

Article

Molecular Simulation of Multi-Factor Coupling Effects on Nanopore Wettability of Typical Shale Minerals

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Featured Application

The findings offer quantitative guidance for optimizing shale oil development schemes, reservoir stimulation design, and enhanced oil recovery technologies.

Abstract

Shale reservoirs feature widely developed nanopores, and the diverse crystal structures and surface functional groups of constituent minerals induce pronounced wettability heterogeneity, rendering conventional experimental methods incapable of characterizing nanoscale interfacial evolution. This work aims to reveal the multi-factor regulated wettability mechanisms of typical shale minerals at the molecular scale. Coupled molecular dynamics (MD) and grand canonical Monte Carlo (GCMC) simulations are performed on four shale minerals (hydroxylated graphene, quartz, calcite, kaolinite) under single-factor conditions (313–373 K, 10–40 MPa, 4–10 nm pores) and coupled pressure–pore deformation scenarios (15–35 MPa, 4–9.1 nm), with wetting mechanisms elucidated from hydrogen bond evolution, water molecular packing, nanoconfinement effect, and mineral crystal structure. The results show that rising temperature linearly reduces contact angles (average 0.33–0.35°/K) by strengthening hydrogen bonding; elevated pressure impairs wettability, with calcite exhibiting the highest-pressure sensitivity; nanoconfinement dominates pore scale wetting; and quartz presents the strongest pore size dependence. Synchronous pressure–pore expansion generates a superimposed wettability deterioration effect. This study quantifies the wettability evolution laws of shale minerals under diverse conditions, providing microscopic theoretical support for reservoir stimulation and enhanced oil recovery.

Keywords: shale; minerals; nanopores; wettability; molecular simulation; contact angle; nanoconfinement effect



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1. Introduction

Shale oil and gas represent core unconventional energy resources underpinning China's energy security. Shale reservoirs feature abundant 4–10 nm nanopores and host diverse inorganic and organic minerals, including quartz, calcite, kaolinite, and carbonaceous graphene [1,2]. Variations in the surface functional groups and crystal structures of these minerals give rise to pronounced spatial heterogeneity in reservoir wettability [3,4]. As a critical interfacial property governing fluid adsorption, spreading, and seepage within

nanopores, wettability directly determines the oil mobilization efficiency of water flooding, thermal injection, and gas displacement in shale oil reservoirs [5]. The wettability of solid surfaces is quantitatively characterized by the solid–liquid–gas three-phase contact angle derived from Young’s equation. A contact angle below 90° indicates hydrophilic surfaces that facilitate water spreading, while angles above 90° correspond to hydrophobic surfaces. However, nanoscale interfacial micro-behaviors cannot be directly observed via conventional macroscale experiments such as core contact angle measurements and nuclear magnetic resonance, rendering it infeasible to quantitatively elucidate the molecular mechanisms underlying wettability evolution under the synergistic effects of temperature, pressure, and pore size [6].

Coupled molecular dynamics and grand canonical Monte Carlo simulations circumvent the scale limitations of conventional experimental approaches, enabling accurate capture of microscopic features including water molecular configuration, hydrogen bond evolution, and interfacial adsorption. This coupled technique has emerged as a mainstream tool for unraveling the wettability mechanisms of shale minerals.

Extensive fundamental studies have been conducted globally on the wettability characterization of individual mineral surfaces. Siddiqui [7] systematically reviewed shale wettability testing methods and summarized critical influencing factors during contact angle measurements, providing guidance for the development of a quantitative wettability evaluation framework. Xue [8] and Chang [9] separately constructed molecular models for representative shale minerals, including quartz, calcite, and graphite to explore the impacts of mineral matrices and oil fractions on inherent wettability and clarified the intrinsic link between solid surface properties and interfacial interactions. For carbonaceous and clay minerals, Sergi [10] investigated the water wetting characteristics of graphite surfaces and uncovered the unique interfacial behaviors of carbon-based materials. Hu [11] and Jimenez-Angeles [12] conducted simulations on media such as kerogen and mica to analyze the regulatory mechanisms governing wettability by organic matter maturity and formation water ions. Furthermore, Shi [13] refined the computational methodology for nanoscale contact angles in molecular simulations, laying a technical foundation for subsequent quantitative research. These works have delineated the fundamental wettability traits of various minerals under single ambient temperature and pressure conditions, yet most fail to replicate the coupled thermobaric environment of subsurface reservoirs.

Regarding the temperature-dependent regulation of wettability, a general consensus has been established in the literature. Chen [14] performed molecular simulations across a range of temperatures and confirmed that elevated temperature increases the number of hydrogen bonds among water molecules and shortens their average bond lengths, thereby enhancing the hydrophilicity of mineral surfaces. For pressure effects, relevant studies have demonstrated that high pressure compacts water molecular clusters and weakens solid–liquid adsorption, giving rise to increased contact angles and degraded water wettability [15].

In terms of pore size dependence, Wu [16] systematically elucidated the nanoconfinement effect. They noted that in small nanopores, molecular force fields from the pore walls fully permeate the entire pore space, so solid–liquid interactions dominate and yield superior wettability. By contrast, fluid in the central region of large pores is free from the constraint of pore walls, and fluid cohesive forces become the dominant governing factor, leading to degraded wettability. Xu [17] used MD simulations to study two-phase flow in shale nanopores.

However, existing molecular simulation studies are mostly limited to single-variable analyses and lack coupled modeling integrating temperature, pressure, and pore size that replicates real in situ reservoir environments. Quantitative cross-comparison of typical

shale minerals under uniform simulation conditions remains scarce. Furthermore, most interpretations are restricted to phenomenological descriptions, and the microscopic superposition mechanism of wettability degradation under the synergistic effects of pressure and pore size has not been fully elucidated [18].

In this work, we employ coupled molecular dynamics and grand canonical Monte Carlo (GCMC) simulations to investigate four typical shale minerals: hydroxylated graphene, quartz, calcite, and kaolinite. We systematically analyze variations in mineral surface contact angles under single-parameter conditions (temperature, pressure, and pore size) as well as the coupled pressure–pore size condition. The mechanisms underlying wettability differences across working conditions and mineral types are elucidated by integrating analyses of water molecular configurations, hydrogen bond characteristics, the nanoconfinement effect, and mineral crystal structures.

The quantitative laws obtained in this work can directly provide theoretical guidance for optimizing hydraulic fracturing construction parameters and screening favorable shale oil development intervals, which fills the gap of microscopic multi-factor coupling research for shale nanopore wettability.

2. Molecular Simulation Models and Methods

2.1. Model Construction

Four typical shale minerals, namely hydroxylated graphene, quartz, calcite, and kaolinite, are selected as research objects. Nanopore wetting models are constructed using Materials Studio 2020 (BIOVIA, Dassault Systems, Vélizy-Villacoublay, France), with a uniform dimension of $40 \times 42.48 \text{ \AA}$ and an interlayer spacing of $3 \text{ \AA}$.

All pore models constructed in this study adopt slit-shaped nanopores, which are the dominant pore geometry of layered inorganic minerals (quartz, kaolinite, calcite) in shale matrix. Cylindrical and conical pores are mainly developed within organic kerogen, which is not included in the research scope of this paper focusing on inorganic mineral wettability. The target pore sizes of 4 nm, 6 nm, 8 nm and 10 nm are precisely controlled by adjusting the vertical interlayer distance between two parallel mineral slabs, and the corresponding lattice parameters for each pore width are recorded to guarantee modeling repeatability.

Lattice optimization and hydroxylation modification are performed on the mineral substrates, and three-dimensional periodic boundary conditions are applied to the entire system to eliminate boundary effects. The established models are illustrated in Figure 1.

For oil–water two-phase nanopore models in Section 3.3, n-decane is selected as the representative component of light shale crude oil, and the TraPPE force field is used to describe the intermolecular interaction of alkane molecules.

2.2. Simulation Methods and Force Fields

The simulations combine molecular dynamics and grand canonical Monte Carlo approaches: MD is utilized to track the dynamic wetting behavior of water molecules, whereas GCMC is applied to compute the equilibrium characteristics of interfacial adsorption. The CLAYFF force field is assigned to mineral pore walls, and the SPC/E force field is adopted for water molecules. The simulation proceeds sequentially, with the NVT ensemble for system relaxation and the NPT ensemble for isothermal–isobaric calculations.

In this work, the Nose–Hoover thermostat was adopted for temperature control, and the Parrinello–Rahman barostat was utilized to regulate system pressure during equilibrium calculations. Although mineral substrates and water molecules present obvious differences in compressibility, all models underwent sufficient NVT relaxation first to stabilize atomic configurations before switching to the NPT ensemble. The reserved vacuum region surrounding the pore channel provides free space for water droplet spreading and

does not introduce extra artificial confinement. Multiple parallel simulations confirm that the vacuum buffer zone exerts negligible influence on the equilibrium solid–water interfacial state, which verifies the validity of the NPT ensemble for our contact angle calculation system.

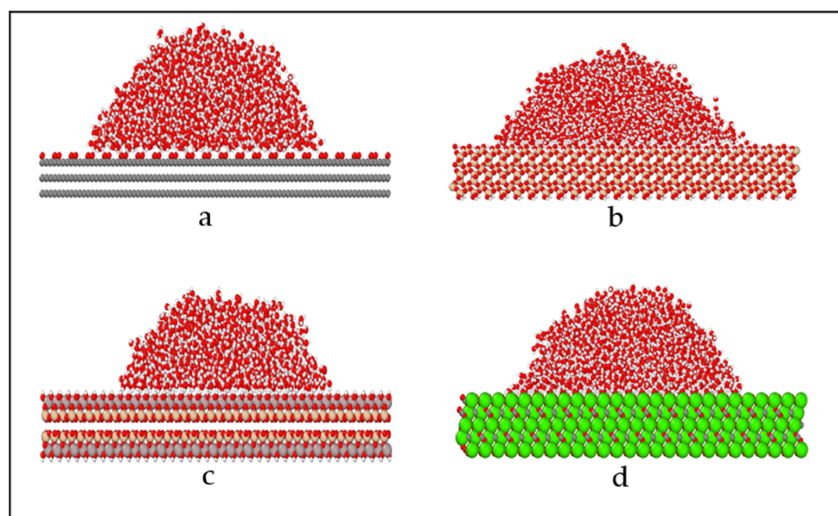


Figure 1. Initial wetting models of water clusters on different mineral surfaces. (a) Hydroxylated Graphene monolayer surface; (b) quartz monolayer surface; (c) calcite monolayer surface; (d) kaolinite monolayer surface; Red spheres represent oxygen atoms, white spheres represent hydrogen atoms, gray spheres represent carbon atoms, green spheres represent calcium atoms, and light brown spheres represent silicon/aluminum atoms.

2.3. Simulation Conditions

Single-factor simulation schemes adopt a temperature range of 313–373 K, a pressure range of 10–40 MPa, and discrete nanopore diameters of 4 nm, 6 nm, 8 nm and 10 nm. This temperature window is chosen to cover the formation temperature gradient of shallow to deep shale oil reservoirs, while the selected pressure interval corresponds to typical in situ formation pressure of continental shale oil strata in China. Such settings make the simulated thermal and pressure conditions consistent with actual subsurface environments, and the derived results can support practical engineering analysis.

Meanwhile, coupled pressure–pore size deformation conditions are configured, with pressure varying from 15 to 35 MPa and corresponding pore sizes synchronously adjusted from 4 to 9.1 nm.

To guarantee data accuracy and reliability, each simulation condition is independently run in triplicate, and the average contact angle is adopted to reduce random calculation errors. All systems undergo sufficient NVT relaxation followed by long-duration NPT equilibrium to eliminate initial molecular configuration disturbance. Under single-factor testing, all other parameters are fixed to strictly realize variable control and avoid interference from coupled factors; the existing literature verifies that the CLAYFF + SPC/E force field system maintains stable computational precision within 313–373 K [19]. The full simulation scheme is summarized in Table 1.

Table 1. Simulation schemes.

Wall Material	Pore Size/nm	Temperature/K	Pressure Gradient/MPa			
Hydroxylated graphene	4~10	313~373	10	20	30	40
Quartz	4~10	313~373	10	20	30	40
Calcite	4~10	313~373	10	20	30	40
Kaolinite	4~10	313~373	10	20	30	40

The pore widths of 4–10 nm are realized by regulating vertical interlayer spacing of mineral slabs in modeling.

2.4. Wettability Evaluation Method

The three-phase solid–liquid–gas contact angle is calculated via Young’s equation to quantitatively evaluate the wettability of mineral surfaces. All simulation conditions are replicated to ensure data reliability, and OVITO 3.8.0 (open-source molecular simulation post-processing visualization software) is employed to perform visualization analysis of molecular configurations and wetting morphologies.

After the simulation system reaches equilibrium, molecular trajectory files are imported into OVITO to extract atomic stress data. The pressure tensor method is adopted to quantitatively calculate solid–vapor, solid–liquid and liquid–vapor interfacial tensions based on molecular density distribution. The three groups of interfacial tension values are substituted into Young’s equation to calculate the equilibrium contact angle of each mineral surface. For asymmetric water droplet morphologies, contact angles on both sides of the droplet are measured three times respectively, outliers are removed, and the average value is taken as the representative contact angle under the corresponding working condition. All contact angle data in this paper are averaged from three parallel simulations to reduce random errors.

3. Results and Discussion

3.1. Effect of Temperature on the Wettability of Different Minerals

The regulatory effect of temperature in the range of 313–373 K on the water wetting characteristics of minerals was systematically investigated to reveal the intrinsic relationship between water molecule adsorption behavior and interfacial wettability under varying temperatures. The simulation results are presented in Figure 2.

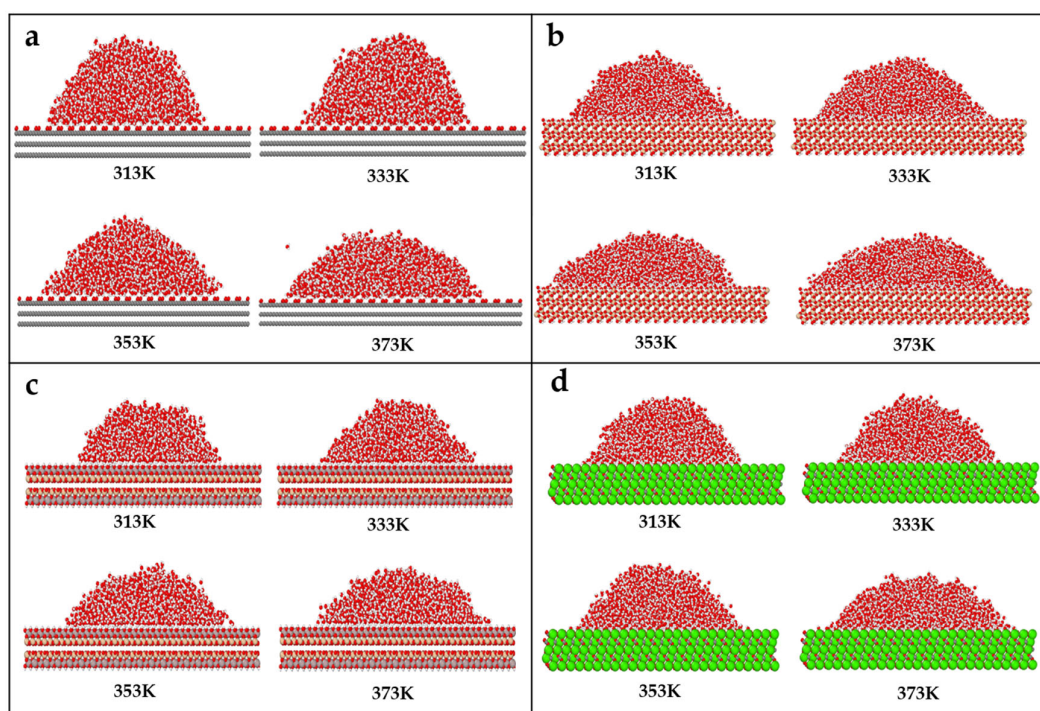


Figure 2. Temperature-dependent wetting models of water clusters on different surfaces. (a) Hydroxylated graphene; (b) quartz; (c) kaolinite; (d) calcite.

Figure 2 intuitively illustrates the wetting evolution of water clusters on the surfaces of hydroxylated graphene, quartz, kaolinite, and calcite. Distinct variations in droplet spreading morphology are observed across different temperatures: droplets exhibit a pronounced

contraction tendency at low temperatures, while uniform spreading characteristics appear at elevated temperatures. The overall simulation process maintains favorable stability.

Each temperature case was run three times for repeatability testing. The standard deviations of contact angles are very small, and the consistent downward trend with temperature is stable across all repeated calculations. Contact angle data for each working condition are extracted from simulation outputs, and the variation in mineral surface contact angle with temperature is presented in Figure 3.

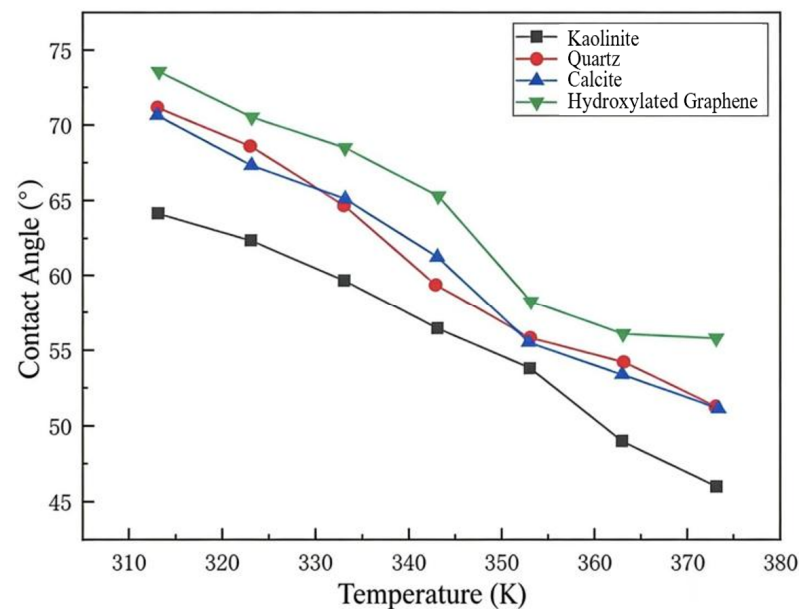


Figure 3. Effect of temperature on the contact angle for different surfaces.

As shown in Figure 3, the contact angles of all four mineral surfaces decrease linearly with rising temperature over the 313–373 K range. Kaolinite exhibits the largest reduction, with its contact angle dropping from 65° to 46°, whereas hydroxylated graphene shows the smallest reduction, decreasing from 75° to 55°. The average decay rate is determined to be 0.33–0.35°/K. Each temperature case was run three times for repeatability testing. The standard deviations of contact angles are very small, and the consistent downward trend with temperature is stable across all repeated calculations.

At the microscopic scale, elevated temperature intensifies the thermal motion of water molecules, leading to an increased number of hydrogen bonds and shortened average bond lengths within the system [14]. This strengthens liquid–solid interfacial interactions and facilitates the spreading of water droplets. The discrepancy in temperature sensitivity among the four minerals is governed by their surface functional groups and surface free energy. Hydroxylated graphene features uniformly distributed functional groups and stable surface free energy, resulting in the smallest contact angle variation and the optimal resistance to temperature fluctuations. Quartz and calcite are abundant in polar functional groups, and their surface free energy responds sharply to temperature changes, endowing them with the strongest temperature sensitivity. Kaolinite exhibits an intermediate overall performance.

3.2. Effect of Pressure on the Wettability of Different Minerals

Grand canonical Monte Carlo (GCMC) simulations are employed to construct single-surface wetting models for the four minerals at a constant temperature of 313 K. The evolution pattern of contact angles over the 10–40 MPa pressure range is investigated, and the regulatory mechanism whereby water molecular adsorption characteristics modulate

mineral water wettability under applied pressure is elucidated. The simulation results are presented in Figure 4.

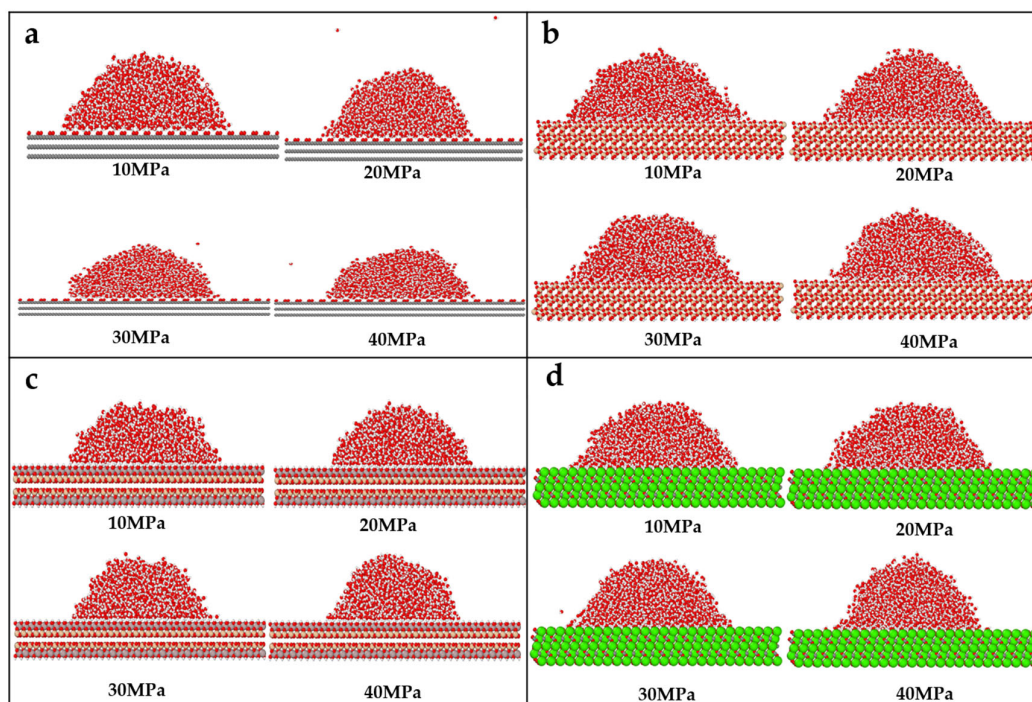


Figure 4. Pressure-dependent wetting models of water clusters on different surfaces. (a) Hydroxylated graphene; (b) quartz; (c) kaolinite; (d) calcite.

Figure 4 clearly illustrates the adsorption and spreading states of water clusters on different mineral surfaces over the 10–40 MPa pressure range. Under high-pressure conditions, water droplets tend to aggregate and contract, resulting in a reduction in the solid–liquid contact area.

Figure 5 summarizes the variation in contact angles on the four mineral surfaces under a pressure gradient of 10–40 MPa. The data demonstrate that elevated system pressure universally impairs the water wettability of mineral surfaces: the contact angles of hydroxylated graphene, quartz, kaolinite, and calcite increase by 9.7°, 8.0°, 11.1°, and 11.4°, respectively. Calcite exhibits the largest contact angle increment, indicating its strongest pressure sensitivity.

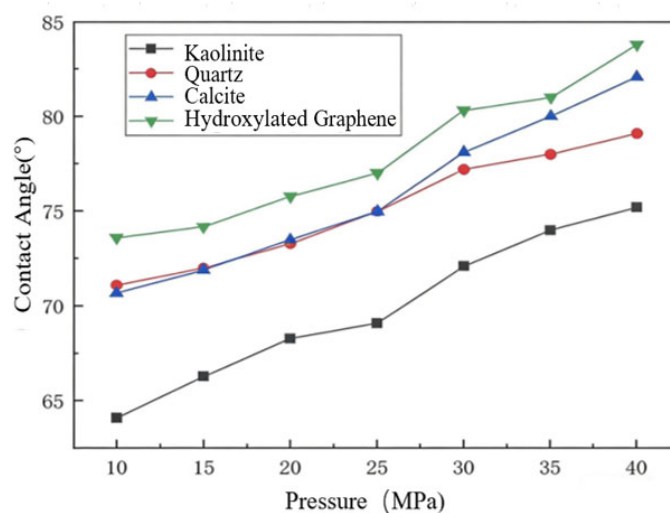


Figure 5. Effect of pressure on the contact angle for different surfaces.

At the microscopic level, an increase in pressure compresses the water molecular system, driving water molecules to transition from loose clusters to a densely packed configuration and leading to droplet contraction. Meanwhile, high pressure induces desorption of water molecules from mineral surfaces, which reduces the solid–liquid contact area and weakens interfacial interactions, ultimately resulting in an enlarged contact angle [20].

The positive correlation between pressure and contact angle is not a universal rule for all water–oil–mineral systems. Within 10–50 MPa, the pressure-induced contact angle rise can be significantly offset by high temperature; the magnitude of pressure influence strongly depends on thermal conditions.

The discrepancy in pressure responsiveness among the four minerals is governed by their crystal structures. Calcite, a carbonate mineral of the trigonal crystal system, is characterized by well-developed cleavage, densely distributed calcium ion active sites on its surface, and high surface free energy. High pressure not only weakens polar solid–liquid interactions but also induces slight lattice deformation; this dual effect results in the most significant wettability degradation in calcite. In contrast, quartz features a compact structure with moderate active site reactivity, kaolinite’s layered structure exerts a pressure buffering effect, and hydroxylated graphene maintains a stable structure. All three minerals are less susceptible to pressure influences than calcite.

3.3. Effect of Pore Size on the Wettability of Different Minerals

Molecular dynamics simulations are carried out at a constant temperature of 333 K and pressure of 20 MPa. Double-layer slit nanopore models of quartz, hydroxylated graphene and calcite are established for wettability characterization. In each model, the left domain of the pore channel is pre-filled with water molecules, while crude oil molecules occupy the right domain, which enables direct visualization of water droplet spreading and oil–water interfacial distribution under pore sizes of 4 nm, 6 nm, 8 nm and 10 nm. The morphological evolution of oil–water two-phase distribution inside nanopores under varying pore diameters is displayed in Figure 6. Kaolinite was excluded from this two-phase visualization model to avoid complex interfacial interference induced by its dual heterogeneous basal planes, which would obscure the independent nanoconfinement effect of pore size.

Figure 6 illustrates the wetting configurations of water clusters in the 4–10 nm slit nanopores of quartz, hydroxylated graphene, and calcite. Within small pores, water droplets maintain intimate contact with the pore walls, whereas those in large pores tend to adopt isolated morphologies.

Figure 7 summarizes the variation trends of contact angles with pore size for different minerals. As indicated by the contact angle versus pore size curves, the contact angle rises markedly with increasing pore diameter: it increases from 53° to 85° for quartz, from 35° to 75° for hydroxylated graphene, and from 47.5° to 75° for calcite. The confinement effect in small pores strengthens water–wall interactions and yields superior wettability, while the weakened confinement in large pores restricts fluid migration. The wettability of quartz surfaces shows the highest sensitivity to pore size changes.

This phenomenon is a typical manifestation of the confinement effect in shale nanopores [21–23]. The smaller the pore size, the stronger the confinement effect and the greater the contribution of solid–liquid interactions, which favors the improvement of water wettability. As pore size expands, the confinement effect attenuates stepwise, and intrinsic fluid properties gradually dominate the wetting behavior, resulting in continuous wettability degradation. Meanwhile, influenced by mineral crystal structures and surface

functional groups, quartz pores exhibit the most sensitive response to the confinement effect, whereas the pore size sensitivity of hydroxylated graphene and calcite is relatively lower.

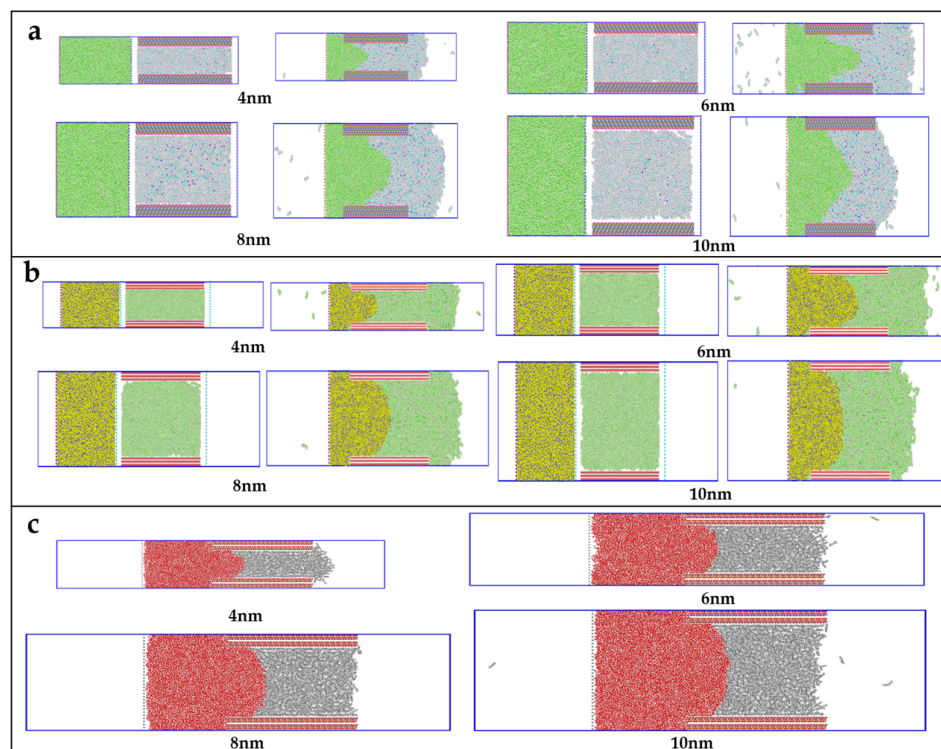


Figure 6. Wettability distribution characteristics within 4–10 nm slit nanopores. (a) Quartz; (b) hydroxylated graphene; (c) calcite. Subgraphs (a–c) in each panel represent pore sizes of 4, 6, 8 and 10 nm. Colored clustered particles on the left of each pore are water molecules, scattered light particles on the right are crude oil, and layered strips at top/bottom denote mineral pore walls. The transverse width of each pore channel equals the target nanopore diameter, revealing how pore size governs water spreading morphology.

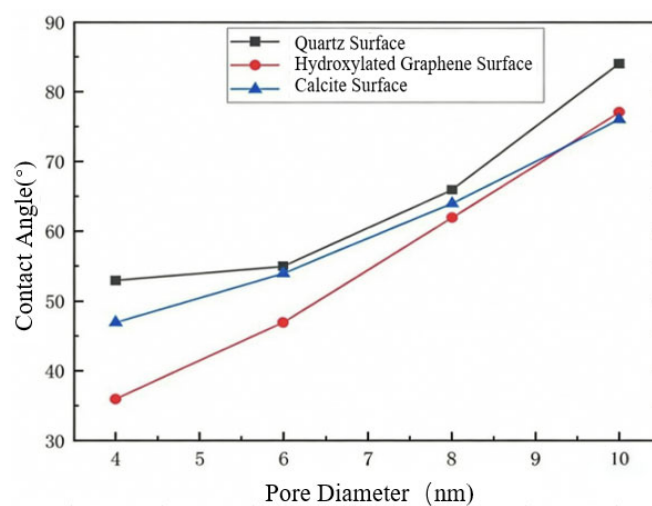


Figure 7. Variation in contact angle with pore size for different mineral pores.

This study only adopts slit-shaped nanopores for all models. For cylindrical and conical nanopores, the radial force field distribution differs obviously from slit pores, leading to distinct nanoconfinement strength and wettability evolution rules. Subsequent research can establish multi-geometric pore models to carry out comparative analysis.

In combination with the temperature and pressure regulation patterns discussed above, there exists a coupling relationship between the nanoconfinement effect and temperature/pressure conditions. Small pores are not only more sensitive to temperature and pressure variations, but their wettability is also continuously modulated by the strong confinement effect. Accordingly, small pores represent a critical pore type that requires focused attention in shale oil reservoir development.

3.4. Coupled Effect of Pressure and Pore Size on Wettability

The aforementioned single-factor analyses have clarified the independent regulatory patterns of pressure and pore size on mineral wettability. However, pressure and pore dimensions evolve dynamically and synchronously throughout reservoir production [24]. To reproduce the in situ coupled deformation characteristics, the stress deformation theory for shale pores is introduced to construct a dynamic wetting model featuring synchronous pressure–pore size evolution, and the wetting evolution behavior under the superimposed effects of the two factors is systematically analyzed.

The basic physical parameters adopted in the model are specified as follows: a Biot coefficient of 0.8, an initial porosity of 0.07, an original formation pressure of 40 MPa, an effective normal stress of 35 MPa, a matrix bulk modulus of 40 MPa, and a pore tortuosity of 1.

Figure 8 quantitatively characterizes the evolution of four sets of initial pore sizes (4, 6, 8, and 10 nm) with formation pressure. Simulation data indicate that all pore diameters expand synchronously as formation pressure rises from 15 MPa to 40 MPa: the initial 4 nm pores increase from 1.67 nm to 4.00 nm, the initial 6 nm pores expand from 2.50 nm to 6.00 nm, the initial 8 nm pores grow from 3.26 nm to 8.00 nm, and the initial 10 nm pores enlarge from 4.00 nm to 10.00 nm.

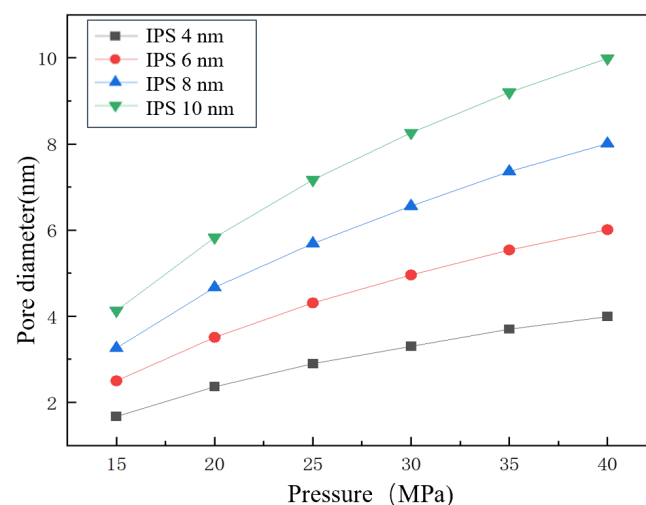


Figure 8. Variation in pore size with formation pressure under different initial pore sizes. IPS: initial pore size.

Figure 8 quantitatively characterizes the evolution of four sets of initial pore sizes (4, 6, 8, and 10 nm) with formation pressure. Under low formation pressure, high effective stress compresses pore space and triggers elastic shrinkage of nanopores, which explains why the curve for the initial 4 nm pores shrinks to 1.67 nm at 15 MPa. Simulation data indicate that all pore diameters expand synchronously as formation pressure rises from 15 MPa to 40 MPa: the initial 4 nm pores recover and increase from the compressed 1.67 nm to 4.00 nm, the initial 6 nm pores expand from 2.50 nm to 6.00 nm, the initial 8 nm pores grow from 3.26 nm to 8.00 nm, and the initial 10 nm pores enlarge from 4.00 nm to 10.00 nm.

Pore size shows a significant positive correlation with formation pressure, which can be explained by the stress deformation mechanism of the shale matrix [25]. Under constant

overburden stress, an increase in formation pore pressure decreases the effective stress borne by the rock skeleton, weakening the compressive constraint on pores and inducing elastic rebound and expansion of the pore space.

Based on the aforementioned pore stress deformation patterns, this work establishes a molecular simulation system for dynamic nanopore wettability incorporating the coupled pore compression effect. The basic model parameters are specified as follows: a baseline initial pore diameter of 10 nm and an original formation pressure of 40 MPa. The formation pressure is artificially regulated over the 15–35 MPa range; as the system pressure decreases progressively, the pore size synchronously contracts to 4 nm in a coupled manner. The parameter settings are listed in Table 2.

Table 2. Deformation of pores with pressure.

Original Pressure/MPa	Current Pressure/MPa	Normal Stress/MPa	Initial Pore Diameter/nm	Pore Diameter/nm
40	40	25	10	10.0
40	35	25	10	9.1
40	30	25	10	8.2
40	25	25	10	7.1
40	20	25	10	5.7
40	15	25	10	4.0

Wettability simulation models with quartz pore walls are constructed based on the current pressure and corresponding pore diameter, and molecular simulations are performed accordingly. The simulation results are presented in Figure 9.

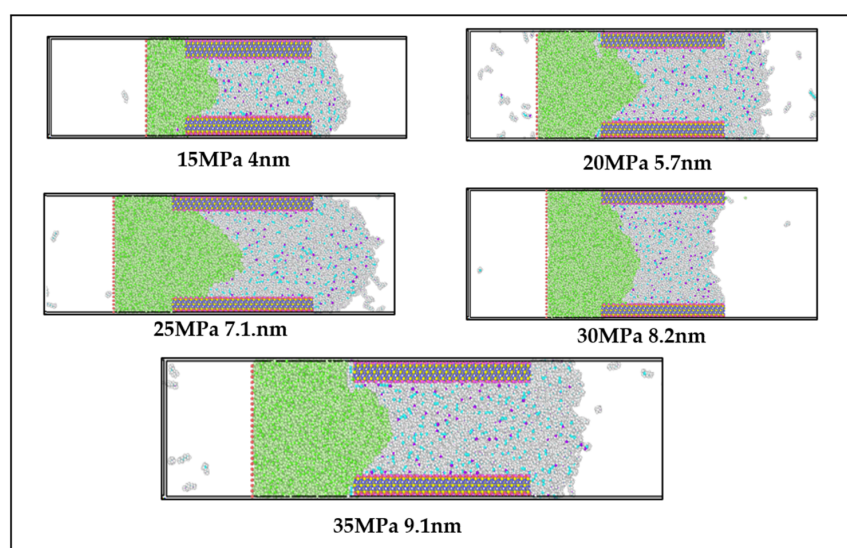


Figure 9. Molecular simulation configurations showing wettability under synergistic pressure–pore size deformation. The light green areas on the left side of the pore channel represent water molecules, while the light gray areas on the right side represent crude oil molecules.

As shown in Figure 9, as the system pressure increases from 15 MPa to 35 MPa, the pores synchronously expand from 4 nm to 9.1 nm. The spreading range of water clusters on the quartz pore walls shrinks continuously, with the solid–liquid contact area decreasing persistently and the spreading extent of water droplets gradually declining.

As can be seen from Figure 10, under the coupled working condition where the formation pressure rises synchronously from 15 MPa to 35 MPa and the corresponding pore diameter expands from 4 nm to 9.1 nm, the contact angle on the quartz surface increases continuously from 63° to 74° overall. The contact angle rises moderately from 63° to 66° within

the range of 15–25 MPa (4–7.1 nm). After entering the interval of 25–35 MPa (7.1–9.1 nm), the growth rate of the contact angle accelerates remarkably and finally reaches 74°.

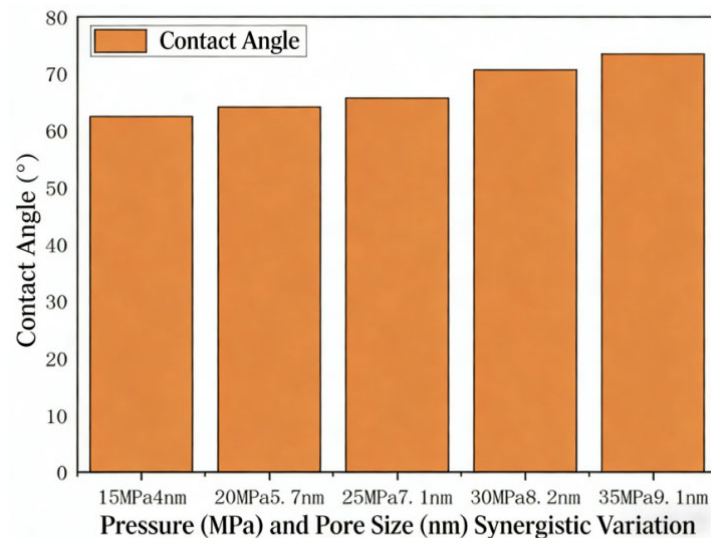


Figure 10. Variation in contact angle under synergistic pressure–pore size deformation.

From a mechanistic perspective, pressure remodels the mineral microstructure and alters the interfacial energy, while pore size governs the permeation and distribution characteristics of water molecules. A superimposed effect is generated by these two factors, which jointly weakens the spreading capacity of the aqueous phase on mineral wall surfaces and leads to the continuous deterioration of reservoir wettability.

4. Conclusions

This study performed coupled molecular dynamics and grand canonical Monte Carlo simulations to quantitatively investigate the contact angle evolution of four shale minerals (hydroxylated graphene, quartz, calcite, and kaolinite). The underlying mechanisms were clarified in terms of hydrogen bond characteristics, water molecular configurations, nanoconfinement effects, and mineral crystal structures. The main conclusions are as follows:

- (1) Increasing temperature effectively enhances the hydrophilicity of shale minerals. In the range of 313–373 K, the contact angles of the four studied minerals decline linearly at an average rate of 0.33–0.35°/K. Elevated temperature increases hydrogen bond quantity and shortens bond length, thereby strengthening liquid–solid interfacial interactions. Although the total contact angle reduction in kaolinite is 19°, its contact angle changes more rapidly with temperature; hydroxylated graphene has a total drop of 20° and shows the most stable wettability under high temperature.
- (2) At a constant temperature of 313 K and 10–40 MPa, elevated pressure weakens mineral surface hydrophilicity. High pressure compresses water clusters and promotes water desorption from mineral surfaces, thus increasing contact angles. This pressure–wettability correlation is not universal and is strongly modulated by temperature. Calcite is the most sensitive to pressure, with contact angle rising by 11.4°, attributed to its trigonal crystal structure and abundant surface calcium active sites prone to interfacial deformation.
- (3) Nanoconfinement governs wetting behavior inside nanopores. Strong solid–liquid interactions in 4 nm pores create favorable hydrophilicity, and the confinement effect weakens drastically as pore size increases to 10 nm. Quartz has the strongest pore size sensitivity, with its contact angle increasing by 32° (53° to 85°) as pores expand.

- (4) Synchronous variations in pressure and pore size exert a superimposed detrimental effect on wettability. For quartz under coupled conditions (15–35 MPa, 4–9.1 nm), contact angle grows by 11° (63° to 74°): the increase is mild at 15–25 MPa and accelerates at 25–35 MPa. Pressure-modulated interfacial energy and pore-size-dependent water distribution jointly restrain water spreading and continuously degrade reservoir hydrophilicity.

The multi-factor coupling rules obtained in this work offer microscopic theoretical support for shale reservoir stimulation design.

- (1) Optimization of hydraulic fracturing parameters: High-temperature deep shale zones have better hydrophilicity for oil displacement; overhigh injection pressure compresses nanopores and impairs wettability. Field fracturing temperature and pressure can be preliminarily adjusted based on formation pore size distribution to boost oil–water displacement capacity.
- (2) Favorable reservoir interval screening: 4–6 nm narrow slit nanopores feature strong nanoconfinement and stable hydrophilicity. In terms of interfacial wettability, these pore intervals serve as priority exploitation targets in fine reservoir evaluation.

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Informed Consent Statement: Not applicable.

Data Availability Statement: All data used during the study are available upon reasonable request. To access the measured experimental data, one can contact Dr. Bai Jinmei by contacting email of baijinmei@cczu.edu.cn.

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Conflicts of Interest: Authors Zhilin Wang and Zhengjun Ge were employed by Research Institute of Exploration and Development of Jiangsu Oilfield Company. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Abbreviations

The following abbreviations are used in this manuscript:

MD	molecular dynamics
GCMC	grand canonical Monte Carlo
IPS	initial pore size

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