Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

Mechanism and Universal Scaling Law for Contact Line Friction of Cassie-State Droplets on Nano-Structured Ultrahydrophobic Surfaces

Lei Zhao and Jiangtao Cheng*
Department of Mechanical Engineering,
Virginia Polytechnic Institute and State University,
Blacksburg, VA 24061, USA

* To whom correspondence should be addressed:

Jiangtao Cheng, Email: chengjt@vt.edu; Tel: +1 (805) 368 7240

1. PTFE model

In the OPLSAA force field, the forces acting on each atom is derived from a generalized potential field consisting of the nonbonded potential V_{LJ}, bond stretching potential V_S, bending potential V_B, dihedral potential V_D and electrical potential V_E, was used in this work. The analytical expressions for each potential are shown in following equations[1]:

$$V_{LJ} = \varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] \tag{S1}$$

$$V_S = \frac{1}{2}k_b\left(r_{ij} - b_0\right)^2 \tag{S2}$$

$$V_B = \frac{1}{2}k_\theta\left(\theta_{ijk} - \theta_*\right)^2 \tag{S3}$$

$$V_D = \sum_{n=0}^{3} S_n \cos^n(\phi_{ijkl} - \pi) \tag{S4}$$

$$V_E = 138.935485\frac{q_i q_j}{r_{ij}} \tag{S5}$$

where r_{ij} is the distance between two atoms, θ_{ijk} is the angle of bond, and ϕ is the dihedral angle. The detailed parameters are excerpted from the OPLSAA force field[1, 2] and listed in Table S1.

To validate the PTFE model, an initial structure with a low density of 800 kg/m^3 was constructed by placing 10 chains of PTFE molecules into a cubic unit cell with dimensions of 3.1724 nm for each edge. As listed in Table 1, the bond length of C-C, which makes up the backbone of polymer chains, is 0.1529 nm, indicative of at least 21 C atoms in each direction of the box. After an energy minimization procedure, the system was brought into an NVT ensemble with temperature of 300 K. Then the system was maintained at temperature of 300 K and pressure of 1 bar to reach a steady density. Then an artificial melting process was applied to the system by increasing the temperature from 300 K to 600 K stepwise at an interval of 50 K in every 40 ps.

The PTFE showed two distinct states corresponding to the rubbery state and glassy state respectively. The specific volume versus temperature profile in rubbery state and glassy state was

fitted into two straight lines using linear regression with 95% confidence interval. The detailed fitted parameters for the rubbery state and glassy state are shown in Table S2. The intersection between these two straight lines defines the glass transition temperature T_g.

Table S1. Force field parameters for PTFE structure[2, 3]

Lennard-Jones Potential	C		F
ε (kJ/mol)	0.276144		0.221752
σ (nm)	0.350		0.295
Bond Stretching Potential	C-C		C-F
k_b (kJ /mol nm^2)	224262.4		307105.6
b_0 (nm)	0.15290		0.13320
Bending Potential	C-C-F	C-C-C	F-C-F
k_θ (kJ/mol rad^2)	418.400	488.273	644.336
θ_*	109.5°	112.7°	109.1°
Dihedral Potential	C-C-C-F	C-C-C-C	F-C-C-F
S_0 (kJ/mol)	1.46440	2.92880	-5.23000
S_1 (kJ/mol)	1.88280	-1.46440	5.23000
S_2 (kJ/mol)	0	0.20920	0
S_3 (kJ/mol)	-3.34720	-1.67360	0
Partial Charge	C (CF_3)	C (CF_2)	F
q(e)	0.360	0.240	-0.120

The cubic thermal expansion coefficient α_V is defined as

$$\alpha_V = \frac{1}{v}\frac{\partial v}{\partial T} \tag{S6}$$

where v is the specific volume. The experimental values of α_V within 35°C -140°C (rubbery state) and 140°C - 200°C (glassy state) can be found in reference[4]. Here we consider the temperature

range of 35°C -140°C be in the rubbery state and the 140°C - 200°C be in the glassy state. The specific volume v was chosen to be the values at midpoints (87.5 °C and 170 °C) and $\frac{\partial v}{\partial T}$ is evaluated as the slope of those two straight lines corresponding to the rubbery state and glassy state.

Table S2. Linear fit $v = aT + b$ for rubbery state and glassy state

	$a\ (10^{-7})$	$b\ (10^{-4})$	R-squared
Rubbery state	1.828 ± 0.128	5.078 ± 0.009	0.8923
Glassy state	3.673 ± 0.259	4.863 ± 0.041	0.8472

2. Derivation of ξ_0 and F_C

The formula for the wetting velocity u_c in the dynamic wetting process can be derived by combing equations (1), (2), (3) and (4).

$$u_c = 2K_0\lambda \sinh\left(\frac{\gamma_{LV}(\cos\theta_0 - \cos\theta)\lambda^2}{2fK_BT}\right) \tag{S7}$$

From Raleigh dissipation function, the overall friction coefficient ξ_f can be written as:

$$\xi_f = \lim_{\theta\to\theta_0} \frac{\gamma_{LV}(\cos\theta_0 - \cos\theta)}{u_c} = f\frac{k_BT}{K_0\lambda^3} \tag{S8}$$

Because the contact line friction only occurs on the asperities of the solid surface and the air cushion applies almost no friction to the droplet, the contact line friction coefficient is calculated as:

$$\xi_0 = \frac{\xi_f - 0\times(1-f)}{f} = \frac{k_BT}{K_0\lambda^3} \tag{S9}$$

The CLF is defined as the product of ξ_0 and E_μ. By combing equations (6) and (21), F_C is calculated as:

$$F_C = \frac{k_BT}{K_0\lambda^3}\sqrt{2K_0D} = \frac{k_BT}{\lambda^3}\sqrt{\frac{2D}{K_0}} \tag{S10}$$

Recall equation (5), F_C can be rewritten as:

$$F_C = \frac{\sqrt{2Dk_BTh}}{\lambda^3} \exp\left(\frac{\Delta G}{2N_A k_B T}\right) \tag{S11}$$

Since ΔG can be decomposed into solid-liquid retarding and viscous damping, F_C can be expressed as:

$$F_C = \frac{\sqrt{2Dk_BTh}}{\lambda^3} \exp\left(\frac{\gamma_{LV}(1+\cos\theta_{0,f})\lambda^2}{2k_BT}\right) \exp\left(\frac{\Delta G_{vis}}{2N_A k_B T}\right) \tag{S12}$$

The overall friction between the droplet and the structured surface can be calculating by averaging F_C and F_a, which represents the friction applied by the air cushion to the droplet.

$$F_T = fF_C + (1-f)F_a \tag{S13}$$

In most cases, F_a is negligible comparing to F_C. Therefore, F_T can be eventually approximated as

$$F_T = f\frac{\sqrt{2Dk_BTh}}{\lambda^3} \exp\left(\frac{\gamma_{LV}(1+\cos\theta_{0,f})\lambda^2}{2k_BT}\right) \exp\left(\frac{\Delta G_{vis}}{2N_A k_B T}\right) \tag{S14}$$

References

1. H. Bekker, H. Berendsen, E. Dijkstra, S. Achterop, R. Van Drunen, D. Van der Spoel, A. Sijbers, H. Keegstra, B. Reitsma and M. Renardus, 1993.
2. W. L. Jorgensen, D. S. Maxwell and J. TiradoRives, *J Am Chem Soc*, 1996, **118**, 11225-11236.
3. G. A. Kaminski, R. A. Friesner, J. Tirado-Rives and W. L. Jorgensen, *J Phys Chem B*, 2001, **105**, 6474-6487.
4. P. Teflon and P. F. Resin, *DuPont Fluoroproducts, Washington*, 1996.