On the onset of surface condensation: formation and transition mechanisms of condensation mode

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Molecular dynamics simulations have been carried out to investigate the onset of surface condensation. On surfaces with different wettability, we snapshot different condensation modes (no-condensation, dropwise condensation and filmwise condensation) and quantitatively analyze their characteristics by temporal profiles of surface clusters. Two different types of formation of nanoscale droplets are identified, i.e. the formations with and without film-like condensate. We exhibit the effect of surface tensions on the formations of nanoscale droplets and film. We reveal the formation mechanisms of different condensation modes at nanoscale based on our simulation results and classical nucleation theory, which supplements the ‘classical hypotheses’ of the onset of dropwise condensation. We also reveal the transition mechanism between different condensation modes based on the competition between surface tensions and reveal that dropwise condensation represents the transition states from no-condensation to filmwise condensation.

Vapor condensation on a cooled surface is conventionally categorized as either dropwise condensation (DWC) or filmwise condensation (FWC). In dropwise condensation, the surface covered by droplets of different sizes is not completely wetted by condensate. Many natural phenomena, for example, condensation on lotus leaves1 and butterfly wings2 show dropwise condensation mode while condensation on metal surfaces often shows filmwise condensation mode3. Dropwise condensation can be obtained on micro/nanostructured surfaces or chemically modified surfaces with lowered surface free energy and desired wettability4. Wettability, typically characterized by the contact angle ($\theta$), is generally described as either hydrophilic ($\theta < 90^\circ$) or hydrophobic ($\theta > 90^\circ$)5. Particularly, with even larger $\theta$ than the naturally achievable maximum ($\theta \approx 120^\circ$), the wettability is further termed as ultra-hydrophobic ($\theta > 120^\circ$) and super-hydrophobic ($\theta > 150^\circ$)5,6.

In dropwise condensation, a typical cycle of the evolution of droplets usually consists of formation, growth, coalescence and departure. The sizes of these droplets are observed at the scales from micrometer, millimeter to centimeter. Their size distribution and development have also been widely investigated7–10. However, the formation of initial nanoscale droplets, on which this report is focused, has not yet been fully understood. Since dropwise condensation was recognized in 193011, the formation mechanism of the initial droplets has been explained from different angles12–22 and two ‘hypotheses’ were proposed, namely ‘the hypothesis of film-rupture’18 and ‘the hypothesis of specific nucleation sites’21. The former suggests that a thin condensate film forms on the surface and then the film ruptures into droplets due to the effect of surface tensions when the film reaches a critical thickness18,19. The latter suggests that nuclei directly initiate at specific nucleation sites, such as pits, caves or grooves20–22. The majority studies seem to support ‘the hypothesis of specific nucleation sites’15, however, the understanding of fundamental physics of the formation of initial droplets is still incomplete.

Dropwise condensation fundamentally originates from nucleation process. The concept of molecular clustering has been introduced to explain the formation mechanism of initial droplets23. The nucleation process has been investigated using the Monte Carlo (MC) simulation24,25 and the molecular dynamics (MD) simulation26–33. This includes the distribution of critical cluster size27, free energy barrier of cluster formation29 and effect of surface

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free energy\(^{22,33}\). Although these investigations have shed some light on the formation mechanism of clusters, few studies concern how the initial droplets appear after the formation of clusters. In this report, nucleation processes are investigated using MD simulation in a relatively large timescale to exhibit how the initial droplets develop. We further reveal the formation mechanisms of different condensation modes and the transition mechanism between them.

**Results**

We apply MD simulation to condensation of Lennard-Jones (L-J) vapor on cooled solid surfaces. The saturated vapor and solid surface are in thermodynamic equilibrium at \(T_v = 1.0 \varepsilon k_B^{-1}\) before the solid surface is suddenly cooled to \(T_s = 0.9 \varepsilon k_B^{-1}\) (\(\Delta T = T_v - T_s\)) at \(t = 0\), \(\tau\) being the time scale. The fluid-solid interaction is also described by the L-J potential function with a fluid-solid bonding strength parameter \(\beta\), representing the relative strength of fluid-solid interaction compared to the fluid-fluid interaction. The relative surface free energy is set at different levels by adjusting the value of \(\beta\) (see Supplementary Table S1).

Although the number of clusters increases after the surface is cooled (Fig. 3a), we monitor the profile and behavior of clusters. Based on Stillinger’s definition\(^{35}\), any two molecules separated by a distance more than the smallest distance between a cluster and the surface (Fig. 2f). Both the size and number of clusters increase with time (see Fig. 3b), but the profile of cluster size we plot the evolution of the number of molecules in all surface clusters (Fig. 3c) and the number of molecules in the maximum size surface cluster \(n_{\text{max}}\). The ratio \(R = n_{\text{max}}/n_{\text{all}}\) is illustrated in Fig. 4b. When \(R\) approaches unity, it indicates that almost all surface clusters are connected as a droplet or a film.

On the super-hydrophobic surface with \(\beta = 0.15\) (\(\theta \approx 153^\circ\)), as shown in Fig. 2a–d, no condensation occurs. Although the number of clusters increases after the surface is cooled (Fig. 3a), \(n_{\text{max}}\) remains less than 50 (Fig. 4a), indicating that almost no cluster ever survives and evolves into a droplet (see Supplementary Video S1).

On the surface with \(\beta = 0.30\) (\(\theta \approx 105^\circ\)), as shown in Fig. 2e–h, the clusters form discretely (Fig. 2e) and randomly deposit on the surface (Fig. 2i). Both the size and number of clusters increase with time (see Fig. 3b), but \(n_{\text{max}}\) increases gradually and its value is less than 100 until \(t = 1000\), \(\tau\), see Fig. 4a. Some clusters are able to migrate on the surface and coalesce with other clusters. Note that the coalescence of large clusters leads to a sudden increase in the value of \(n_{\text{max}}\) as shown by the stepwise evolution of \(R\) in Fig. 4b. A cluster becomes large enough to possibly overcome the free energy barrier of nucleation (see below), it forms a nucleus. Some nuclei continue growing up towards nanoscale droplets while others downsize and fail. This diverse evolution is evidenced by the fluctuation in \(n_{\text{max}}\) as shown in Fig. 4a. Nevertheless, \(n_{\text{max}}\) keeps increasing while the surviving nuclei continue evolving towards nanoscale droplets (Fig. 2g).

On the surface with \(\beta = 0.45\) (\(\theta \approx 60^\circ\)), as shown in Fig. 2i–l, the number of clusters increases after the formation of clusters (Fig. 2g). After numerous coalescences, only one primary droplet is observable (see Fig. 2h). \(\theta\) of this primary droplet is ca. 100° (ca. 105° in Fig. 1). This primary droplet continues growing up by absorbing the clusters and molecules nearby. It is found that an initial droplet develops through three overlapping stages, namely the formation of clusters, generation of nuclei and emergence of nanoscale droplets (see Supplementary Video S2).

On the surface with \(\beta = 0.45\) (\(\theta \approx 60^\circ\)), as shown in Fig. 2i–l, the thermal resistance of the liquid-solid interface decreases due to stronger fluid-solid interaction\(^{36,37}\). Consequently, more clusters are seen to quickly and discretely deposit on the surface (see Fig. 2i) and both the number and size of clusters increase rapidly (see Figs 3c and 4a).

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**Figure 1. Relation between contact angle (\(\theta\)) and fluid-solid bonding strength parameter (\(\beta\)) at \(T = 0.9 \varepsilon k_B^{-1}\).**
Most of the surface clusters are connected at \( t = 1000 \tau \) (\( R \approx 0.85 \) in Fig. 4b), indicating a film-like condensate, despite that part of the surface area is not covered by the condensate (see Fig. 2). Then, vapor molecules keep condensing continuously and directly into the existing film-like condensate. No appreciable stepwise evolution of \( R \) is seen in Fig. 4b. Afterwards, the film-like condensate contracts and ruptures into nuclei and then forms a cap-shaped droplet (see Fig. 2k). \( \theta \) of the cap-shaped droplet is ca. 60° (ca. 60° in Fig. 1). Finally, the droplet is pulled into a film due to the finite system size under a periodic boundary condition (see Supplementary Video S3). To check that the evolution is not affected by the system size, we repeated the simulation on this surface (\( \beta = 0.45 \)) but the surface area is three times larger. The results are shown in Fig. 5. A similar film-like condensate firstly emerges and then contracts and ruptures locally into several, not completely separated nuclei. These nuclei grow up with continuous supplement of vapor molecules, then merge with other nuclei in the vicinity, and eventually develop into one large droplet with \( \theta \approx 60° \) (see Supplementary Video S4).

On the surface with \( \beta = 0.75 \) (\( \theta \approx 16° \)), as shown in Fig. 2m–p, filmwise condensation is observed. The fluid-solid interaction is sufficiently strong so that numerous clusters form randomly on the surface immediately when the surface is cooled. The number of clusters is large enough so that the condensate quickly covers the whole surface (see Fig. 2m) and develops into a film (\( R \approx 1.0 \) since about 500 \( \tau \) in Fig. 4b). The film continues to grow thicker (see Fig. 2n–p) and no condensate film rupturing is seen. Therefore, a filmwise condensation is identified. Note that the initial clusters coalesce into a film-like condensate in both the cases for \( \beta = 0.45 \) and 0.75, however, the difference is that the film-like condensate in the former case contracts and ruptures into several nuclei and evolves into a large droplet while the film-like condensate in the latter case develops into a complete condensate film eventually (see Supplementary Video S5).
Discussion

Different condensation modes have been exhibited above and the mechanisms will be explained below based on the classical nucleation theory (CNT) and our simulation results.

According to CNT, the minimal work required for an \( n \)-cluster to form is equal to the change of the Gibbs free energy \( \Delta G(n) \), which is called the Gibbs free energy of cluster formation, as:

\[
\Delta G(n) = n \Delta \mu - \gamma \frac{36 \pi F}{\rho_l \beta} \frac{1}{n^{3/2}}
\]

where \( \Delta \mu \) is the difference between the chemical potentials of vapor bulk \( \mu_v \) and liquid bulk \( \mu_l \) (\( \Delta \mu = \mu_v - \mu_l \)), \( \gamma \) is the vapor-liquid surface tension, \( \rho_l \) is the density of droplet and \( F = f(\theta) \) is the Fletcher factor with the value between 0 and 1 as \( \theta \) varies from 0° to 180°. The Fletcher factor generally accounts for the geometric effect due to different wetting status. For a droplet on a flat surface, \( F = f(\theta) = (2 - 3\cos \theta + \cos^3 \theta)/4 \). On increasing \( n \), \( \Delta G(n) \) first increases and then decreases after a maximum \( \Delta G^* \) is reached. \( \Delta G^* \) is called the Gibbs free energy barrier of cluster formation, as:

\[
\Delta G^* = \frac{16\pi \gamma^3}{3\rho_l^2 \Delta \mu^2} F
\]

and the corresponding \( n \) is called the critical number of molecules of cluster formation (\( n_c \)), as:

\[
n_c = \frac{32\pi \gamma^3}{3\rho_l^2 \Delta \mu^2} F
\]

Theoretically, only when the Gibbs free energy barrier of cluster formation is overcome and the critical number of molecules of cluster formation is exceeded could a newly-formed cluster survive. In other words, \( \Delta G^* \) and \( n_c \) quantify the difficulty of cluster formation and thus the tendency of condensation to occur. For simplification, Eqs (2) and (3) could be reduced as:

\[
\Delta G^* \propto \frac{F}{\rho_l^2 \Delta \mu^2},
\]
\[ \rho \mu \propto \Delta \nu. \]  

Basically, \( \gamma_{vl} \) is upon the nature of the fluids and primarily determined by the thermodynamic state at vapor-liquid interface. Since throughout all the present simulations the vapor bulk is well confined at the saturation state of \( \varepsilon = -T_k \) and solid temperature is constant at \( \varepsilon = -T_k \), the thermodynamic state at the vapor-liquid interface could be regarded as constant and so does \( \gamma_{vl} \). Previous MD studies have clearly revealed that increasing \( \beta \) significantly decreases the liquid-solid interfacial thermal resistance \( R_t \), which reduces the temperature jump \( T_J \) between solid and liquid and thus lowers the liquid bulk temperature \( T_L \) in the simulations. It is known that \( \rho_L \) increases with decreasing \( T_L \). Meanwhile, decreasing \( T_L \) enlarges \( \Delta \mu \) because \( \mu_v \) is fixed due to constant thermodynamic state of vapor bulk but \( \mu_L \) decreases due to higher stability at lower temperature for liquid bulk. Considering the relations, we find that increasing \( \beta \) tends to reduce \( \Delta G^* \) and \( n_c \) according to the correlations as \( \beta \uparrow \rightarrow R_t \downarrow \rightarrow T_J \downarrow \rightarrow \rho_L \uparrow \& \Delta \mu \downarrow \rightarrow \Delta G^* \downarrow \& n_c \downarrow \). On the other hand, the simulation results clearly illustrate that \( \theta \) decreases with increasing \( \beta \) (see Fig. 1) and we know that \( F = f(\theta) \) is an increasing function of \( \theta \) for the case of a droplet on a flat surface. Considering the relations, we readily obtain the correlations as \( \beta \uparrow \rightarrow \theta \downarrow \rightarrow F \downarrow \rightarrow \Delta G^* \downarrow \& n_c \downarrow \). Therefore, we can conclude that increasing \( \beta \) leads to decreasing \( \Delta G^* \) and \( n_c \). According to CNT, this conclusion suggests that as the relative surface free energy increases, both the Gibbs free energy barrier and the critical number of molecules of cluster formation decrease, which eventually drives the surface condensation to occur more easily (see curve in lower panel of Fig. 6).

Figure 6 is a schematic presentation showing the formation mechanisms of no-condensation, droplet condensation and filmwise condensation. On the surface with \( \beta = 0.15 \) (Fig. 6a), \( \Delta G^* \) and \( n_c \) are so large that no clusters can survive and evolve into droplet or film. Therefore, no condensation is observable.

On the surface with \( \beta = 0.30 \) (Fig. 6b), \( \Delta G^* \) and \( n_c \) decrease, which raises the probability for newly-formed surface clusters to survive. The survived surface clusters continue to grow and coalesce, which leads to the
formation of nuclei and then droplets. The limited number of surface clusters can hardly form any condensate film. This droplet formation mechanism is in line with 'the hypothesis of specific nucleation sites'\(^2\), except that the nuclei occurring here are triggered and located randomly on the perfectly smooth surface rather than specific nucleation sites, e.g. pits, caves or grooves.

However, on the surface with \(\beta = 0.45\) (Fig. 6c), the formation mechanism of nanoscale droplets is significantly different. With \(\Delta G^*\) and \(n_0\) further decreasing, the number of clusters forming and depositing on the surface is large enough to quickly generate a film-like condensate (thickness ca. several nanometers). It then contracts and ruptures into nuclei and droplet. This droplet formation mechanism is in line with 'the hypothesis of film-rupture'\(^1\).
On the surface with $\beta = 0.75$ (Fig. 6d), much larger $\beta$ further reduces $\Delta G^*$ and $n_c$ and drives numerous clusters to immediately generate on the surface. The enhanced liquid-solid interaction makes them rest on the surface rather than condense onto a droplet. The rest of the clusters cover most of the surface area and readily connect to form a film-like condensate. The film-like condensate continues growing up into a complete film, identifying the condensation mode to be filmwise.

As shown in the two cases of $\beta = 0.35$ and 0.45, neither of the 'classical hypotheses' can independently describe the formation mechanisms of nanoscale droplets. In fact, either describes the specific scenario at a certain wettability. They may be complementary processes at nanoscale rather than independent as reported before$^{15}$.

As discussed above, we find that $\beta$ determines $\Delta G^*$ and $n_c$, which quantifies the difficulty of cluster formation based on CNT (see inserts in lower panel of Fig. 6). We also find that the dynamics of surface clusters significantly affects the transition of condensation mode according to our simulation results. Essentially, the dynamics of surface clusters is closely related to the balance of surface tensions at the vapor-liquid-solid triple-phase contact-line, which is generally described by the Young's equation (see insert in Fig. 1):

$$\gamma_{vs} = \gamma_{lv} + \gamma_{vl} \cos \theta.$$  

Then we have

$$\cos \theta = \frac{\gamma_{vs} - \gamma_{lv}}{\gamma_{vl}},$$

where $\gamma_{vl}$ and $\gamma_{vl}$ are the vapor-solid and liquid-solid surface tensions. As is stated above that $\gamma_{vl}$ basically keeps constant throughout the present simulations. With increasing $\beta$, the fluid-solid interaction becomes stronger, therefore the adhesive forces between the fluids and solids spread the cohesive forces within the fluid bulks, which leads to decreases in $\gamma_{vs}$ and $\gamma_{vl}$. On the other hand, the $\beta$-induced variation in $\gamma_{vl}$ is always greater than that in $\gamma_{vs}$ due to much stronger liquid-solid interaction than the vapor-solid one, i.e. $\gamma_{vl}$ is more sensitive to $\beta$. Therefore, we readily have $\beta \uparrow \rightarrow \gamma_{vl} \downarrow$ & $\gamma_{vs} \uparrow \rightarrow (\gamma_{vl} - \gamma_{vl}) \uparrow \rightarrow \cos \theta \uparrow \rightarrow \theta \downarrow$. Note that there exists a critical value of $\beta$ ensuring $\theta = 90^\circ$ (e.g. $\beta \approx 3.5$ in Fig. 1), indicating $\gamma_{vl} = \gamma_{vl}$. The eventual condensation mode is in fact decided by the competition between the surface tensions (see inserts in lower panel of Fig. 6). Take the diverse evolutions of the film-like condensate in the cases of $\beta = 0.45$ and 0.75 for an example. The film-like condensate contracts and ruptures and dropwise condensation arises if the cohesive forces overcome the adhesive forces. Otherwise, the film-like condensate grows thicker and filmwise condensation develops. Specifically, when abundant clusters form on the surface, the surface tensions determine the eventual condensation mode through affecting the dynamics of surface clusters. If the fluid-solid interaction keeps decreasing until it is too weak to possibly generate nuclei on the surface, eventually dropwise condensation disappears and no condensation could ever occur on the surface. It is predictable that there could exist two critical values of $\beta$. The first critical value lies in the no-to-dropwise transition and separates no-condensation mode and dropwise condensation mode. This is essentially a threshold of surface clusters between 'zero' and 'few'. The second critical value lies in the dropwise-to-filmwise transition and separates dropwise and filmwise condensation modes. This is essentially a threshold of surface clusters between 'few' and 'many'. From the view of surface tension competition, dropwise condensation represents the transition states between no-condensation mode and filmwise condensation mode. The transition mechanism between different condensation modes is explicitly illustrated in lower panel of Fig. 6 in terms of relative surface free energy ($\beta$). Other experimental$^{17,40–42}$ and numerical$^{31,33}$ investigations also support the transition mechanism that by physically or chemically lowering the relative surface free energy, e.g. micro/nanomachining$^{37,40,41}$, chemical coating$^{37,42}$ and fluid with higher surface tension$^{41}$, the condensation mode changes from filmwise to dropwise with visible decreasing $\theta$. It is noteworthy that micro/nanomachining and chemical coating are direct resorts of lowering the absolute surface free energy while fluid with higher surface tension is the resort of increasing the cohesive fluid-fluid interaction. Equivalently, there are all resorts of lowering the relative surface free energy ($\beta$).

To determine the critical values of $\beta$ for defining different condensation modes, we borrow the Fletcher factor as the criterion. Since we already acquired the correlations of $F = f(\theta)$ and $\theta = g(\beta)$, we readily have the correlation between $F$ and $\beta$ (see Fig. 7). As is expected, there exist two apparent turning points ($\beta \approx 0.20$ and $\beta \approx 0.55$), which could be generally regarded as the critical values, dividing the range of $\beta$ into three regions, corresponding to non-condensation, dropwise condensation and filmwise condensation. The present cases shown in Fig. 2 lie in the corresponding regions. By analyzing more simulations with a serial values of $\beta$, we further determine within $\beta = 0.18–0.22$ and $\beta = 0.53–0.57$. In summary, we present the evolutions from clusters to nucleus and nanoscale droplets or to liquid film, undergoing different condensation modes. We qualitatively examine the characteristics of different condensation modes by transient snapshots and quantitatively analyze the evolutions of the number and size of clusters. We find that the initial droplets in dropwise condensation could form in two significantly different ways depending on the relative surface free energy. We reveal the formation mechanisms of different condensation modes at nanoscale based on our simulation results and classical nucleation theory, which supplements the 'classical hypotheses' of the onset of dropwise condensation. We also reveal the transition mechanism between different condensation modes based on the competition between surface tensions and reveal that dropwise condensation represents the transition state from no-condensation to filmwise condensation.

**Methods**

The basic simulation system size measures $l_s \times l_s \times l_s = 47.2 \sigma \times 48.0 \sigma \times 92.0 \sigma$. A larger system of $92.7 \sigma \times 93.0 \sigma \times 183.0 \sigma$ is used to examine the effect of finite system size. The fluid-fluid interaction is governed by the Lennard-Jones (LJ) potential function $\phi(r) = 4\varepsilon[(\sigma/r)^{12}-(\sigma/r)^6]$, where $r$ is the intermolecular separation,
\( \sigma \) is the length scale and \( \varepsilon \) is the energy scale. The function is truncated at the cut-off radius \( r_c = 4.0 \, \sigma \), beyond which molecular interactions are neglected. The semi-infinite solid wall at the bottom end is represented by three layers of solid molecules forming a (111) plane of a face-centered cubic lattice with the lattice constant \( c_0 = 0.814 \, \sigma \). Neighboring solid molecules are connected by Hookean springs with the constant \( k = 0.91 \, \sigma \). For temperature control, two extra layers of solid molecules are set below the three layers. The lower layer is stationary as a frame while the upper is governed by the Langevin thermostat \( \frac{dp_i}{dt} = -\alpha p_i + f_i + F_i \), where \( \alpha = 168.3 \, \tau^{-1} \) is the damping constant\(^4\), \( p_i \) is the momentum of the \( i \)th solid molecule; \( f_i \) is the sum of the forces acting on the \( i \)th solid molecule, \( F_i \) is a random force, of which each component is sampled from the Gaussian distribution with zero mean value and variance \( 2 \alpha k_B T / \delta t \) (\( k_B \) is the Boltzmann constant and \( \delta t = 0.002 \, \tau \) is the time step, where \( \tau = \sqrt{m \sigma^2 / \varepsilon} \) is the time scale, \( m \) being the mass of a fluid molecule). This technique of constant temperature control is feasible for both fluid\(^5\)\(^\rightarrow\)\(^6\) and solid\(^5\)\(^\rightarrow\)\(^6\). The fluid-solid interaction is also described by the L-J potential

\[ \varepsilon_{\sigma} = \varepsilon \sigma^6 / \sigma^9. \]

Periodic boundary condition and diffuse reflection boundary condition are employed at the sides and top end, respectively. The leapfrog scheme is used for integrating the equations of motion and the cell subdivision technique is used to improve the computational efficiency\(^4\)\(^\rightarrow\)\(^6\).

Figure 7. Correlation between the Flecher factor (\( F \)) and the fluid-solid bonding parameter (\( \beta \)).

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Author Contributions
Q.S. developed the code, performed the simulations, prepared the manuscript, analyzed the results and reviewed the manuscript. J.S. developed the code, performed the simulations, prepared the manuscript, analyzed the results and reviewed the manuscript. W.W. analyzed the results and reviewed the manuscript. H.S.W. analyzed the results and reviewed the manuscript.

Additional Information
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