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Molecular dynamics simulation of wetting and interfacial behaviors of argon fluid confined in smooth and groove-patterned rough nano-channels

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ABSTRACT

Wetting and interfacial behaviors of argon fluid confined in smooth and groove-patterned rough nano-channels are investigated through molecular dynamics (MD) simulation. The results demonstrate that, for smooth channels, lyophilic channels change to lyophobic as energy factors decrease from 1.0 to 0.1 and contact angles exhibit a simple linear dependence on the energy factors. When energy factor is smaller than 0.6, a novel three-phase solid–vapor–liquid interface takes place of solid–liquid interface, and vapor tunnel is discovered. For rough channels, the wetting and interface properties are similar with those of smooth channels. The roughness makes contact angles smaller for lyophilic channels, and larger for lyophobic channels. There are two density layering effects due to the adsorption in nano-grooves. The patterns of fluid contacting with the solid surfaces conform to Wenzel model at larger energy factors, while it agrees with Cassie model at smaller energy factors.

1. Introduction

Due to the development of nano-materials [1], nanotubes [2,3] porous materials for adsorption separation [4] and drug delivery [5], fluids confined in nano-channel have been attracted serious concern [6–13]. One of properties of fluid confined in nano-channels is the contact angle which can be obtained from experiments, Young's equation or molecular simulation. Because of impurities in solid surfaces and contact angle hysteresis, the experimental errors are evident [14]. Young [15] defined the contact angle of a liquid droplet contacting with an ideal flat surface. However, the interfacial tensions of solid–liquid and solid–vapor are difficult to obtain, the usage of this method is limited. Along with development of computing technology, molecular simulation began to become a priority to study wetting behaviors [16–19]. In 1977, for the first time, Saville [20] obtained the contact angle of liquid film confined between two smooth parallel-plates through solid–liquid, solid–vapor and liquid–vapor tensions by molecular dynamics simulation. The disadvantage of this method is the complexity of computing solid–liquid and solid–vapor tensions. In order to simplify the above method, a visual measurement of contact angles by iso-density lines of the liquid–vapor interfaces has been developed by Nijmeijer et al. [21], and this method has been accepted by many researchers [18,12,22–25].

It is well known that Young's equation only applies to ideal smooth surface, but it is not suitable for rough surface. Actually, there is virtually no ideal smooth surface. Sometimes solid surfaces are even fabricated to be rough by scraping and corroding [26]. Wenzel [27], Cassie and Baxter [28] proposed two different models which are appropriate for liquid droplet contacting with rough surfaces. The two types are wetted (Fig. 1a) and composite contact (Fig. 1b) [29]. Yong and Zhang [30] investigated the wetting behavior of a liquid mercury droplet on groove-patterned copper surface. More interestingly, they compared their results with Wenzel and Cassie models and found that these two models are applicable for nanoscale system.

Interfaces, particularly liquid–vapor, solid–vapor and solid–liquid interfaces, play a major role in mass transfer, heat transfer and phase transition. There is no lack of research on liquid–vapor interface using molecular dynamics simulation. In 1976, Rao and Levesque [31] proposed a sandwiches box to study the liquid–vapor interface, and then it became the standard model of molecular simulation [32]. Density distribution of LJ fluid and profile of the local surface tension of liquid–vapor interface has been investigated using Monte Carlo simulation [33]. However, the error of the interface tensions gained from this method could not be ignored. Subsequently, many papers on the liquid–vapor interface were reported, their research put particular emphasis on

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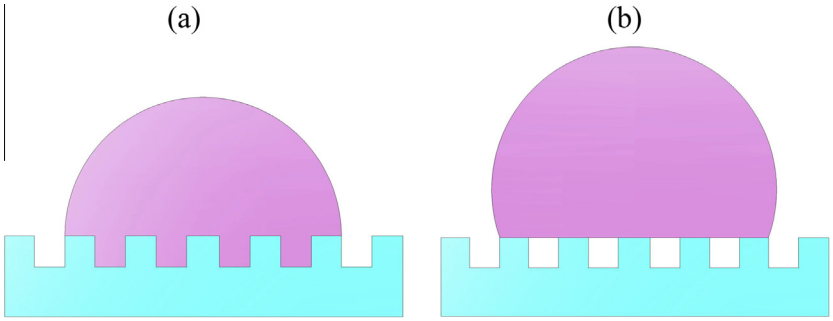

Fig. 1. Droplet in contacting with structured wall: (a) Wenzel model; (b) Cassie model.

increasing the accuracy [32,34,35]. Nijmeijer et al. reported the surface tension of a LJ liquid–vapor interface tensions of LJ fluids was seriously affected by the tail of the interaction potential [36]. Baidakov et al. [37] also point out the cut-off radius influence surface tensions and determined interface effective thickness through a rule named "10–90". For solid–liquid and solid–vapor interfaces, interfacial tensions have been also extensively investigated. Saville [20] computed solid–vapor and solid–liquid interface tensions using the same method which is used for calculating liquid–vapor interface tension. Berim and Ruckenstein [38] determined solid–liquid and solid–vapor as well as the liquid–vapor interface tension on the basis of a nonlocal density functional theory. In addition, some studies have found that there are four layers of ordering water molecules near the solid–liquid interface and the two layers nearest the wall became solid-like substance [39]. As noted above, many researchers have been engaged in simulating liquid bridge formation through L–J potential by MD simulations or experiments [40,41]. In contrast, we explore the changing from liquid bridge to vapor tunnel which may be attract more and more attention due to the development of super-hydrophobic materials.

In this study, we attempt to research wetting and interfacial behaviors of argon fluid confined in smooth and rough nano-channels by using molecular dynamics simulation. We intend to investigate wetting properties of the channels by changing energy factors of solid–liquid interaction and survey the corresponding interfacial behaviors of argon fluid. One-dimensional and two-dimensional mass density distributions are displayed at different energy factors. In addition, the relationship between contact angles and energy factors is also explored.

Table 1
Parameters of argon and solid atoms.

Atoms	Mass/kg	Energy parameter/J	Length parameter/Å
Argon atom	6.636×10^{-26}	1.67×10^{-21}	3.405
Solid atom	3.24×10^{-25}	8.35×10^{-20}	2.77

2. Simulation details

2.1. Simulation models

Simulation models consist of two solid walls and argon fluid filled between smooth (Fig. 2a) and groove-patterned rough (Fig. 2b) which are shown in Fig. 2. The thickness and the width of all the plates are 15 Å and 65 Å. For smooth channels, the length

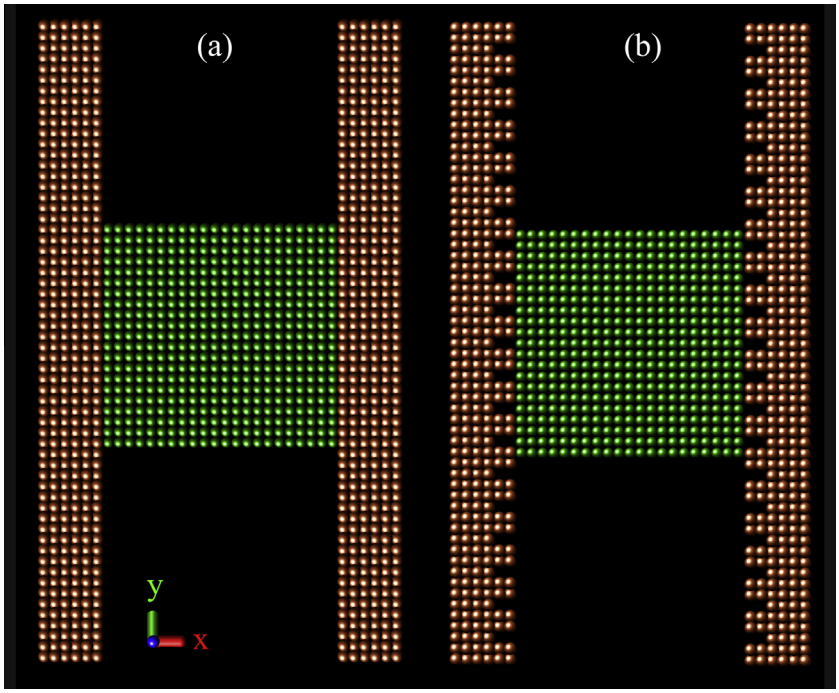

Fig. 2. Models of smooth and groove-patterned rough nano-channels: (a) smooth channel; (b) rough channel.