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2007 Chinese Phys. Lett. 24 1021

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Large Slip Length over a Nanopatterned Surface *

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(Received 18 September 2006)

A thermodynamic method is employed to analyse the slip length of hydrophobic nanopatterned surface. The maximal slip lengths with respect to the hydrophobicity of the nanopatterned surface are computed. It is found that the slip length reaches more than $50\ \mu\text{m}$ if the nanopatterned surfaces have a contact angle larger than 160° . Such results are expected to find extensive applications in micro-channels and helpful to understand recent experimental observations of the slippage of nanopatterned surfaces.

PACS: 68.08. -p, 83.50.Lh, 68.03.Cd

Based on viscosity effect, non-slip boundary condition is a fundamental assumption in continuum hydrodynamics.^[1] However, at nanoscales, this assumption is usually invalid, and instead a slip length is often observed.^[2] In fact, larger slip lengths are required in many practical applications,^[3,4] such as the membranes in polluted water treatment and desalination.^[5] For example, the radius of the channels in the membranes in desalination should be small enough so that the salt can be effectively shielded. A large slip length results in a high water flux for a given pressure difference.

A traditional way to reduce the friction between water and the solid surface is to make the surface as smooth as possible. Very recently, it has been found experimentally that nanopatterned surfaces greatly increase the hydrophobicity and hydrodynamic slippage of the liquid at the surface.^[6] Molecular dynamics (MD) simulations^[7] have also shown that in a non-wetted situation, the slip length of a rough surface is larger than double of that of a smooth surface. However, only small systems can be handled by molecular dynamics simulation. In this Letter, we show an analysis based on wetting theory that the large slip length can reach several tens of micrometres for a nanopatterned surface with the length of the nanopatterns ranging from $30\ \text{nm}$ to $1\ \mu\text{m}$. We also discuss the necessary condition to obtain a large slip length on the hydrophobicity of the solid.

The model system is composed of fluids and a nanopatterned surface. The nanopatterned surface is formed by an ideal flat surface with ideal cubes, with side length d . The hydrophobicity of the material composing the nanopatterned surface is depicted

with a contact angle.^[8] We thus have the following Young equation:

$$\gamma_{vs} - \gamma_{ls} = \gamma_{lv} \cos \theta, \quad (1)$$

where γ_{ls} , γ_{vs} , and γ_{lv} are, respectively, the surface free energies at liquid/surface, vapour/surface, and liquid/vapour interface, θ is the contact angle of the liquid drops on a smooth surface. Here we neglect the changes of contact angle at the nanoscale due to the motion of fluids and other factors.^[9,10]

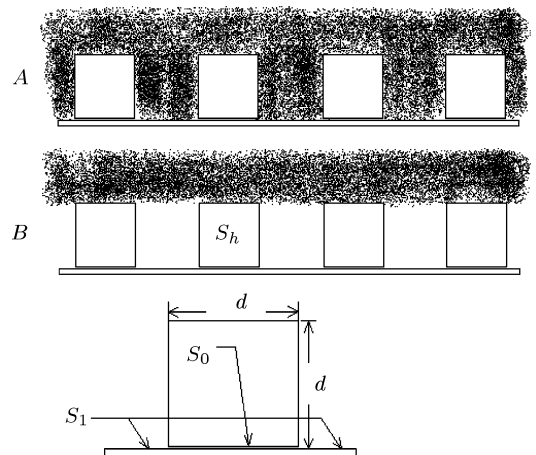


Fig. 1. Thermodynamic stable states of the system. Ideal cubes are uniformly distributed on an ideal flat surface. *A* is the wetting state, and *B* is the dewetting state that there is no water in the space between cubes. The black dots are water molecules.

Figure 1 shows two possible states of the system, the wetting state *A* and dewetting state *B*. To find which one is the thermodynamically stable state, we

* Supported by the 100 Persons Project of the Chinese Academy of Sciences, the National Natural Science Foundation of China under Grant Nos 10474109 and 10674146, the National Basic Research Programme of China under Grant Nos 2006CB933000 and 2006CB708612.

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calculate the grand potentials Ω_A and Ω_B of the system for the wetting state A and dewetting state B , respectively:^[8]

$$\Omega_A = -P_l V_1 + \gamma_{ls}(S_1 + S_h), \quad (2)$$

$$\Omega_B = -P_v V_1 + \gamma_{vs}(S_1 + S_h) + \gamma_{lv} S_1, \quad (3)$$

where $S_0 = d^2$ is the surface area of the substrate which is covered by a nanopattern (cube); S_1 is the residual area of the substrate exposed to the water; $V_1 = S_1 d$ is the volume of the region between neighbouring cubes, where the wetting–dewetting transformation occurs; and $S_h = 4d^2$ is the total side surface area of the cube. The difference between the grand potentials of states A and B is

$$\Delta\Omega = \Omega_A - \Omega_B = \Delta P V_1 - \gamma_{lv} \cos\theta S_h - \gamma_{lv} S_1, \quad (4)$$

where ΔP is the difference of the pressures between liquid and vapour phases. When $\Delta\Omega > 0$, the dewetting state is the stable one, otherwise the wetting state is more stable.

When the dewetting state is stable, we have

$$-\Delta P S_1 d - \gamma_{lv} \cos\theta (S_1 + 4d^2) - \gamma_{lv} S_1 \geq 0. \quad (5)$$

Thus

$$S_1 \leq \frac{-4d^2 \gamma_{lv} \cos\theta}{\gamma_{lv}(1 + \cos\theta) + \Delta P d}, \quad (6)$$

and

$$\frac{S_1}{S_0} \leq \frac{-4\gamma_{lv} \cos\theta}{\gamma_{lv}(1 + \cos\theta) + \Delta P d}. \quad (7)$$

Defining the coverage ratio R as

$$R \equiv \frac{S_0}{S_0 + S_1}, \quad (8)$$

there is a critical coverage ratio R_c with

$$R_c = \frac{1 + \cos\theta + d\Delta P/\gamma_{lv}}{1 + d\Delta P/\gamma_{lv} - 3\cos\theta}. \quad (9)$$

Only when $R > R_c$, the system displays a dewetting state.

Now we calculate the slip length of the dewetting system. For a slip boundary condition, the shear stress σ at fluid/surface interface with the velocity v_s of fluid at the wall can be expressed as

$$\sigma = k v_s, \quad (10)$$

where k is the surface friction coefficient. Denoting by k_0 and k_1 the surface friction coefficients at liquid/cube and liquid/vapour/substrate interfaces, respectively, assuming that the velocity of liquid at liquid/cube and liquid/vapour/substrate is the same of v_s , and neglecting the transient part between the liquid/cube and liquid/vapour interface, the total shear

stress for a unit length of the nanopatterned surface is

$$\sigma_t = (Rk_0 + (1 - R)k_1)v_s. \quad (11)$$

Equating the shear stress to the viscous shear stress in the fluid ($\eta dv(z)/dz$, with the dynamic viscosity η), we can obtain the slip length b as

$$\frac{1}{b} = \frac{(1 - R)k_1 + Rk_0}{\eta} = \frac{1 - R}{b_1} + \frac{R}{b_0}, \quad (12)$$

where $b_0 = \eta/k_0$ and $b_1 = \eta/k_1$ are the slip lengths at liquid/cube and liquid/vapour/substrate interfaces, respectively.

In the macroscopic theory of boundary layer with continuum approximation, the slip length at liquid/vapour/substrate interface can be calculated by $b_1 = \delta(\eta_l/\eta_v - 1)$, where δ is the thickness of the vapour layer, η_l and η_v are the dynamic viscosities of liquid and vapour, respectively.^[12] Under normal condition, η_l/η_v equals 55 for water. This theory gives a large value of slip length when the thickness of vapour layer δ is in scale of micrometre.^[6] When the thickness is at the nanoscale, the continuum approximation is usually invalid and the molecule effect of the vapour layer should be taken into account. De Gennes proposed that the value of b_1 is about $7\mu\text{m}$ ^[11] for typical liquids (water for example) with δ less than 100 nm. This value is much larger than the predictions of $\delta(\eta_l/\eta_v - 1)$ from macroscopic theory. In this Letter, we show the slip length of the patterned surface with the side length d of the cube of the values of 30 nm, and $1\mu\text{m}$, respectively. The De Gennes prediction and macroscopic theory are used for the former and latter systems, respectively.

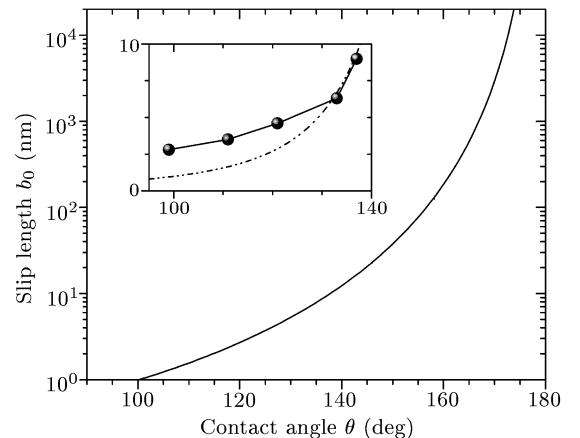


Fig. 2. Slip length at solid/liquid interfaces b_0 vs the contact angle θ for a flat surface. The solid curve and the circles are the results from the present analysis and a MD simulation.^[15]

For a smooth surface, both the slip length at liquid/cube interface and the contact angle are related to the interaction between solid and liquid molecules.

However, the relationship between the slip length and the contact angle are usually not so simple since other factors, such as the relative fluid molecule diameter, also have impact on them.^[13] Using standard Laplace estimate of surface free energies^[14] and neglecting the effect of the radii of different molecules, the relationship between the fluid-solid interaction strength and the contact angle is obtained as^[15]

$$\cos\theta + 1 = \frac{2\rho_S c_{FS}}{\rho_F c_{FF}}, \quad (13)$$

where ρ_S and ρ_F are the densities of solid and fluid, respectively, c_{FF} and c_{FS} are the fluid-fluid and fluid-solid interaction strength, separately. It is clear that the larger the value of c_{FS}/c_{FF} , the larger the contact angle θ . This is consistent with the previous molecular simulation result.^[10] About the relationship between slip length at fluid/solid interface and the interaction strength c_{FS} , Barrat *et al.* have given a theoretical relation^[15]

$$b_0 = \alpha c_{FS}^{-2}, \quad (14)$$

where α is a function of the interface structure which may be regarded as constant when c_{FS} changes in a small range.

Figure 2 shows the picture of b_0 as a function of contact angle θ on a flat surface, where $\alpha = 2.25$ nm and $2\rho_S/(\rho_F c_{FF}) = 0.55$ from MD simulation.^[15] The slip length shows a steep rise when contact angle is larger than 140° and approaches infinite as contact angle approaches 180° . The round dots in the inset are the MD simulation results.^[15] The analytical results are favourable with the MD simulation.

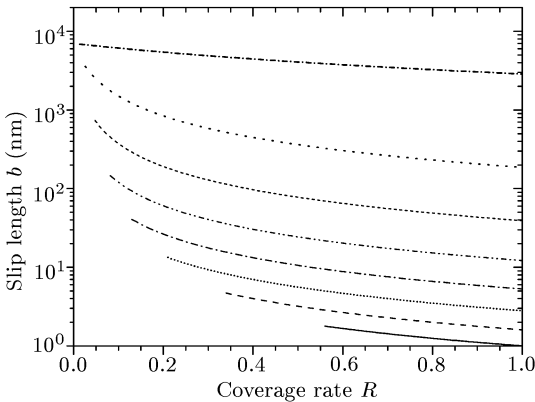


Fig. 3. Slip length b vs the coverage ratio R in dewetting state for the patterned surface for different contact angles θ calculated by our theory. The values of θ corresponding to lines from bottom to upper increases from 100° to 170° with a step of 10° . All the curves start at their critical coverage ratio R_c . Here $\Delta P = 1$ atm,^[8] $d = 30$ nm and $\gamma_{lv} = 72$ mJ/m².

In Fig. 3, we display the slip length for the patterned surface with respect to the coverage ratio for different contact angles. Here we assume $\Delta P = 1$ atm, which is the same as the value in Ref. [8], and $\gamma_{lv} =$

72 mJ/m², which is comparable to the value of surface free energy of water at room temperature. The slip length increases as the coverage ratio decreases and reaches a maximal value at the critical coverage ratio R_c , only below which the system falls in the wetting state. The critical ratio R_c decreases as the contact angle increases.

There is a maximal slip length b_c for a critical coverage ratio of the patterned surface, which can be computed by

$$b_c = \frac{1}{\frac{1-R_c}{b_1} + \frac{R_c}{b_0}}. \quad (15)$$

The results are shown in Fig. 4 for $d = 30$ nm and 1 μ m, respectively. We can find that the slip length increases obviously with the enhancement of hydrophobicity of surface. When the contact angle is close to 180° , due to the decreasing difference between b_0 and b_1 , the increase of b_c tends to slow down and finally b_c is saturated to the value of the slip length of liquid/vapour/substrate interface b_1 , where $b_1 = 7$ μ m for $d = 30$ nm^[11] and 54 μ m for $d = 1$ μ m.^[6] We note that larger cubes obtain lower efficiency of dewetting process. The maximal slip length for $d = 30$ nm is much smaller than that for $d = 1$ μ m.

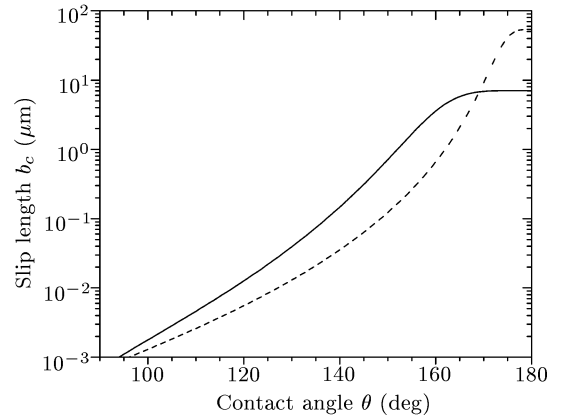


Fig. 4. Slip length at critical coverage ratio b_c vs the contact angle of nanopattern θ for $d = 30$ nm (solid curve) and 1 μ m (dashed curve), respectively. Other parameters are the same as those in Fig. 3.

In summary, we have analysed the behaviour of hydrophobic nanopatterned surfaces by using the thermodynamic method. Unlike a flat surface, the friction between water and nanopatterned surface decreases dramatically when dewetting happens, resulting in considerably larger slip length. We note that the coverage ratio is an important parameter to obtain a dewetting state. The results are expected to find extensive applications in micro-channels and could be helpful to understand some recent experimental observations of the slippage of nanopatterned surfaces.

The nanopatterns are composed of uniformly distributed simple cubes. In real systems, the forma-

tion of nanopatterns can be more complex such as the triangles in Ref. [6] and the distribution varies. The hydrophobicity of the nanopattern and the residual surface can also be different. Nonetheless, we believe the conclusion would remain the same.

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