Computational Materials Science 124 (2016) 190–194

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Letter

The self-propelled movement of the water nanodroplet in different surface wettability gradients: A contact angle view

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ARTICLE INFO

Article history:
Received 4 May 2016
Received in revised form 5 July 2016
Accepted 23 July 2016
Available online 6 August 2016

Keywords:
Wettability gradient
Water nanodroplet
Movement pattern
Molecular dynamics simulation

ABSTRACT

In this work, the movement of the water nanodroplet, which was propelled by the wettability gradient from the view of the contact angle, was investigated by using molecular dynamics (MD) simulations. In the meantime, all of the contact angle range was discussed in detail. Results showed that the average speed of the water nanodroplet propelled by the wettability gradient could be affected by both the wettability of the initial section and the wettability gradient. The phenomenon revealed that a larger gradient and a relatively hydrophilic status of initial section could lead to a higher speed. In addition, the movement pattern of the water nanodroplet propelled by wettability gradient is similar to the principle of the caterpillar band.

1. Introduction

Self-propelled movement is widespread in all around us. Due to its advantage of eliminating the need for pumps [1] or other external devices [2], scientists and engineers paid a great deal of attention to self-propelled movement and succeeded in mimicking some of them using different methods in the past several decades, such as asymmetrically structured surfaces [3,4], thermal gradient [5], curvature gradient [6,7] and wettability gradient [8]. Among these approaches, the wettability gradient has been one of the most popular methods because of its significant application in micro and nanofluidic devices [9–12]. In addition to nanofluidic devices, there have been extensive applications on the mobile droplets in different fields. For example, gradient surface materials were used in self-cleaning, anti-fog, anti-corrosion and so on in daily life [13]. As for the mysterious biological research [14], it was applied in many ways including cell motility [15] and biochips [16]. At the forefront of electronic science and technology, of course, it has also frequently appeared in people's sight, such as condensation heat transfer [17] and design of self-powering actuators [18]. In a word, the wettability gradient materials have already existed around us.

Greenspan [19] and Brochard [20] proposed firstly a theoretical expression of the movement of water droplet on the wettability gradient surface. Chaudhury [21] realized the movement of water droplet on the wettability gradient surface experimentally. Afterward, there existed a lot of such experiments that was conducted to investigate the self-propelled movement. In 2001, Daniel [22] described a fast drop movement of water droplet on a surface with a radial surface tension gradient. Zielke et al. [23] reported that the speed of water droplet would increase as droplet size increased, which maximum speed reached 50 mm/s. Yoshihiro et al. [24] studied the movement speed of water droplet from the hydrophobic to hydrophilic surface depended on the wettability gradient. The results illustrated that the higher the wettability gradient induced the greater speed. The movement of the droplet on radial-wettability gradient surface was researched by tracking the change of advancing and receding angle [25]. Obviously, these investigations mainly focused on relative large-scale water droplet and explained the movement behaviors at macroscopic level. However, as the rapid development of micro and nanofluidic technology, the water droplet would turn to be nanoscale. In order to control the movement of such a small droplet on the micro and nanofluidic devices, the wettability gradient was commonly used. With the decrease of the water droplet size, the moving behaviors and mechanism may have significant difference from the macroscopic water droplet due to the size effect. Therefore, it is necessary to study the movement mechanism of water droplet induced by wettability gradient from both of atomic level and subtle molecular interaction. Unfortunately, such microscopic information is challenging and impossible to be obtained by experiment method [26].

With the rapid development of computational capabilities, MD simulation has attracted enough attention in exploring the microscopic interaction. MD simulation enables us to change individual

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http://dx.doi.org/10.1016/j.commatsci.2016.07.026
0927-0256/

parameters separately, which it is impossible to implement in an experiment. Therefore, MD simulation is a powerful tool to study the influence of independent parameters [27]. Chakraborty [28] mainly studied the effect of temperature variation on the droplet movement by using MD simulations and theory model. Using MD simulations, Wang et al. [26] investigated the microscopic moving mechanism of the water nanodroplet induced by the wettability gradient. Meanwhile, Liu [29] proposed a conceptual design of driving the water nanodroplet on the graphene surface. It is worth mentioned that the direction of the movement propelled by wettability gradient can be controlled via a continuous wettability gradient. For instance, a two-dimensional surface wettability gradient can make the water nanodroplet move along nonlinear arc paths. These researches indicate that MD simulation is a good tool in studying the moving process and microscopic mechanism of water nanodroplet on wettability gradient surface.

Using MD simulations, this paper studied the self-propelled movement of water nanodroplet on the wettability gradient surface from the view of the contact angle. The effect of the gradient magnitude on the movement speed of the water nanodroplet was discussed in detail. In addition, we also explored the self-propelled movement pattern.

2. Models and methods

MD simulations are carried out using the LAMMPS package [30]. The simulations are performed using a time step of 0.001 ps in a canonical (NVT) ensemble, in which the Nose-Hoover thermostat is chosen to maintain a constant temperature (300 K). [31]. The periodic boundary condition is applied in all three spatial dimensions of the simulation box. The simulation system is sufficiently large to avoid the influence of the other periodic surfaces.

In present MD simulations, 8000 water molecules, which initially arranged with face-centered cubic (FCC) crystal structure, are positioned on the graphene surface. As for the choice of potential, the adaptive intermolecular reactive empirical bond order (AIREBO) [32] is employed to describe the interaction of carbon atoms. The atoms of graphene are fixed to their lattice sites by a spring, which can provide a realistic model of a solid surface [33]. Each carbon atoms are treated to be neutral. A rigid-body water model, the simple point charge-extended (SPC/E) model [34], is used. The interaction between the water and graphene surface is also assumed to be 12-6 Lennard-Jones (LJ) particles [35] as follow:

$$V_{CO}(r) = 4(\lambda\varepsilon_{CO})(\sigma_{CO}^{12}/r^{12} - \sigma_{CO}^{6}/r^{6}) \quad (1)$$

where σ_{CO} is the equilibrium distance, $\varepsilon = \lambda\varepsilon_{CO}$ is initial well depth of the potential between atoms with a distance of r, λ is a scaling factor and can be used to tune the wettability of the graphene surface. The cutoff distances for LJ and Coulomb interactions are 10 and 12 Å.

In this paper, only a single surface wettability gradient is needed to be created. It means that there are two sections of the graphene surface, including initial section and adjustable section (Fig. 1). During the simulations, the wettability of two sections can be changed by altering the scaling factor λ. In reality, the surface wettability could be changed through chemical modification [36] or physical treatment [37]. When the simulations started, the water nanodroplet is placed on the graphene surface and its center of mass is located in the dividing line of two different wettability sections. At the moment, the equilibrium state of water nanodroplet is broken, resulting in a movement toward the direction of the decrease of contact angle with a relatively stronger wettability. Then the simulations are executed for some time to make the water nanodroplet reach a uniform position. It is worth mentioned that the movement of the water nanodroplet in the wettability gradient is discussed from the view of the contact angle, because it is a fundamental and relatively straightforward quantity which is usually used to characterize the wetting properties of water on a solid surface.

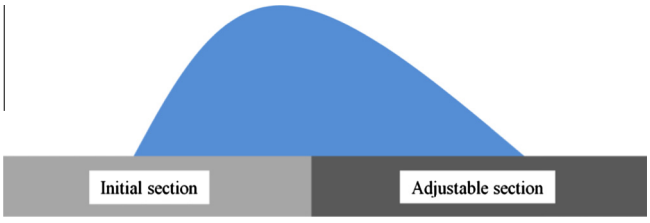

Fig. 1. A single surface wettability gradient: the graphene surface consists of initial section and adjustable section.

3. Results and discussion

The contact angles for different wettability on the graphene surface are firstly measured. Fig. 2 shows the simulation snapshots of the water nanodroplet on the intrinsic graphene surface at equilibrium. To determine the contact angle, a popular circular method [38] is applied to fit the positions of outermost water molecules of the droplet and is illustrated in Fig. 3. It is noted that the disturbance of density fluctuations at the liquid-solid interface, so the interfacial water within a thickness of 8 Å adjacent to the graphene surface are not used in the calculation of the contact angle. The measured intrinsic contact angle of the water nanodroplet on the graphene surface with $\sigma_{CO} = 3.19$ Å and $\varepsilon_{CO} = 0.00406$ eV ($\lambda = 1$) [38] is about 94° at 300 K, which meet the previous experimental result well [39,40]. Depending on the interaction parameters between water molecules and carbon atoms, the computed contact angles range from 34° to 133° with varying λ. Fig. 4 plots the contact angle as a function of liquid-solid interaction parameters ε on the graphene surface. It is noticed that the contact angles vary with liquid-solid interaction parameters linearly.

A single wettability gradient surface can be achieved by fixing the wettability of the initial section and altering the wettability of the adjustable section, and the contact angles are θ_0 and θ_1 ($<\theta_0$) respectively. When the water nanodroplet is placed on the wettability gradient surface, owing to the difference of the surface tension, it moves in the direction of relatively hydrophilic end. The surface wettability gradient is defined as $\Delta\theta$ ($= \theta_0 - \theta_1$), which can be termed a contact angle gradient. During the movement of the water nanodroplet, the coordinates of its center of mass along the direction of the wettability gradient are evaluated. It should be noted that the simulations can be stopped when the water molecules completely lie in adjustable section and the displacement along other directions are negligible.

Fig. 5 shows the displacement of the water nanodroplet center of mass versus time curve in different wettability gradients on the graphene surface when the contact angle of initial section is 94°. It is showed that the water nanodroplet will move on the wettability gradient surface. After the initial period of acceleration, the water nanodroplet will roughly remain a uniform motion. The speed of the water nanodroplet depends on the magnitude of the surface wettability gradient, which a larger wettability gradient leads to a higher speed. Based on the above reasons, one can obtain that a wettability gradient will be only corresponding to an average speed of the water nanodroplet. Therefore, the relationship between the wettability gradients and the average speeds of the water nanodroplet will be further investigated.

Generally speaking, the speed is a basic quantity to characterize the dynamical properties of the interfacial water. In order to get