at -27 kJ/mol gradually diminished, while the peak at -45 kJ/mol increased, indicating the emergence of a second adsorption site alongside the preferred one, although most H<sub>2</sub>O molecules were still adsorbed at the preferred site. The formation of the second adsorption site evolved gradually with increasing adsorption, with adsorbed H<sub>2</sub>O molecules serving as new adsorption sites. When the fugacity reached to 10 kPa, the potential energy peaks at -27 kJ/mol and -45 kJ/mol were close to each other, and the preferred and second adsorption sites occupied the same ratio. The emergence of potential energy bimodal peaks at low fugacity indicated the multilayer adsorption of H<sub>2</sub>O within the LRC slit-pore model and the existence of two adsorption sites for H<sub>2</sub>O molecules. Given that H<sub>2</sub>O molecules exhibit a Boltzmann distribution, the ratio of H<sub>2</sub>O molecules between the potential bimodal peaks at low fugacity was approximately 1:5, as revealed by the simulation of the RDF between H<sub>2</sub>O and H<sub>2</sub>O, with the peak area of the  $RDF_{H2O-H2O}$  bimodal peaks being roughly 1:5. When the fugacity increased to 20 kPa, a peak in the -27 kJ/mol energy region was absent, and the only peak existed in the -45 kJ/mol potential energy region, shifting to a lower energy region (-50 kJ/mol). Thus, H<sub>2</sub>O saturated the preferred adsorption site, and all adsorption shifted to the second adsorption site, leading to enhanced H2O-H2O interactions and a substantial increase in the amount of H2O adsorbed within the LRC slit pores. When the fugacity increased to the range of 50 kPa to 100 kPa, the peak potential energy ranged from approximately -66 kJ/mol to -68 kJ/mol in the low-energy region, indicating a higher concentration of H<sub>2</sub>O adsorption in this region where the H<sub>2</sub>O-H<sub>2</sub>O interaction was the strongest. Specifically, at 50 kPa, the adsorption of H<sub>2</sub>O at the second adsorption site reached saturation, leading to the filling of the LRC slit pores with H<sub>2</sub>O. Svabova et al. conducted isothermal water vapor adsorption tests using three coal samples and concluded that adsorption primarily occurred at the primary adsorption site at lower pressures. However, with increasing pressure, H<sub>2</sub>O molecules gradually shifted to the secondary adsorption site, wherein secondary adsorption became more prominent (Svabova et al., 2011). These findings aligned with the simulation results.

A comparison of the energy distribution of  $H_2O$  adsorbed in the LRC slit pores at various fugacities revealed a shift in adsorption sites for  $H_2O$  molecules. Increasing fugacity resulted in a shift of the potential energy distribution of  $H_2O$  toward lower potential energy, with the high energy region representing the preferred adsorption site. Conversely, in the case of  $CO_2$  gas adsorption in coal, the potential energy distribution occurred in the region with the lowest interaction energy, indicating the

preferential adsorption site for CO<sub>2</sub>. The position of the potential energy peak shifted to the right with increasing fugacity. These differences in the direction of potential energy movement and the preferential adsorption sites of  $H_2O$  molecules and CO<sub>2</sub> gas indicated notable variations in their adsorption properties. The adsorption mechanism of  $H_2O$  in coal was assessed based on the energy distribution of  $H_2O$  in the LRC slit-pore model, confirming the conclusions drawn from the adsorption amount of  $H_2O$  molecules, the distribution of probability density field, and the adsorption heat. These findings provided a deeper understanding of the adsorption behavior of  $H_2O$  molecules in coal.

#### 3.5. Kinetic properties of H<sub>2</sub>O molecules

# 3.5.1. Diffusion properties of $H_2O$

The size of the LRC pore diameter influenced the migratory diffusion characteristics of  $H_2O$ . The mean square displacement (MSD) and the self-diffusion coefficient (*D*) helped elucidate the diffusion rate of  $H_2O$ within the slit pores of varying pore diameters. Stable data from 0 to 250 ps were selected to analyze the MSD and calculate the self-diffusion coefficient using the following expression (Hao et al., 2022):

$$MSD = \frac{1}{N} \sum_{i=1}^{N} \left[ r_i(t) - r_i(0) \right]^2$$
(1)

where N denotes the number of molecules, and  $r_i(t)$  and  $r_i(0)$  represent the position vectors of the center of mass of the molecules at moments t and t = 0, respectively.

The self-diffusion coefficient was derived from the Einstein equation with the following expression (Hao et al., 2022):

$$D = \frac{1}{6N} \lim_{t \to \infty} \frac{d}{dt} \sum_{i=1}^{N} \left[ r_i(t) - r_i(0) \right]^2$$
(2)

$$D = \lim_{t \to \infty} \left(\frac{\text{MSD}}{6t}\right) = \frac{1}{6} K_{\text{MSD}}$$
(3)

where *D* denotes the self-diffusion coefficient of  $H_2O$  molecules, and  $K_{MSD}$  is the slope of the MSD curve. Fig. 7 depicts the MSD of H2O over time in different LRC slit-pore models, exhibiting a linear correlation between the MSD curves and time within the selected 250 ps, with an  $R^2$  value exceeding 0.99 in all instances. The fitted MSD curves are summarized in Table 2. The magnitude of the slope of the MSD curve positively correlated with the diffusion strength of the H<sub>2</sub>O molecules. As depicted in Fig. 7, the larger the pore diameter, the easier the migration of H<sub>2</sub>O in the LRC slit pores, with the mobility of H<sub>2</sub>O in



Fig. 7. Self-diffusion coefficients of H<sub>2</sub>O in the LRC slit-pore model.

#### Table 2

MSD fitting curves and self-diffusion coefficients of  $H_2O$  in different LRC slit pores.

| Slit pore<br>aperture | MSD fitting curves     | R <sup>2</sup> | Self-diffusion coefficient ( <i>D</i> , cm <sup>2</sup> /s) |
|-----------------------|------------------------|----------------|---|
| 0.5 nm                | Y = 0.7232 X + 9.7789  | 0.9981         | $1.21\times10^{-5}$   |
| 1 nm                  | Y = 1.1497 X + 15.2632 | 0.9975         | $1.92\times10^{\text{-5}}$                                  |
| 1.5 nm                | Y = 1.6386 X + 12.7939 | 0.9992         | $2.73\times10^{-5}$   |
| 2 nm                  | Y = 1.7497 X + 20.6512 | 0.9969         | $2.92\times10^{\text{-5}}$                                  |
| 2.5 nm                | Y = 2.1140 X + 20.7099 | 0.9978         | $3.52 	imes 10^{-5}$  |
| 3 nm                  | Y = 2.2496 X + 21.5591 | 0.9974         | $3.75\times10^{\text{-5}}$                                  |

mesopores notably higher than that in micropores. The self-diffusion coefficients of H<sub>2</sub>O in different LRC slit pores were obtained using expression (3), with the results presented in Table 2. As indicated by the data in Table 2 the self-diffusion coefficient of H<sub>2</sub>O tended to increase with the aperture of the slit pores, but the rate of increase had a tendency to increase first and then slow down. The self-diffusion coefficient of H<sub>2</sub>O in the 0.5 nm slit pore was  $1.21 \times 10^{-5}$  cm<sup>2</sup>/s, whereas it was  $3.75 \times 10^{-5}$  cm<sup>2</sup>/s in the 3 nm slit pore, indicating approximately a threefold increase in the self-diffusion coefficient H<sub>2</sub>O exhibited a greater propensity to migrate and diffuse in mesopores, attributed to the strong adsorption on the LRC and the binding effect of the pores on the H<sub>2</sub>O molecules, which had a more notable influence only within a certain distance range. Beyond this range, the effect of adsorption on H<sub>2</sub>O was diminished. The greater the pore diameter of the slit pores, the closer the

diffusion of  $H_2O$  was to that of pure water. Low-rank coal mesopores retained more  $H_2O$  than micropores, with the influence of OFGs and pores on the migration and diffusion of  $H_2O$  being less notable, resulting in a larger self-diffusion coefficient. The self-diffusion coefficient of  $H_2O$ in the 3 nm slit pore did not substantially increase compared to that in the 2.5 nm slit pore, because the self-diffusion coefficient of  $H_2O$  in the 2.5 nm slit pore closely resembled that of pure water, leading to a decrease in the rate of increase of the self-diffusion coefficient in the 3 nm slit pore.

# 3.5.2. Radial distribution function (RDF)

The RDF characterizes the distribution of one class of atoms or molecules in the system relative to another class of atoms or molecules within a specific distance r + dr (Zhao and Liu, 2022; Xiang et al., 2014). It responds to the level of ordering of H<sub>2</sub>O within the LRC slit pores of varying pore sizes using the following expression (Zhou et al., 2022):

$$g_{x-y}(r) = \frac{1}{4\pi\rho_y r^2} \times \frac{dN_{x-y}}{dr}$$
(4)

where *x* and *y* represent the two classes of atoms,  $\rho_y$  denotes the density of class *y* atoms, and  $dN_{x-y}$  denotes the average number of class *y* atoms within a certain distance of class *x* atoms. To further elucidate the diffusion distribution of H<sub>2</sub>O within the LRC slit pores, the RDFs between hydrogen atoms, oxygen atoms in the H<sub>2</sub>O molecule, and H<sub>2</sub>O molecules within the slit pores of different aperture diameters were calculated at an analytical distance of 12 Å. The results are illustrated in Fig. 8 and Fig. 9. Higher peaks in the RDF curve indicated a higher degree of ordering between atoms or molecules. As depicted in Fig. 8 and Fig. 9, for different pore sizes of LRC slit-pore models, the peak-out distances between hydrogen atoms, oxygen atoms, and H<sub>2</sub>O molecules in the H<sub>2</sub>O remained consistent, with only the heights of the peaks



Fig. 8. RDF between atoms in H<sub>2</sub>O molecule.



Fig. 9. RDF between H<sub>2</sub>O molecule and H<sub>2</sub>O molecule.

differing. The position of the first peak of the RDF between hydrogen atoms in an H<sub>2</sub>O molecule was at 1.5 Å, representing the distance between two hydrogen atoms within an H<sub>2</sub>O molecule, while the position of the second peak was at 2.5 Å. The position of the RDF peak between oxygen atoms of an H<sub>2</sub>O molecule was approximately 2.7 Å. Comparing the heights of the inter-atomic oxygen peaks in H<sub>2</sub>O revealed that the smaller the pore size, the higher the RDF peaks between oxygen atoms in the LRC slit pores. This indicated a tighter arrangement between oxygen atoms in H<sub>2</sub>O molecules within smaller aperture slit pores, resulting in more organized H<sub>2</sub>O molecules with lower diffusion rates, consistent with conclusions drawn from the height of the peaks between hydrogen atoms in H<sub>2</sub>O molecules. The RDF between H<sub>2</sub>O molecules exhibited two peaks, at 0.9 Å and 1.5 Å. Given that H<sub>2</sub>O molecules follow a Boltzmann distribution, the ratio of H<sub>2</sub>O molecules between the two peaks was 1:5, consistent with the ratio of peak areas obtained from the RDF calculations, affirming the accuracy of the calculations. At r = 0.9 Å, this corresponded to the bond length between oxygen and hydrogen atoms within the H<sub>2</sub>O molecule, whereas at r = 1.5 Å, it represented the hydrogen bond formed between H<sub>2</sub>O molecules. The height of the hydrogen bonding peak decreased with the increase in the aperture of the LRC slit pores, indicating that with an increase in the pore diameter, the hydrogen bonding force between H<sub>2</sub>O molecules diminished, the degree of ordering weakened, and the diffusion rate increased. This can be attributed to the adsorption of OFGs in the LRC and the binding effect of pores; with an increase in pore diameter, more H<sub>2</sub>O is adsorbed in the slit pores, resulting in weaker binding effects of the LRC pores and stronger H<sub>2</sub>O diffusion. The diffusion performance of H<sub>2</sub>O molecules was the most pronounced when the pore size of the slit holes was 3 nm, consistent with the results of the calculated diffusion coefficients.

# 3.5.3. Effect of pore size of slit pores on the adsorption of $LRC/H_2O$

The strength of  $H_2O$  adsorption was evaluated by calculating the interaction energies between different LRC slit-pore models and  $H_2O$ . The script was utilized to analyze 101 frames of interaction energy post-model adsorption equilibrium, focusing on the last 80 frames to calculate the average interaction energy. The expression for each frame of interaction energy/adsorption energy is as follows (Ding et al., 2023):

$$E_{\rm int} = E_{\rm LRC/H_2O} - E_{\rm LRC} - E_{\rm H_2O}$$
(5)

where  $E_{LRC/H2O}$  represents the total energy of the optimized H<sub>2</sub>O/LRC slit-pore system (kcal/mol);  $E_{LRC}$  and  $E_{H2O}$  denote the energies of LRC and H<sub>2</sub>O, respectively (kcal/mol). A lower interaction energy value indicates stronger H<sub>2</sub>O molecule adsorption. The calculation results of the

interaction energy and non-covalent interaction force between the LRC slit-pore model with different pore diameters and H2O/single H2O molecule are presented in Fig. 10. As illustrated in Fig. 10(a), the interaction energy between the LRC pore model and H<sub>2</sub>O gradually decreases with the increase in the pore diameter of the slit pores, indicating an enhanced adsorption capacity of H<sub>2</sub>O with larger pore diameters, aligning with the results of adsorption isotherm analysis. From the perspective of non-covalent interaction force, electrostatic force constitutes a higher percentage of the interaction energy of the H2O-LRC slit pore model, approximately 60 %, in both micropores and mesopores. Hence, the adsorption of H<sub>2</sub>O in the LRC slit pores was predominantly controlled by electrostatic force. Notably, as depicted in Fig. 10(b), the interaction energy between a single H<sub>2</sub>O molecule and the 0.5-nm pore model was -2.08 kcal/mol, whereas for the 8-nm pore model, it was -0.88 kcal/mol, representing a 57.69 % increase over the 0.5 nm pore model. The interaction between a single H<sub>2</sub>O molecule and the LRC slit pore model gradually decreases with increasing pore diameter, with electrostatic forces still dominating the interaction energy. Thus, when the pore diameter increases, the number of H<sub>2</sub>O molecules also increases, and the farther the H<sub>2</sub>O molecules are from the LRC, the weaker the adsorption of individual H<sub>2</sub>O molecules with the LRC pore model. This can be attributed to the adsorption of H<sub>2</sub>O molecules with those already adsorbed at the primary adsorption site, forming secondary adsorption sites. Subsequently, the adsorption between H<sub>2</sub>O molecules facilitates re-adsorption to form secondary adsorption layers, thus weakening the interaction of the LRC slit-pore model with individual H<sub>2</sub>O molecules. The larger the LRC slit pore, the more secondary adsorption layers are formed, confirming multilayer adsorption of H<sub>2</sub>O in the LRC slit-pore model, as indicated by the energy analysis in Fig. 10.

Fig. 11 illustrates the relative concentration distribution of  $H_2O$  molecules along the Z-axis in the LRC slit-pore/ $H_2O$  system. The adsorption rate of  $H_2O$  in the LRC slit pores was 33.36 % when the pore diameter was 0.5 nm. With an increase in pore diameter, the adsorption rate of  $H_2O$  gradually rises, exceeding 50 % for all pore diameters exceeding 1 nm. When the pore diameter reaches 3 nm, the adsorption rate peaks at 74.75 %. A substantial amount of  $H_2O$  is adsorbed in the LRC slit with larger pore sizes, weakening the interaction of individual  $H_2O$  molecules with the LRC. Conversely, fewer  $H_2O$  molecules are adsorbed in small aperture slit pores, resulting in greater force exerted by low-rank coal in micropores compared to mesopores on individual  $H_2O$  molecules. The pore diameter magnitude significantly influences  $H_2O$  adsorption in the LRC slit-pore model, which is pivotal for the investigation of coal pore wetting.

#### 4. Conclusions

This study investigated the influence of LRC slit pore size on the adsorption-diffusion properties of  $H_2O$  through GCMC and MD simulations, enhancing the understanding of  $H_2O$  adsorption mechanisms in LRC and providing new insights at the molecular scale.

The adsorption of  $H_2O$  in LRC slit pores exhibited a positive correlation with fugacity, and adsorption was enhanced with increasing slit pore diameter. This adsorption followed a multilayer pattern. Adsorption primarily occurred on the LRC surface and within the slit pores.

For adsorption of  $H_2O$  molecules in the LRC slit pores, the potential energy distribution occurred in the region with the highest interaction energy, indicating the preferential adsorption site for  $H_2O$ molecules. The position of the potential energy peak shifted to the left with increasing fugacity. Larger pore diameters corresponded to stronger interactions between  $H_2O$  and the LRC slit-pore model, while interactions between individual  $H_2O$  molecules and the model decreased. The bimodal distribution of energy upon adsorption of  $H_2O$  molecules and the decreasing interaction of individual  $H_2O$ molecules with the LRC slit-pore model with increasing pore



Fig. 10. Interaction energy between H<sub>2</sub>O (individual H<sub>2</sub>O molecules) and LRC slit-pore models.



Fig. 11. Relative concentration distribution of H<sub>2</sub>O molecules along the Z-axis: (a) 0.5 nm, (b) 1 nm, (c) 1.5 nm, (d) 2 nm, (e) 2.5 nm, and (f) 3 nm.

diameter confirmed the occurrence of multilayer adsorption of  $\mathrm{H}_{2}\mathrm{O}$  molecules.

The peak RDF between hydrogen atoms, oxygen atoms, and  $H_2O$  molecules in the  $H_2O$  decreased with increasing pore diameter. Conversely, the diffusion rate gradually enhanced. The increase in LRC slit pore diameter facilitated  $H_2O$  molecule self-diffusion. The analysis of the RDF matched the results of the calculated self-diffusion coefficients.

The microscopic mechanisms governing  $H_2O$  molecules adsorbed by the LRC slit-pore model were elucidated through molecular simulation, which may provide valuable insights for future studies aimed at reducing dust and preventing gas outbursts.

# CRediT authorship contribution statement

Dan Zhao: Conceptualization, Funding acquisition, Methodology,

Supervision. **Xiaoqing Liu:** Data curation, Writing – original draft, Writing – review & editing, Visualization, Software, Investigation, Validation.

# Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

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