Long-range hydrophobic interactions operating under water are important in the mediation of many natural and synthetic phenomena, such as protein folding, adhesion and colloid stability. Here we show that rough hydrophobic surfaces can experience attractive forces over distances more than 30 times greater than any reported previously, owing to the spontaneous evaporation of the intervening, confined water. Our finding highlights the importance of surface roughness in the interaction of extended structures in water, which has so far been largely overlooked.

The existence of long-range hydrophobic interactions has been debated for more than 25 years, because their reported range of 1–100 nanometres exceeds that of van der Waals forces and cannot be explained by water restructuring. However, investigations have been limited to smooth, flat model surfaces, even though most surfaces are rough. Roughness strongly influences wetting — as evidenced by the high water-contact angles (θ > 160°) and rolling of water droplets on lotus leaves.

Knowing that superhydrophobic surfaces occur naturally and that living systems operate mainly in water, we investigated the interaction of rough superhydrophobic surfaces beneath the water surface. Interfacial-force microscopy and optical imaging were used to examine the interaction between two approaching or retracting superhydrophobic surfaces (water contact angle θ of about 170°; see supplementary information) submerged in either air-equilibrated or de-aerated water.

We discovered a very-long-range hydrophobic interaction that was due to out-of-contact evaporation, or cavitation, of the intervening water at tip-to-substrate separations ranging from 0.8 μm to as much as 3.5 μm. Cavitation is a first-order phase transition characterized by a sudden, strong attractive force (Fig. 1a) and by the appearance of a vapour bridge spanning the tip-to-substrate gap (Fig. 1b–e, and see supplementary information for details).

Pre-existing ‘nanobubbles’ of a size commensurate with the interaction length have been proposed as a source of long-range interactions3. We therefore used in situ confocal imaging to search for bubbles on an isolated, flat superhydrophobic surface (for details, see supplementary information). Neither the microscopy nor neutron reflectivity experiments4 provide evidence for bubbles — certainly not micrometre-sized bubbles. We therefore argue that cavitation is a consequence of, and thermodynamically consistent with, the properties of confined water. The critical separation, D, below which cavitation is thermodynamically favoured can be estimated from Laplace’s equation as 1.4 μm (see supplementary information); this is a lower bound and will increase if Δp, the pressure difference across the interface, is reduced by incorporation of air into the cavity.

Unambiguous cavitation has previously been observed only following the contact of smooth hydrophobic surfaces5,6,11. Although it is thermodynamically acceptable, out-of-contact cavitation has been modelled as having a large activation barrier12, so we need to explain why we observe it and how kinetic barriers are surmounted.

First, we used interfacial-force microscopy7, in which interfacial forces are counterbalanced, to avoid snap-to-contact (when the rate of change of the force exceeds the spring constant and the two surfaces snap together uncontrollably, as occurs in atomic-force microscopy and in surface-force apparatus studies8). Second, the calculated D for submerged superhydrophobic surfaces is more than ten times that of smooth surfaces, which increases the probability of cavity nucleation at larger separations. Third, the submerged superhydrophobic surface presents an intrinsic liquid/vapour/solid interface, which may serve as a heterogeneous nucleation surface.

We simulated the molecular dynamics of a model fluid, which showed the necessary liquid—vapour behaviour, confined between two closely spaced surfaces containing opposing (θ = 180°) superhydrophobic patches. The simulations show that cavitation occurs by the growth of capillary-like fluctuations of vapour films extending from the superhydrophobic surfaces, leading to the sudden formation and growth of a vapour bridge.

Our experiments reveal that cavitation can be one source of long-range hydrophobic interactions. For rough surfaces, the interaction length extends to micrometre scales. Correspondingly, interaction lengths of hundreds of nanometres, observed for smooth surfaces (for example, snap-to-contact), might also be explained by cavitation, in agreement with thermodynamic expectations.

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