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An insight into the effects of mix-wettability micro/nano structured surface on droplet spreading and heat transfer: With Molecular Dynamic Simulations

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Abstract

With the advancement of electronic manufacturing technology, electronic devices are rapidly evolving toward higher integration and miniaturization. Consequently, the heat flux generated within limited spatial environments has increased dramatically, creating an urgent need for efficient heat dissipation methods to ensure safe operation. Nucleate boiling heat transfer is characterized by a small temperature difference and a high heat transfer coefficient, making it an effective approach for managing high heat flux.

Compared to macroscopic droplet spreading and capillary flow, the phenomena and mechanisms at the micro/nanoscale are significantly more complex. At this scale, the influence of intermolecular forces becomes non-negligible, and potential scale effects must be carefully considered. Furthermore, theories based on macroscopic behavior may no longer be applicable and require corresponding modifications or supplements. Therefore, an in-depth investigation into the micro-mechanical mechanisms of droplet spreading and capillary flow is urgently needed. Extensive research indicates that composite wettability surfaces (mixed hydrophilic/hydrophobic surfaces) can effectively enhance boiling heat transfer. However, due to constraints in fabrication and experimental costs, it is challenging to conduct microscale boiling heat transfer experiments on these composite surfaces. Moreover, the rules governing how the distribution of hydrophilic/hydrophobic regions affects boiling heat transfer, along with the underlying physical mechanisms, remain incompletely understood.

Therefore, this study focuses on the micro/nanoscale processes of droplet spreading and capillary flow. Addressing the micro-mechanical mechanisms as the core scientific problem, I combine molecular dynamics (MD) simulations with theoretical analysis to deeply investigate how solid-liquid interactions influence surface wettability and droplet spreading, as well as the capillary flow processes and energy dissipation mechanisms under various wettability conditions. Concurrently, using MD simulations, I alter the area fraction and spatial distribution of hydrophobic regions to explore the

physical principles of pool boiling heat transfer on both smooth and structured mixed-wettability surfaces. I analyze the effects of solid-liquid interaction strength (surface wettability), wall temperature, and composite wettability micro/nanostructures on the bubble growth process, the number of evaporated atoms, interfacial thermal resistance, and heat flux. This reveals the physical mechanisms behind boiling heat transfer enhancement and provides a reference for optimizing structured surfaces. The main contributions are as follows:

1. Mechanism of Solid-Liquid Interactions on Surface Wettability and Droplet Spreading Dynamics

I investigated the wetting and spreading processes of droplets on solid surfaces under varying solid-liquid interaction strengths. While solid-liquid interactions are crucial in modulating wettability and spreading, current research covers a limited range of interaction strengths and lacks a deep understanding of how liquid molecular layers form or how precursor films affect spreading. The MD simulations indicate that surface wettability strengthens as the solid-liquid interaction increases. However, the droplet spreading velocity does not increase monotonically; excessively strong interactions actually hinder spreading. Based on the simulation results, I identified the conditions for generating a liquid precursor film and revealed its impact and mechanisms during spreading. Utilizing a simplified solid-liquid interaction model, I elucidated how interaction strength governs wettability and the formation of molecular layered structures. These findings deepen the understanding of micro-mechanical spreading mechanisms and provide a theoretical basis for the targeted regulation of wettability, making them highly relevant for engineering applications like self-cleaning surfaces, anti-icing/fogging, and microfluidic control.

2. Energy Dissipation Mechanisms in Nanoscale Capillary Flow and a Modified Theoretical Model

I revealed the energy dissipation mechanisms during nanoscale capillary flow and proposed a theoretical model incorporating dynamic contact angle effects and asymmetric wall wettability. While wettability dictates micro/nanoscale capillary flow, most studies focus on uniform wettability channels, leaving asymmetric nanochannels and their energy dissipation mechanisms underexplored. Through theoretical analysis and MD simulations, I established the critical conditions for capillary flow based on energy conservation and conversion. I modified the classical Lucas-Washburn model using the Cox-Voinov law to account for dynamic contact angles and asymmetric wettability, verifying the modified model's accuracy via MD simulations. These outcomes provide effective tools for analyzing and controlling micro/nanoscale capillary flow, offering broad application prospects in novel materials, microfluidic chips, ion/water transport in cementitious materials, and spontaneous imbibition of fracturing fluids in shale reservoirs.

3. MD Simulation of Pool Boiling Heat Transfer on Smooth Mixed-Wettability Surfaces

I explored the variations in bubble growth, evaporation atom count, and interfacial thermal resistance on smooth hydrophilic/hydrophobic composite surfaces under different interaction strengths and wall temperatures. The results demonstrate that hydrophobic regions promote bubble nucleation, accelerate growth, and enhance evaporation. Compared to purely hydrophilic surfaces, the time Δt required from bubble nucleation to the coalescence of a vapor film on the wall is reduced by up to 61.3%. Higher wall temperatures also shorten both the initial bubble growth time and the vapor film formation time. However, as the hydrophobic area fraction β increases, solid-liquid heat transfer begins to deteriorate. At $\beta = 0.25$, a 4×4 distribution pattern achieves the minimum thermal resistance (only 2% higher than a purely hydrophilic surface) due to the "dense" layout of surrounding low-potential-energy zones. As the hydrophobic fraction increases further, interfacial thermal resistance rises sharply, reaching up to a 368.68% increase compared to purely hydrophilic walls.

4. MD Simulation of Pool Boiling Heat Transfer on Structured Mixed-Wettability Surfaces

I constructed structured mixed-wettability surfaces using a 4×4 hydrophobic distribution pattern to investigate the changes in bubble growth, evaporation, and heat flux under various wall temperatures and hydrophobic fractions. The results show that as the projected area fraction of the micro/nanostructures β increases, the area of the low-potential-energy zone on the hydrophobic structured surface decreases. Additionally, as the micro/nanostructure height increases, the absolute value of solid-liquid potential energy drops, leading to poorer contact and hindered heat transfer. Consequently, the liquid phase temperature change ΔT during bubble growth and the Critical Heat Flux (CHF) gradually decrease with higher. Conversely, for hydrophilic structured surfaces, an increase in β enlarges the solid-liquid contact area. Driven by capillary forces, the structural voids remain filled with liquid atoms, ensuring stable heat transfer and preventing "dry-out." With increasing, the ΔT improved by 14.0%, 10.1%, and 9.4%, respectively. However, increasing β did not significantly impact CHF, showing only minor improvements of 3.0%, 1.2%, and 1.8% compared to the baseline of $\beta = 0.25$.

Declaration of Originality

I hereby declare that this thesis is my original work and has not been submitted, in whole or in part, for any degree or diploma at any other university or institution. All sources of information used in the thesis have been duly acknowledged. Any ideas, data, charts, or quotations from the work of others are properly cited.

I further declare that this thesis does not contain any material previously published or written by another person except where proper reference is made, and that it does not include any content that has been obtained through unauthorized assistance.

I take full responsibility for the originality and authenticity of the content presented in this thesis.

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1. Introduction

1.1. Research Background and Motivation

The spreading of droplets and capillary flow at micro- and nanoscale, along with the associated heat transfer phenomena, are fundamental scientific issues of common interest across multiple research fields, including hydraulics, materials science, energy, geology, and environmental engineering. Whether it concerns the development of novel materials, the evolution of mechanical and durability properties of hydraulic concrete, geological sequestration of carbon dioxide, or the extraction and utilization of unconventional shale oil and gas resources, these processes inevitably involve droplet spreading and heat transfer at micro- and nanoscale.

Unlike at the macroscale, intermolecular forces become significantly influential at micro- and nanoscale, and materials exhibit pronounced size-dependent properties due to their large specific surface area. This leads to highly complex phenomena and mechanisms in droplet spreading and capillary-driven flow at such scales. Moreover, theories established based on macroscale behaviors may no longer be applicable and thus require modifications or extensions for micro/nanoscale applications. Therefore, an in-depth investigation into the microscopic mechanical mechanisms of droplet spreading and the related heat transfer processes is essential.

The issues of droplet spreading and capillary flow at micro- and nanoscale are fundamental and cross-cutting challenges encountered in various fields, including materials science, energy, and environmental engineering. As illustrated in Figure 1.1a, the advancement of nanotechnology has led to the industrial-scale production of micro/nanostructured materials. Certain surfaces with special micro/nano-scale structures exhibit unique properties such as anti-fogging, anti-icing, and enhanced heat transfer performance (Liu et al., 2017; Pan et al., 2018; Shi et al., 2020; Agudo-Canalejo

et al., 2021; Yang et al., 2021). The regulation of material wettability and the droplet spreading behavior on these surfaces is key to improving material performance (Lü, 2011; Zhu, 2017; Zhang, 2018; Yong et al., 2022).

Calcium silicate hydrate (C-S-H), the main product of cement hydration, is a primary contributor to the mechanical strength of cement-based materials and a critical factor influencing their mechanical and durability properties (Pellenq et al., 2009; Hou et al., 2020; Liu et al., 2021; Zhang et al., 2021). C-S-H is a typical porous medium (Figure 1.1b), with pore sizes primarily distributed in the range of 0.5–10 nm (Yao and He, 2010; Tang et al., 2019). When cement-based materials are exposed to water- and salt-containing environments, water and ions are drawn into the micro/nano-scale pores of C-S-H under capillary forces, thereby affecting material strength, creep, shrinkage, and physicochemical reactions (Hou et al., 2020; Guo et al., 2021; Wang et al., 2021).

Geological carbon sequestration (GCS) is an important strategy for reducing greenhouse gas emissions and mitigating global warming. In this process, CO₂ is pressurized into a supercritical state and injected into deep saline aquifers for long-term isolation (Figure 1.1c). During sequestration, CO₂ can also undergo mineralization to form environmentally friendly carbonate minerals such as calcite and magnesite (Matter et al., 2016; Xie et al., 2017; Li et al., 2022). The wettability of reservoir rock minerals to brine and CO₂, as well as the wetting behavior of CO₂ microdroplets on mineral surfaces, plays a crucial role in both sequestration efficiency and mineralization processes (Tenney and Cygan, 2014; Zhao et al., 2014; Ma et al., 2019).

At present, hydraulic fracturing remains the primary technology for the extraction of unconventional shale oil and gas (Figure 1.1d). During hydraulic fracturing, the injected fracturing fluid induces cracks in shale reservoirs, enhancing fluid pathways (Zhuang et al., 2016; Liu et al., 2019; Wang et al., 2019; You et al., 2021). Meanwhile, fracturing fluid can spontaneously imbibe into the shale matrix through hydraulic and natural fractures, leading to a substantial amount of fluid retention within the formation. This retained fluid significantly impacts the permeability of the shale reservoir and the

productivity of gas wells (Li et al., 2015; Ye, 2019; Hu et al., 2020; Hu et al., 2020). Shale reservoirs typically contain abundant micro- and nanopores, with pore sizes mainly ranging from 2 to 100 nm (Zhao et al., 2015; Neuzil, 2019; Whitelaw et al., 2019; Yu et al., 2020). Therefore, investigating the micro-mechanical mechanisms of capillary flow at micro/nanoscale is of great importance for regulating the spontaneous imbibition behavior of fracturing fluids in shale reservoirs.

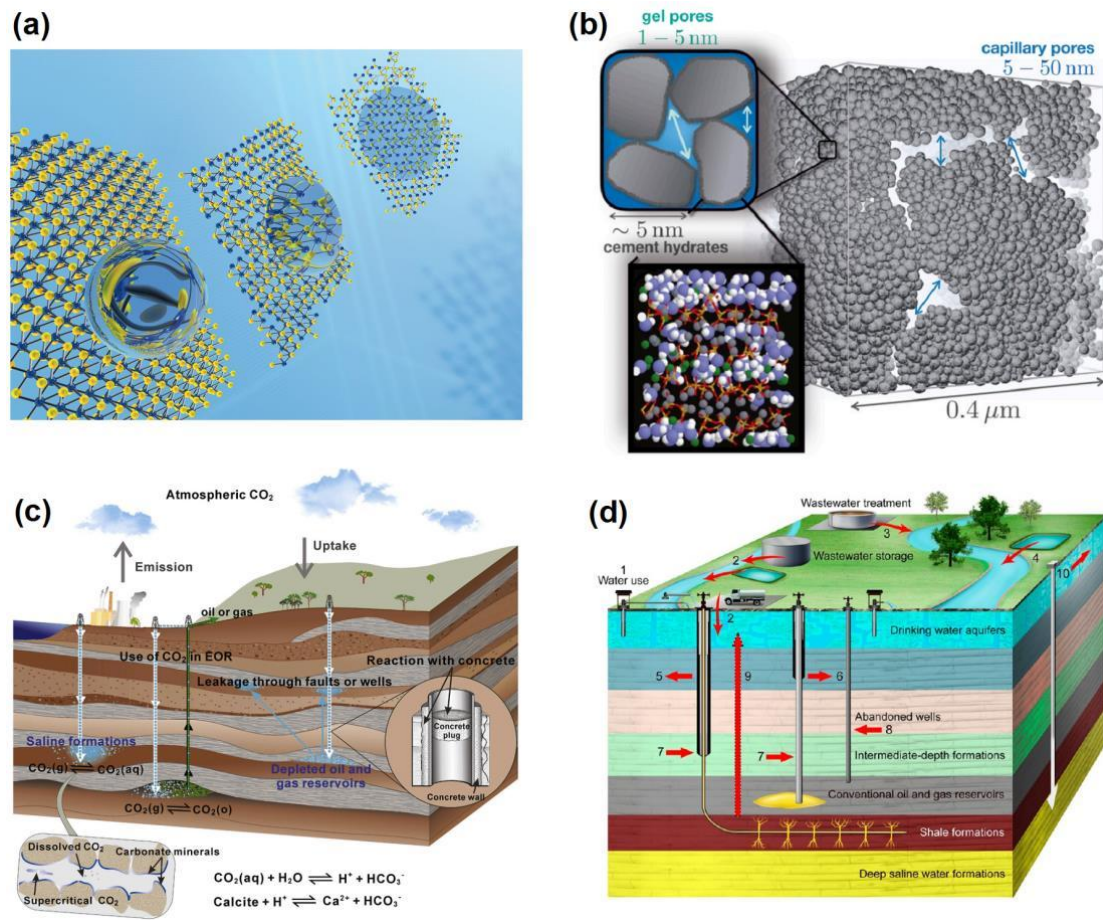


Figure 1.1 Applications of micro/nanoscale droplet spreading and capillary flow: (a) Active control of material wettability and droplet spreading on material surfaces (Jaiswal et al., 2019); (b) Micro/nanoscale pore structures in calcium-silicate-hydrate (C-S-H) gel

Meanwhile, With the widespread application of microelectronic technologies in integrated circuits, electric vehicles, and aerospace systems, electronic devices have become increasingly integrated and miniaturized. Meanwhile, the heat generated during operation has risen sharply (Li et al., 2020), with local heat fluxes sometimes reaching

as high as 1000 W/cm^2 (Mohammadi et al., 2018). If this heat is not removed promptly and efficiently, it may compromise device performance or even lead to severe safety incidents (Pedram et al., 2006; Sohel et al., 2017). Therefore, effective thermal management at increasingly smaller length scales is of critical importance.

Traditional single-phase air cooling and liquid cooling can no longer meet the rapidly growing heat-dissipation demands. Phase-change cooling, which relies on the absorption of latent heat during phase transition, offers advantages such as small temperature differences, large latent heat, and high heat-transfer coefficients. Its heat-removal capability is typically 1–3 orders of magnitude higher than that of single-phase cooling (Nazari et al., 2018). Thus, phase-change heat transfer is undoubtedly a superior choice for high-heat-flux applications (Attinger et al., 2014). Depending on the cooling strategy, phase-change heat transfer includes nucleate boiling, spray cooling, and jet-impingement cooling. Spray and jet-impingement cooling require external power to drive the coolant to impact the heated surface at a certain velocity, after which phase-change heat transfer occurs. Compared with nucleate boiling, these methods not only need external power input but also require high velocities and pressures to counteract flow resistance. In contrast, nucleate boiling requires less energy consumption, involves simpler components, provides high reliability, and ensures long service life. Thus, nucleate boiling heat transfer has broader engineering applicability. However, boiling on conventional smooth surfaces cannot satisfy the increasingly stringent heat-dissipation requirements. Enhancing boiling performance therefore requires surface modification through wettability alteration or the construction of micro/nanostructured surfaces.

Research on nucleate boiling heat transfer at the micro/nanoscale involves both experimental studies and numerical simulations. However, experimental studies face significant challenges due to fabrication limitations and high costs. For example, direct observation of nanoscale boiling processes is extremely difficult, and the acquisition of experimental data is highly restricted. In addition, the fabrication of heating surfaces

with well-defined and uniform micro/nanostructures remains challenging, and further reduction in structure size is limited by current manufacturing technologies.

Consequently, numerical simulation methods have gained increasing attention. Among them, molecular dynamics (MD) is a simulation technique that integrates mathematics, physics, and chemistry to investigate material structure and properties at atomic and molecular scales (Chen et al., 2007). Compared with traditional experiments, MD allows the independent control of surface energy and microstructure geometry, enabling precise manipulation of the distribution and dimensions of surface features at the atomic scale. This makes it possible to investigate the influence of various surface characteristics on boiling heat-transfer processes. Numerous studies have employed MD to examine the effects of working fluids (Gonzalez-Valle et al., 2018; Aksoy et al., 2021; Wu et al., 2022), surface wettability modification (Chen et al., 2018; Wu et al., 2020; Li et al., 2023), micro/nanostructured surfaces (Liu et al., 2019; Surblys et al., 2019), and hybrid-wettability surfaces (Chen et al., 2021; Liao et al., 2021) on microscale convective heat transfer (Chen et al., 2021; Hu et al., 2016) and nucleate boiling (Wu et al., 2020; Liu et al., 2019; Chen et al., 2021; Zhou et al., 2022). These works demonstrate that MD is a feasible and powerful approach for studying boiling heat transfer at small scales.

Therefore, this study adopts molecular dynamics simulations to investigate boiling heat-transfer processes from a microscopic perspective. By modifying surface wettability distributions and constructing micro/nanostructures, the physical mechanisms underlying enhanced boiling heat transfer are explored, providing insights for the design of high-performance boiling surfaces.

1.2. Gaps and limitations in the existing literature

In summary, the droplet spreading process on solid surfaces is influenced by numerous factors and involves complex phenomena, making the study of its mechanisms and regulation challenging. Current research has only explored a limited

range of solid–liquid interaction strengths, and the understanding of the formation mechanisms of layered liquid molecular structures on solid surfaces, as well as the impact of precursor films on droplet spreading, remains insufficient. Systematic investigations are required. Additionally, the movement modes of the three-phase contact line during droplet spreading include both the jumping mode and the rolling mode, with the conditions for the generation of the rolling mode and its regulation mechanisms warranting further study.

Meanwhile, micro- and nanoscale capillary flow exhibits significant scale effects and requires consideration of dynamic contact angles and solid–liquid interfacial slip. Corrections to the Lucas–Washburn model based on these phenomena can effectively describe capillary flow in such regimes. However, current research mainly focuses on channels with homogeneous and symmetric wettability, with fewer studies on channels exhibiting asymmetric wettability. Moreover, while molecular kinetic theory is primarily used to modify the Lucas–Washburn model by incorporating dynamic contact angle effects, it becomes inadequate when the three-phase contact line moves in modes other than the jumping mode. Thus, the applicability and rationality of hydrodynamic models in such cases need further discussion. Additionally, the energy dissipation mechanisms during capillary flow warrant more detailed investigation.

On the other hand, there is limited research on the influence of the distribution of regions with different wettability on boiling heat transfer over smooth surfaces. For smooth surfaces, many researchers have mainly focused on altering the wettability of the entire surface or changing the proportion of hydrophilic/hydrophobic areas. However, insufficient attention has been paid to the effects of different spatial distributions of hydrophilic/hydrophobic regions under the same wettability ratio, as well as the effects of varying hydrophilic/hydrophobic ratios under the same distribution pattern on the solid–liquid heat transfer process. In addition, there is still a lack of three-dimensional observations of bubble nucleation, growth, and coalescence processes, and the visualization quality of bubble dynamics remains unsatisfactory.

For structured surfaces, there is likewise a lack of investigation into how the proportion of hydrophilic/hydrophobic structures and the distribution of microstructures affect the boiling heat transfer process at the solid–liquid interface. Moreover, studies on the dynamic processes of bubble nucleation, growth, and coalescence on structured surfaces under three-dimensional conditions are still insufficient.

Compared with MD simulations, mesoscopic methods such as LBM and DPD can handle larger systems and longer timescales while retaining essential microscopic features and interactions. However, mesoscopic methods require coarse-graining of microscopic structures, which inevitably leads to loss of molecular details. For complex systems, coarse-graining becomes increasingly difficult and may compromise simulation accuracy. In contrast, although the accessible time and length scales in MD simulations remain limited, MD provides a convenient and effective means of studying physicochemical processes at the micro/nanoscale, overcoming experimental limitations and revealing atomic-level mechanisms. Micro/nanoscale droplet spreading and capillary flow involve various factors, including liquid properties, surface wettability, and the composition and arrangement of surface atoms. Understanding these processes thus requires atomic- or molecular-level investigation. Therefore, MD simulations are adopted as the primary research method in this study.

1.3. Research Contents of This Study

This study employs a research approach that integrates molecular dynamics (MD) simulations with theoretical analysis to investigate the mechanisms by which solid–liquid interactions influence surface wettability and droplet spreading, the capillary flow behavior and energy dissipation under different wettability conditions, and the effects of mineral type and surface structure on droplet spreading and capillary transport.

① Molecular dynamics simulations were carried out to examine droplet spreading on solid surfaces under different solid–liquid interaction strengths. The mechanisms by which solid–liquid interaction influences surface wettability and droplet spreading were elucidated. Based on the simulation results, the conditions for precursor-film formation were identified, and the mechanism by which the precursor film affects droplet spreading was revealed. In addition, by combining a simplified solid–liquid interaction model with MD simulations, the effects of interaction strength on surface wettability and the formation of layered molecular structures at the solid surface were clarified.

② By analyzing energy conservation and transformation, the critical conditions for the onset of capillary flow were obtained, and the energy dissipation mechanisms during capillary transport were further revealed. Considering the dynamic contact-angle effect and the influence of asymmetric surface wettability, the classical Lucas–Washburn model was modified. MD simulations of nanoscale capillary flow were then conducted to validate the accuracy and applicability of the modified theoretical model.

③ MD simulations were employed to investigate the effects of different hydrophilic/hydrophobic ratios and spatial distributions on pool-boiling heat-transfer characteristics. A computational model for pool boiling on smooth composite hydrophilic/hydrophobic surfaces was first established. The influence of solid–liquid interaction strength (wettability), hydrophilic/hydrophobic ratio, and spatial arrangement on heat transfer at the solid–liquid interface was analyzed. By examining the variations in the number of evaporated atoms, interfacial thermal resistance, critical heat flux, and bubble evolution, the underlying physical mechanisms governing boiling heat transfer on smooth composite-wettability surfaces were revealed.

④ The effects of structured composite hydrophilic/hydrophobic surfaces on pool-boiling heat transfer were further explored. A pool-boiling MD simulation model incorporating structured composite wettability was constructed. The influence of solid–liquid interaction strength (wettability), wall temperature, and hydrophilic/hydrophobic ratio on boiling heat transfer was investigated. By analyzing the bubble growth dynamics, the number of evaporated atoms, temperature variations, and heat flux during

boiling, the physical mechanisms by which structured composite wettability enhances solid–liquid boiling heat transfer were elucidated.

2. Fundamental Theories and Numerical Simulation Methods

2.1. Research Statement of droplet spreading mechanisms in micro/nano scale

2.1.1. Research Progress on Mechanisms of Droplet Spreading at Micro- and Nanoscale

The spreading of a droplet on a solid surface is a typical thermodynamically irreversible process. Both the spreading dynamics and the final equilibrium state are influenced by various factors, including the intrinsic properties of the liquid and the wettability of the solid surface (Jiao et al., 2016; Yuan et al., 2016). Due to the interplay of these factors, the phenomena and underlying mechanisms involved in droplet spreading are highly complex.

From a microscopic perspective, the droplet spreading process is primarily governed by the competition between two forces: the attractive force exerted by the solid atoms on the liquid molecules (the driving force), and the frictional resistance between the liquid molecules and the solid surface (Bertrand et al., 2009). The interaction between solid atoms and liquid molecules—namely, the solid–liquid interaction—can influence both the magnitude of the driving force and the frictional resistance at the atomic scale, thereby playing a critical role in determining the wettability of the solid surface and the dynamics of droplet spreading (Cazabat et al., 1997; Blake and De Coninck, 2002; Xu et al., 2015; Fan et al., 2020).

Studies have shown that increasing the solid–liquid interaction strength enhances the wettability of the solid surface, resulting in a decrease in the equilibrium contact angle of the droplet. However, stronger solid–liquid interactions also simultaneously increase both the driving force and the frictional resistance during the spreading process. This implies that the spreading speed of a droplet does not increase monotonically with the interaction strength. Instead, the spreading rate reaches a maximum at an intermediate level of solid–liquid interaction strength and decreases as the interaction strength continues to rise (Voué et al., 1998; Blake and De Coninck, 2002).

Moreover, during the spreading process, liquid molecules tend to form layered structures near the solid surface, and their mobility is significantly reduced in the vicinity of the solid–liquid interface (Yuan and Zhao, 2010; Akaishi et al., 2017; Sun et al., 2017; Gonzalez-Valle et al., 2018). Nevertheless, the three-dimensional distribution and dynamic behavior of interfacial liquid molecules, as well as their relationship with the solid–liquid interactions, remain inadequately understood.

The droplet spreading process is typically characterized by the spreading velocity V and the dynamic contact angle θ_D . Two classical models—the Hydrodynamic Model and the Molecular Kinetic Theory—have been developed to describe the relationship between the spreading velocity V and the dynamic contact angle θ_D , based on the dominant mechanisms of energy dissipation during spreading (Blake, 2006; Carbone et al., 2009; Yuan et al., 2016; Khalkhali et al., 2017). In the Hydrodynamic Model, resistance to spreading mainly originates from viscous dissipation within the three-phase contact region, whereas in the Molecular Kinetic Theory, energy dissipation is predominantly due to friction between solid atoms and liquid molecules near the contact line.

The Hydrodynamic Model divides the region near the three-phase contact line into three zones: a macroscopic capillary region, a mesoscopic transition region, and a microscopic molecular region. Within the capillary region, an apparent dynamic contact angle $\theta_{D,App}$ is defined, while in the molecular region, a microscopic dynamic contact angle $\theta_{D,M}$ is introduced. The Cox–Voinov law describes the relationship between the apparent dynamic contact angle $\theta_{D,App}$, the microscopic dynamic contact angle $\theta_{D,M}$, and the contact line velocity V_{CL} . Typically, the microscopic dynamic contact angle $\theta_{D,M}$ is approximated by the equilibrium contact angle θ_E in this law (Voinov, 1976; Fernandez-Toledano et al., 2021).

In contrast, the Molecular Kinetic Theory attributes the motion of the three-phase contact line to the collective displacement of liquid molecules on the solid surface

within the contact region. The velocity of the three-phase contact line V_{CL} is approximately linearly proportional to the difference $\cos\theta_E - \cos\theta_D$ (Blake and Haynes, 1969; Martic et al., 2002).

Scaling analysis links the spreading radius R of the droplet to the elapsed time t through the relation $R \sim t^\alpha$, where the exponent α reflects the underlying energy dissipation mechanism (Heine et al., 2005; Yuan and Zhao, 2010; Yuan and Zhao, 2013). For an initially spherical droplet spreading on a smooth solid surface, the Hydrodynamic Model predicts $\alpha = \frac{1}{10}$, while the Molecular Kinetic Theory predicts $\alpha = \frac{1}{7}$. In the two-dimensional case where the initial droplet shape is cylindrical, the predicted exponents are $\frac{1}{7}$ and $\frac{1}{5}$, respectively (Heine et al., 2005; Yuan and Zhao, 2010).

Yuan et al. (2014) proposed a novel theoretical model incorporating both liquid viscous resistance and solid–liquid friction, enabling a more comprehensive description of the physical mechanisms and corresponding scaling laws during droplet spreading on micropillar surfaces (Yuan et al., 2016).

However, in practical spreading experiments, many studies estimate the exponent α by simply fitting the relation $R \sim t^\alpha$ without distinguishing different spreading stages, which can reduce the accuracy of the results (Heine et al., 2005; Yuan and Zhao, 2010; Qiu et al., 2013; Khalkhali et al., 2017). One simulation study on microdroplet spreading on metal surfaces qualitatively divided the spreading process into two stages and fitted the corresponding exponents α , but did not provide a rationale for this segmentation (Lu et al., 2015). Another study on microdroplet spreading on graphene surfaces demonstrated that solid–liquid interactions influence the spreading dynamics, with the three-phase contact line velocity V_{CL} being relatively low at both the initial and final stages of spreading (Andrews et al., 2016). However, the underlying mechanisms were not further analyzed, and the range of solid–liquid interaction strengths considered was limited, highlighting the need for further investigation.

Moreover, as illustrated in Figure 2.1b, within the Molecular Kinetic Theory, liquid molecules at the three-phase contact line can hop to the next adsorption site driven by capillary forces. This mode of contact line movement is referred to as the jumping mode, which has been extensively validated through simulations and experiments (Bertrand et al., 2009; Yuan and Zhao, 2010; Zhao and Cheng, 2017).

Subsequent simulation studies revealed that water molecules can become strongly adsorbed on the solid surface via hydrogen bonding, losing their mobility. This immobilization of water molecules at the leading edge of the three-phase contact line, as shown in Figure 2.1a, prevents their movement. Instead, water molecules from the upper layers directly bypass the immobile molecules at the front of the contact line and reach the solid surface, causing the three-phase contact line to advance. This mode of contact line motion is termed the rolling mode (Johansson and Hess, 2018).

Johansson and Hess (2018) proposed a new theoretical model specifically for the rolling mode. However, their model fails to capture the observed decrease in the contact line velocity V_{CL} as the dynamic contact angle θ_D decreases during droplet spreading. Furthermore, when θ_D is small, the contact line velocity V_{CL} predicted by the model deviates significantly from experimental or simulated values.

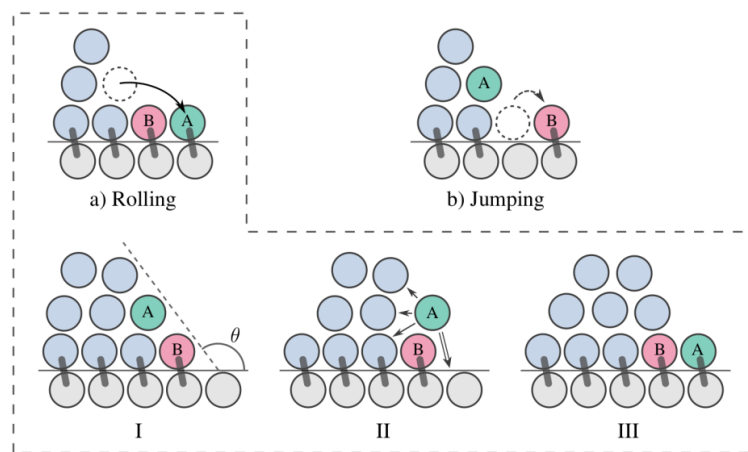


Figure 2.1 Two typical modes of three-phase contact-line motion during droplet spreading on solid surfaces (Johansson and Hess, 2018): (a) Rolling mode; (b) Jumping mode.

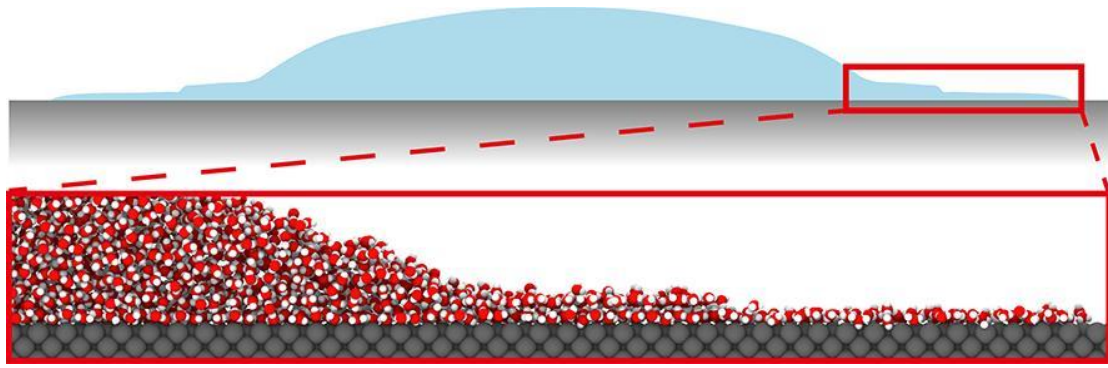


Figure 2.2 Formation of a precursor film ahead of the main droplet during spreading on a solid surface.

In certain cases, a precursor film forms on the solid surface during the droplet spreading process and spreads ahead of the main droplet. The presence of the precursor film leads to distinctly different spreading behaviors (Hardy, 1919; Chibbaro et al., 2008; Popescu et al., 2012; Yuan and Zhao, 2013; Qiu et al., 2013). Hardy (1919) was the first to recognize the existence of the precursor film through experiments on liquid spreading on glass. Subsequent theoretical and experimental studies further confirmed the presence of the precursor film and its significant role in the droplet spreading process (Yuan and Zhao, 2010; Popescu et al., 2012; Akaishi et al., 2017).

Both experimental and simulation studies have shown that the spreading of the precursor film also exhibits scaling invariance, generally expressed as $R \sim t^\alpha$, where the exponent α depends on the specific experimental system and simulation setup. Factors influencing α include the size of liquid molecules, volatility of the liquid, surface structure of the solid, and solid–liquid interaction strength (Bekink et al., 1996; Popescu et al., 2012; Yuan et al., 2016).

Yuan and Zhao (2010) employed molecular dynamics simulations to study the spreading of droplets on solid surfaces and revealed the formation mechanism of the precursor film at the atomic scale. They found that fast-moving liquid molecules at the droplet surface migrate to the precursor film region, where they are attracted and “pinned” by substrate atoms, resulting in reduced mobility until they become part of the precursor film.

2.1.2. Research Progress on Mechanisms of Micro- and Nanoscale Capillary Flow

Capillary flow refers to the process in which a liquid spontaneously flows into narrow channels or porous materials without the assistance of external forces such as gravity. The driving force of capillary flow can be described by the Young–Laplace equation, which relates the pressure difference across the interface (i.e., the Laplace pressure or capillary pressure) to the interface curvature and surface tension (Oyarzua et al., 2015; Cai, 2021).

At the macroscopic scale, the Lucas–Washburn model accurately describes the variation of the capillary rise height L with time t during the capillary flow process, following the scaling relation $L \sim t^{0.5}$ (Huang, 1956; Dimitrov et al., 2007; Cai et al., 2021).

Although the Lucas–Washburn model can accurately describe capillary flow at the macroscopic scale (Oyarzua et al., 2015), it neglects the effect of inertia, resulting in the unrealistic prediction that the initial liquid entry velocity into the capillary is infinite, contradicting experimental observations (Cai and Yu, 2012). Quéré (1997) proposed a model assuming that at the initial stage of capillary flow, viscous forces and the liquid's own gravity are negligible, and only inertia and capillary driving forces need to be considered. This model corrects the infinite initial velocity flaw in Lucas–Washburn and predicts that the capillary rise height L grows linearly with time at the initial stage. The Bosanquet model combines the advantages of both the Lucas–Washburn and Quéré models, converging to the former when time tends to infinity and to the latter as time approaches zero (Karna et al., 2016). Subsequent studies have demonstrated that liquid inertia plays an important role at the early stage of capillary flow, when the capillary diameter is relatively large, and when the liquid viscosity is low (Martic et al., 2002). Furthermore, if factors such as liquid properties, physical characteristics of porous media, boundary conditions, and gravity are considered, the mechanisms and laws governing capillary flow become even more complex (Gao and Hu, 2012; Li et al., 2015; Yang et al., 2019).

With the development of nanotechnology and the exploitation of unconventional shale oil and gas, micro- and nanoscale capillary flow has found increasingly broad applications in emerging engineering fields (van Honschoten et al., 2010; Liu et al., 2019; Zhang et al., 2021; Dong et al., 2021). Studies show that at micro- and nanoscale, intermolecular interaction forces become very significant. Due to the enormous specific surface area at this scale, capillary flow exhibits pronounced scale effects. Some fundamental assumptions of the Lucas–Washburn model are violated; for example, the density and viscosity of liquid near the wall change, requiring necessary adjustments and corrections to the model (Dimitrov et al., 2007; Joly, 2011; Oyarzua et al., 2015; Chu et al., 2019; Hou et al., 2020).

Moreover, the Lucas–Washburn model assumes a constant contact angle of the liquid on the capillary wall, equal to the equilibrium contact angle θ_E . However, during micro- and nanoscale capillary flow, the meniscus shape changes dynamically, and thus the contact angle is not constant. This angle is called the dynamic contact angle θ_D , and generally $\theta_D \geq \theta_E$. If the capillary flow lasts sufficiently long, θ_D gradually converges to θ_E . Therefore, the equilibrium contact angle θ_E in the Lucas–Washburn model should be replaced by the dynamic contact angle θ_D (Dimitrov et al., 2007; Yang and Cao, 2016; Chu et al., 2019; Hou et al., 2020). The value of θ_D during capillary flow is closely related to many factors such as liquid properties, geometry of the capillary, and wettability, making it difficult to predict theoretically. Research indicates a close relationship between the dynamic contact angle θ_D and the three-phase contact line velocity V_{CL} (Ahadian et al., 2010; Fernandez-Toledano et al., 2021). Hydrodynamic models and molecular kinetic theory are frequently used to describe the relationship between θ_D and V_{CL} (Voinov, 1976; Blake and De Coninck, 2002; Ahadian et al., 2010; Fernandez-Toledano et al., 2021).

Martic et al. (2004) corrected the Lucas–Washburn model based on relationships in molecular kinetic theory, achieving good agreement with simulation results (Martic et al., 2002; Martic et al., 2004; Wolf et al., 2010; Hou et al., 2020). Additionally, the

influence of slip at the solid–liquid interface at micro- and nanoscale cannot be ignored. The slip length at the interface significantly alters the capillary flow velocity (Bao et al., 2017; Zhou et al., 2020), and this slip length depends on factors such as the solid–liquid interaction strength, solid surface structure, and liquid flow velocity (Wu et al., 2017; Feng et al., 2018; Zhan et al., 2020; Shi and Lu, 2021).

In some cases, when the capillary wall has strong wettability, a precursor film forms ahead of the meniscus during capillary flow. At this stage, the contact angle of the liquid on the capillary wall is effectively 0° or undefined, and the capillary driving force cannot be calculated using the Young–Laplace equation, leading to significant discrepancies between the Lucas–Washburn model and actual capillary flow (Chibbaro et al., 2008; Popescu et al., 2012; Chu et al., 2019; Cenchu et al., 2020). Zhang et al. (2021) proposed a theoretical model that incorporates the effect of precursor film formation and shows good agreement with experimental and simulation results.

Currently, most studies focus on capillary flow in channels with uniform or symmetric wettability walls. However, asymmetric wettability is common in nature and engineering applications. For example, unconventional oil and gas reservoirs contain numerous micro- and nanoscale channels with walls composed of different minerals (Sun et al., 2017; Singh and Myong, 2018; Mohammed and Gadikota, 2020). Asymmetric wettability is also found in biological channels such as cell membranes and walls (Hou et al., 2010; Tian et al., 2011; Hou et al., 2012; Robertson et al., 2012; Zhang et al., 2014). With the rapid development of nanotechnology, many biomimetic materials, micro-/nano-fluidic chips, and nanoscale ultra-sensitive detection platforms have been developed and applied, involving capillary flow in micro- and nanoscale channels with asymmetric wettability (Zhang et al., 2014; Kelly et al., 2017; Xu et al., 2020; Dai et al., 2022). Furthermore, even for the same wall material, differences in surface roughness may cause wettability variations (Stukan et al., 2010; Vanzo et al., 2016; Hulikal Chakrapani and den Otter, 2020; Fan et al., 2021). At present, research

on capillary flow and related mechanisms in nanoscale channels with asymmetric wettability remains insufficient and requires further in-depth study.

2.1.3. Research Progress on Numerical Simulation Methods for Micro/Nanoscale Droplet Spreading and Capillary Flow

Research methods for micro/nanoscale droplet spreading and capillary flow mainly include experimental observation, theoretical analysis, and numerical simulation (Cencha et al., 2020; Pan et al., 2020; Fan et al., 2021; Cai, 2021). In general, experimental observation is the most direct research approach. When the characteristic length scales approach the micro- or nanoscale, instruments such as atomic force microscopes, particle image velocimetry systems, and nanoindenters enable direct observation of morphology, flow behavior, and mechanical properties at these scales (Lv, 2011; Cencha et al., 2020). However, experimental techniques face many limitations, including high technical difficulty, limited measurement precision, time-consuming procedures, and high cost (Tang et al., 2019; Pan et al., 2020; Fan, 2020). Meanwhile, many existing theories are built upon fundamental assumptions—such as continuum homogeneity and no-slip boundary conditions at solid–liquid interfaces—which are appropriate for macroscopic systems (Yang and Cao, 2016; Fan et al., 2020; Hou et al., 2020). At the micro/nanoscale, however, intermolecular forces become non-negligible and materials exhibit extremely high surface-to-volume ratios, leading to pronounced scale effects. As a consequence, some assumptions valid at the macroscale may no longer apply and require appropriate refinement or correction (Wu et al., 2017; Cencha et al., 2020; Hou et al., 2020).

With the rapid advancement of computational power, numerical simulation has become an essential tool for addressing scientific and engineering problems. Currently, three major numerical approaches are used to study micro/nanoscale droplet spreading and capillary flow: the lattice Boltzmann method (LBM), dissipative particle dynamics (DPD), and molecular dynamics (MD) simulations (Shen and Zhou; Ren, 2019; Chen et al., 2020; Hulikal Chakrapani and den Otter, 2020; Zhang and Pei, 2020).

In MD simulations, atoms are treated as the fundamental units of the simulation system, and their motions are assumed to follow deterministic equations, such as Newton's laws of motion (Plimpton, 1995). The temporal evolution of the system is obtained by numerically integrating the equations of motion, and macroscopic quantities can be extracted through statistical analysis of atomic trajectories. Interatomic interactions are described by potential functions, and the accuracy of the selected potential directly affects the reliability of the simulation results (Thompson et al., 2022). Key aspects of MD include the formulation and solution of atomic equations of motion, the choice and parameterization of interatomic potentials, and the calculation of macroscopic physical quantities. MD is a powerful tool for probing microscopic systems and can reveal molecular-scale mechanisms governing droplet spreading and capillary flow (Zhang and Li, 2018; Fan et al., 2020; Hou et al., 2020).

The lattice Boltzmann method and dissipative particle dynamics are typical mesoscopic simulation methods. The earliest mesoscopic approach is the lattice gas automaton (LGA) model (Dong, 2011; Ren, 2019), which discretizes the domain into a lattice where fluid particles reside on nodes and move along lattice links. Collisions occur when particles arrive at the same node and are constrained by mass and momentum conservation. The macroscopic fluid behavior obtained from LGA is consistent with the Navier–Stokes Equations LBM was later developed from the LGA framework and has since become a powerful tool for fluid simulation. Similar to LGA, LBM discretizes the computational domain into a lattice and uses velocity distribution functions to represent fluid motion between nodes. Macroscopic fluid variables can then be computed from distribution functions. Current multiphase LBM models mainly include pseudopotential (Shan–Chen) models, color-gradient models, free-energy models, and phase-field models, among which the Shan–Chen model is widely used due to its clear physical interpretation and computational efficiency (Rothman and Keller, 1988; Shan and Chen, 1993; Swift et al., 1996; He et al., 1999; Hu et al., 2019).

DPD incorporates advantages of MD and Brownian dynamics and introduces improvements to the LGA framework (Li, 2011). In DPD, coarse-grained particles serve as simulation units and are described in a Lagrangian framework while obeying Newton's laws. Each particle experiences three types of forces—conservative, dissipative, and random forces—whose magnitudes and directions depend on particle positions. The conservative force in classical DPD is a soft repulsive force, while the dissipative force accounts for friction and energy dissipation, and the random force supplies thermal fluctuations. The dissipative and random forces form a thermostat that ensures both temperature control and momentum conservation. Classical DPD, however, contains only repulsive conservative forces, causing particles to disperse throughout the domain, making it unsuitable for problems involving liquid–gas interfaces or free surfaces (Zhang et al., 2012; Chen et al., 2020). For such problems, classical DPD must be modified. One modification introduces a long-range attractive and short-range repulsive conservative force—similar to treatments in smoothed particle hydrodynamics—allowing the formation of liquid–gas interfaces (Liu et al., 2007). Another approach introduces the concept of local density so that repulsive forces depend on both interparticle distance and local density, balancing attraction and repulsion to allow interface formation. This modified approach is known as many-body DPD and is widely used for studying micro/nanoscale droplet spreading and capillary flow (Zhou and Chen, 2014; Chen et al., 2020; Meng et al., 2022).

2.2. Research Statement of Pool Boiling Heat-Transfer Characteristics

2.2.1. Research Progress on MD Simulations of Pool Boiling Heat-Transfer Characteristics on Smooth Surfaces

On smooth surfaces, many researchers have investigated heat-transfer characteristics primarily by modifying surface wettability. By adjusting the strength of solid–liquid interactions, surfaces with different wettabilities can be conveniently constructed (Zhou et al., 2020; Yi et al., 2021), and the degree of wettability is typically quantified using the solid–liquid contact angle.

Li et al. studied the wetting behavior of Ar droplets on smooth surfaces. Using molecular dynamics simulations, they tuned the wettability of the wall by varying the potential-energy coefficient between Ar atoms and wall atoms. Their results showed that as the potential-energy coefficient increased, the solid–liquid contact angle decreased, while the number of evaporated liquid atoms increased.

Yi et al. conducted MD simulations to investigate the wetting behavior of n-heptane droplets on a smooth Fe surface. As shown in Figure 2.3, increasing the solid–liquid potential-energy coefficient increases the magnitude of the solid–liquid interaction potential, causing both the droplet contact angle and the droplet centroid height to decrease nearly linearly with increasing interaction strength.

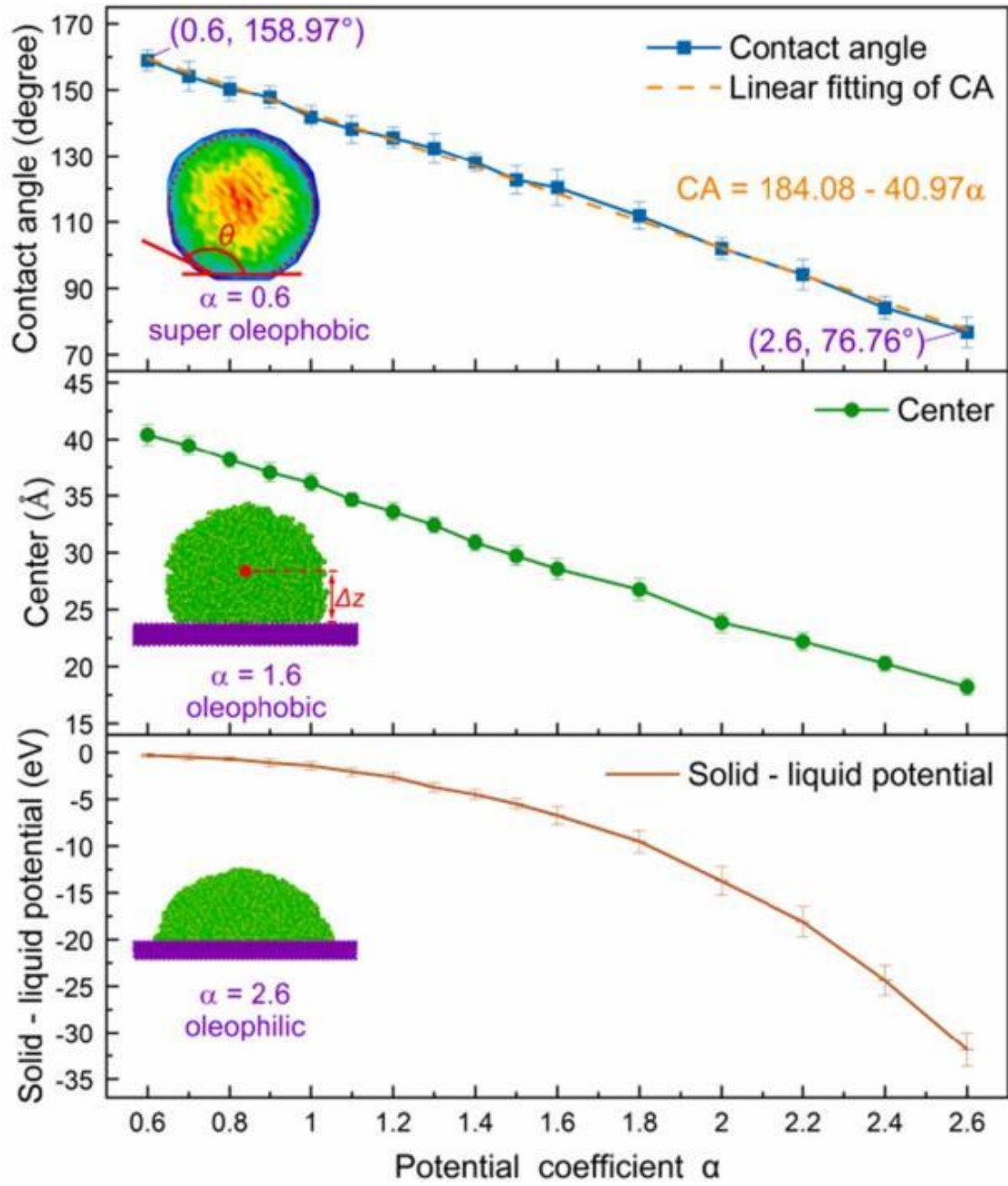


Figure 2.3 Variation of *n*-heptane contact angle, center and solid-liquid potential with potential coefficient (Yi et al., 2021)

For other complex liquid molecules, similar trends are observed between the solid–liquid interaction strength and both the contact angle and the droplet centroid position. As shown in Figure 1.5, on a Cu surface, the contact angle θ of the fluorinated liquid decreases nearly linearly with increasing solid–liquid interaction strength $\epsilon_{\text{C-Cu}}$, and the droplet centroid position z_{cm} also decreases correspondingly. When $\epsilon_{\text{C-Cu}}=0.001 \text{ eV} \sim 0.003 \text{ eV}$, the droplet maintains a contact angle $\theta > 90^\circ$, indicating

hydrophobic behavior. In contrast, when $\varepsilon_{C-Cu}=0.004\text{ eV}\sim 0.006\text{ eV}$, the contact angle becomes $\theta<90^\circ$, and the surface exhibits hydrophilic behavior. Overall, the contact angle decreases approximately linearly with increasing solid–liquid interaction strength.

As shown in Figure 2.4(b), the centroid position z_{cm} decreases monotonically with increasing ε_{C-Cu} . The droplet has the highest centroid position at $\varepsilon_{C-Cu}=0.001\text{ eV}$, whereas the lowest z_{cm} occurs at $\varepsilon_{C-Cu}=0.006\text{ eV}$. In addition to altering the contact angle, the solid–liquid interaction strength also affects the dynamic wetting process. Han et al. constructed hybrid-wettability regions on a smooth wall using molecular dynamics simulations and observed droplet splitting on smooth hybrid-wetting surfaces.

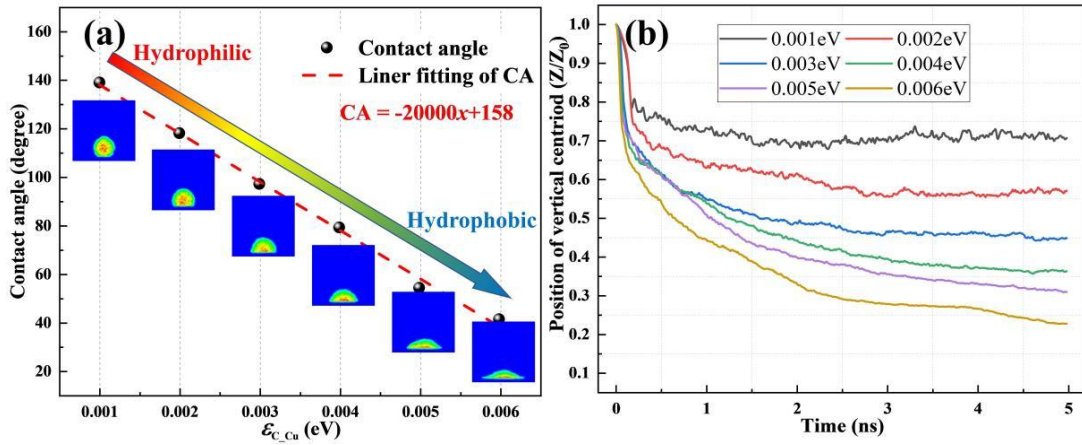


Figure 2.4 Effect of different ε_{C-Cu} on droplet wetting behavior: (a) change in contact angle; (b) change in center of mass position in vertical direction

The solid–liquid interaction strength not only alters the wetting mode between the solid surface and the droplet, influencing the contact angle, but experimental and simulation studies have also shown that it affects heat-transfer behavior at the solid–liquid interface. Wang et al. used molecular dynamics simulations to investigate the evaporation and explosive boiling of liquid films of different thicknesses on hydrophilic and hydrophobic surfaces. Their results indicated that on hydrophilic surfaces, the phase-change mode gradually shifts from evaporation to explosive boiling as the film thickness increases, whereas on hydrophobic surfaces, explosive boiling occurs only when the film thickness reaches 6 nm.

Cao et al. examined the influence of surface wettability on liquid-phase transition behavior. They found that during phase change, a dense liquid layer with a density of 1.4 g/cm^3 forms on hydrophilic surfaces, while a quasi-liquid–vapor layer with a density of $0.7\text{--}0.8 \text{ g/cm}^3$ forms on hydrophobic surfaces. Zhou et al. used molecular dynamics simulations to study the heat-transfer behavior of Ar on Cu surfaces under different potential-energy coefficients. They observed that as the potential-energy coefficient increases, the liquid exhibits different phase-change modes: when the coefficient is $0.2\text{--}0.3$, the liquid undergoes evaporation only without boiling; when it increases to $0.4\text{--}2.0$, the phase-change mode transitions to nucleate boiling, and the most effective nucleate boiling occurs at a coefficient of 1.5 ; when the coefficient exceeds 2.5 , the boiling mode shifts to intense explosive boiling.

Li et al. investigated the effect of surface wettability on bubble nucleation using molecular dynamics. Their results showed that the influence of surface wettability on the nucleation rate and bubble growth rate is completely opposite. When the surface wettability is weak, the weak solid–liquid interaction promotes bubble nucleation, but the increased interfacial thermal resistance weakens heat transfer across the interface, thereby suppressing subsequent bubble growth. They further concluded that the most favorable range of solid–liquid interaction strength for bubble nucleation is $0.00624\text{--}0.052 \text{ eV}$. They also observed that the initial nucleate-boiling process consists of two stages: a slow nucleation stage during which the bubble reaches a critical nucleus, followed by a rapid growth stage where the bubble quickly expands into a stable vapor bubble.

Liu et al. conducted boiling heat-transfer simulations for a mixed Ar–Kr liquid on a smooth Pt surface. As shown in Figure 2.5, the phase-change mode also transitions with increasing potential-energy coefficient, and nucleate boiling occurs earlier as the coefficient increases. To explore the relationship between surface wettability and boiling heat transfer, Bai et al. investigated nanoscale pool boiling from the perspective of surface potential energy. Their results showed that changes in surface potential

energy are the key reason why surface wettability influences heat-transfer performance: increasing surface wettability enhances the surface potential energy between the liquid and the wall, reduces the Kapitza resistance, and improves solid–liquid heat transfer.

Bai et al. further studied the effect of surface wettability on solid–liquid heat-transfer behavior and found that as wettability increases, both bubble nucleation time and liquid-film departure time decrease, accompanied by a reduction in wall thermal resistance. In another study, Bai et al. used molecular dynamics to investigate the mechanisms governing thin-film boiling. They found that the fundamental reason why increasing solid–liquid interaction strength enhances boiling heat transfer is the increase in the absolute value of the surface potential energy.

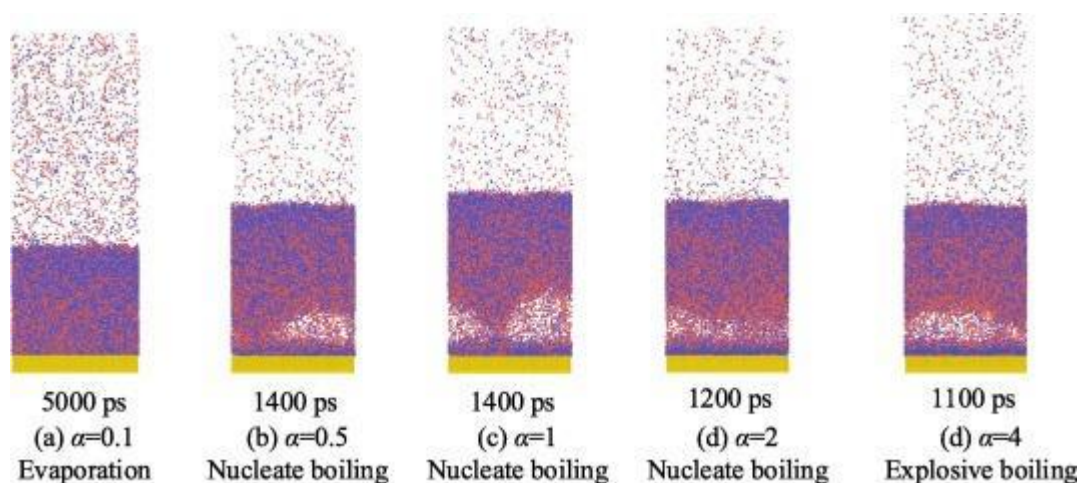


Figure 2.5 Phase change behavior under different surface wettability (Liu et al., 2023)

These findings indicate that on smooth surfaces, the solid–liquid interaction strength not only alters the wetting behavior and influences the contact angle but also affects the heat-transfer behavior at the solid–liquid interface, leading to transitions in phase-change modes and changes in the onset time of nucleate boiling. In addition, related studies have shown that the spatial distribution and relative proportion of hydrophilic and hydrophobic regions on the surface also influence the heat-transfer process at the solid–liquid interface.

Chen et al. conducted molecular dynamics simulations to investigate boiling and bubble nucleation on both uniformly wetting and nonuniformly wetting smooth surfaces. Their results showed that on a nonuniform surface with a hydrophilic center surrounded by hydrophobic regions, the stronger interaction in the hydrophilic area enhances heat transfer between the liquid and the wall, enabling the liquid to reach saturation temperature more easily. As a result, bubble nucleation occurs earlier and bubble growth is faster. Hasan et al. constructed hybrid hydrophilic/hydrophobic surfaces and examined thin-film evaporation using molecular dynamics simulations. They found that due to the stronger solid–liquid interaction, superhydrophilic surfaces exhibited more intense evaporation, with the highest heat flux and mass-evaporation rates. Wu et al. studied the boiling process of water films on smooth copper surfaces with different wettabilities and found that hydrophilic regions facilitate heat transfer at the solid–liquid interface, whereas hydrophobic regions promote evaporation due to weaker solid–liquid interactions.

Zhou et al. used molecular dynamics to examine the effect of wall temperature on bubble nucleation. Their results showed that at lower wall temperatures, bubbles preferentially nucleate on hydrophobic regions, whereas at higher wall temperatures, the nucleation sites shift from hydrophobic to hydrophilic regions. Cao et al. investigated heat-transfer behavior on hybrid-wettability surfaces and found that the interfacial thermal resistance decreases as the hydrophilic proportion increases, resulting in better heat-transfer performance. Additionally, when the liquid-film thickness exceeds 1 nm, increasing the hydrophobic proportion enlarges the vapor–liquid interfacial region, thus promoting evaporation. Deng et al. designed various hybrid hydrophilic/hydrophobic surfaces and simulated their boiling heat-transfer behavior. The results showed that under low heat-flux conditions, bubbles tend to nucleate in hydrophobic regions due to weaker solid–liquid interactions; under high heat-flux conditions, bubble nucleation occurs in both hydrophilic and hydrophobic regions, and bubbles rapidly merge shortly after nucleation.

In summary, most existing studies on smooth surfaces have primarily focused on the role of surface wettability in the solid–liquid boiling heat-transfer process, whereas investigations into how the spatial distribution of hydrophilic and hydrophobic regions affects boiling heat transfer remain limited. There is still a lack of systematic research on how different proportions and spatial arrangements of hydrophilic/hydrophobic regions influence heat transfer at the solid–liquid interface. Given the significant impact of surface wettability on solid–liquid heat transfer, further studies are needed to clarify how the proportion and spatial distribution of hydrophilic and hydrophobic regions regulate the heat-transfer process and to elucidate the underlying physical mechanisms governing boiling enhancement.\

2.2.2. Research Progress on MD Simulations of Pool Boiling Heat-Transfer Characteristics on Structured Surfaces

In addition to surface wettability, surface roughness also plays an important role in heat transfer at the solid–liquid interface (Byon et al., 2012; Kim et al., 2015; Xie et al., 2021; Sun et al., 2022). Previous studies have shown that microstructures on the wall significantly influence bubble nucleation behavior at the interface (Liu et al., 2019; Surblys et al., 2019; Chen et al., 2021). In molecular simulations, rough surfaces are typically constructed by adding microstructures onto a smooth base surface. The presence of such microstructures increases the contact area between the liquid atoms and the heated surface, allowing more liquid atoms to interact with the wall. Compared with smooth surfaces, rough surfaces can absorb more thermal energy from the heated wall within the same period of time, thereby reducing the solid–liquid thermal resistance and enhancing heat-transfer performance (Zhang et al., 2019; Cao et al., 2020). Furthermore, rough structures provide numerous nucleation sites on the wall, accelerating bubble nucleation and promoting mass transport within the liquid phase, ultimately improving the overall heat-transfer capability of the surface (Lavino et al., 2021; Shi et al., 2022; Zhou et al., 2022).

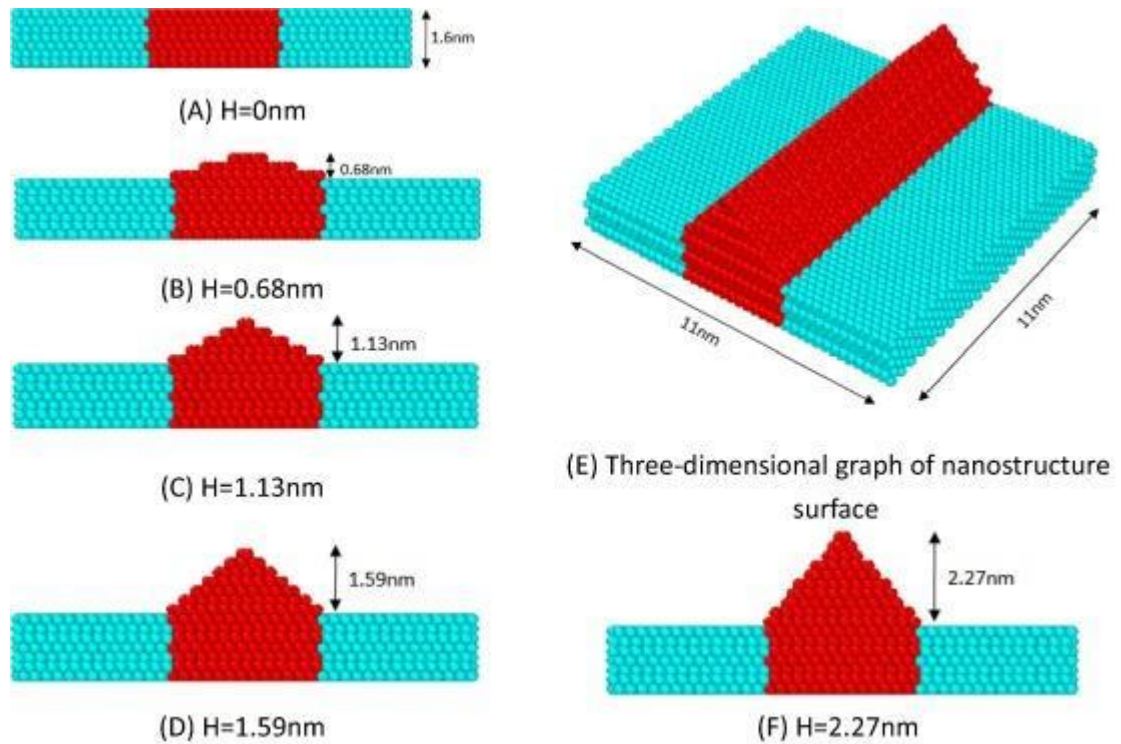


Figure 2.6 Nanostructure surfaces (Chen et al., 2018)

Shavik et al. performed molecular dynamics simulations to study explosive boiling on nanostructured surfaces under different wettability conditions. Their results indicated that heat-transfer efficiency at the solid–liquid interface increases with enhanced surface wettability. On hydrophilic surfaces, increasing the height of nanostructures enlarges the contact area between the liquid and the solid wall, thereby strengthening solid–liquid heat transfer. However, on hydrophobic surfaces, increasing the structure height does not lead to significant improvement in heat-transfer performance. She et al. simulated bubble growth on surfaces using molecular dynamics and found that the presence of surface cavities facilitates bubble growth.

Guo et al. investigated the influence of solid–liquid interaction strength on nucleate boiling heat transfer over rough surfaces using molecular dynamics. They reported that rough structures increase the contact area between the liquid and the solid surface and generate thin liquid layers within the microstructures, ensuring intimate solid–liquid contact and ultimately enhancing heat transfer. Diaz et al. examined the effect of nanostructure spacing on pool boiling and found that when the spacing is $21.7\text{ \AA}$, the

critical heat flux reaches $1.01 \times 10^8 \text{ W/m}^2$. As the spacing increases to $106.6 \text{ \AA}$, the critical heat flux increases to $1.59 \times 10^8 \text{ W/m}^2$, representing an improvement of nearly 57%.

Liu et al. designed smooth concave-pit surfaces and rough concave-pit surfaces and investigated their evaporation and explosive boiling heat-transfer characteristics. Compared with smooth concave-pit surfaces, the presence of rough structures inside the pits deteriorates heat transfer during evaporation but enhances heat transfer during explosive boiling. This difference in performance is closely related to the Kapitza resistance at the solid–liquid interface. Zhang et al. conducted molecular dynamics simulations of nucleate boiling on convex and concave structured surfaces, showing that both types of structures provide additional nucleation sites and shorten bubble nucleation time, thereby enhancing nucleate boiling compared with smooth surfaces. Moreover, nucleate boiling occurs nearly 50% earlier on concave surfaces than on convex surfaces.

Liu et al. studied boiling heat transfer of water on concave structured surfaces using molecular dynamics. Their simulations revealed that bubble nucleation occurs earlier on structured surfaces than on smooth ones. Further analysis showed that as the solid–liquid contact area increases, the interaction energy per unit area grows, enhancing heat-transfer efficiency. Among the studied surfaces, concave structured surfaces exhibited the lowest thermal resistance, whereas smooth surfaces had thermal resistance values nearly 42% higher.

Chen et al. used molecular dynamics simulations to examine the influence of groove geometry on boiling heat transfer. On small-size concave grooves, the kinetic energy of water molecules is insufficient to overcome the strong potential energy of the hydrophilic surface, causing bubble nucleation to occur away from the groove. On larger grooves, some water molecules reside in regions where the potential energy is weaker, enabling them to gain enough kinetic energy to cross the energy barrier, resulting in bubble nucleation inside the groove.

Zhou et al. studied the effects of rectangular micropit nanostructures on nucleate boiling heat transfer and found that these structures increase the contact area between the liquid and the heated surface. Compared with smooth surfaces, the liquid atoms inside the micropits can additionally absorb heat from the sidewalls, promoting bubble nucleation and delaying the transition from nucleate boiling to film boiling. Wang et al. investigated bubble nucleation on three-dimensional recessed nanostructures and found that, compared with smooth surfaces, recessed structures provide stable nucleation sites, leading to consistent bubble nucleation locations. Moreover, recessed structures increase the contact area between the liquid and the surface, reduce thermal resistance, and improve heat-transfer efficiency, although they also partially suppress bubble growth.

Zhang et al. examined the influence of surface wettability and concave/convex hemispherical structures on boiling heat transfer using molecular dynamics simulations. They found that microstructures on hydrophilic surfaces can attract more liquid argon atoms, thereby accelerating heat transfer and promoting bubble generation. In contrast, bubble nucleation occurs later on hydrophobic structured surfaces due to weaker solid – liquid interactions.

In addition to simple concave and convex structures, many researchers have begun investigating heat-transfer processes on surfaces with more complex geometric and topological features. Cao et al. further explored the effect of sinusoidal nanostructures on solid–liquid boiling heat transfer based on the heat-transfer enhancement mechanisms of nanostructured surfaces. Their simulations showed that as the amplitude of the sinusoidal nanostructure increases and the wavelength decreases, the solid–liquid contact area becomes larger, accelerating the temperature variation of liquid atoms near the heated wall. Compared with smooth surfaces, the evaporation rate increased by up to 42%. Furthermore, the presence of nanostructures reduced the interfacial thermal resistance, with the minimum value calculated to be $8.70 \times 10^{-9} \text{ m}^2 \cdot \text{K/W}$, representing a reduction of 27.6% relative to the smooth surface.

Ahmad et al. investigated pool-boiling heat transfer on porous mesh structures and standard mesh structures. Compared with smooth surfaces, the evaporation rates on porous mesh and standard mesh structures increased by 23.89% and 19.16%, respectively, indicating that porous mesh surfaces possess superior heat-transfer enhancement capability. Huang et al. introduced nanoarrays at the heating hotspot on the wall and found that under strong solid–liquid interactions, the nanoarrays continuously attracted surrounding liquid toward the hotspot, delaying the occurrence of dryout and ensuring liquid supply at the hotspot. As the number of nanoarrays increased, both the evaporation performance of the wall and the liquid replenishment capability improved.

Liu et al. designed surfaces with different roughness levels using the multivariable Weierstrass–Mandelbrot function. Compared with smooth surfaces, rough surfaces provided more nucleation sites, accelerated bubble nucleation, promoted the liquid-to-vapor transition, and enhanced evaporation. Moreover, the heat-transfer performance of the wall improved further with increasing roughness.

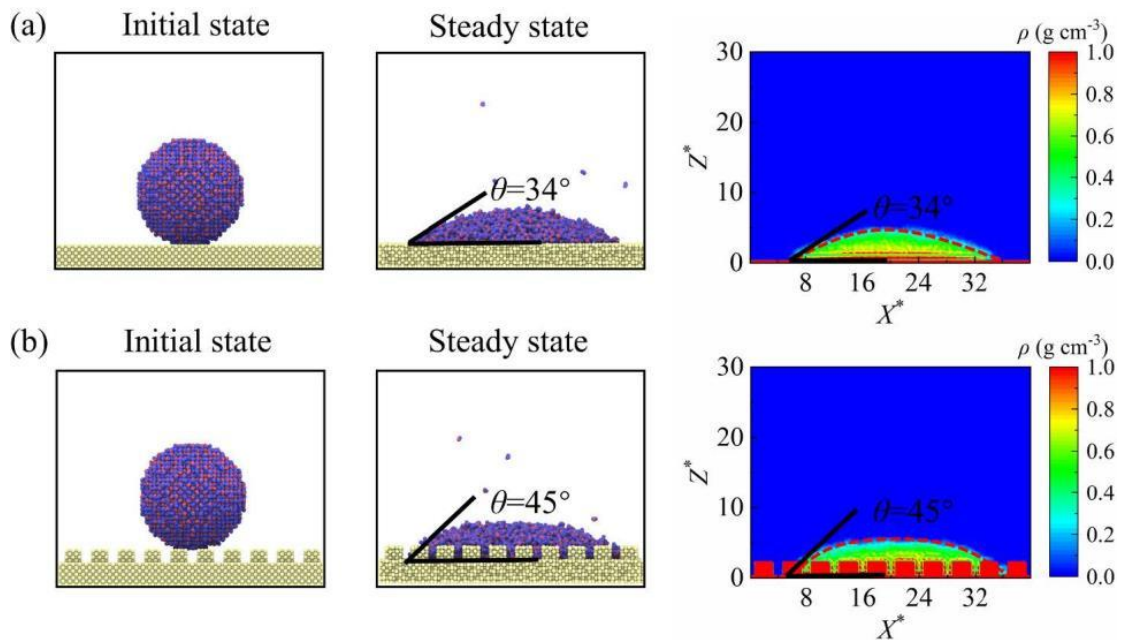


Figure 2.7 Wetting state of water droplets at the initial and steady stages and density contours of water droplets for (a) smooth surface, (b) rough surface. (Guan et al., 2020)

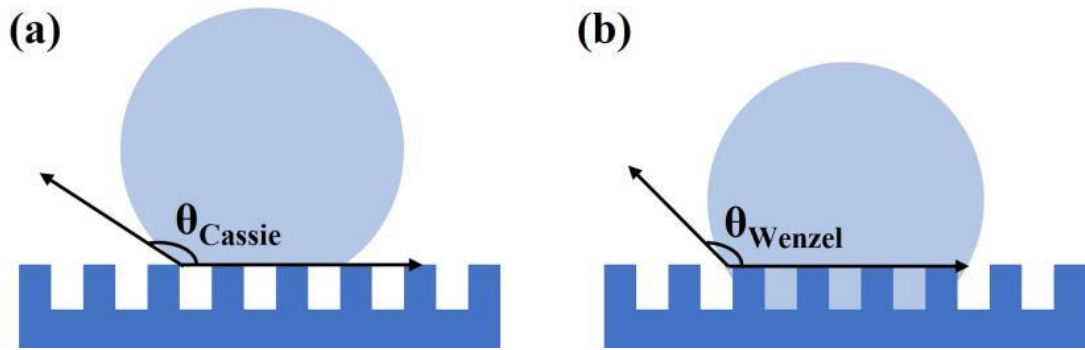


Figure 2.8 Droplet wettability state on structured surface: (a) Cassie wettability state, (b) Wenzel wettability state

In addition to influencing heat transfer at the solid–liquid interface, surface microstructures also affect the wetting behavior of droplets on the wall. Fu et al. used molecular dynamics simulations to investigate the variation in wetting behavior of water on Cu nanostructured surfaces. Their results showed that, compared with smooth surfaces, the contact angle of water decreased from 87° to 71.6° on rough surfaces, indicating that the presence of microstructures enhances the hydrophilicity of the wall to some extent. Guan et al. found through molecular dynamics simulations that as the groove width between surface microstructures increases, the wetting mode transitions from the Cassie state to the Wenzel state, and the droplet contact angle decreases accordingly. The Cassie and Wenzel wetting modes are illustrated in Figure 2.8.

Yi et al. studied the wetting behavior of complex long-chain alkane droplets on pillar-structured surfaces using molecular dynamics simulations. They found that the wetting state is determined jointly by the solid–liquid interaction strength, pillar spacing, and pillar height. When the solid–liquid interaction is either too strong or too weak, the droplet contact angle no longer changes with increasing pillar height, and the droplet remains consistently in either the Cassie or Wenzel wetting state. Sethi et al. reported that the geometric shape of microstructures has a significant influence on wettability. Their simulations showed that shell-shaped microstructures exhibited the smallest contact angle under both hydrophobic and hydrophilic conditions, whereas hollow and solid spheres showed similar contact angles in both cases.

In summary, compared with smooth surfaces, structured surfaces not only increase the solid–liquid contact area and enhance energy transfer across the interface but also provide additional nucleation sites, accelerating bubble growth and strengthening pool-boiling heat transfer. However, in molecular dynamics studies of boiling heat transfer on structured surfaces, most research has focused primarily on the geometric design of micro/nanostructures and on discussing how geometric shape affects solid–liquid heat transfer. There remains a lack of studies examining how the projected area ratio of micro/nanostructures on the wall and the intrinsic wettability of the structures themselves influence the solid–liquid heat-transfer process and bubble growth behavior.

Therefore, it is necessary to further investigate the effects of the projected area fraction of micro/nanostructures and their inherent wettability on pool-boiling performance and bubble dynamics on structured surfaces, so as to clarify the physical mechanisms by which structured surfaces enhance pool-boiling heat transfer.

2.2.3. Research Progress on MD Simulations of Pool-Boiling Heat-Transfer Characteristics on Composite Structured Surfaces

In the previous subsection, the application of molecular dynamics simulations to study pool-boiling heat transfer on structured surfaces was reviewed. Those studies show that the presence of micro/nanostructures increases the solid–liquid contact area and provides numerous nucleation sites, thereby enhancing nucleate boiling heat transfer. However, they did not consider the influence of the intrinsic wettability of micro/nanostructures on heat-transfer behavior at the wall. Consequently, researchers have shifted their attention to composite structured surfaces that combine micro/nanostructures with controlled wettability (Liu et al., 2021; Shahmardi et al., 2021; Zhang et al., 2020), aiming to integrate the advantages of both features and achieve further enhancement of boiling heat transfer. Therefore, this subsection presents recent developments in molecular dynamics studies on composite structured surfaces.

As illustrated in Figure 2.9, compared with conventional structured surfaces, composite structured surfaces integrate micro/nanostructures with regions of different wettability. On one hand, micro/nanostructures increase the solid–liquid contact area and improve heat-transfer efficiency. On the other hand, adjusting the wettability of the structures enables the construction of hybrid hydrophilic/hydrophobic surfaces. Hydrophobic regions help reduce the nucleation temperature and increase the number of vapor embryos, while hydrophilic regions enhance solid–liquid heat transfer and increase the critical heat flux (CHF). Through the combination of these advantages, composite structured surfaces achieve further enhancement of pool-boiling performance beyond that of conventional structured surfaces.

Experimental studies have demonstrated (Betz et al., 2010; Pontes et al., 2020; Sun et al., 2022) that hybrid hydrophilic/hydrophobic composite surfaces effectively increase the number of nucleation sites, accelerate bubble growth and departure, and significantly strengthen pool-boiling heat transfer by leveraging both wettability modulation and structural design.

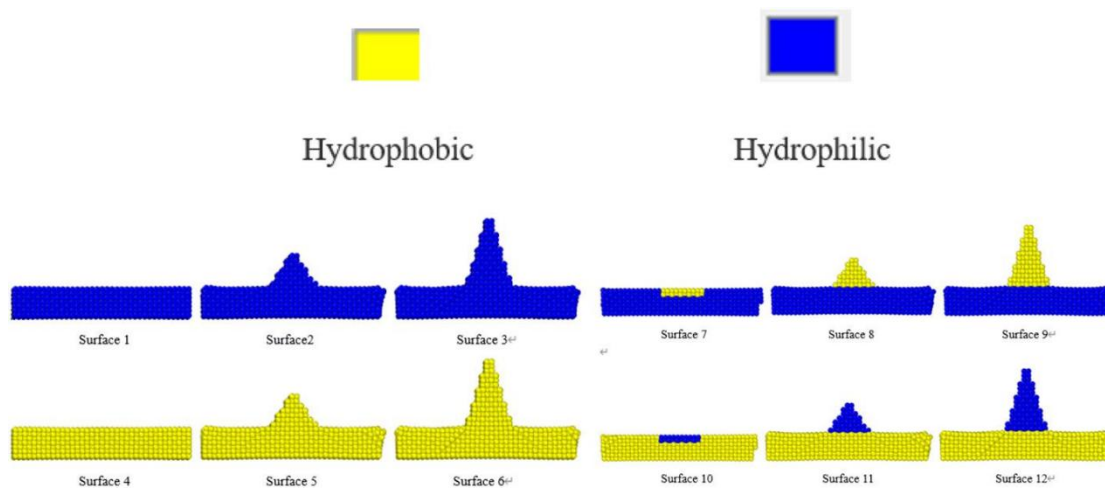


Figure 2.9 Structured surfaces and hybrid-wettability surfacesc (Chen et al., 2021)

Liao et al. used molecular dynamics simulations to investigate the influence of composite hydrophobic–hydrophilic micro/nanostructured surfaces on explosive boiling. Their results showed that compared with fully hydrophilic surfaces, the hydrophobic regions in the composite structures promote bubble formation, accelerate

liquid-film rupture, and reduce the temperature at which explosive boiling occurs. In addition, as the thickness of the hydrophobic coating increases, the onset temperature of explosive boiling decreases with increasing pillar width and liquid-film thickness.

Chen Yujie et al. constructed hydrophilic/hydrophobic composite groove surfaces and examined bubble nucleation behavior and nucleation rates. Their results indicated that bubble nucleation occurs on surfaces with different wettabilities, but the nucleation location depends on the strength of surface wettability. On hydrophilic/hydrophobic composite surfaces, vapor embryos first appear on the hydrophobic side, while the hydrophilic side remains covered by a layer of liquid atoms due to stronger solid–liquid interactions.

Chen et al. constructed micropillar-structured surfaces whose wettability varied with time. They found that time-dependent changes in wettability reduce the viscous force exerted on bubbles by the wall, increasing bubble departure frequency. The micropillar structures also increased bubble curvature locally and formed a vapor film between the bubble and the pillars, preventing dry out.

Gao et al. developed various composite structured surfaces and simulated thin-film boiling using molecular dynamics. Their results showed that increasing surface roughness, enhancing surface wettability, and enlarging the hydrophilic area fraction reduce thermal resistance at the solid–liquid interface and further improve heat and mass transfer. Unlike macroscopic boiling, nanoscale thin-film boiling exhibits superior heat- and mass-transfer characteristics because bubble formation is suppressed.

Zhou et al. examined the influence of microstructure and wettability on bubble nucleation. Their results showed that the nucleation location is closely related to the wettability of the microstructures: on hydrophilic pillar surfaces, nucleation occurs in the bulk liquid region, while on hydrophobic pillar surfaces, nucleation takes place on the pillar surface itself. Wettability also affects nucleation timing—on hydrophilic pillars, weaker wettability delays nucleation, whereas on hydrophobic pillars, weaker

wettability leads to earlier nucleation. Moreover, compared with uniformly hydrophilic pillars, mixed-wettability pillars promote bubble nucleation and enhance heat-transfer performance.

Zhao Hui et al. simulated bubble nucleation and boiling heat transfer on nano–mixed-wettability surfaces under transient temperature boundary conditions. They found that mixed-wettability surfaces enhance bubble nucleation through a pinning effect, and that superhydrophobic modification of nanostructures on superhydrophilic substrates provides the most effective boiling enhancement.

In summary, compared with conventional structured surfaces, composite hydrophilic–hydrophobic structured surfaces further enhance bubble nucleation and improve boiling heat-transfer performance. This enhancement is achieved not only through the increased solid–liquid contact area and the greater number of nucleation sites provided by micro/nanostructures, but also by modifying the wettability of these structures to form hybrid hydrophilic–hydrophobic patterns. Such composite configurations effectively strengthen the nucleation process and promote more efficient boiling heat transfer.

However, in molecular dynamics studies of pool boiling on composite structured surfaces, research remains limited regarding the influence of the projected area fraction of micro/nanostructures on the overall boiling performance. Moreover, the bubble growth and development behaviors and the enhancement mechanisms of solid–liquid boiling heat transfer on micro/nanostructures with different wettabilities require further investigation.

2.3. Fundamental Theories of Droplet Spreading

Droplet spreading refers to the phenomenon in which a liquid droplet, upon contacting a solid surface, spreads under the action of capillary forces. This behavior is widespread in nature and closely associated with the life activities of plants and animals. Moreover, droplet spreading has extensive applications in various industrial and daily

processes, such as adhesion, lubrication, petrochemical operations, cleaning, welding, dyeing, waterproofing, and coating (Zhang et al., 2016; Zhao and Cheng, 2017). The spreading of a droplet depends not only on the intrinsic properties of the liquid and solid but also on the interactions between them. Specifically, liquid and solid molecules (or atoms) exhibit cohesive forces within their respective phases, while adhesive forces act between solid atoms and liquid molecules. The droplet spreading process and its final equilibrium state are determined by the combined effects of these cohesive and adhesive forces.

2.3.1. Equilibrium Contact Angle and Young's Equation

When a microdroplet is placed on a solid surface, the cohesive forces between liquid molecules tend to maintain a spherical shape and minimize contact with the solid, whereas the adhesive forces between solid and liquid molecules promote spreading over the surface. Once the droplet reaches a stable state, it forms a spherical cap under the action of surface tension, and the angle formed at the three-phase contact line is defined as the equilibrium contact angle θ_E . For smooth surfaces, the equilibrium contact angle θ_E is also referred to as the intrinsic contact angle.

The value of the equilibrium contact angle reflects the degree of wettability of the solid surface: a smaller θ_E corresponds to stronger wettability. As illustrated in Figure 2.10, if a droplet spreads completely over the surface, the equilibrium contact angle is $\theta_E=0^\circ$, indicating complete wetting. If the droplet forms a perfect sphere, the contact angle is $\theta_E=180^\circ$, corresponding to complete non-wetting. When the equilibrium contact angle lies between 0° and 180° ($0^\circ<\theta_E<180^\circ$), the surface exhibits partial wetting.

More specifically, an equilibrium contact angle in the range $0^\circ<\theta_E<90^\circ$ indicates hydrophilicity, whereas $90^\circ<\theta_E<180^\circ$ signifies hydrophobicity. Surfaces with an equilibrium contact angle greater than 150° ($\theta_E>150^\circ$) are typically classified as superhydrophobic.

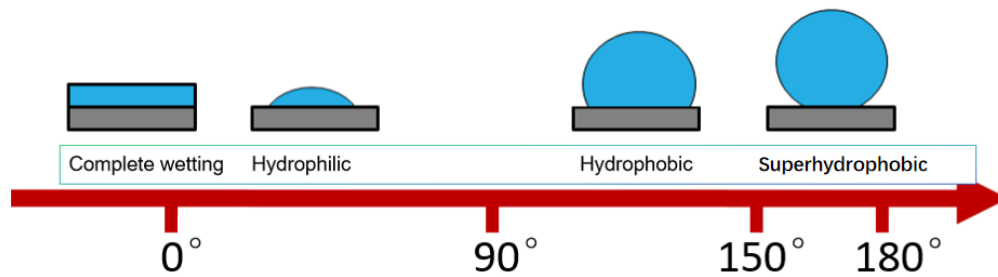


Figure 2.10 Wetting states corresponding to various equilibrium contact angles θ_E

As illustrated in Figure 2.11, when the droplet reaches equilibrium on the solid surface, the net force at the three-phase contact line should be zero in both the horizontal and vertical directions. By considering the force balance in the horizontal direction, the relationship between interfacial tensions and the equilibrium contact angle θ_E can be obtained, which is expressed by the Young equation, shown as Equation 2.1:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta_E \quad \text{Equation 2.1}$$

Where:

- γ_{SV} is the solid–vapor interfacial tension,
- γ_{SL} is the solid–liquid interfacial tension,
- γ_{LV} is the liquid–vapor surface tension.

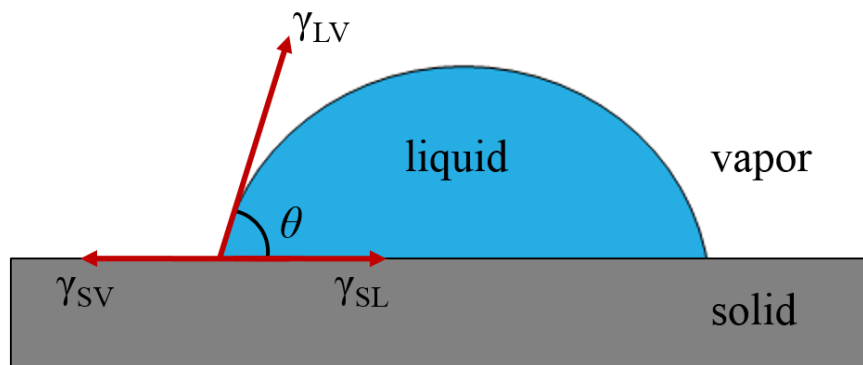


Figure 2.11 Droplet spreading on a smooth solid surface at equilibrium

However, in practical situations, the surfaces of many solids are not smooth and homogeneous but instead possess certain microstructures or chemical heterogeneities. These characteristics alter the wetting behavior of microdroplets on the solid surfaces, rendering the Young's equation inapplicable under such conditions and necessitating appropriate modifications. To quantify the influence of surface roughness on the wettability of solid surfaces, Wenzel introduced the concept of roughness to describe the degree of surface irregularity (Wenzel, 1936). Roughness is defined as the ratio of the actual surface area of the solid to its projected area, as shown in Equation (2.2).

The parameter r represents the roughness of a solid surface, where A_{true} and A_{apparent} denote the actual surface area and the projected area of the solid surface, respectively, as defined in Equation 2.2.

$$r = \frac{A_{\text{true}}}{A_{\text{apparent}}} \quad \text{Equation 2.2}$$

When a droplet contacts a rough surface, there are two classical wetting states: the Wenzel state and the Cassie-Baxter state (Wenzel, 1936; Cassie and Baxter, 1944; Cassie, 1948). As illustrated in Figure 2.12, in the Wenzel state, the droplet completely wets the surface roughness, forming a continuous contact with the solid surface. In this case, the apparent contact angle $\theta_{E,W}$ is related to the intrinsic contact angle θ_E by Equation 2.3 (Wenzel, 1936):

$$\cos\theta_{E,W} = r \cos\theta_E \quad \text{Equation 2.3}$$

In contrast, in the Cassie-Baxter state, the droplet sits atop the rough structure, partially supported by air pockets between the solid features. Here, the apparent contact angle $\theta_{E,C}$ is determined by the surface fraction and intrinsic contact angles of the composite materials, as described by Equation 2.4 (Cassie and Baxter, 1944; Cassie, 1948):

$$\cos\theta_{E,C} = f_1 \cos\theta_{E,1} + f_2 \cos\theta_{E,2} \quad \text{Equation 2.4}$$

In the specific case where the second phase is air (i.e., the droplet is in contact with a solid–air composite interface), assuming no liquid infiltration into the grooves, the liquid–air interface remains unconnected to the solid substrate. In this situation, the apparent contact angle $\theta_{E,C}$ is related to the intrinsic contact angle θ_E as follows (Cassie and Baxter, 1944; Cassie, 1948):

$$\cos\theta_{E,C}=f_1\cos\theta_{E,1}+f_2\cos\theta_{E,2} \quad \text{Equation 2.5}$$

Here, $\theta_{E,W}$ and $\theta_{E,C}$ represent the apparent contact angles of a droplet in the Wenzel and Cassie-Baxter states, respectively. f_1 and f_2 are the area fractions of materials 1 and 2 on the surface, and $\theta_{E,1}$ and $\theta_{E,2}$ are the intrinsic contact angles of the droplet on materials 1 and 2, respectively.

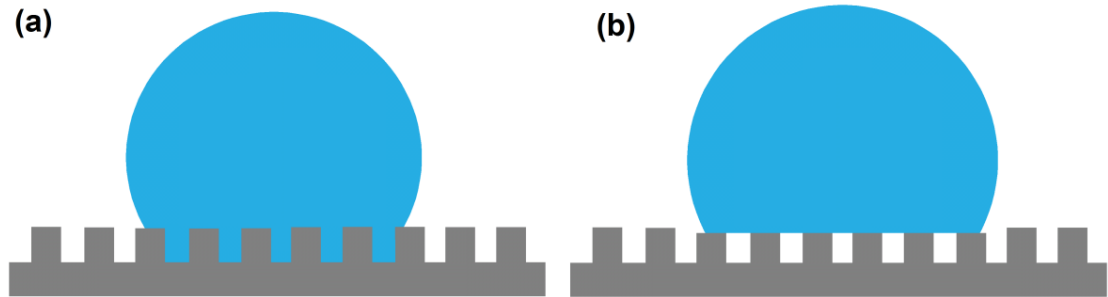


Figure 2.12 Two typical wetting states of a droplet on a rough solid surface: (a) Wenzel state; (b) Cassie–Baxter state

As shown in Figure 2.13, when a droplet spreads on a solid surface, the effect of line tension should also be considered. Taking line tension into account, the modified Young’s equation is given by Equation 2.6 (Amirfazli and Neumann, 2004; Schimmele et al., 2007):

$$\cos\theta_E=\frac{\gamma_{SV}-\gamma_{SL}}{\gamma_{LV}}-\frac{\lambda}{R\gamma_{LV}} \quad \text{Equation 2.6}$$

$$\lambda\approx 4\delta'\sqrt{\gamma_{SV}\gamma_{LV}}\cot\theta_E \quad \text{Equation 2.7}$$

Here, λ represents the line tension, and $1/R$ is the local curvature of the three-phase contact line, where R is the spreading radius. The smaller the value of R , the larger the curvature and the greater the influence of line tension. As the droplet radius approaches zero, the above expression reduces to the classical Young's equation. When the droplet size decreases to the micro- or nanoscale, behaviors differing from those at the macroscopic scale may emerge, and the effect of line tension must be considered.

In general, line tension λ can be estimated using Equation 2.7 (Marmur, 1997), where δ' represents the average distance between solid molecules at the interface. From Equation 2.7, it can be seen that the sign of the line tension determines whether it promotes or suppresses droplet spreading. When the solid surface is hydrophobic ($\theta_E > 90^\circ$), λ is negative, indicating that line tension inhibits spreading. In contrast, when the surface is hydrophilic ($\theta_E < 90^\circ$), λ is positive, meaning that line tension facilitates droplet spreading.

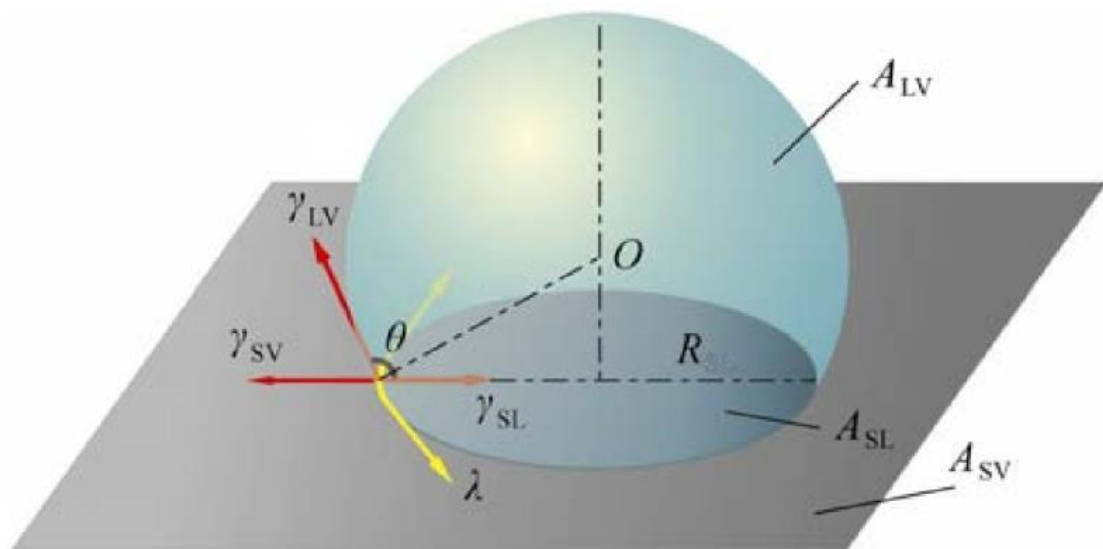


Figure 2.13 Wetting state of a droplet on a solid surface considering the effect of line tension (Lü Cunjing, 2011)

2.3.2. Droplet Spreading Process and Classical Theories

When a droplet is placed on a solid surface, liquid molecules near the three-phase contact line move outward under the influence of capillary forces. The static wetting model, namely the Young's equation, characterizes the relationship among interfacial tension, line tension, and equilibrium contact angle when the droplet reaches a steady state. Compared to the static model, the dynamic spreading process better reflects the flow characteristics of liquid molecules on the solid surface. The droplet spreading velocity or the contact line velocity V_{CL} , along with the dynamic contact angle θ_D , are the main parameters used to describe the dynamic spreading behavior (Yuan et al., 2016). Droplet spreading is a thermodynamically irreversible and dissipative process, during which the three-phase contact line advances at a finite speed. As the wetted area increases, both the droplet shape and the dynamic contact angle θ_D also evolve.

Depending on the underlying mechanisms of energy dissipation, two classical theoretical frameworks are commonly used to describe dynamic wetting: the hydrodynamic model and the molecular kinetic theory (Voinov, 1976; Blake and De Coninck, 2002; Fernandez-Toledano et al., 2021). In the hydrodynamic model, viscous dissipation near the contact line is considered the primary source of energy loss. In contrast, the molecular kinetic theory attributes the energy dissipation to the adsorption and desorption of liquid molecules at the solid surface near the contact line, driven by external forces—i.e., molecular friction dominates the energy loss.

As shown in Figure 2.14, the hydrodynamic model divides the region near the three-phase contact line into three different length-scale zones: the macroscopic, mesoscopic, and microscopic regions. The macroscopic region is on the same length scale as the droplet spreading radius R , within which the apparent dynamic contact angle $\theta_{D,App}$ can be defined to describe the droplet shape. The mesoscopic region is a transitional zone where the curvature of the interface changes from positive to negative. The microscopic region spans only a few nanometers near the contact line. Within this microscopic region, a corresponding microscopic dynamic contact angle $\theta_{D,M}$ can be

defined. Here, molecular interactions and the statistical dynamics of liquid molecules govern the behavior of the three-phase contact line.

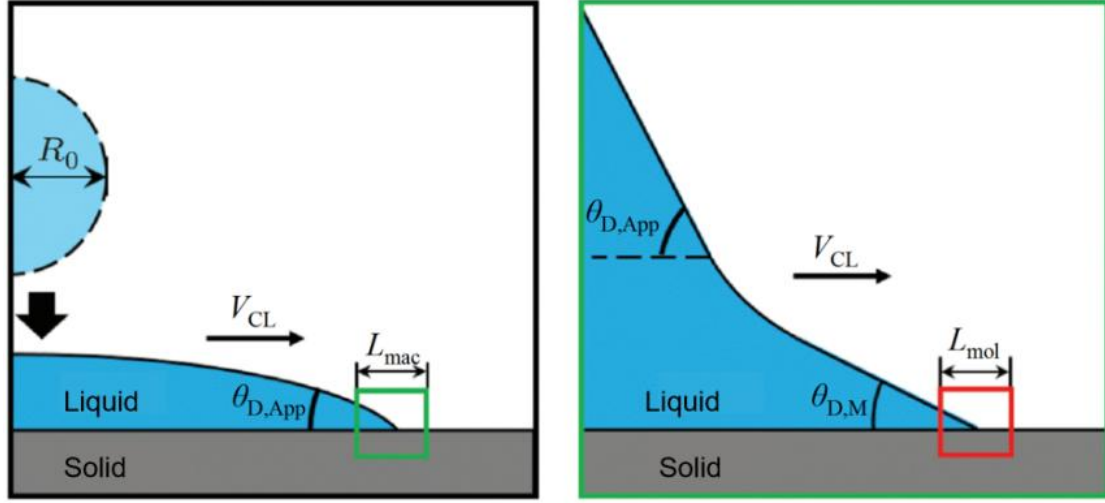


Figure 2.14 Schematic of the hydrodynamic model for droplet spreading. $\theta_{D,App}$ and $\theta_{D,M}$ denote the apparent and microscopic dynamic contact angles, respectively (Yuan et al., 2016).

The relationship among the apparent dynamic contact angle $\theta_{D,App}$, the microscopic dynamic contact angle $\theta_{D,M}$, and the contact line velocity V_{CL} is generally described by Equations 2.8 and 2.9, collectively known as the Cox–Voinov law:

$$G(\theta_{D,App}) = G(\theta_{D,M}) + \ln\left(\frac{L_{mac}}{L_{mol}}\right) Ca \quad \text{Equation 2.8}$$

$$Ca = \frac{V_{CL}\mu}{\gamma_{LV}} \quad \text{Equation 2.9}$$

Here, Ca is the capillary number, μ is the dynamic viscosity of the liquid, and L_{mac} and L_{mol} are the characteristic length scales in the macroscopic and molecular regions, respectively.

The values of $G(\theta_{D,App})$ and $G(\theta_{D,M})$ depend on the viscosity ratios between the liquid and gas phases. For systems in which the viscosity of the gas phase is negligible compared to that of the liquid, $G(\theta)$ can be calculated by Equation 2.10. Expanding

this expression as a Taylor series, when the dynamic contact angle $\theta_D < 135^\circ$, Equation 2.11 provides a simplified estimation of $G(\theta_D)$, and Equation 2.8 reduces to the following form Equation 2.12:

$$G(\theta_D) = \int_0^{\theta_D} \frac{\theta' \sin \theta' \cos \theta'}{2 \sin^2 \theta'} d\theta' \quad \text{Equation 2.10}$$

$$G(\theta_D) = \frac{\theta_D^3}{9} \quad \text{Equation 2.11}$$

$$\theta_{D,App}^3 = \theta_{D,M}^3 + 9 \ln \left(\frac{L_{mac}}{L_{mol}} \right) Ca \quad \text{Equation 2.12}$$

In practical applications of Equation 2.12, a common approach is to replace the microscopic dynamic contact angle $\theta_{D,M}$ with the equilibrium contact angle θ_E . Under this approximation, Equation 2.8 can be further simplified to:

$$\theta_{D,App}^3 = \theta_E^3 + 9 \ln \left(\frac{L_{mac}}{L_{mol}} \right) Ca \quad \text{Equation 2.13}$$

In the framework of molecular kinetic theory, the motion of the three-phase contact line is governed by the statistical dynamics of molecules transitioning between the solid–liquid and solid–vapor interfaces (Blake and De Coninck, 2002). As shown in Figure 2.15, when the system is at equilibrium, the forward and backward molecular jump frequencies of liquid molecules at the contact line are equal, and denoted as κ_0 . Under this condition, no net movement of the contact line occurs. The molecular vibration frequency κ_0 is given by:

$$\kappa_0 = \left(\frac{k_B T}{h} \right) \exp \left(\frac{-\Delta G}{k_B T} \right) \quad \text{Equation 2.14}$$

Here, k_B is the Boltzmann constant, h is Planck's constant, T is the absolute temperature, and ΔG is the energy barrier associated with molecular displacement at the interface.

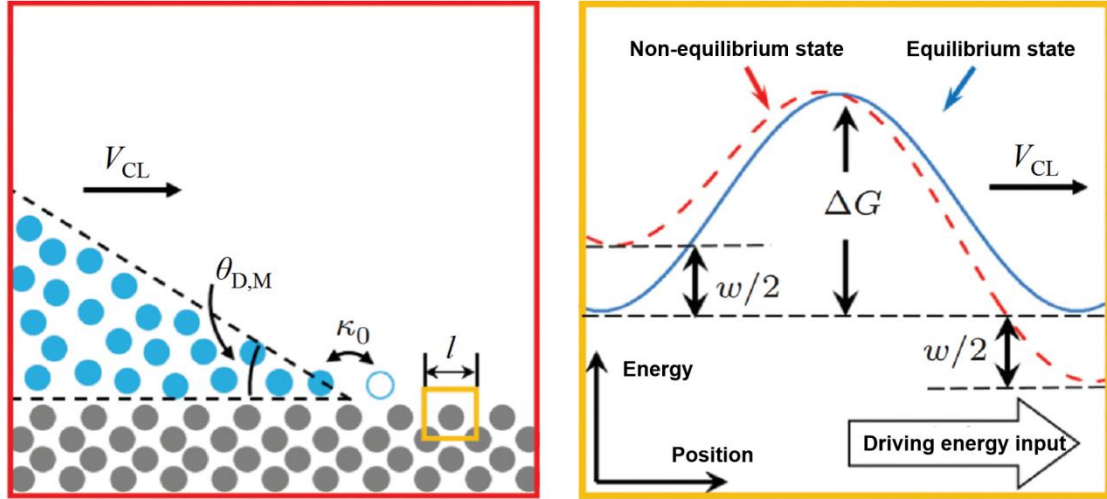


Figure 2.15 Schematic of the molecular kinetic theory of droplet spreading, where the driving energy input induces a tilt in the potential energy surface of liquid molecules on the solid surface (Yuan Quanzi et al., 2016).

When water molecules at the three-phase contact line are subjected to an external driving force, the potential energy surface at the solid interface becomes tilted. As a result, the forward hopping frequency κ^+ of liquid molecules increases, while the backward hopping frequency κ^- decreases accordingly. The expressions for κ^+ and κ^- are given by Equations 2.15 and 2.16, respectively:

$$\kappa^+ = \left(\frac{k_B T}{h} \right) \exp \left(\frac{-\Delta G}{k_B T} + \frac{w}{2nk_B T} \right) \quad \text{Equation 2.15}$$

$$\kappa^- = \left(\frac{k_B T}{h} \right) \exp \left(\frac{-\Delta G}{k_B T} - \frac{w}{2nk_B T} \right) \quad \text{Equation 2.16}$$

Here, w is the driving work per unit area, n is the number of liquid molecules (or atoms) per unit area.

As shown in Figure 2.15, let l be the distance between two atoms on the solid surface. Combining Equations 2.15 and 2.16, the displacement velocity of liquid molecules at the three-phase contact line, i.e., the contact line velocity V_{CL} , can be expressed as:

$$V_{CL} = l(\kappa^+ - \kappa^-) = 2\kappa_0 l \sinh\left(\frac{w}{2nk_B T}\right) \quad \text{Equation 2.17}$$

Typically, $nl^2 = 1$.

When $w \ll 2nk_B T$, Equation 2.17 can be further simplified to a linear relationship:

$$V_{CL} = \frac{w}{\zeta} \quad \text{Equation 2.18}$$

$$\zeta = \frac{k_B T}{\kappa_0 l^2} = \left(\frac{\hbar}{l^2}\right) \exp\left(\frac{\Delta G}{k_B T}\right) \quad \text{Equation 2.19}$$

When a microscopic droplet spreads over a solid surface, as shown in Equation 2.20, the unit-area driving energy w can be related to the difference in surface energies between the equilibrium contact angle θ_E and the microscopic dynamic contact angle $\theta_{D,M}$. Given that the liquid–vapor surface tension is γ_{LV} , the driving force becomes:

$$w = \gamma_{LV}(\cos\theta_E - \cos\theta_{D,M}) \quad \text{Equation 2.20}$$

Substituting this into Equation 2.17 gives the contact line velocity as:

$$V_{CL} = 2\kappa_0 l \sinh\left(\frac{\gamma_{LV}(\cos\theta_E - \cos\theta_{D,M})}{2nk_B T}\right) \quad \text{Equation 2.21}$$

If $\gamma_{LV}(\cos\theta_E - \cos\theta_{D,M}) \ll 2nk_B T$, then Equation 2.21 can be further linearized:

$$V_{CL} = \kappa_0 l \frac{\gamma_{LV}}{nk_B T} (\cos\theta_E - \cos\theta_{D,M}) \quad \text{Equation 2.22}$$

From Equation 2.22, it is evident that the contact line velocity V_{CL} is linearly dependent on the difference in cosine values between the equilibrium contact angle and the microscopic dynamic contact angle.

For spreading of microscopic droplets on smooth solid surfaces, assuming the droplet shape remains approximately hemispherical and ignoring gravitational effects, the droplet radius R varies with time t as a result of contact line motion. Since the

contact line velocity V_{CL} is defined as $\frac{dR}{dt} = \dot{R}$, and from geometric considerations we have:

$$\cos\theta_{D,M} - \cos\theta_E \propto \frac{1}{R^2}$$

Combining with Equation 2.22, we find the contact line velocity is inversely proportional to R^2 :

$$V_{CL} = \dot{R} \propto \frac{1}{R^2} \quad \text{Equation 2.23}$$

$$V_{CL} = \dot{R} \propto \frac{1}{R^6} \quad \text{Equation 2.24}$$

It can thus be concluded that the droplet spreading radius R exhibits different scaling relationships with time t in the hydrodynamic model and the molecular kinetic theory. Specifically, for three-dimensional droplets, the spreading follows $R \sim t^{1/10}$ in the hydrodynamic model and $R \sim t^{1/7}$ in the molecular kinetic theory, corresponding to scaling exponents $\alpha=1/10$ and $\alpha=1/7$, respectively.

For two-dimensional droplets with an initial cylindrical shape, the droplet evolves into a segment of a cylinder during the spreading process. In this case, the scaling laws become $R \sim t^{1/7}$ for the hydrodynamic model and $R \sim t^{1/5}$ for the molecular kinetic theory, corresponding to scaling exponents $\alpha=1/7$ and $\alpha=1/5$, respectively.

2.4. Fundamental Theory of Capillary Flow

Capillary flow refers to the spontaneous movement of a liquid into narrow channels or porous materials without the assistance of external forces such as gravity. This phenomenon is not only widespread in nature but also plays a vital role in various aspects of human life and industrial applications, including water uptake by plant roots, moisture retention in soil, and oil and gas recovery (Prodanovic and Bryant, 2006; Li et al., 2019).

The capillary flow process is primarily governed by capillary driving forces, viscous resistance, gravity, and inertial forces of the liquid (Washburn, 1921; Bosanquet, 1923; Quéré, 1997). At the micro- and nanoscale, additional factors must be considered, such as the dynamic effects of the contact angle, slip at the solid–liquid interface, and potential scale-dependent phenomena (Xiao et al., 2006; Dimitrov et al., 2007; Joly, 2011).

2.4.1. Capillary Dynamics Equation

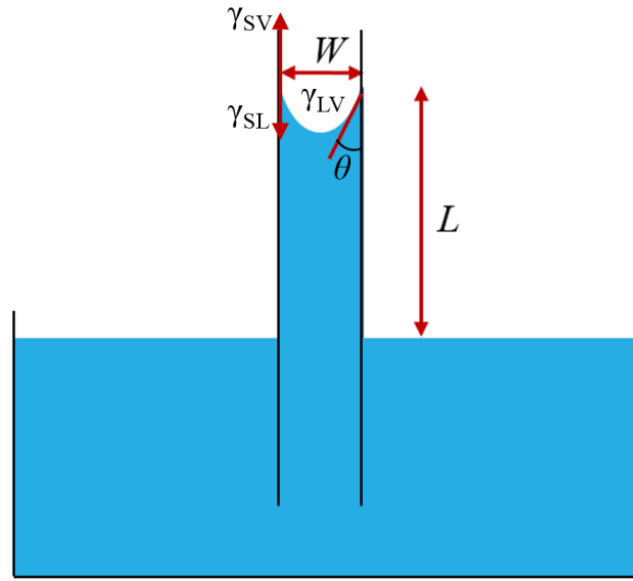


Figure 2.16 Schematic of capillary flow in a vertically oriented capillary tube

To maintain generality, consider the system shown in Figure 2.16, in which a cylindrical capillary tube with radius $W/2$ is vertically inserted into a liquid reservoir. Driven by the capillary force F_{Cap} , the liquid rises into the capillary. During the capillary flow process, the liquid primarily experiences two resisting forces: the viscous resistance from the capillary wall F_{Vis} and the gravitational force of the liquid column F_G (Washburn, 1921; Bosanquet, 1923; Quéré, 1997).

The capillary driving force F_{Cap} can be obtained from the Young–Laplace equation. If the contact angle of the liquid on the capillary wall is θ , the capillary driving force during the rise process is computed using Equation 2.25 (Washburn,

1921). Let L denote the height of the capillary rise; then the gravitational force exerted by the liquid column inside the capillary can be calculated using Equation 2.26.

$$F_{cap} = \frac{2\gamma_{LV} \cos \theta}{W/2} \quad \text{Equation 2.25}$$

$$F_G = \pi \left(\frac{W}{2}\right)^2 L \rho g \quad \text{Equation 2.26}$$

Here, θ is the contact angle between the liquid and the capillary wall, typically taken as the equilibrium contact angle θ_E ; ρ is the liquid density, and g is the gravitational acceleration.

Assuming that the liquid is Newtonian and that the flow inside the capillary follows the Hagen–Poiseuille profile during capillary rise, the viscous resistance F_{vis} can be obtained by combining Newton’s law of internal friction with the Hagen–Poiseuille equation (Washburn, 1921). According to Newton’s law of viscosity, the viscous shear force exerted by the capillary wall on the liquid is given by Equation 2.27. When the liquid flow inside the capillary satisfies the Hagen–Poiseuille equation and slip at the solid–liquid boundary is neglected, the axial velocity profile across the capillary cross-section exhibits a parabolic distribution, as shown in Equation 2.28, where P denotes the pressure acting on the liquid inside the capillary. Taking the derivative of both sides of Equation 2.28 with respect to the radial coordinate r_c yields Equation 2.29. Because the liquid velocity varies along the radial direction, an average velocity is introduced to facilitate calculation. The average velocity $\bar{V}$ is defined as the volumetric flow rate per unit cross-sectional area of the capillary, as expressed in Equation 2.30. By combining Equations 2.29 and 2.30, Equation 2.31 is obtained. Finally, from Equations 2.27 and 2.31, the viscous resistance F_{vis} during capillary flow can be evaluated by substituting the radial coordinate $r_c = W/2$, i.e., the capillary radius, leading to Equation 2.32.

$$\tau = \mu \left. \frac{dV}{dr_c} \right|_{r_c=W/2} \quad \text{Equation 2.27}$$

$$V = \frac{1}{4\mu} \int_{r_c}^2 \left(\frac{W}{2}\right)^2 \left. \frac{\partial P}{\partial L} \right| \quad \text{Equation 2.28}$$

$$\frac{dV}{dr_c} = \frac{2r_c}{4\mu} \frac{\partial P}{\partial L} \quad \text{Equation 2.29}$$

$$\bar{V} = \frac{(W/2)^2}{8\mu} \frac{\partial P}{\partial L} \quad \text{Equation 2.30}$$

$$\frac{dV}{dr_c} = \frac{2r_c}{4\mu(W/2)^2} 8\mu \bar{V} \quad \text{Equation 2.31}$$

$$F_{vis} = 8\pi\mu L \bar{V} \quad \text{Equation 2.32}$$

Since the liquid enters and rises within the capillary under the combined action of the capillary driving force F_{cap} , the viscous resistance F_{vis} , and the gravitational force of the liquid column F_G , the momentum theorem yields Equation 2.33. Further simplification of Equation 2.33 leads to Equation 2.34.

$$\frac{d(m\bar{V})}{dt} = F_{cap} - F_G - F_{vis} \quad \text{Equation 2.33}$$

$$\frac{2\gamma_{LV}\cos\theta}{W/2} - \frac{8\mu L \bar{V}}{(W/2)^2} - L\rho g - d\rho \frac{d(L\bar{V})}{dt} = 0 \quad \text{Equation 2.34}$$

where m is the mass of liquid inside the capillary tube, and $m = \pi(W/2)^2 L \rho$, while the average velocity is $\bar{V} = dL/dt$.

2.4.2. Stage Classification of Capillary Flow Dynamics

As described above, under the action of the capillary driving force F_{Cap} , the liquid spontaneously enters the capillary tube. The liquid inside the capillary is simultaneously subjected to the viscous resistance F_{vis} , inertial forces, and its own gravitational force F_G . Capillary flow is therefore the outcome of the combined action of multiple forces, and the dominant force varies across different stages of the flow, resulting in distinct underlying mechanisms. At the instant when the capillary first contacts the liquid reservoir, only a very small amount of liquid enters the tube. At this moment, both the viscous resistance F_{vis} and the gravitational force F_G are negligible. The capillary driving force F_{Cap} and the inertial force of the liquid dominate the flow behavior. According to Equation 2.34, the relationship between the capillary rise height L and time t is given by Equation 2.35, known as the Quéré model (Quéré, 1997). The stage

in which the capillary flow is dominated by F_{Cap} and the inertial force is referred to as the inertial regime of capillary flow.

$$L = \sqrt{\frac{2\gamma_{LV}\cos\theta}{\rho W/2}} t \quad \text{Equation 2.35}$$

As the capillary flow progresses, in addition to the capillary driving force F_{Cap} and the inertial force of the liquid, the viscous resistance F_{Vis} can no longer be neglected. Under these conditions, the relationship between the capillary rise height L and time t can be obtained from Equation 2.34, leading to 2.36, known as the Bosanquet model (Bosanquet, 1923). This stage corresponds to the inertial–viscous regime, in which both inertia and viscosity jointly govern the capillary flow.

$$L^2 = \frac{2b}{a} \left[t - \frac{1}{a^2} (1 - e^{-at}) \right] \quad \text{Equation 2.36}$$

$$\text{Where } a = \frac{8\mu}{\rho(W/2)^2}, \quad b = \frac{2\gamma_{LV}\cos\theta}{\rho(W/2)}.$$

As the capillary rise height L continues to increase, the influence of liquid inertia gradually diminishes. When the gravitational force F_G of the liquid column is still relatively small, the capillary flow becomes dominated by the viscous resistance F_{Vis} and the capillary driving force F_{Cap} . Under these conditions, the relationship between the capillary rise height L and time t can be derived from Equation 2.34, yielding Equation 2.37, which corresponds to the classical Lucas–Washburn model (Washburn, 1921). This stage is referred to as the viscous regime of capillary flow.

$$L = \sqrt{\frac{\gamma_{LV}\cos\theta W t}{2\mu}} \quad \text{Equation 2.37}$$

As the capillary flow further progresses and the rise height L continues to increase, the gravitational force of the liquid column F_G can no longer be neglected.

At this stage, the capillary driving force F_{Cap} , the viscous resistance F_{Vis} , and the

gravitational force F_G jointly govern the capillary flow. This regime is therefore referred to as the viscous–gravitational regime.

Washburn (1921) and Fries and Dreyer (2008) respectively provided an implicit and an explicit solution for the relationship between the capillary rise height L and time t in this regime, as given in Equations 2.38 and 2.39. Due to mathematical complexity, no analytical solution has been obtained thus far that simultaneously accounts for the capillary driving force F_{Cap} , viscous resistance F_{Vis} , inertial force, and gravitational force F_G .

$$t(L) = -\frac{L}{\beta} - \frac{\alpha}{\beta^2} \ln \left(1 - \frac{\beta L}{\alpha} \right) \quad \text{Equation 2.38}$$

$$L(t) = \frac{\alpha}{\beta} \left[1 + W_L(-e^{-\beta t/\alpha - 1}) \right] \quad \text{Equation 2.39}$$

Where $\alpha = \frac{\gamma_{LV} \cos \theta (W/2)}{4\mu}$, $\beta = \frac{\rho g (W/2)^2}{8\mu}$, and $W_L(z)$ is the Lambert W function, with $z = W_L(z) e^{W_L(z)}$.

When the capillary tube is placed horizontally, the effect of the liquid's gravitational force can be neglected. In this case, the horizontal capillary flow process consists of two stages: an inertial–viscous combined stage and a viscous-dominated stage.

2.4.3. Modifications to the Classical Lucas–Washburn Model at the Micro–Nano Scale

At the micro–nano scale, the influence of the gravitational force of the liquid column F_G can be neglected. Because the capillary radius $W/2$ is extremely small, the inertial regime is very short, and the capillary flow can typically be described by considering only the capillary driving force F_{Cap} and the viscous resistance F_{Vis} (Chu et al., 2019).

During micro/nanoscale capillary flow, the contact angle of the liquid at the capillary wall varies continuously and generally differs from the equilibrium contact angle. Therefore, the dynamic effect of the contact angle must be taken into account, as expressed in Equation 2.40 (Xiao et al., 2006).

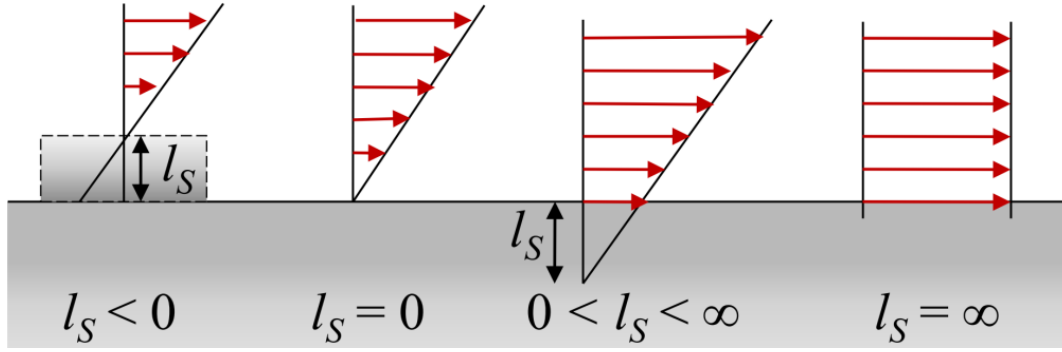


Figure 2.17 Schematic of the velocity slip boundary at the solid–liquid interface, where l_s denotes the slip length

In addition, at the micro–nano scale, the influence of solid–liquid interfacial slip on capillary flow cannot be neglected. As illustrated in Figure 2.17, the slip at the solid–liquid interface can be described using the Navier slip model, with the slip length denoted as l_s (Navier, 1823). In general, the slip length l_s varies with the solid–liquid interaction strength (or the wettability of the solid surface) (Joly, 2011; Wu et al., 2017). The Lucas–Washburn model that simultaneously incorporates both the dynamic contact angle effect and solid–liquid interfacial slip is expressed in Equation 2.41.

$$L = \sqrt{\frac{\gamma_{LV} \cos \theta_D W/2}{2\mu}} t \quad \text{Equation 2.40}$$

$$L = \sqrt{\frac{\gamma_{LV} \cos \theta_D (W/2 + l_s)^2}{2\mu W/2}} t \quad \text{Equation 2.41}$$

If the capillary channel is formed by two parallel walls separated by a distance W , Equations 2.40 and 2.41 can be rewritten as Equation 2.42 and 2.43, respectively:

$$L = \sqrt{\frac{\gamma_{LV} \cos \theta_D W}{3\mu}} t \quad \text{Equation 2.42}$$

$$L = \sqrt{\frac{\gamma_{LV} \cos \theta_D (W + 6l_s)}{3\mu}} t \quad \text{Equation 2.43}$$

3. Methodology

3.1. Molecular Dynamics Simulation Method

Molecular dynamics (MD) is a simulation method that investigates materials from the microscopic scale by solving the motions of atoms or molecules. The method is based on Newton's fundamental equations of motion; by integrating the trajectories of microscopic particles, their positional coordinates and related information can be obtained, from which macroscopic thermodynamic properties are subsequently derived. Compared with conventional experiments, molecular dynamics allows the decoupling of surface wettability and surface microstructures at the atomic scale, enabling independent manipulation of these factors. Consequently, MD has been widely applied in the study of nano/micro-scale spreading process, capillary flow and boiling heat transfer

This part introduces the basic principles of molecular dynamics simulations. It further presents the potential functions, ensembles, and thermostat methods used in this work, as well as the setup of initial and boundary conditions and the numerical solution of the equations of motion. In addition, the data analysis methods and implementation procedures required for the subsequent simulations in this study are described.

3.1.1. Fundamental Principles of the Molecular Dynamics Simulation Method

Figure 3.1 illustrates the fundamental computational procedure of a molecular dynamics simulation. Once the interatomic potential function governing the interactions among particles is specified, the initial state of the system—characterized by parameters such as t .

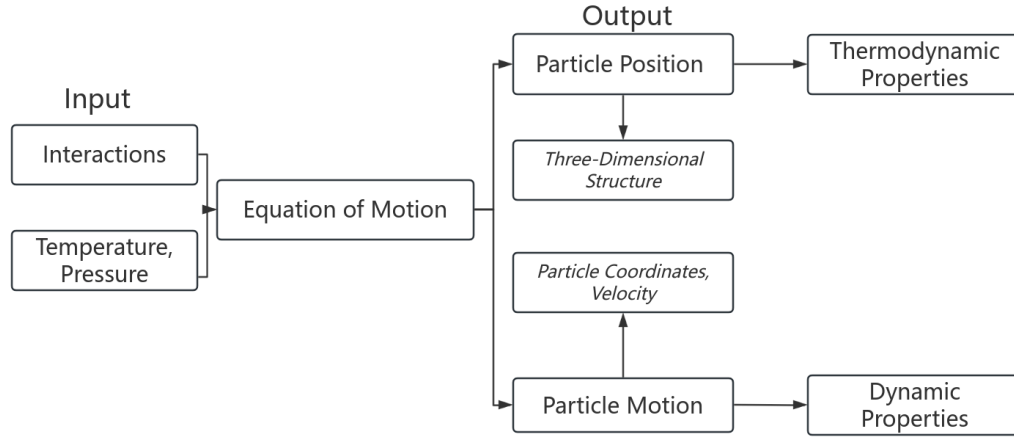


Figure 3.1 Flowchart of Molecular Dynamics simulation

3.1.2. Selection of Potential Functions

In molecular dynamics simulations, the interactions between atoms are described by potential functions, also referred to as force fields. During the simulation, atomic interactions are computed based on the selected potential function, and the resulting calculations are used to determine corresponding macroscopic physical properties. Therefore, the choice of potential function plays a critical role in ensuring the accuracy and reliability of the simulation results. In the following, brief introductions to the Lennard–Jones (LJ) potential and the embedded-atom method (EAM) potential are provided, in accordance with the specific simulation requirements of this study.

(1) Lennard-Jones Potential

The Lennard-Jones (LJ) potential has a relatively simple functional form. Based on the positional information of two atoms, it can determine the interaction between them, and the potential can roughly describe certain characteristic behaviors of simple substances, small molecular systems, and noble-gas systems. Therefore, LJ potentials have been widely used in early molecular dynamics simulations to describe related interactions. Its mathematical expression is given as:

$$E(r_{ij}) = \begin{cases} 4\varepsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right], & (r_{ij} < r_c) \\ 0, & (r_{ij} \geq r_c) \end{cases} \quad \text{Equation 3.1}$$

In this equation, ε is the depth of the potential well, σ is the characteristic distance at which the potential energy between two atoms is zero, r_{ij} represents the distance between atoms i and j , and r_c is the cutoff radius. To save computational resources, when the distance between two atoms is larger than or equal to the cutoff radius, the interaction is approximated as zero.

When multiple types of atoms are present in the simulated system, the potential parameters between different atom types are usually determined using the Lorentz–Berthelot mixing rules, expressed as:

$$\varepsilon_{12} = \sqrt{\varepsilon_1 \varepsilon_2} \quad \text{Equation 3.2}$$

$$\sigma_{12} = \frac{\sigma_1 + \sigma_2}{2} \quad \text{Equation 3.3}$$

When adjustment of the interaction strength between atoms is required—for example, to achieve controllable solid–liquid interaction strength and thus regulate the wetting performance at the wall–fluid interface—the Lennard-Berthelot mixing rules are often modified by introducing an energy-scaling factor:

$$\varepsilon_{sl} = \alpha \sqrt{\varepsilon_s \varepsilon_l} \quad \text{Equation 3.4}$$

Here, α is the energy-scaling coefficient. By adjusting the value of α , the solid–liquid interaction strength can be modified, allowing control of the surface wetting characteristics.

(2) Embedded Atom Method (EAM)

The Embedded Atom Method (EAM) is a type of many-body potential that can more accurately describe the interactions between metal atoms. Its mathematical expression is given by:

$$E = \sum_i F_i(\rho_i) + \frac{1}{2} \sum_{j \neq i} \phi_{ij}(r_{ij}) \quad \text{Equation 3.5}$$

In this equation, $F_i(\rho_i)$ represents the embedding energy of atom i in the electron cloud, ϕ_{ij} denotes the pairwise potential between atoms i and j , and r_{ij} is the distance between atoms i and j . ρ_i represents the local electron density at the position of atom i contributed by the surrounding atoms (excluding atom i itself). Its mathematical form is:

$$\rho_i = \sum_j f_j(r_{ij}) \quad \text{Equation 3.6}$$

Here, $f_j(r_{ij})$ is the electron density contribution from the valence electrons of atom j at the position of atom i , and r_{ij} is the distance between the two atoms.

Based on the formulation of the EAM potential, extensive studies have developed various EAM parameter sets for different metals, such as the parameter set for pure Cu atoms and the EAM potential for Fe–Cu–Ni alloys. In this work, the EAM potential for pure Cu is used to describe the interactions between metal atoms within the copper substrate.

3.1.3. Ensemble Principle

(1) Canonical Ensemble (NVT)

In the canonical ensemble, the number of particles N , the system volume V , and the temperature T all remain constant. In the simulation process of this work, the NVT ensemble is used during the relaxation stage after the model is constructed in order to control the system temperature and ensure that the simulation domain reaches a quasi-steady equilibrium state at the preset temperature. Therefore, during the relaxation stage,

the NVT ensemble is applied to control the temperature of both the liquid Ar atoms and the Cu solid wall.

(2) Microcanonical Ensemble (NVE)

In the microcanonical ensemble, the number of particles N , the system volume V , and the total energy E remain constant. Under these conditions, there is no exchange of matter or energy between the system and the external environment. Although the total energy is conserved, the kinetic and potential energies are not individually conserved and can transform into each other.

In this study, once the system reaches a quasi-stable equilibrium state after relaxation, the NVE ensemble is subsequently applied to regulate the temperature of the fixed solid wall.

3.1.4. Temperature Control Methods

During the molecular dynamics simulations in this study, it is necessary to control the temperatures of both the solid wall and the working fluid in real time during the relaxation stage after model construction, ensuring that they remain within the preset temperature range. The temperature control methods employed in this work—namely the Nose–Hoover thermostat and the Langevin thermostat—are introduced below.

(1) The Nose–Hoover thermostat

The Nose–Hoover thermostat couples the real simulated system with an adequately large heat bath system, forming an extended ensemble. The Hamiltonian of this extended ensemble is given by:

$$H = \sum_{i=1}^N \frac{p_{wi}^2}{2m_i s} + E_{pe} + \frac{p_s^2}{2Q} + g k_B T_0 \ln s \quad \text{Equation 3.7}$$

This expression consists of four parts: the first two terms represent the kinetic and potential energies of all particles in the extended system, while the last two terms represent the kinetic and potential energies of the heat bath. Here, p_{wi} denotes the momentum of particle i in the extended system, m_i is the mass of particle i , s is a

scaling variable that couples the real system to the heat bath, E_{pe} is the potential energy of all particles in the extended system, p_s is the momentum corresponding to s , Q is the “mass” of the variable s , g is the number of degrees of freedom, k_B is the Boltzmann constant (1.38×10^{-23} J/K), and T_0 is the target temperature preset for the simulation.

The relationship between the variables of the real system and those of the extended ensemble is given by:

$$\tilde{p}_i = \frac{1}{s} p_{wi}, \quad \tilde{q}_i = q_{wi}, \quad dt = s dt_w \quad \text{Equation 3.8}$$

where $\tilde{p}_i$, $\tilde{q}_i$, and dt represent the momentum, position coordinates, and time of the real system, respectively. Thus, the equations of motion of the real system become:

$$\dot{\tilde{q}}_i = \frac{\tilde{p}_i}{m} \quad \text{Equation 3.9}$$

$$\dot{\tilde{p}}_i = -\frac{\partial E_{pe}}{\partial \tilde{q}_i} - \eta \tilde{p}_i \quad \text{Equation 3.10}$$

$$\eta = \tau^2 \frac{T(t) - T_0}{T_0} \quad \text{Equation 3.11}$$

$$\tau = \sqrt{\frac{g k_B T_0}{Q}} \quad \text{Equation 3.12}$$

Here, η is the friction coefficient of the thermostat, used to adjust system temperature via feedback control during computation; τ is the relaxation time that governs the rate at which the temperature approaches the target value; and $T(t)$ is the instantaneous system temperature at time t .

The Nose–Hoover thermostat is one of the most commonly used temperature control methods in molecular dynamics simulations. It is typically paired with the NVT ensemble for simulations near equilibrium to maintain the system temperature.

(2) Langevin Thermostat

The Langevin thermostat regulates the system temperature by modifying Newton's equations of motion. Its mathematical formulation is given by:

$$m_i \frac{\partial \vec{v}_i}{\partial t} = \vec{F}_i(t) + \vec{\eta}_i(t) - \gamma_i \vec{v}_i \quad \text{Equation 3.13}$$

where $\vec{\eta}_i(t)$ denotes the random force, and $\gamma_i \vec{v}_i$ represents the viscous damping force, with γ_i being the damping coefficient.

Although the Langevin thermostat can yield the particle velocity at the next time step, the corresponding particle positions are not updated simultaneously by the random force. As a result, the Langevin thermostat alone cannot achieve temperature control. Therefore, the Langevin thermostat must be used in combination with the NVE ensemble to regulate system temperature. In this study, after the relaxation stage of model initialization, the NVE ensemble is applied to the fluid atoms in the interaction region, while the solid metal wall atoms are thermostatted using the Langevin method to maintain the desired temperature.

3.1.5. Selection of Initial and Boundary Conditions

(1) Initial Conditions

Before starting the simulation, it is necessary to assign initial positions and velocities to all particles in the simulated system. After the simulation environment is fully constructed, the spatial coordinates of particles are known, so their velocities must be initialized.

The initial velocities of particles are generally assigned according to the Maxwell–Boltzmann distribution at the preset simulation temperature:

$$p(v_{ix}) = \left(\frac{m_i}{2\pi k_B T} \right)^{1/2} \exp \left[-\frac{m_i v_{ix}^2}{2k_B T} \right] \quad \text{Equation 3.14}$$

where T is the desired simulation temperature, and v_{ix} is the velocity component of particle i in the x -direction.

The velocity distribution is often obtained through Gaussian sampling:

$$p(x) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp \left[-\frac{(x - \langle x \rangle)^2}{2\sigma^2} \right] \quad \text{Equation 3.15}$$

where $\langle x \rangle$ denotes the mean value and σ is the standard deviation.

(2) Boundary Conditions

Due to the limitation of the simulation length scale in molecular dynamics, the computation can be significantly affected by finite-size effects. To address this issue, periodic boundary conditions are typically applied in simulations. These conditions ensure accuracy while controlling system size efficiently and reducing computational cost.

As illustrated in Figure 3.2, applying periodic boundary conditions means that the simulated domain is surrounded by identical mirror-image regions. When a particle reaches one side of the simulation box, a corresponding image particle simultaneously appears on the opposite side to maintain continuity. This effectively allows particles leaving the system to re-enter through the opposite boundary, preventing loss of atoms and preserving the density and number of particles.

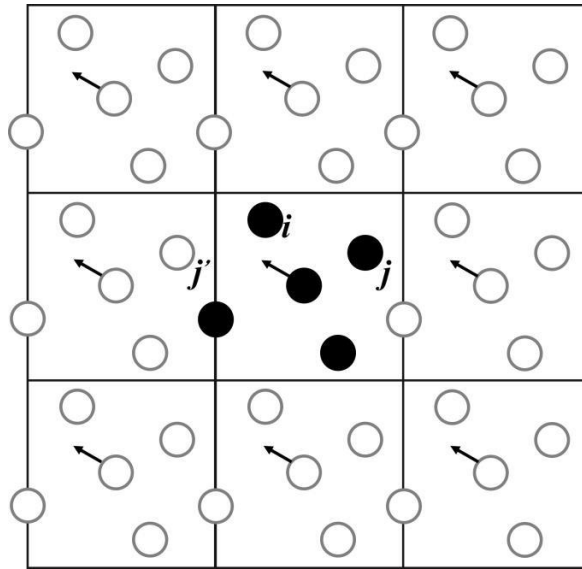


Figure 3.2 Schematic of periodic boundary condition

It should be noted that under periodic boundary conditions, a given particle iii may simultaneously interact with particle jjj in the real system and with its image particle $j'j'j'$ in the virtual replicated system. Therefore, when constructing the

simulation domain, the size of the simulation box must be greater than twice the cutoff radius to prevent a particle from interacting with both the real and the corresponding image particle at the same time. Moreover, depending on the requirements of the simulation, different boundary conditions may be applied in different spatial directions. For example, in pool-boiling simulations, non-periodic boundary conditions are typically applied in the direction perpendicular to the heated surface, while periodic boundary conditions are imposed in the directions parallel to the heated surface.

3.1.6. Equations of Motion and Numerical Solution Methods

(1) Equations of Motion

After specifying the interatomic potential function, the forces acting between particles can be obtained by taking the gradient of the potential. The mathematical expression is:

$$\vec{F}_i = -\nabla U(\vec{r}_i) = -\left(\mathbf{i} \frac{\partial}{\partial x_i} + \mathbf{j} \frac{\partial}{\partial y_i} + \mathbf{k} \frac{\partial}{\partial z_i}\right) U_i \quad \text{Equation 3.16}$$

Here, i represents the index of the atom, U is the potential function, and $\vec{r}_i$ is the position vector of atom i .

Once the force acting on each atom is obtained, the acceleration of the atom can be determined according to Newton's second law. Based on the calculated acceleration and the initial velocity, the velocity and position of each atom at the next time step can be predicted, thereby determining the atomic trajectories throughout the simulation.

$$\vec{a}_i = \frac{\vec{F}_i}{m_i} \quad \text{Equation 3.17}$$

$$\vec{v}_i(t_1) = \vec{v}_i(0) + \vec{a}_i \Delta t \quad \text{Equation 3.18}$$

$$\vec{r}_i(t_1) = \vec{r}_i(0) + \vec{v}_i(0) \Delta t + \frac{1}{2} \vec{a}_i \Delta t^2 \quad \text{Equation 3.19}$$

Here, $\vec{a}_i$ represents the acceleration of atom i , m_i is its mass, $\vec{v}_i(t_1)$ is the velocity at time t_1 , $\vec{r}_i(0)$ is the initial position, $\vec{v}_i(0)$ is the initial velocity, and Δt is the timestep.

(2) Numerical Solution Methods

Molecular dynamics relies on finite-difference numerical methods to solve particle trajectories. Common integration methods include the Verlet algorithm, Gear predictor–corrector method, Leapfrog algorithm, and the Velocity-Verlet algorithm. Among these, the Velocity-Verlet algorithm can simultaneously obtain acceleration, velocity, and position at the next timestep while maintaining high computational accuracy. Therefore, it is adopted in this study for subsequent simulation calculations. The mathematical expressions of the Velocity-Verlet algorithm are:

$$\vec{r}_i(t+\Delta t) = \vec{r}_i(t) + \vec{v}_i(t)\Delta t + \frac{1}{2}\vec{a}_i(t)\Delta t^2 \quad \text{Equation 3.20}$$

$$\vec{v}_i(t+\Delta t) = \vec{v}_i(t) + \frac{1}{2}[\vec{a}_i(t+\Delta t) + \vec{a}_i(t)]\Delta t \quad \text{Equation 3.21}$$

3.2. Calculation Methods of Relevant Physical Quantities

3.2.1. Surface Tension

At the liquid–gas interface, the cohesive attractive forces within the liquid cause the molecules located at the interface to experience an unbalanced force. This imbalance leads to a tendency for the surface layer of the liquid to contract, and the magnitude of this tendency is reflected by the surface tension (Townsend et al., 1985; Chen and Smith, 2007). According to the Young equation and the Lucas–Washburn model, surface tension plays an important role in phenomena such as droplet spreading and capillary flow. In molecular dynamics simulations, the surface tension can be calculated using the method proposed by Kirkwood and Buff (1949). Specifically, the stress components in the directions perpendicular and parallel to the liquid–gas interface are first obtained. Then, the surface tension is computed by integrating the difference between these two stress components along the direction normal to the interface.

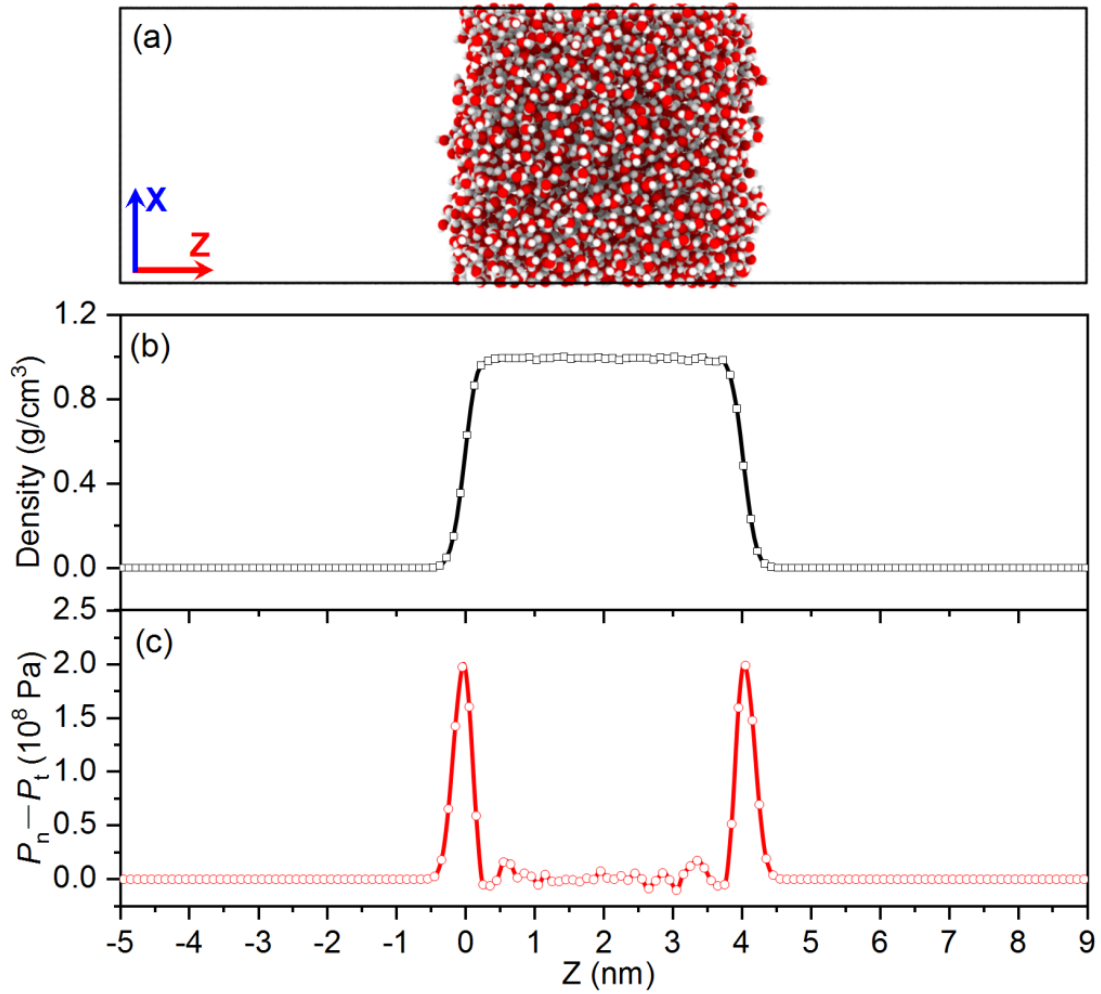


Figure 3.3 Calculation of surface tension in molecular dynamics simulations: (a) Molecular dynamics model of a liquid–gas two-phase system; (b) Liquid density distribution; (c) Distribution of the difference between normal and tangential stresses. In panel (a), the red and white spheres represent the oxygen and hydrogen atoms of water molecules, respectively.

As an example, the surface tension of bulk water at room temperature (300 K) is calculated. As shown in Figure 3.3(a), a liquid–gas two-phase simulation domain is constructed, in which water molecules are modeled using the classical SPC/E model (Chen and Smith, 2007). The Z -direction is perpendicular to the liquid–gas interface, while the X - and Y -directions are parallel to the interface. The lengths of the simulation box in the three directions are denoted as L_X , L_Y , and L_Z , respectively. Periodic boundary conditions are applied in all three directions. To ensure a sufficiently large vapor region and to avoid possible finite-size effects, the typical requirement is $L_X=L_Y$ and $L_Z>3L_X$. In the model shown in Figure 3.3a, $L_X=4$ nm and $L_Z=14$ nm, which

satisfies the condition $L_Z > 3L_X$. After the simulation system relaxes and reaches thermodynamic equilibrium, the surface tension can be calculated using Equations 2.65 – 2.67.

$$\gamma_{LV} = \frac{l}{2} \int_{-\infty}^{\infty} [P_n(z) - P_t(z)] dz \quad \text{Equation 3.22}$$

$$P_n(z) = P_{ZZ}(z) \quad \text{Equation 3.23}$$

$$P_t(z) = \frac{l}{2} [P_{XX}(z) + P_{YY}(z)] \quad \text{Equation 3.24}$$

Here, P_{XX} , P_{YY} , and P_{ZZ} represent the stress components of the simulation system in the X -, Y -, and Z -directions, respectively. Correspondingly, P_n and P_t denote the normal and tangential stress components, i.e., the stress perpendicular and parallel to the liquid–vapor interface.

In practical calculations, the simulation domain is typically divided into several slabs along the Z -direction (denoted as N_{num} slabs). In this work, the simulation domain is divided into 140 slabs, each with a thickness of 0.1 nm. The stress distribution in each slab is obtained, and the surface tension is then computed by numerically integrating Equation 3.25:

$$\gamma_{LV} = \sum_{i=1}^{N_{\text{num}}} \frac{l}{2} \frac{L_Z}{N_{\text{num}}} [P_n(z_i) - P_t(z_i)] \quad \text{Equation 3.25}$$

With SPC/E model, the surface tension calculated by this method at room temperature (300 K) is approximately 64.3 mN/m.

3.2.2. Viscosity

Viscosity is another key physical property that influences droplet spreading and capillary flow. In molecular dynamics simulations, commonly used viscosity calculation methods can be categorized into equilibrium and non-equilibrium approaches (Sunda and Venkatnathan, 2013).

The equilibrium approach is primarily the Green–Kubo method (also referred to as the pressure autocorrelation method). This method is straightforward to implement and can be used to calculate the viscosity of Newtonian fluids as well as unsheared non-

Newtonian fluids (Backer et al., 2005). However, in practical simulations, the atomic pressure tensor exhibits strong fluctuations, requiring long simulation times to obtain converged results, making the computation costly. In addition, the Green–Kubo method shows significant dependence on simulation parameters, such as system size and the chosen correlation time for evaluating the pressure autocorrelation function, both of which can affect the final viscosity value (Sunda and Venkatnathan, 2013).

Non-equilibrium methods, on the other hand, apply external forces to the system to generate a steady shear flow, from which viscosity can be determined based on velocity profiles or other physical quantities. Common non-equilibrium methods include the shear-flow method, the Muller–Plathe method, the Poiseuille flow method, and the periodic Poiseuille flow method (Muller-Plathe, 1999; Varnik and Binder, 2002; Backer et al., 2005). Among them, the periodic Poiseuille flow method, which is an improved version of the traditional Poiseuille flow approach, exhibits faster convergence, produces accurate and stable results, and shows minimal sensitivity to the simulation domain size.

Therefore, in this work, we first introduce the fundamental principles and methodology of calculating liquid viscosity using the Poiseuille flow method, and then describe how to compute viscosity using the periodic Poiseuille flow method based on this foundation.

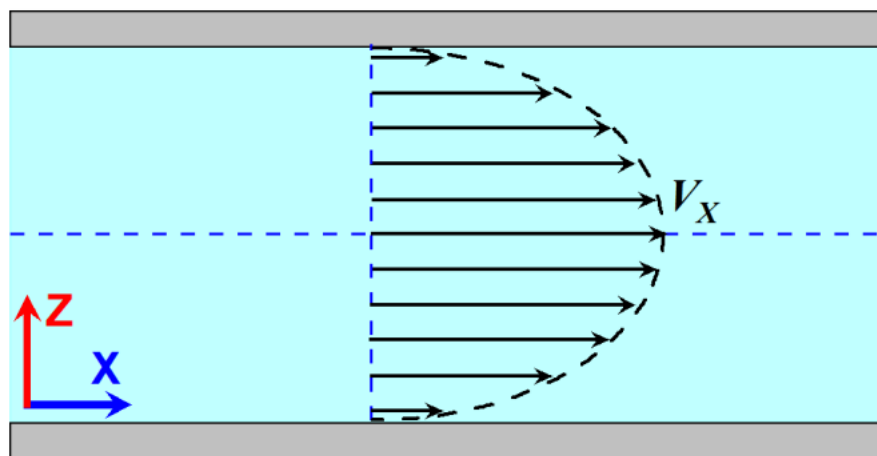


Figure 3.4 Schematic diagram of calculating fluid viscosity using the Poiseuille flow method in molecular dynamics simulations

As shown in Figure 3.4, the model used for calculating liquid viscosity with the Poiseuille flow method consists of a flow channel bounded by two parallel solid walls and filled with liquid molecules. During the simulation, a constant body force f_X is applied in the X -direction to every liquid molecule in the flow channel. After the system reaches a steady dynamic state, a stable Poiseuille flow is established within the channel, and the velocity profile of the liquid becomes parabolic.

At this point, the distribution of the X -direction velocity V_X along the Z -direction is related to the water molecule mass m , the applied body force f_X , the density ρ , and the viscosity μ , as described by Equation 3.26. Therefore, by fitting the velocity distribution in the flow channel using a quadratic function and extracting the quadratic coefficient (denoted as A), the viscosity can be calculated using Equation 3.27 (Backer et al., 2005).

$$V_X = -\frac{\rho f_X}{2\mu} (z - z_{axis})^2 + V_s \quad \text{Equation 3.26}$$

$$\mu = \frac{\rho f_X}{2mA} \quad \text{Equation 3.27}$$

Here, z_{axis} is the Z -coordinate of the axis of symmetry of the parabolic velocity profile, and V_s is the slip velocity at the solid–liquid interface. Because velocity slip may occur near the boundary, it is necessary to include V_s in the fitting function. However, when calculating viscosity using the Poiseuille flow method, the results depend not only on the intrinsic properties of the liquid but also on the interaction strength between solid and liquid atoms and the width of the flow channel. These factors can influence the final viscosity value to varying degrees (Joly, 2011; Hou et al., 2020).

Taking the calculation of the viscosity of bulk water under ambient conditions (temperature of 300 K and pressure of 1 atm, i.e., 1.01325 kPa) as an example, the basic principles and procedures of the periodic Poiseuille flow method are introduced. First, the simulation system shown in Fig. 2.12a is constructed, in which water molecules are modeled using the SPC/E model. The dimensions of the simulation box are 5 nm in the

X -, Y - and Z -directions, and periodic boundary conditions are applied in all three directions. After the system is relaxed and reaches thermodynamic equilibrium, it is divided into two subsystems along the Z -direction, as indicated by the blue dashed lines in Fig. 2.12a. As shown by the green arrows, equal-magnitude but oppositely directed body forces f_X are applied to each water molecule within the upper and lower subsystems, respectively. After the system reaches a steady state, Poiseuille flows with opposite directions are formed in the two subsystems (as illustrated in Figure 3.5(b)).

In the periodic Poiseuille flow method, the influence of solid atoms on liquid molecules does not need to be considered, and no velocity slip occurs at the boundaries between the two subsystems. Therefore, the relationship between the X -direction velocity V_X and the Z -direction coordinate within each subsystem is expressed by Equation 2.27, which depends on the molecular mass m , the applied body force f_X , the density ρ , and the viscosity μ . By fitting the velocity distribution within each subsystem using a quadratic function and extracting the quadratic coefficient (denoted as A), the viscosity can be calculated using Equation 2.28.

$$V_X = -\frac{\rho f_X}{2\mu} (z - z_{axis})^2 \quad \text{Equation 3.28}$$

Here, z_{axis} represents the Z -coordinate of the symmetry axis of the velocity distribution curve within the subsystem, ρ is the simulated liquid density (approximately 1 g/cm^3), and m is the mass of a single water molecule. Using the SPC/E model, the viscosity of water at ambient conditions is calculated to be approximately $0.792 \text{ mPa}\cdot\text{s}$.

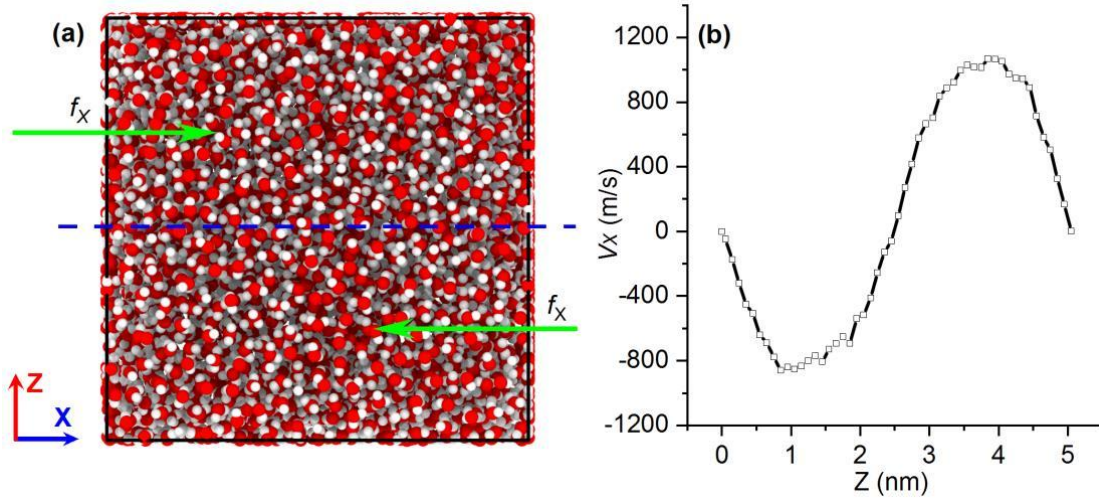


Figure 3.5 Viscosity calculation of a fluid using the periodic Poiseuille flow method in molecular dynamics simulations: (a) Molecular dynamics model used for the calculation; (b) Velocity distribution of water molecules in the X-direction as a function of the Z-coordinate.

3.2.3. Contact Angle

The contact angle θ is defined as the angle formed at the three-phase contact line where the liquid–gas interface meets the solid–liquid interface. Its value typically ranges from 0° to 180° . In this work, the contact angles involved include the equilibrium contact angle θ_E and the dynamic contact angle θ_D . The equilibrium contact angle θ_E characterizes the wettability of a liquid on a solid surface. A smaller θ_E indicates stronger surface wettability, meaning the liquid more readily wets the solid surface. The dynamic contact angle θ_D , on the other hand, plays a crucial role in quantitatively describing droplet spreading and capillary flow processes. In this study, the contact angle is calculated using the sessile drop method (Kumar and Prabhu, 2007).

As shown in Figure 3.6a, a liquid droplet is placed on the solid surface. During the simulation, a small number of molecules may evaporate from the droplet surface. Typically, the liquid–gas interface is defined as the isosurface whose density equals half of the bulk liquid density (Zhang et al., 2015). Once the system reaches a dynamic equilibrium state, the liquid–gas interface (the red dashed region in Figure 3.6b is fitted with a circular arc according to Equations 3.29 – 3.30 to obtain the contact angle. To obtain a statistically meaningful equilibrium contact angle θ_E , the density distribution

data at multiple time instants during the dynamic equilibrium period must be averaged. This method can be used not only to calculate the equilibrium contact angle θ_E , but also to determine the dynamic contact angle θ_D during the droplet spreading process. However, when calculating the dynamic contact angle θ_D , only density data over a short time interval—within which θ_D is assumed to vary only slightly—should be averaged. This allows the temporal evolution of the dynamic contact angle $\theta_D(t)$ to be obtained.

$$(x-a_{cir})^2+(z-b_{cir})^2=R_{cir}^2 \quad \text{Equation 3.29}$$

$$\theta=\arccos\left(\frac{z_a-b_{cir}}{R_{cir}}\right) \quad \text{Equation 3.30}$$

Here, R_{cir} is the radius of the fitted circle, while a_{cir} and b_{cir} denote the coordinates of the circle center in the X - and Z -directions, respectively. To avoid the influence of density fluctuations near the solid surface on circle fitting accuracy, the fitting point z_a is chosen at least 0.5 nm above the solid surface. Therefore, z_a represents the coordinate in the Z -direction located 0.5 nm above the solid surface.

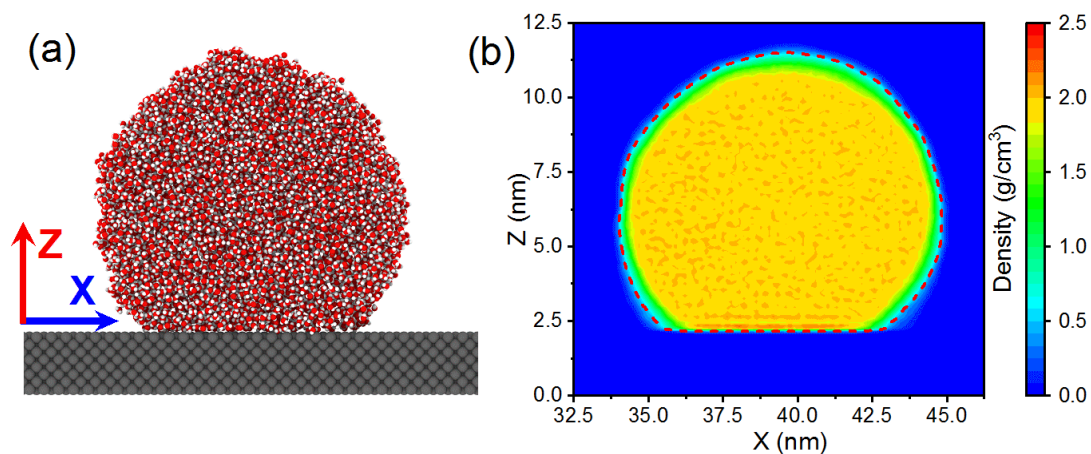


Figure 3.6 Determination of the contact angle using the sessile drop method in molecular dynamics simulations: (a) Molecular dynamics model; (b) Density distribution of the liquid droplet, where the red dashed line represents the liquid–gas interface, defined as the isosurface with a density equal to half of the bulk liquid density.

Similarly, during the capillary flow process, the liquid forms a meniscus after entering the capillary channel. By fitting the liquid–gas interface of the meniscus with

a circular arc, the dynamic contact angle at different moments during capillary flow can be obtained.

3.2.4. Temperature

Temperature reflects the intensity of the thermal motion of particles and is a very important physical parameter. In molecular dynamics simulations, the kinetic energy of the system is closely related to the velocities of the particles within the system and to the macroscopic temperature of the system. By calculating the velocities of all particles in the simulation system, the macroscopic temperature can be obtained. The mathematical relationship is expressed as:

$$\overline{E_k} = \sum_{i=1}^N \frac{m_i |v_i|^2}{2} = \frac{(3N - N_c) k_B T}{2} \quad \text{Equation 3.31}$$

where $\overline{E_k}$ is the average kinetic energy of the system, m_i and v_i are the mass and velocity of particle i , N is the total number of particles, N_c is the number of constraints, and k_B is the Boltzmann constant.

In practical calculations, in addition to evaluating the overall temperature of the system, it is often necessary to compute the local temperature at specific positions within the simulation domain to determine the spatial distribution of the system temperature field. Therefore, the simulation region is divided into grids, and the temperature of each grid is computed as:

$$T_l = \frac{1}{N_l} \sum_{n=1}^{N_l} \frac{2}{3k_B} \sum_{d=1}^3 \frac{1}{2} m_n (v_{n,d} - V_d)^2 \quad \text{Equation 3.32}$$

In Equation 2.32, the subscript l denotes a grid in the flow direction, representing the mathematical form of a one-dimensional temperature distribution. Here, T_l and N_l refer to the temperature of the l -th grid and the total number of atoms located within that grid, respectively. m_n is the mass of atom n , $v_{n,d}$ is the velocity component of atom n in direction d , and V_d is the average velocity in direction d for atoms inside the grid. In the simulation calculations of this work, this method is used to analyze the temperature distribution of both the liquid and the solid wall

surfaces in the simulation system. This allows for detailed investigation of heat transfer characteristics during liquid–solid boiling processes.

3.2.5. Heat Flux Density

Heat flux density reflects the amount of heat transferred across an interface during the heat transfer process. In molecular dynamics simulations, the heat flux density can be calculated using the following expression (Eapen et al., 2007):

$$\vec{q} = \frac{1}{V} \left[\sum_{k=1}^{\alpha} \sum_{n=1}^{N_k} \frac{1}{2} m_n^k (v_n^k)^2 \vec{v}_n^k + \sum_{k=1}^{\alpha} \sum_{l=1}^{\beta} \sum_{n \in k} \sum_{j \in l} \left\{ U(r_{ij}^{kl}) \vec{v}_i^k - \frac{r_{ij}^{kl}}{r_{ij}} \frac{\partial U(r_{ij}^{kl})}{\partial r_{ij}} \vec{v}_i^k \right\} - \sum_{h=1}^{\alpha} h^k \vec{v}_i^k \right] \quad \text{Equation 3.33}$$

Here, V is the volume of the simulation domain; α and β denote the numbers of different atom types; k and l represent the labels of two atom types; N_k is the number of atoms of type k ; m_n^k and v_n^k are the mass and velocity of the n -th atom of type k , respectively; i denotes the spatial direction; U represents the pairwise potential between atoms; r_{ij}^{kl} is the distance between two atoms; and h^k denotes the average energy of atoms of type k . For steady heat flow, the last term in Equation 3.34 becomes negligible, and thus the heat flux density can be rewritten as:

$$\vec{q} = \frac{1}{V} \left[\sum_{k=1}^{\alpha} \sum_{n=1}^{N_k} \frac{1}{2} m_n^k (v_n^k)^2 \vec{v}_n^k + \sum_{k=1}^{\alpha} \sum_{l=1}^{\beta} \sum_{n \in k} \sum_{j \in l} \left(U(r_{ij}^{kl}) \vec{v}_i^k - \frac{r_{ij}^{kl}}{r_{ij}} \frac{\partial U(r_{ij}^{kl})}{\partial r_{ij}} \vec{v}_i^k \right) \right] \quad \text{Equation 3.34}$$

In this work, the above method is used to calculate the heat flux density during the solid–liquid heat transfer process.

3.2.6. Number of Evaporated Atoms

In pool boiling, the liquid near the heated wall undergoes phase change and evaporates into vapor. In macroscopic experiments, this process is typically characterized by the evaporation rate, i.e., the rate of change in the mass of the liquid phase. In molecular dynamics simulations, however, the process is described using the variation in the number of evaporated atoms. Therefore, it is necessary to introduce the method used to identify and count evaporated atoms.

At present, a commonly used method for determining whether a target atom is in the “vapor phase” is based on the number of neighboring atoms within a certain cutoff distance around that atom (Maroo et al., 2008). As illustrated in Figure 3.7, if the number of atoms located within a distance of 1.5σ from the target atom is fewer than 7, the atom is identified as a “vapor-phase atom.” By counting all vapor-phase atoms in the system, the number of evaporated atoms at a given moment can be obtained. The evaporation rate of the simulated system can then be calculated from the temporal change in this number. In this work, the above method is adopted to calculate the evaporation rate during the simulation process.

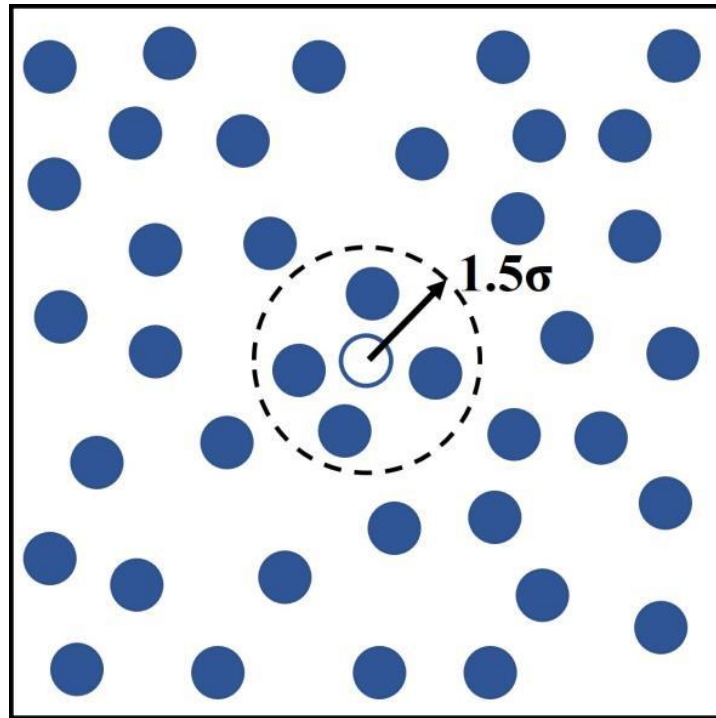


Figure 3.7 Schematic of vapor atom determination

3.2.7. Bubble Volume

In the simulation of solid–liquid boiling heat transfer, bubble growth is an inevitable phenomenon, and the variation of bubble volume during its growth is of particular importance. In molecular dynamics simulations, the bubble volume is typically determined by performing a three-dimensional grid division of the liquid phase region. For each grid, the potential energy and kinetic energy of the particles within it are calculated. If the sum of the potential and kinetic energies of the particles

in a grid is greater than zero, the grid is identified as being in the “vapor phase.” By repeating this procedure for all grids and counting the number of vapor-phase grids, the bubble volume at that specific moment can be obtained (Chen et al., 2021; Wang et al., 2023). Applying this statistical method at different time steps enables the determination of bubble volume evolution during the simulation process.

3.2.8. Onset Time of Bubble Growth

In molecular dynamics simulations, the onset time of bubble growth is typically determined based on the density variation within the liquid region. This allows the identification of the moment at which boiling initiates.

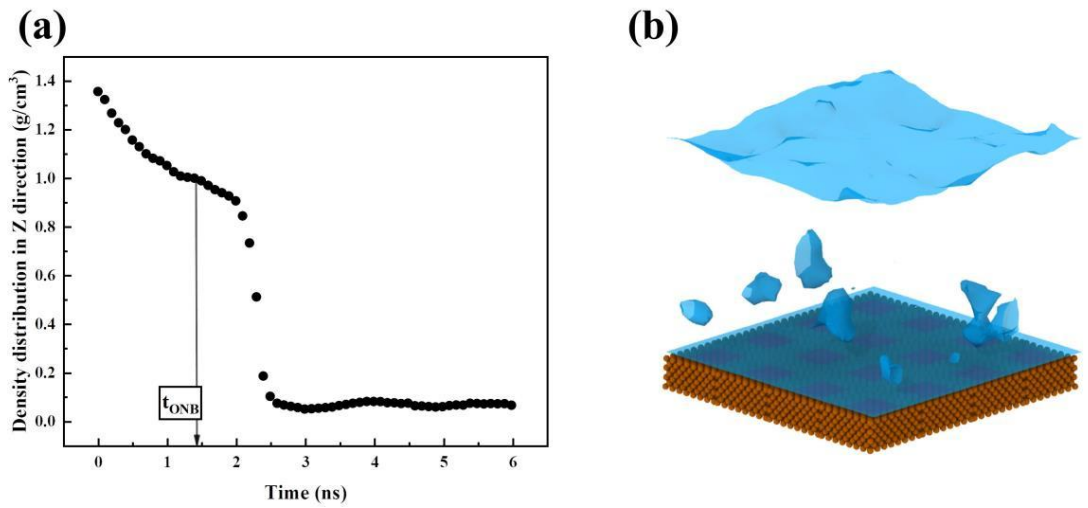


Figure 3.8 (a) Density distribution in Z direction, (b) Schematic of liquid region in t_{ONB}

As shown in Figure 3.8(a), during the initial stage of the simulation, the density of Ar in the liquid region gradually decreases following a concave-down (“ $\cap$ -shaped”) trend. At approximately 1.44 ns, the curve reaches an inflection point. After this inflection point, the density of Ar in the liquid region rapidly decreases following a convex (“U-shaped”) trend. At the moment corresponding to the inflection point, the state of the liquid region is shown in Figure 3.8 (b). At this time, a stable vapor bubble has already formed on the heated surface. Therefore, the time at which the inflection point occurs is identified as the onset time of bubble growth.

4. Mechanisms of Solid–Liquid Interactions on Surface Wettability and Droplet Spreading

Droplet spreading on solid surfaces is a phenomenon widely observed in nature as well as in industrial applications. It plays an important role in lubrication, spray coating, surface treatment, and oil and gas extraction (Vanzo et al., 2016; Hung and Shiomi, 2018). Among the many factors that influence this process, the interaction between the solid and liquid phases is crucial for regulating both surface wettability and the droplet spreading behavior.

Although extensive studies have been conducted on droplet spreading on solid surfaces (Blake and De Coninck, 2002; Yuan and Zhao, 2010; Xu et al., 2015; Wang et al., 2019), phenomena and mechanisms at the micro- and nanoscale are significantly more complex than those at the macroscale, posing considerable challenges for research. In particular, the mechanistic influence of the solid–liquid interaction strength on surface wettability and droplet spreading still requires further clarification.

In this chapter, the 12-6 Lennard–Jones (12-6 LJ) potential is employed to describe the interactions between solid atoms and liquid molecules. The 12-6 LJ potential contains two key parameters—the collision diameter (σ) and the potential well depth (ϵ). By varying the values of σ and ϵ , the strength of the solid–liquid interactions can be adjusted.

On this basis, molecular dynamics simulations are performed to investigate droplet spreading on solid surfaces under different solid–liquid interaction strengths. The results reveal the mechanisms by which the solid–liquid interaction regulates surface wettability and the droplet spreading process. Furthermore, the simulations identify the conditions for the formation of precursor films on solid surfaces and elucidate the mechanism by which these films influence droplet spreading. Finally, by combining a simplified solid–liquid interaction model with molecular dynamics

simulations, the chapter further clarifies how the interaction strength affects surface wettability and the formation of layered liquid structures near the solid surface.

4.1. Molecular Dynamics Model of Droplet Spreading on a Solid Surface

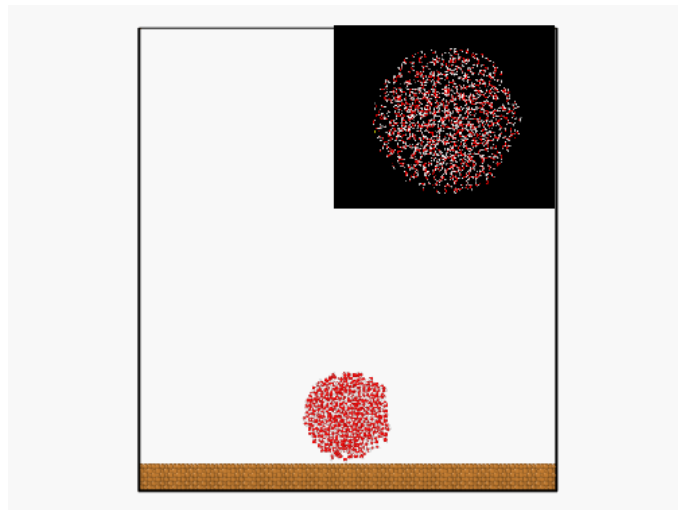


Figure 4.1 Molecular dynamics model of a droplet spreading on a solid surface, where the gray, red, and white spheres represent Cu atoms, O atoms, and H atoms, respectively.

As shown in Figure 4.1, The simulation system consists of a water droplet (diameter = 40 Å, 1000 water molecules) with a density of bulk water (≈ 1 g/cm³) and a copper (Cu) substrate with a face-centered cubic (fcc) structure. The size of the substrate is 180 Å × 180 Å × 50 Å (X × Y × Z) while the size of the simulation domain is set 180 Å × 180 Å × 200 Å (X × Y × Z). The simulation domain in the Z direction is set big enough to avoid none-physical interactions and phenomena caused by cycle simulation, which ensures that the droplet above is not affected by the substrate. Using a cylindrical droplet in the simulation is more computationally efficient than using a spherical droplet and eliminates the influence of line tension. Moreover, according to Heine et al. (2004), the spreading behavior obtained using cylindrical droplets is essentially the same as that using spherical droplets.

For simplicity, computational efficiency, and reliability, this work adopts the extended simple point charge (SPC/E) model for water. In this model, electrostatic (Coulomb) forces, van der Waals interactions, and bonded contributions—including

bond stretching and angle bending—are all taken into account, as described in Equations 4.1 – 4.4.

$$U_{Coul} = \frac{e^2}{4\pi\epsilon_0} \sum_{i \neq j} \frac{q_i q_j}{r_{ij}} \quad \text{Equation 4.1}$$

$$U_{VDW} = \sum_{i \neq j} 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad \text{Equation 4.2}$$

$$U_{bond\ stretch} = \sum_{Bonds} k_1 (l_{ij} - l_0)^2 \quad \text{Equation 4.3}$$

$$U_{angle\ bend} = \sum_{Angles} k_2 (\theta_{ijk} - \theta_0)^2 \quad \text{Equation 4.4}$$

where U_{Coul} , U_{VDW} , $U_{bond\ stretch}$, and $U_{angle\ bend}$ represent the potential energy contributed by the Coulombic (electrostatic) interactions, van der Waals interactions, bond stretch, and angle bend terms, respectively. In Equations 4.1 – 4.2, r_{ij} is the distance between two atoms, e is the charge of an electron, ϵ_0 is the dielectric permittivity of vacuum, and q_i and q_j represent the partial charges of atom i and j , respectively; symbols ϵ_{ij} (the depth of the potential well) and σ_{ij} (collision diameter) represent the 12-6 LJ potential parameters. In eq 3.3, k_1 represents a force constant, l_{ij} is the instantaneous length of the O–H bond, and l_0 is the equilibrium O–H bond length. Similarly, in eq 3.4, k_2 represents a force constant, θ_{ijk} is the instantaneous bond angle of the H–O–H angle, while θ_0 is the equilibrium H–O–H bond angle. For the SPC/E water model, the force constants k_1 and k_2 equal 554.1349 (kcal/mol $\text{\AA}^2$) and 45.7696 (kcal/mol rad^2), respectively, the equilibrium O–H bond length l_0 is 1 $\text{\AA}$, and the equilibrium H–O–H bond angle is 109.47°.

The interaction parameter σ_{O-S} can be obtained based on the arithmetic mean rule, $\sigma_{O-S} = (\sigma_O + \sigma_S)/2$, and σ_{O-S} is in the range of 2.7195–3.1708 $\text{\AA}$. ϵ_{O-S} is about 0.6748–1.1010 kcal/mol according to the geometric mean rule, $\epsilon_{O-S} = \sqrt{\epsilon_O \times \epsilon_S}$, where the subscripts O and S in σ_{O-S} and ϵ_{O-S} represent the oxygen atoms and substrate solid atoms, respectively. In this work, to find out different wetting statuses, we set a wider range for ϵ_{O-S} ($1 \times \epsilon_{O-O}$ – $10 \times \epsilon_{O-O}$ or 0.1554–1.554 kcal/mol). Given that the copper (Cu) substrate is used, we first fix σ_{O-S} equal to σ_{O-S} (2.8907 $\text{\AA}$) and tune ϵ_{O-S} to determine the influence of the depth of the potential well (ϵ_{O-S}) and then, we investigate the influence of σ_{O-S} . Tables 3.1 and 3.2 list the non bond potential parameters used in this work.

Table 4.1 Non-bond Potential Parameters of Water Molecules and Copper (Cu) Atoms

Species	Symbol	Mass(g/mol)	$q(e)$	ϵ (kcal/mol)	σ (Å)
Hydrogen	H	1.008	0.52	0	0
Oxygen	O	15.9994	-1.04	0.1554	3.1655
Copper	Cu	63.546	0	4.07	2.75

Table 4.2 12-6 LJ Potential Parameters between the Water Oxygen Atoms (O) and Solid Substrate Atoms (S)

ϵ_{O-S} ($\times \epsilon_{O-O}$)	1	2	3	4	6	8	10
ϵ_{O-S} (kcal/mol)	0.1554	0.3108	0.4662	0.6216	0.9324	1.2432	1.544
σ_{O-S} (Å)	2.8907/2.5132						

All simulations in this paper use the canonical ensemble (NVT), with the Nose-Hoover approach controlling the temperature. To get rid of the so-called border effects, all directions adopt periodic boundary conditions. As a result, the droplet can be thought of as infinitely long in the X direction, resulting in a typical two-dimensional system that has the advantage of minimizing scale effects by reducing droplet curvature and doing away with three-phase line tensions, so the contact angle is hardly impacted by the curvature-induced line tension.

All MD simulations are run using the large-scale atomic/molecular massively parallel simulator, a conventional MD algorithm (LAMMPS). The particle-particle particle-mesh method is used to calculate the long-range Coulombic forces with a 99.99% accuracy, and the LJ 12-6 and Coulomb interactions are both reduced to 10. Water molecules are held stiff by the LAMMPS-integrated SHAKE algorithm, and the solid substrate is maintained constant throughout the simulations to minimise computational costs. The velocity-Verlet algorithm integrates Newton's equations of motion every 1.0 fs.

Each simulation mainly includes the following steps:

- ① the water droplets are placed far from the substrate to ensure that there are no interactions between them, and the possible potential energy excess existing in the initial configuration is removed by performing energy minimization;
- ② the water droplets are equilibrated at the set temperature with a time step of 2 fs during 0.2ns;
- ③ the equilibrated droplets are moved near the substrate surface;
- ④ The computational domain is divided into rectangular bins with a size of $1 \times$

1 Å² (Y × Z). The desired properties in each bin are obtained by analyzing the collected information during the simulation. For each parameter specified by the collision diameter (σ_{O-S}) and depth of the potential well (ϵ_{O-S}), we perform at least three independent simulations, each starting from an independent initial state, to reduce the effect of statistical fluctuations.

4.2. Role of Solid–Liquid Interactions in the Droplet Spreading Dynamics

4.2.1. Dynamics and Phenomena of Droplet Spreading

The variation in the droplet's center-of-mass position during spreading reflects the rate of spreading and can also be used to determine whether the simulation system has reached equilibrium. As shown in Figure 4.2, during the initial stage of spreading ($t < 0.5$ ns), the droplets in all cases move rapidly downward. When the value of ϵ_{O-Cu} is relatively small, the system quickly reaches a dynamic equilibrium within 1 ns. At this point, the solid–liquid interaction is weak, resulting in noticeable fluctuations in the center-of-mass position of the droplet; moreover, the amplitude of these fluctuations decreases as the strength of the solid–liquid interaction increases.

Generally speaking, before the droplet begins to spread, the droplet must first establish contact with the substrate, that is, the water molecule reaches the substrate surface attracted by the solid atoms. The larger the ϵ_{O-S} , the stronger the solid atoms attract to the water molecules, and the faster the water molecules move down, and the shorter the time it takes to reach the substrate surface, which is shown in Figure 4.3&4.4.

Also, in the initial phase of droplet spreading, the water molecules near the substrate below the droplet are more easily attracted to the solid atoms, and thus they move down faster to the substrate surface and forming several layers of water molecules thick. At this time of the time, the shape of the droplet is not an ideal spherical crown, and the water molecular layer on the basement surface and the main droplet above it are connected by a sunken "liquid bridge", which is more obvious when the ϵ_{O-S} is large. With the spread of the droplet, the sunken "liquid bridge" gradually disappears, and the main droplet interacts with the water molecular layer on the substrate surface, and there is no obvious distinction.

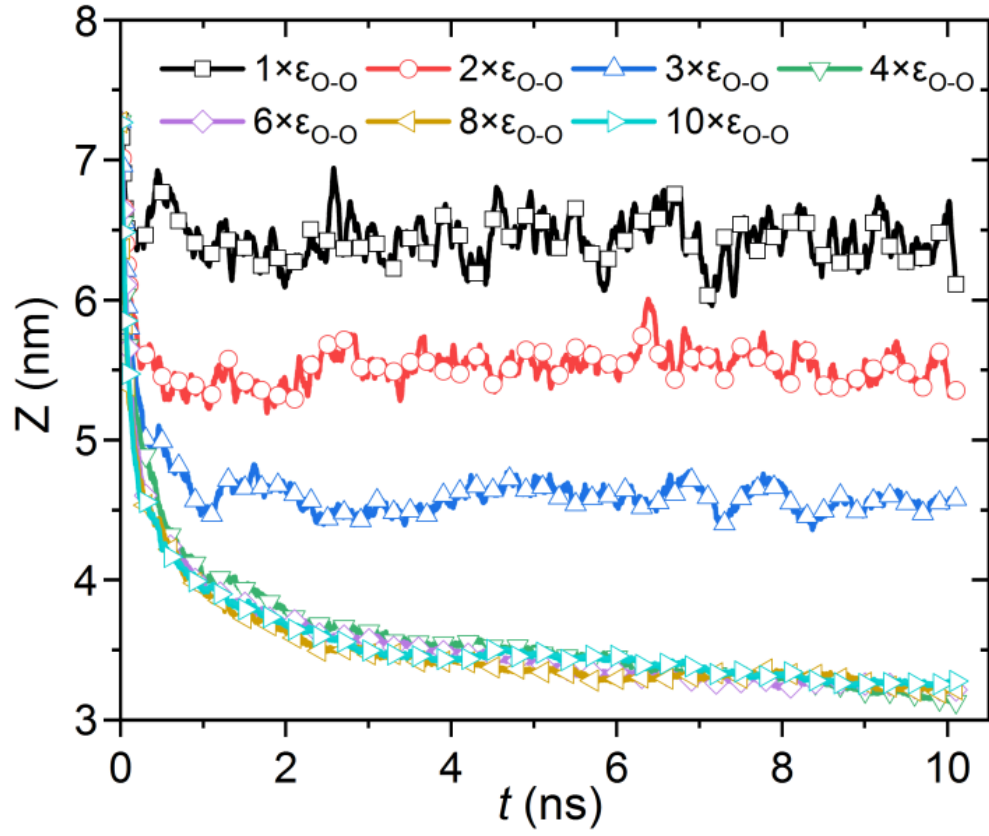


Figure 4.2 Variation of the droplet center-of-mass Z-coordinate over time for different solid-liquid interaction strengths

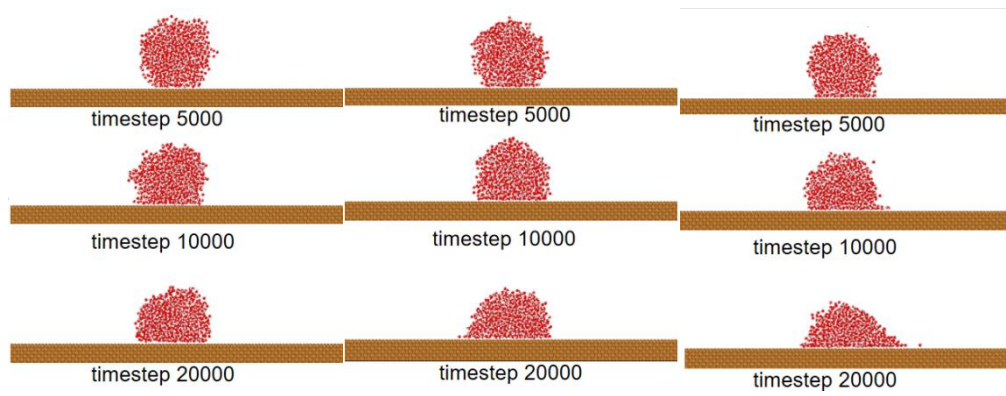


Figure 4.3 the initial spreading phenomenon, from left to right:
 $\epsilon O-S = \epsilon O-O$, $\epsilon O-S = 2 \times \epsilon O-O$, $\epsilon O-S = 3 \times \epsilon O-O$

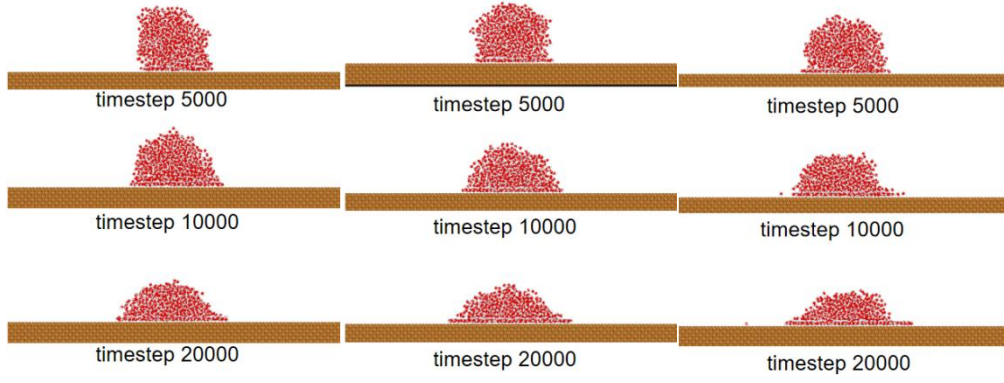


Figure 4.4 the initial spreading phenomenon, from left to right:

$$\varepsilon_{O-S}=4\times\varepsilon_{O-O}, \varepsilon_{O-S}=6\times\varepsilon_{O-O}, \varepsilon_{O-S}=8\times\varepsilon_{O-O}$$

In general, before spreading begins, the droplet must first establish contact with the substrate. This occurs when water molecules, driven by the attractive force from the solid atoms, migrate downward to the substrate surface. A larger ε_{O-Cu} corresponds to a stronger attraction between the solid atoms and the water molecules, causing the water molecules to move downward more rapidly and reducing the time required for them to reach the substrate. It should also be noted that, as illustrated in Figures. 3.3–3.4, during the initial stage of spreading, the water molecules located near the bottom of the droplet—closest to the substrate—are more readily attracted by the solid atoms. These molecules move downward more quickly, forming several molecular layers on the substrate surface. At this stage, the droplet does not exhibit an ideal spherical-cap geometry. Instead, the molecular layers on the substrate and the main droplet above them are connected by a concave “liquid bridge,” a feature that becomes more pronounced when ε_{O-Cu} is large. As spreading proceeds, this concave liquid bridge gradually disappears, and the main droplet merges seamlessly with the water layers on the substrate, eliminating any clear distinction between them.

4.2.2. Relationship Between the Equilibrium Contact Angle and Solid–Liquid Interactions

Since the temperature is not considered in this part, all simulations and data collected or shown here is under 300K while ε_{O-S} and σ_{O-S} are tuned to find out the effect of solid-liquid interactions on surface hydrophilicity.

The change in the radius of the droplet during spreading can reflect the speed of

spreading as well as the wettability of the surface. To characterize the strength of the wettability of the substrate, the spreading process is shown in figure 4 which show how radius of the droplet increases with different ϵ_{O-S} . The σ_{O-S} is fixed as $2.8907\text{\AA}$.

In the cases of low ϵ_{O-S} , the droplet tends to achieve equilibrium more easily as the increase of the radius soon becomes gentle. When ϵ_{O-S} is higher, the radius increases more quickly and the value is bigger too while the trend line of the radius is sharper than it in low ϵ_{O-S} . This is because the attraction between the substrate and water droplet grows when ϵ_{O-S} is tuned larger. As the water molecules are more easily to be captured by the substrate, the contact between the droplet and substrate is built sooner which resulted the spreading process starts sooner. Obviously, with the higher ϵ_{O-S} , the radius of water droplet firstly increases rapidly at the beginning of the simulation, then continuously increases slowly throughout the whole process until equilibrium. It shows that the copper substrate is more wetting and the droplet tends to spread on the substrate surface. Also, when ϵ_{O-S} increases, the radius of droplet over time is less affected by the value of ϵ_{O-S} because the final radii differ less among larger ϵ_{O-S} .

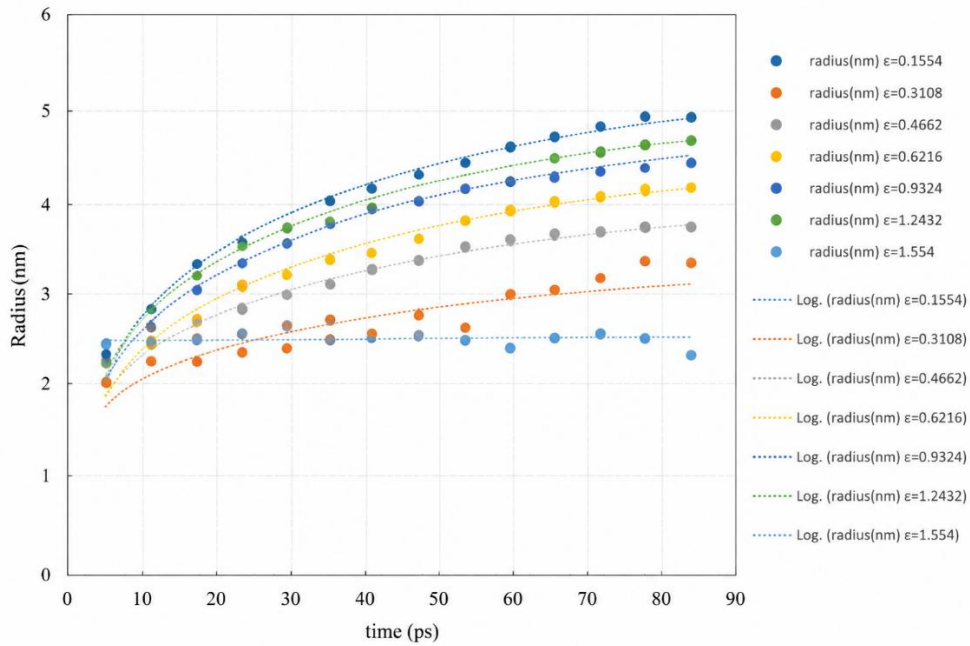


Figure 4.5 Radius increases during the simulation($\sigma_{O-S}=2.8907\text{\AA}$)

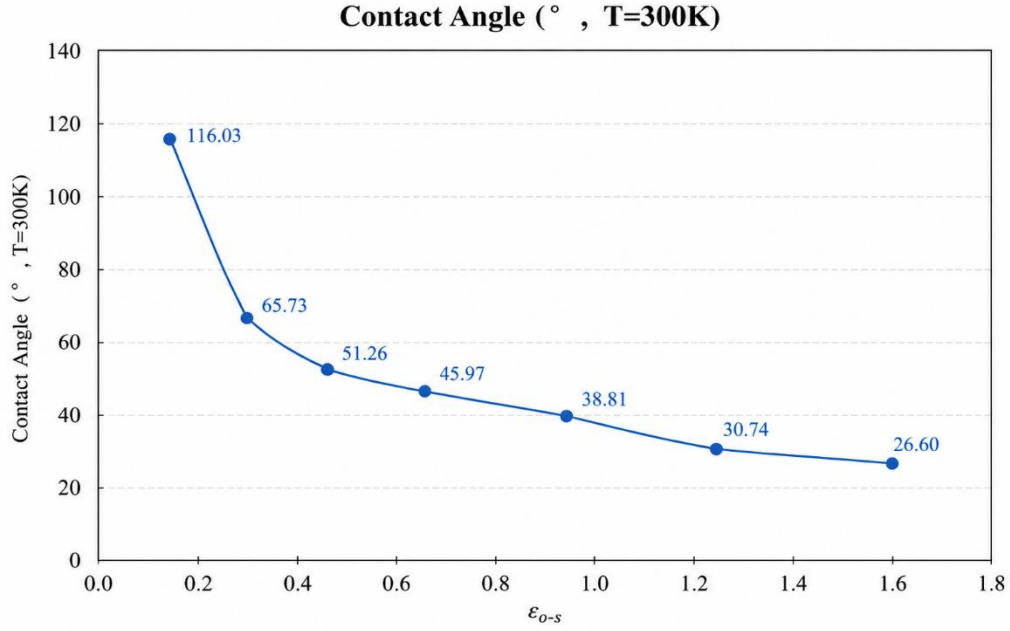


Figure 4.6 Contact angle decreases during the simulation($\sigma_{O-S}=2.8907\text{\AA}$)

In order to quantitatively characterize the strength of the wettability of the substrate, as shown in Figure 4.6, the value of the equilibrium contact angle θ_E of the droplets in different conditions was calculated after the simulated system reached the dynamic equilibrium state.

With the increase of ϵ_{O-S} , the interaction between liquid molecules and solid atoms gradually increased, and the wettability of the substrate is also significantly improved. The contact angle of the equilibrium water droplet θ_E is sharply decreased from 116° to 26° , where $\epsilon_{O-Cu} = 1 \times \epsilon_{O-O}$, $\epsilon_{O-Cu} = 10 \times \epsilon_{O-O}$ respectively. When the value of ϵ_{O-Cu} is changed from $1 \times \epsilon_{O-O}$ to $2 \times \epsilon_{O-O}$, the substrate changes from a hydrophobic state to a hydrophilic state. If ϵ_{O-Cu} continues to increase until beyond a critical value, it is possible that the droplet will become a liquid film on the base surface with a contact angle of 0° .

Meanwhile, σ_{O-Cu} is also part of solid-liquid interaction which has an influence on the wettability of the copper substrate. Figure 6 gives an insight into whether σ_{O-Cu} affects contact angles like ϵ_{O-Cu} . We can find out that larger σ_{O-Cu} makes the substrate hydrophilic. The difference between contact angles tends to be larger when ϵ_{O-Cu} are larger.

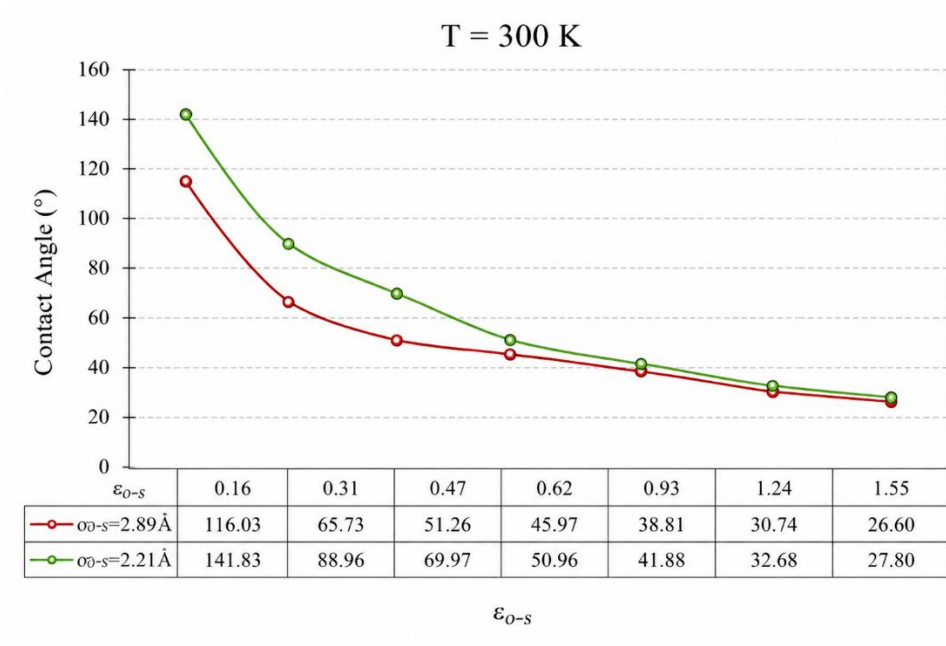


Figure 4.7 Variations of contact angles in different $\sigma O-Cu$

The solid-liquid interaction is also affected by different temperature as the force between the intrinsic dipoles of the molecule—— the orientation force is related to the temperature of the molecules.

As shown in Figure 4.8, the simulations have been down with fixed σ_{O-Cu} and tuned ϵ_{O-Cu} and temperature. The contact angles of equilibrium water droplets are 116° , 109° , 106° , 104° as temperatures are 300K, 325K, 350K and 375K($\sigma_{O-Cu}=2.8907\text{\AA}$, $\epsilon_{O-Cu} = 1 \times \epsilon_{O-O}$) respectively which means that the higher temperature benefits the hydrophilicity of the substrate. The results of other simulations of ϵ_{O-Cu} show the same trend. According to molecular kinetic theory, temperature will affect the average translational kinetic energy of molecules. Since the contact between solid and liquid is direct contact once the contact has been established, the temperature of the molecules increases, the kinetic energy increases and the momentum increases. Therefore, the interaction force increases which explains why the wettability of the base is improved with increasing temperature.

Table 4.3 shows the detailed data of the simulations ($\sigma_{O-Cu}=2.8907\text{\AA}$) .

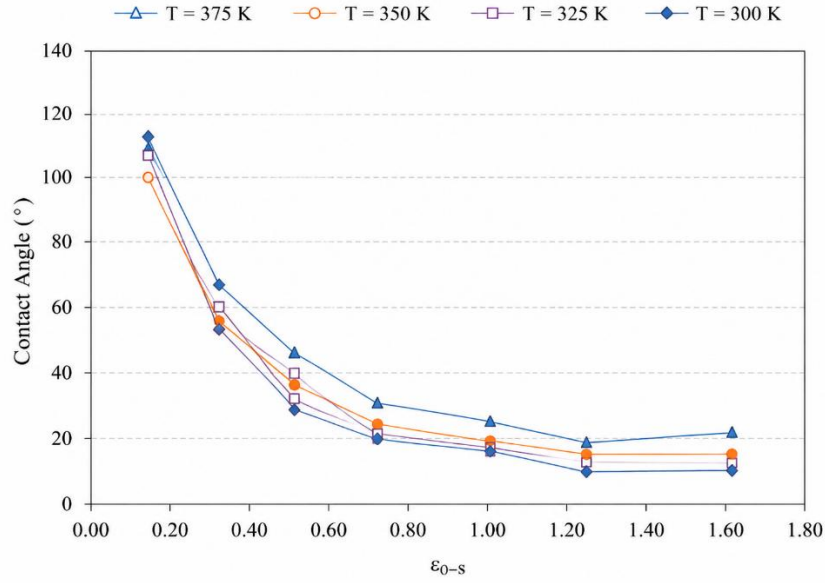


Figure 4.8 Contact angle decreases with higher temperature

Table 4.3 shows the detailed data of the simulations ($\sigma_{O-Cu}=2.8907\text{\AA}$)

ϵ_{O-Cu}	Contact Angle (°, T=375K)	Contact Angle (°, T=350K)	Contact Angle (°, T=325K)	Contact Angle (°, T=300K)
0.1554	104.56	106.88	109.00	116.03
0.3108	58.48	61.45	63.36	65.73
0.4662	34.19	37.68	42.64	51.26
0.6216	23.00	26.93	29.62	45.97
0.9324	19.41	21.12	23.20	38.81
1.2432	15.30	20.59	22.64	30.74
1.554	11.88	17.83	19.19	26.60

4.3. Control the spreading process of liquid droplet with honeycomb structure hydrophilic-hydrophobic mixed surface

With the mechanism above, in this research, we employ the honeycomb structure to create a new mixed hydrophilic and hydrophobic surface to observe how mix wettability structure with honeycomb effects the wettability of the surface and how droplets spread on these surfaces to further the insight into the enhancement of boiling heat transfer.

The simulation system consists of a cylindrical water droplet (diameter = 100 Å, length = 22 Å, 2000 water molecules) with a density of bulk water ($\approx 1 \text{ g/cm}^3$) and a copper (Cu) substrate with etched hexagonal structures (lattice constant equals 3.61 Å), as shown in Figure 4.9. Using cylindrical droplets in simulations is computationally

more efficient than using spherical droplets, and the line tension effect can be avoided. Moreover, according to Heine et al., the simulations with cylindrical droplets show the same behavior as those with spherical ones.

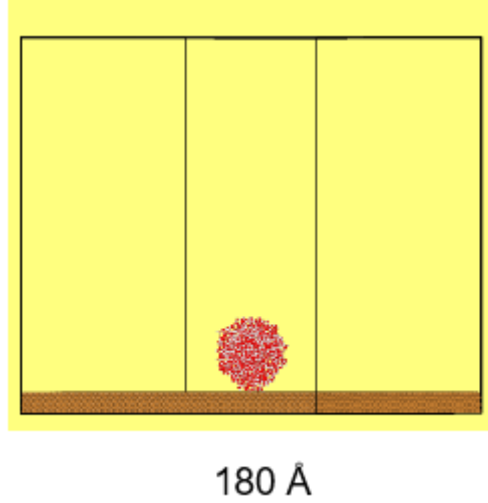


Figure 4.9 Schematic diagram of the simulation model.

The size of the substrate is $180 \text{ Å} \times 180 \text{ Å} \times 50 \text{ Å}$ ($X \times Y \times Z$) while the size of the simulation domain is set $180 \text{ Å} \times 180 \text{ Å} \times 200 \text{ Å}$ ($X \times Y \times Z$). The simulation domain in the Z direction is set big enough to avoid non-physical interactions and phenomena caused by cycle simulation, which ensures that the droplet above is not affected by the substrate.

The etched honeycomb structure is designed as shown in Figure 4.10. The hexagonal honeycomb structure has a unit size of 9 Å (angstroms), with 20 units evenly distributed along both the X and Y directions on the substrate. The etching depth of the area is 1.8 Å .

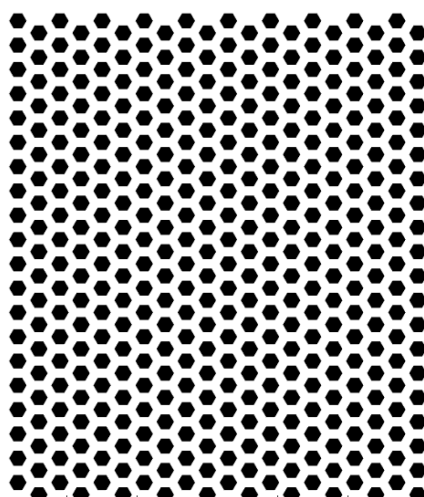


Figure 4.10 honeycomb structure in 2D (black part is etched)

Table 4.4 12-6 L-J Potential Parameters between the Water Oxygen Atoms (O) and Solid Substrate Atoms (S)

	1	2	3	4	5	6
$\epsilon_{O-S}(\text{kcal/mol})$	0.0154	0.3108	0.4662	0.9324	1.2432	1.154
$\epsilon_{O-S}(\text{kcal/mol}), \text{etched}$	0.6216	0.6216	0.6216	0.6216	0.6216	0.6216

4.3.1. The spreading process of a droplet on a honeycomb-structured etched surface

The variation in the centroid position of a droplet during the spreading process can reflect the spreading rate and serve as an indicator of whether the simulation system has reached equilibrium. In the initial stage of droplet spreading, the droplet in all cases moves rapidly downward. Since the etched area in the simulation corresponds to a hydrophobic surface, while most areas are hydrophilic, the droplet exhibits a tendency for complete spreading under strong solid-liquid interactions, forming a stable structure. However, the presence of regularly etched hydrophobic areas introduces significant fluctuations in the spreading process. Under the influence of the hydrophobic surface, the droplet's spreading becomes oscillatory, accompanied by more intense molecular motion. Additionally, variations in the degree of hydrophobicity can further affect the final wettability of the surface.

As shown in Figure 4.11, during the initial stage of droplet spreading ($t < 0.5\text{ns}$), the droplet in all cases rapidly moves downward. This effect is particularly pronounced when the smooth substrate of the surface exhibits stronger hydrophilicity, allowing the simulation system to reach a dynamic equilibrium state more quickly. Due to the contrasting wettability between the etched and smooth areas of the surface at this stage, the centroid position of the droplet exhibits noticeable fluctuations. The magnitude of these fluctuations increases with greater differences in wettability. Conversely, when the wettability of the surface areas is more similar (e.g., Case 3 and Case 4), the fluctuations in the droplet's centroid position are largely reduced.

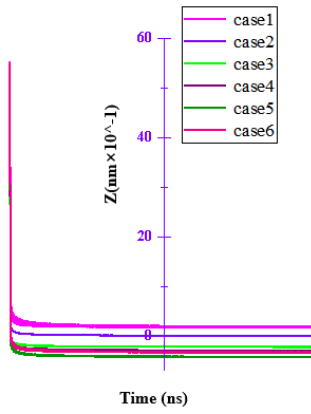


Figure 4.11 Trajectories of the droplet centroid in all cases

4.3.2. How honeycomb structure changes the wettability of the surface

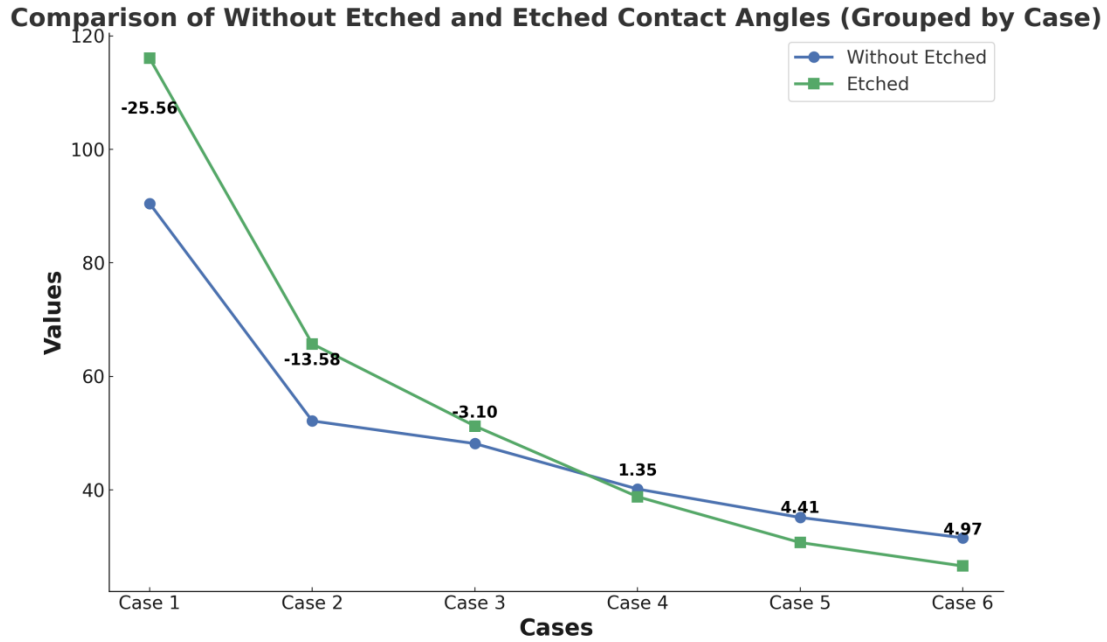


Figure 4.12 Equilibrium contact angles are changed after applying the etched honeycomb structure

As shown in Figure 4.12, increasing the hydrophilicity of the smooth area transforms the etched area from relatively more hydrophilic to relatively more hydrophobic, thereby altering the overall surface wettability. In Cases 1, 2, and 3, the equilibrium contact angle of the surface becomes smaller than that of the original, indicating an enhancement in hydrophilicity. Conversely, in Cases 4, 5, and 6, because the etched area is more hydrophobic than the original smooth surface, the equilibrium contact angle increases, leading to a reduction in overall hydrophobicity. In case1, the original equilibrium contact angle of the surface is 116° while it decreased by 25.56 to 90.4° after the honeycomb structure is etched while in case 6, the equilibrium contact angle increases from 26° to 31.51° . The simulation results are shown in Table 4.5.

Notably, according to Table 4.5, we can observe that when the wettability difference between the etched area and the smooth area is greater, the variation in the equilibrium contact angle also becomes more pronounced. Since the wettability of the etched area is quantified by an equilibrium contact angle of 45.96° , the etched surface of the honeycomb structure always lies between the wettability of the etched area and that of the smooth area.

Table 4.5 Simulation results of equilibrium contact angles

Equilibrium Contact Angle	Without Etched	Etched	Difference
90.47	116.03	90.47	-25.56
52.16	65.73	52.16	-13.58
48.16	51.26	48.16	-3.1
40.17	38.81	40.17	1.35
35.15	30.74	35.15	4.41
31.57	26.6	31.57	4.97

This finding demonstrates that etching a honeycomb structure into the surface and modifying its wettability can effectively alter the overall hydrophilicity or hydrophobicity of the substrate. Correspondingly, coating a smooth surface with a honeycomb structure made from materials possessing different wettability can also serve as an effective strategy for tuning the surface's wettability.

4.3.3. Dynamic Analysis of Droplet Spreading on a Honeycomb-Etched Surface

As shown in Figure 4.13, the time evolution of the droplet spreading radius under different conditions is presented. Overall, the final spreading radius depends on the overall wettability of the surface; the greater the wettability, the larger the final spreading radius.

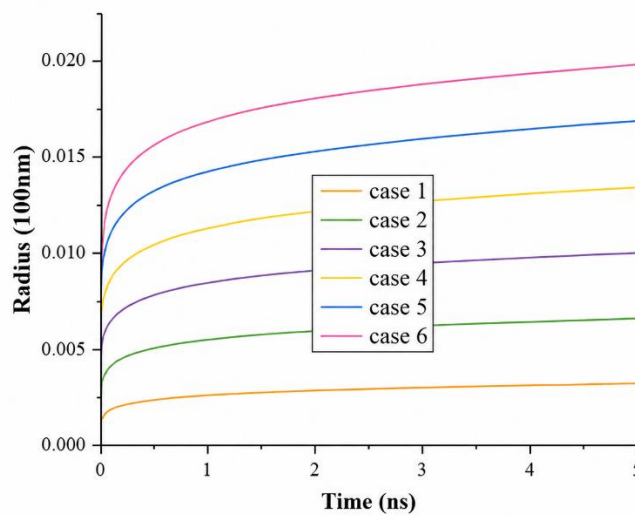


Figure 4.13 Equilibrium radius of different cases. Furthermore, examining changes in

the dynamic contact angle throughout the spreading process remains necessary to further elucidate the influence of the honeycomb structure on droplet spreading.

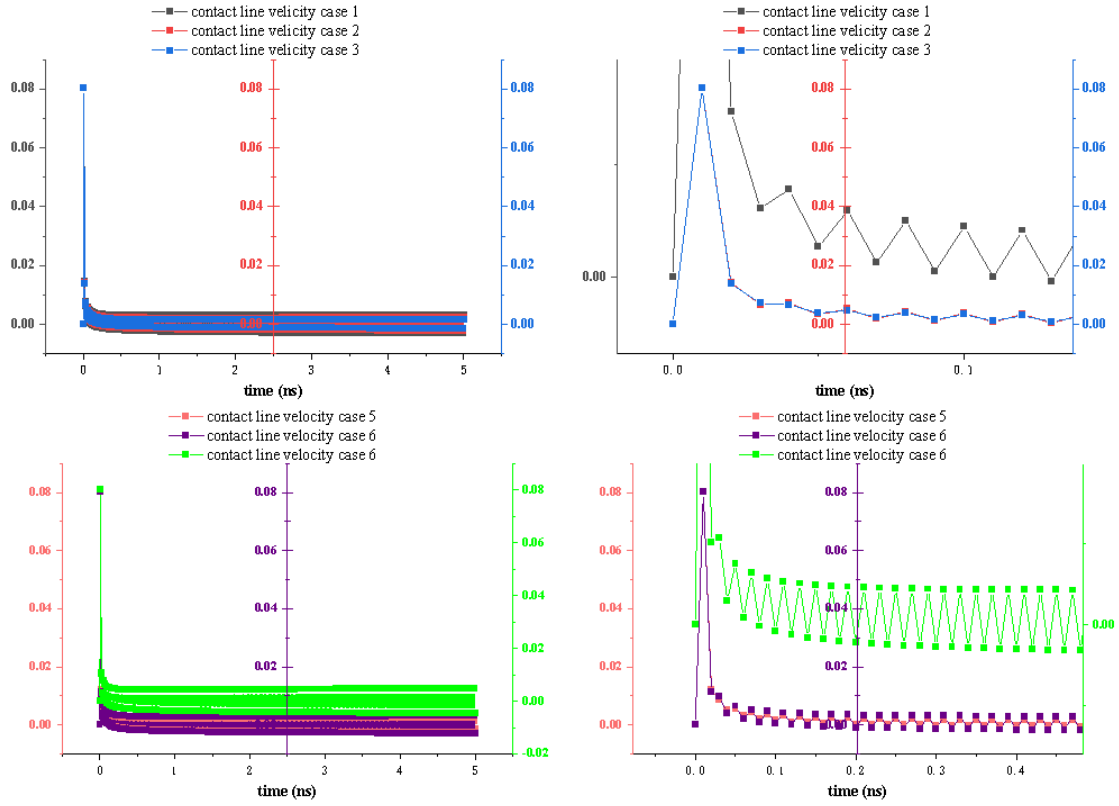


Figure 4.14 Contact line velocity of different cases

Therefore, we tracked the droplet's dynamic contact angle and contact line velocity during the spreading process. Figure 4.14 illustrates the time evolution of the dynamic three-phase contact line velocity for Cases 1 – 6. Based on these profiles, we observe that the droplet initially establishes contact with the surface very rapidly, resulting in a high contact line velocity, which then decreases sharply. According to droplet spreading theory, water molecules first need to establish contact with the surface; subsequently, under the influence of solid-liquid interactions, they spread out across the substrate. During this initial contact phase, the effect of wettability on the contact line velocity is relatively small. However, once contact is established, the droplet's further spreading behavior becomes closely linked to the substrate's wettability.

On surfaces featuring a honeycomb-etched pattern, the contact line velocity exhibits noticeable fluctuations due to the periodic honeycomb structures, in contrast

to the relatively smooth behavior on flat surfaces without etching. These fluctuations persist until the droplet reaches equilibrium and ceases to spread. Moreover, the amplitude of these fluctuations varies across different cases. In particular, Cases 1 and 6 exhibit the largest oscillations in contact line velocity, because the wettability contrast between the smooth and etched areas is most pronounced in these two cases. In the other four cases, as the wettability of the smooth and etched areas becomes increasingly similar, the magnitude of the velocity fluctuations diminishes accordingly.

Because the etched area in this simulation follows a regular honeycomb pattern, we observe that fluctuations in the contact line velocity correspond closely to the alternating etched and smooth areas. This finding demonstrates that the honeycomb structure indeed influences the motion of water molecules at the microscopic level, impeding their movement in a manner distinct from that on a smooth surface.

In this study, the influence of honeycomb-structured, mixed-wettability surfaces on droplet spreading dynamics and surface wettability modulation was comprehensively investigated through molecular dynamics simulations. The results reveal that the honeycomb structure provides a versatile platform for tailoring surface properties, enabling precise control over the spreading process and equilibrium contact angle. The etched honeycomb areas, with their periodic alternation of hydrophilic and hydrophobic areas, introduce unique oscillatory behaviors during droplet spreading, which are absent on smooth surfaces. These findings underscore the critical role of surface morphology and wettability in determining droplet dynamics at the nanoscale.

The adoption of molecular dynamics simulation allowed for the detailed analysis of atomic-level interactions, providing insights that are challenging to achieve through experimental or macroscale numerical approaches. By simulating water droplets on honeycomb-etched surfaces, the study highlights how differences in wettability between etched and smooth areas influence the spreading rate, contact line velocity, and final equilibrium state of the droplet. This work further demonstrates that honeycomb

structures can effectively modulate surface wettability, transitioning surfaces from hydrophilic to hydrophobic or vice versa, depending on the design parameters.

4.4. Conclusion

In this chapter, molecular dynamics simulations were employed to investigate the mechanisms by which solid–liquid interactions influence substrate wettability and the spreading behavior of droplets on solid surfaces. The results show that, as the solid–liquid interaction strength increases, the substrate becomes progressively more wetting. The cosine of the equilibrium contact angle, $\cos\theta_E$, increases linearly with the interaction strength, and there exists a critical value $\varepsilon_{\text{critical}}$ at which the equilibrium contact angle becomes $\theta_E=0^\circ$. When the solid–liquid interaction strength exceeds $\varepsilon_{\text{critical}}$, a precursor film forms ahead of the main droplet during spreading. Moreover, stronger solid–liquid interactions also promote the formation of layered liquid structures at the substrate surface, which is closely associated with the potential energy distribution and its evolution near the interface.

According to the scaling relation $R\sim t^\alpha$ between the spreading radius R and time t , the spreading process can be roughly divided into two stages, with a relatively large exponent α at the early wetting stage and a smaller value at the later stage. When the solid–liquid interaction is weak, the droplet rapidly reaches equilibrium. Once the interaction strength becomes sufficiently large, a precursor film develops ahead of the main droplet. Comparison with previous studies shows that the liquid type and substrate structure affect the exponent α to some extent (Isele-Holder et al., 2015; Lu et al., 2015; Lu et al., 2017). In addition, during spreading, the contact-line velocity V_{CL} exhibits a clear linear relationship with $\cos\theta_D$, which agrees with predictions from kinetic theory. This indicates that, in the simulation system used in this chapter, energy dissipation during droplet spreading is primarily governed by friction between solid atoms and liquid molecules near the three-phase contact line.

Further analysis reveals that the spreading speed of droplets does not always increase monotonically with solid–liquid interaction strength. In particular, once a precursor film

forms, excessively strong solid–liquid interactions can actually hinder further spreading and reduce spreading efficiency. This occurs for two main reasons: (i) strong solid–liquid interactions favor the formation of a stable precursor film, thereby restricting the exchange of liquid molecules between the precursor film and the rest of the droplet; and (ii) when the solid–liquid interaction becomes too strong, the solid–liquid friction coefficient increases further, solid–liquid friction becomes dominant, and the spreading speed is reduced.

In this chapter, solid–liquid interactions were described using the 12–6 Lennard–Jones (LJ) potential. The results indicate that the two key LJ parameters—the well depth ϵ_{O-S} and the collision diameter σ_{O-S} —influence substrate wettability and droplet spreading in similar ways: larger values of either parameter deepen the potential well experienced by interfacial liquid molecules, thereby enhancing wettability. However, their mechanisms differ. Increasing ϵ_{O-S} directly strengthens the interaction between each solid atom and each liquid molecule, whereas increasing σ_{O-S} does not directly enhance the interaction for a single solid atom. Instead, a larger σ_{O-S} slows the decay of the interaction with distance. Consequently, when many solid atoms are present, the collective solid–liquid interaction becomes stronger, enhancing wettability.

5. Capillary Flow and Energy Dissipation Mechanisms under Different Wettability Conditions

Capillary flow—the phenomenon in which a liquid spontaneously infiltrates narrow tubes or porous media without the aid of gravity or other external forces—is widespread in nature and has numerous practical applications, such as water uptake in plant roots, moisture storage in soils, and oil–gas recovery (Zhud et al., 2000; Prodanovic and Bryant, 2006; Li et al., 2019; Liu et al., 2019; Zhang et al., 2021). At the macroscopic scale, models such as the Lucas–Washburn model, the Quéré model, and the Bosanquet model can accurately describe capillary flow processes (Zhang et al., 2021; Cai et al., 2021).

However, capillary flow at the micro- and nanoscale is not only governed by the wettability of capillary walls and the physicochemical properties of the liquid, but is also significantly influenced by intermolecular forces (Hou et al., 2020). Moreover, the contact angle at the liquid–wall interface is not constant during nanoscale capillary flow, necessitating the consideration of dynamic contact-angle effects. Possible scale effects and solid–liquid interfacial slip must also be taken into account (Joly, 2011). In short, capillary flow at the micro- and nanoscale involves more factors and exhibits more complex mechanisms than its macroscopic counterpart.

In addition, most current studies on micro/nanoscale capillary flow focus on channels with uniform and symmetric wall wettability (Cao et al., 2016; Cai et al., 2021; Zhang et al., 2021). Capillary flow in nanochannels with asymmetric wettability and the corresponding governing mechanisms remain insufficiently understood, and therefore require further investigation.

In this chapter, a combination of theoretical analysis and molecular dynamics simulations is used to study capillary flow in nanochannels with different wettability characteristics. To ensure generality, two types of nanochannels are examined: those

with symmetric wettability and those with asymmetric wettability. First, based on energy conservation and conversion principles, the mechanisms of energy transfer and dissipation during capillary flow are analyzed. Then, considering dynamic contact-angle effects and the influence of wall-wettability asymmetry, the classical Lucas–Washburn model is modified using the Cox–Voinov law.

The results show that the modified Lucas–Washburn model can accurately describe capillary flow in various nanochannels and is in good agreement with simulation results. For nanochannels with asymmetric wettability, this chapter also focuses on how differences in wall wettability affect the capillary flow process.

5.1. Theoretical Models for Capillary Flow in Nanochannels

5.1.1. Critical condition for the onset of capillary flow

As shown in Figure 5.1, and without loss of generality, the wettability of the upper and lower walls of the nanochannel considered in this chapter can be specified independently, so that both symmetric (identical wettability on the two walls) and asymmetric (different wettability on the two walls) cases are taken into account. When liquid molecules enter the nanochannel under capillary driving, the solid–gas interface is progressively replaced by a solid–liquid interface. Assuming that the shape of the liquid–gas interface remains constant during the capillary flow process, the decrease in the system’s surface energy, ΔE_S , can be expressed by Equation 5.1. According to Young’s equation, Equation 5.1 can be further rewritten in the form of Equation 5.2.

$$\Delta E_S = [(\gamma_{SV,L} - \gamma_{SL,L}) + (\gamma_{SV,U} - \gamma_{SL,U})]YdL_B \quad \text{Equation 5.1}$$

$$E_S = \gamma_{LV}(\cos\theta_{E,L} + \cos\theta_{E,U})YdL_B \quad \text{Equation 5.2}$$

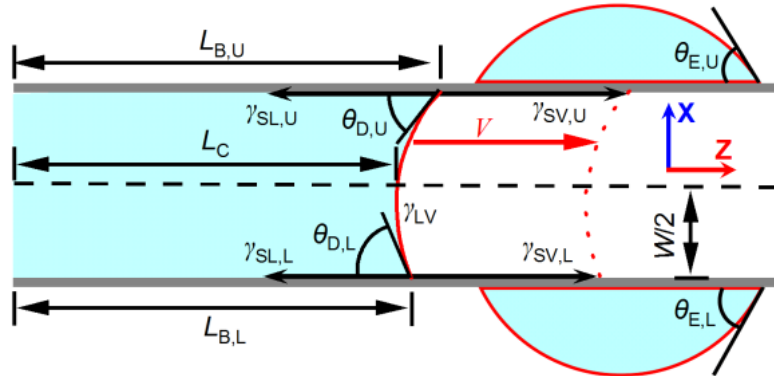


Figure 5.1 Schematic diagram of capillary flow process in a nanochannel, where the red arrows indicate the direction of capillary flow. $\theta_{D,L}$ and $\theta_{D,U}$ represent the dynamic contact angles of the liquid on the upper and lower walls of the channel, respectively.

Where γ_{SV} , γ_{SL} , and γ_{LV} are the interfacial tensions between the solid and gas phases, solid and liquid phases, and liquid and gas phases (surface tension of the liquid), respectively. Y represents the thickness of the nanochannel perpendicular to the plane, and dL_B is the increment of the capillary rise height. $\gamma_{SL,L}$ and $\gamma_{SL,U}$ are the solid-liquid interfacial tensions between the liquid and the lower and upper walls of the channel, respectively. $\gamma_{SV,L}$ and $\gamma_{SV,U}$ are the solid-gas interfacial tensions between the gas phase and the upper and lower walls of the channel, respectively. $\theta_{E,L}$ and $\theta_{E,U}$ represent the equilibrium contact angles of the liquid on the upper and lower walls of the channel, respectively.

During capillary flow, part of the decrease in the system's surface energy, ΔE_S , is converted into the kinetic energy of the liquid, while the remaining portion is dissipated. The primary pathways of energy dissipation include viscous losses within the liquid and frictional losses near the three-phase contact line (Primkulov et al., 2020). Therefore, to ensure that capillary flow proceeds, the following condition must be satisfied—that is, the decrease in surface energy ΔE_S during the capillary flow process must be positive:

$$\sum \cos \theta_E = \cos \theta_{E,L} + \cos \theta_{E,U} > 0 \quad \text{Equation 5.3}$$

where $\theta_{E,L}$ and $\theta_{E,U}$ denote the equilibrium contact angles at the lower and upper walls of the nanochannel, respectively.

A larger value of $\sum \cos \theta_E$ indicates that a greater amount of surface energy is reduced in the system during capillary flow. Because both the kinetic energy of the liquid, E_k , and the rate of energy dissipation, Φ_{dis} , are closely related to the capillary flow velocity V_B —that is, both E_k and Φ_{dis} increase as V_B increases (Primkulov et

al., 2020)—a large $\sum \cos\theta_E$ implies that the liquid enters the nanochannel at a higher velocity. Therefore, it is reasonable to assume that, regardless of whether the upper and lower walls of the nanochannel have identical wettability, the capillary flow process is governed by $\sum \cos\theta_E$.

In fact, the dynamic contact angle θ_D is not constant during capillary flow but gradually decreases toward the equilibrium contact angle θ_E . This implies a tendency for the liquid–vapor interface to expand, which corresponds to an increase in the surface energy of the liquid–vapor interface. The energy required for this increase must also be supplied by the decrease in surface energy ΔE_S .

It should be noted, however, that the variation of the dynamic contact angle θ_D is typically slow, and the liquid–vapor interface undergoes only very small changes during capillary flow. Thus, the assumption that the shape of the liquid–vapor interface remains constant is reasonable.

When the upper and lower walls of the nanochannel have different wettability, the liquid–vapor interface exhibits slight fluctuations but remains in dynamic equilibrium. Consequently, the change in the surface energy of the liquid–vapor interface oscillates around zero and can be neglected in the overall energy analysis.

5.1.2. Energy Dissipation Mechanisms During Capillary Flow

During capillary flow, the cumulative decrease in the system's surface energy E_S must be equal to the liquid kinetic energy E_k plus the dissipated energy E_{dis} , where E_k and E_{dis} are given by Equations 5.4 – 5.11. To determine the instantaneous flow velocity V_B , one may equate the rate of decrease of surface energy with the sum of the dissipation rates, as shown in Equation 5.6. If the energy dissipation associated with changes in the liquid–vapor interfacial area can be neglected, then only viscous dissipation within the liquid and frictional dissipation near the three-phase contact line need to be considered (Primkulov et al., 2020). Among these, the three-phase contact-line friction is dominated by the interactions between liquid molecules and solid atoms and is quantified via the dissipation power Φ_{CL} , computed using Equation 5.7.

Assuming that capillary flow in a nanoscale channel resembles Hagen–Poiseuille flow in a capillary tube and combining this with the Navier–Stokes equations as well as the characteristic velocity boundary layer near the wall, the viscous dissipation power Φ_{vis} can be obtained from Equation 5.8 (Johansson and Hess, 2018; Primkulov et al., 2020). The ratio between Φ_{CL} and Φ_{vis} , denoted as R_{CL} and R_{vis} , is given by Equations 5.9 - 5.10. Furthermore, integrating Φ_{CL} and Φ_{vis} over time yields the dissipated energies E_{CL} and E_{vis} during capillary flow.

$$E_S = 2\gamma_{LV} \cos \theta_E Y L_B \quad \text{Equation 5.4}$$

$$E_k = \frac{1}{2} \rho W Y L_B V_B^2 \quad \text{Equation 5.5}$$

$$\Phi_S = \frac{dE_S}{dt} = 2\gamma_{LV} \cos \theta_E Y V_B \quad \text{Equation 5.6}$$

$$\Phi_{CL} = 2\gamma_{LV} (\cos \theta_E - \cos \theta_D) Y V_B \quad \text{Equation 5.7}$$

$$\Phi_{vis} = 6\mu L_B \frac{V_B^2 W/2}{H^2} \quad R_{CL} = \frac{\Phi_{CL}}{\Phi_S} \quad \text{Equation 5.8}$$

$$R_{vis} = \frac{\Phi_{vis}}{\Phi_S} \quad \text{Equation 5.9}$$

$$E_{dis} = E_{CL} + E_{vis} \quad \text{Equation 5.10}$$

If the capillary flow process can be described using the Lucas–Washburn model incorporating the dynamic contact-angle effect, then the capillary flow velocity V_B can be obtained from Equation 5.11. Substituting Equation 5.11 into Equations 5.8 – 5.10 yields Equations 5.12 – 5.14:

$$V_B = \frac{\gamma_{LV} W \cos \theta_D}{6\mu L_B} \quad \text{Equation 5.11}$$

$$\Phi_{vis} = \frac{\gamma_{LV}^2 W Y \cos^2 \theta_D}{3\mu L_B} \quad \text{Equation 5.12}$$

$$R_{CL} = \frac{\Phi_{CL}}{\Phi_S} = \frac{\cos \theta_E - \cos \theta_D}{\cos \theta_E} \quad \text{Equation 5.13}$$

$$R_{vis} = \frac{\Phi_{vis}}{\Phi_S} = \frac{\cos \theta_D}{\cos \theta_E} \quad \text{Equation 5.14}$$

Based on Equations 5.12 - 5.14, Φ_S is approximately equal to the sum of Φ_{CL} and Φ_{vis} , i.e., $R_{CL} + R_{vis} \approx 1$, which indicates that nearly all of the reduced surface energy during capillary flow is dissipated through solid–liquid friction near the contact

line and viscous losses within the liquid. In other words, if the Lucas–Washburn model incorporating dynamic contact-angle effects is valid, then E_{CL} and E_{vis} dominate the dissipation, whereas the kinetic energy E_k can be neglected. Furthermore, previous studies have shown that the dynamic contact angle θ_D gradually decreases during capillary flow and approaches its equilibrium value θ_E . Thus, R_{vis} is expected to increase with increasing $\cos\theta_D$, while R_{CL} decreases with increasing $\cos\theta_D$. This implies that viscous dissipation progressively becomes the dominant mechanism during capillary flow.

5.1.3. Modification of the Classical Lucas–Washburn Model

When the dynamic effect of the contact angle is considered, the classical molecular kinetic theory becomes invalid if the motion of the three-phase contact line does not follow a molecular-jump mechanism. Instead, a hydrodynamic model (i.e., the Cox–Voinov law) must be adopted to describe the relationship between the capillary flow velocity V_B (or the three-phase contact-line velocity V_{CL}) and the dynamic contact angle θ_D . In this chapter, the Cox–Voinov law is therefore used to relate V_B to θ_D . Fernandez-Toledano et al. (2021) pointed out that the microscopic length scale L_{mol} in the Cox–Voinov law may vary for different liquid–solid systems and surface wettabilities. Hence, the selection of L_{max} and L_{mol} enables the description of the relationship between θ_D and V_B under different conditions.

To account for the dynamic contact-angle effect, the classical Lucas–Washburn model is modified using the Cox–Voinov law, yielding Equations 5.15 – 5.16. Since the analytical solution of the resulting differential equation is complex, numerical integration with a Euler–Raphson scheme is used for solving Equations 5.15 – 5.16, as shown in Equations 5.17 – 5.20. In the calculations, the initial condition is set as $L_B=0$, $\theta_{D,0}=90^\circ$, and the initial capillary velocity $V_{B,0}$ is obtained using Equation 5.17. Then, the capillary velocity and penetration length at the next time step, $V_{B,n+1}$ and $L_{B,n+1}$, are computed using Equations 5.18 – 4.19. The corresponding dynamic contact angle $\theta_{D,n+1}$ is calculated using Equation 5.20. Finally, the capillary velocity $V_B(t)$ at any time can be obtained by integrating Equation 5.19.

$$\frac{2\gamma_{LV}\cos\theta_D}{W} = \frac{12\mu L_B}{W^2} \frac{dL_B}{dt} \quad \text{Equation 5.15}$$

$$\cos\theta_D = \cos\left[\theta_E^3 + 9\left(\frac{dL_B}{dt}\right)\frac{\mu}{\gamma_{LV}} \ln\left(\frac{L_{max}}{L_{mol}}\right)\right]^{1/3} \quad \text{Equation 5.16}$$

$$V_{B,0} = \frac{(\theta_{D,0}^3 - \theta_E^3)\gamma_{LV}}{9\mu \ln(L_{max}/L_{mol})} \quad \text{Equation 5.17}$$

$$L_{B,n,0} = L_{B,n-1} + V_{B,n-1}\Delta t \quad \text{Equation 5.18}$$

$$L_{B,n} = L_{B,n-1} + (V_{B,n-1} + V_{B,n,0}) \frac{\Delta t}{2} \quad \text{Equation 5.19}$$

$$V_B = \frac{\gamma_{LV}W\cos\theta_D}{6\mu L_B} = \frac{[(\theta_D)^3 - (\theta_E)^3]\gamma_{LV}}{9\mu \ln(L_{max}/L_{min})} \quad \text{Equation 5.20}$$

Where Δt is an appropriately chosen integration time step.

5.1.4. Influence of Asymmetric Wall Wettability

In nanochannels with asymmetric wall wettability, the difference in surface wettability between the two channel walls leads to unequal capillary rise heights. The wall with stronger wettability exhibits a significantly greater capillary rise. When the liquid first contacts the channel entrance, liquid molecules are preferentially adsorbed onto the more wetting wall and climb upward along that wall at a faster rate. Without loss of generality, and as illustrated in Figure 5.1, we assume that the upper wall of the channel is more wetting than the lower wall, i.e., $\theta_{E,U} < \theta_{E,L}$. To ensure the occurrence of capillary flow, it is necessary that $\theta_{E,U} < 90^\circ$, meaning that the upper wall must be hydrophilic. If the lower wall is hydrophobic, i.e., $\theta_{E,L} > 90^\circ$, liquid molecules will initially climb only along the upper wall. Once the dynamic contact angle on the upper wall, $\theta_{D,U}$, decreases to a sufficiently small value, liquid molecules begin to climb along the hydrophobic lower wall. During this stage, the dynamic contact angle on the lower wall, $\theta_{D,L}$, is obtuse, such that $\theta_{D,U} < 90^\circ < \theta_{D,L}$, indicating that the hydrophobic wall hinders the progression of capillary flow. If the lower wall is also hydrophilic, i.e., $\theta_{E,U} < \theta_{E,L} < 90^\circ$, the dynamic contact angles during capillary flow satisfy $\theta_{D,U} < \theta_{D,L} < 90^\circ$, meaning that both walls facilitate capillary infiltration. Moreover, the difference in capillary rise heights between the two walls, ΔL , is expected to depend on the difference in their wettability, quantified by $\Delta\cos\theta_E$, where $\Delta L = L_{B,U} - L_{B,L}$, $\Delta\cos\theta_E = \cos\theta_{E,U} - \cos\theta_{E,L}$.

In nanochannels with asymmetric wettability, the capillary flow process is significantly more complex than that in channels with symmetric wettability, and the corresponding capillary rise heights on the two walls, $L_{B,U}$ and $L_{B,L}$, cannot be directly obtained using the classical Lucas–Washburn model. As discussed above, the stronger the wall wettability (i.e., the larger the value of $\cos\theta_E$), the higher the resulting capillary rise height. To provide a unified description of capillary flow in asymmetric nanochannels, an effective average capillary rise height, L_{ave} , is defined as $L_{ave}=(L_{B,U}+L_{B,L})/2$. An effective equilibrium contact angle θ_E^* characterizing the wettability of asymmetric nanochannels may then be introduced, as shown in Equation 4.21 (Berthier et al., 2015), by conceptually replacing the asymmetric-wettability channel with a channel whose two walls possess identical wettability. Substituting θ_E^* into the Lucas–Washburn equation as the positive cosine term yields the corresponding average capillary rise height $L_{ave}(t)$. Furthermore, the relationship between ΔL and $\Delta\cos\theta_E$ allows the individual capillary rise heights on the upper and lower walls, $L_{B,U}$ and $L_{B,L}$, to be obtained. Specifically, the capillary rise heights on the two walls can be expressed as $L_{B,U}=L_{ave}+\Delta L/2$, $L_{B,L}=L_{ave}-\Delta L/2$. The effective contact angle θ_E^* is defined by

$$\cos\theta_E^*=f_L\cos\theta_{E,L}+f_U\cos\theta_{E,U}, \quad \text{Equation 5.21}$$

Where f_L and f_U are the weighting factors associated with the lower and upper channel walls, respectively. For the nanochannel model adopted in this chapter, the values $f_L=f_U=0.5$ are used.

5.2. Molecular Dynamics Model for Capillary Flow in Nanochannels

In this chapter, molecular dynamics (MD) simulations are employed to verify the validity and accuracy of the theoretical analysis presented above. Two types of nanochannels are considered: one with symmetric wall wettability and the other with asymmetric wall wettability. Correspondingly, two sets of simulations are conducted.

In the first set, the two channel walls possess identical wettability; in the second set, the wettability of the upper wall is kept constant, while that of the lower wall is varied by adjusting the solid–liquid interaction strength.

As shown in Figure 5.2, the simulation system for capillary flow consists of a nanochannel with two parallel walls and an adjacent liquid reservoir. The nanochannel walls are composed of lead (Pb) atoms arranged in a face-centered cubic lattice with a lattice constant of 0.495 nm (Heinz et al., 2008). Each wall contains six atomic layers, of which the three inner layers are treated as Newtonian layers, while the three outer layers serve as thermostat layers. The channel length H and width W are 60 nm and 8 nm, respectively. To the left of the nanochannel is a water reservoir with a length comparable to that of the channel.

The overall dimensions of the MD model in the X, Y, and Z directions are approximately 11 nm, 3 nm, and 127 nm. The simulation system contains 17,424 wall atoms and 65,173 water molecules.

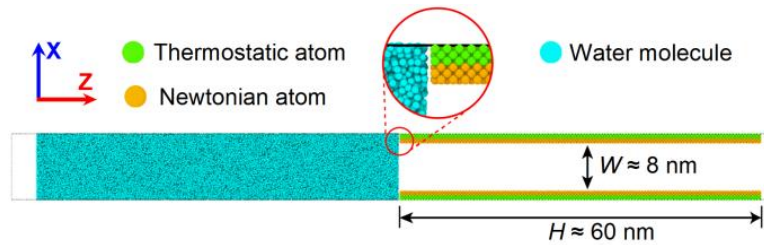


Figure 5.2 The molecular dynamics model for simulating capillary flow processes.

The liquid molecules are modeled using the mW model developed by Molinero and Moore (2009), based on the Stillinger-Weber potential function. In this model, a single particle represents a water molecule. The mW model accurately describes physical properties of water, such as density and surface tension. Despite the mW model's viscosity being relatively lower compared to experimental values and classical water models like SPC/E, SPC, TIP3, its widespread adoption in studying fluid-solid coupling issues is due to its extremely high computational efficiency, surpassing classical models by two orders of magnitude. Under conditions of pressure at one atmosphere (101.325 kPa) and room temperature (300 K), using the mW model, the calculated density (ρ) of

water is approximately 0.996 g/cm^3 . The surface tension is approximately $66 \pm 2.7 \text{ mN/m}$, and the viscosity (μ) is approximately $0.306 \pm 0.015 \text{ mPa}\cdot\text{s}$.

Because the wall atoms and water molecules used in this chapter carry no electric charge, electrostatic interactions do not need to be considered. Therefore, the non-bonded interactions between wall atoms, as well as those between wall atoms and water molecules, are described using the 12–6 Lennard-Jones (LJ) potential, as expressed in Equation 5.22. The LJ parameters for the solid atoms adopted in this chapter are $\epsilon_{\text{Pb}}=2.93 \text{ kcal/mol}$ and $\sigma_{\text{Pb}}=0.31761 \text{ nm}$ (Heinz et al., 2008).

$$U_{VDW}=4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12}-\left(\frac{\sigma_{ij}}{r_{ij}}\right)^6\right] \quad \text{Equation 5.22}$$

Here, ϵ_{ij} and σ_{ij} are the two LJ parameters, representing the well depth and the collision diameter, respectively, and r_{ij} is the distance between atoms i and j .

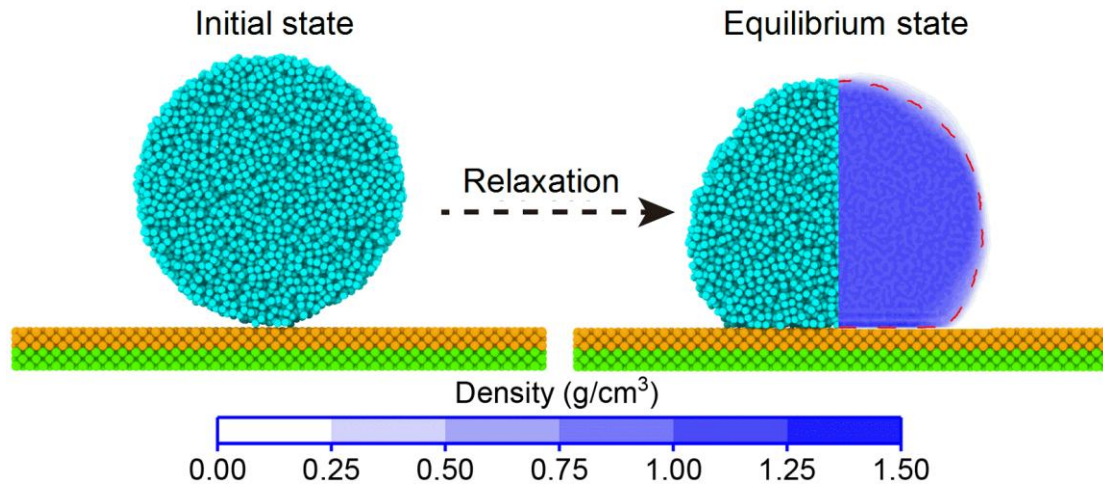


Figure 5.3 for calculating the equilibrium contact angle θ_E of a liquid droplet on the inner surface of the nanochannel wall (illustrated using the case $\epsilon_{\text{Pb}}-W=0.1554 \text{ kcal/mol}$), where the red dashed line represents the liquid–vapor interface.

To investigate the influence of nanochannel wall wettability on the capillary flow process, it is first necessary to determine how the wettability of the channel walls varies with the Lennard–Jones parameters ϵ_{ij} and σ_{ij} used for the wall–water interactions. In this chapter, $\sigma_{\text{Pb-W}}=0.31761 \text{ nm}$ is fixed, and $\epsilon_0=0.1554 \text{ kcal/mol}$ is defined as a

reference value. The interaction strength $\varepsilon_{\text{Pb-W}}$ is then varied as a multiple of ε_0 . Here, the subscripts Pb and W refer to the solid wall atoms and water molecules, respectively. Since wettability is commonly characterized by the equilibrium contact angle θ_E , the static sessile-droplet method is employed. Molecular dynamics simulations are performed to model the spreading of a cylindrical water droplet on the inner surface of the nanochannel wall, as illustrated in Figure 5.3. The droplet has a diameter of 10 nm and contains 4000 water molecules, ensuring that size effects are negligible (Andrews et al., 2016). During the simulation, a small number of water molecules evaporate from the droplet surface. The liquid–vapor interface is defined as the isodensity surface at half the bulk water density (i.e., 0.5 g/cm^3). After the system reaches dynamic equilibrium, a circular arc is fitted to the liquid–vapor interface to obtain the equilibrium contact angle θ_E . To achieve statistically reliable contact-angle values, the density fields of the droplet at different times within the final 5 ns of dynamic equilibrium are averaged. A total of 5000 density snapshots are used, with a sampling interval of 1 ps. The solid–liquid interaction strengths $\varepsilon_{\text{Pb-W}}$ used and their corresponding equilibrium contact angles θ_E are listed in Table 5.1. As shown in Figure 5.4, before $\varepsilon_{\text{Pb-W}}$ reaches the critical value $\varepsilon_{\text{critical}}$ (where $\theta_E=0^\circ$), the cosine of the equilibrium contact angle $\cos\theta_E$ increases linearly with $\varepsilon_{\text{Pb-W}}$. For the model adopted in this chapter, the critical value is approximately $\varepsilon_{\text{critical}}\approx 0.6815 \text{ kcal/mol}$. According to the analysis presented in Chapter 3, when $\varepsilon_{\text{Pb-W}}$ exceeds $\varepsilon_{\text{critical}}$, the droplet exhibits complete spreading on the solid surface, with a precursor film forming ahead of the main droplet.

Table 5.1 interaction parameters and their corresponding equilibrium contact angles

$\varepsilon_{\text{Pb-W}}$ (kcal/mol)	0.1554	0.3108	0.4351	0.4662	0.5439	0.5828	0.6216	0.6371	0.6527
θ_E (°)	135.41	105.26	82.40	76.90	56.80	43.12	35.50	30.18	27.09
$\cos\theta_E$	−0.71	−0.26	0.13	0.23	0.55	0.73	0.81	0.86	0.89

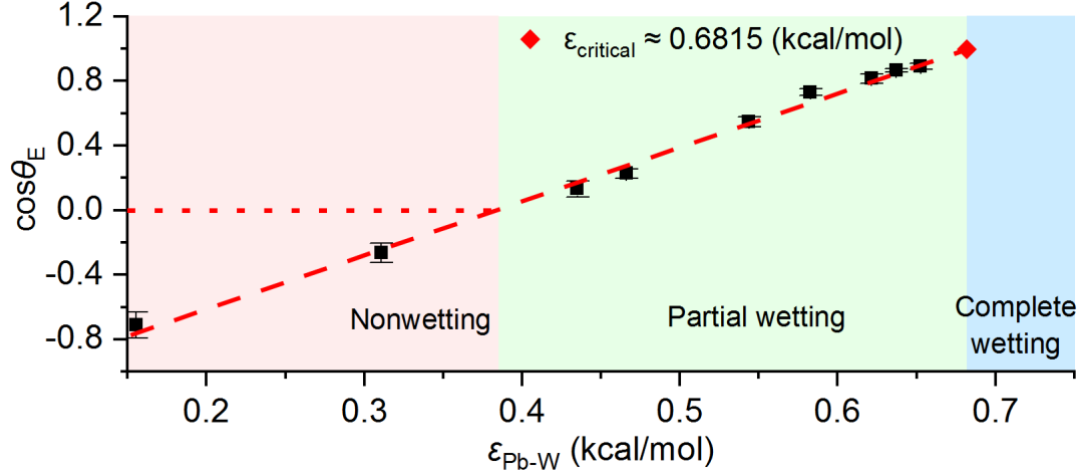


Figure 5.4 between the solid–liquid interaction parameter $\epsilon_{\text{Pb-W}}$ and the corresponding equilibrium contact angle θ_E .

After establishing the relationship between the wettability of the nanochannel walls and the parameter $\epsilon_{\text{Pb-W}}$, different wettability conditions can be simulated by varying $\epsilon_{\text{Pb-W}}$. Two sets of simulations are conducted in this chapter. In the first set, the two channel walls have identical wettability, and this wettability is varied simultaneously. In the second set, capillary flow in nanochannels with asymmetric wall wettability is examined by fixing the wettability of the upper wall and adjusting that of the lower wall.

The solid–liquid interaction parameters used in the simulations and the corresponding nanochannel wettability characteristics are summarized in Table 5.2. In the table, $\sum \cos \theta_E$ and $\Delta \cos \theta_E$ denote, respectively, the sum and the difference of the cosine values of the equilibrium contact angles on the upper and lower walls: $\sum \cos \theta_E = \cos \theta_{E,L} + \cos \theta_{E,U}$, $\Delta \cos \theta_E = \cos \theta_{E,U} - \cos \theta_{E,L}$. These two quantities represent the overall wettability of the nanochannel and the wettability difference between its two walls.

The main steps of the simulation are as follows: (1) A virtual wall is first introduced between the water reservoir and the nanochannel, and the interactions between water molecules and wall atoms are temporarily switched off. The water reservoir and the nanochannel are then relaxed separately to equilibrium under the NVT ensemble at 300 K, with temperature controlled using a Nosé–Hoover thermostat. (2) The interactions between water molecules and wall atoms are subsequently restored, and the virtual wall

introduced in step (1) is removed, allowing water molecules to enter the nanochannel. Throughout the capillary flow process, in order to prevent significant displacement of wall atoms—which would result in deformation of the channel—virtual spring constraints are applied to the solid atoms, allowing them to vibrate only near their equilibrium positions. The positions, velocities, and forces of the water molecules and the Newtonian layers of the solid walls are updated using the NVE ensemble, while the thermostat layers are maintained at 300 K under the NVT ensemble with a Nosé–Hoover thermostat. The temperature of the entire system is thus regulated by the thermostat layers. To ensure that the capillary flow process proceeds sufficiently, the total simulation time is set to 10 ns.

Table 5.2 Relevant Parameters Used in the Capillary Flow Simulations

Group	Case	Sidewall	$\epsilon_{\text{Pb-W}}$ (kcal/mol)	θ_E (°)	$\cos\theta_E$	$\sum\cos\theta_E$	$\Delta\cos\theta_E$
1	1	Lower wall	0.4662	76.90	0.23	0.45	0.00
		Upper wall	0.4662	76.90	0.23		
	2	Lower wall	0.5439	56.80	0.55	1.10	0.00
		Upper wall	0.5439	56.80	0.55		
	3	Lower wall	0.5828	43.12	0.73	1.46	0.00
		Upper wall	0.5828	43.12	0.73		
	4	Lower wall	0.6371	30.18	0.86	1.73	0.00
		Upper wall	0.6371	30.18	0.86		
2	5	Lower wall	0.1554	135.41	-0.71	0.87	1.58
		Upper wall	0.6371	30.18	0.86		
	6	Lower wall	0.3108	105.26	-0.26	0.60	1.13
		Upper wall	0.6371	30.18	0.86		
	7	Lower wall	0.4662	76.90	0.23	1.09	0.64
		Upper wall	0.6371	30.18	0.86		
	8	Lower wall	0.5439	56.80	0.55	1.41	0.32
		Upper wall	0.6371	30.18	0.86		
	9	Lower wall	0.5828	43.12	0.73	1.59	0.13
		Upper wall	0.6371	30.18	0.86		
	10	Lower wall	0.3108	105.26	-0.26	0.49	0.26
		Upper wall	0.4662	76.90	0.23		

During the simulations, periodic boundary conditions are applied in the X, Y, and

Z directions. The equations of motion are integrated using the velocity–Verlet (leapfrog) algorithm with a time step of 5 fs, and a cutoff distance of 1 nm is used for non-bonded interactions. To record the evolution of velocity, capillary rise height, and contact angle during the capillary flow process, the system configuration is output every 1 ps. Because the liquid–vapor interface evolves rapidly at the onset of capillary flow, the output interval is reduced to 0.1 ps during this initial stage. All molecular dynamics simulations in this chapter are performed using the open-source software LAMMPS (Plimpton, 1995; Thompson et al., 2022). The atomic trajectory files generated during the simulations are visualized using the open-source software OVITO (Stukowski, 2010).

As shown in Figure 5.1, to better characterize the capillary flow process, the capillary rise height L is defined as the distance from the channel entrance to the liquid–vapor interface at the meniscus. Two types of capillary rise heights are introduced: the capillary rise height along the channel wall and the capillary rise height at the channel center.

5.3. Capillary Flow in Nanochannels with Symmetric Wall Wettability

5.3.1. Capillary Flow Process and Phenomena

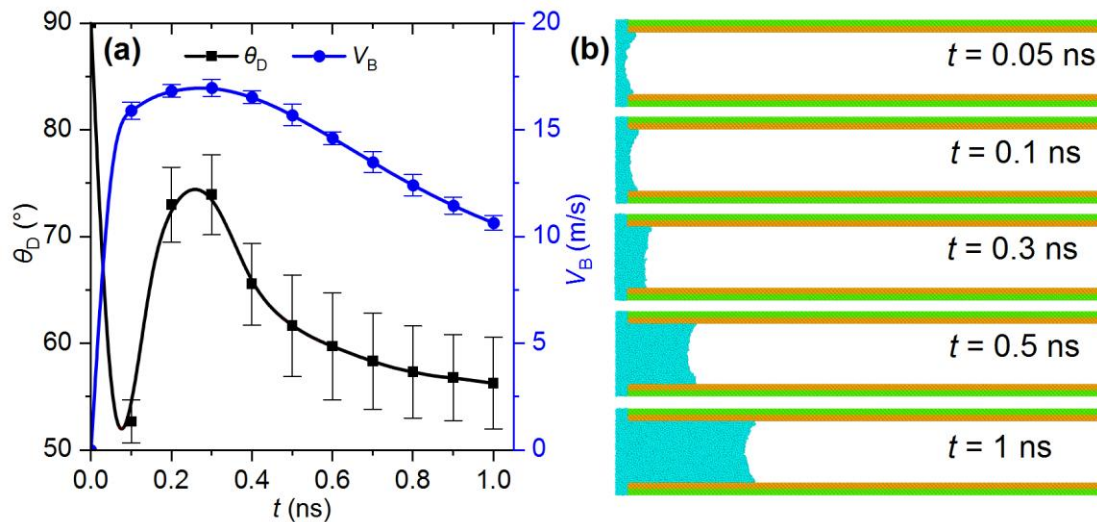


Figure 5.5 Capillary flow velocity V_B and dynamic contact angle θ_D at different times for Case 4 when $t < 1$ ns; (b) configurations of the simulation system at different times for Case 4 when $t < 1$ ns.

As shown in Figure 5.5, we first examine the initial stage of the capillary flow process, namely the *meniscus formation stage* (Kornev and Neimark, 2001; Wolf et al., 2010). Initially, the liquid surface is approximately planar, and there is no relative motion between the liquid and the channel. Once the liquid approaches the channel entrance, capillary flow begins: liquid molecules accelerate under the influence of the solid atoms and enter the channel. A characteristic feature of the meniscus formation stage is the non-monotonic evolution of the dynamic contact angle θ_D . At the onset of capillary flow, water molecules near the channel entrance and close to the walls climb upward along the wall. The shape of the liquid–vapor interface therefore changes from a flat surface to a curved meniscus, causing a rapid decrease in θ_D . Subsequently, water molecules located farther from the channel walls are driven into the channel by those near the walls. As a result, the difference between the capillary rise height along the walls, L_B , and that at the channel center, L_C , begins to diminish, leading to an increase in the dynamic contact angle θ_D .

5.3.2. Energy Dissipation Analysis

To analyze the energy dissipated due to viscous losses during capillary flow, the relevant fluid properties inside the nanochannel—namely the density, viscosity, and velocity distribution—must first be evaluated. As shown in Figure 5.6, the effective liquid density ρ^* inside the nanochannel is very close to the bulk water density, indicating that the channel dimensions used in the simulations are sufficiently large compared with the molecular scale, and that the influence of the channel walls on the intrinsic fluid properties is minimal. In addition, the velocity profile of the liquid during capillary flow exhibits a parabolic shape, consistent with the characteristics of Hagen–Poiseuille flow, confirming the validity of the assumption used in Equation 5.11.

To determine the fluid viscosity inside the nanochannel, the Poiseuille flow method is employed, as illustrated in Figure 5.7, and the calculated viscosity is found to be essentially identical to that of bulk water. For the mW model, water molecules in the liquid phase at room temperature (300 K) do not easily evaporate, and only a negligible number of water molecules exist in the vapor phase (Molinero and Moore, 2009).

Therefore, energy dissipation associated with the vapor phase can be neglected.

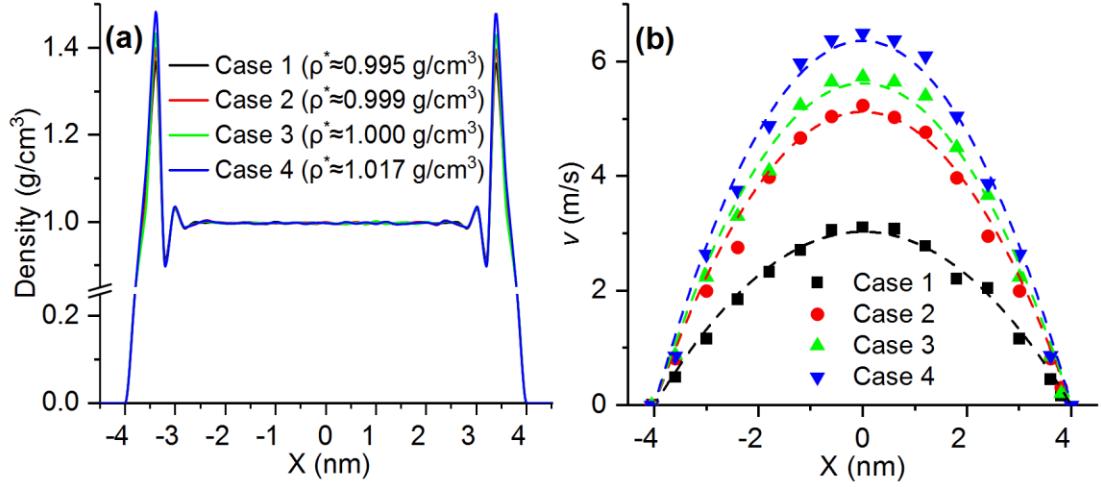


Figure 5.6 (a) Liquid density distribution inside the nanochannel during capillary flow, where the effective density ρ^* is defined as the weighted average of the local liquid density; (b) average velocity profile of the liquid inside the nanochannel during $t=7-8$ ns, with the dashed line representing a parabolic fit to the simulation results.

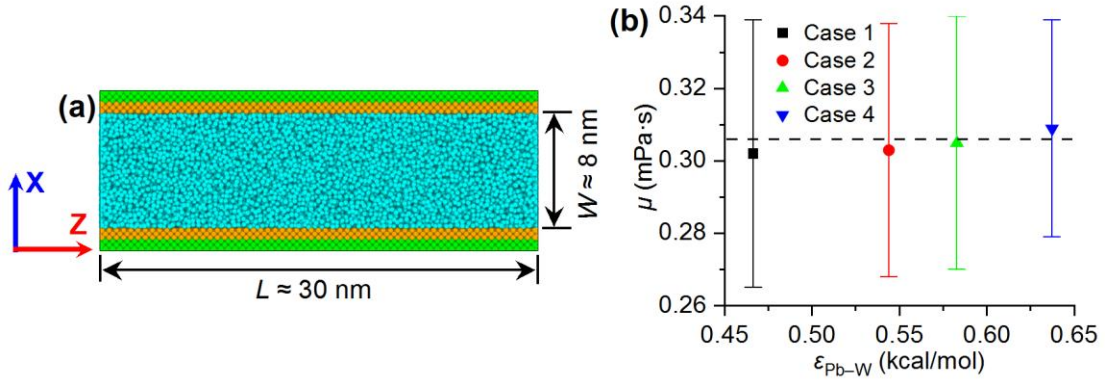


Figure 5.7 (a) Model used for calculating the liquid viscosity inside the nanochannel via the Poiseuille-flow method. The channel width is set to 8 nm, the length to 30 nm, and the depth in the Y -direction to 3 nm; (b) liquid viscosity in nanochannels with different wettability, where the black dashed line represents the viscosity of bulk water.

Because periodic boundary conditions are applied in the Y -direction during the capillary flow simulations, the nanochannel effectively has an infinite length in this direction; for convenience, it may therefore be treated as having a unit length of 1 m. As shown in Figure 5.8, during capillary flow, the kinetic energy of the liquid E_k is 2–3 orders of magnitude smaller than the viscous dissipation energy E_{vis} within the liquid and the contact-line dissipation energy E_{CL} caused by molecular friction near the three-phase contact line. This demonstrates that nearly all of the surface-energy

reduction E_S is dissipated during the capillary flow process. The sum of E_{CL} and E_{vis} is close to E_S , especially after capillary flow becomes fully developed, in agreement with the theoretical analysis. Since both the capillary flow velocity V_B and the capillary rise height L_B increase continuously during the meniscus formation stage, Equations 5.11 and 5.13 indicate that Φ_S and Φ_{vis} should also increase with increasing V_B , which is consistent with the simulation results. According to Equation 5.12, the evolution of Φ_{CL} depends on both the capillary flow velocity V_B and the dynamic contact angle θ_D . Because the evolution of θ_D is non-monotonic during the early stage of capillary flow, the behavior of Φ_{CL} is correspondingly more complex. As θ_D increases during the later part of the meniscus formation stage, Φ_{CL} also exhibits an increasing trend. After the meniscus formation stage, the capillary flow process can be described using the Lucas–Washburn model with dynamic contact-angle correction. According to Equations 5.11 – 5.12, both Φ_S and Φ_{CL} gradually decrease as θ_D and V_B decrease. Meanwhile, the capillary rise height L_B continues to increase throughout the process, whereas the dynamic contact angle θ_D varies only slowly at later times. Thus, Equation 5.13 indicates that Φ_{vis} should also decline as time progresses. Overall, the simulation results show excellent agreement with the theoretical analysis.

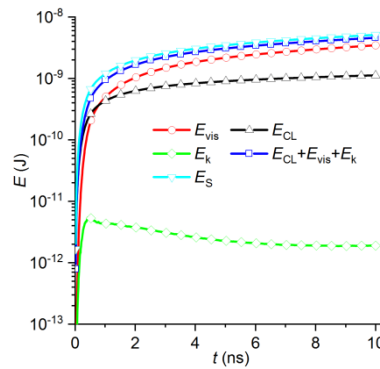


Figure 5.8 The variation of E_k , E_S , E_{CL} , and E_{vis} at different time intervals in Case 4 with respect to time t .

As shown in Figure 5.9, the sum of R_{CL} and R_{vis} is less than 1 during the simulations, particularly during the meniscus formation stage. This indicates the presence of additional energy dissipation mechanisms, which may include pronounced

changes in the shape of the liquid–vapor interface and the influence of the flow pattern at the channel entrance (Kornev and Neimark, 2001; Wolf et al., 2010). During the meniscus formation stage, the liquid–vapor interface undergoes substantial deformation, inevitably leading to energy dissipation. Moreover, when liquid molecules first enter the channel, the capillary flow velocity V_B is relatively high, and the velocity distribution at the channel entrance is non-uniform, both of which may contribute to additional dissipation.

In the later stages of the simulation, the shape of the liquid–vapor interface becomes more stable, and the value of V_B decreases significantly. Consequently, the reduction in surface energy E_S is primarily dissipated through viscous losses within the liquid and molecular friction near the three-phase contact line. As capillary flow progresses and the dynamic contact angle θ_D gradually decreases, viscous dissipation increasingly becomes the dominant mechanism.

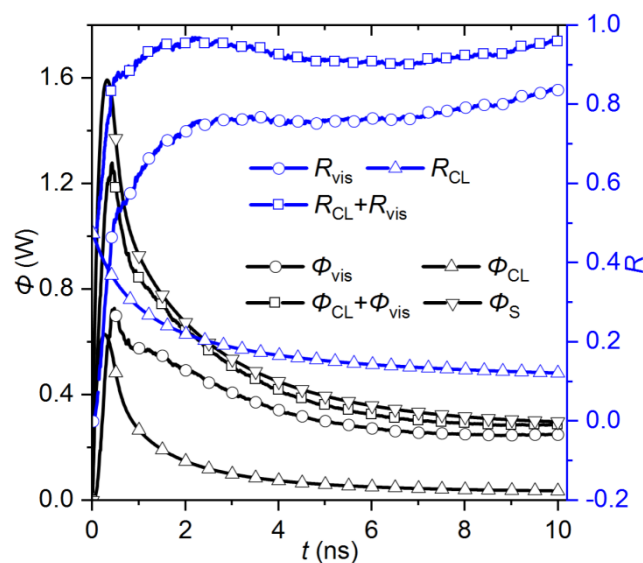


Figure 5.9 evolution of Φ_S , Φ_{CL} , Φ_{vis} , R_{CL} , and R_{vis} at different moments in Case 4.

5.3.3. Validation of the Modified Lucas–Washburn Model

In the theoretical analysis presented earlier, the Cox–Voinov law was employed to describe the relationship between the contact-line velocity V_B and the dynamic contact angle θ_D , leading to a modified Lucas–Washburn model. However, at the micro–

nanoscale, when the driving force and the direction of fluid motion are aligned, the two forms of dynamic contact angle—the apparent dynamic contact angle $\theta_{D,App}$ and the microscopic dynamic contact angle $\theta_{D,M}$ —are known to be very similar (Fernandez-Toledano et al., 2021). Moreover, the influence of thermal molecular motion cannot be neglected. Continuous molecular collisions cause persistent fluctuations of the contact line, the liquid–vapor interface, and the solid–liquid interface, which severely affect the accuracy of dynamic contact-angle measurements during imbibition (Fernandez-Toledano et al., 2019; Fernandez-Toledano et al., 2021). As a result, distinguishing between $\theta_{D,App}$ and $\theta_{D,M}$ becomes challenging.

Therefore, following previous studies, the two dynamic contact angles are not strictly differentiated in this chapter unless otherwise specified, such that $\theta_D \approx \theta_{D,App} \approx \theta_{D,M}$ (Joly, 2011; Chu et al., 2019; Primkulov et al., 2020). In addition, Fernandez-Toledano et al. (2021) noted that fitting θ_D and V_B using Equation 2.22 is applicable when the directions of the contact-line velocity and the external driving force are consistent.

In the simulations conducted in this chapter, the parameter $\ln(L_{mac}/L_{mol})=2.64$, corresponding to $L_{mac}/L_{mol} \approx 14$. Considering the measurement method for θ_D , half of the nanochannel width can be defined as L_{mac} , i.e., $L_{mac}=W/2=4$ nm. This gives $L_{mol}=0.286$ nm, which is close to the diameter of a water molecule (approximately 0.275 nm). Thus, the value of $\ln(L_{mac}/L_{mol})$ is strongly dependent on both the channel dimensions and the molecular size of the liquid.

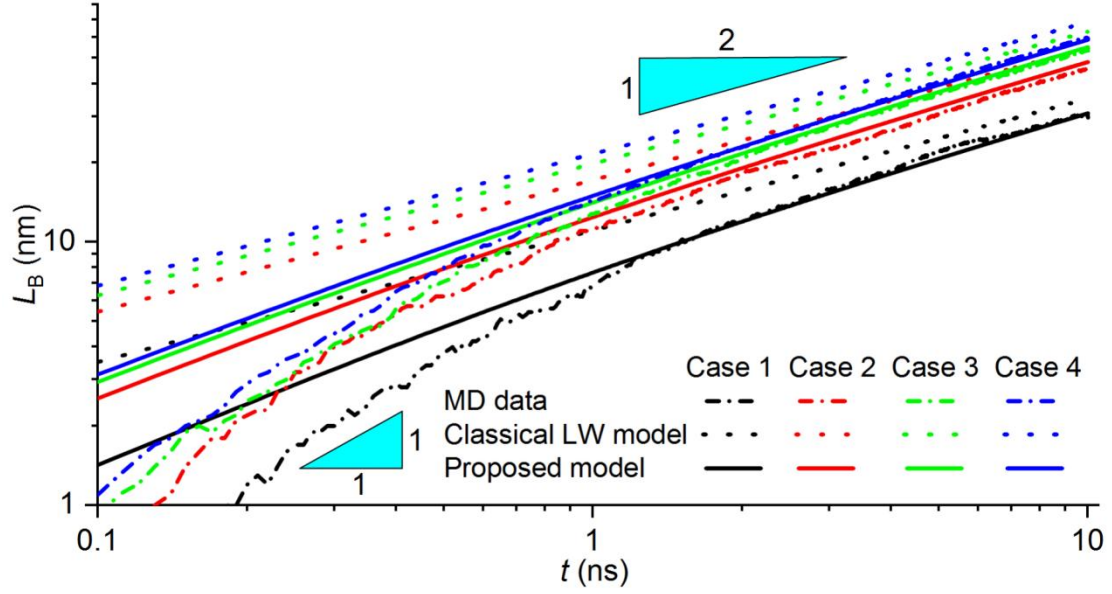


Figure 5.10 Time evolution of the capillary rise height L_B during the capillary flow process. The simulation results are compared with the predictions of the classical Lucas–Washburn model and the modified Lucas–Washburn model.

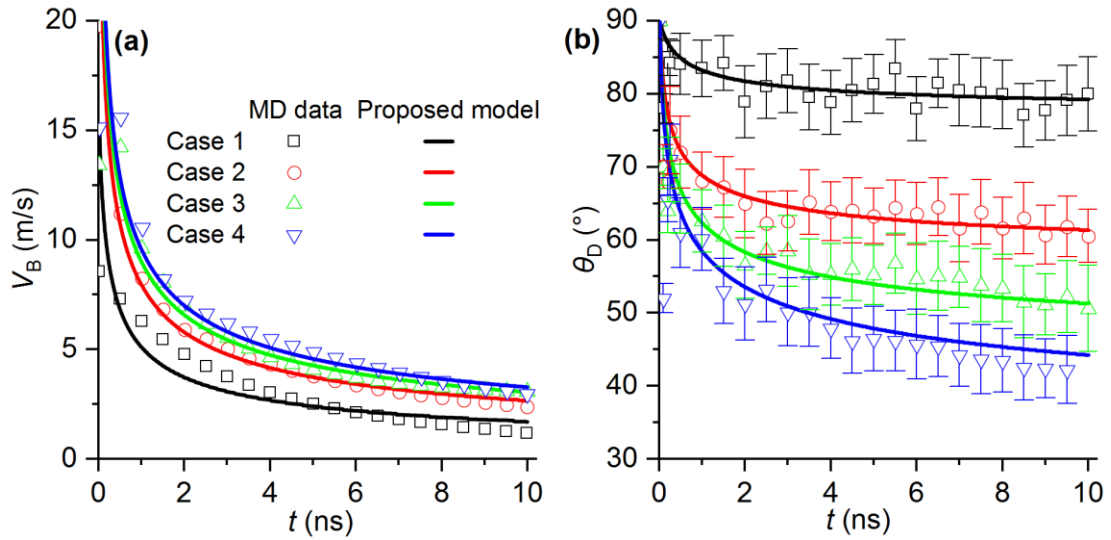


Figure 5.11 evolution of (a) the capillary flow velocity V_B and (b) the dynamic contact angle θ_D during the capillary flow process. The simulation results are compared with the predictions of the classical Lucas–Washburn model and the modified Lucas–Washburn model.

As shown in Figure 5.10, stronger nanochannel wettability leads to faster capillary flow and larger capillary rise height L_B at any given time, which is consistent with the theoretical analysis. As discussed earlier, the capillary flow velocity V_B increases continuously during the meniscus formation stage and then gradually decreases during

the subsequent capillary flow process. As illustrated in Figure 5.11, the decrease in the dynamic contact angle θ_D becomes progressively slower as the capillary rise height L_B increases, and the influence of θ_D on V_B also diminishes. According to the modified Lucas–Washburn model, the late-stage capillary flow tends toward the scaling relation $L_B \sim t^{1/2}$. Consequently, throughout the entire capillary flow process, the slope of $L_B(t)$ on the log–log plot (Figure 5.10) gradually converges from values greater than 1 to the limiting value of 1/2.

Overall, the classical Lucas–Washburn model overestimates the capillary infiltration rate in nanochannels, whereas the modified Lucas–Washburn model based on the Cox–Voinov law, which incorporates dynamic contact-angle effects, provides accurate predictions of the capillary rise height L_B , flow velocity V_B , and dynamic contact angle θ_D at different times. It should be noted that the Lucas–Washburn framework does not describe the meniscus formation stage (Wolf et al., 2010). Accordingly, the modified Lucas–Washburn model also does not account for this early stage, leading to discrepancies between the theoretical predictions and the simulation results. However, because the meniscus formation stage is typically very short at the micro–nanoscale, this limitation does not affect the accuracy of the modified Lucas–Washburn model in the subsequent capillary flow regime.

5.4. Capillary Flow in Nanochannels with Asymmetric Wall Wettability

When the two walls of a nanochannel exhibit identical wettability, the capillary rise heights along the upper and lower walls are the same throughout the capillary flow process. In contrast, when the wall wettability is asymmetric, the capillary rise heights differ on the two sides, with the higher value occurring on the more wettable wall. Figures 4.12 and 4.13 show the evolution of the imbibition lengths $L_{B,U}$ and $L_{B,L}$ along the upper and lower walls, respectively, as well as the height difference $\Delta L = L_{B,U} - L_{B,L}$ as a function of time t . A higher overall wettability of the nanochannel results in a faster increase in capillary rise height. Another notable feature of asymmetric-wettability channels is the evolution of ΔL . When the nanochannel first contacts the liquid reservoir, water molecules preferentially adsorb onto the more wettable wall and

rise along it at a relatively higher speed.

For the less wettable wall, two cases may occur. In the first case, the equilibrium contact angle θ_E on the weaker-wetting wall exceeds 90° , indicating hydrophobicity. In the second case, the wall is hydrophilic, i.e., $\theta_E < 90^\circ$, but still less wettable than the opposite wall. In the first scenario, the height difference between the two walls increases rapidly, accompanied by a significant disparity between the two dynamic contact angles. As shown in Figure 5.14, the dynamic contact angle on the strongly wetting side is acute and thus drives the capillary flow, whereas the dynamic contact angle on the weakly wetting side is obtuse, impeding the flow. In the second scenario, the height difference ΔL decreases and soon reaches a steady value, and the dynamic contact angle on the weaker-wetting wall becomes acute as well, thereby contributing to the driving force for capillary flow. In general, as the wettability contrast between the two walls decreases, the capillary rise heights on both sides converge. In Case 10, where $\cos\theta_E^* < 0$, the simulation results show that capillary flow does not occur.

Moreover, in nanochannels with asymmetric wall wettability, the liquid–vapor interface oscillates continuously during capillary flow, and the larger the wettability contrast, the stronger the oscillations. As shown in Figure 5.13, both the magnitude of oscillations and the value of ΔL increase with increasing wettability difference $\Delta\cos\theta_E$. To elucidate the mechanism underlying these interfacial oscillations, the capillary flow process can be divided into two stages based on whether the liquid–vapor interface has reached a dynamically stable configuration. As illustrated in Figure 5.14, during the initial stage of capillary flow, water molecules rise preferentially along the more wettable wall, causing ΔL to increase rapidly. In this stage, interfacial oscillations are not prominent, and the dominant effect is the rapid growth of the height difference ΔL . Once the liquid–vapor interface reaches a dynamically stable shape, ΔL fluctuates around its equilibrium value, as shown in Figure 5.13.

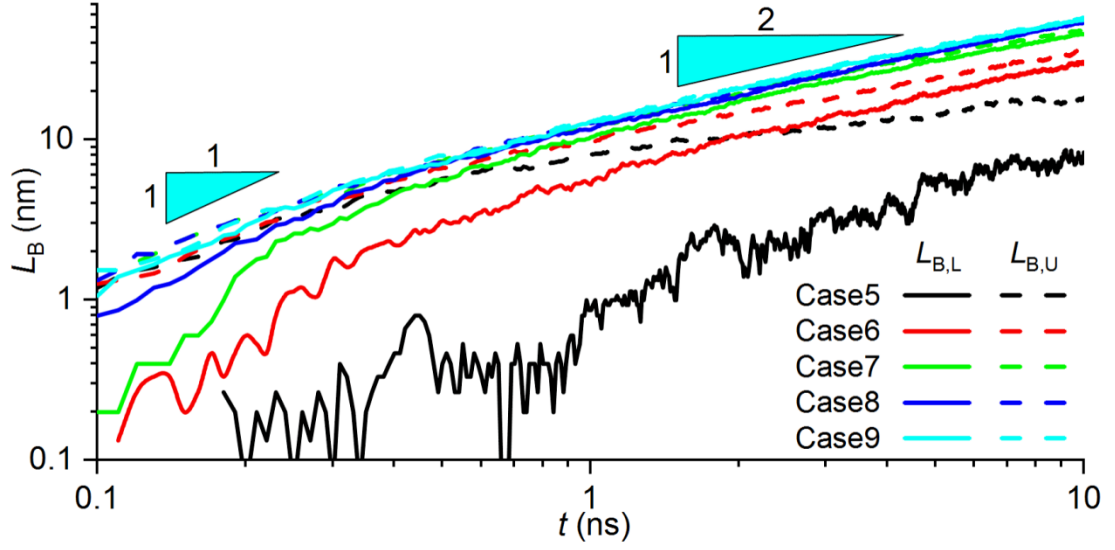


Figure 5.12 Time evolution of the capillary rise heights $L_{B,U}$ and $L_{B,L}$ along the upper and lower walls, respectively, during the capillary flow process.

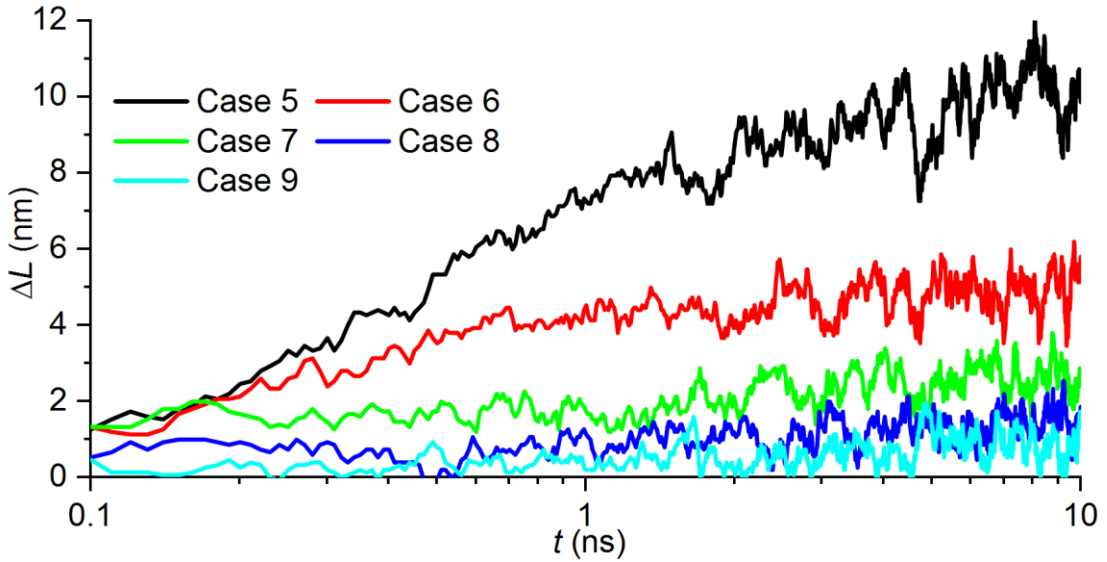


Figure 5.13 Time evolution of the height difference $\Delta L = L_{B,U} - L_{B,L}$ between the upper and lower walls during the capillary flow process.

During capillary flow, the net force acting on the liquid in the direction parallel to the channel walls must be aligned with the direction of flow, i.e., $\gamma_{LV}(\cos\theta_{D,U} + \cos\theta_{D,L}) > 0$. However, in the direction perpendicular to the flow, the net force $\gamma_{LV}(\sin\theta_{D,U} - \sin\theta_{D,L}) \neq 0$, indicating a force imbalance in this direction. As a result, the liquid–vapor interface continuously oscillates. The closer $\gamma_{LV}(\sin\theta_{D,U} - \sin\theta_{D,L})$ is to zero, the weaker the interfacial oscillations become. When $\sin\theta_{D,U} - \sin\theta_{D,L} = 0$, the

liquid experiences only the net driving force along the capillary flow direction. According to trigonometric relations, this condition requires either $\theta_{D,U}=\theta_{D,L}$ or $\theta_{D,U}+\theta_{D,L}=180^\circ$. The case $\theta_{D,U}=\theta_{D,L}$ corresponds to symmetric wall wettability, whereas $\theta_{D,U}+\theta_{D,L}=180^\circ$ leads to $\cos\theta_{D,U}+\cos\theta_{D,L}=0$, meaning the capillary driving force vanishes and capillary flow cannot proceed. Therefore, for nanochannels with asymmetric wall wettability, oscillations of the liquid–vapor interface are unavoidable. If the lower wall is hydrophobic, oscillations of the liquid–vapor interface during capillary flow may cause liquid molecules near the contact line to detach from the lower wall, resulting in a receding contact line—an effect that becomes more pronounced as the hydrophobicity increases. When the lower wall is hydrophilic, the value of $\gamma_{LV}(\sin\theta_{D,U}-\sin\theta_{D,L})$ decreases as $\Delta\cos\theta_E$ decreases, leading to weaker oscillations of the liquid–vapor interface. In summary, regardless of the wettability of the lower wall, the amplitude of interfacial oscillations decreases as the wettability contrast between the two channel walls decreases.

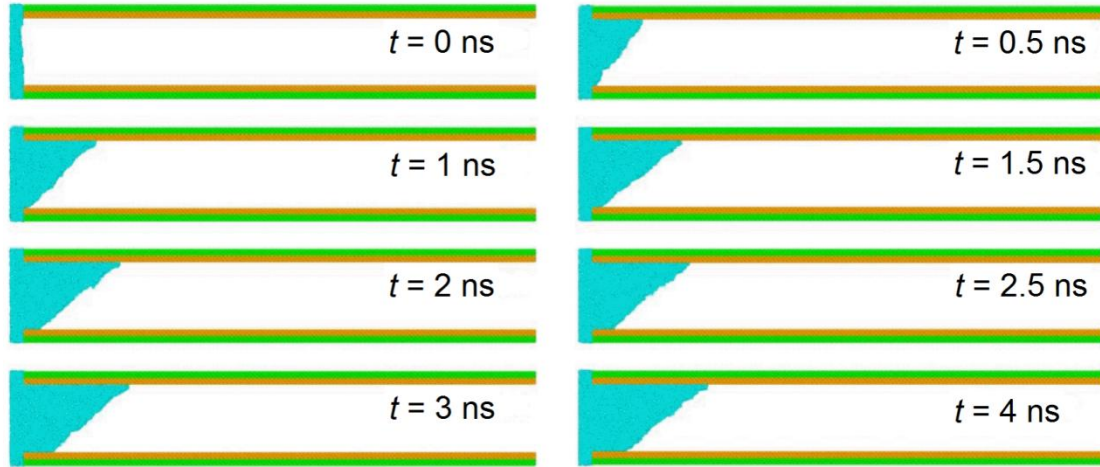


Figure 5.14 of the simulation configuration at different times for Case 5.

As shown in Figure 5.15, the relationship between the capillary rise height difference ΔL on the two channel walls and the wettability contrast $\Delta\cos\theta_E$ can be approximated by $\Delta L=k(\Delta\cos\theta_E)^\beta$, where k and β are fitting parameters determined by the properties of the solid and liquid, as well as external conditions such as pressure and temperature. In the simulations of this chapter, $\Delta\cos\theta_E$ varies between 0 and 1.58;

given that the theoretical upper bound of $\Delta\cos\theta_E$ is 2 (based on trigonometric considerations), the present simulations cover the vast majority of possible scenarios. This indicates that the proposed relationship possesses broad applicability. It should also be noted that, in addition to the wettability contrast between the two walls, thermal molecular motion can induce fluctuations of the liquid–vapor interface, especially when the capillary flow velocity is relatively small.

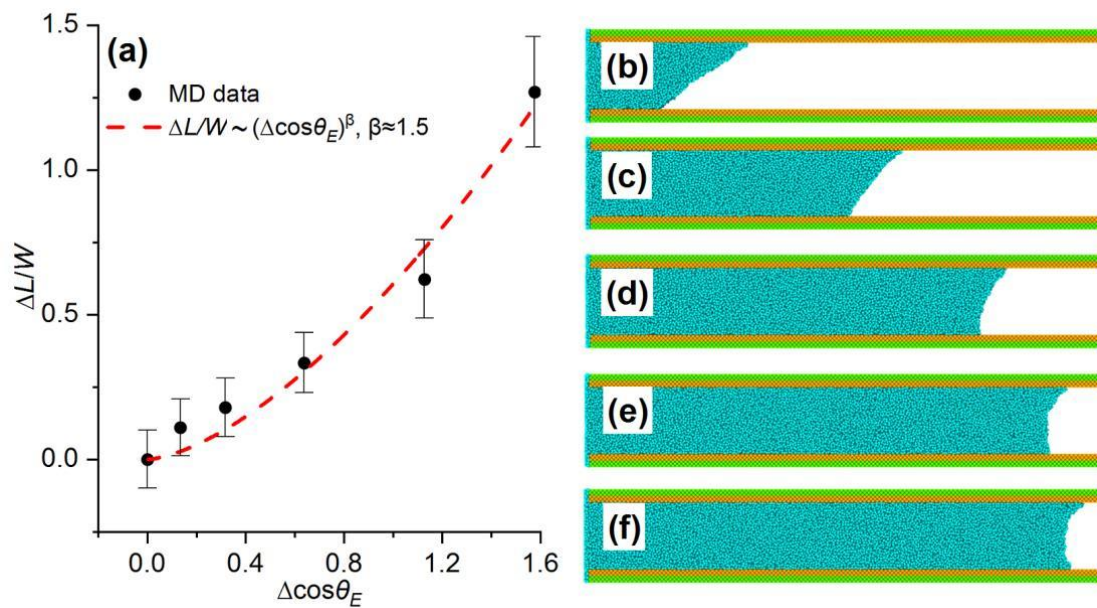


Figure 5.15 Relationship between the capillary rise height difference ΔL on the two channel walls and the wettability contrast $\Delta\cos\theta_E$; (b)–(f) simulation snapshots of Cases 5–9 at $t=10$ ns.

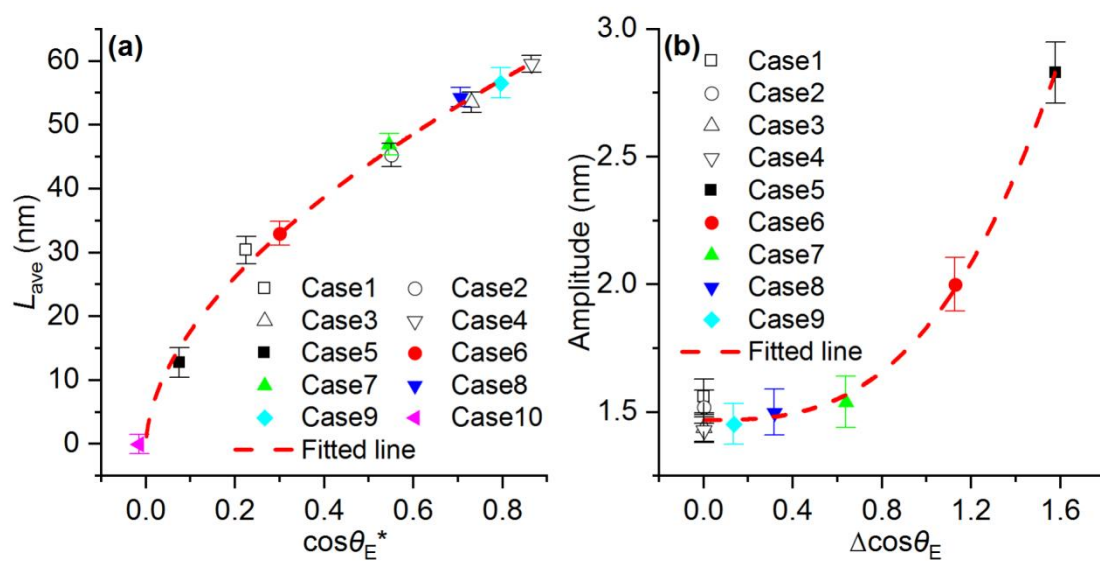


Figure 5.16 (a) Relationship between the average capillary rise height L_{ave} at

$t=10\text{ ns}$ and the effective equilibrium contact angle θ_E^* ; (b) relationship between the fluctuation amplitude of the capillary rise height difference ΔL (for $t>5\text{ ns}$) and the wettability contrast $\Delta\cos\theta_E$.

As shown in Figure 5.16a, the average capillary rise height L_{ave} during capillary flow increases with the cosine of the effective equilibrium contact angle $\cos\theta_E^*$. Moreover, when the effective equilibrium contact angles θ_E^* of the nanochannels are similar, the corresponding values of L_{ave} are also similar, regardless of whether the wall wettability is symmetric or asymmetric.

As illustrated in Figure 5.16b, the fluctuation amplitude of ΔL increases with the wettability contrast $\Delta\cos\theta_E$. In Cases 5 and 6, the upper wall of the nanochannel is hydrophilic while the lower wall is hydrophobic, producing a large wettability difference between the two sides; consequently, the fluctuation amplitude of ΔL is significantly larger than in other cases. In Cases 7–9, both channel walls are hydrophilic (i.e., $\theta_{E,U}<\theta_{E,L}<90^\circ$), and the fluctuation amplitude of ΔL rapidly diminishes to a level comparable to that in Cases 1–4. This indicates that, in these cases, the oscillations of the liquid–vapor interface are primarily caused by thermal molecular fluctuations.

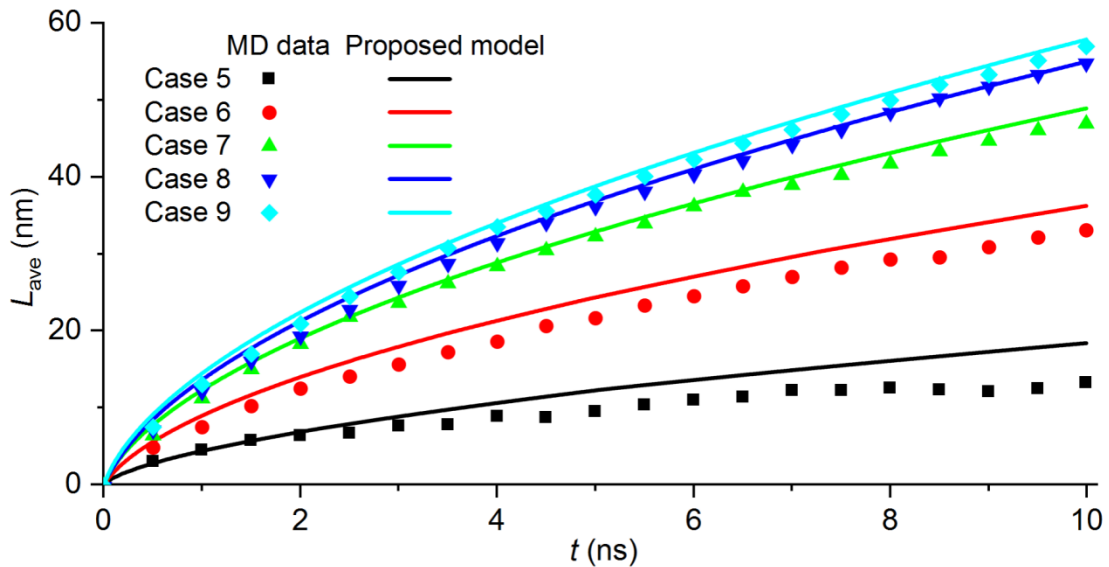


Figure 5.17 evolution of the average capillary rise height L_{ave} during the capillary flow process.

As shown in Figure 5.17, overall, using the effective equilibrium contact angle θ_E^* to characterize the wettability of nanochannels with asymmetric wall properties, and substituting θ_E^* into the modified Lucas–Washburn model, enables accurate prediction of the time evolution of the average capillary rise height L_{ave} . Combined with the relationship between ΔL and $\Delta \cos \theta_E$, the capillary rise heights along the upper and lower walls, $L_{B,U}$ and $L_{B,L}$, at different times can also be determined. Moreover, the good agreement between the simulation results and the theoretical predictions indicates that the underlying energy dissipation mechanisms during capillary flow are similar regardless of whether the wall wettability is symmetric or asymmetric.

It should be noted that in Cases 5–6, the upper wall of the nanochannel is hydrophilic while the lower wall is hydrophobic, i.e., $\theta_{E,U} < 90^\circ < \theta_{E,L}$. In these cases, the theoretically predicted evolution of L_{ave} is slightly faster than the simulation results. This discrepancy is likely caused by oscillations of the liquid–vapor interface. Because the wettability contrast between the walls is large in Cases 5–6, the amplitude of interfacial oscillations is significantly greater than in other cases, resulting in additional energy dissipation. In the preceding theoretical analysis, it was assumed that nearly all of the reduced surface energy during capillary flow is dissipated through viscous losses in the liquid and molecular friction near the contact line, without accounting for dissipation associated with interfacial oscillations. Therefore, when the influence of liquid–vapor interface fluctuations is non-negligible, discrepancies between the theoretical model and simulation results may arise.

5.5. Conclusion

This chapter systematically investigates the mechanisms by which wall wettability influences capillary flow and energy dissipation in nanochannels, considering both symmetric and asymmetric wettability conditions. The overall wettability of the channel is characterized by the sum of the cosine values of the equilibrium contact angles on the two walls, i.e., $\sum \cos \theta_E = \cos \theta_{E,L} + \cos \theta_{E,U}$. Based on energy conservation and transformation analysis, the necessary condition for capillary flow to occur is found

to be $\sum \cos \theta_E > 0$. The results show that the reduction in surface energy during capillary flow is primarily dissipated through viscous losses within the liquid and molecular friction near the three-phase contact line. When the wettability contrast between the two walls is large, additional dissipation associated with oscillations of the liquid–vapor interface must also be considered.

Accounting for dynamic contact-angle effects, the classical Lucas–Washburn model was modified using the Cox–Voinov law. The modified Lucas–Washburn model accurately predicts the capillary rise height, flow velocity, and dynamic contact angle at different times. In nanochannels with asymmetric wall wettability, oscillations of the liquid–vapor interface are observed, and these oscillations become more pronounced as the wettability contrast $\Delta \cos \theta_E$ increases. A height difference ΔL between the two walls emerges, and once capillary flow is fully established, ΔL oscillates around an equilibrium value and follows the relationship $\Delta L \sim (\Delta \cos \theta_E)^{1.5}$.

To facilitate comparison between channels with symmetric and asymmetric wettability, the average capillary rise height is defined as $L_{\text{ave}} = \frac{L_{B,U} + L_{B,L}}{2}$, i.e., the mean of the rise heights along the upper and lower walls. Regardless of whether the wall wettability is symmetric, a larger $\sum \cos \theta_E$ corresponds to a faster increase in L_{ave} . When $\sum \cos \theta_E$ is equal or similar across channels, the temporal evolution $L_{\text{ave}}(t)$ is likewise similar. For nanochannels with asymmetric wall wettability, substituting the effective equilibrium contact angle θ_E^* into the modified Lucas–Washburn model enables accurate prediction of the time-dependent average capillary rise height $L_{\text{ave}}(t)$.

6. Molecular Dynamics Study of Pool Boiling Heat Transfer on Smooth Hydrophilic/Hydrophobic Composite Surfaces

Extensive research has demonstrated that modifying surface wettability can enhance boiling heat transfer at solid–liquid interfaces. However, the roles of the spatial distribution of hydrophilic and hydrophobic regions on the surface, as well as their respective area fractions, in strengthening interfacial boiling heat transfer remain insufficiently explored, and the underlying physical mechanisms are not yet fully understood. Therefore, it is necessary to construct surfaces with different spatial arrangements and area fractions of hydrophilic/hydrophobic regions and to examine bubble growth, the variation in the number of evaporated atoms, and interfacial thermal resistance. Such analyses can clarify the physical laws governing how the spatial distribution and proportion of hydrophilic/hydrophobic regions affect boiling heat transfer and reveal the mechanisms by which these factors enhance interfacial heat transfer.

In this chapter, to investigate the enhancement of boiling heat transfer on hydrophilic/hydrophobic composite surfaces, molecular dynamics (MD) simulations are performed to construct smooth composite surfaces with mixed wettability. The effects of solid–liquid interaction strength and hydrophilic/hydrophobic area ratios on pool-boiling heat transfer characteristics are examined. The bubble nucleation, growth, and coalescence dynamics are visualized using the Construct Surface Mesh function in OVITO, enabling detailed observation of bubble evolution during the boiling process. In addition, the number of evaporated atoms and interfacial thermal resistance are quantitatively analyzed to elucidate the physical mechanisms governing boiling heat transfer on surfaces with different wettability distributions. This chapter clarifies how solid–liquid interaction strength and wettability patterns enhance pool-boiling heat transfer at the nanoscale, providing the theoretical foundation for the investigation of structured hydrophilic/hydrophobic composite surfaces in Chapter 6.

6.1. Computational Model of Pool Boiling Heat Transfer on Smooth Hydrophilic/Hydrophobic Composite Surfaces

6.1.1. Physical Model

The simulation model for pool boiling on smooth hydrophilic/hydrophobic composite surfaces and the corresponding wall configurations are shown in Figure 6.1. As illustrated in Figure 6.1(a), the computational domain has dimensions of $L_x \times L_y \times L_z = 108.3 \text{ \AA} \times 108.3 \text{ \AA} \times 108.3 \text{ \AA}$. The bottom boundary of the model is a metallic substrate, where Cu atoms are arranged in a face-centered cubic (FCC) lattice structure with a lattice constant of $3.615 \text{ \AA}$. The wettability distribution on the wall surface is shown in Figure 6.1(b). According to the spatial arrangement of the hydrophobic regions, the wall surfaces are labeled sequentially as #LPi (entirely hydrophilic), #LPo (entirely hydrophobic), $\#\beta_L1$, $\#\beta_L2$, $\#\beta_L3$, $\#\beta_L4$, and $\#\beta_L5$, where β denotes the ratio of the hydrophobic area to the total wall surface. Figure 6.1(b) displays the distribution of hydrophilic and hydrophobic regions for $\beta = 0.25$; under this condition, the surfaces are denoted as $\#0.25_L1$, $\#0.25_L2$, $\#0.25_L3$, $\#0.25_L4$, and $\#0.25_L5$.

In the direction normal to the wall surface, the substrate metal is divided into three layers based on their functional roles, as shown in Figure 6.1(c). The bottommost layer is the fixed layer, where atomic positions and velocities remain zero throughout the simulation to ensure system stability. The middle layer functions as the heat source, where adjusting its temperature enables control of the wall temperature during pool boiling simulations. The uppermost layer is the thermal conduction layer, responsible for transferring energy from the heat source layer to the Ar atoms in the liquid region above.

During the simulation, periodic boundary conditions are applied in both the X and Y directions, while non-periodic boundary conditions are imposed in the Z direction. To prevent atoms from escaping from the top of the computational domain and causing atomic loss, a reflective boundary layer is placed at the top of the model. When atoms reach the upper boundary, they undergo elastic collisions with this reflective layer and are redirected back into the simulation domain. Throughout this process, both the

energy and momentum of the atoms are conserved, ensuring that no energy loss occurs.

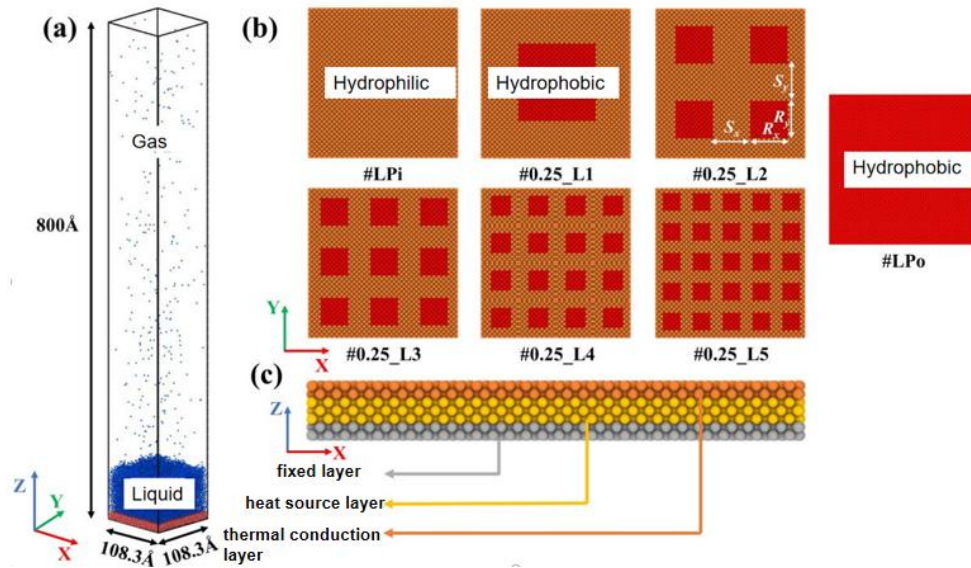


Figure 6.1 (a) MD simulation model of pool boiling, (b) Surface wettability distribution, (c) Function layers distribution of solid surface

6.1.2. Potential Parameter Settings

The interaction between Cu atoms and Ar atoms is described by the Lennard–Jones (LJ) potential, and the corresponding potential parameters are listed in Table 6.1. For the interactions among Cu atoms within the metallic substrate, the embedded-atom method (EAM) potential is employed. Since the EAM potential has already been briefly introduced in Chapter 2, it is not repeated here.

Table 6.1 LJ potential function parameters for Ar–Ar and Ar–Cu

Interaction pair	ε [eV]	σ [Å]
Ar–Ar	0.0104	3.405
Ar–Cu (hydrophilic, $\alpha=0.7$)	0.0455	2.8725
Ar–Cu (hydrophilic, $\alpha=1.5$)	0.0975	2.8725
Ar–Cu (hydrophobic, $\alpha=0.04$)	0.0026	2.8725

6.1.3. Simulation steps

Before the production run, the entire simulation system is first relaxed. In this stage, the NVT ensemble is applied to the whole system, and the system temperature is

maintained at 86 K using the Nosé–Hoover thermostat. The relaxation is performed for 1 ns to ensure that the system reaches a stable equilibrium state.

After relaxation, temperature control of both the solid Cu substrate and the Ar working fluid is removed. The temperature of the heat source layer is then increased to the target wall temperature using the Langevin thermostat, according to the requirements of each simulation case. The system is subsequently switched to the NVE ensemble. Under these conditions, the heat source layer transfers energy to the liquid region through the conductive layer, initiating the pool-boiling process.

A timestep of 0.001 ps is used, and the simulation is executed for 6 ns, during which all relevant physical quantities are recorded for analysis.

6.2. Effects of Solid–Liquid Interaction Strength on the Pool Boiling Heat Transfer Characteristics of Smooth Hydrophilic/Hydrophobic Composite Surfaces

6.2.1. Variations in Bubble Dynamic Growth on Smooth Hydrophilic/Hydrophobic Composite Surfaces

Previous studies have demonstrated that the solid–liquid interaction strength has a significant influence on heat transfer across solid–liquid interfaces. However, the mechanism by which this interaction strength affects boiling heat transfer on hydrophilic/hydrophobic composite surfaces remains insufficiently understood. Therefore, in this section, molecular dynamics simulations are employed in which the interaction strength between Cu atoms in the hydrophilic regions and Ar atoms in the liquid phase is set to 0.0455 eV and 0.0975 eV, respectively. In the hydrophobic regions, the Cu–Ar interaction strength is kept constant at 0.0026 eV. This setup allows for a comparative investigation of boiling heat transfer on hydrophilic/hydrophobic composite surfaces under different solid–liquid interaction conditions. Meanwhile, during the molecular dynamics simulations, the vapor–liquid interface of the liquid phase is visualized using the *Construct Surface Mesh* function in the visualization software Ovito, enabling a three-dimensional observation and analysis of bubble growth.

Under the conditions of solid–liquid interaction strength $\varepsilon_{\text{Ar-Cu}}=0.0455$ eV and wall temperature $T_m=160$ K, the evolution of the liquid phase during boiling on the fully hydrophilic surface #LPi and composite surfaces #0.25_L1, #0.25_L2, #0.25_L3, #0.25_L4, and #0.25_L5 is illustrated in Figure 6.2. As shown in Figure 6.2, the complete process of bubble nucleation, growth, and coalescence on the wall surface can be clearly observed. On the fully hydrophilic surface #LPi, bubble nucleation sites are relatively random and sparsely distributed. Due to the stronger solid–liquid interaction on this wall, energy transfer occurs more rapidly. As the simulation progresses, the distances between isolated bubbles in the liquid phase gradually decrease, leading to bubble coalescence on the wall and ultimately forming a vapor film at around 2000 ps.

In contrast, on the hydrophilic/hydrophobic composite surfaces, bubbles predominantly grow on the hydrophobic regions, and the overall number of bubbles is increased relative to #LPi. However, because the hydrophobic regions weaken solid–liquid heat transfer, the initial bubble growth and subsequent vapor-film formation are delayed on surfaces #0.25_L1, #0.25_L2, #0.25_L3, and #0.25_L5 compared with #LPi. Among these, the behavior of surface #0.25_L4 is the closest to that of the fully hydrophilic surface #LPi, with smaller discrepancies.

To further examine the boiling heat transfer characteristics on surfaces #LPi and #0.25_L4, the distributions of potential energy and kinetic energy are analyzed in this chapter. Contour maps of the potential energy, kinetic energy, and total energy of Ar atoms in the liquid phase are plotted to provide deeper insight into the underlying thermal transport behaviors.

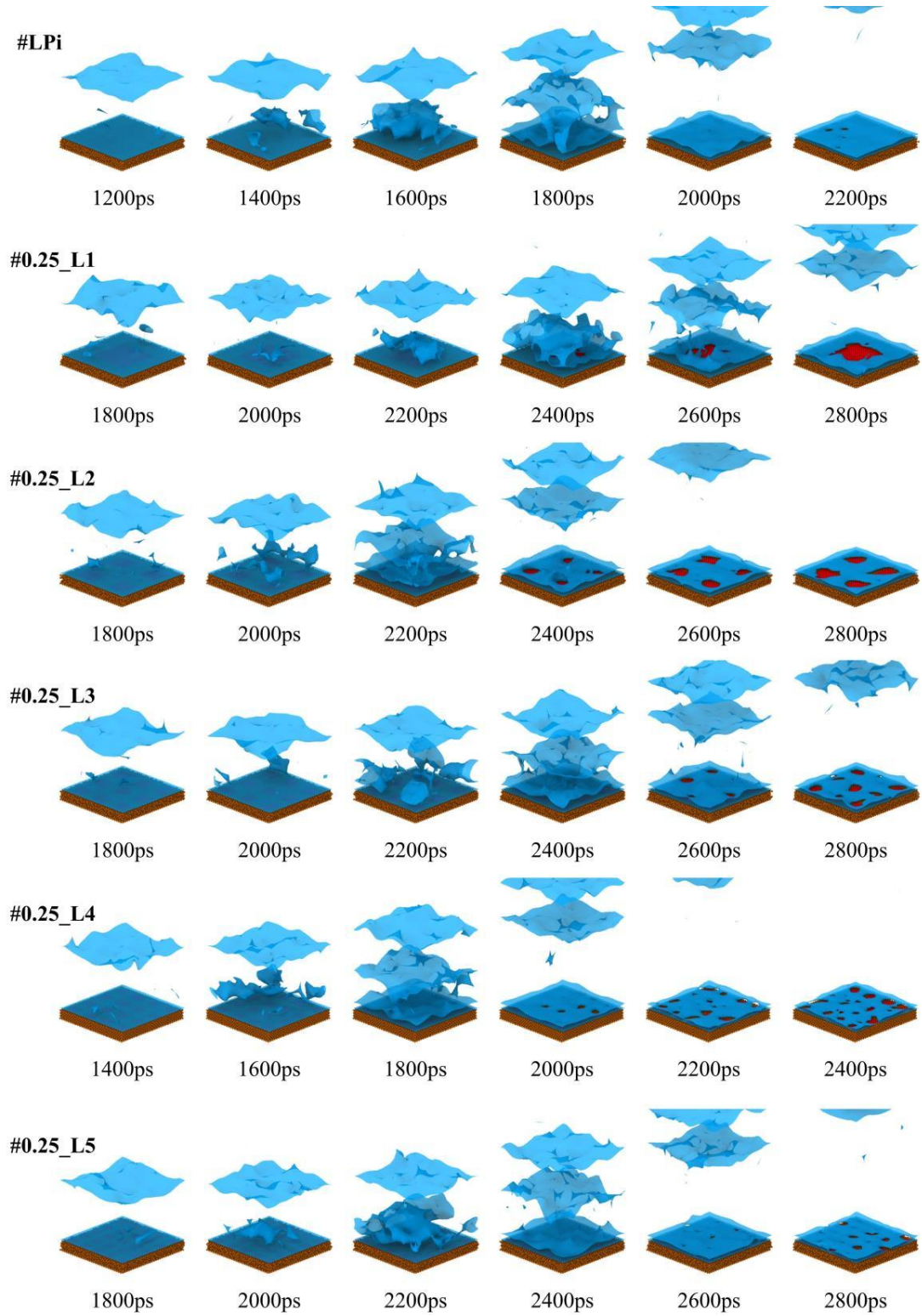


Figure 6.2 Schematic of bubble growth with $\epsilon_{Ar_Cu} = 0.0455$ eV, $T_m = 160$ K and $\beta = 0.2$

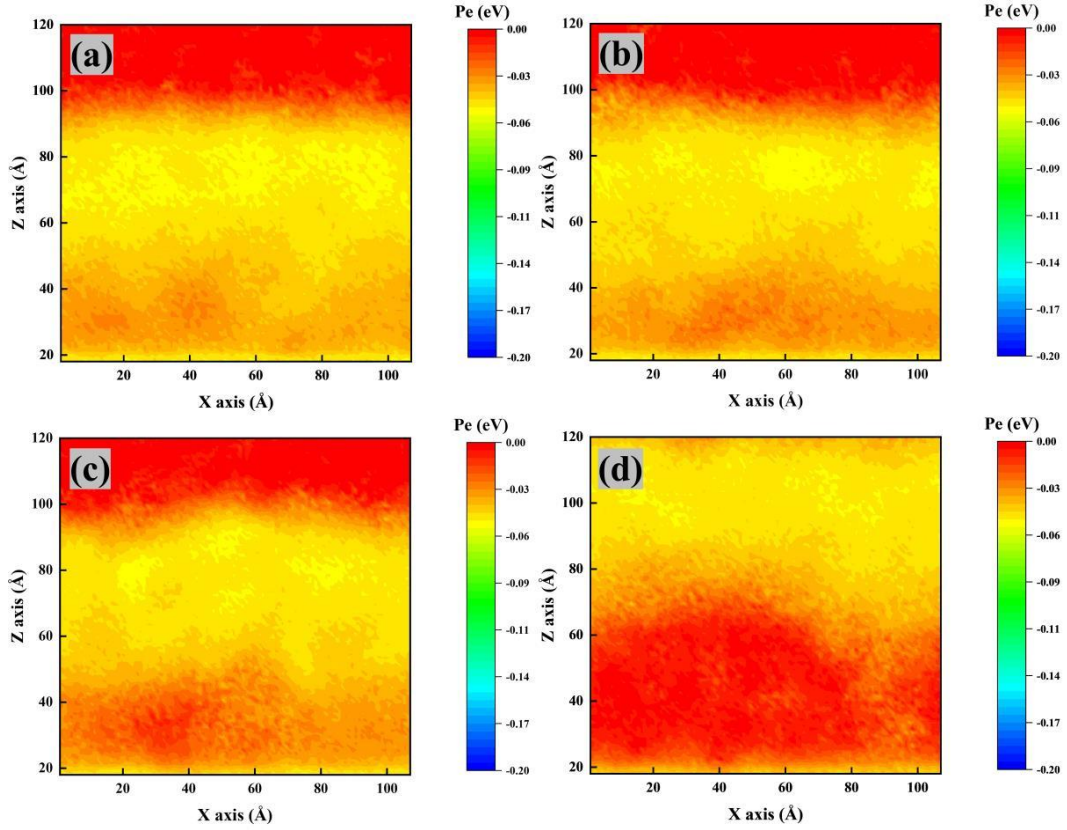


Figure 6.3 Potential energy distribution contours on #LPi surface with $\epsilon_{Ar_Cu} = 0.0455$ eV: (a) $t = 1200$ ps, (b) $t = 1400$ ps, (c) $t = 1600$ ps, (d) $t = 1800$ ps

The simulation results indicate that the distribution of the potential energy of Ar atoms is closely related to the bubble growth process. Figure 6.3 presents two-dimensional contour maps of the potential energy distribution of Ar atoms at 1200 ps, 1400 ps, 1600 ps, and 1800 ps, respectively. As shown in the figure, the potential energy of Ar atoms exhibits pronounced variations near the wall surface. At 1400 ps, the potential energy (its magnitude) of Ar atoms near the wall begins to decrease. By comparing this phenomenon with the bubble states shown in Figure 6.2 at 1400 ps, it can be observed that bubble generation is correlated with the potential energy distribution. At 1600 ps, as shown in Figure 6.3(c), the low-potential-energy region near the wall expands relative to Figure 6.3(b), corresponding to the bubble growth process.

The distribution of the kinetic energy of Ar atoms is shown in Figure 6.4. As the simulation progresses, from 1200 ps to 1600 ps, the Ar atoms near the wall are heated by the wall surface, leading to an increase in their kinetic energy. By 1800 ps, due to

bubble coalescence and the formation of a vapor film, a low-kinetic-energy region appears near the wall surface. The distribution of the total energy near the wall is presented in Figure 6.5. It can be observed that the variation in total energy of Ar atoms near the wall exhibits similarities to their potential energy distribution. From 1200 ps to 1600 ps, a continuously expanding high-energy region develops near the wall, corresponding to the bubble growth process.

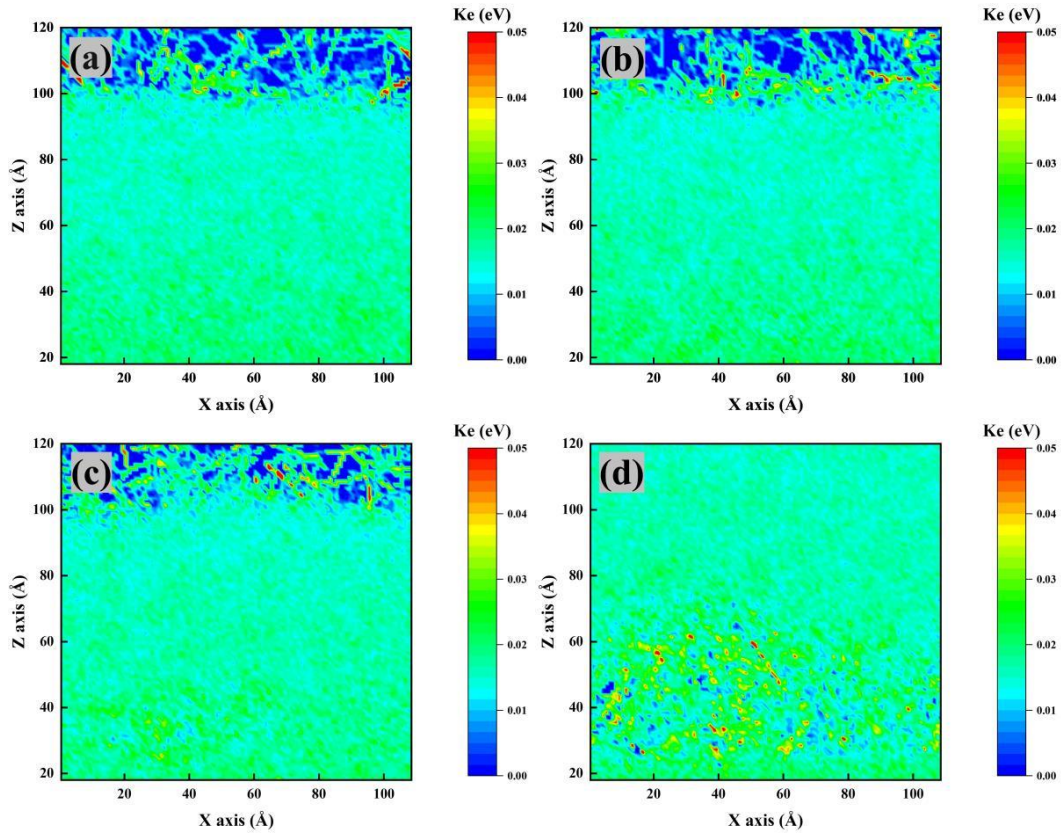


Figure 6.4 Kinetic energy distribution contours on #LPi surface with $\epsilon_{Ar_Cu} = 0.0455$ eV: (a) $t = 1200$ ps, (b) $t = 1400$ ps, (c) $t = 1600$ ps, (d) $t = 1800$ ps

By comparing the distributions of potential energy, kinetic energy, and total energy near the wall, it can be observed that the variations in the potential energy and total energy of Ar atoms exhibit a certain degree of similarity. The expansion of the low-potential-energy region (in terms of potential energy magnitude) corresponds to the bubble growth process on the wall surface. Therefore, bubble growth can be regarded as a process in which Ar atoms in the near-wall region absorb energy and overcome the potential-energy constraints imposed by the wall.

During the simulation, Ar atoms in the near-wall region absorb heat from the wall. A portion of this energy is converted into atomic potential energy, which weakens the potential-energy barrier and allows the atoms to escape from the potential constraints imposed by the wall. Another portion of the absorbed energy is transformed into kinetic energy, which is subsequently transferred to Ar atoms located farther away through interatomic interactions, thereby enabling energy transport within the liquid phase and causing its temperature to rise continuously. In the near-wall region, once the Ar atoms receive sufficient heating from the wall and acquire enough kinetic energy to overcome the potential-energy constraint, their total energy becomes greater than zero. At this moment, bubble nucleation begins to occur at the wall surface, corresponding to the variations observed in the total-energy distribution contour maps of Ar atoms in Figure 6.5.

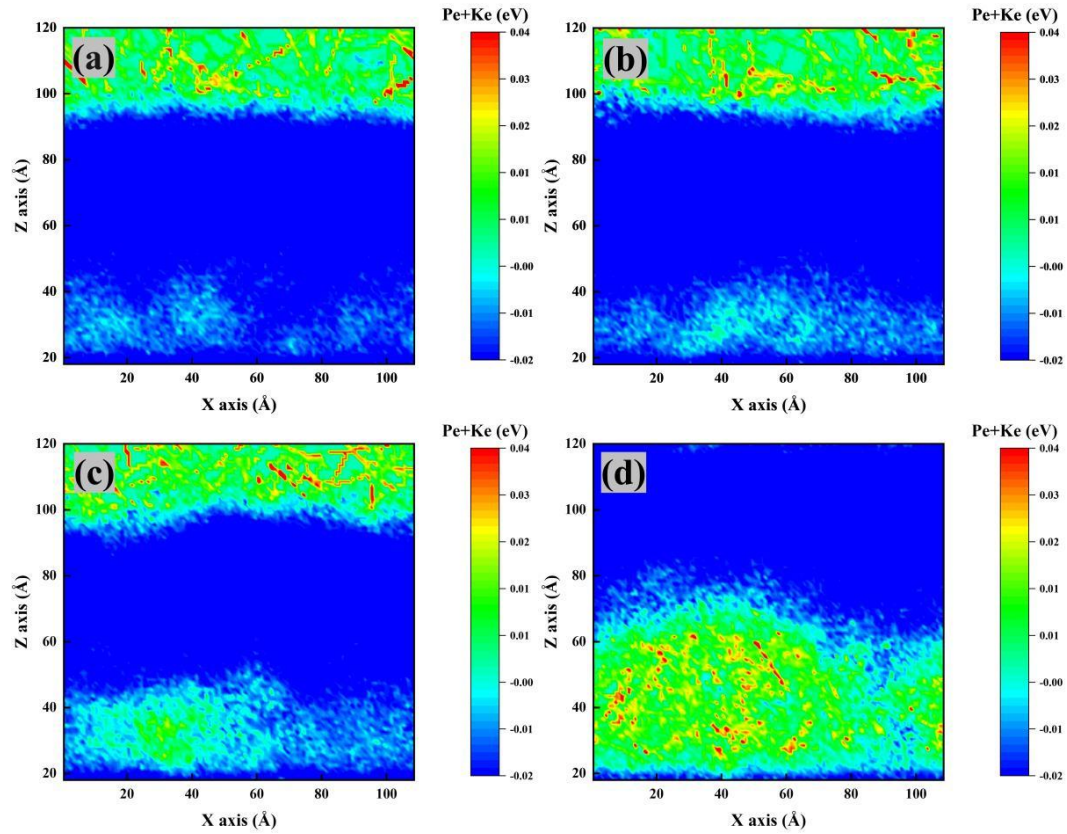


Figure 6.5 Total energy distribution contours on #LPi surface with $\epsilon_{Ar_Cu} = 0.0455$ eV: (a) $t = 1200$ ps, (b) $t = 1400$ ps, (c) $t = 1600$ ps, (d) $t = 1800$ ps

The analytical results obtained for the fully hydrophilic surface are likewise applicable to the hydrophilic/hydrophobic composite surfaces. As shown in Figure 6.6, the bubble growth process is also observed on the #0.25_L4 surface using the vapor–liquid interface visualization tool in Ovito, and the evolution of bubble growth corresponds to the changes in the near-wall total-energy distribution shown in Figure 6.6(a)–(d). Therefore, the statistical method for bubble volume presented in Chapter 2.4.7 is demonstrated to be effective.

It is important to note, however, that although the bubble growth behavior on the #0.25_L4 and #LPi surfaces both undergo the stages of nucleation, growth, and coalescence, differences arise due to the distinct wettability distributions on the two types of surfaces. The variation in surface wettability alters the solid–liquid energy transfer process, which ultimately leads to differences in bubble volume evolution, bubble nucleation time, and vapor-film formation time. To further investigate bubble growth on the wall surfaces, this work conducts a statistical analysis of bubble volume evolution, the onset of bubble nucleation t_{ONB} , and the vapor-film formation time t_{FB} during the bubble growth process.

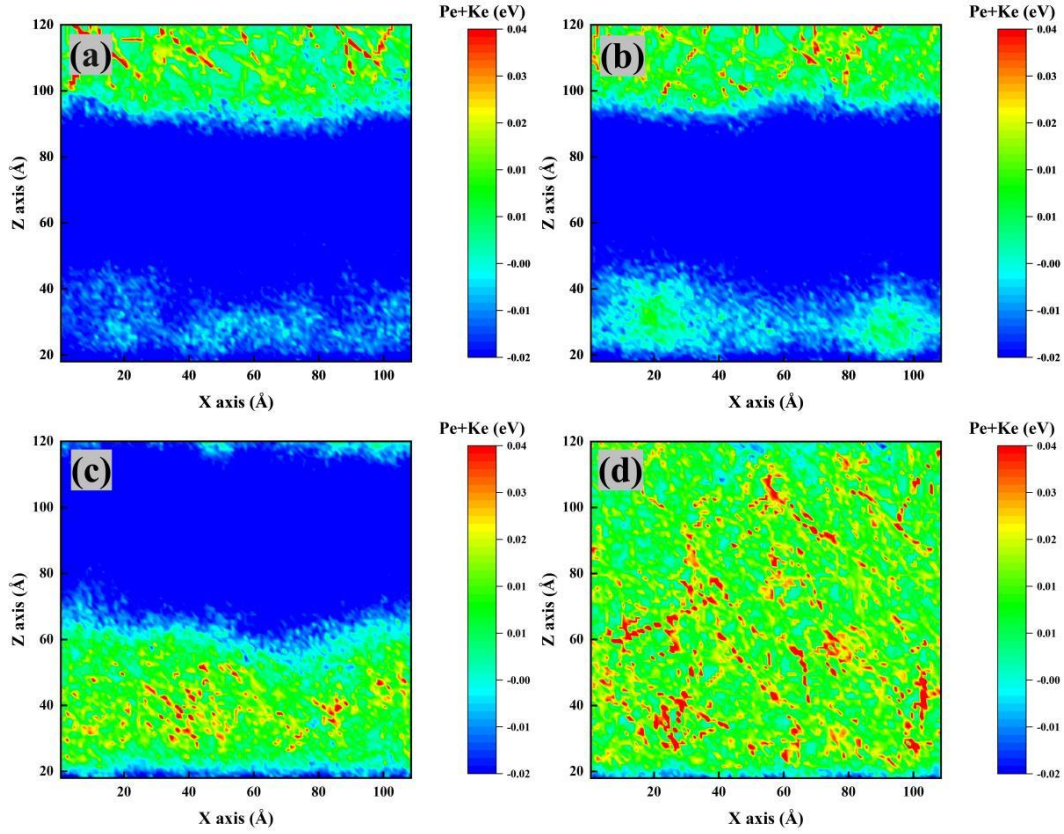


Figure 6.6 Total energy distribution contours on #0.25_L4 surface with $\epsilon_{Ar-Cu}=0.0455$ eV: (a) $t=1400$ ps, (b) $t=1600$ ps, (c) $t=1800$ ps, (d) $t=2000$ p

The variation in bubble volume on the wall surfaces is shown in Figure 5.7(a) and (b). As illustrated in the figure, bubbles on the wall undergo a period of slow growth followed by rapid coalescence. When the bubble growth curve reaches its maximum value, all bubbles on the wall have merged, forming a vapor film on the surface. When the solid–liquid interaction strength in the hydrophilic regions is $\epsilon_{Ar-Cu}=0.0455$ eV, the bubble volume on the #0.25_L4 surface in the hydrophilic/hydrophobic composite wall begins to change first, followed sequentially by #0.25_L2, #0.25_L5, #0.25_L3, and #0.25_L1. However, when the solid–liquid interaction strength in the hydrophilic regions increases to 0.0975 eV, the order in which bubble-volume evolution occurs changes: the bubble volume on #0.25_L3 changes first, while the differences in the onset time of bubble-volume evolution among the remaining composite surfaces become relatively small.

It is noteworthy that no bubbles are generated on the fully hydrophobic surface

#LPo throughout the simulation. Due to the weak solid–liquid interaction on this surface, energy transfer is insufficient, and the surface remains in a state of slow evaporation during the entire simulation. Among all other surfaces, the bubble growth curve on the fully hydrophilic surface #LPi consistently lags behind those of the composite surfaces, indicating the latest bubble growth onset and the weakest boiling heat transfer performance mediated by solid–liquid interactions.

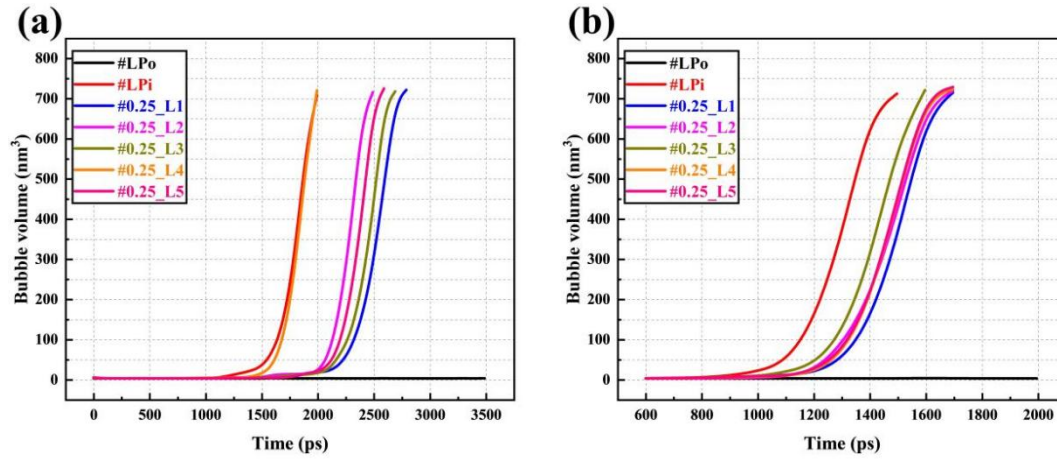


Figure 6.7 Curves of bubble volume growth: (a) $T_m = 160\text{ K}$, $\epsilon_{Ar_Cu} = 0.0455\text{ eV}$, (b) $T_m = 160\text{ K}$, $\epsilon_{Ar_Cu} = 0.0975\text{ eV}$

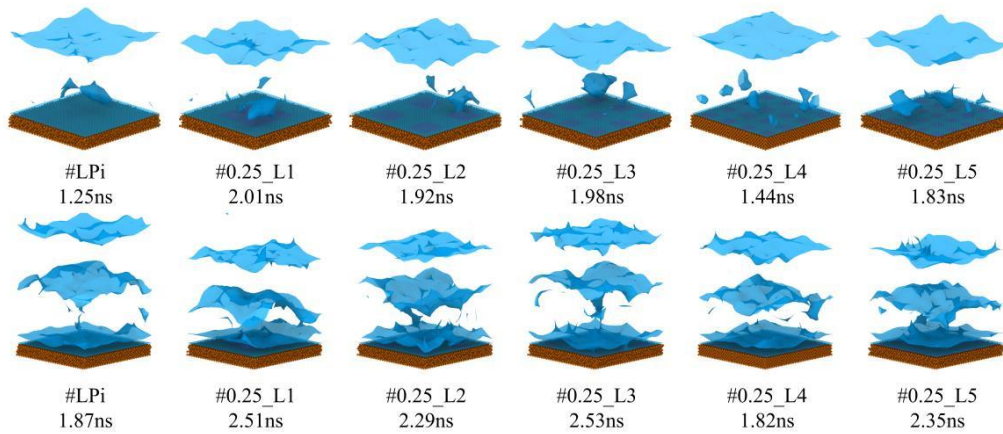


Figure 6.8 Diagrams of bubble nuclear and vapor film formation with $T_m = 160\text{ K}$ and hydrophilic region $\epsilon_{Ar_Cu} = 0.0455\text{ eV}$

By utilizing the visualization capabilities of Ovito, the initial bubble growth time and the vapor-film formation time on the wall surfaces were determined with improved accuracy. As shown in Figure 6.8 and Figure 6.9, compared with the fully hydrophilic

surface, a larger number of bubbles appear at the onset of bubble growth on the hydrophilic/hydrophobic composite surfaces, and these bubbles tend to nucleate preferentially in the hydrophobic regions. At the instants of initial bubble growth and vapor-film formation, the temperature at the onset of nucleation T_{ONB} , the temperature at vapor-film formation T_{FB} , and the time interval from initial bubble growth to vapor-film formation Δt were statistically analyzed for all wall surfaces. The corresponding parameters are summarized in Table 6.2.

From Table 6.2, it can be observed that, compared with the fully hydrophilic surface #LPi, all hydrophilic/hydrophobic composite surfaces #0.25_L1 to #0.25_L5 reduce Δt to varying degrees. Among them, surface #0.25_L4 exhibits the best performance in promoting bubble growth, coalescence, and solid-liquid heat transfer. The value of Δt on this surface is reduced by 61.3% relative to #LPi, significantly shortening the bubble development period on the wall. However, the onset time t_{ONB} on the composite surfaces still lags behind that of the fully hydrophilic surface #LPi, indicating that the composite-wall configuration does not substantially improve the reduction of t_{ONB} .

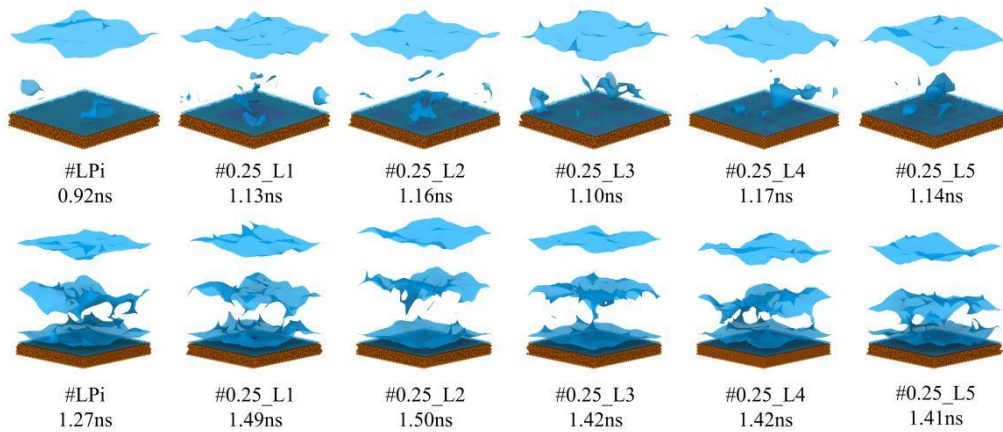


Figure 6.9 Diagrams of bubble nuclear and vapor film formation with $T_m = 160 \text{ K}$ and hydrophilic region $\varepsilon_{\text{Ar-Cu}} = 0.0455 \text{ eV}$

Table 6.2 State parameters at bubble initial growth and vapor film formation times with $T_m=160$ K and hydrophilic region $\epsilon_{Ar-Cu}=0.0455$ eV

Surface	t_{ONB} [ns]	t_{FB} [ns]	Δt [ns]	T_{ONB} [K]	T_{FB} [K]	ΔT [K]
#LPi	1.25	1.87	0.62	130.89	133.17	2.28
#0.25_L1	2.01	2.51	0.50	133.96	136.72	2.74
#0.25_L2	1.92	2.29	0.37	135.42	138.24	2.82
#0.25_L3	1.98	2.53	0.55	135.81	138.46	2.65
#0.25_L4	1.46	1.98	0.52	132.19	134.96	2.77
#0.25_L5	1.83	2.35	0.52	133.51	136.64	3.13

To shorten the t_{ONB} on hydrophilic/hydrophobic composite surfaces, the solid–liquid interaction strength in the hydrophilic regions was increased. As shown in Table 6.3, when the solid–liquid interaction strength in the hydrophilic regions increases from 0.0455 eV to 0.0975 eV, both t_{ONB} and t_{FB} on the fully hydrophilic surface #LPi are reduced. Bubble nucleation and vapor-film formation occur earlier on the wall surface, and compared with the case of $\epsilon_{Ar-Cu}=0.0455$ eV, the value of Δt is shortened by 43.5%. Moreover, the liquid-phase Ar temperatures T_{ONB} and T_{FB} also decrease, with ΔT reduced by 38.6%.

For the hydrophilic/hydrophobic composite surfaces, the differences in t_{ONB} among the surfaces become smaller when the hydrophilic-region solid–liquid interaction strength is $\epsilon_{Ar-Cu}=0.0975$ eV, consistent with the bubble-growth curves of the composite surfaces shown in Figure 6.7(b). Among these surfaces, #0.25_L4 exhibits the smallest Δt .

Table 6.3 State parameters at bubble initial growth and vapor film formation time with $T_m=160$ K and hydrophilic region $\epsilon_{Ar-Cu}=0.0975$ eV

Surface	t_{ONB} [ns]	t_{FB} [ns]	Δt [ns]	T_{ONB} [K]	T_{FB} [K]	ΔT [K]
#LPi	0.92	1.27	0.35	128.94	130.34	1.40
#0.25_L1	1.13	1.49	0.36	129.17	132.86	3.69
#0.25_L2	1.16	1.50	0.34	128.98	133.64	4.66
#0.25_L3	1.10	1.42	0.32	128.92	133.28	4.37
#0.25_L4	0.94	1.20	0.25	128.93	131.56	2.72
#0.25_L5	1.14	1.41	0.27	128.93	131.65	2.72

6.2.2. Variation in the Number of Evaporated Atoms on Smooth Hydrophilic/Hydrophobic Composite Surfaces

During the simulation, in order to evaluate the boiling rate of different hydrophilic/hydrophobic composite surfaces under various solid–liquid interaction strengths, the interaction strength in the hydrophilic regions was further refined. The number of evaporated atoms on each surface was statistically analyzed, and the evaporation rate was calculated accordingly. The results are presented in Figure 6.10.

The calculations show that although the hydrophilic/hydrophobic composite surfaces differ from the fully hydrophilic surface in terms of the spatial distribution of wettability, the evaporation rate on all six surfaces decreases as the solid–liquid interaction strength increases. Specifically, when the interaction strength increases from 0.0455 eV to 0.0975 eV, the evaporation rate on the fully hydrophilic surface #LPi decreases from 50.1% to 42.3%, representing a reduction of 7.8%. For the composite surfaces #0.25_L1, #0.25_L2, #0.25_L3, #0.25_L4, and #0.25_L5, the evaporation rates likewise decrease with increasing interaction strength, and the reduction magnitudes are generally larger than that of #LPi. Among these, surface #0.25_L3 exhibits the greatest decrease, with the evaporation rate dropping from 57.6% to 43.3%—a reduction of nearly 14.3%. Surface #0.25_L4 shows the smallest decrease, with the evaporation rate decreasing from 50.4% to 42.8%, corresponding to a reduction of only 7.6%.

Furthermore, compared with the fully hydrophilic surface #LPi, all hydrophilic/hydrophobic composite surfaces exhibit varying degrees of enhancement in evaporation rate. When the solid–liquid interaction strength is 0.0455 eV, the surface with the highest evaporation rate is #0.25_L1, whose evaporation rate is 7.7% higher than that of #LPi. As the interaction strength continues to increase, although the evaporation rate of #0.25_L1 decreases slightly, its enhancement relative to #LPi continues to grow. When the solid–liquid interaction strength reaches 0.0585 eV, the evaporation rate of #0.25_L1 shows the largest improvement, exceeding that of #LPi by 8.1%.

However, with further increases in the interaction strength, the surface exhibiting

the highest evaporation rate begins to change, and the difference from the fully hydrophilic surface gradually decreases. When the solid–liquid interaction strength increases to 0.0650 eV and 0.0975 eV, the surface with the highest evaporation rate becomes #0.25_L2, whose evaporation rate exceeds that of #LPi by 7.9% and 2.5%, respectively.

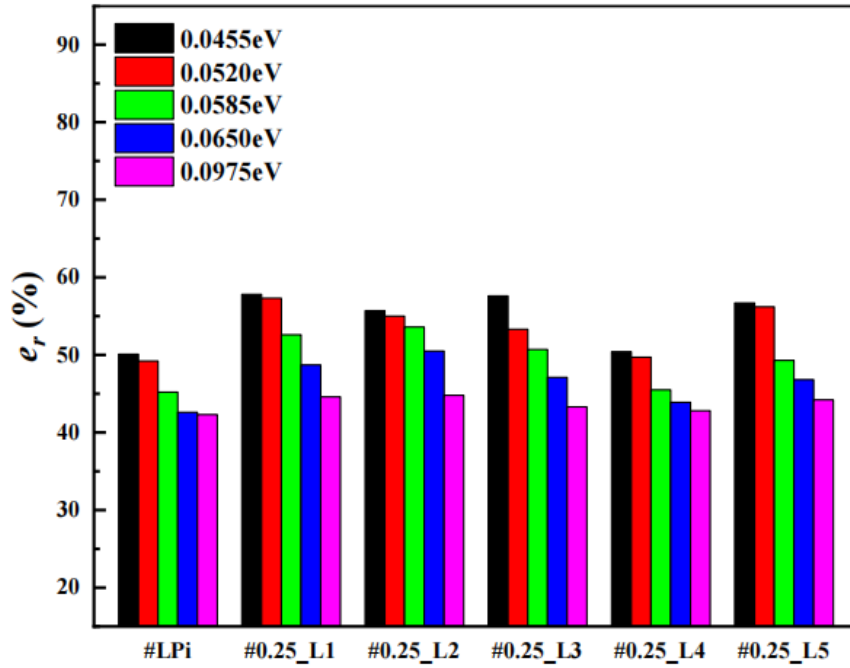


Figure 6.10 Evaporation rate of hybrid-wettability surfaces with different solid-liquid interaction

By comparing the evaporation rates of the hydrophilic/hydrophobic composite surfaces with that of the fully hydrophilic surface, it can be observed that the enhancement of solid–liquid interactions suppresses the increase in evaporation rate. However, the strength of this suppression does not exhibit a monotonic or synergistic relationship with the magnitude of the solid–liquid interaction. As indicated by the preceding analysis, when the interaction strength is 0.0585 eV, the composite surfaces actually achieve the greatest improvement in evaporation rate. In contrast, when the solid–liquid interaction reaches its maximum value, the differences in evaporation rate among the various surfaces become very small, with the maximum difference being only 2.5%.

6.2.3. Variations in Interfacial Thermal Resistance on Smooth Hydrophilic/Hydrophobic Composite Surfaces

From the evaporation-rate results presented in Chapter 5.2.1, it can be seen that the solid–liquid interaction strength and the spatial distribution of hydrophilic/hydrophobic regions on the wall surface both influence the heat-transfer process at the solid–liquid interface. To further investigate the underlying mechanisms, this section examines the interfacial thermal resistance between the solid and liquid phases. The selected surfaces are #LPi, #0.25_L1, #0.25_L2, #0.25_L3, #0.25_L4, and #0.25_L5, and the interaction strength between Cu atoms in the hydrophilic regions and Ar atoms is kept consistent with that used in Chapter 5.2.2.

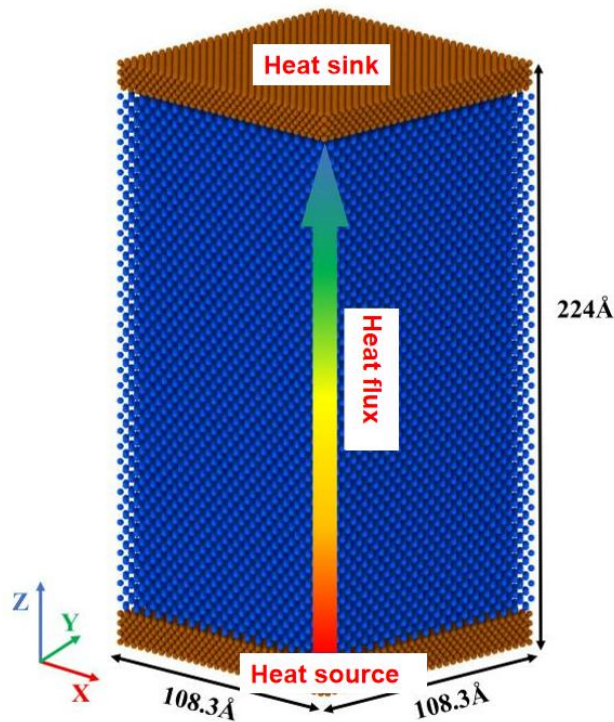


Figure 6.11 Calculation model of interfacial thermal resistance

Heat transfer resistance between the solid and liquid phases is investigated. The thermal-resistance calculation model is constructed as shown in Figure 6.11. The dimensions of the heat source and heat sink layers are the same as those of the metal substrate in Chapter 5.1.1, with a size of $L_x \times L_y = 108.3 \text{ Å} \times 108.3 \text{ Å}$. This ensures consistency between the thermal-resistance model and the boiling model in terms of the

size and spatial distribution of hydrophilic/hydrophobic regions in the heat source and heat sink layers.

In the thermal-resistance model, the temperature of the heat source layer is set to 160 K, and that of the heat sink layer is set to 86 K. The interfacial thermal resistance is calculated using the following expression:

$$R = \frac{\Delta T}{q} \quad \text{Equation 6.1}$$

where ΔT is the temperature difference between the heat source layer and the first layer of Ar atoms above the wall surface, and q represents the heat flux density.

When the solid–liquid interaction strength is 0.0455 eV, the variations in the data obtained from the thermal-resistance model are shown in Figure 6.12. Figure 6.12(a) illustrates the time-dependent energy accumulation in the heat source and heat sink layers, where negative values represent energy released from the layer and positive values represent energy absorbed. Under the combined influence of the heat source and heat sink, the system energy reaches a steady state, and a stable temperature gradient is established in the liquid phase along the heat-flux direction (the Z-direction), as shown in Figure 6.12(b).

Based on the slope of the curves in Figure 6.12(a) and the temperature-gradient distribution in Figure 6.12(b), the heat flux density q and the temperature difference ΔT can be obtained, respectively. The interfacial thermal resistance can then be calculated using Equation 6.1.

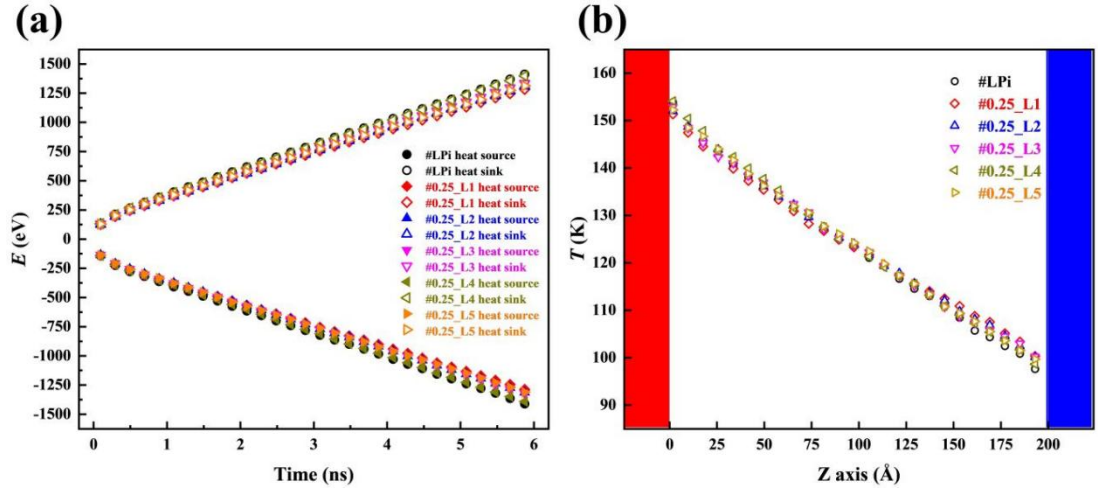


Figure 6.12 Variation of thermal resistance model data when solid-liquid interaction equals 0.0455 eV: (a) Variation of accumulated energy of heat source and heat sink, (b) Temperature distribution in Z axis.

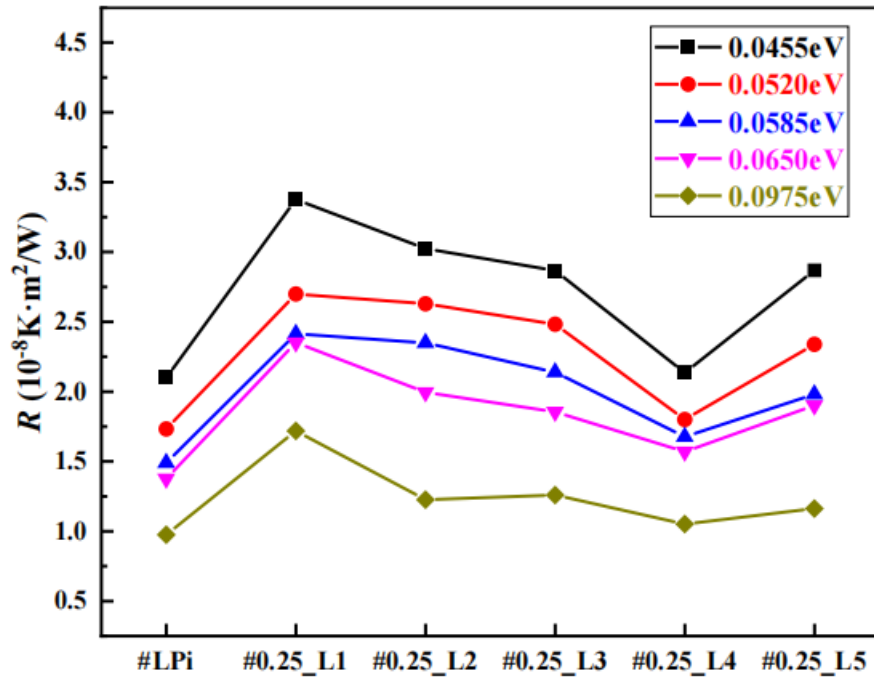


Figure 6.13 Variation of interfacial thermal resistance with different solid-liquid interaction

The calculated thermal resistances of the wall surfaces are shown in Figure 6.13. It can be observed that as the solid-liquid interaction strength increases, the thermal resistance of all six surfaces decreases. This is because stronger solid-liquid interactions enhance the energy exchange at the interface, allowing more energy to be

transferred across the solid–liquid boundary per unit time. As a result, interfacial heat-transfer performance is strengthened, which manifests as a reduction in interfacial thermal resistance. This finding further explains the variation in evaporation rate with interaction strength discussed in Chapter 5.2.2.

In addition, the calculated results reveal that the spatial distribution of hydrophilic and hydrophobic regions on the wall surface also influences the interfacial thermal resistance. Among the surfaces #0.25_L1 to #0.25_L5, the thermal resistance first decreases and then increases as the number of segmented hydrophobic regions increases. Notably, compared with the other composite surfaces, #0.25_L4 exhibits a significantly lower thermal resistance. As the solid–liquid interaction increases, the thermal resistance of #0.25_L4 becomes 37%, 33%, 13%, and 8% lower than that of the surface with the highest resistance, #0.25_L1. Compared with the fully hydrophilic surface #LPi, which has the lowest overall thermal resistance, the resistance of #0.25_L4 is only 2% higher at minimum and 14% higher at maximum.

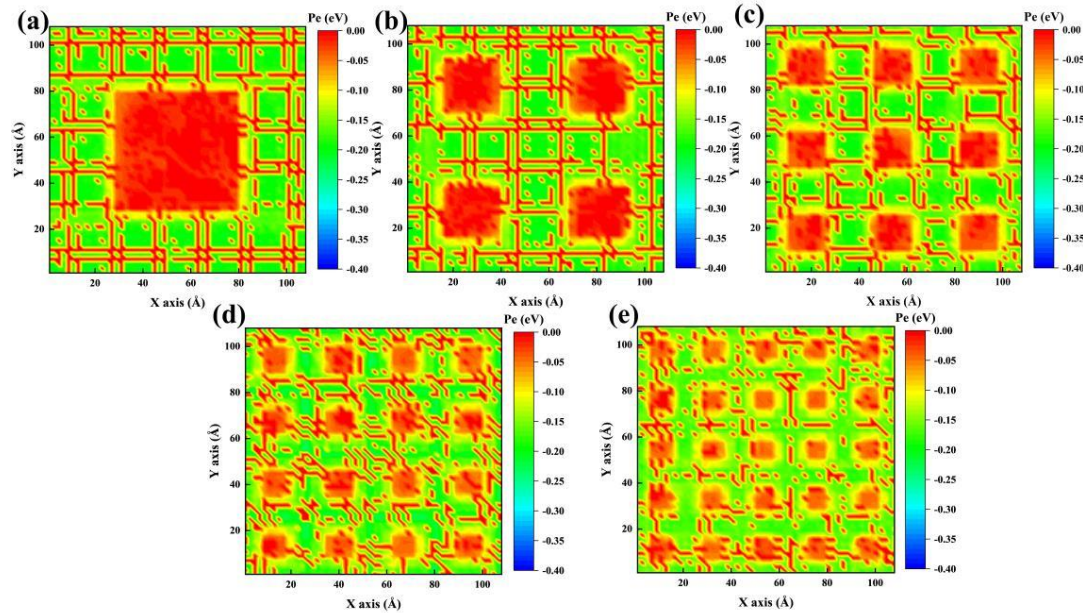


Figure 6.14 Potential energy distribution with hydrophilic region $\epsilon_{Ar_Cu} = 0.0455$ eV: (a) #0.25_L1, (b) #0.25_L2, (c) #0.25_L3, (d) #0.25_L4, (e) #0.25_L5

From the above analysis, it can be concluded that as the solid–liquid interaction strength increases, the potential energy in the low–potential-energy region near the wall

also increases (i.e., its magnitude becomes larger). This raises the potential-energy barrier between solid and liquid atoms, requiring liquid-phase atoms to absorb more energy in order to overcome the “confinement” imposed by the solid wall atoms. Consequently, the solid–liquid heat-transfer process becomes more stable, the interfacial heat-transfer efficiency is enhanced, and the interfacial thermal resistance is reduced.

Moreover, as the number of hydrophobic regions on the wall increases, the thermal resistance exhibits a trend of first decreasing and then increasing. Calculations of the potential-energy distribution on the wall surface show that from surfaces #0.25_L1 to #0.25_L4, the low-potential-energy regions surrounding the hydrophobic patches become more compact. However, when the number of hydrophobic segments is further reduced, as in surface #0.25_L5, the potential energy in the low-potential-energy region begins to decrease, with the effect becoming particularly significant when the solid–liquid interaction strength reaches 0.0975 eV.

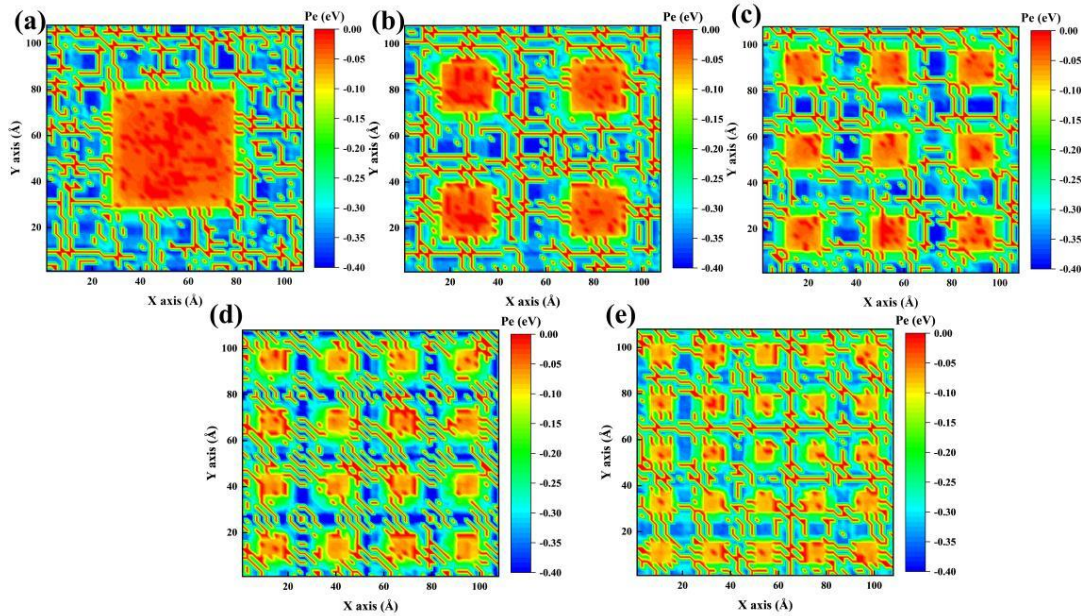


Figure 6.15 Potential energy distribution with hydrophilic region $\epsilon_{Ar_Cu} = 0.0975$ eV: (a)#0.25_L1, (b)#0.25_L2, (c)#0.25_L3, (d)#0.25_L4, (e)#0.25_L5

6.3. Effects of Hydrophilic/Hydrophobic Surface Coverage Ratio on the Pool Boiling Heat Transfer Characteristics of Smooth Composite Surfaces

The previous section examined the influence of solid–liquid interaction strength within hydrophilic regions on the pool-boiling heat transfer characteristics of smooth hydrophilic/hydrophobic composite surfaces. In this section, the focus shifts to the effect of the hydrophobic-area coverage ratio β on bubble dynamic growth, evaporation rate, and interfacial thermal resistance. Additionally, in order to investigate the influence of β on pool-boiling heat transfer under comparable boiling conditions, the wall temperature is increased to 180 K in this section. This ensures that boiling can still occur at relatively low solid–liquid interaction strengths when β is large, thereby facilitating consistent comparison of the simulation results.

6.3.1. Variations in Bubble Dynamic Growth on Smooth Hydrophilic/Hydrophobic Composite Surfaces

To investigate the influence of the hydrophobic-area coverage ratio β on the solid–liquid heat-transfer process, hydrophilic/hydrophobic composite surfaces with $\beta=0.25$, $\beta=0.36$, $\beta=0.49$, and $\beta=0.64$ are constructed at a wall temperature of $T_m=180$ K. The variations in bubble volume on these surfaces are compared with those on the fully hydrophobic surface #LPo and the fully hydrophilic surface #LPi. As shown in Figure 6.16, the hydrophobic surface undergoes only a slow evaporation process due to its weak solid–liquid interactions, and no bubble nucleation occurs; consequently, its bubble-growth curve remains a straight line. In contrast, bubble formation and boiling occur on the fully hydrophilic surface #LPi and on all hydrophilic/hydrophobic composite surfaces.

Moreover, the bubble growth curve of the fully hydrophilic surface #LPi consistently leads those of the composite surfaces, and this leading effect becomes more pronounced as β increases. Among the composite surfaces, #0.25_L4, #0.36_L4, #0.49_L4, and #0.64_L4 exhibit more advanced bubble-growth behavior than the other composite configurations. In contrast, the surfaces #0.25_L1, #0.36_L1, #0.49_L1, and #0.64_L1 show the slowest bubble-growth progression. Therefore, in terms of hydrophobic-region spatial arrangement, the 4×4 segmentation pattern demonstrates superior performance in promoting bubble growth, whereas the 1×1 pattern is

comparatively less favorable. The performance of the other hydrophobic-region configurations falls between these two extremes.

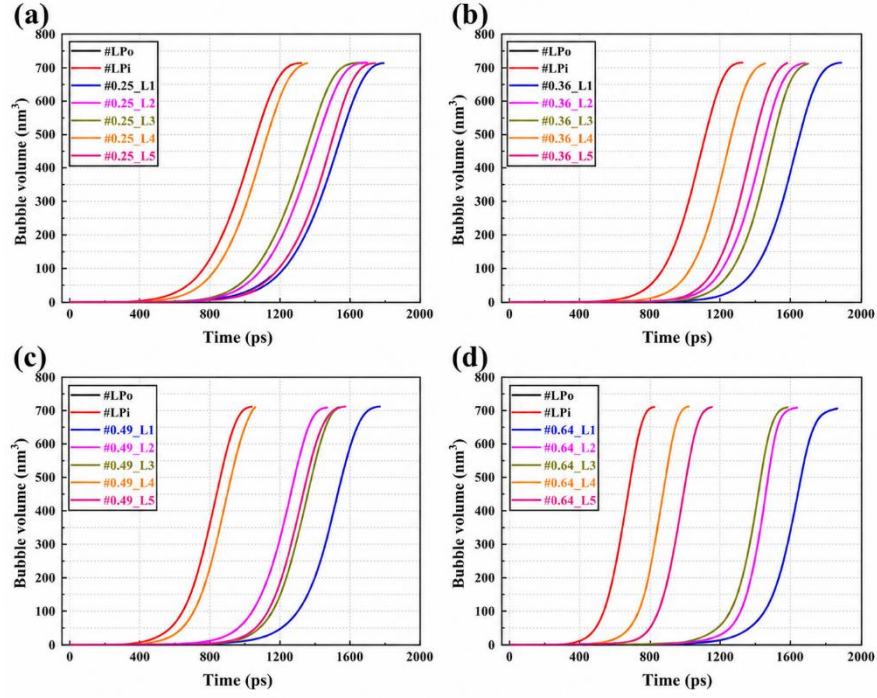


Figure 6.16 Curves of bubble volume growth with $T_m = 180$ K and hydrophilic region solid-liquid interaction $\varepsilon_{Ar_Cu} = 0.0455$ eV: (a) $\beta = 0.25$, (b) $\beta = 0.36$, (c) $\beta = 0.49$, (d) $\beta = 0.64$

Furthermore, due to the increased wall temperature, both the initial bubble growth time t_{ONB} and the vapor-film formation time t_{FB} occur earlier. As shown in Figure 6.17, the t_{ONB} on the fully hydrophilic surface shortens to 0.50 ns, representing a 60% reduction compared with the case of $T_m = 160$ K. The vapor-film formation time is reduced to 0.74 ns, a decrease of 63.2%. Among the hydrophilic/hydrophobic composite surfaces, #0.25_L4 exhibits the shortest t_{ONB} and t_{FB} , consistent with the bubble-growth curve in Figure 6.16(a), where #0.25_L4 leads the other composite surfaces. Compared with the fully hydrophilic surface, the differences are only 10% and 1.4%, respectively. Relative to the case of $T_m = 160$ K, its t_{ONB} and t_{FB} are reduced by 61.8% and 58.8%, respectively. For surface #0.25_L3, the increases in T_m lead to the largest reductions in t_{ONB} and t_{FB} , which decrease by 67.7% and 65.6%, respectively.

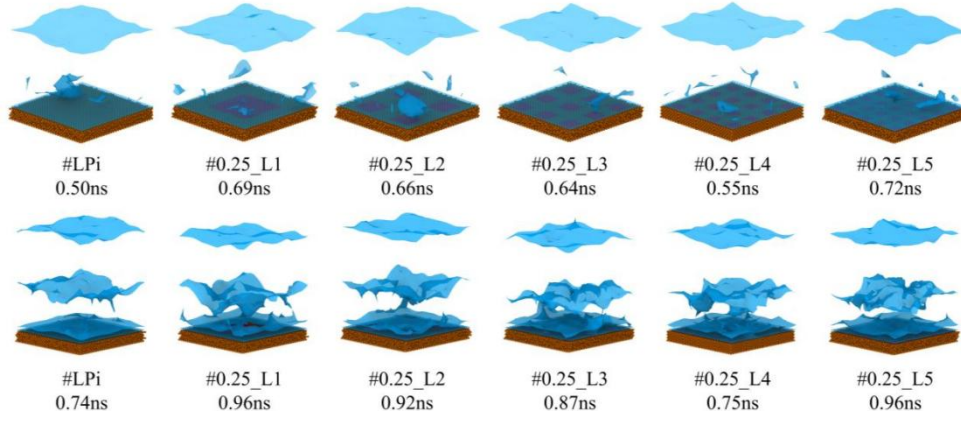


Figure 6.17 Diagrams of bubble nuclear and vapor film formation with $T_m = 180\text{ K}$, hydrophilic region $\epsilon_{\text{Ar_Cu}} = 0.0455\text{ eV}$ and $\beta = 0.25$

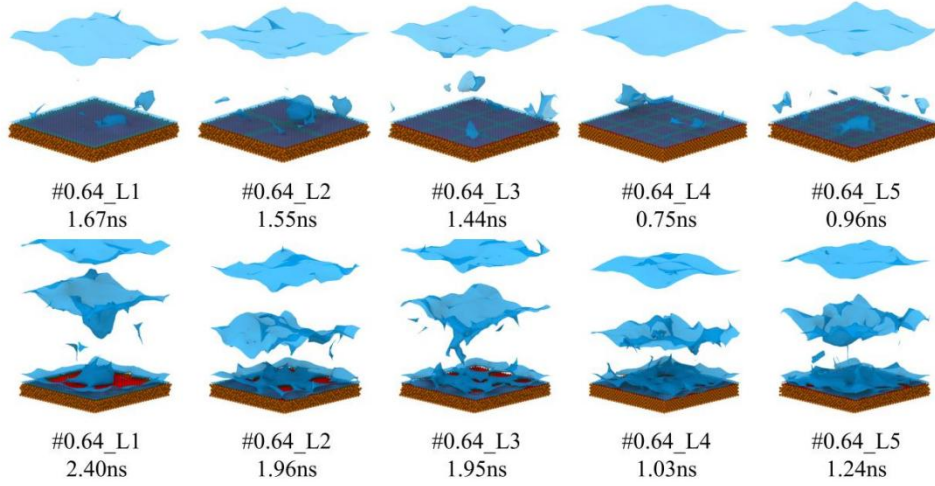


Figure 6.18 Diagrams of bubble nuclear and vapor film formation with $T_m = 180\text{ K}$, hydrophilic region $\epsilon_{\text{Ar_Cu}} = 0.0455\text{ eV}$ and $\beta = 0.64$

As the hydrophobic-area coverage ratio β increases, both t_{ONB} and t_{FB} on the hydrophilic/hydrophobic composite surfaces begin to increase. As shown in Figure 6.18, when $\beta = 0.64$, the t_{ONB} and t_{FB} of the #0.64_L4 surface increase to 0.75 ns and 1.03 ns, respectively, which are 50% and 39.2% higher than those of the fully hydrophilic surface #LPi. For the #0.64_L1 surface, t_{ONB} and t_{FB} increase by 234% and 224.3%, respectively.

From the above simulation results, it can be observed that increasing the wall temperature promotes the reduction of t_{ONB} and t_{FB} . However, the t_{ONB} on hydrophilic/hydrophobic composite surfaces remains higher than that of the fully hydrophilic surface, and the difference in t_{ONB} and t_{FB} among different surfaces

becomes larger as β increases. As discussed in Chapter 5.2.1, increasing the solid–liquid interaction strength on the wall can shorten t_{ONB} and t_{FB} . Therefore, in this section, the solid–liquid interaction strength $\varepsilon_{\text{Ar-Cu}}$ in the hydrophilic regions is increased to investigate its influence on bubble dynamic growth.

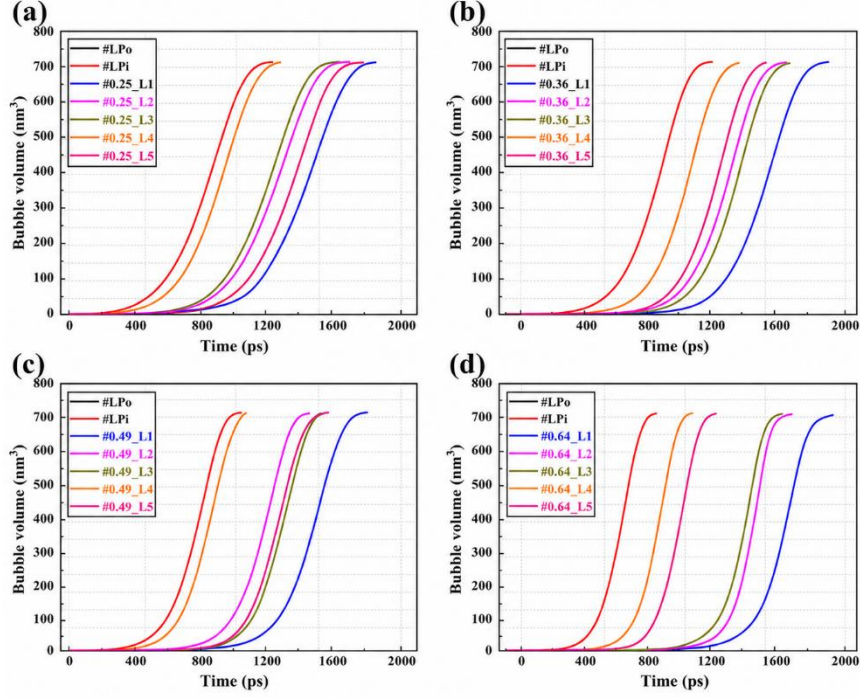


Figure 6.19 Curves of bubble volume growth with $T_m = 180$ K and hydrophilic region solid-liquid interaction $\varepsilon_{\text{Ar-Cu}} = 0.0975$ eV: (a) $\beta=0.25$, (b) $\beta=0.36$, (c) $\beta=0.49$, (d) $\beta=0.64$

As shown in Figure 6.19, when the solid–liquid interaction strength in the hydrophilic regions $\varepsilon_{\text{Ar-Cu}}$ is increased to 0.0975 eV, the bubble-growth curves on different surfaces diverge progressively as β increases. For surfaces with $\beta=0.25$, the bubble-growth curves of #0.25_L3 and #0.25_L4 lead that of the fully hydrophilic surface #LPi. When the solid–liquid interaction strength increases, the differences in t_{ONB} and t_{FB} among the surfaces become smaller, as shown in Figure 6.20. Compared with #LPi, the values of t_{ONB} and t_{FB} on #0.25_L1 differ by only 11.4% and 12.9%, respectively. Moreover, on surfaces #0.25_L2, #0.25_L3, and #0.25_L4, both t_{ONB} and t_{FB} are shorter than those on #LPi, with maximum reductions of 6.8% and 4.8%, respectively.

In addition to the statistical analysis of t_{ONB} and t_{FB} , the temperatures and other

thermodynamic quantities in the liquid phase at these two moments were also evaluated. The detailed data are summarized in Table 6.4.

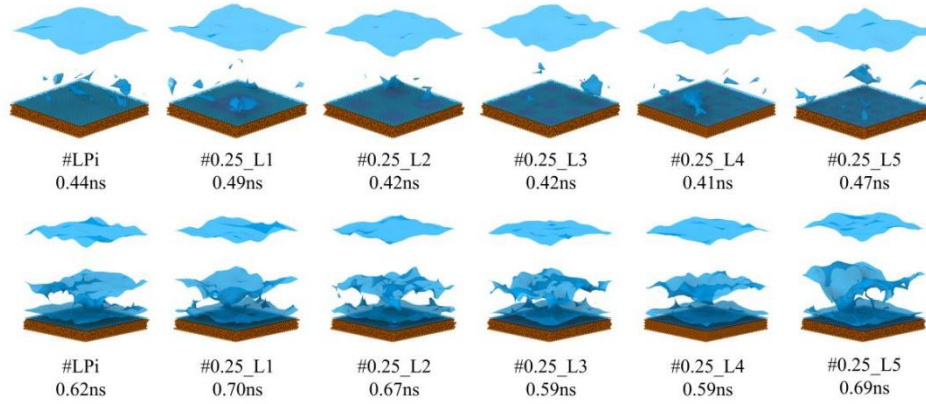


Figure 6.20 Diagrams of bubble nuclear and vapor film formation with $T_m = 180$ K, hydrophilic region $\epsilon_{Ar-Cu} = 0.0455$ eV and $\beta = 0.25$

Table 6.4 State parameters at bubble initial growth and vapor film formation time with $T_m = 180$ K, hydrophilic region $\epsilon_{Ar-Cu} = 0.0975$ eV and $\beta = 0.25$

Surface	t_{ONB} [ns]	t_{FB} [ns]	Δt [ns]	T_{ONB} [K]	T_{FB} [K]	ΔT [K]
#LPi	0.44	0.62	0.18	124.12	130.31	6.19
#0.25_L1	0.49	0.70	0.21	124.72	127.75	3.03
#0.25_L2	0.42	0.67	0.25	124.89	129.98	5.09
#0.25_L3	0.42	0.59	0.17	125.01	129.37	4.36
#0.25_L4	0.41	0.59	0.18	125.15	130.53	5.38
#0.25_L5	0.47	0.69	0.22	125.08	128.51	3.43

6.3.2. Variations in the Evaporation Rate on Smooth Hydrophilic/Hydrophobic Composite Surfaces

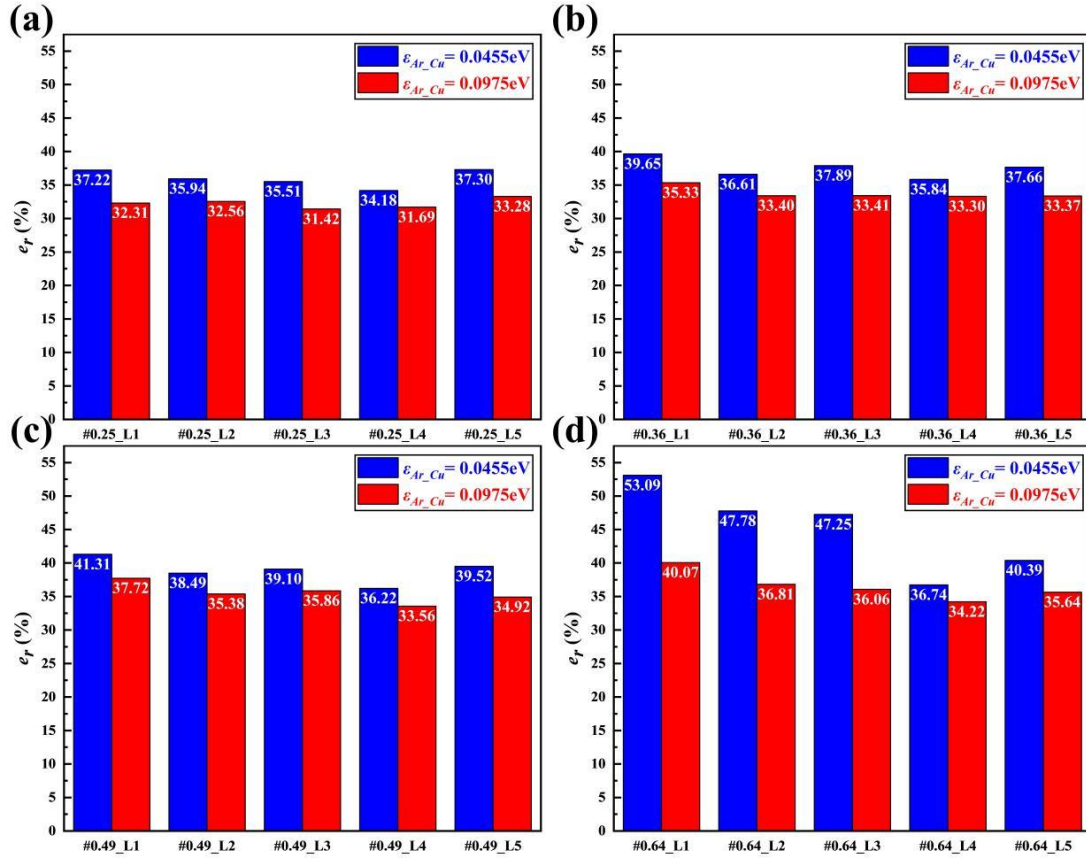


Figure 6.21 Variation of evaporation rate on hybrid-wettability surfaces with different β : (a) $\beta=0.25$, (b) $\beta=0.36$, (c) $\beta=0.49$, (d) $\beta=0.64$

The hydrophobic-area coverage ratio β not only alters the bubble growth process on the wall surface but also affects the evaporation rate. As shown in Figure 6.21, when the solid–liquid interaction strength in the hydrophilic regions is relatively low ($\epsilon_{Ar-Cu}=0.0455 \text{ eV}$), the evaporation rate increases with increasing β , as the proportion of hydrophobic regions becomes larger. When $\beta=0.64$, the wall surface exhibits the strongest evaporation performance; for example, the evaporation rate of surface #0.64_L1 is 42.6% higher than that of #0.25_L1. This demonstrates that the size of the hydrophobic region promotes the evaporation process.

However, when the solid–liquid interaction in the hydrophilic regions is increased ($\epsilon_{Ar-Cu}=0.0975 \text{ eV}$), the evaporation rate decreases compared with the case of $\epsilon_{Ar-Cu}=0.0455 \text{ eV}$. Moreover, this decrease becomes more pronounced as β increases.

For instance, on the #0.64_L1 surface, increasing the interaction strength leads to a 24.5% reduction in evaporation rate. Therefore, at high solid–liquid interaction strengths, the promoting effect of hydrophobic regions on evaporation is suppressed, and differences in evaporation rates among the surfaces become smaller. This trend is consistent with the observations discussed in Chapter 5.2.2.

Among the hydrophilic/hydrophobic composite surfaces, surface #0.64_L4 maintains a relatively low evaporation rate when $\varepsilon_{\text{Ar-Cu}}=0.0455$ eV. As shown in Figure 6.18, #0.64_L4 is the first surface to form a vapor film, suggesting that its reduced evaporation rate may be related to the early formation of the vapor film. To verify this hypothesis, the energy absorbed by Ar atoms was statistically analyzed for $\beta=0.64$ and $\varepsilon_{\text{Ar-Cu}}=0.0455$ eV, and the results were compared with the number of evaporated atoms on the wall surface, as shown in Figure 6.22.

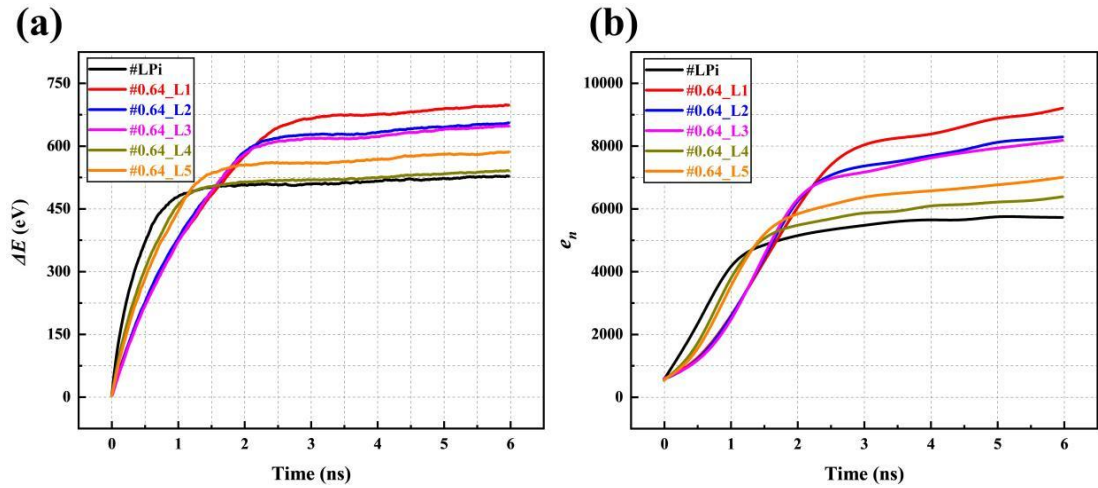


Figure 6.22 (a) Variation of absorbed energy by Ar atoms, (b) Variation of evaporated atom number

In Figure 6.22(a), the surfaces can be ranked in ascending order of the total absorbed energy as #LPi, #0.64_L4, #0.64_L5, #0.64_L3, #0.64_L2, and #0.64_L1. This ordering matches the sequence of evaporation rates from lowest to highest shown in Figure 6.21(d). Furthermore, by comparing Figure 6.22(a) and Figure 6.22(b), it can be observed that the curve representing the energy absorbed by Ar atoms exhibits a similar trend to the curve representing the number of evaporated atoms. A positive correlation exists between the evaporation rate of the wall surface and the amount of

energy absorbed by the Ar atoms. Additionally, the inflection point of the curves in Figure 6.22(a) occurs at a time very close to the vapor-film formation moment. For the #0.64_L4 surface, the energy-absorption curve exhibits an inflection point around 1 ns, which is consistent with the vapor-film formation time of 1.03 ns shown in Figure 6.18.

Therefore, it can be concluded that the relatively low evaporation rate of the #0.64_L4 surface is associated with the early formation of the vapor film. The presence of the vapor film hinders direct contact between the liquid phase and the solid wall, thereby disrupting the solid–liquid heat-transfer process. As a result, Ar atoms in the liquid phase can no longer continue absorbing heat from the wall, leading to a slowdown in the evaporation process. Consequently, the total number of evaporated atoms decreases, and the evaporation rate of the wall surface is reduced.

6.3.3. Variations in Interfacial Thermal Resistance on Smooth Hydrophilic/Hydrophobic Composite Surfaces

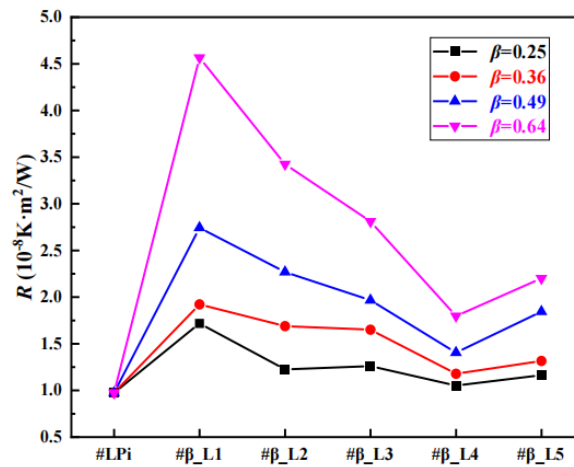


Figure 6.23 Variation of surfaces kapitza resistance with different β

In Chapter 5.2.3, the influence of solid–liquid interaction strength on interfacial thermal resistance was discussed. In this section, the same computational model and methodology are used to evaluate the interfacial thermal resistance of surfaces with different hydrophobic-area coverage ratios. The results are shown in Figure 6.24. As the hydrophobic-area ratio β increases, the interfacial thermal resistance of all surfaces increases accordingly. Among the composite surfaces, # β _L1 consistently exhibits the

highest thermal resistance. Compared with the fully hydrophilic surface #LPi, its thermal resistance increases by 76.39%, 97.28%, 181.57%, and 368.68% as β increases.

It is worth noting that for all values of β , the order of interfacial thermal resistance from smallest to largest is # β _L4, # β _L5, # β _L3, # β _L2, and # β _L1. This ordering is consistent with the ranking of absorbed energy at $\beta=0.64$ shown in Figure 6.22(a), where surfaces with larger absorbed energy correspond to lower interfacial thermal resistance.

Additionally, by comparing Figure 6.24 with the potential-energy distributions in Figure 6.25, it can be observed that as the number of hydrophobic segments increases, the contact contour between the hydrophobic and hydrophilic regions also increases. As a result, the low-potential-energy zones around the hydrophobic regions become more “compact.” When the number of hydrophobic segments increases from 4 to 5, as shown in Figure 6.24(d) and Figure 6.24(e), the potential energy within the surrounding low-potential-energy region becomes “diluted” due to the expanded hydrophobic segmentation, weakening the solid-liquid interaction at the wall. A similar “dilution” effect occurs when β increases from 0.36 to 0.64, as shown in Figure 6.25(d) and Figure 6.25(e).

Therefore, when the hydrophobic region is divided into four segments, the surface exhibits the lowest interfacial thermal resistance. In contrast, for the # β _L5 surface, the potential energy in the low-potential-energy region is further diluted, leading to weaker solid-liquid interactions and consequently a reduced interfacial heat-transfer capability.

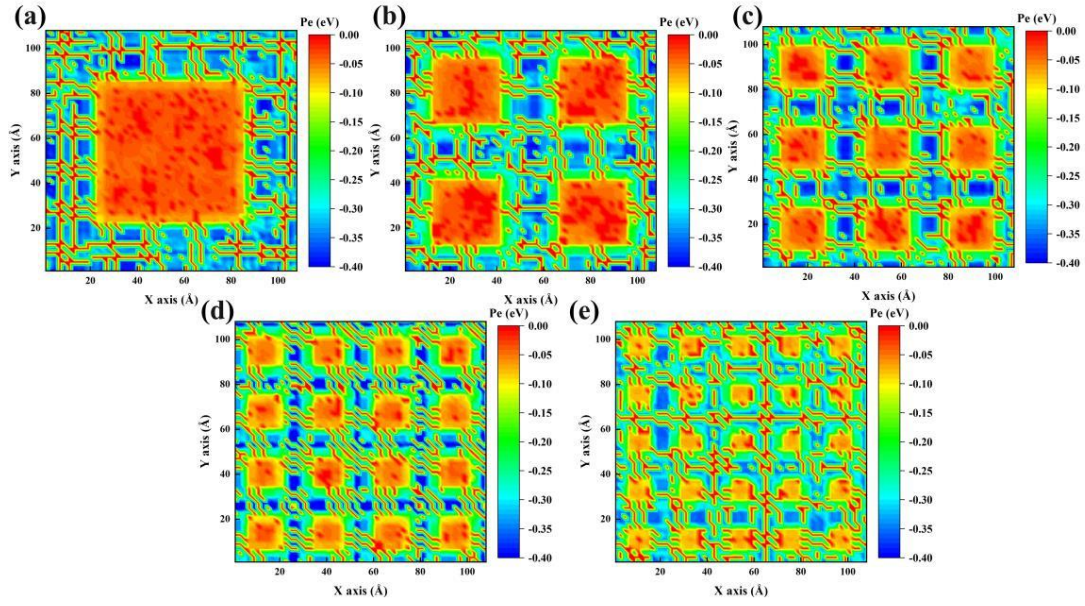


Figure 6.24 Potential energy distribution with hydrophilic region $\epsilon_{Ar_Cu} = 0.0975$ eV: (a) #0.36_L1, (b) #0.36_L2, (c) #0.36_L3, (d) #0.36_L4, (e) #0.36_L5

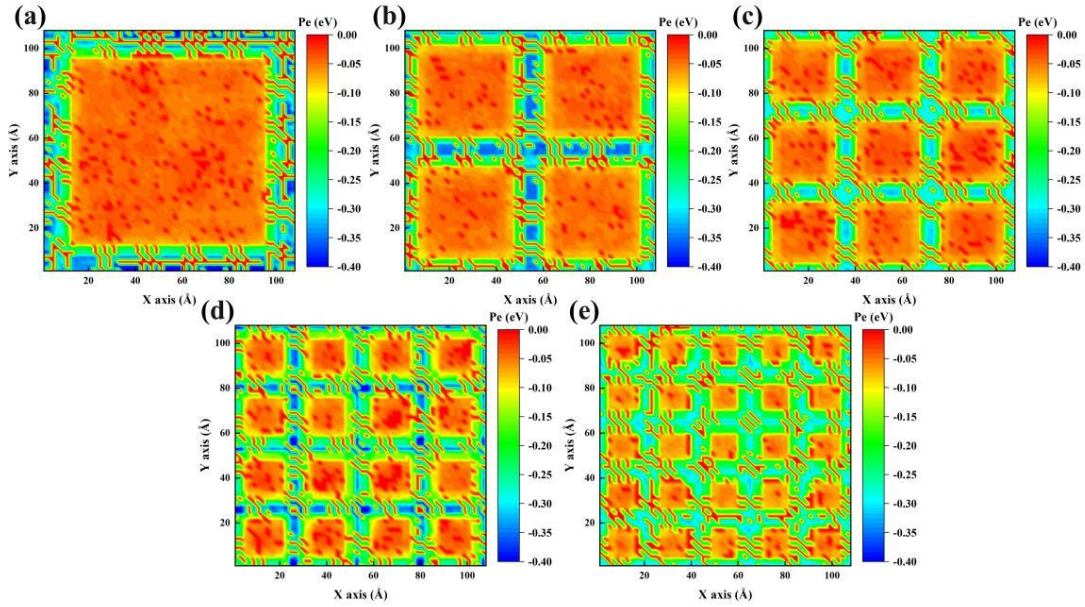


Figure 6.25 Potential energy distribution with hydrophilic region $\epsilon_{Ar_Cu} = 0.0975$ eV: (a) #0.64_L1, (b) #0.64_L2, (c) #0.64_L3, (d) #0.64_L4, (e) #0.64_L5

6.4. Conclusion

In this chapter, five hydrophilic/hydrophobic composite surfaces with different hydrophobic-region distributions (β_L1 , β_L2 , β_L3 , β_L4 , and β_L5) were constructed, and their pool-boiling heat transfer processes were investigated through

molecular dynamics simulations. The effects of solid–liquid interaction strength in the hydrophilic regions and the hydrophobic-area coverage ratio β on interfacial heat transfer were examined. Subsequently, the bubble-volume evolution, the onset of bubble nucleation and vapor-film formation (t_{ONB} , t_{FB}), the corresponding liquid-phase temperatures (T_{ONB} , T_{FB}), the evaporation rate, and the interfacial thermal resistance were analyzed and compared across surfaces. The results show that increasing the solid–liquid interaction strength shortens the bubble nucleation time, accelerates bubble growth, and enhances the evaporation rate. In addition, the spatial configuration of the hydrophobic regions also influences bubble growth, interfacial heat transfer, and thermal resistance.

The bubble nucleation process on hydrophilic/hydrophobic composite surfaces was investigated. At the onset of bubble growth, the number of bubbles increases significantly on the composite surfaces, and bubble nucleation tends to occur preferentially in the hydrophobic regions. Although the composite surfaces accelerate bubble growth, their ability to shorten t_{ONB} remains limited due to weaker solid–liquid interactions and relatively low wall temperatures. When the solid–liquid interaction strength in the hydrophilic regions increases to 0.0975 eV, the enhanced interactions strengthen interfacial energy transfer, causing earlier bubble nucleation and earlier vapor-film formation. Consequently, both T_{ONB} and T_{FB} decrease, and bubble growth is accelerated.

The evaporation behavior on hydrophilic/hydrophobic composite surfaces was examined. When the solid–liquid interaction strength is 0.0455 eV, surface #0.25_L1 exhibits the highest evaporation rate, increasing by 7.7% compared with the fully hydrophilic surface #LPi. However, increasing the interaction strength shortens t_{FB} , allowing the vapor film to form earlier. This interrupts contact between the liquid atoms and the solid wall, disrupts the solid–liquid heat-transfer process, and prevents liquid-phase Ar atoms from continuously absorbing energy and transitioning into vapor. When the interaction strength increases to 0.0975 eV, the maximum difference in evaporation rates decreases to only 2.5%.

The heat-transfer process on hydrophilic/hydrophobic composite surfaces was analyzed. When the wall temperature increases to 180 K, both t_{ONB} and t_{FB} occur earlier. However, as β increases, the solid–liquid heat-transfer process begins to deteriorate. The earlier formation of the vapor film prematurely disrupts the liquid–solid contact, reducing the amount of energy absorbed by the liquid phase.

The interfacial thermal resistance of hydrophilic/hydrophobic composite surfaces was studied. As the solid–liquid interaction strength increases, the interfacial heat-transfer process is enhanced, leading to reduced interfacial thermal resistance. Among the composite surfaces, #0.25_L4 exhibits the lowest thermal resistance owing to its compact low–potential-energy region surrounding the hydrophobic patches. Compared with the fully hydrophilic surface #LPi, the minimum difference is only 2%. In contrast, #0.64_L1 shows the highest interfacial thermal resistance, exceeding that of #LPi by 368.68%.

7. Molecular Dynamics Study of Pool Boiling Heat Transfer on Structured Hydrophilic/Hydrophobic Composite Surfaces

In Chapter 5, the effects of solid–liquid interaction strength (wettability), the spatial distribution of hydrophobic regions, and the hydrophobic-area coverage ratio on the pool-boiling heat transfer characteristics of smooth hydrophilic/hydrophobic composite surfaces were examined. The results showed that the presence of hydrophobic regions effectively accelerates bubble growth, and among the investigated configurations, surface # β_L4 exhibits superior performance in shortening the bubble nucleation time and reducing interfacial thermal resistance. These findings provide a basis for optimizing wall-surface designs to enhance boiling heat transfer. However, the enhancement achievable on smooth surfaces remains limited. As indicated in the literature, micro/nanostructured surfaces can increase the solid–liquid contact area and provide additional bubble nucleation sites, thereby further improving boiling heat transfer compared with smooth surfaces. Nevertheless, the underlying physical mechanisms by which different projected-area ratios of micro/nanostructures promote bubble growth and enhance boiling heat transfer remain unclear. Moreover, the ways in which structural parameters influence the heat-transfer process on such surfaces have yet to be elucidated. Therefore, building upon the smooth hydrophilic/hydrophobic composite surfaces studied in Chapter 5, it is necessary to construct structured hydrophilic/hydrophobic composite surfaces and investigate the effects of projected-area ratio β and structural parameters on boiling heat transfer.

To further enhance the boiling heat transfer performance of the surfaces, this chapter extends the work of Chapter 5 by constructing structured hydrophilic/hydrophobic composite surfaces based on the hydrophilic/hydrophobic distribution pattern of surface # β_L4 . First, under the condition of $\beta=0.25$, the effects of micro/nanostructure wettability and wall temperature on bubble growth and the number of evaporated atoms are analyzed. The corresponding bubble-growth

parameters (t_{ONB} , t_{FB} , T_{ONB} , and T_{FB}) are statistically evaluated to examine how structural distribution, wettability, and geometric parameters influence the bubble growth process. Meanwhile, the variations in the number of evaporated atoms and the energy absorbed by Ar atoms at different wall temperatures are also analyzed, thereby revealing the physical mechanisms through which structural distribution, wettability, and structural parameters influence boiling heat transfer under varying thermal conditions.

Subsequently, structured surfaces with $\beta=0.49$ are designed, and the effects of the hydrophilic/hydrophobic structural coverage ratio on bubble growth, the number of evaporated atoms, and the heat flux are systematically compared. The underlying physical laws governing the influence of these parameters on boiling heat transfer are thereby elucidated.

7.1. Computational Model for Pool Boiling Heat Transfer on Structured Hydrophilic/Hydrophobic Composite Surfaces

7.1.1. Physical Model

The computational model for pool boiling on structured hydrophilic/hydrophobic composite surfaces and the corresponding wall configurations are shown in Figure 7.1. The dimensions of the computational domain are $L_x \times L_y \times L_z = 108.3 \text{ \AA} \times 108.3 \text{ \AA} \times 108.3 \text{ \AA}$, which are identical to those used in the pool-boiling simulations of smooth hydrophilic/hydrophobic composite surfaces. The bottom wall of the model consists of Cu atoms arranged in a face-centered cubic (FCC) lattice structure with a lattice constant of $3.615 \text{ \AA}$.

The distribution of microstructures on the wall surface is illustrated in Figure 7.1(b). Based on the simulation results of smooth hydrophilic/hydrophobic composite surfaces presented in Chapter 5, two types of microstructured surfaces—#0.25_L4_hR and #0.49_L4_hR—are constructed in this chapter. The geometric parameters of the microstructures, including size, spacing, and height, are listed in Table 7.1.

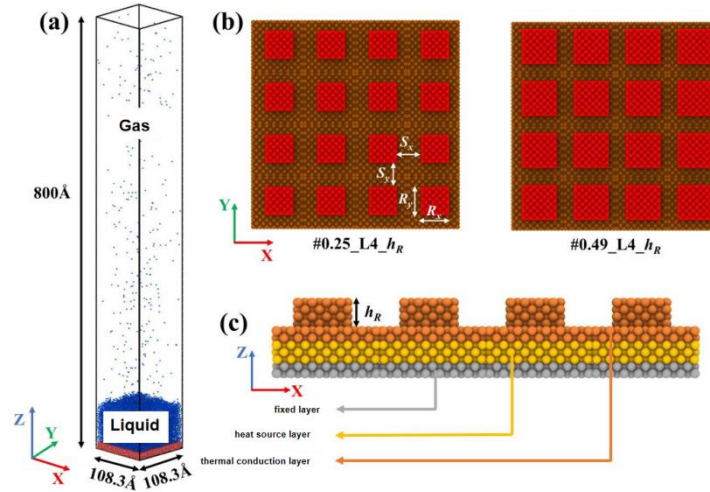


Figure 7.1 (a)MD simulation model of pool boiling, (b)Micro/nano structures distribution, (c)Function layers distribution of solid surfaces

Table 7.1 Parameters of micro/nano structures

Surface	$S_x=S_y$ [Å]	$R_x=R_y$ [Å]	h_R [Å]
#0.25_L4_hR	13.54	13.54	3.61
	13.54	13.54	7.22
	13.54	13.54	10.83
#0.49_L4_hR	18.95	4.06	3.61
	18.95	4.06	7.22
	18.95	4.06	10.83

Based on different projected-area ratios β of the micro/nanostructures, a total of twelve structured surfaces were designed by varying the height and wettability of the micro/nanostructures. The corresponding structural heights and wettability conditions are listed in Table 7.2. Throughout the simulations, the underlying substrate surface was maintained in a hydrophilic state.

Table 7.2 Micro/nano structured surfaces simulated in this chapter

Surface	β	h_R [Å]	Wettability of micro/nano structures
#0.25_Case1	0.25	3.61	Hydrophobic
#0.25_Case2	0.25	7.22	Hydrophobic
#0.25_Case3	0.25	10.83	Hydrophobic

Surface	β	h_R [Å]	Wettability of micro/nano structures
#0.25_Case4	0.25	3.61	Hydrophilic
#0.25_Case5	0.25	7.22	Hydrophilic
#0.25_Case6	0.25	10.83	Hydrophilic
#0.49_Case1	0.49	3.61	Hydrophobic
#0.49_Case2	0.49	7.22	Hydrophobic
#0.49_Case3	0.49	10.83	Hydrophobic
#0.49_Case4	0.49	3.61	Hydrophilic
#0.49_Case5	0.49	7.22	Hydrophilic
#0.49_Case6	0.49	10.83	Hydrophilic

7.1.2. Potential Parameter Settings

The potential functions used in this chapter are identical to those described in Chapter 5.1.2, where the Lennard–Jones (LJ) potential and the embedded-atom method (EAM) potential are employed to describe the interactions between Cu and Ar atoms, and among Cu atoms within the metallic wall, respectively. In this chapter, different interaction strengths are assigned to the wall surface and the microstructures, as summarized in Table 7.3.

Table 7.3 LJ potential function parameters for Ar–Ar and Ar–Cu

Interaction Pair	ε [eV]	σ [Å]
Ar–Ar	0.0104	3.405
Ar–Cu (substrate hydrophilic)	0.0975	2.8725
Ar–Cu (microstructure hydrophilic)	0.0975	2.8725
Ar–Cu (microstructure hydrophobic)	0.0026	2.8725

7.1.3. Simulation steps

Similar to the simulation procedure described in Chapter 5.1.3, the entire simulation system is first relaxed using an NVT ensemble, where the system temperature is maintained at 86 K via the Nose–Hoover thermostat and run for 1 ns. Subsequently, temperature control on the solid Cu wall and the Ar base fluid is removed, and the system is switched to an NVE ensemble. The temperature of the heat-source layer is then raised to the target wall temperature T_{mT_mTm} using the Langevin thermostat. At this stage, heat is transferred from the heat-source layer to the fluid region, initiating the boiling process. The simulations are performed with a time step of

0.001 ps for a total duration of 6 ns, during which the relevant data are collected.

7.2. Effect of Wall Temperature on Pool Boiling over Structured Surfaces

7.2.1. Bubble Dynamic Growth on Structured Hydrophilic–Hydrophobic Composite Surfaces

As shown in Figure 7.2, when the wall temperature is $T_m=160$ K, it can be observed that on hydrophobic structured surfaces, bubbles tend to nucleate within the microstructures, whereas on hydrophilic structured surfaces, bubble nucleation occurs above the structured region. This difference arises because hydrophobic structures, due to their weaker solid–liquid interactions, provide numerous nucleation sites. Within the structured region, these nucleation sites are densely distributed, causing bubbles to preferentially form and grow inside the microstructures.

In contrast, on fully hydrophilic structured surfaces, the capillary effect of the micro/nano structures keeps the base surface continuously wetted by a layer of liquid-phase atoms. As a result, bubbles do not form between the microstructures but rather above them. Consequently, the potential-energy confinement imposed by the wall on the bubbles is relatively reduced. Moreover, the stronger solid–liquid interaction enhances interfacial heat transfer, leading to earlier bubble nucleation and vapor-film formation. Therefore, both t_{ONB} and t_{FB} on hydrophilic structured surfaces occur earlier than those on hydrophobic structured surfaces.

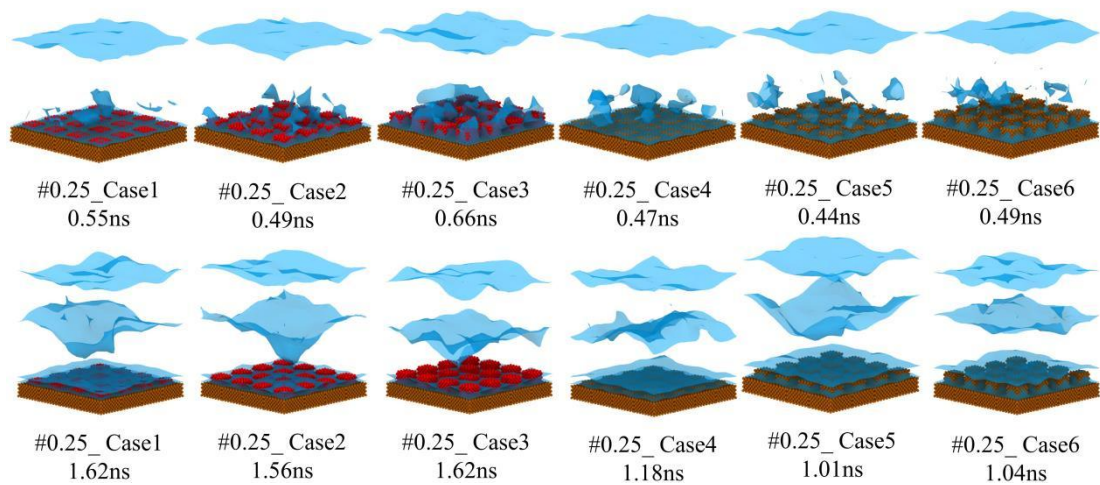


Figure 7.2 Diagrams of bubble nuclear and vapor film formation with $T_m=160$ K

and $\beta=0.25$

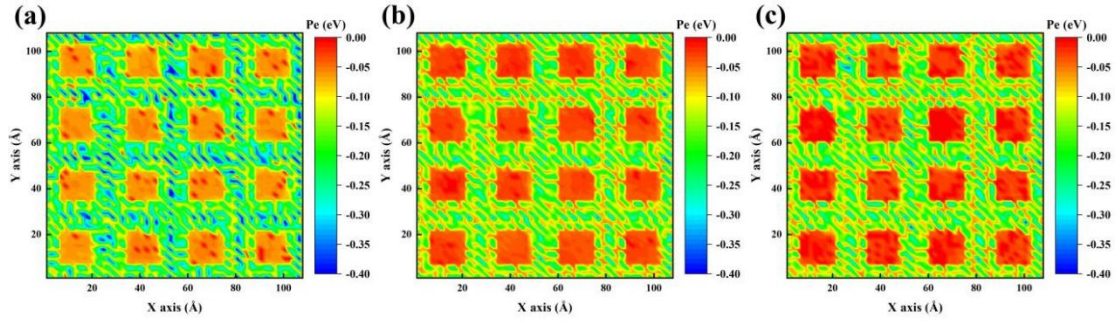


Figure 7.3 Surface potential energy distribution with $T_m = 160$ K: (a)#0.25_Case1, (b)#0.25_Case2, (c)#0.25_Case3

As shown in the potential energy distributions of the hydrophobic structured surfaces in Figure 7.3, when $h_R = 3.61$ Å, the low-potential-energy region surrounding the hydrophobic structures is relatively small, providing fewer bubble nucleation sites. This is consistent with Figure 7.2, where the number of bubbles generated at t_{ONB} on surface #0.25_Case1 is relatively low. As h_R increases to 7.22 Å, the area of the low-potential-energy region expands, leading to an increase in the number of bubbles nucleated on the surface. When h_R is further increased to 10.83 Å, the potential energy distribution on the surface exhibits almost no additional change.

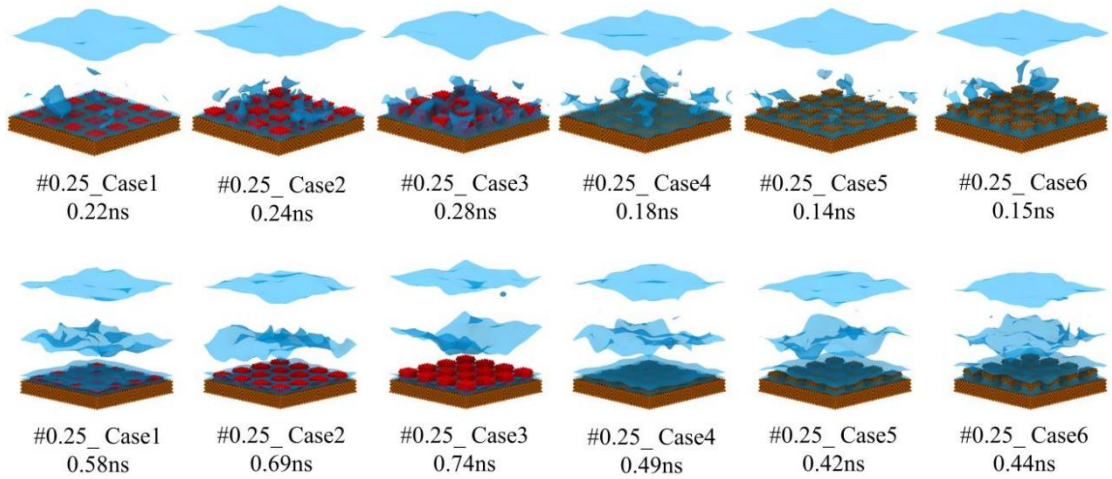


Figure 7.4 Diagrams of bubble nuclear and vapor film formation with $T_m = 180$ K and $\beta=0.25$

When the wall temperature T_m is increased to 180 K, both bubble nucleation and

vapor-film formation occur earlier, as shown in Figure 7.4. By comparing the number of bubbles on surfaces #0.25_Case1, #0.25_Case2, and #0.25_Case3, it can be observed that when $h_R=7.22 \text{ \AA}$, the number of bubbles generated on the surface reaches a saturation limit. Further increasing h_R does not significantly enhance bubble formation. This observation is consistent with the potential energy distributions of surfaces #0.25_Case1, #0.25_Case2, and #0.25_Case3 shown in Figure 7.3. For hydrophilic structured surfaces, the increase in wall temperature further strengthens the solid–liquid heat-transfer process. Among these surfaces, #0.25_Case5 exhibits the shortest t_{ONB} and t_{FB} , indicating the most rapid bubble nucleation and vapor-film formation.

The variations in liquid-phase temperature under different wall-temperature conditions are shown in Figure 7.5(a) and Figure 7.5(b). At both wall temperatures, the temperature rise in the liquid above hydrophilic structured surfaces is faster than that above hydrophobic structured surfaces. Moreover, as h_R increases, the temperature variation on hydrophilic structured surfaces accelerates, whereas the temperature variation on hydrophobic structured surfaces gradually slows down. These trends indicate that hydrophilic structured surfaces possess a greater advantage in facilitating solid–liquid heat transfer.

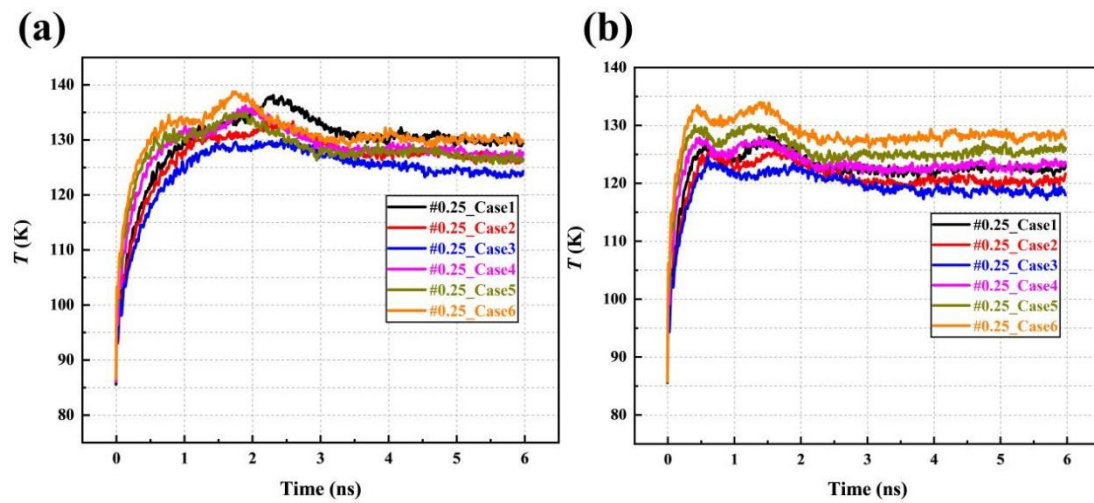


Figure 7.5 Variation of temperature at the micro/nano structured surfaces: (a) $T_m = 160 \text{ K}$, (b) $T_m = 180 \text{ K}$

Furthermore, as the wall temperature increases, the inflection point in the liquid-phase temperature curves on the structured surfaces also changes. When $T_m=160$ K, the liquid temperature above the hydrophilic and hydrophobic structured surfaces begins to level off at approximately 1 ns and 1.5 ns, respectively, which corresponds closely to the vapor-film formation times shown in Figure 7.2. When T_m is increased to 180 K, the temperature curve begins to flatten at around 0.5 ns, again matching the vapor-film formation time in Figure 7.4. This behavior occurs because once bubbles merge and form a vapor film on the wall surface, the vapor layer obstructs direct solid–liquid contact and disrupts interfacial heat transfer. As a result, the liquid phase can no longer absorb heat from the wall effectively, leading to a slowdown in its temperature rise. To further analyze the temperature evolution at the wall, the liquid-phase temperature at t_{ONB} and t_{FB} was statistically evaluated, as summarized in Tables 6.4 and 6.5.

From Table 7.4, it can be observed that hydrophobic structured surfaces not only increase the number of nucleation sites but also reduce the bubble nucleation temperature. Compared with the fully hydrophilic surface #0.25_L4, the maximum reduction in T_{ONB} is 6.2%. Moreover, as the micro/nano structural height increases, the vapor-film formation temperature on hydrophobic structured surfaces gradually decreases. This is because, while hydrophobic structures reduce the nucleation temperature, the increased number of nucleation sites also shortens the time between bubble nucleation and coalescence into a vapor film. Consequently, the duration of liquid heating is reduced. Additionally, due to the relatively weak solid–liquid interaction on hydrophobic structures, the interfacial heat-transfer process is weakened, ultimately leading to a reduction in T_{FB} and ΔT .

For hydrophilic structured surfaces, the stronger solid–liquid interaction and the increased heated surface area (as h_R increases) enhance interfacial heat transfer. As a result, both t_{ONB} and t_{FB} decrease, while T_{ONB} and T_{FB} increase accordingly. From Table 7.5, it can also be seen that as the wall temperature increases, the temperature variation in the liquid phase during bubble growth and coalescence

becomes more pronounced, indicating further enhancement of the solid–liquid heat-transfer process. Correspondingly, t_{ONB} and t_{FB} are further shortened, and the liquid-phase temperatures at bubble nucleation and vapor-film formation decrease.

Table 7.4 State parameters at bubble initial growth and vapor film formation time with $T_m=160$ K and $\beta=0.25$

Surface	t_{ONB} [ns]	t_{FB} [ns]	Δt [ns]	T_{ONB} [K]	T_{FB} [K]	ΔT [K]
#0.25_Case1	0.55	1.62	1.07	125.12	139.14	14.02
#0.25_Case2	0.49	1.56	1.07	122.78	133.71	10.93
#0.25_Case3	0.66	1.62	0.96	123.48	130.82	7.34
#0.25_Case4	0.47	1.18	0.71	128.81	139.70	10.89
#0.25_Case5	0.44	1.01	0.57	132.16	142.49	10.33
#0.25_Case6	0.49	1.04	0.55	134.07	144.35	11.55

Table 7.5 State parameters at bubble initial growth and vapor film formation time with $T_m=180$ K and $\beta=0.25$

Surface	t_{ONB} [ns]	t_{FB} [ns]	Δt [ns]	T_{ONB} [K]	T_{FB} [K]	ΔT [K]
#0.25_Case1	0.22	0.58	0.36	117.24	135.83	18.59
#0.25_Case2	0.24	0.69	0.45	118.20	133.82	15.62
#0.25_Case3	0.28	0.74	0.46	119.40	130.82	11.42
#0.25_Case4	0.18	0.62	0.44	128.76	139.50	10.74
#0.25_Case5	0.14	0.42	0.28	132.70	148.22	15.52
#0.25_Case6	0.15	0.44	0.29	125.96	144.32	18.36

7.2.2. Count Change of Evaporated Atoms on Structured Hydrophilic/Hydrophobic Composite Surfaces

At $T_m=160$ K, the number of evaporated atoms on the structured surfaces was statistically analyzed, as shown in Figure 7.6. The results indicate that on hydrophobic structured surfaces, the number of evaporated atoms increases with increasing h_R . At 2 ns, the numbers of evaporated atoms are 7155, 6390, and 5827 for the three

hydrophobic cases, corresponding to evaporation rates of 48.1%, 43.2%, and 39.4%, respectively.

In contrast, the differences in the number of evaporated atoms among the hydrophilic structured surfaces are relatively small. At 2 ns, the numbers of evaporated atoms on surfaces #0.25_Case4, #0.25_Case5, and #0.25_Case6 are 6627, 6431, and 6674, respectively, corresponding to evaporation rates of only 43.3%, 42.2%, and 42.6%.

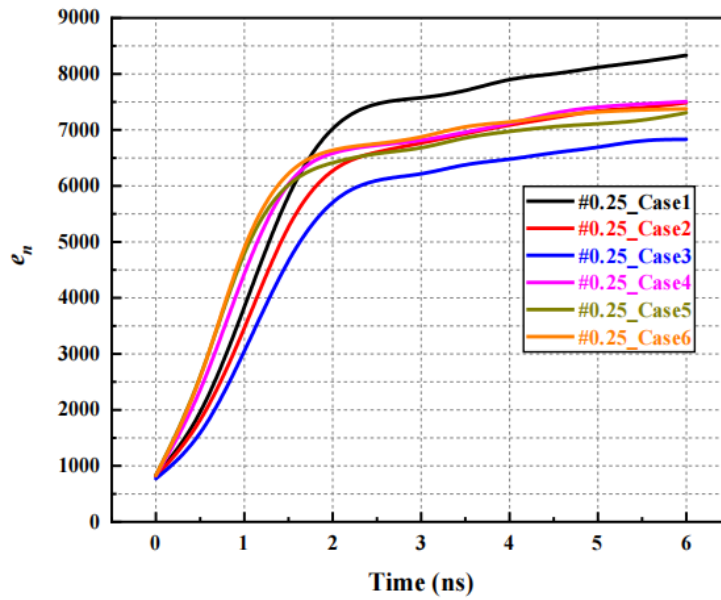


Figure 7.6 Variation of evaporated atom at the micro/nano structured surfaces with $T_m = 160\text{ K}$

In Chapter 5.3.2, it was shown that differences in the number of evaporated atoms among surfaces are related to the formation of vapor films. A similar correlation is observed on structured surfaces. As shown in Table 7.4, surface #0.25_Case1 exhibits a relatively late t_{FB} , and the time interval required for bubbles to grow and subsequently merge into a vapor film on the wall (Δt) is comparatively long. This extended heating duration results in a higher evaporation rate. In contrast, on hydrophilic structured surfaces, the stronger solid–liquid interactions enhance interfacial heat transfer. As a result, the time Δt for bubbles to grow and merge into a vapor film is shortened compared with hydrophobic structured surfaces. This earlier

disruption of the solid–liquid heat-transfer process prevents liquid-phase atoms from continuously absorbing heat and transitioning into vapor, ultimately leading to evaporation rates comparable to that of the hydrophobic surface #0.25_Case2.

The above analysis indicates that the bubble growth and coalescence behavior on the wall strongly influences the evaporation rate. However, when the wall temperature decreases, the number of evaporated atoms exhibits different trends. As shown in Figure 7.7, when the wall temperature T_m is reduced to 140 K, the phase-change mode transitions from boiling to pure evaporation. During the simulation, the number of evaporated atoms increases nearly linearly on all surfaces. For hydrophilic structured surfaces, the absence of bubble generation and coalescence means that the liquid maintains stable thermal contact with the heated wall. As h_R increases, the solid–liquid contact area increases, resulting in enhanced evaporation. Consequently, the final evaporation rates on surfaces #0.25_Case4, #0.25_Case5, and #0.25_Case6 reach 78.5%, 78.6%, and 75.8%, respectively.

For hydrophobic structured surfaces, although increasing h_R enlarges the potential contact area, the inherently weak solid–liquid interactions do not improve interfacial heat transfer. Therefore, the evaporation rate decreases with increasing h_R , with final evaporation rates of 74.1%, 68.5%, and 63.9% for the respective hydrophobic surfaces.

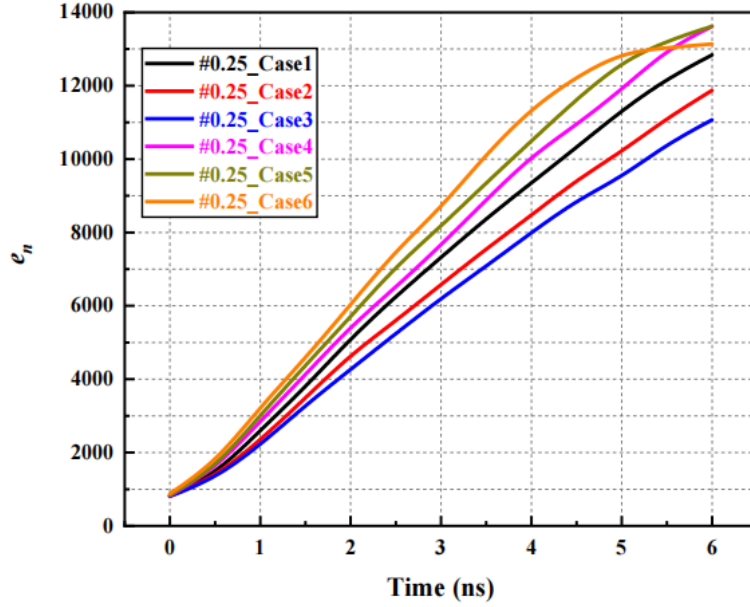


Figure 7.7 Variation of evaporated atom at the micro/nano structured surfaces with $T_m = 140\text{ K}$

Figures 6.8(a) and 6.8(b) present the variations in liquid-phase temperature and absorbed energy on the different structured surfaces. A comparison of Figures 6.7 and 6.8 shows that the trends in the number of evaporated atoms are consistent with the trends in both temperature rise and energy absorption.

For hydrophobic structured surfaces, as h_R increases, both the liquid-phase temperature and the absorbed energy decrease. This is because, at lower wall temperatures, the phase-change mode transitions from boiling to evaporation. Although increasing h_R enlarges the nominal solid–liquid contact area, the inherently weak interaction between the hydrophobic micro/nano structures and the liquid prevents any significant enhancement of interfacial heat transfer.

In contrast, on hydrophilic structured surfaces, the stronger solid–liquid interaction ensures that increasing h_R effectively enlarges the solid–liquid contact area, thereby strengthening interfacial heat transfer. Moreover, due to the shift from boiling to pure evaporation, the liquid remains in continuous and intimate contact with the micro/nano structures. As a result, the heat-transfer process is no longer disrupted by vapor film formation, and both the liquid temperature and the absorbed energy increase steadily

with h_R .

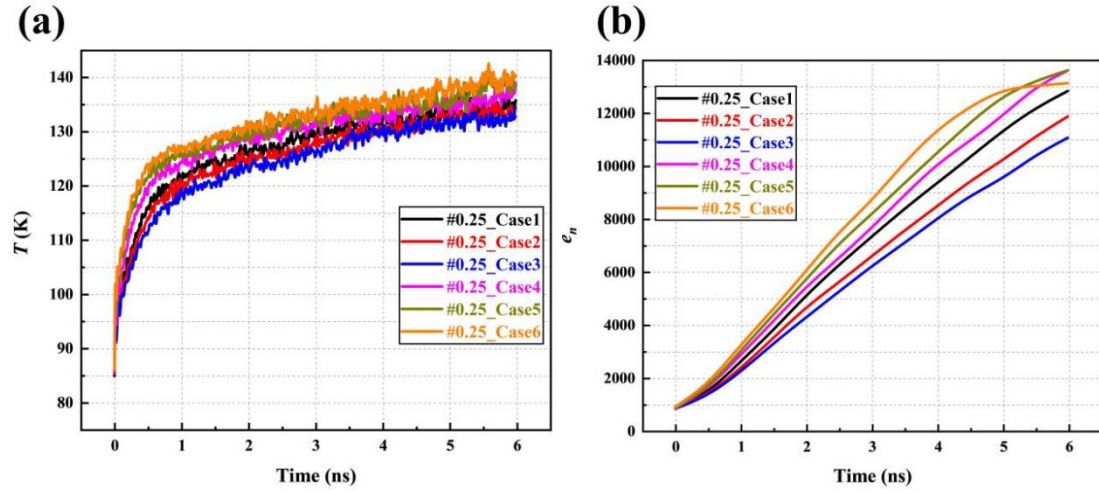


Figure 7.8 Variation of (a) liquid-phase temperature and (b) absorbed energy by Ar atom at the micr/nano structured surfaces with $T_m = 140$ K

7.3. Effect of Hydrophilic–Hydrophobic Structural Ratio on Pool Boiling of Structured Surfaces

7.3.1. Bubble Dynamic Growth on Structured Hydrophilic – Hydrophobic Composite Surfaces

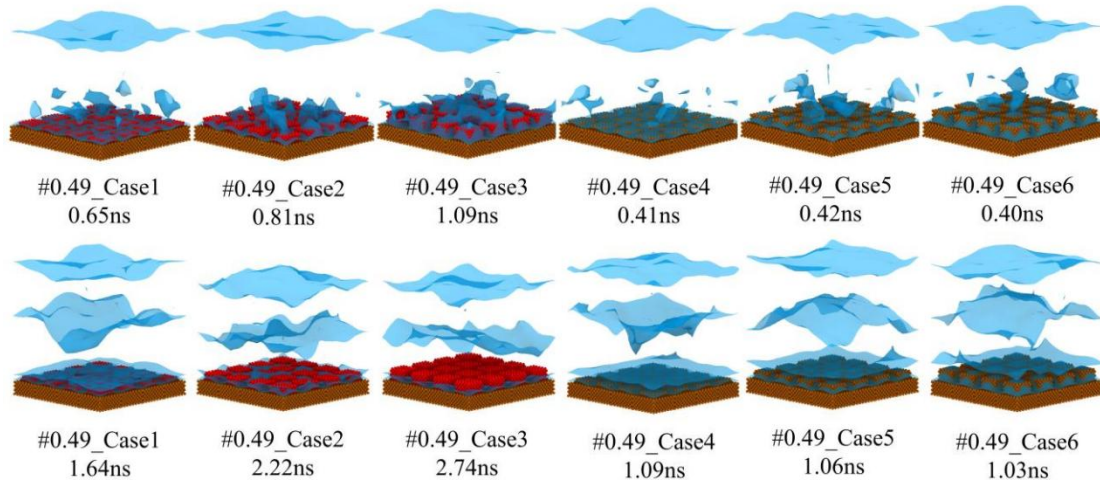


Figure 7.9 Diagrams of bubble nuclear and vapor film formation with $T_m = 160$ K and $\beta = 0.49$

Figure 7.9 presents the bubble nucleation and vapor-film formation snapshots for the structured hydrophilic/hydrophobic surfaces at a wall temperature of $T_m = 160$ K

and a coverage ratio of $\beta=0.49$. The results show that, on hydrophobic structured surfaces, bubbles still preferentially nucleate within the micro/nanostructures. As the structural height h_R increases, the void space within the hydrophobic microstructures accommodates more liquid-phase atoms; however, due to the weak solid–liquid interactions at hydrophobic sites, the interfacial heat-transfer process is not strengthened. Consequently, the bubble nucleation time t_{ONB} becomes progressively delayed, and the vapor-film formation time t_{FB} is similarly postponed. In contrast, on hydrophilic structured surfaces, bubbles tend to nucleate above the structured region rather than within it. As h_R increases, the differences in t_{ONB} and t_{FB} remain small, indicating that the increase in structure height has only a modest effect on bubble nucleation and vapor-film formation for hydrophilic configurations.

Table 7.6 State parameters at bubble initial growth and vapor film formation time with $T_m=160\text{ K}$ and $\beta=0.49$

Surface	t_{ONB} [ns]	t_{FB} [ns]	Δt [ns]	T_{ONB} [K]	T_{FB} [K]	ΔT [K]
#0.49_Case1	0.65	1.64	0.99	125.98	136.94	10.96
#0.49_Case2	0.81	2.22	1.41	123.98	132.64	8.66
#0.49_Case3	1.09	2.74	1.65	122.57	128.78	6.21
#0.49_Case4	0.41	1.09	0.68	127.76	138.17	10.41
#0.49_Case5	0.42	1.06	0.64	130.02	141.39	11.37
#0.49_Case6	0.40	1.03	0.63	131.11	143.75	12.64

As shown in Table 7.6, with increasing h_R , both t_{ONB} and t_{FB} on the hydrophobic structured surfaces (#0.49_Case1, #0.49_Case2, and #0.49_Case3) are delayed, while the bubble growth time Δt becomes longer. It is noteworthy that the increase in Δt does not lead to a higher liquid temperature; instead, it results in a reduction, which is consistent with the trend observed for hydrophobic structured

surfaces at $\beta=0.25$. However, the temperature variation ΔT for #0.49_Case1, #0.49_Case2, and #0.49_Case3 is smaller than that for #0.25_Case1, #0.25_Case2, and #0.25_Case3, with reductions of 21.8%, 20.8%, and 15.4%, respectively. In contrast, for hydrophilic structured surfaces, ΔT increases with increasing h_R . Compared with #0.25_Case1, #0.25_Case2, and #0.25_Case3, the values of ΔT on the hydrophilic structured surfaces increase by 14.0%, 10.1%, and 9.4%, respectively.

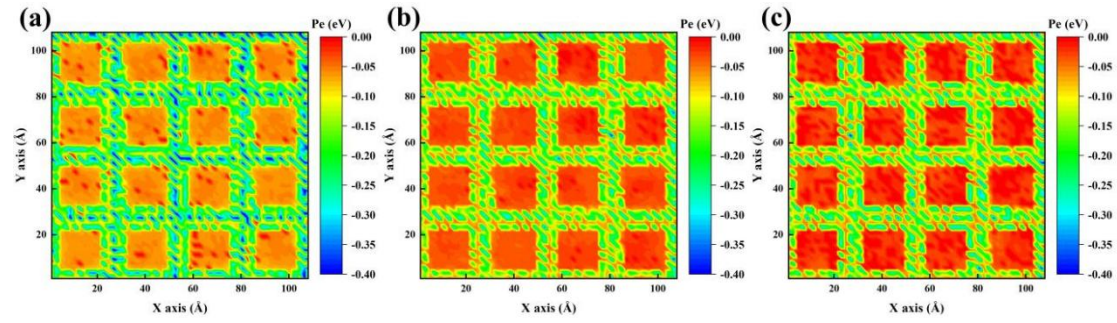


Figure 7.10 Surface potential energy distribution with $T_m = 160$ K and $\beta=0.49$:

(a)#0.49_Case1, (b)#0.49_Case2, (3)#0.49_Case3

The potential energy distributions of the hydrophobic structured surfaces are shown in Figure 7.10. As illustrated, the area of the low-potential-energy regions decreases with increasing β . When $h_R=3.61$ Å, the hydrophobic structures are still relatively shallow, and noticeable low-potential-energy regions remain on the surface, indicating that the solid-liquid interaction is still relatively strong. However, as h_R increases, although the nominal contact area between the hydrophobic structures and the liquid enlarges, the absolute value of the potential energy between liquid atoms and the wall decreases. Consequently, the solid-liquid contact becomes less intimate and the energy-transfer capability is weakened, ultimately impeding the heat-transfer process across the solid-liquid interface.

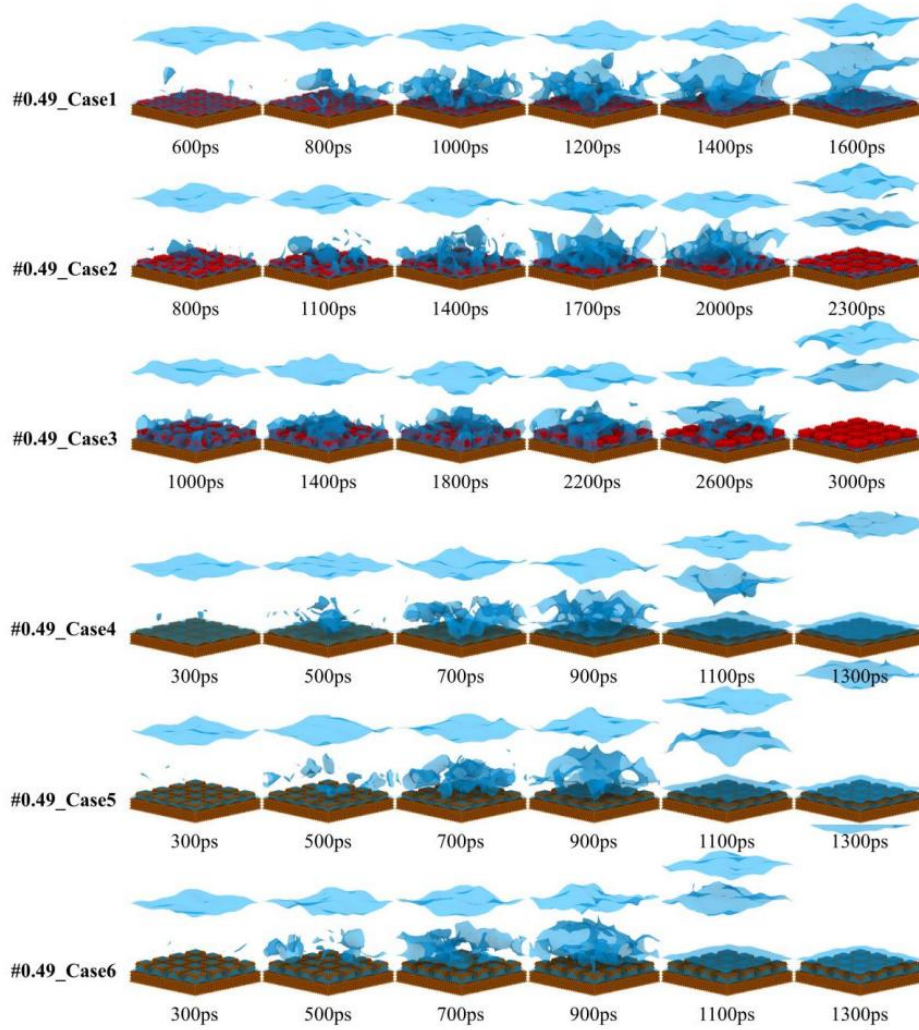


Figure 7.11 Schematic of bubble growth with $T_m=160K$ and $\beta=0.49s$

Figure 7.11 illustrates the bubble growth process on the structured surfaces. As shown, on hydrophobic structured surfaces, bubble nucleation and coalescence preferentially occur within the gaps between the micro/nanostructures, and this behavior becomes more pronounced as the structural height h_R increases. Although increasing h_R enlarges the nominal solid–liquid contact area and provides more potential nucleation sites, the inherently weak interaction between the hydrophobic microstructures and the liquid prevents any substantial enhancement of interfacial heat transfer. As a result, bubbles have difficulty growing, departing, and coalescing, leading to prolonged bubble growth times and a delayed vapor-film formation time t_{FB} . In contrast, on hydrophilic structured surfaces, the strong solid–liquid interaction ensures that the cavities within the structures remain fully filled with liquid atoms due to

capillary effects. This continuous liquid supply maintains stable solid–liquid heat transfer and prevents the “dryout” of the heated wall. As h_R increases, the effective contact area between the hydrophilic structures and the liquid becomes larger, thereby further strengthening the interfacial heat-transfer process.

7.3.2. Evaporation Behavior on Structured Hydrophilic – Hydrophobic Composite Surfaces

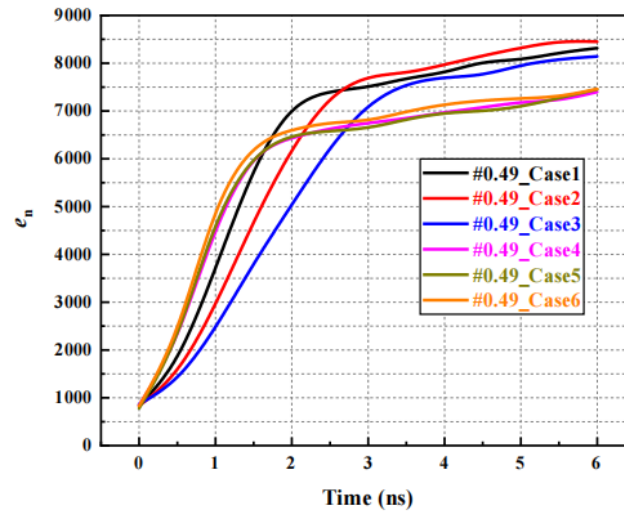


Figure 7.12 Variation of evaporated atom on the micr/nano structured surfaces with $T_m = 160\text{ K}$ and $\beta = 0.49$

Figure 7.12 shows the variations in the number of evaporated atoms on the different structured surfaces. It can be observed that the differences among the hydrophilic structured surfaces are relatively small. At 2 ns, the numbers of evaporated atoms on surfaces #0.49_Case4, #0.49_Case5, and #0.49_Case6 are 6447, 6515, and 6619, respectively. In contrast, for the hydrophobic structured surfaces, the weaker solid–liquid interaction results in a slower increase in the number of evaporated atoms compared with the hydrophilic cases. Moreover, as the micro/nanostructure height h_R increases, the growth rate of the evaporated atoms decreases accordingly.

A comparison between Figures 6.9 and 6.12 reveals that the evaporation behavior is closely related to the timing of vapor-film formation. Due to the weaker solid–liquid interaction on hydrophobic structured surfaces, the vapor film forms later, resulting in

a longer duration of direct contact between the liquid phase and the wall. This extended contact time enhances evaporation, leading to relatively high evaporation rates. At 6 ns, the evaporation rates for #0.49_Case1, #0.49_Case2, and #0.49_Case3 reach 48.0%, 48.8%, and 47.0%, representing increases of 4.7%, 6.6%, and 4.4% compared with #0.25_Case1, #0.25_Case2, and #0.25_Case3.

When the wall temperature T_m is reduced to 140 K, as shown in Figure 7.13, the phase-change mode transitions from boiling to pure evaporation. At $\beta=0.49$, the strong solid–liquid interaction on hydrophilic structured surfaces enhances interfacial heat transfer. As h_R increases, the evaporation rates reach 79.7%, 79.0%, and 76.3%, which represent increases of 1.2%, 0.4%, and 0.5% compared with the case of $\beta=0.25$.

For hydrophobic structured surfaces, although increasing β enlarges the nominal contact area between the liquid and the hydrophobic structures, the inherently weak solid–liquid interaction leads to evaporation rates lower than those of the hydrophilic counterparts. Ultimately, the evaporation rates reach 70.9%, 62.4%, and 56.8%, which are reductions of 3.2%, 6.1%, and 7.1% compared with the $\beta=0.25$ cases.

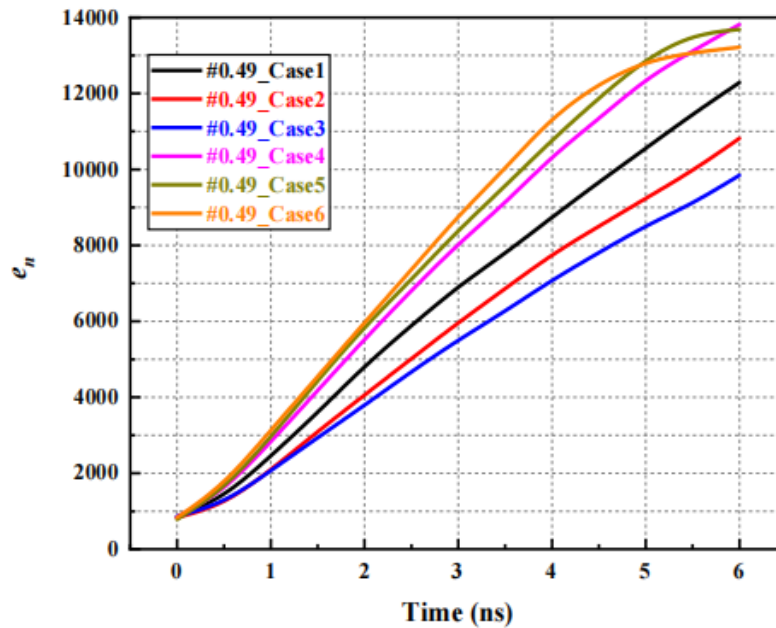


Figure 7.13 Variation of evaporated atom on the micr/nano structured surfaces with

$$T_m = 140 \text{ K}$$

Moreover, the evolution of the number of evaporated atoms shows a trend similar to that of the temperature and energy absorption of Ar atoms, consistent with the observations at $\beta=0.25$. As shown in Figure 7.14, in Figure 7.14(a), the temperature rise of Ar atoms on hydrophilic structured surfaces increases with increasing h_R , and the temperature rises more rapidly compared with the $\beta=0.25$ cases. In contrast, the temperature variation on hydrophobic structured surfaces exhibits the opposite trend.

Similarly, the energy absorbed by Ar atoms also changes with increasing β . On hydrophilic structured surfaces, Ar atoms on #0.49_Case4, #0.49_Case5, and #0.49_Case6 absorb 886.21 eV, 883.18 eV, and 858.76 eV of energy, respectively, representing increases of 1.5%, 0.8%, and 1.0% compared with their counterparts at $\beta=0.25$. In contrast, for hydrophobic structured surfaces, the absorbed energy decreases significantly as β increases, with reductions of 2.6%, 5.9%, and 8.9% relative to #0.25_Case1, #0.25_Case2, and #0.25_Case3.

These results indicate that increasing β only slightly enhances the solid–liquid energy-transfer capability of hydrophilic structured surfaces, whereas its influence on hydrophobic structured surfaces is much more.

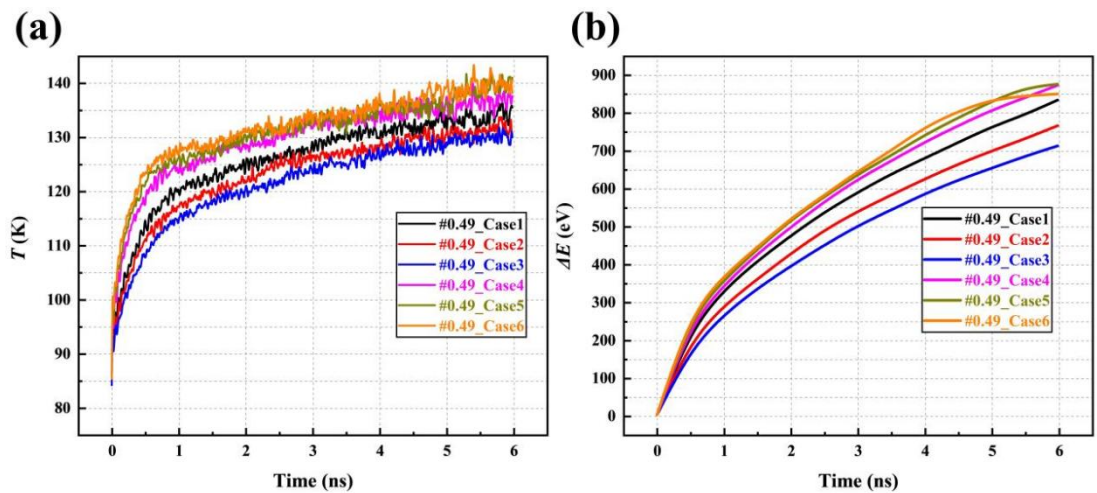


Figure 7.14 Variation of (a) Ar temperature and (b) absorbed energy by Ar atoms on the micr/nano structured surfaces with $T_m = 140 \text{ K}$ and $\beta = 0.49$

7.3.3. Heat Flux Characteristics of Structured Hydrophilic – Hydrophobic Composite Surfaces

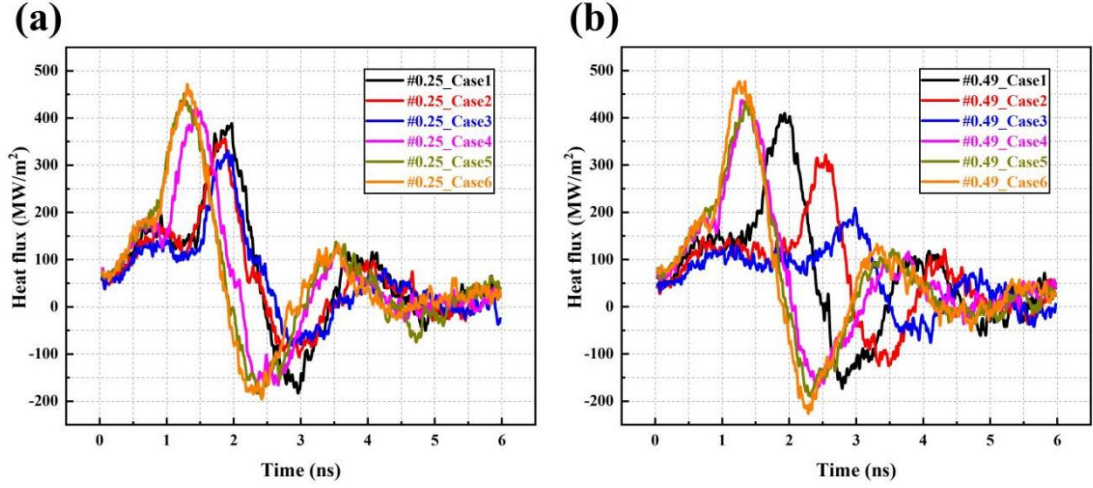


Figure 7.15 Variation of heat flux on micro/nano structured surfaces: (a) $T_m = 160\text{ K}$, $\beta = 0.25$, (b) $T_m = 160\text{ K}$, $\beta = 0.49$

As shown in Figure 7.15, the heat flux on each structured surface reaches a maximum value at a certain moment and subsequently decreases to negative values, which is attributed to the pressure waves reflected from the upper boundary of the system [96]. A comparison between Figures 6.15(a) and 6.15(b) reveals that hydrophilic structured surfaces reach the critical heat flux (CHF) earlier than hydrophobic structured surfaces. This observation indicates that hydrophilic structures exhibit better conformity with the liquid phase, thereby facilitating solid–liquid heat transport and enhancing interfacial heat transfer.

For $\beta = 0.25$, as shown in Figure 7.15(a), the heat-flux curves for hydrophilic and hydrophobic structured surfaces follow similar trends. With increasing h_R , the CHF values for the hydrophilic structured surfaces rise sequentially, with CHF values of 429.82 MW/m^2 , 458.26 MW/m^2 , and 480.44 MW/m^2 for #0.25_Case4, #0.25_Case5, and #0.25_Case6, respectively. Among them, #0.25_Case5 reaches CHF first at 1.27 ns, followed by #0.25_Case6 at 1.32 ns and #0.25_Case4 at 1.46 ns. In contrast, due to the weaker solid–liquid interactions on hydrophobic structured surfaces, the wall–liquid contact quality is lower than that of hydrophilic surfaces. As a result, the hydrophobic

surfaces reach CHF later and exhibit lower CHF values. With increasing h_R , the CHF for hydrophobic surfaces decreases from 390.94 MW/m² to 330.67 MW/m², while the CHF times remain relatively unchanged at 1.98 ns, 1.88 ns, and 1.93 ns.

As β increases, Figure 7.15(b) shows that the differences in CHF among the surfaces become more pronounced. The CHF values for the hydrophobic structured surfaces continue to decrease with increasing h_R , declining from 409.66 MW/m² to 213.72 MW/m², and the time to reach CHF is further prolonged. For the hydrophilic structured surfaces, however, the increase in β leads to only modest improvement in CHF. The CHF values for #0.49_Case4, #0.49_Case5, and #0.49_Case6 are 442.89 MW/m², 463.55 MW/m², and 489.13 MW/m², representing only slight increases of 3.0%, 1.2%, and 1.8% relative to #0.25_Case4, #0.25_Case5, and #0.25_Case6, respectively.

7.4. Conclusion

In this chapter, micro/nanostructures were introduced on the basis of the smooth hydrophilic/hydrophobic composite surfaces investigated in Chapter 3, thereby constructing structured hydrophilic/hydrophobic composite surfaces. A total of twelve types of structured surfaces were designed by varying the hydrophilic–hydrophobic structural coverage ratio β , the micro/nanostructure height h_R , and the wettability of the structures. Molecular dynamics simulations were then performed to investigate the corresponding solid–liquid heat transfer processes.

First, for structured surfaces with $\beta=0.25$, the influence of wall temperature T_m on bubble dynamic growth was analyzed, including the bubble incipient nucleation time t_{ONB} , the vapor–film formation time t_{FB} , and the liquid-phase temperatures T_{ONB} , T_{FB} , and ΔT . These analyses elucidated the physical mechanisms governing bubble growth under different wall temperatures. Subsequently, the evolution of the number of evaporated atoms was examined, along with the changes in liquid temperature and absorbed energy under different thermodynamic phase-change regimes. Finally, the

influence of the structural coverage ratio β on boiling heat transfer was investigated by comparing bubble growth behavior, evaporated atom evolution, and heat flux variations on structured surfaces with $\beta=0.49$.

On hydrophobic structured surfaces, the weak solid–liquid interaction provided numerous nucleation sites within the inter-structural cavities, causing bubbles to preferentially nucleate inside these gaps. In contrast, on hydrophilic structured surfaces, the strong solid–liquid interaction and capillary action ensured that the cavities remained fully filled with liquid atoms. Because the potential energy constraint on liquid atoms is weaker above the structures, bubbles tended to nucleate above the micro/nanostructures rather than within them. As a result, hydrophilic structured surfaces exhibited shorter t_{ONB} and t_{FB} values compared with hydrophobic ones.

For hydrophobic surfaces, increasing β reduced the area of low–potential-energy regions on the wall, and increasing h_R further decreased the absolute potential experienced by liquid atoms, weakening solid–liquid contact and hindering interfacial heat transfer. Consequently, the temperature rise ΔT in the liquid decreased. In contrast, for hydrophilic structured surfaces, increasing β enlarged the solid–liquid contact area. Meanwhile, capillary forces ensured persistent liquid replenishment within the structures, enabling stable heat transfer and effectively preventing wall dryout.

The wall temperature determines the phase-change mode and strongly influences the number of evaporated atoms. At $T_m=160$ K, hydrophobic structured surfaces exhibited higher evaporation rates, though these rates decreased with increasing h_R . Hydrophilic structured surfaces showed relatively small variations in evaporation rate with increasing h_R . When the wall temperature was reduced to 140 K, the phase-change mode shifted from boiling to pure evaporation. For hydrophobic structured surfaces, the weak solid–liquid interaction became more pronounced with increasing h_R , weakening energy transfer across the interface and slowing the liquid temperature rise. In contrast, on hydrophilic structured surfaces, bubble formation and vapor-film

disruption no longer occurred, and the evaporation rate increased with increasing h_R . Furthermore, the influence of increasing β was found to be more significant for hydrophobic structured surfaces than for hydrophilic ones.

Increasing β enlarged the disparity in CHF among the different surfaces. On hydrophobic structured surfaces, CHF decreased progressively with increasing h_R . For hydrophilic structured surfaces, however, increasing β produced only modest improvements in CHF, indicating a relatively limited influence on their heat-transfer capability.

8. Conclusion and outlook

8.1. Conslusions

Research on micro/nanoscale droplet spreading and capillary flow is of great significance in engineering practices, such as the development of novel materials, the enhancement of mechanical properties and durability in cementitious materials, geological sequestration of carbon dioxide, and the exploitation and utilization of unconventional energy sources like shale oil and gas. Against the background of these engineering applications, this study focuses on the processes of micro/nanoscale droplet spreading and capillary flow. Taking the micro-mechanical mechanisms of droplet wetting and capillary flow as the core scientific problem, this study employs a research method combining molecular dynamics (MD) simulations and theoretical analysis to deeply investigate these mechanisms.

We conducted MD simulations of droplet spreading on solid surfaces under varying solid-liquid interaction strengths, revealing how solid-liquid interactions influence solid surface wettability and droplet spreading dynamics. Based on energy conservation and conversion analysis, the critical conditions for the occurrence of capillary flow were established, and the energy dissipation mechanisms during capillary flow were revealed. Furthermore, by considering the dynamic effects of the contact angle and the influence of asymmetric wall wettability, the classical Lucas-Washburn theoretical model for capillary channel imbibition was modified based on the Cox-Voinov law and subsequently validated by MD simulation results. We also conducted MD simulations of the contact between bulk water and minerals, revealing the three-dimensional distribution characteristics and motion properties of water molecules on mineral surfaces. By analyzing the interaction characteristics between water and different minerals, we quantified the mobility of water molecules and elucidated how surface crystal structures affect the droplet spreading process, three-

phase contact line motion, precursor film migration modes, and capillary flow in nanochannels. The main research achievements and conclusions are as follows:

(1) Influence of Solid-Liquid Interactions on Surface Wettability and Droplet Spreading Dynamics MD simulations of droplet spreading on solid surfaces under different solid-liquid interaction strengths were conducted. The results indicate that when solid-liquid interactions are relatively weak, an increase in interaction strength enhances surface wettability and accelerates the droplet spreading process. There exists a critical solid-liquid interaction strength that yields an equilibrium contact angle of 0° on the solid surface; once exceeded, a precursor film will appear during spreading. However, the spreading velocity does not increase monotonically with interaction strength. Particularly after liquid molecules form a precursor film, an excessively strong solid-liquid interaction actually hinders further spreading. There are two main reasons for this: First, a stronger interaction favors the formation of a stable precursor film, thereby restricting liquid molecular exchange between the precursor film and other droplet regions. Second, when the interaction is excessively strong, the solid-liquid friction coefficient increases significantly, and the friction effect begins to dominate, causing the spreading velocity to decrease.

(2) Mechanisms of Molecular Layering and Surface Potential Energy Based on a simplified solid-liquid interaction model and MD simulations, the mechanisms by which interaction strength affects wettability and molecular layered structures were investigated. The results show that differences in interaction strength lead to variations in the potential energy distribution of liquid molecules on the surface. Specifically, a stronger interaction results in a deeper potential well, making it easier for liquid molecules to adsorb and enhancing surface wettability. When the potential well is sufficiently deep, liquid molecules tend to adsorb and form a high-density layer. Once the solid surface is covered by a monolayer of liquid molecules, the potential well depth diminishes significantly, greatly weakening the surface's ability to adsorb further molecules. After the adsorption of a bilayer (or multiple layers), the potential well depth

continues to decrease until it reaches a hydrophobic level, at which point the surface no longer generates high-density liquid molecular layers. These findings provide a theoretical foundation for the targeted regulation of surface wettability, spreading processes, and molecular layering, holding important reference value for engineering applications such as self-cleaning surfaces, anti-icing/fogging, and microfluidic control.

(3) Critical Conditions and Energy Dissipation in Capillary Flow Based on energy conservation and conversion analysis, the critical conditions for capillary flow were established, and its energy dissipation mechanisms were revealed. Capillary flow can occur if the total surface energy of the system decreases when the solid-gas interface transitions to a solid-liquid interface. Only a small fraction of this reduced surface energy is converted into kinetic energy for liquid flow; the remainder is primarily dissipated through viscous losses within the liquid and molecular friction near the three-phase contact line. The energy dissipated through these pathways correlates with the dynamic contact angle. As capillary flow proceeds, the dynamic contact angle gradually decreases, and the proportion of internal viscous loss increases. Furthermore, in capillary channels with asymmetric wall wettability, the fluctuation of the liquid-gas interface also dissipates a portion of the energy.

(4) Modification of the Lucas-Washburn Capillary Flow Model The classical Lucas-Washburn model was modified to account for dynamic contact angle effects and asymmetric wall wettability. First, for channels with symmetric wettability, the model was modified based on the Cox-Voinov law. When the channel possesses asymmetric wall wettability, both the wettability and the capillary rise height differ between the two side walls; therefore, an effective equilibrium contact angle is adopted to characterize the overall wettability. By substituting this effective equilibrium contact angle into the modified Lucas-Washburn model, the average capillary rise height over time can be accurately predicted. The rationality and accuracy of this modified model were verified via MD simulations. These findings provide effective tools for analyzing and controlling micro/nanoscale capillary flow, presenting broad application prospects in

novel materials, microfluidic chips, ion/water transport in cementitious materials, and spontaneous imbibition in shale reservoirs.

Investigating bubble growth and solid-liquid heat transfer characteristics in pool boiling is of vital significance for the thermal management of high-heat-flux components in practical engineering. Many researchers have enhanced solid-liquid heat transfer by altering wall wettability or increasing wall roughness. Based on wall wettability, hydrophobic area fraction, distribution patterns, and structure height, this study designed various mixed hydrophilic/hydrophobic composite surfaces. Using MD simulations, the dynamic bubble growth processes and enhanced heat transfer characteristics on both smooth and structured mixed-wettability surfaces were studied from a microscopic perspective. The main contents and conclusions are as follows:

(1) Pool Boiling on Smooth Mixed-Wettability Surfaces MD simulations of pool boiling on smooth composite surfaces clarified the physical mechanisms governing solid-liquid boiling heat transfer under various wettabilities and hydrophobic distributions.

The presence of hydrophobic regions promotes bubble nucleation, accelerates bubble growth, and enhances evaporation. However, as the solid-liquid interaction strength increases, the time required to form a vapor film shortens, disrupting the heat transfer process and gradually reducing the number of evaporated atoms.

The composite surface with a hydrophobic fraction of $\beta = 0.25$ exhibits excellent heat transfer characteristics. Compared to the purely hydrophilic surface #LPi, its onset of nucleate boiling time t_{ONB} and film boiling time t_{FB} are reduced by up to 6.8% and 4.8%, respectively. However, as β increases, vapor film formation occurs earlier, and the heat transfer deteriorates.

Surface #0.25_L4 achieves the minimum interfacial thermal resistance—differing by only 2% compared to the purely hydrophilic surface #LPi—due to the relatively "dense" distribution of low-potential-energy zones surrounding its hydrophobic regions.

As β increases, interfacial thermal resistance rises significantly; surface #0.64_L1 yields the maximum thermal resistance, a 368.68% increase compared to #LPi.

(2) Pool Boiling on Structured Mixed-Wettability Surfaces Building upon the smooth surface study, structured mixed-wettability surfaces were constructed to explore the effects of wall temperature on bubble growth and evaporation.

Increasing the wall temperature shortens both bubble nucleation time and vapor film formation time, while lowering the nucleation temperature. For hydrophobic structured surfaces, surface #0.25_Case1 showed the most significant variations, with t_{ONB} and t_{FB} shortened by 60% and 64.2%, respectively; for hydrophilic structured surfaces, the reduction is relatively modest.

The wall temperature dictates the liquid's phase change mode. At $T_m = 160$ K, the evaporation rate of the hydrophobic structured surface gradually decreases as the structure height h_R increases, whereas on the hydrophilic structured surface, the evaporation rate varies little. When T_m is lowered to 140 K, the mode transitions from boiling to pure evaporation. Due to weaker solid-liquid interactions on the hydrophobic surface, the liquid phase temperature changes slowly with increasing h_R . Conversely, on the hydrophilic surface—where a vapor film no longer forms—the liquid maintains stable contact, and the evaporation rate sequentially increases with higher h_R .

On hydrophobic structured surfaces, as β increases, the area of the low-potential-energy zone decreases, leading to a smaller liquid phase temperature change ΔT . Compared to baseline configurations ($\beta = 0.25$), the ΔT for configurations with $\beta = 0.49$ dropped by 15.4% to 21.8%. For hydrophilic structured surfaces, an increase in β enlarges the solid-liquid contact area; as h_R increases, their ΔT improved by 14.0%, 10.1%, and 9.4%, respectively. Driven by capillary action, structural voids remain continually filled with liquid atoms, preventing wall "dry-out".

At $T_m = 160$ K, increasing β has a more pronounced effect on the evaporation atom count of hydrophobic surfaces, with evaporation rates for $\beta = 0.49$ configurations

increasing by 4.4% to 6.6% compared to $\beta = 0.25$. As T_m decreases, the evaporation atom counts on hydrophilic structured surfaces increased slightly (up to 1.2%), whereas evaporation rates on hydrophobic surfaces fell below those of hydrophilic surfaces, decreasing by 3.2% to 7.1%.

8.2. Future Research Directions

Although this study has made certain progress in investigating the micro-mechanical mechanisms of droplet spreading and capillary flow, the phenomena and mechanisms involved remain highly complex. This complexity arises because intermolecular forces cannot be ignored at the micro/nanoscale, and potential scale effects must also be taken into account. Therefore, numerous issues warrant further in-depth research and exploration, as detailed below:

(1) Effect of solid surface roughness In both nature and engineering applications, most solid surfaces possess a certain degree of roughness. Some roughness is inherent to the solid surface, while some is artificially fabricated through processes such as etching, coating, and lamination to meet specific practical needs. The presence of surface roughness induces contact angle hysteresis and dynamic contact angle variations, thereby further complicating the phenomena and underlying mechanisms of micro/nanoscale droplet spreading and capillary flow. Therefore, it is necessary to build upon this study to further investigate the effects of solid surface roughness on droplet spreading and capillary flow processes.

(2) Droplet spreading and capillary flow in multi-component and multiphase systems The research in this study focuses on the effects and mechanisms of solid-liquid interactions, solid surface wettability, and mineral types and their surface structures on droplet spreading and capillary flow. Consequently, it primarily concerns single-phase wetting of droplets on solid surfaces and single-phase capillary flow within capillary channels. It does not account for the diversity of fluid components in practical engineering applications, nor does it sufficiently consider droplet spreading

and capillary flow in multiphase systems. Therefore, it is essential to conduct research on the micro-mechanical mechanisms of droplet spreading and capillary flow within multi-component and multiphase systems.

(3) Capillary flow in capillary channels with different geometric shapes In nature and many practical applications, there are numerous micro/nanoscale capillary channels with diverse geometric shapes. However, current research is predominantly focused on capillary flow within cylindrical channels or channels formed by two parallel walls, with relatively fewer studies dedicated to other geometric configurations. Therefore, further in-depth studies can be carried out on capillary flow in channels of different geometric shapes to reveal the influence and mechanisms of channel geometry on micro/nanoscale capillary flow processes.

(4) Establishment of multi-scale theoretical models This study mainly focuses on the micro-mechanical mechanisms of droplet spreading and capillary flow, systematically investigating capillary flow phenomena under different wettability conditions at the micro/nanoscale and within typical mineral capillary channels, and establishing corresponding theoretical models. Meanwhile, the continuous advancement in the precision of experimental instruments and equipment facilitates the observation of spatial variability in porous media components and pore structures. By obtaining the structure and components of porous media and combining them with image processing techniques, three-dimensional digital cores can be acquired to characterize porous media precisely. On this basis, combined with the micro-mechanical mechanisms of droplet spreading and capillary flow, pore-scale spontaneous imbibition experiments, simulations, and theoretical studies can be further conducted to reveal pore-scale flow laws. Furthermore, a "bottom-up" strategy can be adopted to transfer the laws and parameters obtained from the pore-scale research to larger scales, thereby establishing a systematic multi-scale theoretical model.

Although the bubble growth and heat transfer processes on smooth and structured mixed hydrophilic/hydrophobic surfaces have been investigated from a microscopic

perspective, several limitations remain in this study due to insufficient experimental conditions and time constraints, which need further supplementation and improvement:

(1) Refinement of hydrophobic area fractions Regarding the area fraction of the hydrophobic regions on the wall, this study only considered four fractions: 0.25, 0.36, 0.49, and 0.64. Other area fractions were not investigated in greater detail. Future research could further subdivide the hydrophobic area fractions to thoroughly discuss the effects of the hydrophobic area fraction on solid-liquid bubble growth and heat transfer.

(2) Complexity of hydrophobic region distributions Regarding the spatial distribution of the hydrophobic regions, this study only considered ideal uniform distributions of 1x1, 2x2, 3x3, 4x4, and 5x5. Future work could examine the impacts of more complex and irregular distribution patterns on the solid-liquid heat transfer process.

(3) Optimization of micro/nanostructured walls Regarding the structured walls, the micro/nanostructures constructed in this study are simple cylindrical shapes, without considering the influence of other geometric shapes on the wall heat transfer characteristics. Furthermore, the constructed rough surfaces do not fully replicate real-world rough walls. Future molecular dynamics simulations could further optimize the wall models to construct rough surfaces that conform better to realistic conditions, thereby achieving a better alignment with actual experimental setups.

(4) Expansion of simulation scales and real working fluids Due to the limitations of computational resources, the simulation system size in this study is restricted to a dozen nanometers. Moreover, a commonly used argon fluid was selected to substitute for liquid water during the simulations. In the future, it is necessary to expand the simulation system size and carry out pool boiling heat transfer research using real working fluids on both smooth and structured mixed-wettability surfaces, thereby

laying a foundation for the practical application of composite hydrophilic/hydrophobic walls in enhancing solid-liquid heat transfer processes.

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