Superlyophilic spreading of a droplet on the forest of pillar arrays

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INTRODUCTION

Superlyophilic spreading of a droplet on the pillar-arrayed surface attracted considerable attentions during the last decade, for its important applications in biomedicine, fuel cell, antifogging and etc [1, 2]. To meet the superlyophilic desire from practical applications, we should understand and control the superwetting behaviours and governing rules.

When a droplet is deposited on a lyophilic smooth surface, the wetting behaviour has been intensely studied for decades [3, 4]. Driven by the interface tension and dissipating in the vicinity of the moving contact line, the droplet wets the surface with a scaling law of $R\sim t^{1/7}$ from molecular kinetic theory (MKT) [5]. When the solid surface is patterned with pillars, the surface topology enhances its wettability, a transition of the substrate from lyophilic to superlyophilic happens. The lower part of the droplet (the fringe) penetrates into the pillars, while the upper part (the bulk) propagates on the base of the fringe, as shown in figure 1. The previous works made efforts on determining the scaling law of the fringe in the wicking/hemiwicking process based on the Washburn law at continuum level [6]. But, the superwetting process is essentially a multiscale process, the physics behind phenomena is now far from well understood. To comprehend the complex liquid-solid interactions of droplet on a pillar-arrayed superlyophilic substrate from the atomic to the continuum level, a multiscale study is required.

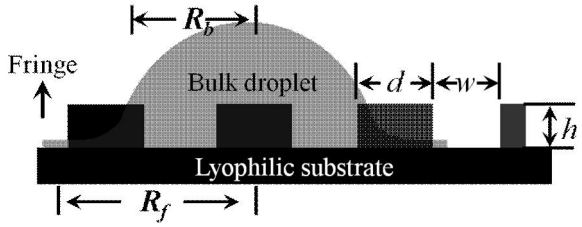

Figure 1. A schematic model of a droplet on pillar-arrayed surface

In this article, the superlyophilic spreading was studied employing multiscale experiments and molecular dynamics (MD) simulations. The details of the spreading process were revealed from atomic to continuum level. The scaling analysis was performed using MKT and the governing rules for superlyophilic wetting was obtained. Our results can be a first step in completely understanding the superwetting behaviours and assisting the future design in practical applications.

RESULTS AND DISCUSSIONS

In the macro and microscale experiments, a droplet was deposited on lyophilic micropillar arrays with different roughness, $r=1+4dh/(d+w)2$, as shown in figure 1. In the nanoscale MD simulations, a geometrical and physical similar simulation domain, which is dominated by the Suratman number $\mathrm{Su}=\gamma\rho L/\mu^2$, was constructed. The whole superwetting process could hence be studied in detail from the atomic to continuum level. The multiscale process was illustrated in figure 2.

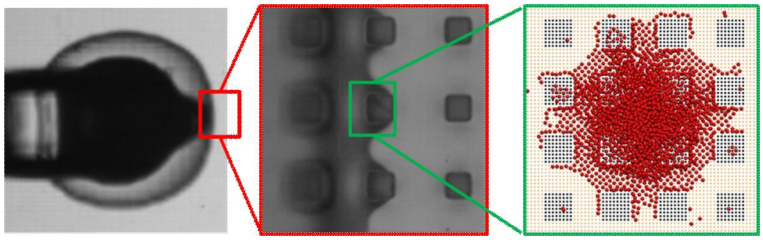

Figure 2. Top view of the macroscale, microscale experiments and nanoscale MD simulations.

At the atomic level, there is a very thin liquid film, usually 1-2 molecular layer, propagating ahead of the nominal contact line. This liquid film is called the precursor film (PF) [7], which could be one answer to the "Huh-Scriven paradox" and is very important in the wetting process. In the dynamic spreading process of a droplet on the pillar arrays, the PF also played an important role to eliminate the stress singularity at the solid-liquid interface. The PF advanced very fast and formed a molecular layer on the solid surface. Once the PF encountered the pillars, the interior corner between the pillars and the substrate would provide excess driving force to the liquid, known as the Concus-Finn effect [8]. The excess force dragged the PF to form a single-molecule precursor chain (PC) [9] along the interior

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corner. The PC quickly advanced around the pillars and was pinned by the interior corner until PF caught up, in figure 3(a). The PF reached the front of the contact line and climbed up the pillars, in figure 3(b). The fringe spread on the base of the PF and filled the space among pillars, in figure 3(c). The fringe advanced with a characteristic capillary velocity $U_{CA}\sim\gamma/\mu\sim0.1$ m/s. The bulk droplet then spread on the base of the fringe with a slower velocity. In the next period of the pillars, this process repeated but with lower velocity, because of the reduction in the difference of interfacial tensions. On one hand, the grooves between the pillars provide excess driving force to the liquid; on the other hand, the pillars bring extra resistance to the liquid. These two opposite effects introduced by the lyophilic pillars achieve a balance in the fast advancing contact line region. The pillar array accelerated the wetting process from the atomic PC and PF to the microscale fringe, making the macroscale superwetting process. The macroscale smooth circular contact line was a complicated curve depending on the spreading direction. Hence, the fast radius expansion of the droplet at continuum level and the liquid penetration among lyophilic pillars at atomic level could be comprehended.

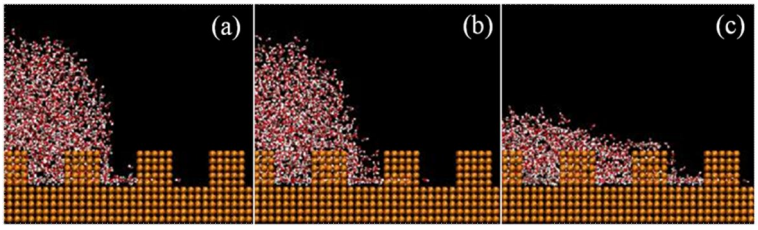

Figure 3. (a) the precursor chain propagated around the pillars; (b) the precursor film climbed up the pillars; (c) the fringe filled the space among pillars.

The scaling law of the superwetting on the pillar arrayed surface could be analyzed using MKT, which was proposed by Eyring et al. [10] and developed by Blake et al. [5]. According to the viewpoint of the bottom-up theory MKT, the wetting process is a stress-modified molecular rate process. The motion of the moving contact line is determined by the statistical dynamics of the liquid molecules near the three phase zone. Actually, when liquid moves across a solid surface, the solid adsorbs and tries to immobilize the liquid molecules, while the liquid molecules desorb and try to transport. Considering the liquid molecules driven by w (driving work per unit area) jump between surface sites separated by a distance λ with a frequency κ_0, their advancing velocity is $U=2\kappa_0\lambda\sinh\left(w\lambda^2/2k_BT\right)$. Taking account of the lubrication approximation ($h\ll R$, $\theta=h/R\ll1$), the mass conservation relation, and the roughness of the surface, the advancing velocity could be derived:

$$U=dR/dt\sim U_{CA}\left[1-d^2/\left(d+w\right)^2\right]^2 h^2/R^2 \tag{1}$$

The corresponding scaling law for a droplet on pillar arrays is $R_f\sim t^{1/3}$, which is in accordance with our experiments and MD simulations. The characteristic time scale for the spreading is controlled by both the liquid properties, i.e., surface tension, the viscosity and the droplet radius, as well as the properties of the lyophilic pillars, i.e., the pillar density and the pillar height.

CONCLUSIONS

In summary, the superlyophilic spreading was explored using a combination method of multiscale experiments and MD simulations. The multiscale superwetting process was revealed from PC and PF at atomic level to the fringe and radius expansion at continuum level. The physics and mechanism behind the phenomena were studied using the MKT analysis. The pillars brought both excess driving force and extra resistance to the liquid, which reached a dynamic balance in the three phase zone. The surface topology enhanced its wettability and resulted in superlyophilic wetting phenomena with a scaling law of $R_f\sim t^{1/3}$. Our results can be a first step in completely understanding the superwetting behaviours and assisting the future design in practical applications.

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