Improving the wetting stability on submersed superhydrophobic surfaces for drag reduction applications using hierarchical structures

Yahui Xue[*], Shigan Chu[*], Pengyu Lv[*] & Huiling Duan [*&**]
[*]*State Key Laboratory for Turbulence and Complex System, Department of Mechanics and Aerospace Engineering, College of Engineering, Peking University, Beijing 100871, China*
[**]*Key Laboratory of High Energy Density Physics Simulation (HEDPS), CAPT, Peking University, Beijing 100871, ChinaDepartment of Mechanics and Aerospace Engineering, College of Engineering, Peking University,Beijing, 100871, China*

Summary Superhydrophobic surfaces exhibit great potentials for reducing drag in micro-fluidic devices. In this work, by comparison with existing numerical and experimental studies, we confirm that a new metastable state, which happens after depinning of the three-phase contact line (TCL), exists on submersed superhydrophobic surfaces. We show that a strategy of using hierarchical structures can strengthen the TCL pinning in the metastable state, and thus is important to improve the stability of superhydrophobicity under high liquid pressure.

Introduction

The wetting state of liquid on rough surfaces can be generally described by the Wenzel and Cassie-Baxter (CB) states. Researchers around the world have done many studies on wetting transitions between these two states. Recent research interest arises in studying the behavior of submersed superhydrophobic surfaces due to the emergent requirement for drag reduction in micro-fluidic devices or submersed bodies.[1] The existence of the liquid-air interface in a large-area fraction is essential for significant drag reduction on those surfaces. However, the collapse of the liquid-air interface will induce the failure of the superhydrophobic state and thus the drag reduction ability.

Several experiments have been carried out to study the wetting transitions of the submersed super-hydrophobic surfaces. For example, Forsberg et al.[2] used the method of light reflection to study the decay of the plastron to study the wetting transitions on superhydrophobic surfaces under hydrostatic pressure. They demonstrated that a closed film of trapped air helps stabilize the submersed CB state, especially in the low pillar densities. However, there exists a significant deviation between their predicted collapse pressure and that obtained by their experiments, and the deviation is especially high as the increase of the pillar densities.

On the other hand, inspired by the unique water-repellent capabilities of some plant leaves and insect legs, researchers have studied the special hierarchical structures of these plant leaves and insect legs and shown that the nano- micro hierarchical structure is crucial for their stability. For example, Lee et al.[3] investigated the influence of hierarchical structures of superhydrophobic surfaces on liquid slip by experiments. Though the experiments have shown that the stability of submersed superhydrohphobic surfaces can be improved by hierarchical structures with nano-structured sidewalls, there lacks of a quantitative explain and understanding.

In this paper, we investigate the wetting stability on the submersed superhydrophobic surfaces under hydrostatic pressure by a theoretical approach.

Theoretical model

From the energy point of view, the wetting transition can be regard as a process of overcoming the energy barrier between the CB and Wenzel states. Our formulation is based on minimizing the total free energy of the system. We first consider a structure with the cylindrical cavities on a periodic square lattice. The surface structure is submersed in an incompressible liquid (e.g. water), and a hydrophobic solid material is considered. The free energy *G*, which governs the equilibrium and stability of the system, includes three parts: the bulk energy, the potential energy due to body forces (e.g., gravity), and the total surface energy. The bulk energy is increased by compressing the trapped air by the liquid, where the idea-gas law is assumed. For a specific surface structure, the total free energy *G* is a function of the meniscus shape (θ), the pinning position (h) and the trapped-air pressure (p_1) at a given liquid pressure (p_l). A minimization of *G* will lead to the equilibrium states of the system under the different liquid pressures.

Stabilities of equilibrium states

Besides the Wenzel state due to the collapse of the liquid-air interface, two equilibrium states are obtained by derivation of *G* with respect to θ, h and p_1. The first one is the CB state with considering the actual shape of the liquid-air interface before depinning. The other is a new equilibrium state, which happens after the TCL depinning from the tops. The new equilibrium is reached as a result of the increasing air pressure by the liquid pressurization. The free energies with respect to different equilibrium states can be obtained by substituting equations of the equilibrium states into the expression for *G*. It can be easily estimated that both states are local stable ones. The global stabilities of these equilibrium states can be simply analyzed by an energy comparison with the Wenzel state.

The analysis shows that at low hydrostatic pressure, the CB state with lower free energy than that of the Wenzel state, is stable and always preferential in general cases; As the hydrostatic pressure increases, the Wenzel state turns to have a lower energy than that of the CB state after a critical pressure (P1), where, though the free energy of the Wenzel state is relatively lower, the CB state (from P1 to P2) is still the more preferential than that of the Wenzel state due to the stabilization induced by the TCL pinning; When the pressure increases further, beyond a critical pressure (P2) the TCL depinning will happen, where the wetting state is not immune to external disturbances. On the other hand, by achieving the metastable state after depinning, the liquid pressure, which the structured surface can support, will be significantly increased.

Comparison with experiments

Recently, Forsberg et al.[2] carried out experiments to study the wetting transition on submersed superhydrophobic surfaces under hydrostatic pressure, and demonstrated that a closed film of trapped air helps stabilize the Cassie-Baxter state, especially in the low pillar densities. We carry out a comparison between the present theory and the experiment results of Forsberg et al.[2]. Before that, we extend the formulation developed in the above sections so as to analyze the behavior on submersed pillared surfaces by adopting certain approximations.

Comparison between our theoretical results and the experimental ones of Forsberg et al.[2] shows that almost all experiment datum fall into the region after pressure P2 (see above), that is, when the collapse happened, the liquid-air interfaces had slipped into the cavities at certain distances. Our calculated depinning pressures are in good agreement with the numerical ones of Forsberg et al.[2] within their tested pillar-fraction range. The further calculation shows the protrusion depth h ranges from 1%H to 8%H (where H is the height of the pillar) when the collapse happened during their experiments. A relative protrusion depth of 4% contributes about 40% to the pressure (i.e., $p_l - p_0$) just before the collapse of the liquid-air interface.

Wetting stability on hierarchical structured surfaces

The comparison between our analytical results and the numerical and experimental ones of Forsberg et al.[2] in above Section confirms that a metastable state exists after the TCL depins from the tops. The metastable state helps the submersed superhydrophbic surface stand higher liquid pressure. Increasing the stability of the metastable state will strengthen the superhydrophobicity. To maintain a metastable state, the TCL should be strongly pinned on the cavity sidewalls, or the collapse transition will happen. Therefore, technique assisting the pinning of TCL will help to obtain stable and large area liquid-air interfaces on the rough surfaces.

It has been shown that microstructures or defects on substrates can significantly increase the wetting hysteresis due to TCL pinning.[4] Thus, a two-level hierarchical surface with sub-structured sidewalls helps for a stable liquid-air interface. This is because, when the TCL depins from the pillar tops, the sub-level structures will provide the new pinning positions for the TCL. The metastable state after depinning can be strengthened by the sub-level structures. Therefore, the TCL can slip into the cavity at a great depth h with a large apparent advancing contact angle $\theta_{\mathrm{adv}}^{\mathrm{app}}$ due to the assistance given by the sub-level structures. Calculation shows that the critical (or collapse) pressure increases significantly as the increases of $\theta_{\mathrm{adv}}^{\mathrm{app}}$ and h. It is consistent with the experiments of Lee et al.[3] by using structured sidewalls to enhance the stability of the liquid-air interface on superhydrophobic surfaces.

Conclusions

In this paper, we have theoretically investigated the wetting stability on the submersed superhydrophobic surfaces under hydrostatic pressure. Comparison with the available experimental results shows that a metastable state after depinning exists due to the increase of air pressure by the liquid pressurization. The advantage of the metastable state is that it can increase the liquid pressure that can be stood by superhydrophobic surfaces, and the disadvantage is that the depined metastable state is not immune to external disturbances. It is shown that a two-level hierarchical surface with structured sidewalls is important for the stability of submersed superhydrophobicity in the way that it helps enhance the pinning of the liquid-air interface on the cavity sidewalls in the metastatble state. The present theory can provide guides for designing new stable superhydrophobic surfaces for drag reduction applications.

References

[1] Rothstein J. P.: Slip on Superhydrophobic Surfaces. *Annu. Rev. Fluid Mech.* **42**: 89-109, 2010.

[2] Forsberg P., Nikolajeff F. & Karlsson M.: Cassie-Wenzel and Wenzel-Cassie Transitions on Immersed Superhydrophobic Surfaces under Hydrostatic Pressure. *Soft Matter* **7**: 104-109, 2011.

[3] Lee C. & Kim C.J.: Maximizing the Giant Liquid Slip on Superhydrophobic Microstructures by Nanostructuring their Sidewalls. *Langmuir* **25**: 12812, 2009.

[4] Reyssat M. & Quéré D.: Contact Angle Hysteresis Generated by Strong Dilute Defects. *J. Phys. Chem. B* 113: 3906, 2009.