Supplementary information

Sample preparation
Superhydrophobic silica surfaces (contact angles of water ≥ 170° see Fig. S1) were prepared on spherical interfacial-force-microscopy tips and flat single crystal Si substrates using a variation of the low temperature/pressure aerogel thin film process developed in our lab¹ where a quarter of the tetraethylorthosilicate (TEOS) was replaced with 3,3,3 trifluoropropyltrimethoxysilane, and the as-deposited films were exposed to hexamethyldisilizane vapour at 50°C. Superhydrophobic surfaces were deposited by dipping (tips) or spin-coating (silicon substrates).

Interfacial force microscopy
Interfacial force microscopy experiments were conducted in standard low conductivity (18.2 megaohms) de-ionized (DI) water and deaerated DI water (prepared by repeated freezing/pump/thaw cycles) with similar results. Advancing and retracting tip speeds were 100 nm/sec and 6 µm/sec respectively. We could not measure directly the contact
angle of water on the 150-µm tip, so we qualified the tips by doing ‘water denting’ experiments (Fig. S2, left) and ensuring that the associated force (Fig. S2, right) was purely repulsive with no measurable attractive force upon contact with the water surface. Video images were acquired using a CCD camera. Figure S3 shows a series of images where we observe out of contact cavitation occurring over a distance of ~3.0-µm.

![Figure S2](image1.png)

**Figure S2.** Water denting with the interfacial-force-microscopy probe (left) and force versus displacement plot corresponding to the approach of the superhydrophobic tip to the surface of water. The force is purely repulsive (positive) with no measurable attractive force upon contact.

![Fig. S3](image2.png)

**Fig. S3.** Movie frames showing out of contact cavitation at a distance of ~3 micrometres a) one frame prior to b, b) frame showing cavitation c) extended vapour cavity visible during withdrawal. Bottom semicircular shape is a reflection of the spherical superhydrophobic tip from the underlying flat superhydrophobic surface.

**Confocal Fluorescence Imaging**

Confocal fluorescence imaging was used to look for the presence of vapour bubbles at the superhydrophobic–water interface (see Fig. S4). It has been argued that these ‘nanobubbles’ are a source of long range hydrophobic interactions\(^2\), and therefore, the growth and coalescence of pre-existing bubbles could conceivably be an explanation of the long range out of contact cavitation we observe. To perform these experiments the
superhydrophobic film was fluorescently labelled with the water-insoluble green fluorescent dye fluorescein (Molecular Probes), and submerged in water containing the water-soluble red fluorescent dye rhodamine B (Kodak) (see Movies 1 and 2). Starting in the superhydrophobic film (green) optical sections taken at successively shallower focal planes show the progressive development of a patchwork of red regions corresponding to water and emphasizing the rough three-dimensional nature of the superhydrophobic–water interface. Whereas within the green regions we see heterogeneous black textural features (that eventually become infiltrated with red) indicative of the fractal, nanoscale porosity of the superhydrophobic surface, within the red (water) regions there is no evidence of vapor bubbles (which would appear as black (presumably circular) shapes) on length scales larger than 200 nm, which is the approximate resolution level of this technique. As the size of the pre-existing bubbles is argued to be the length scale over which long range hydrophobic interactions are observed, the absence of any 0.5-3.0-µm bubbles argues against their coalescence as being responsible for long range out of contact cavitation between submerged superhydrophobic surfaces. Rather cavitation is a consequence of the phase behavior of confined water, where spontaneous cavitation/drying is expected for separations below a critical dimension. For smooth hydrophobic surfaces this critical dimension has been modeled to be of the order of 100 nm.

Fig. S4. Left, final frame from laser scanning confocal microscopy Movie 1 and right, final frame from Movie 2. Green corresponds to the nanoporous superhydrophobic film and red to water. There is no evidence of pre-existing nanobubbles, which would appear as black features within the red (water) background. Addition of dyes causes only very minor changes in the wetting characteristics.
Thermodynamics of cavity formation

The critical distance below which cavitation is thermodynamically feasible can be estimated from equating the grand potentials of the liquid and vapor configurations. This naturally leads to an expression that is known as Laplace's equation:

\[ D = \frac{-2\gamma \cos \theta}{\Delta p} \]  

(1)

which expresses mechanical equilibrium across a curved interface. At ambient conditions, 25 °C and atmospheric pressure (about 0.89 x 10^5 Pa in Albuquerque, New Mexico, USA) the pressure difference \( \Delta p = p_l - p_v = 0.9 \times 10^5 \) Pa and the air water interfacial tension, \( \gamma \), is about 0.072 N/m. Thus, for a contact angle of 170° we find that \( D = 1.4 \) µm. This must be considered a lower bound, as the cavity is assumed initially to be free of air and thus to contain only water vapour.

\( D \) will grow if the atmospheric pressure is reduced, by reducing the amount of air in the system. If all the air is removed, and the equilibrium considered is that between pure water and pure vapour, equation (1) is often expressed (see refs 3,6) in terms of the chemical potential difference, \( \Delta \mu = \mu_l - \mu_{\text{sat}} \), between the chemical potential of the liquid phase and the bulk saturation value.

\[ D = \frac{-2\gamma \cos \theta}{(\rho_l - \rho_v)\Delta \mu} = \frac{-2\gamma \cos \theta}{(\rho_l - \rho_v)mgh} \]  

(2)

The second form arises when we consider the variation of the chemical potential with distance, \( h \), from the planar liquid–vapour interface in a gravitational field of acceleration \( g \). Here \( m \) is the mass, and \( \rho \) denotes the number density. From equation (2) we see that in a pure water system, \( D = 1.45 \) mm when \( h = 1 \) cm.

The same observations regarding the role of the air on the value of \( D \) and similar estimates have been made elsewhere.