

The Superhydrophobic State Is Metastable, Not Stable

- One surface holds two contact angles: at $r = 2.0$ and $f = 0.30$ they are **133.1602** and **143.3797** degrees
- The Young angle at which the two balance is **114.3157** degrees, and the actual **110** does not reach it — The state that repels better is the one losing thermodynamically — [Paper 376]

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September 2026

— *From thinking to syncing.* —

Abstract

A superhydrophobic surface is described as one that repels water. This paper asks whether that state is stable—the answer is that under some conditions it is metastable, not stable. No new mathematical theorem and no new law is claimed. First, one rough surface holds two states, Wenzel and Cassie (Section 2). Second, at $r = 2.0$ and $f = 0.30$ the contact angles split into **133.1602** and **143.3797** degrees (Section 2). Third, this is the core of the paper. The Young angle at which the two balance is **114.3157** degrees, and the actual **110** does not reach it (Section 3). Fourth, so under these conditions the repelling Cassie state is the one losing thermodynamically (Section 3). Fifth, lowering the contact fraction raises the boundary; stabilising it takes a roughness of **2.3467** or more (Section 4). Sixth, the separator is which state has the lower energy, not the size of the contact angle (Section 5).

Scope of this paper (scope note): No new mathematical theorem and no new law is claimed—Young’s equation, Wenzel’s equation, and the Cassie–Baxter equation are all standard. We do not build interface science—the height of the barrier between states and its kinetics are not entered. They are named and no more. We perform no experiment—no measurement on a real surface is made. A Young angle of 110 degrees is a stated assumption. Contact-angle hysteresis is not treated—the difference between advancing and receding angles is not the subject. Only equilibrium contact angles are computed. We design no materials—no guidance on what structure to build is given. Dynamics are not treated—state transitions from droplet impact or evaporation are not the subject. Relation to earlier papers: Paper 363 showed a bat to have three sweet spots—there one word named several things; here one surface holds two states. Paper 365 showed a standard explanation failing on geometry—there too a prediction was overturned by checking the condition numerically. Paper 300 showed whether two things share a root is decidable—by that test, “it repels” and “that state is stable” have distinct roots. Paper 373 showed the initial condition setting the amplitude—here which state the droplet was placed in settles the outcome. What is added is setting the two contact angles side by side at five roughnesses, solving backwards for the boundary Young angle 114.3157 degrees, showing that the actual Young angle does not reach it, solving backwards for the roughness 2.3467 that stabilises it and confirming the formula closes, and putting the separator on which energy is lower.

1. Notation and the Question

Setting: Take a Young angle of $\theta_Y = 110$ degrees on the smooth solid and write the two states with roughness r and contact fraction f .

$$\cos \theta_W = r \cos \theta_Y, \quad \cos \theta_C = f \cos \theta_Y + f - 1$$

r is the true area over the apparent area and f the fraction of area in contact with the liquid.

Observation 1.1

In the Wenzel state the liquid fills the grooves. The contact area is r times larger—on a hydrophobic solid, roughness makes it more hydrophobic.

Observation 1.2

In the Cassie state the liquid bridges the grooves. Air remains beneath—only the fraction f is in contact.

Observation 1.3

The two live on the same surface. Which one occurs is not decided by the surface——this paper gives, as numbers, which has the lower energy.

Question: Is the superhydrophobic state stable?

2. One Surface, Two Contact Angles

Calculation 2.1: The two contact angles against roughness and contact fraction (computed in this paper, $\theta_Y = 110$ degrees).

r / f	Wenzel angle [deg]	Cassie angle [deg]	Difference
1.0 / 1.00	110.0000	110.0000	+0.0000
1.5 / 0.50	120.8659	132.1451	+11.2792
2.0 / 0.30	133.1602	143.3797	+10.2195
3.0 / 0.10	(no solution)	159.0996	—
4.0 / 0.05	(no solution)	165.2624	—

Observation 2.2

At $r = 1$ and $f = 1$ both return the Young angle. Both 110.0000 degrees——a check that the formulae close.

Observation 2.3

Wenzel's equation breaks down beyond $r = 3$. $|r \cos \theta_Y|$ exceeds 1——outside the range of the cosine, so no Wenzel state exists. That is what “no solution” marks.

Observation 2.4

The Cassie angle rises to 165.2624 degrees. At $f = 0.05$ —beyond the 150 degrees taken as the mark of superhydrophobicity.

Observation 2.5

At one roughness the two angles differ by over 10 degrees. 133.1602 against 143.3797 at $r = 2.0$, $f = 0.30$ —one cannot write “this surface’s contact angle” without saying which state was measured.

3. The Balancing Young Angle Is 114.3157 Degrees

Calculation 3.1: Solving for the Young angle at which the two energies are equal (computed in this paper, $r = 2.0$, $f = 0.30$).

Quantity	Value
$\cos \theta_{\text{crit}} = (f - 1)/(r - f)$	−0.411765
Boundary Young angle	114.3157 deg
Actual Young angle	110.0 deg
Thermodynamically stable	Wenzel

Observation 3.2

This is the core of the paper. The actual 110 degrees does not reach the boundary 114.3157—so here the Cassie state is metastable, not stable.

Observation 3.3

And still the Cassie angle is the larger. 143.3797 against 133.1602 degrees—the state that repels better is the one losing thermodynamically.

Observation 3.4

The two are easily confused. “It repels well” and “that state persists” are different things——distinct roots by the criterion of Paper 300: the first is settled by a contact-angle formula, the second by comparing energies.

Observation 3.5

And a metastable state collapses on a trigger. A droplet falls, is pressed, or shrinks by evaporation——once it drops into the Wenzel state it does not come back.

Observation 3.6

That is the shape in which superhydrophobic surfaces wet with use. This paper has not computed the kinetics of the transition——what is shown is only that its direction was settled from the start.

4. Stabilising It Means Raising the Roughness

Calculation 4.1: The roughness needed to stabilise Cassie at $f = 0.30$ (computed in this paper).

Quantity	Value
Required roughness $r = f + (f - 1) / \cos \theta_Y$	2.3467 or more
Boundary Young angle at that r	110.0000000000 deg (check)
Present r	2.0

Observation 4.2

The formula closes. Putting $r = 2.3467$ back gives a boundary of 110.0000000000 degrees——not an arithmetic error.

Observation 4.3

The direction needs care. Lowering the contact fraction f raises the boundary—in the limit $f = 0$ it becomes 120 degrees, still further from 110.

Observation 4.4

So “make it finer” is the wrong way. Fewer contact points raise the Cassie angle and lower the stability—the strength of repulsion and the stability of the state move in opposite directions.

Observation 4.5

The right way is to raise the roughness. From $r = 2.0$ to 2.3467 at the same f —deeper grooves. That real superhydrophobic surfaces are hierarchical answers this requirement.

Observation 4.6

To be stated honestly—this paper has not computed hierarchical structures. A model with r and f set independently was used—in a real structure the two are coupled.

5. The Separator: Which Energy Is Lower?

Observation 5.1

The separator—which of the two states has the lower energy; not the size of the contact angle.

Condition	Cassie angle	Stable state	Cassie is
$\theta_Y = 110, r = 2.0, f = 0.30$	143.3797 deg	Wenzel	metastable
$\theta_Y = 110, r = 2.3467, f = 0.30$	the same	exactly balanced	on the boundary
$\theta_Y = 120, r = 2.0, f = 0.30$	larger	Cassie	stable

Observation 5.2

The first row does not have the largest Cassie angle and is the least stable. Looking at the contact angle says nothing about stability——what to look at is the distance from the boundary.

Observation 5.3

The separator can be moved. Raise the Young angle (a more hydrophobic material) or raise the roughness——either crosses the boundary. Lowering f works against it.

Observation 5.4

The Young angle has a ceiling. Few smooth solids go far beyond 120 degrees——so the margin has to come from roughness. This paper has not computed that ceiling.

Observation 5.5

To be stated honestly——114.3157 degrees and 2.3467 are values under stated conditions: $\theta_Y = 110$ degrees and $f = 0.30$. Another material gives other numbers——what does not move is the structure: repellence and stability are fixed by different formulae.

Observation 5.6

One last thing——working well does not mean the state will be kept. An excellent 143.3797 degrees of repellence occurring in a state that is losing thermodynamically——when the formula for performance and the formula for persistence are different, looking only at performance misses the lifetime.

6. The Census and the Close

1. Both give 110.0000 at $r = 1$, $f = 1$ (Observation 2.2): the formulae close.
2. 133.1602 and 143.3797 at $r = 2.0$, $f = 0.30$ (Calculation 2.1): a gap of 10.2195.
3. Wenzel breaks down beyond $r = 3$ (Observation 2.3): outside the cosine's range.

4. Cassie reaches **165.2624** at $f = 0.05$ (Calculation 2.1): **past 150 degrees**.
5. The boundary is **114.3157** degrees (Calculation 3.1): **110 does not reach it**.
6. Wenzel is the stable state (Calculation 3.1): **Cassie is metastable**.
7. The better repeller is losing (Observation 3.3): **143.3797** against **133.1602**.
8. Stabilising takes $r \geq 2.3467$ (Calculation 4.1): **back-substitution gives 110.0000000000**.
9. Lowering f raises the boundary (Observation 4.3): **the opposite direction**.
10. Repellence and stability move oppositely (Observation 4.4): **they cannot be had together**.

Closing: A superhydrophobic surface is described as one that repels water—but the state doing the repelling is not necessarily stable. One rough surface holds two states—Wenzel, with the liquid filling the grooves, and Cassie, with it bridging them over trapped air. At $r = 2.0$ and $f = 0.30$ the contact angles split into **133.1602** and **143.3797** degrees, 10.2195 apart. One cannot write “this surface’s contact angle” without saying which state was measured. And the Young angle at which the two balance is **114.3157** degrees—the actual 110 does not reach it. So here the Cassie state is metastable, not stable, and the thermodynamic winner is Wenzel. And still the Cassie angle is the larger (143.3797 against 133.1602) — the state that repels better is the one losing. A metastable state collapses on a trigger—a droplet falls, is pressed, or shrinks by evaporation, and once it drops into the Wenzel state it does not come back. That is the shape in which superhydrophobic surfaces wet with use. This paper has not computed the kinetics, and shows only that the direction was settled from the start. Stabilising it needs care about direction—lowering the contact fraction raises the Cassie angle but also raises the boundary (to 120 degrees in the limit $f = 0$), so “make it finer” is the wrong way: repellence and stability move oppositely. The right way is more roughness — at $f = 0.30$, $r \geq 2.3467$ (back-substitution gives a boundary of 110.0000000000 degrees). That real superhydrophobic surfaces are hierarchical answers this requirement. One thing separates them—which of the two states has the lower energy; not the size of the contact angle. Looking at the contact angle says nothing about stability; what to look at is the distance from the boundary. Either a higher Young angle or more roughness crosses it, but few smooth solids go far beyond 120 degrees, so the margin has to come from roughness. To be said honestly —this paper used a model with r and f set independently, while in a real structure the two are coupled. The 114.3157 degrees and 2.3467 hold for $\theta_Y = 110$ degrees and $f = 0.30$. One last thing—working well does not mean the state will be kept. An excellent 143.3797 degrees of repellence is occurring in a state that is losing thermodynamically. When the formula for performance and the formula for persistence are different, looking only at performance misses the lifetime.

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