Cluster Evolution and Transition From Adsorption to Capillary Condensation in Nanostructure With Varying Wettability[#]

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ABSTRACT

To capture the transformation mechanism from adsorption to capillary condensation in nanostructures, argon adsorption on regularly arranged nanostructures model is established based on Monte Carlo and molecular dynamics simulation in this work. The variation of clusters and the effect of surface wettability during adsorption and capillary condensation are examined. Results indicate that the adsorption starts with the filling of the adsorption site by the single molecular cluster. The atoms in the bulk vapor coalesce with a single molecular cluster to form the multi molecular cluster after the adsorption site is filled. And the coalesce of clusters induces the formation of liquid film. Subsequently, the bending of the liquid film brings a negative pressure to the bulk liquid, which induces the onset of capillary condensation. During this process, the number of single clusters decreases rapidly, while the number of multi molecular clusters increases. With the decrease of surface wettability, the argon atoms tend to gather at the bottom of nanostructures, directly forming into multi molecular clusters. Finally, the adsorption and capillary condensation map exhibit that the critical relative pressure decrease from 0.6 to 0.2 as the surface wettability parameter increase from 0.33 to 0.67. And the increase in spacing leads to an increase in critical relative pressure.

Keywords: adsorption, capillary condensation, nanostructure, wettability, cluster evolution

1. INTRODUCTION

The adsorption and capillary condensation phenomenon that happened inside the nanostructure can be observed in many situations. Such as the regulation of surface wettability [1], the design of thermal diodes [2-3]. Based on the demand of expanding the application scope and improving the performance of nanostructures, it is necessary to fully the mechanism of adsorption and capillary condensation within the nanostructure.

For the adsorption process, based on the assumption that the molecular is adsorbed on the adsorption site in form of clusters, the Zeta adsorption model successfully predicts the adsorption amount as a function of relative pressures [4]. Moreover, the Zeta model predicts the transition from adsorption to condensation, and its rationality was verified in both experiments and simulations [5-7]. However, the real surface often has microstructures and non-uniform wettability, which induce the transition from adsorption to capillary condensation before the bulk vapor pressure reaches saturation. Luisa et al. [8] point out that the adsorption structure changes from layered to clustered as the surface wettability decreases. Tan and Jia [9] invested in the separation efficiency of graphite for methane ethane mixtures vapor by the kinetic Monte Carlo method. Results indicate that the smaller pore size graphite has stronger ethane selection, but the desorption also requires extremely low pressure. As for the transition from adsorption to capillary condensation, Tan et al. [10] present a serious critical relative bulk vapor pressure required for the transition from adsorption to capillary condensation as a function of pore diameter and point out that the capillary condensation is induced by the cluster coalesce

Additionally, with the maturity of nanostructure manufacturing technology, the use of nanostructures to optimize the surface phase transition process has been widely promoted. However, the adsorption and capillary condensation processes in the nanostructure are rarely considered. Tadeh et al. [11] used the molecular dynamics simulation method to reproduce the adsorption and capillary condensation behavior that

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happened in nanostructure. Result shows that the critical relative pressure can be significantly decreased with the decrease of surface wettability. But the atomic behavior in the process of adsorption and capillary condensation within nanostructure still needs to be further explored.

In summary, the adsorption and capillary condensation that happened inside the nanostructure plays an important role during the phase change process. But the underlying mechanism needs further exploration. To make up for this deficiency, the molecular dynamics simulation combined with the grand canonical Monte Carlo (GCMC) method is adopted in this work to explore the atomic behavior and cluster evolution during adsorption and capillary condensation transition process. The effect of surface wettability on adsorption and capillary condensation transition are revealed. Finally, a map of adsorption and capillary condensation state distribution under various surface wettability and nanostructure spacing is obtained.

2. PHYSICAL MODEL AND SIMULATION RESULTS

The simulation domain with a length of 9×9×44nm in x, y, and z dimensions is demonstrated in Fig.1. There are only copper and argon atoms in the system. To prevent the deformation of solid substrate from deformation, a solid wall with a velocity of zero (marked in red) is performed at the bottom of simulation system. The adsorbent is composed of a copper substrate (represent by dark blue) and a 3×3 nano-pillar array (marked by light blue) with a spacing of s.
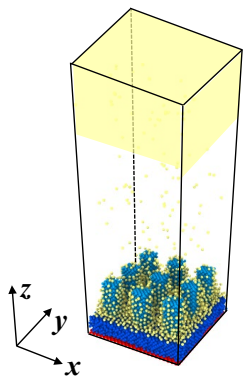

Fig. 1. Diagram of the simulation system. A GCMC region is placed on the upper part of the simulation box.

In this work, the value of s varies from 10Å to 30Å. To maintain a constant bulk vapor chemical potential and relative pressure, a grand canonical Monte Carlo region is applied in the upper part of the simulation box to suppled argon atoms (yellow atoms) required for adsorption. The interaction between atoms is described by the Lennard-Jones 12/6 potential. The temperature of the system is minted at 90K by the Berendsen

thermostat. And Verlet integrator is applied to update the atom position and velocity with a times step of 5fs and $3.5\sigma_{Ar-Ar}$ cutoff. The periodic boundary conditions are adopted in three dimensions.

3. RESULTS AND DISCUSSION

3.1 General adsorption process

Firstly, the cluster evolution snapshot is illustrated in Fig.2, including single molecular clusters (ζ_1) and multi cluster clusters (ζ_n). The Stillinger method of cluster definition is as follows: if the distance between two atoms is less than $1.15\sigma_{Ar-Ar}$, they are considered to belong to the same cluster. To facilitate observation, the atoms belonging to the same multi molecular clusters are connected with red short lines. It is obviously observed that the single cluster domain the adsorption site is the main adsorption behavior before 5ns. And sporadic multi clusters are randomly distributed near the nanostructure. After 5ns, the adsorption sites are filled, the subsequent adsorbed atoms coalesce with single clusters to form multi clusters. It is worth noting that the multi clusters are preferentially formed at the bottom of nanopillars due to the stronger force filed. At 7.5ns, the multi clusters formed at the bottom of the nanostructure coalesced with each other to form a liquid film and grow steadily upward. The number of single clusters continues to decrease at 10 ns, and the growth of liquid film induces the enlargement of maximum cluster volume.
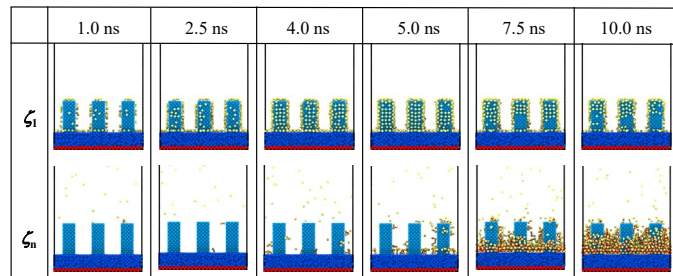

Fig. 2. The evolution snapshot of single molecular clusters (upper) and multi-molecular clusters (lower).

To quantitative describe the above process, the evolution of various types of clusters over time is described in Fig. 3. During 0-5ns, the number of single molecular (ζ_1) increases linearly with time. The number of ζ_1 decreases quickly after 5ns, while the number of multi molecular clusters ($\zeta_{Connect}$) increases rapidly. It can be reasonable considering that most of the multi molecular clusters coalesce into a liquid film, and the upper part of the liquid film forms a meniscus under the combined action of the complex force field in the nanostructure. The negative pressure generated by the

2

meniscus induces the transition from adsorption to capillary condensation. Different from the evolution of clusters on the smooth surface, there still exist some single molecular clusters near solid surfaces as presented in Fig.3. After the formation of liquid film, The difference between ζ_{max} and n^{sv} is attributed to the residual atoms located at the bottom of nanopillars. Moreover, the accumulation of argon atoms increases linearly with time during this period. This is because the morphology of the meniscus is basically unchanged, and the meniscus with a constant radius of curvature continues to grow upward during this period. As the meniscus approaches the upper of nanopillars, the increase of curvature radius leads to a continuous decrease of capillary rate until the nanostructure is completely covered by liquid film.
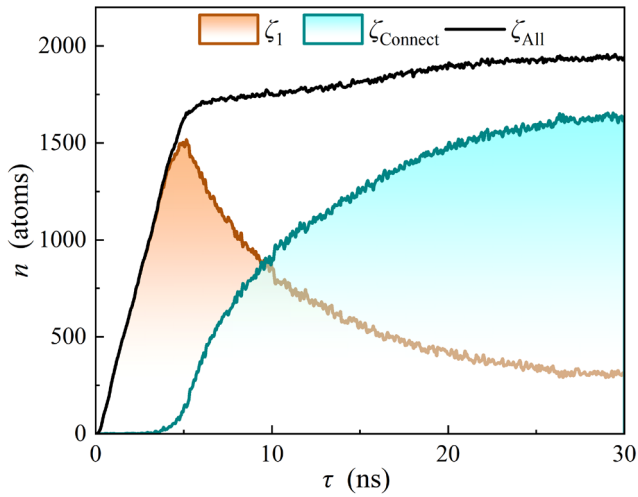

Fig. 3. Snapshot of the transition from adsorption to the formation of liquid and the evolution of liquid film.

3.2 Effect of surface wettability and capillary condensation map

To explore the effect of surface wettability on adsorption and capillary condensation, Fig. 4 shows the variation of single molecular clusters as a function of time under various surface wettability. The surface wettability is controlled by adjusting the size of α, a larger α brings a more hydrophilic surface. It is noted that the number of single molecular clusters reaches the maximum value in a similar time, but with the increase of solid surface wettability, the maximum value increases significantly. The above phenomenon can be attributed to the variation of cluster growth path with the change of surface wettability. When $\alpha>0.44$, argon atoms in the bulk vapor are preferentially adsorbed on the adsorption site, making the number of ζ_1 reach the maximum. After the adsorption sites are filled with a single molecular cluster, the subsequently adsorbed atoms and single molecular clusters would coalesce into various multi

molecular clusters, which reduce the number of single molecular clusters decrease rapidly. For comparison, when $\alpha<0.44$, due to the lower strength of the force filed from the adsorption site, the argon atoms tend to gather at the bottom of nanostructures, directly forming into various types of multi molecular clusters. Therefore, the maximum value of ζ_1 is not observed. Moreover, the number of remaining single molecular clusters is basically unchanged after the capillary condensation reaches equilibrium, independent of the surface wettability.
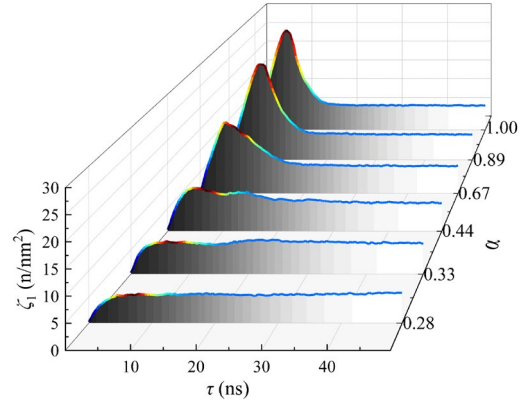

Fig. 4. Variation of single molecular clusters as a function of time under various surface wettability.

Finally, the adsorption and capillary condensation map under various surface wettability and nanostructure spacing is exhibited in Fig. 5.
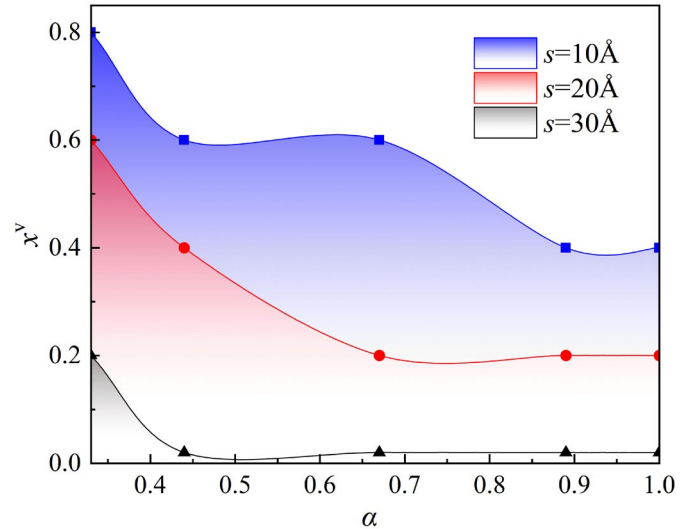

Fig. 5. Adsorption and capillary condensation state distribution, the filling region at the bottom of the curve denotes that the region is in adsorption state, and above the curve represents the capillary condensation region.

Below the curve is the adsorption region, and above the curve is the region where capillary condensation can

occur. The surface wettability is an essential factor that affects the critical relative pressure. Such as for s=20Å, the critical relative pressure decrease from 0.6 to 0.2 as the surface wettability parameter increase from 0.33 to 0.67. However, with the further increase of surface wettability, its effect on the reduction of the critical pressure ratio is weakened. Another key factor affecting the critical x^v is the nanostructure spacing, when s=10Å, since the clusters are easy to contact and coalesce with each other, capillary condensation can be observed under very low relative pressure (x^v=0.05 and α=0.67) or surface wettability (x^v=0.20 and α=0.33). With the increase of s, the possibility of cluster coalesces decreases, and a greater surface wettability or bulk vapor pressure is required for the onset of capillary condensation.

4. *CONCLUSIONS*

In this work, combining grand canonical Monte Carlo and molecular dynamics simulation method, a serious simulation is devoted to exploring the mechanism of adsorption and capillary condensation happening within nanostructures. The following main conclusions are obtained:

(1)   The evolution of clusters in the process of adsorption and capillary condensation is clarified. The adsorption starts with the filling of the adsorption site by the single molecular cluster. After the adsorption site is filled, the subsequently gathered atoms coalesce with the single molecular cluster to form various types of multi molecular clusters. The coalescence of multi cluster induces the formation of the liquid film. And the liquid film preferentially formed at the bottom of nanostructures. The bending of the liquid film brings a negative pressure to the bulk liquid, which induces the onset of capillary condensation. During this process, the number of single clusters decreases rapidly.

(2)   The cluster evolution is affected by surface wettability. When the surface wettability parameter α>0.44, the argon atoms would occupy the adsorption sites and reaches the maximum value, subsequently the atom in the bulk vapor coalesce with single molecular cluster forming into various multi molecular clusters. In comparison, when α<0.44, the argon atoms would gather at the bottom of nanopillars and directly form into multi molecular clusters.

(3)   Finally, the adsorption and capillary condensation state distribution map under various surface wettability and nanostructure spacing s is obtained. For s=20Å, the critical relative pressure decrease from 0.6 to 0.2 as the surface wettability parameter increase from 0.33 to 0.67. But with the further increase of surface wettability, its effect on the reduction of critical pressure ratio is weakened. With the increase of s, the possibility of cluster coalesces decreases, and a greater surface wettability or bulk vapor pressure is required for the onset of capillary condensation.

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