How to control bubble nucleation from superhydrophobic surfaces

Alberto Giacomello, Matteo Amabili and Carlo Massimo Casciola
Dipartimento di Ingegneria Meccanica e Aerospaziale, Sapienza Università di Roma, via Eudossiana 18, 00184 Roma, Italy
E-mail: alberto.giacomello@uniroma1.it

Abstract. Superhydrophobicity is realized by entrapping gas bubbles inside surface roughness. While this strategy affords remarkable surface properties, it enhances the risk of cavitation from these gas nuclei at negative pressures. Here we use free energy molecular dynamics simulations and an extension of the classical nucleation theory to show that the relevant nucleation rates and barriers can be controlled by engineering the surface structure. Mimicking the re-entrant and chemically heterogeneous structure found in the leaves of the Salvinia molesta allows one both to stabilize the gas pockets against liquid intrusion and to reduce the risk of cavitation.

1. Introduction
Superhydrophobicity is emerging as a means to control the macroscopic properties of surfaces in contact with a liquid. Superhydrophobic properties include self-cleaning [1], anti-(bio)fouling [2], and drag reduction [3]. At the same time, however, the superhydrophobic state in surfaces under flow conditions may facilitate the nucleation of gaseous bubbles [4], starting the cavitation process. Here we discuss the issue of controlling such nucleation process by a suitable design of the nanopatterns [5].

Superhydrophobic properties are linked to the entrapment of gas pockets inside of surface roughness or patterns – the so-called Cassie state [6]. Capillary forces sustain this “suspended” state. The Cassie state can be achieved by combining surface roughness and hydrophobic coatings [7] or by special re-entrant structures [8]. Superhydrophobicity is lost if the liquid wets the surface realizing the transition to the so-called Wenzel state [9].

Similarly to nucleation, the Cassie-Wenzel transition is a thermally activated event over a broad range of pressures. For superhydrophobic surfaces, in the realm of negative pressures which is relevant to cavitation, at least three (meta)stable states can exist: Wenzel, Cassie, and pure vapor or nucleated state; free energy barriers make of the Wenzel-Cassie and of the Cassie-vapor transition two activated events, see Fig. 1. Special techniques are required in order to compute the path and the relevant free energy barriers for such transitions; these are usually referred to as rare events methods [10]. Among those, restrained molecular dynamics and the string method have proved useful in studying superhydrophobicity and nucleation [11, 12]; the atomistic approach is computationally expensive but yields a complete and assumptionless picture of molecular phenomena, non-classical effects, and nano-confinement.

On the other end, classical nucleation theory (CNT) [13, 14] is based on a macroscopic description of the fluid and works well in predicting the nucleation barriers relatively close to
2. Results & Discussion

2.1. Catalytic effect on nucleation due to surface heterogeneities

It is well known that the presence of topographical and chemical heterogeneities in walls and solid impurities may promote the nucleation of bubbles thus favoring the inception of cavitation. For instance, the crevice model by Atchley and Prosperetti predicts how the presence of pre-existing vapor bubbles entrapped in surface asperities influence the cavitation pressure [17].

One can extend the picture of the crevice model to consider also the Wenzel-Cassie transition which is part of the overall process of nucleating a bubble from the liquid. This has been investigated in [4] for various kinds of crevices. Figure 1 shows that the nucleation process of a gas bubble is divided into two activated sub-steps when it happens from a crevice: the Wenzel-Cassie and the Cassie-vapor transitions. The two free energy barriers are lower than the one needed to nucleate the same bubble from a flat surface with the same properties. In other words, the crevice acts as a catalyst, enormously increasing the nucleation rate from the surface [4] (see also the similar case of crystal nucleation in pores [18]).

2.2. Barriers in a typical case

The picture emerging from the above discussion is that nucleation can be a multistep process, especially for superhydrophobic surfaces, and that the nucleation rate depends heavily on the status of the surface in contact with the liquid and in particular on the geometry and chemistry of the surface. A question of technological interest is whether cavitation can be controlled, by tuning such surface properties in such a way that the surface maintains its superhydrophobic character (Cassie state) and, at the same time, reduces the nucleation rates.

In order to answer to this question, in Fig. 2 we show the free energy barriers computed via restrained molecular dynamics for a re-entrant decoration of the surface with a heterogeneous chemistry: hydrophobic within the crevice and hydrophilic on the top layer. This peculiar configuration is inspired by the air-retaining properties of the water fern Salvinia molesta [19] which has been shown to have optimal stability properties of the Cassie state against nucleation and wetting [5].
The free energy barriers for nucleation, $\Delta \Omega^\dagger_{\text{CV}}$, diverge as the coexistence pressure $\Delta P \equiv P_l - P_g = 0$ is approached. What is more interesting is that for pressures below $\Delta P_{\text{min}} \Delta \Omega^\dagger_{\text{CV}}$ vanishes: this is the spinodal for the Cassie-vapor transition. This spinodal occurs at very low pressures for the nanocavities ($\sim 5$ nm) here considered, $\Delta P_{\text{min}} = -3.5$ MPa. The bulk spinodal of pure liquids is observed at even lower pressures ($\Delta P \approx -120$ MPa for water [20]). Below $\Delta P_{\text{min}}$, therefore, the nucleation of bubbles is a deterministic event happening preferentially at the surface cavity. It is interesting that also the Wenzel state has a spinodal pressure $\Delta P_W$ at which it becomes unstable. In our case $\Delta P_W \approx -1.8$ MPa, which means that the Cassie state survives at lower pressures than the Wenzel one.

The wetting of the groove by the liquid is governed by the free energy barrier between the Cassie and the Wenzel state, $\Delta \Omega^\dagger_{\text{CW}}$; this barrier monotonically decreases with pressure, see Fig. 2. In this case the spinodal is found at positive pressures, $\Delta P_{\text{max}} = 3.5$ MPa.

### 2.3. Pinning of the contact line

Both the barriers and the spinodal pressures depend on the geometry and the chemistry of the surface, which can be used to control the stability of the Cassie state against bubble nucleation and liquid intrusion. In particular, it can be shown [5] that hydrophilic chemistry of the top layer dramatically increases $\Delta \Omega^\dagger_{\text{CV}}$ while the hydrophobic interior increases $\Delta \Omega^\dagger_{\text{CW}}$.

Also the spinodals $\Delta P_{\text{min}}$ and $\Delta P_{\text{max}}$ can be controlled by tuning the geometry and chemistry of the surface decorations. For the re-entrant geometry shown in Fig. 2, this dependence can be made explicit with macroscopic models of capillarity as follows. The mechanical equilibrium of a liquid-gas meniscus is described by the Laplace law, which reads for the cavity in Fig. 2:

$$\Delta P = -2\gamma \cos \beta / w,$$

where $\gamma$ is the liquid-gas surface tension, $\beta$ is the angle formed by the vertical and the tangent to the liquid-vapor interface (Fig. 2), and $w$ is the width of the crevice mouth. The maximum and minimum of Eq. 1 represent the maximum and minimum pressures that can be balanced by capillary forces, i.e., the spinodals $\Delta P_{\text{max}}$ and $\Delta P_{\text{min}}$, respectively. The angle $\beta$ in Eq. 1 is determined by the pinning of the contact line at the crevice mouth, which is dictated on sharp corners or chemical contrasts by the Gibbs criterion [21]:

$$\theta_{Y,\text{out}} - 90^\circ < \beta < 90^\circ + \theta_{Y,\text{in}},$$

Figure 2. a) Salvinia-inspired geometry for the surface nanodecoration. The surface has an hydrophilic top (dark brown, contact angle $\theta_{Y,\text{out}} = 55^\circ$), a hydrophobic interior (light brown, $\theta_{Y,\text{in}} = 110^\circ$), and $w \approx 5$ nm. b) Nucleation ($\Delta \Omega^\dagger_{\text{CV}}$) and wetting ($\Delta \Omega^\dagger_{\text{CW}}$) free energy barriers as a function of the pressure difference between the gas and the vapor phase $\Delta P \equiv P_l - P_g$. The vertical lines indicate the nucleation spinodal pressure $\Delta P_{\text{min}}$, the intrusion one $\Delta P_{\text{max}}$, and the (confined) liquid spinodal $\Delta P_W$ where the Wenzel state becomes unstable (see text).
where $\theta_Y$ denotes the Young contact angles ($\cos \theta_Y < 0$ for hydrophobic and $> 0$ for hydrophilic surfaces, respectively) for the top surface ($\theta_{Y,\text{out}}$) and the inner surface ($\theta_{Y,\text{in}}$). Combining Eq. 1 with the limits for $\beta$ imposed by Eq. 2 for the case under exam one obtains the spinodals $\Delta P_{\text{max}} = 2\gamma/w$ and $\Delta P_{\text{min}} = -2\gamma/w$, which is the maximum range of pressures in which the Cassie state is stable. In general, it is possible to write down the Laplace equation and the Gibbs criterion for a given surface and design its chemistry and geometry such that it minimizes the risk of cavitation, while maintaining the desired superhydrophobic properties.

3. Conclusions

We presented molecular dynamics simulations and continuum calculations of the free energy barriers and spinodals for the nucleation of bubbles from surfaces with hydrophobic cavities. Our results show that superhydrophobicity indeed increases the nucleation rates as compared to a perfectly smooth surface, but it is possible to decrease them substantially by a careful design of the surface microstructure. In particular, a hydrophilic top layer in combination with a hydrophobic cavity interior achieve the optimal results.

Acknowledgments

The research leading to these results has received funding from the European Research Council under the European Union’s Seventh Framework Programme (FP7/2007-2013)/ERC Grant agreement n. [339446]. We acknowledge PRACE for awarding us access to resource FERMI based in Italy at Casalecchio di Reno.

References

[1] Barthlott W and Neinhuis C 1997 Planta 202 1–8
[2] Ferrari M and Benedetti A 2015 Adv. Colloid Interface Sci. 222 291–304
[3] Rothstein J P 2010 Annu. Rev. Fluid. Mech. 42 89–109
[4] Giacomello A, Chinappi M, Meloni S and Casciola C M 2013 Langmuir 29 14873–14884
[5] Amabili M, Giacomello A, Meloni S and Casciola C 2015 Adv. Mater. Interf.
[6] Cassie A B D and Baxter S 1944 T. Faraday Soc. 40 546–551
[7] Lafuma A and Quéré D 2003 Nat. Mater. 2 457–460
[8] Tuteja A, Choi W, Mabry J M, McKinley G H and Cohen R E 2008 Proc. Natl. Acad. Sci. USA 105 18200–18205
[9] Wenzel R 1936 Ind. Eng. Chem. 28 988–994
[10] Bonella S, Meloni S and Cicotti G 2012 Eur. Phys. J. B 85 97
[11] Giacomello A, Meloni S, Chinappi M and Casciola C M 2012 Langmuir 28 10764–10772
[12] Giacomello A, Meloni S, Müller M and Casciola C M 2015 J. Chem. Phys. 142 104701
[13] Volmer M 1939 Kinetik der Phasenbildung (Dresden: Theodor Steinkopff)
[14] Turnbull D 1950 J. Chem. Phys. 18 198–203
[15] Talanquer V and Oxtoby D W 1996 J. Chem. Phys. 104 1483–1492
[16] Giacomello A, Chinappi M, Meloni S and Casciola C M 2012 Phys. Rev. Lett. 109 226102
[17] Atchley A A and Prosperetti A 1989 J. Acoust. Soc. Am. 86 1065–1084
[18] Page A J and Sear R P 2006 Phys. Rev. Lett. 97 065701
[19] Barthlott W, Schimmel T, Wiersch S, Koch K, Brede M, Barczewski M, Walheim S, Weis A, Kaltenmaier A, Leder A et al. 2010 Adv. Mater. 22 2325–2328
[20] El Meuki Azouzi M, Ramboz C, Lenain J F and Caupin F 2013 Nat. Phys. 9 38–41
[21] Oliver J, Huh C and Mason S 1977 J. Colloid Interface. Sci. 59 568–581