Supporting Information for:

Nano to Micro Structural Hierarchy is Crucial for Stable Superhydrophobic and Water-Repellent Surfaces

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For the derivation of equation 2:

Consider the liquid-solid system shown in Figure 1c. We assume that a) the substrate can be considered rigid in comparison with water and b) the effect of gravity is negligible. The latter assumption is justified as the structure size of concern here is much smaller than the capillary length. Furthermore, since typical dimensions of the surface structure, *h* and λ, are much smaller than the diameter of a water droplet, we simplify the liquid geometry as a semi-infinite space.

Young's equation $\cos\theta_0 = (\gamma_{SA} - \gamma_{LS})/\gamma_{LA}$ is assumed to hold at the triple-junction of liquid, air and solid, where θ_0 is the contact angle, and γ_{SA}, γ_{LS}, γ_{LA} are the solid-air, liquid-solid and liquid-air interfacial energies, respectively.

The contact angle is equal to the angle between the tangent vectors ***l*** and ***m*** (see Figure 1c) as

$$\cos\theta_0 = -\frac{\beta kh\sin(ka)/r + (1-\beta^2/r^2)^{1/2}}{[1+(kh)^2\sin^2(ka)]^{1/2}} \tag{s1}$$

where $\beta = a + d$. The relationship between the pressure *P* and the radius of curvature of the liquid-air interface is defined by the Young-Laplace equation (see Figure 1c),

$$P = \gamma_{LA}/r \tag{s2}$$

By substituting equation (s2), equation (s1) can be rewritten in a normalized form as

$$\bar{P}\bar{\beta}\bar{h}\sin\bar{a} + (1-\bar{P}^2\bar{\beta}^2)^{1/2} + (1+\bar{h}^2\sin^2\bar{a})^{1/2}\cos\theta_0 = 0 \tag{s3}$$

where $\overline{P} = P/(k\gamma_{LA})$, $\overline{a} = ka$, $\overline{h} = kh$, $\overline{d} = kd$, and $\overline{\beta} = k\beta$. Solving Equation (s3), we can get the analytical solution of nondimensional pressure $\overline{P}$, i.e., equation 2 in the main text.

For the derivation of equation 5:

Consider the theoretical model for an N-level hierarchical structure as shown in Figure 1c. The contact area fraction of the first level structure is (see the lowest panel in Figure 1c),

$$\overline{S}_1 = S_1 \Big/ \lambda_1 = \frac{2}{\lambda_1}\int_{a_1}^{\lambda_1/2}(1+\overline{h}^2\sin^2 x)^{1/2}dx = \frac{1}{\pi}\int_{\overline{a}_1}^{\pi}(1+\overline{h}^2\sin^2\overline{x})^{1/2}d\overline{x} \tag{s4}$$

where S_1 and λ_1 are the contact area and the structure size of the first level structure, respectively; a_1 is the position of the triple line at the first level structure, and $\overline{a}_1$ is the nondimensional value of a_1.

The contact area fraction of the second level structure is,

$$\overline{S}_2 = \overline{S}_1\int_{\overline{a}_2}^{\pi}(1+\overline{h}^2\sin^2\overline{x})^{1/2}d\overline{x} \Big/ \pi \tag{s5}$$

Defining $\overline{s}_1 = \int_{\overline{a}_1}^{\pi}(1+\overline{h}^2\sin^2\overline{x})^{1/2}d\overline{x} \Big/ \pi$, and $\overline{s}_2 = \int_{\overline{a}_2}^{\pi}(1+\overline{h}^2\sin^2\overline{x})^{1/2}d\overline{x} \Big/ \pi$, we have

$$\overline{S}_1 = \overline{s}_1,\ \overline{S}_2 = \overline{s}_1\overline{s}_2 \tag{s6}$$

Therefore, for the Nth level structure, equation (s6) can be generalized to be,

$$\overline{S}_N = \prod_{n=1}^{N}\overline{s}_n \tag{5}$$

where $\overline{s}_n = \phi(\overline{a}_n, \pi)$, $\phi(x_1, x_2) = \int_{x_1}^{x_2}(1+\overline{h}^2\sin^2\overline{x})^{1/2}d\overline{x} \Big/ \pi$, and $\overline{a}_n$ denotes the position of the triple line at the nth level structure.

For the derivation of equation 7:

We begin with the first-level structure from which we can then consider the higher-level structures level by level. Considering the N-level hierarchical structure as shown in Figure 1c, the apparent energy per unit area (unit length in the 2D model) of the first-level structure can be described by the Helmholtz free energy as,

$$\overline{F}_1^{CB} = F_1^{CB} / \lambda_1 = (\gamma_{LS,1}^{CB} - \gamma_{SA,1}) . \quad \text{(s7)}$$

Here, $\gamma_{LS,1}^{CB}$ is the apparent solid-liquid interface energy of a typical Cassie wetting state, consisting of interface energy of the solid-liquid interface, liquid-air interface, and solid-air interface as (see the lowest panel in Figure 1c),

$$\gamma_{LS,1}^{CB} = \gamma_{LS}\,\phi(\overline{a}_1, \pi) + \gamma_{LA}\,\psi(\overline{a}_1, \overline{r}_1) + \gamma_{SA}\,\phi(0, \overline{a}_1) \quad \text{(s8)}$$

where we define $\phi(x_1, x_2) = \int_{x_1}^{x_2} (1 + \overline{h}^2 \sin^2 \overline{x})^{1/2} d\overline{x} \Big/ \pi$, and $\psi(x_1, x_2) = x_2 \arcsin(x_1 / x_2)/\pi$. $\overline{a}_1$ denotes the position of the triple line at the first-level structure, and λ_1 denotes the size of the first-level structure; $\gamma_{SA,1}$ is the apparent solid-air interface energy,

$$\gamma_{SA,1} = \gamma_{SA}\,\phi(0, \pi) \quad \text{(s9)}$$

It is noted that $\gamma_{SA,1}$ is a constant which does not change with the wetting state. Substituting equation (s8) and (s9) into equation (s7), we have $\overline{F}_1^{CB} = \overline{F}_0^{CB}\,\phi(\overline{a}_1, \pi) + \gamma_{LA}\,\psi(\overline{a}_1, 1/\overline{P}_1)$, where $\overline{F}_0^{CB} = \gamma_{LS} - \gamma_{SA}$ and $\overline{P} = P/(k\gamma_{LA}) = 1/\overline{r}$. Generalizing this to the Nth level of hierarchy in a self-similar hierarchical surface, we obtain the recursive equation for the apparent surface energy of a hierarchical surface in Cassie state,

$$\gamma_{SA,N} = \gamma_{SA,N-1}\phi(0, \pi) \quad \text{(s10)}$$

$$\gamma_{LS,N} = \gamma_{SA,N-1}\phi(0, \overline{a}_N) + \gamma_{LS,N-1}\phi(\overline{a}_N, \pi) + \lambda_{LA}\psi(\overline{a}_N, 1/\overline{P}_N) \quad \text{(s11)}$$

The Helmholtz free energy for each level can be calculated from,

$$\overline{F}_N^{CB} = -\left(\gamma_{SA,N} - \gamma_{LS,N}\right) \tag{s12}$$

in combination with the recursive equation

$$\overline{F}_N^{CB} = \overline{F}_{N-1}^{CB}\,\phi\left(\overline{a}_N, \pi\right) + \gamma_{LA}\,\psi\left(\overline{a}_N, 1/\overline{P}_N\right) \tag{s13}$$

where $\overline{a}_N$ denotes the position of the triple line at the Nth level structure, and $\overline{P}_N$ denotes the normalized pressure of the Nth level structure.

In a similar manner, the Helmholtz free energy of the first level structure in Wenzel state is

$$\overline{F}_1^W = F_1^W / \lambda_1 = (\gamma_{LS}^W - \gamma_{SA,1}) \tag{s14}$$

where $\gamma_{LS}^W = \gamma_{LS}\,\phi(0,\pi)$ is the apparent solid-liquid interface energy of the Wenzel state. Therefore $\overline{F}_1^W = F_0^W\,\phi(0,\pi)$, where $\overline{F}_0^W = \gamma_{LS} - \gamma_{SA}$. Thus we have the recursive equation of Helmholtz free energy for the N-level hierarchical surface in the Wenzel state,

$$\overline{F}_N^W = \overline{F}_{N-1}^W\,\phi(0,\pi) \tag{s15}$$

The energy difference between the Cassie and Wenzel states of the surface with *N* levels of hierarchy can be obtained based on equations (s13) and (s15),

$$\Delta\overline{F}_N = \overline{F}_N^W - \overline{F}_N^{CB} \tag{7}$$

For the derivation of V' :

The Gibbs free energy of the system loaded by a pressure *P* is written as, $G = F - PV$, where $V = h\lambda - V'$ is the volume of liquid penetrating into the structure, and

$$V' = \frac{\lambda}{k\pi}\left[-\overline{h}\overline{a}\cos\overline{a} - \frac{1}{2\overline{P}^2}\arcsin(\overline{P}\overline{a}) + \frac{\overline{a}}{2\overline{P}}\left(1-\overline{P}^2\overline{a}^2\right)^{1/2} + \overline{h}\sin\overline{a}\right]. \tag{s16}$$

The free energy per unit area of the surface is $\overline{G} = G/\lambda = \overline{F} - \gamma_{LA}\overline{P}\overline{V}/2\pi$, where $\overline{V} = k^2 V$. Then, we can calculate the change of free energy as the liquid penetrates into the surface under fixed pressure.