Chemical Physics Letters 694 (2018) 29–34

Contents lists available at ScienceDirect

Chemical Physics Letters

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

Research paper

Dewetting transition of water confined between atomically rough surfaces: A lattice gas Monte Carlo simulation study

Liyi Bai, Jihye Jang, Zhengqing Zhang, Joonkyung Jang *

Department of Nanoenergy Engineering, Pusan National University, Busan 46241, Republic of Korea

ARTICLE INFO

Article history:
Received 18 November 2017
In final form 16 January 2018

ABSTRACT

Using lattice gas Monte Carlo simulations, we studied the dewetting transition of water confined between a spherical tip and a plate, which is relevant to atomic force microscopy measurements conducted in water. The dewetting transition was investigated by varying the tip-plate distance, tip size, and the pressure of water. With introduction of an atomic scale roughness (1 < nm) in the tip and the plate, the dewetting transition significantly increased in range and yielded an enhanced hydrophobic force between the tip and the plate. This finding is in agreement with the experimental results previously reported by Singh et al.

1. Introduction

A liquid water droplet sandwiched between hydrophobic surfaces spontaneously evaporates when the surfaces are within a certain distance (D_c). This *dewetting transition* occurs due to the confinement of water and gives rise to a strong attractive force between the two hydrophobic surfaces, which is known as the *hydrophobic force*. The hydrophobic force is much stronger and longer in range compared to the van der Waals force. The dewetting transition and the resultant hydrophobic force are manifested in various phenomena, including protein folding [1–3], self-assembly of amphiphilic molecules into micelles and membranes [4,5], and the opening and closing of ionic channels [6,7].

Given its ubiquity and importance, various theoretical and simulation studies have been carried out to understand the dewetting transition [8,9]. Huang et al. [10] have used molecular dynamics simulations to investigate the dewetting transition in ideal $\alpha_2 D$ *de novo* protein chains. Zhou and Berne have studied the dewetting transition in the protein folding [11–14] by modelling mellitin tetramers [13]. These theoretical studies assumed ideal geometries of the surfaces such as two plates or two ellipsoids [11]. On the contrary, real surfaces are rough to some extent. In fact, the presence of an atomic or nano-scale roughness on a surface is a rule rather than an exception. However, it is not completely understood how such a small roughness affects the dewetting transition and the resultant hydrophobic force. Interestingly, Singh et al. reported that the hydrophobic force acting between a spherical tip and a plate [15] is greatly enhanced in its range and magnitude in the presence of a microscale (not atomic or nanoscale) surface roughness.

Herein, we theoretically studied the effect of an atomic scale surface roughness on the hydrophobic force between an atomic force microscope (AFM) tip and a plate. Specifically, we performed extensive Monte Carlo (MC) simulations by employing the lattice gas model for water [16–21]. The lattice gas model enabled us to simulate mesoscale tip and plate geometries that were not accessible in a fully atomistic simulation. By systematically varying the pressure and the tip-plate distance, we examined the dewetting transition and the hydrophobic force. Therefore, the effects of surface roughness on the dewetting transition and hydrophobic force have been investigated in this work.

2. Theory and Monte Carlo simulation methods

The present work focuses on the molecular simulation of the dewetting transition of water confined between a spherical tip and a plate (Fig. 1a). We however introduce a simple continuum theory for the dewetting process to present a theoretical background and to compare with the present simulation. Suppose the dewetting gives rise to a cylindrical cavity of radius r and height D between the tip and the plate. Let Ω_V and Ω_L be the grand potentials of the dewetted and wetted systems, respectively. Then, the difference in the grand potentials, $\Delta\Omega$, is given by Eq. (1) [22].

$$\Delta\Omega = \Omega_V - \Omega_L = (\Delta P)V - (\Delta\gamma)A_S + \gamma_{LV}A_{LV} \tag{1}$$

where V is the volume of the cylindrical cavity, A_S is the area of the solid-vapor interface, A_{LV} is the area of the liquid-vapor interface, and ΔP is the difference between the pressure of the liquid (P_L) and vapor pressure (P_V) (both have the same chemical potential

---

* Corresponding author.
E-mail address: jkjang@pusan.ac.kr (J. Jang).

https://doi.org/10.1016/j.cplett.2018.01.032

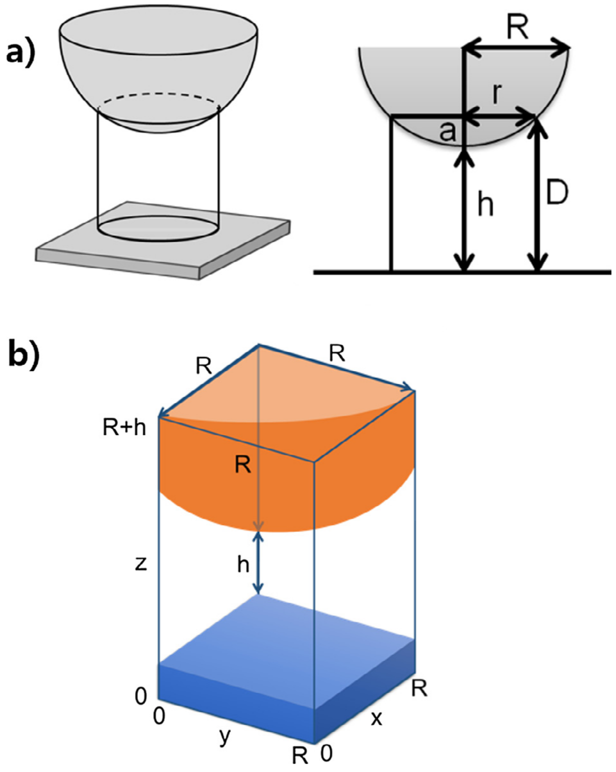

Fig. 1. Geometry of the dewetting transition between a spherical tip (with a radius *R*) and a plate. (a) Cylindrical cavity assumed in the theory of the dewetting transition. The radius and height of the cylinder are denoted by *r* and *D*, respectively. The tip-plate distance is given by *h*, and *a* = *D* – *h*. (b) Simulation cell for the present lattice gas Monte Carlo simulation. Only the first quadrant (*x*, *y* > 0) is simulated and the rest three quadrants are taken to be mirror images of the first quadrant.

μ). γ_{LV} is the liquid-vapor interfacial tension, and $\Delta\gamma \equiv \gamma_{LS} - \gamma_{VS}$ where γ_{LS} and γ_{VS} are the liquid-solid and vapor-solid interfacial tensions, respectively. By inspection of the geometry, it can be noted that $V = \pi r^2 D - V_{trunc}$, $A_S = A_{trunc} + \pi r^2$, and $A_{LV} = 2\pi r D$, where V_{trunc} and A_{trunc} are the volume and surface area of the tip inside the cylinder, respectively. $V_{trunc} = \pi(Ra^2 - a^3/3)$ and $A_{trunc} = 2\pi Ra$, where $a = D - h$.

By imposing the condition that $\Delta\Omega = 0$, it is possible to solve the equations for the tip-plate distance at the dewetting transition h_c as given in Eq. (2).

$$h_c = \frac{\Delta p(Ra^2 - a^3/3) - \gamma_{LV}\cos\theta(2Ra + r^2)}{\Delta p r^2 + 2\gamma_{LV} r} - a \tag{2}$$

where θ refers to the intrinsic contact angle of a water droplet on a flat surface. The Young equation ($\Delta\gamma = -\gamma_{LV}\cos\theta$) was used to derive Eq. (2). Although Eq. (2) applies to a cylindrical cavity, a real cavity is rather close to an axis symmetric meniscus for which a simple analytical expression such as Eq. (2) cannot be obtained.

The present Monte Carlo simulation is based on the lattice gas model, wherein water molecules reside on the sites of a cubic lattice between a sphere and a plate. A molecule interacts with its nearest neighbor (NN) with an attraction energy ε and has its own chemical potential μ. When it is located adjacent (nearest neighbors) to the surfaces of the tip and plate, it experiences a binding energy of *b*. The Hamiltonian in the lattice gas model is given by Eq. (3),

$$H = -\varepsilon \sum_{i,j=n,n} c_i c_j - b \sum_{i=surf} c_i - \mu N \tag{3}$$

where c_i is the occupation number at the i^{th} lattice site (0 or 1). In this model, the μ value for the bulk vapor-liquid phase transition, μ_C, is exactly -3ε. The *saturation* of the system is defined as $\exp[(\mu - \mu_C)/(k_B T)]$, which is exact in the ideal gas limit. The bulk critical temperature, T_C, for the lattice gas is given by $1.128\varepsilon/k_B$. In order to emulate a liquid, the saturation was set to 105%. Identifying the liquid as water, ε was set to 4.8 kJ mol^{-1} (because T_C of water is 647.3 K) and the lattice spacing, *l*, was set to 0.37 nm (molecular diameter of water). The surface binding energy was set to $b = 0.01\varepsilon$, in order to mimic a hydrophobic surface and the temperature was fixed to 300 K.

The present lattice gas model is a standard method to study both gas and liquid phases and the transition between these phases. Numerous previous studies [23–25] on the liquid-gas transitions employed the lattice gas model. This coarse-grained model cannot capture the full molecular features of water such as the dipole moment and the long-ranged Coulomb interaction. However, it has proven to reproduce the essential features of the phase behavior of water. For example, the present lattice gas model was used to successfully simulate the phase transition of water confined in a carbon nanotube [26–28]. Also, the lattice gas simulation reproduced the humidity dependence of the capillary force due to the liquid water formed between an atomic force microscope tip and a surface [22].

The Glauber single spin flip using the Metropolis importance sampling was used for the MC move [29]. Initially, every lattice site was taken to be in the liquid state (by setting its occupancy to 1). In each simulation, 100,000 MC moves were attempted for every lattice site. The initial 60,000 flips were discarded for equilibration and the remaining 40,000 flips were used for calculating the average quantities. We used 5000 configurations to calculate the averages and standard deviations in the densities and cavity widths. A lattice site with an average occupancy larger (less) than 0.5 was considered to be in the liquid (vapor) phase. The density profile, ρ (*x*, *y*, *z*), defined as the average occupancy of the site located at (*x*, *y*, *z*), was also calculated. The width of the cavity was determined from the density profile as follows. For each horizontal position (*x*, *y*), we checked vertically the average occupancies of the sites of the column ranging from the lower plate to the upper tip. If all the sites of a column were less than half-full on average, it was declared to be a vapor column. A collection of such vapor columns was cylindrically symmetric around the *Z* axis. The cavity width was defined as the diameter of this cylinder, and half of this diameter was the radius of the cylindrical cavity *r* used in Eq. (2). In estimating the cavity width, we also estimated the stability of a cavity. The standard deviation in the diameter relative to its average diameter was defined as the fluctuation of the cavity. A cavity with a fluctuation of more (or less) than 20% was declared as an unstable (or stable) cavity [28]. Only the stable cavities are considered for the calculation of the cavity widths. The unstable cavities are taken to have zero widths.

By varying the tip-plate distance *h*, we investigated the formation of a stable cavity (with a fluctuation less than 20%). As *h* decreased to a certain distance h_c, a cavity appeared and broadened with further decreasing *h*. The cavity width at $h = h_c$ was taken to be the minimum width of the cavity.

The attractive force [24] between the tip and plate separated by *h* was calculated by Eq. (4),

$$F(h) = -\left(\frac{\partial\Omega}{\partial h}\right)_{\mu,T} - p\left(\frac{\partial V}{\partial h}\right)_{\mu,T} \tag{4}$$

where *V* is the volume of the cavity, and *p* is the bulk pressure. The value of Ω was calculated by using the following thermodynamic integration method [30],