# Effects of pressure on wetted area of submerged superhydrophobic granular coatings. Part II: poly-dispersed coatings

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## HIGHLIGHTS

- New formulations to characterize performance of superhydrophobic coatings.
- Predictions of wetted area and hydrostatic critical pressure for the coatings.
- Wetted area is important for predicting the water drag force on a surface.
- The proposed method is analytical, easy to use, and relatively accurate.
- Includes poly-dispersed coatings of randomly distributed heterogeneous particles.

## GRAPHICAL ABSTRACT

A simple method is developed to characterize the wettability of superhydrophobic coatings comprised of poly-dispersed particles of different diameters and contact angles by defining mono-dispersed equivalent particle diameters and contact angles for such poly-dispersed coatings.

$$\Delta P_p^{cr} = \Delta P_m^{cr}$$

$$n_1 = n_2 = n_3 = n_4 = 0.25$$
$$\theta_1 = 120^\circ, \theta_2 = 100^\circ, \theta_3 = 80^\circ, \theta_4 = 60^\circ$$
$$d_1 = 72, d_2 = 57, d_3 = 40, d_4 = 31 \ \mu m$$

$$\theta_{eq} = \frac{2\pi \cos\theta_i + \sum_{j=1}^{k} \beta_{ji} \cos\theta_j}{k\pi} = 107^\circ$$

$$d_{eq} = \frac{2\pi d_i + \sum_{j=1}^{k} \beta_{ji} d_j}{k\pi} = 63 \ \mu m$$

## ARTICLE INFO

## ABSTRACT

The effects of hydrostatic pressure on the stability of the air–water interface over submerged superhydrophobic coatings comprised of mono-dispersed particles was studied in the first part of this two-part publication [Colloids and Surfaces A, 465 (2015) 87–98]. In this second part, our formulations are extended to cover granular coatings comprised of randomly arranged particles having bi-dispersed or poly-dispersed size and contact angle distributions. Simple analytical formulations are developed to predict how the air–water interface transitions from a non-wetted (Cassie) state to the fully-wetted (Wenzel) state through a series of intermediate wetting states. In particular, a simple mono-dispersed equivalent particle diameter is proposed to be used in predicting the critical pressure and wetted area of poly-dispersed coatings comprised of particles of different diameters and contact angles as a function of hydrostatic pressure. Numerical simulations conducted via the Surface Evolver finite element code have been used to examine the accuracy of the analytical formulations developed in this study.

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## 1. Introduction

The reduced cost of manufacturing has played an important role in making spray-on granular superhydrophobic coatings attractive alternatives to superhydrophobic surfaces produced via microfabrication (see e.g., [1–3]). Such surfaces can be used for applications ranging from self-cleaning and drag reduction to corrosion resistance and heat transfer [4–7]. The essential attribute of superhydrophobic (SHP) surfaces is the reduced water–solid contact area (wetted area), which helps to reduce the friction between a moving body of water and the surface [6–9]. An analytical force

## Nomenclature

| | |
|---|---|
| $A_{SL}$ | Solid liquid area |
| $A_w$ | Wetted area, the ratio of solid liquid area over the unit cell area |
| $b$ | Slip length |
| $b_1$ | Geometric parameter in Fig. 8a |
| $b_2$ | Geometric parameter in Fig. 8a |
| $C$ | Compression ratio |
| $d_{eq}$ | Equivalent diameter |
| $d_{eq}^{cc}$ | Equivalent diameter calculated using constant curvature concept for meniscus |
| $d_i$ | Diameter of particle $i$ |
| $d_c$ | Diameter of coarse particle |
| $F_\sigma$ | Capillary force |
| $L$ | Center-to-center distance between two particles |
| $L_{m,i}$ | Center-to-center distance between two particles in mono-dispersed coatings |
| $L_b$ | Center-to-center distance between two particles in bi-dispersed coatings |
| $k$ | Number of particles which surround particle number $i$ in Voronoi diagram |
| $M_i$ | Intersection of the meniscus and particle with center $o_i$ at the cell boundary |
| $n_i$ | Number fraction of particles with diameter $d_i$ |
| $O_0$ | Center of meniscus |
| $O_i$ | Center of particle $i$ |
| $P_{bub}$ | Bubble pressure |
| $P_{cap}$ | Capillary pressure |
| $P_h$ | Hydrostatic pressure |
| $P_\infty$ | Atmospheric pressure |
| $R^*$ | Radius of curvature of a meniscus |
| $R_{di}^*$ | Radius of curvature of a meniscus over particles with a diameter of $d_i$ |
| $S_i$ | Center-to-center distance between the particles and the center of the radius of curvature of meniscus |
| $V$ | Volume of entrapped air |
| $V_\infty$ | Volume of entrapped air at a hydrostatic pressure of zero |
| $z_0$ | $z$-Coordinate of the center of a meniscus |
| $z_1$ | Minimum point of the meniscus at the cell boundary |
| $z_2$ | minimum point of the meniscus at the cell center |
| $\alpha_i$ | Immersion angle for particle $i$ |
| $\alpha_\infty$ | Immersion angle at atmospheric pressure |
| $\alpha_{cr}$ | Immersion angle correspondent to critical pressure |
| $\beta_{ji}$ | Angle (in radian) by which particle $j$ sees particle $i$ |
| $\gamma$ | Heat capacity ratio of air |
| $\Delta P$ | Capillary pressure |
| $\Delta P^{cr}$ | Critical capillary pressure |
| $\Delta P_{bi}^{cr}$ | Critical capillary pressure for bi-dispersed coatings |
| $\Delta P_{m,i}^{cr}$ | Critical capillary pressure for mono-dispersed coatings |
| $\epsilon_b$ | Solid volume fraction of bi-dispersed coatings |
| $\epsilon_{m,i}$ | Solid volume fraction of mono-dispersed coatings with a diameter $d_i$ |
| $\epsilon_p$ | Solid volume fraction of poly-dispersed coatings |
| $\eta$ | Coarse-to-fine particle diameter ratio |
| $\theta$ | Young–Laplace contact angle |
| $\theta_{eq}$ | Equivalent contact angle of particle $i$ |
| $\sigma$ | Surface tension |

part publication (referred to here as Part I) [10]. In current paper, referred to as Part II, we extend our formulations to the most general case of SHP coatings made up of particles of different diameters and YLCAs. As in Part I, the instantaneous shape and position of the air–water interface (AWI) between the particles is also used to predict the effective slip length of the surface, when used in a microchannel for instance. An introductory discussion along with a thorough literature review is given in Part I to put this study in the proper context of prior studies, and so it will not be repeated here (see [11–18] for additional information). Here we present a condensed overview of the background information needed for the continuity of our discussion.

The shape and position of the AWI over a SHP surface may be explained using the balance of the forces that act on the interface. For a submerged SHP surface, these forces are due to hydrostatic pressure $P_h$, ambient pressure $P_\infty$, pressure of the air trapped in the pore, referred to here as the bubble pressure $P_{bub}$, and the pores' capillary pressure $P_{cap}$. The bubble and capillary pressures, if positive, tend to balance the hydrostatic pressure [10]. A submerged SHP surface may not always be in the Cassie state (fully-dry); depending on the hydrostatic pressure and the surface morphology, the surface may move to the Wenzel state (fully-wetted) or to a transition state between the two extreme states [19–22]. There are two main paths by which a submerged SHP surface may reach a transition state: a gradual transition from the Cassie state over a certain period of time under a moderate hydrostatic pressure, or a sudden transition upon exposure to an elevated pressure. The former takes place due to the dissolution of the entrapped air in the ambient water, whereas the latter occurs because of the imbalance of the mechanical forces acting on the air–water interface [16–22]. Therefore, the drag-reduction effect generated by a SHP surface varies depending on both the operating pressure and the time in service. The hydrostatic pressure at which a SHP surface starts departing from the Cassie state (where the capillary pressure is at its highest value) is referred to as the critical hydrostatic pressure (CHP) [22–24] for a SHP surface with sharp-edged pores/grooves. We assume the CHP for a pore with round entrance to be the hydrostatic pressure at which the AWI reaches the maximum capillary pressure, unless the AWI deflects enough to touch the bottom of the pore at a lower pressure [25]. In that case, the latter pressure will be considered as the CHP.

In the following section, we first start with a force balance (FB) formulation for an AWI formed between the particles of a submerged granular SHP coating. This is followed by a simple method to relate the hydrostatic pressure of water above the surface to the capillary pressure of the coating's pores in Sections 2.2 and 2.3, we propose mono-dispersed equivalent diameter definitions for bi-dispersed and poly-dispersed coatings to be used for critical capillary pressure (CCP) and wetted area predictions. Comparison between the predictions of our analytical method and those from the numerical simulations carried out using the Surface Evolver (SE) finite element code are given in Section 3. This section also contains detailed analyses for the effects of randomness in the spatial distribution of the particles, among many other parameters, in a poly-dispersed SHP coating. The condensed summary of the calculation procedure developed in our work is given in Section 4 in the form of a flowchart. The conclusions drawn from the work are given in Section 5.

## 2. Analytical formulations

### 2.1. Critical capillary pressure

Consider an idealized condition for a single-layer bi-dispersed granular coating in which the particles with identical YLCAs are

balance method to approximate the wetted area of a SHP surface comprised of particles of equal size but different Young–Laplace contact angles (YLCAs) was presented in the first part of this two-