Soft Matter

Supplementary Information

Title: Design of a robust superhydrophobic surface: thermodynamic and kinetic analysis.

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Supporting information A

A1. Determination of the free energy and APCA for a sagged state

The free surface energy for a sagged state (G_{Msag}^{unit}) is expressed in terms of the surface chemistry (θ_Y), interfacial tension (γ_{LA}), the LA interfacial area (A_{LA}^{unit}) and the SL interfacial area (A_{SL}^{unit}) (equations A1-A3). It is assumed that the LA interface is pinned to the center of the unit, thereby forming a square pyramid. The free surface energy can be reduced to a dimensionless form (G_{Msag}^{*}) (equation A4). The dimensionless free surface energy is expressed in terms of the APCA for the sagged state (θ_{Msag}) and the wetting parameter (j_{Msag}){Sarkar, 2013 #1314}.

$$G_{Msag}{}^{unit} = \gamma_{LA}(A_{LA}{}^{unit} - A_{SL}{}^{unit}\cos\theta_Y) \quad \text{A1)}$$

$$A_{LA}{}^{unit} = \frac{2(a+b)^2}{1+\cos\theta_{Msag}} + 2ab + b\sqrt{b^2+4c^2} \quad \text{A2)}$$

$$A_{SL}{}^{unit} = a^2 \quad \text{A3)}$$

$$G_{Msag}{}^{*} = \frac{G_{Msag}{}^{unit}}{\gamma_{LA}(a+b)^2} = \frac{2}{1+\cos\theta_{Msag}} + 1 + j_{Msag} \quad \text{A4)}$$

Where

$$j_{Msag} = -\left(\frac{a}{a+b}\right)^2(1+\cos\theta_Y) + \frac{b\sqrt{b^2+4c^2}-b^2}{(a+b)^2} \quad \text{A5)}$$

Upon minimization of surface energy minimization, the wetting parameter j_{Msag} can be directly correlated with θ_{Msag} (equation A6).

$$\frac{dj_{Msag}}{d\theta_{Msag}} = 0; 1 + \cos\theta_{Msag} + j_{Msag} = 0 \quad \text{A6)}$$

Using equations A5 and A6, an empirical relationship can be found for θ_{Msag} (equation A7).

$$\cos\theta_{Msag} = \left(\frac{a}{a+b}\right)^2(1+\cos\theta_Y) - 1 + \frac{b^2+b\sqrt{b^2+4c^2}}{(a+b)^2} \quad \text{A7)}$$

A2. Domain of surface parameters for a thermodynamically feasible sagged state

For a sagged state to be thermodynamically feasible, θ_{Msag} should assume geometrically realizable values (equation A8). Equation A8 comprises two inequalities and is consequently simplified (equations A9-A12).

$$-1 \leq \cos\theta_{Msag} \leq 1 \quad \text{A8)}$$

$$-1 \leq \left(\frac{a}{a+b}\right)^2 (1 + \cos\theta_Y) - 1 + \frac{b^2 - b\sqrt{b^2+4c^2}}{(a+b)^2} \leq 1 \quad \text{A9)}$$

$$0 \leq \frac{a^2(1+\cos\theta_Y) + b^2 - b\sqrt{b^2+4c^2}}{(a+b)^2} \leq 2 \quad \text{A10)}$$

$$0 \leq a^2(1 + \cos\theta_Y) + b^2 - b\sqrt{b^2 + 4c^2} \leq 2(a + b)^2 \quad \text{A11)}$$

$$b\sqrt{b^2 + 4c^2} \leq a^2(1 + \cos\theta_Y) + b^2 \leq 2(a + b)^2 + b\sqrt{b^2 + 4c^2} \quad \text{A12)}$$

Equation A12 is split into two inequalities (equations A13 and A14). Since the cosine of a function must be bounded by -1 and 1, both equations A13 and A14 must be correct.

$$a^2(1 + \cos\theta_Y) + b^2 \leq 2(a + b)^2 + b\sqrt{b^2 + 4c^2} \quad \text{A13)}$$

$$b\sqrt{b^2 + 4c^2} \leq a^2(1 + \cos\theta_Y) + b^2 \quad \text{A14)}$$

Equation A13 can be expressed as the sum of equations A15 and A16, which are individually true without any loss of generality. Hence, equation A13 is always correct.

$$a^2(1 + \cos\theta_Y) \leq 2a^2 \leq 2(a + b)^2 \quad \text{A15)}$$

$$b^2 \leq b\sqrt{b^2 + 4c^2} \quad \text{A16)}$$

Thus, the sagged state is feasible if and only if equation A14 is true. Equation A14 is squared and simplified to give the range of permissible spacing to width ratios (equations A17-A20). The spacing to width ratio is limited by a maximum value, here termed as sagged spacing to width ratio.

$$b^4 + 4b^2c^2 \leq b^4 + a^4(1 + \cos\theta_Y)^2 + 2b^2a^2(1 + \cos\theta_Y) \quad \text{A17)}$$

$$4b^2c^2 \leq a^4(1 + cos\,\theta_Y)^2 + 2b^2a^2(1 + cos\,\theta_Y) \qquad \text{A18)}$$

$$b^2(4c^2 - 2a^2(1 + cos\,\theta_Y)) \leq a^4(1 + cos\,\theta_Y)^2 \qquad \text{A19)}$$

$$\frac{b}{a} \leq (\frac{b}{a})_{sag} = \frac{(1+cos\,\theta_Y)}{\sqrt{4\frac{c^2}{a^2}-2(1+cos\,\theta_Y)}} \qquad \text{A20)}$$

However, the sagged limit must exceed the critical limit for $\theta_Y > 90°$. The difference between the sagged limit and the critical limit is plotted with respect to the height to width ratio (c/a) for multiple surface chemistries (figure A1). For $\theta_Y > 105°$, the critical limit exceeds the sagged limit, and hence a feasible sagged limit cannot exist for the corresponding surface chemistries.

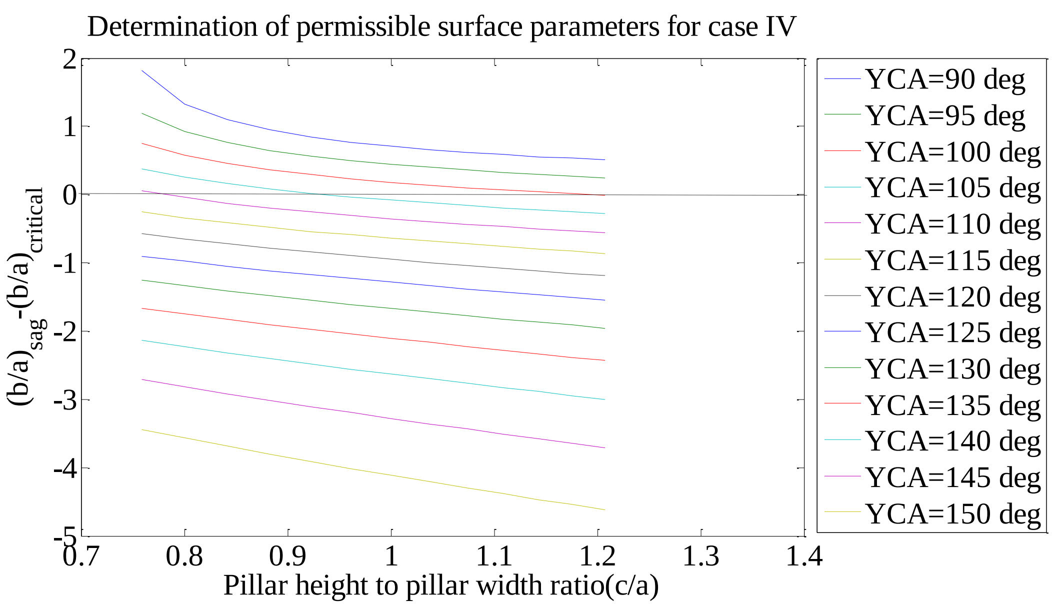

Figure A1 Variation of difference in sagged and critical limits with pillar height to width ratios

It is seen that the sagged limit assumes a real, positive value for a pillar height to width ratio greater than 0.7.The sagged limit exceeds the critical limit for $90° < \theta_Y < 105°$ (figure A2).

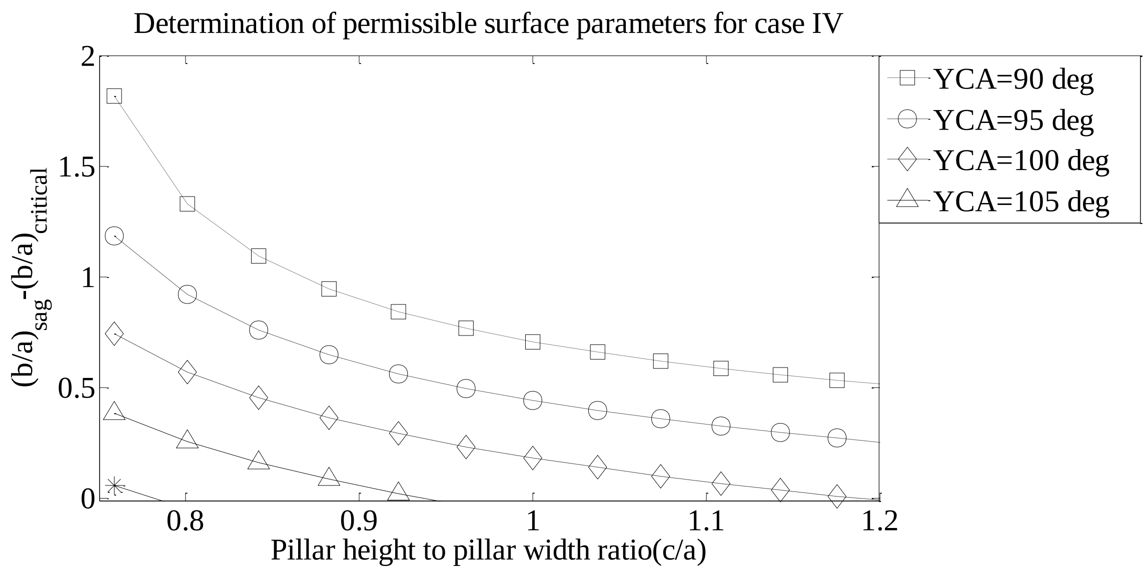

Figure A2 Domain of permissible height to width ratios and surface chemistry

Supporting information B: General equation of wettability for square pillar geometry

For a depinned state to exist, the APCA (θ_{Mdep}) should hold appropriate values for surfaces with $\theta_Y > 90°$ (equation B1). The APCA of a depinned state shares an implicit correlation with the penetration depth, and is given as the characteristic set of equations (Sarkar and Kietzig 2013) (equation B2).

$$\forall\theta_Y \geq 90°;\ 0° \leq \theta_{Mdep} \leq 180°; -1 \leq \cos\theta_{Mdep} \leq 1 \qquad \text{B1)}$$

$$\frac{4ahcos\theta_Y(1+cos\,\theta_{Mdep})}{(a+b)^2} + cos\,\theta_{CB}(1+\cos\theta_{Mdep}) - 2 + \varphi = 0 \qquad \text{B2)}$$

where $= (2+cos\,\theta_{CB})^{\frac{1}{3}}(1-cos\,\theta_{CB})^{\frac{2}{3}}\left(1-cos\,\theta_{Mdep}\right)^{\frac{1}{3}}\left(2+cos\,\theta_{Mdep}\right)^{\frac{2}{3}}$.

The aforementioned symbols are presented in Table 1. The expression φ is a non-linear function of θ_{Mdep} and θ_{CB}.

Table B1: Glossary of the symbols used

Symbol	**Description**
θ_Y	Young's contact angle (YCA)
a	Width of micrometer sized pillar
b	Spacing between consecutive pillars
h	Penetration depth of liquid in roughness valleys.
θ_{Mdep}	Apparent contact angle (APCA) corresponding to $h>0$
θ_{CB}	Cassie contact angle
Φ	Nonlinear function of θ_{CB} and θ_{Mdep}

To analyze the surface characteristics related to equation B2, it is extremely important to convert the fractional exponents of φ to linear formulations. To aid the simplification, the number B1 is rearranged as the product of 4 non-linear functions of $\cos\theta_{CB}$, such that two of the functions are reciprocals to each other (equation B3).

$$1 = (2 + \cos\theta_{CB})^{\frac{2}{3}}(2 + \cos\theta_{CB})^{-\frac{2}{3}}(1 - \cos\theta_{CB})^{\frac{1}{3}}(1 - \cos\theta_{CB})^{-\frac{1}{3}} \qquad \text{B3)}$$

The expression φ is multiplied with equation B3 (equation B4).

$$\varphi(1) = \varphi(2 + \cos\theta_{CB})^{\frac{2}{3}}(2 + \cos\theta_{CB})^{-\frac{2}{3}}(1 - \cos\theta_{CB})^{\frac{1}{3}}(1 - \cos\theta_{CB})^{-\frac{1}{3}} \qquad \text{B4)}$$

On simplification, φ is re-written as a product of two linear functions and two non-linear functions, where the nonlinear functions are expressed as ratios of $\cos\theta_{CB}$ (equation B5).

$$\varphi = (2 + \cos\theta_{CB})(1 - \cos\theta_{CB})\left(\frac{1-\cos\theta_{Mdep}}{1-\cos\theta_{CB}}\right)^{\frac{1}{3}}\left(\frac{2+\cos\theta_{Mdep}}{2+\cos\theta_{CB}}\right)^{\frac{2}{3}} \qquad \text{B5)}$$

Next, the part of the expression consisting of a nonlinear expression of $\cos\theta_{Mdep}$ must be linearized. The difference in the cosines of θ_{Mdep} and θ_{CB}, δ, plays an important role in the conversion of the nonlinear function to its linear counterpart (equation B6).

$$\delta = \cos\theta_{Mdep} - \cos\theta_{CB}\,;\ \therefore \cos\theta_{Mdep} = \delta + \cos\theta_{CB} \qquad \text{B6)}$$

The two nonlinear functions present in φ (equation B5) are individually simplified. The cosine of θ_{Mdep} is expressed in terms of δ, and

$$\left(\frac{1-\cos\theta_{Mdep}}{1-\cos\theta_{CB}}\right)^{\frac{1}{3}} = (1 - \frac{\delta}{1-\cos\theta_{CB}})^{\frac{1}{3}} \qquad \text{B7)}$$

$$\left(\frac{2+\cos\theta_{Mdep}}{2+\cos\theta_{CB}}\right)^{\frac{2}{3}} = (1 + \frac{\delta}{2+\cos\theta_{CB}})^{\frac{2}{3}} \qquad \text{B8)}$$

In the next steps, binomonal equation of fractional exponents is used to simplify and expand φ. The binomial expansion of an algebraic function with a coefficient s and a fractional exponent n is given as follows.

$$(1+s)^n = 1 + ns + \frac{n(n-1)}{2!}s^2 + \frac{n(n-1)(n-2)}{3!}s^3 + \frac{n(n-1)(n-2)(n-3)}{4!}s^4 \quad \text{B9)}$$

Using binomial expansion, equations B7 and B8 are simplified to the 3rd term (equations B10-B13).

$$(1-\frac{\delta}{1-\cos\theta_{CB}})^{\frac{1}{3}} = 1 + \frac{1}{3}\left(-\frac{\delta}{1-\cos\theta_{CB}}\right) + \frac{1}{3}(\frac{1}{3}-1)\frac{1}{2!}\left(-\frac{\delta}{1-\cos\theta_{CB}}\right)^2 \quad \text{B10)}$$

$$(1-\frac{\delta}{1-\cos\theta_{CB}})^{\frac{1}{3}} = 1 - \frac{\delta}{3(1-\cos\theta_{CB})} - \frac{\delta^2}{9(1-\cos\theta_{CB})^2} \quad \text{B11)}$$

$$(1+\frac{\delta}{2+\cos\theta_{CB}})^{\frac{2}{3}} = 1 + \frac{2}{3}\left(\frac{\delta}{2+\cos\theta_{CB}}\right) + \frac{2}{3}(\frac{2}{3}-1)\frac{1}{2!}\left(\frac{\delta}{2+\cos\theta_{CB}}\right)^2 \quad \text{B12)}$$

$$(1+\frac{\delta}{2+\cos\theta_{CB}})^{\frac{2}{3}} = 1 + \frac{2\delta}{3(2+\cos\theta_{CB})} - \frac{\delta^2}{9(2+\cos\theta_{CB})^2} \quad \text{B13)}$$

Upon simplification, equations B11 and B13 are multiplied. Since δ is the difference between two cosines, its absolute value is always less than unity. Hence, the coefficients of the higher exponents δ (δ^3 and δ^4) are neglected (equation B 14).

$$(1-\frac{\delta}{1-\cos\theta_{CB}})^{\frac{1}{3}}(1+\frac{\delta}{2+\cos\theta_{CB}})^{\frac{2}{3}} = 1 - \frac{\delta\cos\theta_{CB}}{(1-\cos\theta_{CB})(2+\cos\theta_{CB})} - \frac{\delta^2}{(1-\cos\theta_{CB})^2(2+\cos\theta_{CB})^2} \quad \text{B14)}$$

Equation 14 is substituted in equation B5 (equation B15).

$$\varphi = (2+\cos\theta_{CB})(1-\cos\theta_{CB})(1 - \frac{\delta\cos\theta_{CB}}{(1-\cos\theta_{CB})(2+\cos\theta_{CB})} - \frac{\delta^2}{(1-\cos\theta_{CB})^2(2+\cos\theta_{CB})^2}) \quad \text{B15)}$$

$$\varphi = (2+\cos\theta_{CB})(1-\cos\theta_{CB}) - \delta\cos\theta_{CB} - \frac{\delta^2}{(1-\cos\theta_{CB})(2+\cos\theta_{CB})} \quad \text{B16)}$$

The parameter δ is expressed in terms of θ_{CB} and θ_{Mdep} (equation B17).

$$\varphi = 2 - \cos\theta_{CB}(1 + \cos\theta_{Mdep}) - \frac{(\cos\theta_{Mdep} - \cos\theta_{CB})^2}{(1-\cos\theta_{CB})(2+\cos\theta_{CB})} \quad \text{B17)}$$

The simplified form of φ is substituted to equation B2 (equation B18).

$$\frac{4ahcos\theta_Y(1+\cos\theta_{Mdep})}{(a+b)^2} - \frac{(\cos\theta_{Mdep} - \cos\theta_{CB})^2}{(1-\cos\theta_{CB})(2+\cos\theta_{CB})} = 0 \quad \text{B18)}$$

Equation B18 is re-arranged to generate a quadratic expression of $\cos\theta_{Mdep}$ (equation B19).

$$\cos^2\theta_{Mdep} + \cos\theta_{Mdep}(-2\cos\theta_{CB} - \tau) + (\cos^2\theta_{CB} - \tau) = 0 \quad \text{B19)}$$

where $\tau = \frac{4ahcos\theta_Y(1-\cos\theta_{CB})(2+\cos\theta_{CB})}{(a+b)^2}$

Equation B19 marks the first instance, where the APCA for a depinned state θ_{Mdep} is expressed as a function of θ_Y, h, a, b. Thus, to have a realizable θ_{Mdep}, the discriminant of equation B19 (Δ) must be positive (necessary condition, equation B20). In addition, one root of equation B19 must possess a realizable value (sufficient condition, equation B1).

$$\Delta = (-2\cos\theta_{CB} - \tau)^2 - 4(\cos^2\theta_{CB} - \tau) = \tau(\tau + 4 + 4\cos\theta_{CB}) \quad \text{B20)}$$

<u>NECESSARY CONDITION: $\Delta > 0$</u>

The discriminant (Δ) is expressed as the product of two functions, namely τ and ($\tau+4+4\cos\theta_{CB}$). For $\Delta > 0$, both the functions must possess the identical sign. A case study is performed, where we analyze the ramifications when both the functions are positive (case i) or negative (case ii).

Case i: $\tau > 0$, and $(\tau + 4 + 4\cos\theta_{CB}) > 0$

Case ii: $\tau < 0$ and $(\tau + 4 + 4\cos\theta_{CB}) < 0$

The above mentioned cases are analyzed as follows.

<u>Case i</u>

The function τ is a product of several expressions.

$$\tau = \frac{4ahcos\theta_Y(1-cos\,\theta_{CB})(2+cos\,\theta_{CB})}{(a+b)^2} > 0 \qquad \text{B21)}$$

The terms a, $(a+b)^2$, h, $(2+cos\ \theta_{CB})$ and $(1\text{-}cos\ \theta_{CB})$ are each positive. Thus, the expression is true when $cos\ \theta_Y>0$.

$$cos\theta_Y > 0; 0° < \theta_Y < 90° \qquad \text{B22)}$$

The domain of case i is mutually exclusive to that in the current discussion (θ_Y>90°, equation B 1). Since case i falls beyond the scope of this discussion, it is not analyzed any further.

Case ii

For case ii to be true, each of the expressions τ and (τ+4+4cosθ_{CB}) ought to be negative. From the analysis of case i, it can be inferred that θ_Y >90° (which is compatible with the domain of θ_Y in discussion) is associated with τ<0. Thus, the sufficient condition can be determined by pinpointing the surface characteristics with $\tau+4+4\cos\theta_{CB} < 0$ (equation B23).

$$\frac{4ahcos\theta_Y(1-cos\,\theta_{CB})(2+cos\,\theta_{CB})}{(a+b)^2} + 4 + 4\,cos\,\theta_{CB} < 0 \qquad \text{B23)}$$

Equation B23 is simplified to render the surface characteristics for case ii, and hence, the phenomenon of a depinned state for a surface with θ_Y >90°.Since cos θ_Y <0, $|cos\,\theta_Y| = -\,cos\,\theta_Y$. Equation B23 is re-arranged to give a minimum permissible value for penetration depth h (equation B25).

$$\frac{4ah|cos\,\theta_Y|(1-cos\,\theta_{CB})(2+cos\,\theta_{CB})}{(a+b)^2} > 4 + 4\,cos\,\theta_{CB} \qquad \text{B24)}$$

$$h > \frac{(a+b)^2}{a}\frac{(1+cos\,\theta_{CB})}{(1-cos\,\theta_{CB})(2+cos\,\theta_{CB})|cos\,\theta_Y|} \qquad \text{B25)}$$

Thus, to have Δ >0, the penetration depth has a minimum value determined by a, b, θ_Y. It is seen that h typically assumes values of the order of mm, much higher than the μm sized pillar height *c*. This clearly shows that in general, it is not feasible to have a penetration with θ_Y>90°. In the following section, the sufficient condition to have a mathematically deductible θ_M is described.

Sufficient condition to have a θ_{Mdep} with θ_Y>90°

Since the general equation of wettability has been simplified to a quadratic equation of cos θ_M (equation B19), feasible results can be obtained when -1< cos θ_{Mdep} <1. The sufficient condition is analyzed for the case θ_Y>90°. The simplified form of the general equation of wettability is expressed in the form of a quadratic equation (equation B26).

$$cos^2 \theta_{Mdep} + \beta \, cos \, \theta_{Mdep} + \chi = 0 \qquad \text{B26)}$$

Where $\beta = -\tau - 2 \, cos \, \theta_{CB}$; $\chi = -\tau + cos^2 \theta_{CB}$

So, to have a valid θ_{Mdep}, -1< cos θ_{Mdep} <1

The root corresponding to $cos \, \theta_{Mdep} = \frac{-\beta - \sqrt{\beta^2 - 4\chi}}{2}$ is ignored as it renders values less than -1, the minimum possible value of cos θ_{Mdep}. The other root, namely $cos \, \theta_{Mdep} = \frac{-\beta + \sqrt{\beta^2 - 4\chi}}{2}$ is considered, and substituted to equation B1 (equation B27).

$$-1 \leq cos \, \theta_{Mdep} = \frac{-\beta + \sqrt{\beta^2 - 4\chi}}{2} \leq 1 \qquad \text{B27)}$$

On simplification, equation B27 gives rise to an inequality (equation B28). Now, both the inherent inequalities comprising equation B28 must be correct.

$$\beta - 2 \leq \sqrt{\beta^2 - 4\chi} \leq \beta + 2 \qquad \text{B28)}$$

To further analyze the result, the inequality must be squared. It should be noted that the inequality, on being squared, may not necessarily retain its sign. The modulus of each term must be squared and compared. To demonstrate this, a corollary is presented as follows.

Corollary

On squaring the inequality $-4 < 2 < 5$ without changing signs, a wrong result is obtained, i.e. $16 < 4 < 25$. The squared inequality is not correct, since 16 > 4. The domain of β plays a very crucial role in further analysis.

$$\forall\theta_Y > 90°; \because \tau < 0;\ \beta > 0; \therefore |\beta + 2| > |\beta - 2| \qquad \text{B29)}$$

For θ_Y>90°, the inequality can be simply squared without changing signs.

$$\forall\theta_Y > 90°; \because \tau < 0;\ \beta > 0; \therefore |\beta + 2| > |\beta - 2| \qquad \text{B30)}$$

$$|\beta - 2| \leq \sqrt{\beta^2 - 4\chi} \leq |\beta + 2| \qquad \text{B31)}$$

$$(\beta - 2)^2 \leq \beta^2 - 4\chi \leq (\beta + 2)^2 \qquad \text{B32)}$$

Inequality B32 is simplified to generate inequality B33.

$$-1 - \beta \leq \chi \leq \beta - 1 \qquad \text{B33)}$$

Substituting $\beta = -\tau - 2\cos\theta_{CB}$; $\chi = -\tau + \cos^2\theta_{CB}$, inequality B33 is simplified in the following steps to render inequality B36.

$$-1 + \tau + 2\cos\theta_{CB} \leq -\tau + \cos^2\theta_{CB} \leq -\tau - 2\cos\theta_{CB} - 1 \qquad \text{B34)}$$

$$-1 + 2\tau + 2\cos\theta_{CB} - \cos^2\theta_{CB} \leq 0 \leq -2\cos\theta_{CB} - 1 - \cos^2\theta_{CB} \qquad \text{B35)}$$

$$2\tau - (1 - \cos\theta_{CB})^2 \leq 0 \leq -(1 + \cos\theta_{CB})^2 \qquad \text{B36)}$$

The above inequality suggests that $0 \leq -(1 + \cos\theta_{CB})^2$, which is absurd. Hence, it can be inferred that no sufficient condition exists for a depinned state with θ_Y>90°. Since neither the necessary condition, nor the sufficient condition render mathematically plausible surface characteristics, it is found that surface energy minimization cannot solely account for a depinned state for surfaces with θ_Y>90°.

Supporting information C: Proof of the existence of a intermediate wetting state

The evolution of the apparent contact angle with increasing pillar spacing to pillar width ratios follows a unique trend for surfaces with $\theta_Y > 90°${He, 2003 #127;Zhu, 2006 #1313;Zhang, 2007 #1312;Barbieri, 2007 #1310;Varanasi, 2009 #893}. In the following figure, the APCA is plotted against spacing to width ratio for square pillar geometry with pillar width of 25 μm and Young's contact angle (θ_Y) of 114° {He, 2003 #127}. Cassie and Wenzel equations are also plotted for the same series of surfaces (Figure C1).

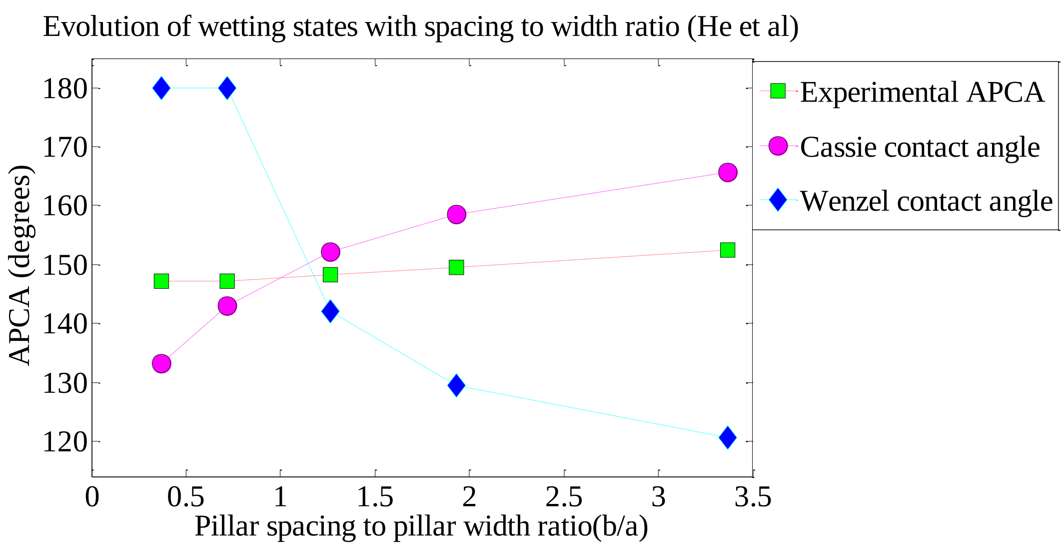

Figure C1 Variation of APCA with spacing to width ratio

There exists a unique spacing to width ratio, also known as critical spacing to width ratio (*b/*a=1.15) for a given surface chemistry for which the calculated Cassie and Wenzel contact angles are equal. For b/a ratios greater than the critical b/a ratio, the Wenzel state becomes energetically favorable to the Cassie state, and the static contact angle assumes values in between those predicted by Cassie and Wenzel models. Here, for b/a ratios between 1.15 and 3.0, the APCA is closer to the Cassie contact angle. Light transmission experiments revealed the existence of the liquid-air interface under the apex of the surface roughness for b/a ratios exceeding 1.15. {He, 2003 #127;Varanasi, 2009 #893}. For very high b/a ratios (> 3), the static contact angle measurements follow the Wenzel model. Erbil et al. have investigated the existing static contact angle measurements for a set of surfaces with square pillar topologies, distinct chemistries, and increasing spacing to width ratios {Erbil, 2009 #1209;Zhang, 2007 #1312;Zhu, 2006 #1313}. To understand the wetting states of the aforementioned set of data, the collected APCAs from the above experiments were listed. Assuming the wetting states were either Cassie (equation C1) or Wenzel, and with the knowledge of the YCA of the surfaces used (θ_Y), the experimentally determined APCAs (θ_{exp}) were substituted into the Cassie equation (equation C 2). The solid fraction $f_{exp,Erbil}$, as obtained from the substitution was expressed in terms of θ_{exp} and θ_Y (equation C3), and compared to the solid fraction as defined by the surface geometry (f).

$$\cos\theta_{CB} = f\cos\theta_Y + f - 1 \qquad \text{C1)}$$

$$\cos\theta_{exp} = f_{exp,Erbil}\cos\theta_Y + f_{exp,Erbil} - 1 \qquad \text{C2)}$$

$$f_{exp,Erbil} = \frac{(1+\cos\theta_{exp})}{(1+cos\,\theta_Y)} \qquad \text{C3)}$$

The change in solid fraction, measured as $\Delta f_{exp,Erbil}$ (equation C4), is tabulated (table C1).

$$\Delta f_{exp,Erbil} = f - f_{exp,Erbil} = \frac{(\cos\theta_{CB} - cos\,\theta_{exp})}{(1+cos\,\theta_Y)} \qquad \text{C4)}$$

A negative change, i.e. $\Delta f_{exp,Erbil} < 0$ denotes penetration of water in the roughness valleys. It has been seen that for the 31 surfaces investigated, only 6 surfaces exhibit a negative change. For the remaining 25 cases, a positive change is recorded. This means that the liquid does not completely wet the apex of the roughness features, which is absurd. The error in the determination of solid fraction arises from overestimation of the contribution of the liquid-air fraction in equation 1 {Milne, 2012 #1315}. We postulate that the area occupied by the liquid-air interface (liquid-air fraction) is independent of the degree of liquid penetration inside the roughness valleys (solid fraction). Equation C2 is corrected (equation C5), and the corrected solid fraction $f_{exp,corrected}$, is determined (equation C6).

$$\cos\theta_{exp} = f_{exp,corrected}\cos\theta_Y + f - 1 \qquad \text{C5)}$$

The change in solid fraction ($\Delta f_{exp,corrected}$) is calculated (equations C6 and C7) and listed for the set of 31 surfaces (table C1).

$$f_{exp,corrected} = \frac{(\cos\theta_{exp}+1-f)}{\cos\theta_Y} \quad \text{C6)}$$

$$\Delta f_{exp,corrected} = f - f_{exp,corrected} = \frac{(\cos\theta_{CB}-\cos\theta_{exp})}{\cos\theta_Y} \quad \text{C7)}$$

Only 6 of the 31 surfaces show a positive change in solid fraction (highlighted in grey). The remaining 25 surfaces exhibit a negative change in solid fraction, thereby indicating a penetration in the roughness valleys. Thus, it is safe to infer that the intermediate state exists for surfaces with $\theta_Y > 90°$.

Table C1 Evidence of an intermediate state: penetration observed for 25 of 28 surfaces.

	Surface	θ_Y **(°)**	***F***	$\Delta f_{CB,Erbil}$	$\Delta f_{CB,corrected}$
{Zhang, 2007 #1312}	1.	107	0.24	0.05	-0.12
	2.		0.29	0.07	-0.17
	3.		0.41	0.17	-0.41
	4.		0.45	0.22	-0.53
	5.		0.50	0.27	-0.65
	6.		0.59	0.33	-0.80
	7.		0.77	0.49	-1.18
	8.		0.97	0.04	-0.10
	9.		0.14	-0.06	0.15
	10.		0.29	0.09	-0.21
	11.		0.40	0.18	-0.43
	12.		0.45	0.20	-0.49
	13.		0.47	0.22	-0.53
	14.		0.60	0.34	-0.82
	15.		0.70	0.41	-0.99
	16.		0.94	0.12	-0.29
	17.		0.97	-0.03	0.07
{Zhu, 2006 #1313}	18.	111	0.21	0.03	-0.05
	19.		0.32	0.15	-0.27
	20.		0.38	0.15	-0.26
	21.		0.44	0.17	-0.30
	22.		0.47	0.25	-0.46
	23.		0.72	0.38	-0.68
	24.		0.39	0.14	-0.26
	25.		0.33	0.09	-0.16
	26.		0.29	0.05	-0.10
	27.		0.21	0.03	-0.05
	28.		0.14	-0.02	0.04

Supporting information D: Determination of quasi-static limit for robustness

The antiwetting pressure must be higher than 117.23 Pa for a quasi-statically robust surface. Equation 17 of the main text (shown here as equation D1) is solved, where all the parameters constituting the antiwetting pressure are converted to their respective SI units. The pillar width and spacing, originally expressed in µm are converted to m. The expression is simplified (equations D1- D6) to generate the quasi-static limit of spacing to width ratios.

$$P_{antiwetting} = -\frac{4\,\gamma_{LA} a \cos\theta_Y}{b(2a+b)} = \frac{4\,\gamma_{LA} a|\cos\theta_Y|}{b(2a+b)} \qquad 17.$$

$$\frac{4\times 0.072\times a|\cos\theta_Y|\,10^{-6}}{b(2a+b)\,10^{-12}} > 117.23\,Nm^{-2} \qquad D1)$$

$$\frac{a|\cos\theta_Y|}{b(2a+b)}\,10^{6} > 407.06\,Nm^{-2} \qquad D2)$$

$$\frac{|\cos\theta_Y|}{a}\frac{10^{6}}{(1+\frac{b}{a})^2-1} > 407.06\,Nm^{-2} \qquad D3)$$

$$(1+\frac{b}{a})^2 - 1 \leq \frac{10^6|\cos\theta_Y|}{407.06a} \qquad D4)$$

$$\frac{b}{a} \leq \sqrt{1+\frac{2456.64|\cos\theta_Y|}{a}} - 1 \qquad D5)$$

$$\frac{b}{a} \leq (\frac{b}{a})_{QS} = \sqrt{1-\frac{2456.64\cos\theta_Y}{a}} - 1 \qquad D6)$$

In order to have a quasi-static limit, the quasi-static spacing to width ratio must exceed its critical counterpart (equation D7). Expressions for both the limits are substituted, and the inequality is simplified to determine the domain of a, b and θ_Y (equations D7- D14). A unique relationship is established between the height to width ratio and the surface chemistry (equation D15).

$$(\frac{b}{a})_{critical} \leq (\frac{b}{a})_{QS} \qquad D7)$$

$$\sqrt{1-\frac{4c\cos\theta_Y}{a(1+\cos\theta_Y)}} - 1 \leq \sqrt{1-\frac{2456.64\cos\theta_Y}{a}} - 1 \qquad D8)$$

$$\sqrt{1+\frac{4c|\cos\theta_Y|}{a(1-|\cos\theta_Y|)}} - 1 \leq \sqrt{1+\frac{2456.64|\cos\theta_Y|}{a}} - 1 \qquad D9)$$

$$\frac{4c|cos\,\theta_Y|}{a(1-|cos\,\theta_Y|)} \leq \frac{2456.64|cos\,\theta_Y|}{a} \qquad \text{D10)}$$

$$\frac{c}{(1-|cos\,\theta_Y|)} \leq 614.16 \qquad \text{D11)}$$

$$1-|cos\,\theta_Y| \geq \frac{c}{614.16} \qquad \text{D12)}$$

$$1+cos\,\theta_Y \geq \frac{c}{614.16} \qquad \text{D13)}$$

$$cos\,\theta_Y \geq \frac{c}{614.16}-1 \qquad \text{D14)}$$

$$\theta_Y \leq \cos^{-1}(\frac{c}{614.16}-1) \qquad \text{D15)}$$