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Formation of Liquid Film in Heterogeneous Condensation of Water Vapor: Effects of Solid–Fluid Interaction and Sulfuric Acid Component

Shuhang Lyu, Zuozhou Tang, Qiang Song,* Zhen Yang, and Yuanyuan Duan

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ABSTRACT: Und densation on solid air pollutant contr formation of con	derstanding the phenomenon surfaces is vital for industrial ol and desalination. In this we idensed liquid films via mo	of filmwise con- processes such as ork, we study the lecular dynamics		Solid-fluid Interaction

simulations, and the effects of solid-fluid interactions and the sulfuric acid component are given major attention. Water is chosen as the fluid, while the solid-fluid interaction is modified to characterize different solid surfaces. The results show that as the solid-fluid interaction decreases, the solid surface transforms from a completely wetting surface to a partially wetting surface, and the



film formation process shows significant differences. The condensed liquid on the completely wetting surface forms small liquid films, which merge to form a complete film covering the surface. With the enhancement of solid-fluid interaction, the condensation rate increases first and then remains virtually invariant, resulting in a film formation time that decreases first and then maintains constant. The condensed liquid on the partially wetting surfaces appears as nanodroplets, and the coalescence between nanodroplets leads to the formation of the liquid film. It is found that the stronger the solid-fluid interaction, the more the coalesced droplets tend to be pinned at nucleation sites, the easier it is to form a liquid film, and the shorter the time required for droplet merging. The sulfuric acid component accelerates liquid film formation on both completely wetting and partially wetting surfaces, but the effect of sulfuric acid is more significant on partially wetting surfaces. The 5% molar fraction of sulfuric acid reduces the nucleation time by 72% and increases the condensation rate by 137% under partial wetting, while the same amount of sulfuric acid only increases the nucleation rate by 6% on the completely wetting surface.

INTRODUCTION

Heterogeneous condensation of supersaturated vapor on solid surfaces is a ubiquitous phenomenon in nature.¹⁻⁴ Due to its broad application prospects, heterogeneous condensation has attracted extensive attention in recent years. Many industrial processes need the control of vapor condensation on solid surfaces. For example, the effective generation of aerosol needs the regulation of heterogeneous condensation on seed particles;^{5,6} reducing pollution emissions from thermal power plants requires a clear understanding of the heterogeneous condensation on ash particles and pipe surfaces;⁷⁻¹⁰ and rapid heterogeneous condensation is important for achieving the efficient production of desalinated water.¹¹

Based on the morphology of condensed liquid, the heterogeneous condensation can be categorized into two modes, i.e., dropwise and filmwise condensation.¹² In dropwise condensation, the condensed liquid stays on the surface in the form of droplets,^{3,4} while in filmwise condensation, the solid surface is covered by a condensed liquid film. Filmwise condensation is quite common in the industry, especially for hydrophilic surfaces, such as metal and suspending particles. The filmwise condensation process can be divided into two

stages: the formation and growth of the liquid film. In the film formation stage, condensation nuclei are first formed on the solid surfaces, and with the development and coalescence of liquid clusters, the condensed liquid forms a film to cover the entire surface. After that, since the liquid film has fully covered the surface, vapor condensation occurs on the liquid-vapor interface, rendering the growth of the liquid film.

A complete description of filmwise condensation needs a detailed understanding of the two stages, i.e., the formation and growth of the condensed liquid film. Many numerical and experimental studies have been carried out on film growth, and several well-developed theories were established to describe the growth of condensation film.¹³⁻¹⁵ However, for the formation of liquid film, although some studies have been conducted to investigate the morphology 16,17 and stability 18,19

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of condensed liquid film, these works mainly focused on the macroscopic film. The knowledge of the nanoscale film formation corresponding to the onset of filmwise condensation is still lacking. In addition, several important influencing factors are involved in heterogeneous condensation, and the roles of these influencing factors in the formation process of the condensed film have not yet been elucidated. Among these factors, solid-fluid interaction and condensable components are two of the most common ones. Even if the fluids are the same, solid-fluid interactions often differ for different solid surfaces, leading to various condensation phenomena. The heterogeneous condensation of multicomponent vapor is also very common in nature and industry. Among these multicomponent vapors, water/sulfuric acid binary mixtures are typical in many condensation scenarios, for example, the condensation of water/sulfuric acid binary vapor on ash particles in the flue gas of power plants²⁰ and on the surface of nanoparticles in the stratospheric atmosphere.²¹ Therefore, the condensation of water/sulfuric acid binary mixtures is significant for some industrial applications, such as the removal of SO₃ from flue gas.^{9,10} The presence of the condensable sulfuric acid component significantly affects the condensation process of water vapor, resulting in the distinctive condensation phenomena of water/sulfuric acid binary vapor compared to those of water vapor. The solid-fluid interaction and sulfuric acid component are two common factors affecting heterogeneous condensation, whereas current studies are still insufficient to understand the effects of these two factors on the formation of the liquid film.

Many studies have been conducted to investigate the condensation phenomena under different solid-fluid interactions and found that the effect of the solid-fluid interaction is quite significant for heterogeneous condensation. Che et al.² ² performed molecular dynamics (MD) simulations to study the condensation of water vapor on smooth surfaces and observed that with the enhancement of the solid-fluid interaction, the surface wettability increases and the condensed liquid film gradually becomes complete. Niu et al.²³ simulated the condensation of water vapor in a nanochannel and proposed that the interfacial thermal resistance decreases with the solid-fluid interaction, leading to a better heat transfer performance. Sheng et al.²⁴ investigated the onset of heterogeneous condensation via MD simulations and found that the solid-fluid interaction would change the solid-vapor and solid-liquid interfacial tensions, thus affecting the critical conditions for liquid film formation. Pu et al.²⁵ constructed a phase diagram of the argon vapor condensation mode based on the solid-fluid interaction and solid-fluid temperature difference to reveal critical conditions for the formation of the condensed liquid film. Although many studies have been conducted on the effect of solid-fluid interaction, previous works mainly focused on the heat transfer characteristics of liquid film and the critical conditions for film formation. However, the specific analysis of the formation pathways and the morphology of the nanoscale liquid film is still lacking. It has been demonstrated in previous studies that solid-fluid interactions impact multiple factors in heterogeneous condensation, such as surface wettability, 2^{2-29} thermal resistance, $2^{2,23,26}$ and interfacial properties. $2^{24,28}$ With the variation of solid-fluid interaction, the alteration of these key factors is expected to change the liquid film morphology and affect the condensation rate, thus influencing the film formation process. However, due to the complicated influencing factors, the

effects of solid-fluid interaction on the liquid film formation process cannot be easily predicted, and thus it is of great importance to conduct a comprehensive study on this issue.

It has been found that the multicomponent condensations differ greatly from the condensation of pure substances, indicating that the presence of condensable components can significantly affect the water vapor condensation. Several differences have been distinguished between the condensation of water/sulfuric acid and pure water vapors. Wu et al.³⁰ found that the rate of heterogeneous condensation can be promoted by the sulfuric acid component. Kulmala et al.³¹ noted that the saturation vapor pressure of water/sulfuric acid binary mixtures is much less than that of pure water, leading to rapid condensation of the mixture vapor, even at low air humidity. Sipilä et al.³² and Berndt et al.³³ measured the critical nucleus size for the homogeneous nucleation of water/sulfuric acid binary vapors, showing that 1-2 sulfuric acid molecules are sufficient to form a stable condensation nucleus. Zhang et al.³⁴ suggested that the strong hydrogen bonds between water and sulfuric acid molecules could prevent the evaporation of sulfuric acid molecules on the solid surface, thus enhancing the stability of condensed sulfuric acid molecules. Matsubara et al.³⁵ found via MD simulations that small amounts of sulfuric acid can effectively increase the condensation rate, and hydrate growth plays a significant role in this enhancement. Toivola et al.³⁶ showed that the bisulfate and hydronium ions generated by sulfuric acid ionization are well separated to form a large dipole moment, thus enhancing the attraction of polar molecules to liquid cluster and increasing the condensation rate. Previous studies have shown that the sulfuric acid component significantly affects the production and growth of condensation nuclei, which is the origin of the condensed liquid film. Therefore, the sulfuric acid component is bound to affect the film formation process. However, the role of sulfuric acid has rarely been discussed in film formation, and the comparison and analysis of water/sulfuric acid binary condensation on surfaces with various solid-fluid interactions are also lacking. There is still a strong need to carry out exhaustive research on the effects of the sulfuric acid component on the heterogeneous condensation of water vapor, especially the film formation stage.

In this work, we couple grand canonical Monte Carlo (GCMC) with molecular dynamics (MD) simulations to simulate the condensation process on solid surfaces from a nanoscale perspective. We classify the solid surfaces into completely and partially wetting surfaces and discuss the formation of nanoscale condensed films on both types of surfaces, respectively. For completely wetting surfaces, we show the pathway of liquid film formation, analyze the changes in the liquid film morphology and condensation rate, and reveal the influence of solid-fluid interaction on the formation time of the liquid film. For partially wetting surfaces, we investigate the nucleation characteristics, present the formation process of liquid films on rough surfaces, analyze the coalescence of adjacent liquid clusters, and answer how solid-fluid interactions affect the critical condition for liquid film formation. Additionally, to reveal the influence of sulfuric acid components on the formation process of condensed liquid films, we compare the heterogeneous condensation process of water/sulfuric acid mixtures on the two types of surfaces and analyze the similarities and differences of the effects of sulfuric acid components.



Figure 1. Simulation systems for heterogeneous condensation on (a) the smooth surface and (b) the rough surface with two nucleation sites.

METHODOLOGY

Molecular Models. In this work, molecular dynamics simulations are performed to study the heterogeneous condensation process. The simulations are implemented by the open-source software LAMMPS,³⁷ and the visualization is achieved by Ovito.³⁸ Three types of molecules, i.e., sulfuric acid, water, and α -iron, are involved, and various force field models are used to describe the inter- and intramolecular interaction potentials. Water molecules are described by the SPC-E/F (flexible SPC/E) model proposed by Berendsen et al.³⁹ The intermolecular interaction energy E_{inter} of water molecules can be expressed as

$$E_{\text{inter}} = \underbrace{\sum_{ij} 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right]}_{\text{Lennard-Jones potentials}} + \underbrace{\sum_{ij} \frac{1}{4\pi\varepsilon_{0}} \frac{q_{i}q_{j}}{r_{ij}}}_{\text{Coulomb potentials}}$$
(1)

where ε_{ij} is the potential well depth, r_{ij} is the distance between atoms, σ_{ij} is the size of particles, ε_0 is the permittivity of vacuum, and q_i and q_j are the charges of atoms *i* and *j*, respectively. The first term in E_{inter} is the Lennard-Jones 12-6 potential and the second term is the Coulomb potential. The intramolecular interactions in water molecules are described by harmonic bonds

$$E_{\rm intra} = \sum_{n} k_{\rm b} (r_n - r_n^{\ 0})^2$$
(2)

where *n* is the bond number, r_n is the bond distance, r_n^0 is the equilibrium bond length, and k_b is the elastic force constant. The interaction between iron atoms is described by the Lennard-Jones 12-6 potential energy model, and the model parameters are referred to as the force field model proposed by Filippova et al.⁴⁰ The parameters for the force fields of water molecules and α -iron atoms are shown in Table S1.

The sulfuric acid molecules are described by the OPLS-AA model,⁴¹ where the potential energy consists of bond, angle, dihedral, and intermolecular potentials

$$E_{\rm p} = E_{\rm bonds} + E_{\rm angles} + E_{\rm dihedrals} + E_{\rm inter}$$
(3)

where E_{bonds} , E_{angles} , and $E_{\text{dihedrals}}$ are two-, three-, and four-body interactions, respectively. E_{inter} represents the intermolecular interaction, which is described in eq 1. The force field parameters for sulfuric acid molecules are all referenced to the model proposed by Loukonen et al.⁴² and are listed in Tables S2–S5.

The interaction potentials between different types of molecules are described by the Lennard-Jones 12-6 potential and the Coulomb potential, where the relevant parameters of the Lennard-Jones 12-6 potential are obtained from the Lorentz-Berthelot mixing rule

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2}, \ \varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}}$$
(4)

According to the simulation results, the normal α -iron surface is completely wetting for water. Therefore, we have to modify the interaction parameters between water and α -iron molecules to characterize surfaces with different wettabilities. The interaction energy between iron atoms and fluid atoms can be expressed as

$$E_{\rm Fe-fluid} = k E_{\rm Fe-fluid}^{0} \tag{5}$$

where $E_{\text{Fe-fluid}}^{0}$ is the interaction energy calculated by the Lorentz–Berthelot mixing rule and k is the interaction parameter. The magnitude of intramolecular energy between fluid and solid molecules is controlled by the interaction parameter, and thus the condensation of water vapor on different solid surfaces can be achieved by varying k.

GCMC+MD Simulation of Heterogeneous Condensation. The simulated systems are set up as shown in Figure 1 and can be divided into two groups, namely, heterogeneous condensation on smooth surfaces (Figure 1a) and on rough surfaces (Figure 1b). In all of the simulations, periodic boundary conditions are applied to the boundaries in the xand y-directions, and the z-direction boundaries are set as reflecting walls to avoid atom loss. Similar setups are used in the vertical direction (z-direction) for both types of systems. α -Fe metal substrates with a body-centered cubic lattice (bcc) are placed at the bottom of the simulation system, and the lattice constant is set to $a_{\rm Fe} = 0.28664$ nm.⁴⁰ A vapor space with a height of 40 nm is arranged above the substrate and divided into three regions. The top region is the GCMC region with a thickness of 10 nm, in which the density and temperature of the supersaturated water vapor are maintained by the GCMC method to provide a reliable source of water vapor for the heterogeneous condensation process. Below the GCMC region is the transition region, where positions and velocities of particles are integrated every time step without any additional constraints. The lowermost part of the vapor space, i.e., the region near the metal substrate, is set as the condensation region. The condensation region is maintained at a low temperature to ensure vapor supersaturation during the condensation process. The metal substrates used in the two types of systems differ in that the smooth substrate consists of eight layers of α -iron with a length of 20.06 nm in both the xand y-directions, while the rough substrate has a length of 29.81 nm in the x-direction and 24.08 nm in the y-direction.



Figure 2. (a) Calculation of contact angle. (b) Wettability of solid surfaces with different solid-fluid interaction parameters.

The morphology of the rough surface is shown in Figure S1, and the corresponding parameters are listed in Table S6. The nucleation sites are located at the center of the rough substrate with a depth of 1.72 nm, a width of 0.86 nm, and a spacing of 5.73 nm. The smooth part of the rough substrate consists of 8 layers of α -iron atoms, and the part of the substrate near the nucleation sites is thickened to 16 layers to ensure that the thickness of the substrate exceeds the cutoff distance of the solid–fluid interaction.

The condensation simulations are performed using the GCMC+MD method, which has been demonstrated to be effective in simulating condensation processes.⁴³⁻⁴⁵ The GCMC method is adopted to maintain the vapor pressure of the system through the whole simulation by inserting or deleting fluid molecules in a specific region. The velocity-Verlet algorithm⁴⁶ is utilized to update the particle velocities and positions. The time step is set to $\tau = 0.0005$ ps (for the systems containing sulfuric acid) or $\tau = 0.001$ ps (for the pure water systems). The time step is different for systems with and without sulfuric acid as the sulfuric acid molecule has a complex structure, requiring a smaller time step to avoid the loss of atoms. The simulation of heterogeneous condensation can generally be divided into two stages, namely, the relaxation and condensation stages. In the relaxation stage, the temperature of the entire vapor is controlled by the Nose-Hoover thermostat,47 and the density of water vapor in the GCMC region is maintained by the GCMC method. The corresponding vapor pressure used in the GCMC method is set to p_{GCMC} = 0.379 MPa. After 1 ns, an equilibrium vapor with a temperature of T = 600 K and a density of $\rho_v = 1.37 \text{ kg} \cdot \text{m}^{-3}$ is obtained. The vapor density is slightly higher than the saturated water vapor density at 400 K to ensure a certain degree of supersaturation and suppress the homogeneous condensation. The interaction parameter is fixed at k = 0.01 in the relaxation stage to reduce the adsorption of fluid molecules on the solid surface. In the condensation stage, the temperature and vapor density in the GCMC region are still maintained in the same way, and no additional constraints are imposed on the vapor molecules in the transition region. At the same time, the vapor in the condensation region is cooled down to T = 400 K by the Nose-Hoover thermostat to achieve condensation on solid surfaces. As surface nucleation is

a highly stochastic process, the formation of liquid nuclei on nucleation sites would be rather random. The randomity of nucleation can pose significant difficulties in the quantitative analysis of droplet growth and coalescence while only having a minor impact on the conclusions. Besides, instead of the nucleation process, the growth and coalescence of condensed droplets are the major concern on partially wetting surfaces. Therefore, in the simulations of condensation on rough surfaces, the two nucleation sites are prefilled with liquid water to obtain stable simulation results and save computational resources.

In addition, simulations are also carried out to investigate the heterogeneous condensation process of the water/sulfuric acid binary vapors. The simulation procedures are the same as that of the pure water system, except that a 5% molar fraction of sulfuric acid molecules is added to the vapor at the onset of the relaxation stage. No additional temperature constraint is imposed on the sulfuric acid molecules, and the temperature of sulfuric acid is regulated by collision with water molecules.

Validation of MD Code. To validate the effectiveness of the GCMC method, we monitor the number of vapor molecules in the GCMC region. As shown in Figure S2, the number of vapor molecules remains at the equilibrium value during the condensation, demonstrating that the GCMC settings are appropriate. In all simulations, the GCMC settings are adjusted to ensure a stable number of vapor molecules in the GCMC region, maintaining a reliable source of water vapor.

Additionally, the growth curve of a condensed water droplet is calculated to validate the MD code. In the simulation, the solid-fluid interaction parameter is set to k = 0.15, corresponding to a large contact angle of $\theta = 116^{\circ}$. The hydrophobic surface is employed to reduce the number of liquid nuclei and prevent the coalescence of liquid clusters. As shown in Figure S3, the growth curve of the nanodroplet is obtained by calculating the number of water molecules in the droplet. According to Toxvaerd's work,⁴⁸ the number of molecules in a condensed droplet grows with a time exponent of 1.25 after the onset of condensation. As shown in Figure S3, the droplet growth curve is double-logarithmically fitted, which is in good agreement with the work of Toxvaerd⁴⁸ and proves the validity of the MD code.



Figure 3. Image sequences of heterogeneous condensation of water vapor on a completely wetting surface at a temperature of T = 400 K and an interaction parameter of k = 1.

RESULTS AND DISCUSSION

Formation of Liquid Film on Completely Wetting Surfaces. The wettability of the solid surface prominently affects the heterogeneous condensation process. Previous studies have shown that the condensation phenomena differ significantly on completely and partially wetting surfaces.^{22,24,25} The discrepancies in condensation phenomena indicate that the formation of the condensed liquid film is likely to be varied with the surface wettability. Therefore, it is necessary to investigate the formation of liquid film and analyze the role of solid–fluid interactions under complete wetting and partial wetting conditions, respectively.

The surface wettability is first evaluated under different solid-fluid interactions. The equilibrium contact angles characterize the wettability of partially wetting surfaces. Thus, a group of MD simulations is performed to calculate the equilibrium contact angles. In the simulations, the density distributions of the equilibrium cylindrical droplets are calculated to obtain the contact angles. As shown in Figure 2a, the iso-density line with the average density of liquid and vapor is considered the liquid-vapor boundary, and the equilibrium contact angle is derived from the circular regression. The dependence of the equilibrium contact angle θ on the interaction parameter k is shown in Figure 2b. According to the equilibrium contact angle, Figure 2b is divided into three regions corresponding to different surface wettabilities, including hydrophobic ($\theta > 90^{\circ}$), hydrophilic $(90^{\circ} > \theta > 0^{\circ})$, and complete wetting regions ($\theta = 0^{\circ}$, flat liquid film). The simulation results illustrate that with the enhancement of the solid-fluid interaction, the surface wettability gradually increases, and the solid surface transforms from a hydrophobic surface to a hydrophilic surface and finally becomes a completely wetting surface. The simulating procedures to achieve the equilibrium states of droplets are detailed in our previous work.44

In this section, the heterogeneous condensation of water vapor on completely wetting surfaces is investigated. According to Figure 2b, complete wetting occurs when the solid-fluid interaction parameter exceeds 0.35. We select completely wetting surfaces with various solid-fluid interaction parameters in the range of k = 0.5-5 and simulate the heterogeneous condensation on smooth surfaces. The general condensation process on a smooth and completely wetting surface is shown in Figure 3. The liquid clusters first occur at different locations via nucleation and then grow and merge with neighboring ones to create an incomplete liquid film. As the condensation proceeds, the liquid film gradually becomes complete and eventually covers the whole solid surface.

The number of liquid clusters is calculated to evaluate the film formation process. The Stillinger criterion⁵⁰ is employed to analyze the liquid clusters. The oxygen atoms are considered the characteristic atoms, and water molecules are assumed to be in the same liquid cluster once the spatial distance between the two oxygen atoms is less than 0.35 nm.⁵¹ The variation of the number of liquid clusters n_{cluster} during the condensation process is shown in Figure 4a. As the condensation proceeds, n_{cluster} first increases, then decreases, and finally reaches $n_{\text{cluster}} =$ 1. According to Figure 4a, the heterogeneous condensation on completely wetting surfaces can be divided into three stages, i.e., the nucleation stage, the coalescence stage, and the film stage. In the nucleation stage, the condensed liquid only covers a minor part of the solid surface, and most of the solid surface is exposed to vapor. As there is no energy barrier for nuclei formation on completely wetting surfaces,⁵² the number of condensation nuclei increases rapidly, resulting in a sharp increase in the number of liquid clusters. Subsequently, as the liquid clusters grow, on the one hand, the number of existing clusters is reduced by merging of clusters; on the other hand, the solid surface is gradually covered by the liquid, suppressing the emergence of new nuclei. Therefore, the number of liquid clusters begins to decrease at a certain point, marking the initiation of the coalescence stage. Eventually, the liquid clusters merge to form a large liquid film covering almost the entire solid surface, and the solid-vapor interface virtually vanishes. After that, only one cluster, the liquid film, is left on the surface, and the condensation of vapor molecules merely takes place at the liquid-vapor interface, which we refer to as the film stage here.

Based on the number of liquid clusters, the film formation time τ_{film} , defined as the boundary between the coalescence stage and the film stage, can be calculated, allowing us to analyze film formation speed. The liquid film is formed when n_{cluster} reaches 1 for the first time, marking the beginning of the film stage. As shown in Figure 4b, τ_{film} is calculated on the completely wetting surfaces with different solid—fluid interactions. The film formation time first decreases with increasing interaction parameter k and then remains almost invariant. Thus, the film formation time can be divided into two regimes, as shown in Figure 4b. The factors influencing the liquid film formation are analyzed to explore the mechanism behind the two regimes.

The film formation time is mainly affected by two key factors: condensation rate $\dot{N}_{\rm liq}$ and film density $\rho_{\rm film}$. The condensation rate refers to the number of liquid molecules condensed on the solid surface per unit time, and the higher the condensation rate, the larger the increasing rate of liquid



Figure 4. Formation of liquid film. (a) Temporal revolution of the number of liquid clusters n_{cluster} on the solid surface. The condensation process is divided into three stages according to the trend of n_{cluster} . (b) The time required to form a complete liquid film τ_{film} first decreases and then remains almost invariant with the increase of solid–fluid interaction.

molecules and the shorter the film formation time. The liquid film density is defined as the number of condensed fluid molecules per unit area of the solid surface. The film density is calculated at the corresponding film formation time to illustrate the minimum film density required for the film formation. The higher the film density, the more liquid molecules are required to form the liquid film, and the longer the film formation time.

We calculate the condensation rate and the film density at different solid-fluid interactions. The number of liquid molecules on the solid surface $N_{\rm liq}$ is calculated to compare the condensation rate under different solid-fluid interactions. As shown in Figure 5a, an approximately linear relationship between $N_{\rm liq}$ and the condensation time τ is observed on completely wetting surfaces. The condensation rate at $N_{\rm liq} = 1000$, obtained by polynomial fitting of the $N_{\rm liq}-\tau$ curve, is compared under various interaction parameters in the range of k = 0.5-5. As shown in Figure 5b, the condensation rate follows an increasing trend with increasing k, but the slope

gradually decreases, and the condensation rate remains almost invariant at k > 1.5. As the solid–fluid interaction increases, the attraction of solid surfaces to vapor molecules is improved, leading to the increase in the condensation rate. However, the finite diffusion rate of vapor limits the maximum number of vapor molecules captured by the solid surface, hindering the increase of the condensation rate. Therefore, the condensation rate is dominated by the diffusion rate of vapor molecules instead of the solid-fluid interaction at k > 1.5. Besides, it is worth noting that some points in Figure 5b depart from the smooth curve. Such a departure can be attributed to the randomity of heterogeneous condensation and the deviation in the fitting process. Due to the limited computational resource, we do not conduct multiple simulations to calculate the condensation rate. We hope a more accurate condensation rate can be obtained in future studies.

The dependence of the film density ρ_{film} on the interaction parameter k is shown in Figure S4. The film density only shows a slightly decreasing trend with k, indicating that the influence of film density is insignificant for the simulated range of interaction parameters. Furthermore, it is worth noting that the decreasing trend of film density is consistent with the theory of wetting films. de Gennes et al.⁵³ pointed out that the equilibrium thickness of the wetting film declines with the surface wettability. In our simulation, with the enhancement of solid—fluid interaction, the surface becomes more wettable, leading to the thinning of liquid films and the drop in film density.

The variation of film density and condensation rate with solid—fluid interaction contributes to the changing trend of the film formation time. In the simulated range of solid—fluid interaction, the film density only shows a minor difference, and thus, the film formation time predominantly depends on the condensation rate. In regime I, the solid—fluid interaction is relatively weak. The condensation rate remarkably increases with the enhancement of solid—fluid interaction, leading to a noticeable decline in the film formation time. In regime II, with the further increase of k, the increment of condensation rate is limited by the finite diffusion rate. The condensation rate is primarily determined by the vertical diffusion rate of vapor molecules and hardly varies with the solid—fluid interaction. Therefore, the film formation time maintains almost constant at k > 1.5.

Formation of Liquid Film on Partially Wetting Surfaces. The heterogeneous condensation on partially wetting surfaces is simulated to illustrate the pathway of film formation on partially wetting surfaces. First, the solid-fluid interaction parameter is set to k = 0.15, and the simulations are performed to investigate the condensation process on smooth surfaces. As shown in Figure S5, the snapshots show that no condensation occurs on the partially wetting surface at $\tau = 500$ ps, and at $\tau = 1000$ ps, a single nucleus appears, which gradually grows. At $\tau = 2000$ ps, a relatively large nanodroplet is formed on the surface. The temporal evolution of the number of liquid molecules is calculated and compared with a completely wetting surface (k = 1) to characterize the condensation process. As shown in Figure 6a, the number of liquid molecules first oscillates around $N_{\text{liq}} = 10$ and then increases rapidly at $\tau = 1000$ ps on the partially wetting surface while showing an instant increase once the vapor temperature drops to 400 K ($\tau = 0$ ps) on the completely wetting surface. This distinctive condensation process on the partially wetting surface has also been observed in previous studies,⁴⁵ indicating



Figure 5. (a) Number of condensed molecules on the solid surfaces N_{iiq} shows an approximately linear relationship with time. (b) Condensation rate increases with k.



Figure 6. Comparison between condensation on a partially wetting surface (k = 0.15) and a completely wetting surface (k = 1). (a) Number of liquid molecules on the surfaces and (b) size of the largest cluster. The number of liquid molecules on the partially wetting surface rapidly increases after forming a stable cluster.

the significant differences between the heterogeneous condensation on partially and completely wetting surfaces.

The difference in nucleation serves as one significant contributing factor to the different condensation phenomena on the two types of surfaces. According to the classical nucleation theory, the occurrence of heterogeneous condensation requires stable condensation nuclei, which are created by the thermal fluctuations and contain at least a critical number of molecules. The critical size of condensation nuclei depends on the free-energy barrier, which is associated with surface wettability. The free-energy barrier gradually falls with the enhancement of wettability, resulting in a decreasing critical nucleus size with the decrease of contact angle. On completely wetting surfaces, the contact angle drops to zero, leading to the vanish of the free-energy barrier and critical nuclei with zero molecules. The discrepancy in the free-energy barriers contributes to the divergent condensation phenomena on partially wetting surfaces and completely wetting surfaces. In the case of complete wetting, even a single molecule can act as a stable liquid cluster, indicating that the molecules

adsorbed on the solid surface can hardly re-evaporate to the vapor space. In contrast, small liquid clusters are not stable on partially wetting surfaces and will spontaneously evaporate due to the chemical potential difference.⁵² The heterogeneous condensation takes place on partially wetting surfaces only if the size of condensation nuclei created by thermal fluctuations exceeds the critical value.

The size of the largest liquid cluster is calculated to support the above analysis for the nucleation characteristics on the two types of surfaces. As shown in Figure 6b, within the first 700 ps, the number of water molecules in the largest cluster remains less than 7. At $\tau = 700$ ps, the first stable nucleus appears, and the number of liquid molecules condensed on the surface begins to increase rapidly, indicating that the heterogeneous nucleation triggers the condensation on partially wetting surfaces. Additionally, according to the variation of the size of the largest liquid cluster, the critical size of condensation nuclei on the simulated surface (k = 0.15, $\theta = 116^{\circ}$) with the corresponding water vapor state ($\rho_v = 1.37$ kg·m⁻³, T = 400 K) can be estimated as $N_c = 7$. In contrast to the partially wetting surface, the size of the largest cluster shows an instant growth from the initial moment on the completely wetting surface. The variation of the cluster size indicates that the liquid cluster can grow with only one water molecule, demonstrating that the free-energy barrier to nucleation does not exist on the completely wetting surface. Our result shows good consistency with the classical nucleation theory. According to the classical nucleation theory, the free-energy barrier of heterogeneous nucleation decreases monotonically with decreasing contact angle and reaches zero when the surface becomes completely wetting ($\theta = 0^{\circ}$).⁵²

The above simulations suggest that the condensed liquid on completely wetting surfaces forms a liquid film and covers the entire solid surface, while the condensed liquid on the smooth and partially wetting surface appears in the form of liquid droplets, which grow and merge with each other to create larger droplets. On the smooth and partially wetting surfaces, a certain contact angle always exists between the liquid droplets and the solid surface, and thus it is difficult to form a complete liquid film on these surfaces. However, the phenomena of heterogeneous condensation do occur on partially wetting surfaces in practice.⁵⁴ These surfaces are generally not ideally smooth and often have a prominent surface roughness, which is assumed to affect the formation of filmwise condensation.⁵⁵ To reveal the pathway of liquid film formation on rough surfaces, we have carried out simulations on the heterogeneous condensation on surfaces with nucleation sites.

The setting of the rough surface is shown in Figure 1b. Two pyramid-like pits are created in the center of the substrate as nucleation sites, and the heterogeneous condensation is simulated under various solid-fluid interaction parameters. As the solid-fluid interaction changes, four different outcomes are revealed. The surface is relatively hydrophobic at small interaction parameters, and the condensation nuclei appear only on the nucleation sites. As shown in Figure 7a, droplets growing on adjacent nucleation sites merge with each other, and the coalesced droplet is depinned from one of the nucleation sites and continues to grow on the other one, which is named the "depinning" coalescence. As the solid-fluid interaction increases, the condensation nuclei still appear only at the nucleation sites, but the coalesced droplet is flattened and pinned at both nucleation sites, called the "pinning" coalescence, as shown in Figure 7b. With the further increase of the interaction parameter k, the surface contact angle is close to 0. As shown in Figure 7c, the condensation nuclei will not only appear at the nucleation sites but also appear on the surrounding smooth surface at k = 0.3. A large liquid film is formed via the merging of liquid clusters, including those on the nucleation sites and the smooth surface, and both nucleation sites remain wetted during the formation of the liquid film. Once k exceeds 0.35, the surface is transformed into a completely wetting surface. To compare the film formation process on smooth and rough surfaces under the condition of complete wetting, we simulate the condensation process on the completely wetting surface (k = 1) with nucleation sites, as shown in Figure 7d, and the condensation phenomenon is virtually the same as that on the smooth surface (Figure 3). The simulation results suggest that the coalesced droplet tends to be pinned at the nucleation sites with large solid-fluid interactions, leading to the formation of the liquid film. With the increase of the interaction parameter, the surface wettability is enhanced, resulting in a large adhesion work of droplets. On hydrophilic surfaces, the stronger



Figure 7. Growth and coalescence of liquid clusters on rough surfaces at different solid–fluid interaction parameters. (a) k = 0.15, (b) k = 0.20, (c) k = 0.30, and (d) k = 1.0.

adhesion between the surfaces and droplets shifts the coalescence of droplets from the "depinning" type to the "pinning" type.

The growth curves of the condensed droplets, i.e., the number of molecules in the liquid clusters, are calculated to analyze the coalescence of droplets quantitatively. The calculated results for k = 0.15 are shown in Figure 8a. The left droplet shows a similar growth curve to the right one, and the coalescence occurs at a certain point to form a large droplet, which is called the coalescence time τ_{coa} . The effect of solid-fluid interaction on the coalescence time is shown in Figure 8b, where τ_{coa} decreases with the interaction parameter, illustrating that the coalescence of condensed droplets occurs more frequently on hydrophilic surfaces. The slope of the τ_{coa} k curve is larger on hydrophilic surfaces ($\theta < 90^{\circ}$), implying that the coalescence time on hydrophilic surfaces is more sensitive to the variation of solid-fluid interaction than that on hydrophobic surfaces. We assume that the different modes of droplet coalescence contribute to the divergent slope of $\tau_{coa}-k$ curves on the hydrophobic and hydrophilic surfaces. As shown in Figure S6, droplet merging on hydrophobic surfaces is triggered by the contact at their diameters, while the merging of triple-phase contact lines leads to coalescence on hydrophilic surfaces. It is worth noting that since the liquid clusters on nucleation sites merge not only with those on adjacent sites



Figure 8. (a) Number of water molecules in condensed droplets. The interaction parameter is fixed at k = 0.15. (b) Time required for the coalescence of droplets at different interaction parameters.



Figure 9. Effect of the sulfuric acid component with a molar fraction of $x_{H_2SO_4} = 5\%$ on the heterogeneous condensation on the (a) partially wetting surface and (b) completely wetting surface.

but also may contact with clusters on nearby smooth surfaces for k > 0.25, the uncertainties of τ_{coa} are so large on these surfaces that the coalescence time cannot be accurately calculated. Therefore, the coalescence time in this range is not addressed in Figure 8b. In addition, the states of coalesced droplets are also analyzed at various solid—fluid interactions. As shown in Figure 8b, the circles represent "pinning", while triangles denote "depinning" coalescence. The critical value of the interaction parameter for the occurrence of "pinning" coalescence is k = 0.175, which is exactly the boundary between hydrophobic and hydrophilic surfaces. It has been demonstrated by previous studies that the pinning effect can be overcome by the coalescence of adjacent Wenzel droplets, indicating that the coalescence mode can affect the wetting states of coalesced droplets.

The simulation results show that the enhanced solid-fluid interaction can effectively promote the formation of the liquid film due to the pinning of coalesced droplets at nucleation sites and the short time of coalescence on hydrophilic surfaces, which reveal the pathways of film formation on partially wetting surfaces and explain the microscopic mechanism behind the transition between condensation modes.

Effects of the Sulfuric Acid Component on the Film Formation. The heterogeneous condensation processes of water/sulfuric acid mixtures on partially wetting surfaces and completely wetting surfaces are simulated to investigate the effects of the sulfuric acid component on the formation of the condensed liquid film. At the initiation of the simulations, sulfuric acid molecules are randomly added to the vapor space to create a water/sulfuric acid binary vapor with a molar fraction of $x_{H_2SO_4}$ = 5%. The interaction parameters are set to k = 0.3 and 1 to represent the typical condensation processes on partially wetting surfaces and fully wetting surfaces, respectively. The calculated number of condensed molecules is shown in Figure 9. As shown in Figure 9a, on the partially wetting surface, the presence of sulfuric acid in water vapor reduces the nucleation time, i.e., the time required for the appearance of the first condensation nucleus, by 72%, indicating that the sulfuric acid component highly enhances

the heterogeneous nucleation. Additionally, the condensation rate of the water/sulfuric acid binary vapor is 137% higher than that of pure water. For completely wetting surfaces, the effect of the sulfuric acid component is relatively minor. As shown in Figure 9b, the sulfuric acid component only results in a 6% increase in condensation rate, much smaller than the partially wetting surface.

Three major effects of the sulfuric acid component on the heterogeneous condensation of water vapor are considered here. First, the saturation vapor pressure of the water/sulfuric acid mixture is significantly lower than that of water vapor, resulting in a larger supersaturation of the binary vapor. Second, the attraction of the condensation nuclei to the vapor molecules is increased by the condensed sulfuric acid molecules, thus increasing the growth rate of the liquid clusters. Finally, the sulfuric acid component alters the interfacial tension and thus affects the contact angle of condensed droplets.

To qualitatively characterize the effect of the sulfuric acid component on wettability, we simulate the equilibrium contact angle of a water/sulfuric acid droplet with $x_{\rm H_2SO_4} = 5\%$ at various solid—fluid interactions and compare the calculated contact angles with those of a pure water droplet. As shown in Figure S7, at a particular solid—fluid interaction, the equilibrium contact angle of the binary droplet is smaller than that of the pure water droplet, indicating that the sulfuric acid component enhances the surface wettability, leading to the drop of the free-energy barrier.

On partially wetting surfaces, the condensation of vapor molecules begins with the formation of stable condensation nuclei, and thus the nucleation rate prominently affects the condensation rate. The sulfuric acid component not only effectively shortens the nucleation time and increases the nucleation rate but also increases the growth rate of condensation clusters. Thus, the sulfuric acid component can greatly facilitate the film formation process on partially wetting surfaces. In contrast, no energy barrier exists in the heterogeneous nucleation on completely wetting surfaces, and the vapor molecules can be directly "adsorbed" onto the solid surface without re-evaporation. Although the sulfuric acid component enhances the surface wettability, no effect on the free-energy barrier is found, and the effect of the sulfuric acid component on nucleation is relatively insignificant. Additionally, the condensation on completely wetting surfaces is dominated by the strong solid-fluid interaction, while the increment of liquid-vapor interaction caused by the sulfuric acid component plays a minor role. Therefore, the sulfuric acid component should only have an insignificant influence on the film formation process on completely wetting surfaces. We calculate the film formation time during the condensation of a water/sulfuric acid binary vapor on completely wetting surfaces to confirm our conjecture. When the solid-fluid interaction is relatively weak, the sulfuric acid component shows a relatively noticeable impact on the film formation time. As shown in Figure 10, the film formation time is reduced by 16% at k =0.5. However, when k exceeds 1.5, the film formation time of water/sulfuric acid binary vapor is almost the same as that of pure water, implying that with the increment of the solid-fluid interaction parameter k, the effect of the sulfuric acid component on film formation becomes diminishing.

Furthermore, it is worth noting that the condensation of binary mixtures can be affected by competitive adsorption.



Figure 10. Comparison between the film formation time of pure water and water/sulfuric acid mixture.

Several MD simulations are performed to analyze the effects of competitive adsorption. The typical distribution of water molecules and sulfuric acid molecules is shown in Figure S8. The molar fraction of H₂SO₄ significantly increases near the solid-liquid interface, indicating that the attraction between H₂SO₄ and solid molecules is stronger than that between water and solid molecules. Due to the competitive adsorption, the sulfuric acid molecules are preferentially adsorbed onto the solid surface. Previous studies have demonstrated that the condensed sulfuric acid molecules are especially stable^{21,34} and can hardly re-evaporate. Therefore, the concentration of sulfuric acid molecules in the condensed liquid is relatively high in the initial stage of condensation. The concentrated sulfuric acid molecules can attract the water molecules to the solid surface and enlarge the condensation rate with the assistance of the strong interaction between water and sulfuric acid molecules. As the condensation proceeds, the solid surface is covered by the liquid bulk, and the effect of competitive adsorption will gradually diminish.

CONCLUSIONS

In this work, molecular dynamics simulations are performed to study the formation of liquid films on solid surfaces in the heterogeneous condensation of water vapor. The formation of liquid films on completely wetting surfaces and partially wetting surfaces is investigated. The effects of solid-fluid interactions and sulfuric acid component are analyzed. The main conclusions are as follows:

(1) The formation time of the liquid film on completely wetting surfaces is mainly affected by two factors, namely, condensation rate and liquid film density. The calculation results show that the liquid film density remains virtually invariant with the enhancement of the solid-fluid interaction, and the film formation time is mainly decided by the condensation rate. When the solid-fluid interaction is relatively weak, the condensation rate increases with the solid-fluid interaction, leading to a remarkable decline in the film formation time. With the further increase of solid-fluid interaction, the diffusion rate of vapor gradually dominates the

condensation rate, and the liquid film formation time remains almost constant.

- (2) On partially wetting and rough surfaces, the condensation nuclei grow to nanodroplets and merge, yielding divergent outcomes. At weak solid-fluid interactions, the condensed droplet is depinned from one of the nucleation sites, leading to the dropwise condensation. With the increase of the solid-fluid interaction, the merged droplet is pinned at both nucleation sites, facilitating the occurrence of the liquid film. The coalescence time between the condensed droplets decreases with the solid-fluid interaction, and the different merging modes of droplets result in the divergent sensitivity of coalescence time to the solid-fluid interaction on hydrophobic and hydrophilic surfaces.
- (3) The effect of the sulfuric acid component on the film formation is much more significant on partially wetting surfaces than on completely wetting surfaces. On partially wetting surfaces, the sulfuric acid component decreases the nucleation time and enhances the attraction of liquid clusters to vapor molecules, leading to a noticeable increase in the condensation rate. However, the condensation is dominated by the strong solid-fluid interaction on completely wetting surfaces, and the sulfuric acid component only slightly improves the condensation rate.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.langmuir.2c00949.

Potential parameters for SPC-E/F, α -iron, and sulfuric acid; morphology of the rough surface; the number of water molecules in the GCMC region; validation of MD code; liquid film density at the film formation time; image sequences of heterogeneous condensation of water vapor on partially wetting surface; schematics of the droplet coalescence; the equilibrium contact angle of water/sulfuric acid binary droplets; and the spatial distribution of water molecules and sulfuric acid molecules (PDF)

AUTHOR INFORMATION

Corresponding Author

Qiang Song – Key Laboratory for Thermal Science and Power Engineering of MOE, Tsinghua University, Beijing 100084, People's Republic of China; orcid.org/0000-0002-5484-3594; Phone: +86-10-62781740; Email: qsong@ tsinghua.edu.cn

Authors

- Shuhang Lyu Key Laboratory for Thermal Science and Power Engineering of MOE, Tsinghua University, Beijing 100084, People's Republic of China
- Zuozhou Tang Key Laboratory for Thermal Science and Power Engineering of MOE, Tsinghua University, Beijing 100084, People's Republic of China
- Zhen Yang Key Laboratory for Thermal Science and Power Engineering of MOE, Tsinghua University, Beijing 100084, People's Republic of China; ◎ orcid.org/0000-0001-6261-4399

Yuanyuan Duan – Key Laboratory for Thermal Science and Power Engineering of MOE, Tsinghua University, Beijing 100084, People's Republic of China; orcid.org/0000-0002-4117-7545

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.langmuir.2c00949

Notes

The authors declare no competing financial interest.

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