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The mechanism for the motion of nanoscale water droplet induced by wetting gradient: A molecular dynamic study

Tao Wang [a,b], Wen Li [a,b], Liang Liu [a,b], Haixiang Chen [a,b], Yefei Wang [c], Jun Zhang [a,b,*], Youguo Yan [a,b,*]

[a] College of Science, China University of Petroleum, 266580 Qingdao, Shandong, People's Republic of China
[b] Key Laboratory of New Energy Physics & Materials Science in Universities of Shandong, China University of Petroleum, 266580 Qingdao, Shandong, People's Republic of China
[c] School of Petroleum Engineering, China University of Petroleum, 266580 Qingdao, Shandong, People's Republic of China

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ABSTRACT

In this work, molecular dynamics simulations were employed to investigate the motion behavior of water nanodroplet on wetting gradient surface. Research exhibited that the water nanodroplet could move from the hydrophobic segment to the hydrophilic segment, spontaneously. Detailed observation revealed that the motion of nanodroplet included spreading and shrinking processes, and a precursor film forming on the $-NH_2$ segment played a pivotal role on the transportation of nanodroplet. The microscopic motion mechanism was discussed, and the intricate and intriguing effects of E_{bind} and E_{water} were analyzed to unveil the driving and resisting forces. Furthermore, the modified segment width and wetting gradient were also discussed, and results unraveled that the narrow modified segment and large wetting gradient promoted the motion of the nanodroplet. Our work provides fundamental insights into the microscopic motion mechanism of nanodroplet, and the results are expected to facilitate the design and fabrication of wetting gradient surface.

1. Introduction

Recent years have witnessed explosive growth of interest in motion and transportation of liquid droplet on solid surface for its significant application in micro/nano-fluidic devices [1–6], condensation heat transfer [7], cell motility [8–10] and biochips [11–15]. Therefore, in order to manipulate the motion of liquid droplet in these application fields, many approaches have been proposed such as applying electric field [16,17], external force [18] or implementing a gradient [19–22] (e.g., wetting gradient and thermal gradient [23]). Among these approaches, wetting gradient has been one of the most interesting methods, which could transport liquid droplet, spontaneously, due to the surface tension heterogeneity [24,25].

The droplet motion on wetting gradient surface was firstly predicted by Greenspan [26] in theory. Since then, a large number of scientific researches have been performed to investigate the motion of liquid droplet induced by wetting gradient. Chaudhury and Whitesides [24] firstly realized the motion of macroscopic water droplet on wetting gradient surface experimentally. Then Nakajima et al. [27] reported that the moving velocity of water droplet was highly related to the surface gradient, i.e., the higher the gradient, the faster the water droplet moved. Meanwhile, during the motion of the water droplet, the advancing angle and receding angle of the droplet would also change correspondingly [28–31]. Obviously, these investigations mainly focused on relative large droplets and elucidated the moving behaviors at macroscopic level. However, as the rapid development of micro/nano-fluidic technology, the water droplet would turn to be nanoscale. In order to control the motion of such a small droplet on the micro/nano-fluidic devices, the wetting gradient is commonly used. But, for nanodroplet, the moving behaviors and mechanism may have significant differences from the macroscopic droplet due to the size effect. Therefore, atomic level structural details and subtle molecular interactions during moving process are crucial to give insights into the mechanism for the motion of liquid droplet induced by wetting gradient. But unfortunately, such microscopic information are challenging or impossible to be probed experimentally.

Benefitting from the rapid development in computational power, molecular dynamics simulations have been widely used to explore the microscopic interactions at atomic level [32–35]. Koishi et al. [36] studied the transition behavior between Wenzel state and Cassie state of water nanodroplet on periodic nanopillared hydrophobic surfaces, and the microscopic mechanism for the transformation of two states were investigated by computing the free-energy barrier. Other simulations relating to the wetting

* Corresponding authors at: College of Science, China University of Petroleum, 266580 Qingdao, Shandong, People's Republic of China.
E-mail addresses: zhangjun.upc@gmail.com (J. Zhang), yyg@upc.edu.cn (Y. Yan).

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behaviors of water droplets on various wettability surfaces were also carried out [37–43]. These researches demonstrate that the molecular dynamics simulation can be used to investigate the moving process and microscopic mechanism of water droplets on wetting gradient surface.

In this work, we employed molecular dynamics simulation methods to study the moving process and mechanism of water nanodroplet on the wetting gradient surfaces. The wetting gradient surface was constructed by modifying SiO_2 substrate with $(CH_2)_9CH_3$, $(CH_2)_9SH$, $(CH_2)_9NH_2$ and $(CH_2)_9OH$. The structural transition of the water droplet during the moving process was described, and the fundamental mechanism for the spontaneous motion of water droplet was also analyzed. Furthermore, during the transport process, a phenomenon of precursor film (PF) was observed and the morphology as well as formation mechanism of PF was discussed. This work would be hoped to extend our understandings about the moving mechanism of nanodroplet on wetting gradient surface more scientific and deep, and to stimulate further studies on the motion of droplet and emerging applications.

2. Theoretical models and methods

Molecular dynamics simulations were utilized with Discover and Amorphous Cell modules in Materials Studio of Accelrys Inc to study the motion of water nanodroplet on wetting gradient surface.

2.1. The construction of the wetting gradient surface

In order to construct the wetting gradient surface, the wettability of different functional groups terminated silica surfaces were first evaluated, respectively. Initially, four silica substrates were derived from the initial silica lattices which were imported from the structural database of Material Studio. Then repeat units of silica were cleaved along (001) crystallographic orientation with dimension of 98.2 Å × 58.8 Å × 18.9. After that, these four silica substrates were completely modified by methyl-terminated $(CH_2)_9CH_3$ group ($-CH_3$), thiol-terminated $(CH_2)_9SH$ group (–SH), amine-terminated $(CH_2)_9NH_2$ group ($-NH_2$) and alcohol-terminated $(CH_2)_9OH$ group (–OH), respectively. Finally, four same water droplets were put onto these four surfaces, respectively. After 800 ps simulations, the water droplets reached the equilibrium state. The ultima contact angles of the water droplets were calculated using the method of Fan and Cagin [44]. And the measured contact angles were 93°, 52°, 28° and 23° on $-CH_3$, –SH, $-NH_2$ and –OH modified surfaces, respectively. It is well known that the smaller the contact angle is, the stronger the surface hydrophily is. Therefore, the order of the hydrophily of the modified silica surfaces is $-CH_3 < -SH < -NH_2 < -OH$.

Then, the wetting gradient surface consisting of a silica substrate and different modifying groups was constructed. The silica substrate with dimensions of 98.2 Å × 58.8 Å × 18.9 Å was first completely modified by $-CH_3$ to ensure that the surface was large enough for accommodating water droplet to move. After that, along the x direction, the terminal $-CH_3$ was replaced by –SH, $-NH_2$ and –OH in sequence. Then a water nanodroplet with the radius of 15 Å was constructed and the water droplet was put onto the hydrophobic segment of the wetting gradient surface to produce the initial simulation system (Fig. 1).

2.2. Molecular dynamics simulations

The condensed-phase-optimized molecular potentials for atomistic simulation studies (COMPASS) force field was used in all the simulations [45]. This was the first ab initio force field that was parametrized and validated using condensed-phase properties in addition to various ab initio and empirical data. The force field was expressed as a sum of valence, cross-terms, and nonbonding interactions:

$$\begin{aligned} E_{pot} = & \sum_b [k_2(b-b_0)^2 + k_3(b-b_0)^3 + k_4(b-b_0)^4] + \sum_\theta [k_2(\theta-\theta_0)^2 \\ & + k_3(\theta-\theta_0)^3 + k_4(\theta-\theta_0)^4] \\ & + \sum_\varphi [k_1(1-\cos\varphi) + k_2(1-\cos 2\varphi) + k_3(1-\cos 3\varphi)] + \sum_\chi k_2\chi^2 \\ & + \sum_{b,b'} k(b-b_0)(b'-b'_0) \\ & + \sum_{b,\theta} k(b-b_0)(\theta-\theta_0) + \sum_{b,\varphi}(b-b_0)[k_1\cos\varphi + k_2\cos 2\varphi + k_3\cos 3\varphi] \\ & + \sum_{\theta,\varphi}(\theta-\theta_0)[k_1\cos\varphi + k_2\cos 2\varphi + k_3\cos 3\varphi] + \sum_{b,\theta} k(\theta-\theta_0)(\theta'-\theta'_0) \\ & + \sum_{\theta,\theta'\varphi} k(\theta-\theta_0)(\theta'-\theta'_0)\cos\varphi + E_{ele} + E_{vdW} \end{aligned} \tag{1}$$

The non-bond interactions were represented by electrostatic potential $E_{ele} = \sum_{i>j} \frac{q_i q_j}{r_{ij}}$ and van der Waals potential

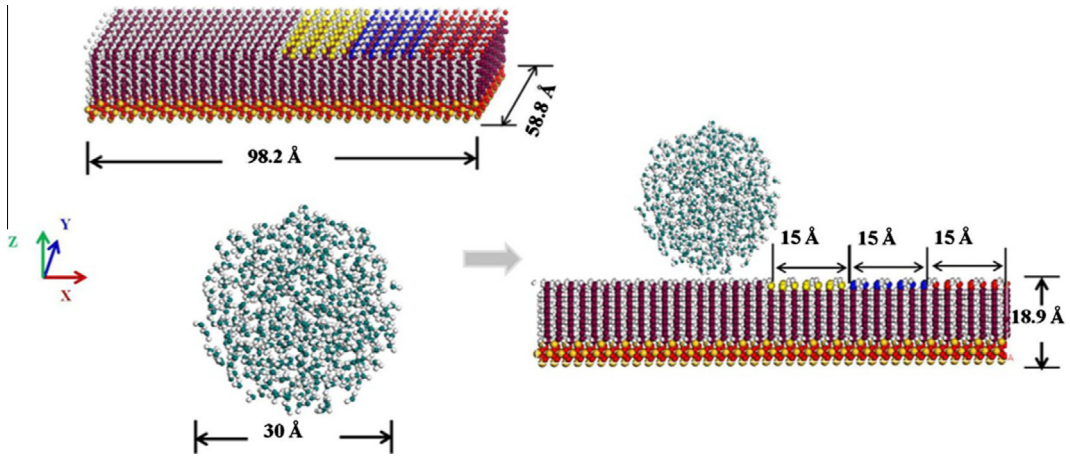

Fig. 1. Preparation of initial configuration of water droplet on the wetting gradient surface. The atoms are colored as follows: C, purple; O connected by Si or C, red; O in the water droplet, aquamarine blue; S, yellow; N, blue; Si, orange; and H, white. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)