Supporting Information for "Measurement of the Hydrophobic Force in a Soft Matter System"

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1 Measuring hydrophobic attraction between solids and drops – a comparison

We highlight the similarities and differences between using the Atomic Force Microscope (AFM) to measure hydrophobic attraction between coalescing drops in this paper and using the Surface Forces Apparatus (SFA) to measure hydrophobic attraction between solid mica surfaces that have been rendered hydrophobic⁴.



Fig. S1: Schematics of the operations of the SFA and AFM with typical experimental results.

1.1 Atomic Force Microscope (AFM) – deformable drops

The operation of the Atomic Force Microscope (AFM) is illustrated schematically in Fig S1. The object is to measure the force between a drop attached to the end of the force sensing cantilever and a drop on the substrate. The separation X(t) between the end of the cantilever and the substrate is first decreased and then increased in what is called an "approach and retract" cycle. At each time step during the cycle, the change in the separation, $\Delta X(t)$ is measured by a linear variable differential transformer.

The force F(t) can be deduced from concomitant changes in the spring deflection $\Delta S(t)$ using the measured spring constant, K and Hooke's Law: $F(t) = K \Delta S(t)$. The time variation of this measured force F(t) during an approach and retract cycle is the key result of such AFM experiments.

In the presence of a hydrophobic attraction, the variations of the force with time can take three general forms:

(a) if during the approach phase, the drops do not approach to close enough together to result in coalescence so they will separate during the retract part of the cycle,

(b) if during the approach phase, the drops become close enough to coalesce under the hydrophobic attraction, the two drops will fuse into a single large drop and the experiment will come to an end, or

(c) the drops may not coalesce during the approach phase but may instead coalesce during the retraction phase when they are being separated. This coalescence is caused by the attractive hydrodynamic suction as the drops are being separated²⁸.

In cases (b) and (c) when the drops do coalesce, the time of coalescence and the value of the force at the point of coalescence are the key characteristic parameters of each coalescence event.

Variables of the experiment such as the initial value of *X*, the maximum displacement of the approach phase, the speed of the approach and retract phases and the drop sizes can all be specified or measured.

The detailed operation of the AFM is modelled theoretically (see section 9) and any assumed form of the hydrophobic attraction must be able to predict the time variations of the measured force, F(t), over the entire approach and retract cycle, the time of coalescence, the value of the force at coalescence for experiments conducted at different speeds, with different maximum displacements and different drop sizes. Therefore, any posited form of the hydrophobic attraction must be consistent with a suite of experimental results obtained by changing a number of control variables.

1.2 Surface Force Apparatus (SFA) - rigid solids

The operation of the Surface Force Apparatus (SFA) is illustrated schematically in Fig S1. The separation X(t) between the end of the force measuring spring and the substrate is decreased at constant velocity, V. At each time step, the change in the separation, $\Delta D(t)$ is measured optically by monitoring spectral shifts in interference fringes of equal chromatic order that has sub-nanometre resolution under ideal conditions.

The force F(t) can be deduced from concomitant changes in the spring deflection $\Delta S(t)$ using the measured spring constant, *K* and Hooke's Law: $F(t) = K \Delta S(t)$.

An schematic of the time variation of the separation D(t) is shown in Fig S1 where an attraction is manifested as a deviation that falls below the straight line whose slope is the

constant velocity V, finishing with a jump into contact. The point of hard contact between the interacting rigid bodies establishes the datum D(t) = 0 from which a force, F(t) vs separation, D(t) curve can be constructed⁴.

In general the molecularly smooth solid mica surfaces are rendered hydrophobic by (a) chemisorption of organic molecules, (b) by physical adsorption of surfactants by Langmuir-Blodgett deposition or self-assembled monolayers or (c) by chemical silanation. Each class of hydrophobic surfaces exhibit attractions with different characteristics.

The force, F_{ad} required to separate the solids after they have come into contact, is the adhesion or the pull-off force. Its magnitude depends on the extent of solid deformation and how long the solids have been held in contact, suggesting modifications of surface energies after contact⁴.

In summary:

(a) AFM force measurements between deformable drops focuses on the time variation of the force, whereas SFA force measurements between solids deduces the force-separation relation that is a less precise concept when deformation is involved,

(b) in our approach to measuring the intrinsic hydrophobic attraction between drops using the AFM, we select materials and system conditions whereby the hydrophobic attraction is one of the dominant forces – see sections 2 and 3 in this document, whereas

(c) with SFA experiments, forces due to van der Waals attraction, electrostatic repulsion as well as any steric effects and surface structural effects of the chemisorbed or physisorbed hydrophobising agents may have to be subtracted to extract the hydrophobic interaction.

2 Design considerations to measure the intrinsic hydrophobic attraction

The observed nature of the hydrophobic attraction deduced from measurements between solid surfaces depends strongly on the method used to render the solid surfaces hydrophobic. Mechanisms that have been advanced to explanation such variations include the possibility of the hydrophobic surface moieties forming patches or domains that may have different charge states or have different degrees of hydrophobicity or have the capacity of exposing or masking the underlying charge on the solid substrate. The presence of surface entrained nanobubbles and surface roughness (for superhydrophobic surfaces) have also been implicated.

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Our objective is to use the simplest, smoothest and pristine hydrophobic surfaces with minimal complexity to characterise the intrinsic hydrophobic attraction and to avoid the complexities associated with using solid surfaces that have been rendered hydrophobic.

Using a simple, inert, non-polar oil ensures molecularly smooth interfaces.

With any aqueous system, an interface invariably carries or develops a surface charge. This will give rise to a electrostatic repulsion due to the overlap of electrical double layers at such surfaces⁸. By working at a high salt concentration, say around 0.5 M, but not too high for ion specific effects to be important, the electrical double layer repulsion can be screened.

Furthermore, the surface charge at interfaces is also pH-sensitive because of the preferential adsorption of hydroxide ions from water. So by working close to the solution pH equal to the isoelectric point of the oil-water interaface, the magnitude of the surface charge is minimised.

The dispersive van der Waals attraction between non-polar materials across water is largely controlled by the refractive index difference between the material and water. Thus using a liquid that is refractive index matched to water will minimise the dispersive van der Waals attraction. Naturally, the complete optical spectra of such oil and water are not identical, but this effect, as well shall see, will be small.

Also working at high salt, the so called zero-frequency term of the van der Waals interaction will also be screened.

Therefore by suppressing as far as possible, the magnitude of all known interactions in an inert index-matched non-polar oil system in high salt near the material's isoelectric point optimises the condition to detect the intrinsic hydrophobic attraction.

The only interaction that remains in such systems is the hydrodynamic interaction between the oil drops in relative motion. The magnitude of the hydrodynamic interations that can be repulsive or attractive can be controlled using the speed of approach and retraction between the drops. The AFM is ideally suited for this application.

Due to refractive index matching, it is of course difficult to make direct visual observations of the system.

3 Perfluorinated oils: reasons for choice and their properties

Perfluorinated oils offer a range of desirable properties over their hydrocarbon counterparts for the purpose of isolating and elucidating the hydrophobic attraction:

- the water incompatibility of perfluorinated oils, an indicator of hydrophobicity, is ٠ greater than that of equivalent hydrocarbons, as evidenced by their higher interfacial tensions with water and significantly lower water solubilities, by about a factor of 10 or more $(Table S1)^{29}$, and
- the incompatiblity of perfluorinated oils with most hydrocarbon-based molecules • means that they are less prone to absorbing potentially surface-active contaminants than hydrocarbon oils³⁰,
- the molecules chosen perfluorooctane (PFO, C_8F_{18}) and perfluorobenzene (PFB, C_6F_6) – are centro-symmetric and completely miscible as is typical of perfluorocarbon mixtures³¹ so they have no amphiphilic character, and thus no propensity to orient at interfaces, and
- they have refractive indices that straddle that of water so that a miscible mixture PFX ٠ that comprises PFO:PFB = 54:46 by volume is refractive index matched to water (n =1.33) – see Table S1.

Table S1: Physical parameters of the fluorinated oils used to make index-matched drops.

Oil ^a	n	$\rho \; (kg/m^3)$	$\gamma_{o/a} (mN/m)$	$\gamma_{o\!/\!w}(mN\!/\!m)$	χ
Perfluorooctane (PFO, C ₈ F ₁₈)	1.255	1691	14.5 ^b	56.2 ^c	$^{\rm d}6.9 \times 10^{-11}$
Octane	1.398	703	21.6	52.5	1.1×10^{-6}
Perfluorobenzene (PFB C ₆ F ₆)	1.377	1610	22.0 ^b	48.4 ^c	${}^{\text{b,f}}6.0\times10^{\text{-5}}$
Benzene	1.501	877	28.9	35.0	$4.0 imes 10^{-4}$

a Data from ref.³² unless otherwise stated.

e at 301 K.

f Ref.³⁵

Refractive index, *n*; density, ρ ; oil/air interfacial tension, $\gamma_{o/a}$; oil-water interfacial tension, $\gamma_{o/w}$; solubility in water (mole fraction), χ . The properties of their hydrocarbon counter parts are given for comparison but these are not used in our experiments.

Interfacial tensions for pure PFO and PFB phases with water were measured at 20°C using pendant drop tensiometry, and found to be 56.2 ± 1 mN/m and 48.4 ± 1 mN/m respectively. Given the proximity of the values and their ideal miscibility, the interfacial tension of PFX with water was thus 51.5 ± 1 mN/m.

b Ref.³³

c Ref.³⁴

4 Force measurements between drops on the AFM

The main components of the atomic force microscope are illustrated in Fig S1 in which the force between the drop attached to the cantilever and the drop on the substrate is measured as the distance, X(t) between the base of the force sensing cantilever and the substrate is varied.

4.1 Atomic Force Microscope (AFM)

We use a commercial AFM (Asylum Research MFP-3D, equipped with ARC1 controller) for our force measurements. The distance, X(t) is controlled by a piezoelectric actuator driven by an applied voltage waveform, but the actual variation X(t) is measured by a linear variable differential transformer. The measured time variation of X(t) will be used for data analysis.

4.2 *Force sensing cantilever*

The cantilever is custom fabricated with a rectangular beam design, $450 \times 50 \ \mu m^2$, and approximately 2 μm in thickness, etched from a silicon wafer using nanolithography. The free end of the cantilever was fashioned to terminate in a circular region, slightly wider in diameter than the cantilever beam, providing a paddle-type shape. This circular paddle was chemically modified by reaction with 1-decanethiol in ethanol (1 mM) to produce a hydrophobic anchor to pick up a drop.

The spring constant of the cantilever is determined by the Hutter-Bechhoefer method⁷. The spring constants of cantilevers used in these experiments ranged between 0.15 and 0.30 N/m. A correction factor to account for the loading effect of a drop accurately positioned on the gold disc of the cantilever was applied³⁶.

The deflection of the cantilever is measured by a voltage difference at the splitphotodiode where a laser beam reflected from the cantilever is incident. This voltage is calibrated in terms of the inverse optical-lever sensitivity (InvOLS, which takes units of nm/V) that can be readily measured by driving the cantilever down against a solid surface, and measuring the change in deflection. Once the cantilever is in contact with the solid surface, the motion of the piezo motor that drives the back of the cantilever-substrate separation is reflected as an increasing deflection of the cantilever, measured in Volts at the photodiode. Hence, the reciprocal of the slope of this theoretically linear region, termed 'constant compliance' is taken to be the InvOLS.

As our measurements were conducted in water, the effects of noise, vibrations and stray electrostatic charges are much less important than AFM experiments undertaken in air, as the effect of fluid damping is much greater. In addition, vibrations were sequestered by mounting the AFM on an active vibration-isolation table (Herzan TS-150), resulting in a characterstic maximum deflection noise of the cantilever in contact with a solid surface of <50 pm.

4.3 Drop generation, immobilisation and capture

PFX mixtures were generated by using glass syringes to dispense appropriate amounts of each oil underwater into a macroscopic 'bulk' drop. This method was preferred to mixing in air in order to increase precision when considering the highly volatile nature of the oils.

Micro-droplets could be readily generated on a substrate by dispersing a few microlitres of the PFX mixture from the macroscopic drop by back-filling a glass syringe with a few microlitres of this oil and a few hundred microlitres of water. Discharging this oil-water mixture underwater provides a coarse emulsion with a distribution of droplet sizes, including those appropriate for AFM measurements. Because fluorinated oils are denser than water (Table S1), the droplets settle onto the substrate.

Solution pH was adjusted by addition of nitric acid (HNO₃, Chem Supply reagent grade) to achieve a final concentration of 0.32 mM. The solution pH was independently measured with a standard glass pH electrode to be 3.5 ± 0.05 .

The cantilever can then be positioned over a selected drop and used to pick it up from the substrate. The alkanethiolated gold disc on the cantilever is significantly more hydrophobic (contact angle of water in air $\sim 100^{\circ}$) than the substrate onto which the drops settle (contact angle of water in air $\sim 30^{\circ}$), and so a drop will readily attach to the cantilever to minimise its surface energy. It is then aligned axisymmetrically with another drop on the substrate for force measurement using an inverted optical microscope (Nikon TE-2000). See Fig S2. The contact angle of oil droplets on the surface was calculated by measuring the droplet radius and the contact area with the substrate and calculating assuming a spherical cap. The contact angle of droplets on the cantilever was obtained similarly, using the size of the gold disc as the contact area (confirmed by optical microscopy).

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Fig. S2: A schematic guide on steps to pick up a drop on the AFM cantilever and subsequent alignment with another drop on the substrate for force measurement.

4.4 Drop alignment effects

To estimate the effect of imperfect axisymmetric alignment on the measured force, we consider the interaction of two spheres of radius *R* at a distance of closest approach, *h* as indicated in Fig S3. For $R \gg h$, the Derjaguin expression for the interaction free energy, $V_D(h)$ is given by

$$V_D(h) = \pi R \int_h^\infty E_P(z) \, dz \quad + \quad O\left(\frac{h}{R}\right)$$

where $E_P(h)$ is the interaction energy per unit area between parallel plates. The corresponding force, assuming axisymmetric interaciton is

$$F_D(h) = -\frac{dV_D(h)}{dh} = \pi R E_P(h) + O\left(\frac{h}{R}\right)$$

We now consider a displacement ds along the line that is offset from the the line of centres between the spheres a distance d and calculate the resulting force. From the geometric relation (see Fig S3)

$$s^2 + d^2 = (2R + h)^2$$

we find

$$\frac{dh}{ds} \approx \left[1 - \frac{d^2}{8R^2} + O\left(\frac{d^4}{R^4}, \frac{h}{R}\right)\right]$$

for R >> h and R >> d. Therefore the force due to an offset displacement ds is

$$F_{offset}(s) = -\frac{dV_D(h)}{ds} = -\frac{dV_D(h)}{dh}\frac{dh}{ds} = F_D(h) \left[1 - \frac{d^2}{8R^2} + O\left(\frac{d^4}{R^4}, \frac{h}{R}\right) \right]$$

So even for a 20% offset, (d/R) = 0.2, the percentage correction to the Derjaguin result is

$$\frac{d^2}{8R^2} \sim \frac{(0.2)^2}{8} \sim 0.5\%$$

In Fig S3 we show variations of the measured force with displacement between two PFO drops (radii 42 μ m and 43.5 μ m) in deionised water at pH 5.5 for varying degrees of deliberate mis-alignment on a 10 μ m × 10 μ m and a 25 μ m × 25 μ m grid. The spring constant of the cantilever used here was 0.308 N/m. The drive velocity was 10 μ m/s. The results indicate no discernable systematic variations with misalignment of less than 10 μ m. In practice, axisymmetric drop alignment can easily be achieved to within ± 2 μ m.



Fig. S3: Variation of the force with displacement between two PFO drops (radii 42 and 43.5 μ m) in deionised water at pH 5.5 for varying degrees of mis-alignment on a 10 μ m x 10 μ m and a 25 μ m x 25 μ m grid. The drive velocity was 10 μ m/s. The spring constant of the cantilever was 0.308 N/m.

5 Visualisation of stealth drops - PFX

PFX drops that are a mixture of perfluorooctane (PFO) and perfluorobenzene (PFB) [PFO:PFB = 54:46] index-matched to water (refractive index 1.33) are virtually invisible under normal illumination conditions.

However, because the dielectric spectra for the PFX oil phase and aqueous solutions are not matched perfectly at all frequencies, the drop can be detected via a dispersion effect. This was exploited using phase contrast illumination to increase their visibility during experiments.

As we have previously demonstrated³⁷, laser scanning confocal microscopy (LSCM), a fluorescence imaging technique, can be used to selectively illuminate the oil-water interface of small emulsion droplets, via adsorption of a fluorescent dye at the interface. This technique was used *only* to confirm the validity of alignment using phase contrast illumination, and was not used in drop interaction measurements. A comparison of these three visualisation techniques is given in Fig. S4. The fluorescent dye used to make the LSCM image was Acid Red 88 (~0.01 mM).

Using a Nikon TE-2000 inverted microscope, experiments were arranged and observed using phase contrast illumination. This provided sufficient visibility of the drops to ensure that axisymmetry was achieved during interactions.



Fig. S4: Images of index matched PBX droplets, made using brightfield (conventional, diffuse) and phase contrast illumination, and visualised with laser scanning confocal microscopy.

6 Electric double layer repulsion

In Fig. 1a of the paper, we compare the disjoining pressure between two flat surfaces composed of different oil phases and under different conditions, to demonstrate the magnitude and range of surface forces from the Derjaguin-Landau-Verway-Overbeek (DLVO) model that comprises electric double layer repulsion and Lizshitz-van der Waals attraction.

To generate the result for index matched drops at pH 3.5 (red solid curve, Fig. 1), electric double layer (EDL) disjoining pressure Π_{EDL} was calculated using the superposition approximation of the non-linear Poisson-Boltzmann theory for electrical double-layer interactions in a 1:1 electrolyte³⁸:

$$\Pi_{\text{EDL}}(D) = \left[64 \, k_{\text{B}} T \, n_{\text{bulk}} \tanh^2 \left(e \Phi / 4 k_{\text{B}} T \right) \right] \exp\left(-\kappa \, D\right) \tag{6.1}$$

where $k_{\rm B}$ is Boltzmann constant, *T* is the temperature, $n_{\rm bulk}$ is the number concentration of ions in the bulk electrolyte, *e* is the fundamental charge, Φ is the surface potential, κ is the inverse Debye length and *D* is the separation. Eq. (6.1) is an overestimate of the magnitude of the electrical double-layer repulsion but is sufficiently accurate for the range of *D* in Fig. S4.

For PFX drops at pH 3.5, which is close to the isoeletric point, the surface potential (16 mV) was assumed to be that of PFO drops in water, measured previously¹⁷. Creux *et al.* measured zeta potentials for a wide range of chemically-different oil drops and found them to be nearly identical³⁹, suggesting that the assumption made here is valid.

7 Lifshitz-van der Waals attraction

For the result for PFO drops at pH 3.5 in Fig. 1 of the paper (green dashed curve), the disjoining pressure Π was calculated assuming the same electrical double-layer parameters, but including a van der Waals component for non-matched pure PFO drops, to generate a classical DLVO curve.

The Lifshitz-van der Waals disjoining pressure is given by

$$\Pi_{\rm vdW}(D) = \Pi_{\rm disp}(D) + \Pi_0(D) \tag{7.1a}$$

$$\equiv -\frac{A_{disp}(D)}{6\pi D^2} - \frac{A_0(D)}{6\pi D^2} \equiv -\frac{A_{vdW}(D)}{6\pi D^2}$$
(7.1b)

where $A_{vdW}(D)$ is defined to be the Hamaker function, see Fig S4.

The full Lifshitz model^{40,41} that includes the effect of electromagnetic retardation on the dispersion contribution where the dispersion force per unit area, Π_{disp} between two half-spaces at separation *D* is given by

$$\Pi_{\rm disp}(D) = -\frac{kT}{\pi c^3} \sum_{n=1}^{\infty} \varepsilon^{3/2} \xi_n^3 \int_{1}^{\infty} p^2 \left\{ \left[\overline{\Delta} - 1 \right]^{-1} + \left[\Delta - 1 \right]^{-1} \right\} dp$$
(7.2)

where k is Boltzmann's constant, T absolute temperature, c the velocity of light in vacuum and

$$\Delta = \left(\frac{s\varepsilon_f + p\varepsilon}{s\varepsilon_f - p\varepsilon}\right)^2 \exp\left(\frac{2p\xi_n\varepsilon^{1/2}D}{c}\right), \quad \overline{\Delta} = \left(\frac{s+p}{s-p}\right)^2 \exp\left(\frac{2p\xi_n\varepsilon^{1/2}D}{c}\right)$$
(7.3)
$$s = \sqrt{p^2 - 1 + (\varepsilon_f/\varepsilon)}, \quad \xi_n = \left(\frac{2\pi kT}{\hbar}\right)n$$
(7.4)

with $(2\pi\hbar)$ the Planck's constant, $\varepsilon_f(i\xi_n)$ and $\varepsilon(i\xi_n)$ the dielectric permittivity of fluorocarbon and water, respectively, evaluated at imaginary frequencies $(i\xi_n)$.

An approximate expression for the dispersive part of the Hamaker function in the non-retarded limit has been given⁸ in terms of the refractive indices of the fluorocarbon, n_f and water, n and the mean UV absorption angular frequency, ω_o (rad/s) of these two materials

$$A_{disp} \approx \frac{1}{16\sqrt{2}} \frac{(n_f^2 - n^2)^2}{(n_f^2 + n^2)^{3/2}} (\hbar \,\omega_o) \qquad \text{(non-retarded)}$$
(7.5)

For refractive-index matched materials: $n_f = n$, this expression vanishes and we must consider the effects of dispersion that arise from the difference in the absorption spectra of fluorocarbon and water where the leading order expression for the dispersive part of the Hamaker function in the non-retarded limit become

$$A_{disp} \approx \frac{3}{16} \frac{(n^2 - 1)^2}{(n+1)^3} \left(\frac{\Delta\omega}{\omega_o}\right)^2 (\hbar \,\omega_o) \quad \text{(non-retarded, index-matched } n_f = n) \quad (7.6)$$

where $\Delta \omega$ is the difference between the absorption frequency of fluorocarbon and of water. Although Eqs. (7.5) and (7.6) provide estimates of the effects of index-matching and dispersion effect, but we use Eq. (7.2) to give more accurate results.

The zero frequency term of the force per unit area, Π_0 that includes the effects of electrolyte screening is calculated using⁴²

$$\Pi_0(D) = -\frac{kT}{2\pi} \int_0^\infty q \sqrt{q^2 + \kappa^2} \left[\Delta_0 - 1 \right]^{-1} dq$$
(7.7)

where $(1/\kappa)$ is the Debye length of the electrolyte and

$$\Delta_0 = \left(\frac{\sqrt{q^2 + \kappa^2} \,\varepsilon(0) + q \,\varepsilon_f(0)}{\sqrt{q^2 + \kappa^2} \,\varepsilon(0) - q \,\varepsilon_f(0)}\right)^2 \exp\left(2\sqrt{q^2 + \kappa^2} D\right)$$
(7.8)

with the dielectric permittivities $\varepsilon_f(0)$ and $\varepsilon(0)$ evaluated at zero frequency.

The formulae given in Eq. (7.2) and (7.7) give the most detailed and complete approach to calculating the Lifshitz-van der Waals attraction.



Fig. S5: The Hamaker function $A_{vdW}(D)$ defined in Eq. (7.1) for two half spaces of PFO and PFX across a 0.5 M aqueous solution as a function of separation, *D*.

For water, we use the recent dielectric function constructed by Dagastine *et al.*⁴³. The dielectric function for PFO was obtained using a Cauchy plot with data extrapolated from Drummond *et al.*⁴⁴.

An estimate of the maximum possible Hamaker function $A_{vdW}(D)$ for matched PFX drops in water was obtained by approximating the dielectric function of PFX as intermediate between those of PFO⁴⁴ and PFB⁴⁵, and is shown in Fig. S5. The variation of $A_{vdW}(D)$ with separation is a consequence of the effects of electromagnetic retardation.

At any separation, the Hamaker function for the index-matched PFX-water-PFX system is over 30 times smaller than that for PFO-water-PFO. The very small residual Hamaker function in the index-matched PFX-water-PFX system is the consequence of the small difference in the spectral properties between water and the index-matched PFX above

the visible range, cf Eq. (7.6). We use this dispersion effect to help visualise the PFX drops in water using phase contrast microscope during handling and alignment.

In 0.5M salt where the Debye screening length is ~ 0.4 nm, then at a separation D = 3 nm, the zero frequency component of the Hamaker function, $A_0(D)$ is over 2000 times smaller than the dispersion component, $A_{disp}(D)$ for the PFX-water-PFX system.

We use the dielectric data for tetradecane given by Hough and White⁴⁶ to calculate the Hamaker function of the tetradecane-water-perfluorooctane system given in Fig. 2b of the main text.

8 Range of the intrinsic hydrophobic interaction – Lum-Chandler-Weeks model

The self-consistent field theory developed by Lum, Chandler and Weeks²² (LCW) to calculate the hydrophobic interaction and de-wetting phenomena at an air-water interface is used to estimate the range of hydrophobic interaction in the stealth system.

Following the notation of LCW, we have from their Eq. (13)

$$\frac{\gamma}{\sqrt{m}} = \int_{n_g}^{n_l} \mathrm{d}n \sqrt{2[w(n) - w(n_g)]}$$
(8.1)

where w(n) is the local free energy density of water at the local fluid density *n*, that take on the bulk liquid value n_l , and gas phases value n_g (see Eq. 12 of LCW). The parameter *m* is defined in terms of the characteristic length λ in which water molecules attract each other by

$$m = a \lambda^2 \tag{8.2}$$

where *a* is the bulk energy density parameter in the self-consistent field theory. For water, LCW estimated $a = 0.23 \text{ J m}^3 \text{ mol}^{-2}$ and $\lambda = 0.38 \text{ nm}$ at the air-water interface with interfacial tension $\gamma = 72 \text{ mJ m}^{-2}$.

The evaluation of the integral in Eq (8.1) requires a coarse graining prescription and the local structure of water is extrapolated from the experimental structure factor – see LCW for details. However, we expect the value of the integral at the air-fluorocarbon interface to be similar to that at the air-water interface because the additional van der Waals interaction would only give a small contribution⁴⁷.

At the PFX-water interface, $\gamma = 51 \text{ mJ m}^{-2}$, and assuming the integral in Eq. (8.1) is constant, we have: $\lambda = 0.38 \text{ nm} \times (51/72) = 0.27 \text{ nm}$ at the fluorocarbon-water interface.

Therefore we estimated that the decay length in Eq. (1) in the main text to be

$$D_0 \approx \lambda \approx 0.3 \text{ nm.}$$
 (8.3)

We note that Eq. (1) is only used to model the hydrophobic attraction that triggers coalescence experiments when the water films thin to around 3 nm. Thus the current coalescence experimental results provided no information about thinner films. However, for films of water 3 nm or thicker, it would be reasonable to assume that the state of the water molecules in the film would not be too different from that of water at a single interface as was considered by LCW. Had the critical film thickness been substantially thinner than 3 nm, the self-consistent analysis of LCW would have needed to be modified.

9 The Stokes-Reynolds-Young-Laplace model

The Stokes-Reynolds-Young-Laplace (SRYL) model is used to analyse the coalescence experiments described in this paper. The accuracy of this model has been tested on experimental data acquired on a variety of instruments including the atomic force microscope and the surface forces apparatus²⁰.

The deformation of the surfaces of the drop, expressed in terms of the axisymmetric water film thickness h(r, t) during interaction is described by the Young-Laplace equation²⁰

$$\frac{\gamma}{2r}\frac{\partial}{\partial r}\left(r\frac{\partial h}{\partial r}\right) = \frac{2\gamma}{R} - p - \Pi, \qquad \qquad \frac{1}{R} = \frac{1}{2}\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$
(9.1)

where R_1 and R_2 are the undeformed radii of the drops and γ is the interfacial tension. Eq. (9.1) takes into account the disjoining pressure, Π that has contributions from electric double layer, van der Waals and hydrophobic attraction. The effects of fluid flow is contained in the hydrodynamic pressure, *p*.

Evolution of the film thickness is obtained from Reynolds lubrication theory that gives

$$\frac{\partial h}{\partial t} = \frac{1}{12\mu r} \frac{\partial}{\partial r} \left(r h^3 \frac{\partial p}{\partial r} \right)$$
(9.2)

where μ is the Newtonian viscosity of water. Implicit in Eq (9.2) is that the hydrodynamic boundary condition at the air-oil interfaces is tangentially immobile, like that at a sold-liquid surface.

The details involved in applying this model to analyse force measurements between deformable drops using the atomic force microscope are documented extensively in the literature²⁰. From an initial separation, h_0 , at which the drops are undeformed, Eqs. (9.1) and (9.2) are solved in the range $0 \le r \le r_{max}$. The AFM displacement function X(t) enters in the boundary condition at r_{max}

$$\frac{\partial h(r_{\max},t)}{\partial t} = \frac{dX(t)}{dt} + \frac{dF(t)}{dt} \left\{ \left| \frac{1}{K} - \frac{1}{2\pi\gamma} \left[\log\left(\frac{r_{\max}^2}{4R_1 R_2}\right) + B(\theta_1) + B(\theta_2) \right] \right| \right\}$$
(9.3)

where

$$B(\theta) = 1 + \log\left(\frac{1 + \cos\theta}{1 - \cos\theta}\right) \tag{9.4}$$

with θ being the contact angle of the drop on the cantilever, θ_1 or on the substrate, θ_2 and F(t) is the force given by

$$F(t) = 2\pi \int_{0}^{\infty} \left[p(r,t) + \Pi(r,t) \right] r \, dr \tag{9.5}$$

Given the measured displacement function X(t), Eq. (9.1) – (9.5) can be solved to give the force F(t) as a function of time *t* to be compared directly to experimental values.

The modelling experimental data at low driving speeds $\sim 0.1 \ \mu m/s$ this model gives identical results to the equilibrium approach of Chan, Dagastine and White⁴⁸.

In the absence of deformation, the hydrodynamic pressure at the line of symmetry between two drops has the form

$$p(0,t) = -\frac{3\mu R}{\left[h(0,t)\right]^2} \frac{dX(t)}{dt} \qquad \text{(non-deforming)}$$
(9.6)

This is the expression used to estimate the hydrodynamic pressure in Fig. 4 of the paper. To include the effects of drop deformation, the governing equations must be solved numerically.

The system parameters such as contact angle on the substrate, contact radius on the cantilever and the undeformed radius of curvature of the drops can be measured independently, in situ by optical microscopy. Interfacial tension is measured ex situ by standard drop-shape tensiometry. Previous studies have also used needle tipped AFM cantilevers in a micro-Wilhelmy rod geometry⁴⁹ to confirm surface and interfacial tension measurements for immobilized drops and bubbles in the AFM fluid cell. These measurements agree with standard drop-shape tensiometry measurements. Instrument parameters such as the cantilever spring constant and the inverse optical lever sensitivity (InvOLS) can be measured. All such measurements have known experimental uncertainties.

In static force measurements using the AFM, one obtains a single force vs displacement curve. On the other hand, in our measurement of the time dependent force, we can, using the same drop pair, vary the speeds with which the drops are driven together or separated as well as the maximum distance over which we drive the drops. We can check the repulsive force maximum and the attractive force minimum for interactions that remain stable and we can also monitor the time of coalescence. After drop coalescence, we have to work with a new drop pair.

Thus for the same pair of drops we have a large number of force vs time data traces, each with their characteristic shape, maximum and minimum. To model such sets of force data, using the above measured system parameters (which are identical within each data set), we ensure that the values used are within their known experimental uncertainties.

We further check that the quality of the agreement between experimental data and model calculations is equally good for different drop pairs. This gives us confidence that we have an accurate, quantitative description of the experimental data.

10 Comparisons between experiment and theory

In the absence of an attractive disjoining pressure, the Stokes-Reynolds-Young-Laplace (SRYL) model predicts that the drop-drop interaction will be stable and coalescence will not occur. Thus a sufficiently strong attractive disjoining pressure – due to hydrophobic interaction in our system, would be required to cause drop coalescence.

We expect this hydrophobic attraction to depend on separation between the perfluorocarbon drops but to be independent of velocity. Thus any posited form of this hydrophobic attraction should be able to predict the coalescence time and the magnitude of the force at the point of coalescence for

- the range of drop sizes studies,
- the range of drop interaction velocity used, between 0.1 to 25 μ m/s,
- coalescence events that occurr as the two drops approached other other, and
- coalescence events that occurr as the drops are being separated from each other.

In our comparison between experiment and theory, we use the exponential form given in Eq. (1) where the exponential dependence is anticipated by the Lum-Chandler-Weeks model. Since the magnitude of the attractive hydrophobic interaction free energy at contact is dictated by thermodynamic considerations (see main text), then the exponential form contains

only one parameter – the decay length D_0 . From the Lum-Chandler-Weeks, we estimated in Section 8 that $D_0 \sim 0.3$ nm. As we have seen, with this value we obtain excellent quantitative agreement with all experimental results. In Section 10.3, we quantify the sensitivity of this agreement with variations of the decay length D_0 . In Section 10.4 we consider the effects of using other functional forms for the attractive hydrophobic disjoining pressure, noting that using another functional form will require invoking additional parameters.

10.1 Hydrodynamic boundary condition and film viscosity

The Stokes-Reynolds-Young-Laplace (SRYL) model described in Section 9 contain the following assumptions:

- the no-slip hydrodynamic boundary condition holds at the molecularly smooth perfuorocarbon-water interface, and
- the viscosity of water retains its bulk value at all thicknesses.

Numerous detailed experimental studies of flow and film drainage of down to nanometre thickness at the smooth interface between water-hydrocarbons (decane, tetradecane, hexadecane, glycerol), water-mercury or water-air interfaces are all consistent with the above assumptions. These experiments and detailed comparisons with the predictions of the SRYL model have been summarised in recent reviews^{20,28}. A variety of experimental techniques with different characteristic system sizes were used and involve the drainage of thin films of water:

- between an air bubble pressed onto a silica plate in a bubble expansion experiment⁵⁰
- trapped drainage between a mercury drop and a mica place in the SFA⁵¹
- during force measurements between an oil drop and a sold surface¹⁶
- between a bubble and a sold surface⁵², and
- between two bubbles¹⁶.

Furthermore, the drainage rate or flow rate indicates that the viscosity of water retains its bulk value down to nm thickness⁵³.

As with previous studies, the assumptions of

- 1. the no-slip boundary condition at the perfluorocarbon-water interface and
- 2. that water retains its bulk viscosity near such interfaces

are both required to give quantitative agreement with present results obtained over

- the range of drop sizes,
- the range of drop interaction velocity between 0.1 to 25 μ m/s,
- coalescence that occurred as the two drops approached other other, and
- coalescence that occurred as the two drops are being separated from each other.

Relaxing either one of these identified conditions above does not give the agreement we observe. The consistent behaviour across many different experimental variables is compelling evidence that these assumptions hold for our experiments.

Studies of fluid flow near solid surfaces that have been rendered hydrophobic⁵⁴ found that the hydrophobisation process also induces surface roughness (~ 8 nm) on an originally smooth surface (roughness ~ 1 nm). The effects of this surface roughness or heterogeneity associated with hydrophobisation on fluid transport were subsumed as an apparent hydrodynamic slip boundary condition at an otherwise smooth surface. This provided a simple one-parameter characterisation of observed deviations expected from a model smooth surface in terms of a slip length. However, this cannot be generalised to the notion that "hydrodynamic slip occurs at all hydrophobic surfaces". The same phenomenology does not appear to apply at hydrophobic but molecularly smooth oil-water or air-water interfaces.

10.2 Coalescence times

The hydrophobic attraction characterised by the exponential form given Eq. (1) of the main text can be used in the Stokes-Reynolds-Young-Laplace model to predict the coalescence times on approach or on retraction. The results shown in Fig S6, together with the force at coalescence and the critical film thickness results in Fig. 4 in the main text, indicate we have succeeded in quantifying the spatial and temporal behaviour of drop coalescence triggered by the intrinsic hydrophobic attraction.



Fig. S6: A comparison of experimental and predicted coalescence times due to hydrophobic attraction of the exponential form given by Eq. 1 of the main text with a decay length of 0.3 nm (circles).

10.3 Decay length of the hydrophobic attraction

An exponential decaying hydrophobic attraction has been reported in the literature^{3,4,6} with the longer decay length of \sim 1 nm. However, if we use a 1 nm decay length for the exponential hydrophobic attraction, the predicted coalescence would occur too early compared to experimental observations – see Fig. 2 and 3 in the main text and a comparison with the experimental coalescence time is given in Fig S5.

10.4 Functional form of the hydrophobic attraction

Instead of the exponential form of the hydrophobic attraction that is anticipated in the Lum-Chandler-Weeks theory, we can consider using a decaying power law to represent the hydrophobic attraction. In this case, we need to specify two parameters: the decay length scale, D_0 and the power law index, n. This power law will take the following form for the hydrophobic interaction free energy per unit area

$$E_{HB}(D) = -2\gamma \left(\frac{D_o}{D+D_o}\right)^n \tag{10.1}$$

in order to satisfy the thermodynamic limiting behaviour $E(D \rightarrow 0) \rightarrow -2\gamma$. Thus the disjoining pressure becomes

$$\Pi_{HB}(D) = -\frac{dE_{HB}(D)}{dD} = -\frac{2n\gamma}{D_o} \left(\frac{D_o}{D + D_o}\right)^{n+1}$$
(10.2)



Fig. S7: A comparison of exponential (Eq. 1 main text) and power law (Eq. 10.2) form for the attractive hydrophobic disjoining pressure with $\gamma = 50 \text{ mJ/m}^2$ and $D_0 = 0.3 \text{ nm}$. The power law index is varied from n = 2 to 5.

In Fig S7, we see that the exponential law is intermediate between a power law index n = 4 and 5. If we use n = 4, coalescence is predicted to occur too early, similar to when we a decay length of 1 nm was used for the exponential law. On the other hand, with n = 5, no coalsecence would be predicted at all under the experimental conditions. Thus a power law would not be able to produce any quantitative match with experiments. Furthermore there is no known theoretical foundation for a power law index of 4 or 5.

10.5 Robustness of the analysis

With respect to the robustness of our analysis of experimental results, the following remarks are relevant:

- For the low speed $(0.1 \,\mu\text{m/s})$ coalescence results shown in
 - Fig 2a between index-matched drops (with electric double layer repulsion but negligble van der Waals attraction) and
 - in Fig 2b between a pure perfluorooctane drop and a pure tetradecane drop (with van der Waals repulsion but negligible electric double layer repulsion),

hydrodynamic effects are neglibibly small. In both cases, coalescence is caused by the same attractive hydrophobic interaction. The exponential form with a decay length of 0.3 nm predicted the variation of the measured force with time and also predicted correctly the coaleacence time and as well as the force magnitude at which coalescence occurred.

Using the same functional form for attractive hydrophobic interaction (between index matched drops), but at a high velocity of 20 μm/s (see Fig 2c) or at intermediate velocities 4 μm/s and 6 μm/s (Fig 3), equally good agreements were observed.

Here DLVO interactions are minimal but at these higher velocities, hydrodynamic interactions play an important role – particular for the observed coaleacence on retraction seen in Fig 3. If hydrodynamic slip is assumed at the index-matched perfluorocarbon oil-water interface, the attractive hydrophobic interaction will have to take a different form to that used to model the results in Figs. 2a and b (taken at 0.1 μ ms) to accommodate this. There is no reason to assume that the attractive hydrophobic interaction should be velocity dependent.

Therefore, the across the board agreement with all experiments is consistent with the assumptions of the no-slip or tangentially immobile hydrodynamic boundary condition, constant viscosity of the aqueous phase and a decay length for the intrinsic hydrophobic attraction of ~ 0.3 nm, with around $\pm 10\%$ uncertainty.

10.6 Model and experimental parameters

The measured parameters and theoretical values used to model the force data between two index-matched PFX drops in 1 M NaClO₄ electrolyte shown in Figs. 2 and 3 of the main text are given in Table S2. The inverse optical lever sensitivity (InvOLS) was obtained by driving the cantilever (without drop) against the solid substrate in the working solution and measuring the response at the photodiode to a given vertical displacement of the cantilever. This method has been verified previously to be accurate and appropriate using both indepentent methods of cantilever calibration⁴⁹ and laser scanning confocal microscopy³⁷.

		Fig 2A		Fig 2B		Fig 2C		Fig 3	
Parameter	Units	Expt	Model	Expt	Model	Expt	Model	Expt	Model
Drop radius (CL)	μm	40	40	39	39	30	31	37	37
Drop radius (SS)	μm	43	43	41	41	33	34	40	40
Surface potential	mV	-12	-12	-12	-12	-12	-12	-12	-12
Electrolyte conc.	mol/L	3.2×10 ⁻⁴	3.2×10 ⁻⁴	1	1	1	1	1	1
Contact radius (CL)	μm	22	22	22	22	22	22	22	22
Contact radius (SS)	μm	26	26	25	25	19	20	24	24
Unloaded spring const.	N/m	0.180	n/a	0.177	n/a	0.236	n/a	0.155	n/a
Loaded spring const.*	N/m	n/a	0.198	n/a	0.192	n/a	0.26	n/a	0.17
InvOLS	nm/V	94	94	88	88	83	80	72	70
Solution viscosity	mPa s	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Reduced interfacial tension**	mN/m	51.5	52	54	54	51.5	50	51.5	50
Hydrophobic decay length	nm	n/a	0.3	n/a	0.3	n/a	0.3	n/a	0.3

 Table S2: Measured parameters and theoretical values used to model the force data between two
 index-matched PFX drops shown in the main text.

*For a thorough discussion of the effects of loading on cantilever spring constants, refer to ref.⁵⁵

**Harmonic mean interfacial tension for the oil-water interfaces of the drop on the cantilever and surface.

Abbreviations used: CL = cantilever; SS = substrate; InvOLS = inverse optical lever sensitivity.

11 Movies of coalescence of PFX drops

A movie collage comparing stable and coalescent experiments with theory for indexmatched PFX drops under stealth conditions: aqueous solutions at the isoelectric point, 0.5 M NaNO₃, in which van der Waals and electrical double layer forces are suppressed so that only hydrodynamic interaction and hydrophobic attraction operate.

11.1 Sampling the hydrophobic interaction: Movie_1_Energy_and_Pressure.avi

The three vertical frames in the centre compare the time variation of the measured force with theoretical prediction:

Top: velocity 5 µm/s; radii 30 µm, 31 µm (Stable)

Middle: velocity 3 µm/s; radii 30 µm, 31 µm (Coalescent on retraction)

Bottom: velocity 25 µm/s; radii 34 µm, 27 µm (Coalescent on approach)

For clarity, only a small subset of the experimental data points are shown.

The Top and Middle frames show results from the same drop pair driven together with the same maximum displacement and then separated, but at slightly different speeds $-3 \mu m/s$ and $5 \mu m/s$. The comparison demonstrates the competition between the hydrophobic attraction and the hydrodynamic interaction. At a speed of 5 $\mu m/s$, the drops remain stable upon separation because at this higher approach speed, the hydrodynamic repulsion on approach is larger, and so the drops deform and are further apart when the retraction starts. Although the hydrodynamic attraction that appears on retraction will pull the drop surfaces closer together, the minimum separation is still beyond the range when the hydrophobic attraction can be effective to cause coalescence.

However, at the lower speed of 3 μ m/s, the magnitude of the hydrodynamic repulsion on approach is smaller and hence the drop surfaces will be closer together when the retraction phase begins. Now the hydrodynamic attraction that appears on retraction is sufficient to pull the drop surfaces close enough together for the hydrophobic attraction to take hold and cause coalescence.

In the bottom frame, the drops are driven together at a very high approach velocity of 25 μ m/s. Only when the hydrodynamic force has reached a much higher value of ~ 50 nN

does the drop separation became sufficiently small for the hydrophobic attraction to take hold and cause coalescence.

The above description is illustrated in the frame on the left that depicts the locus of the three experiments along the hydrophobic disjoining pressure on a linear scale as a function of film thickness:

 $\Pi_{\rm HB}(D) = -(2\gamma/D_{\rm o}) \exp(-D/D_{\rm o}).$

The frame on the right depicts the locus of the three experiments along the hydrophobic interaction energy per unit area on a logarithmic scale as a function of film thickness:

$$E_{\rm HB}(D) = -(2\gamma) \exp(-D/D_{\rm o}).$$

with $D_0 = 0.30$ nm in both cases.

11.2 Drop profiles: Movie_2_Drop_profiles.avi

The top row of three frames compare the time variation of the measured force with theoretical prediction. These are the same experiments and model calculations as those in the previous section, 11.1 shown in Movie 1 Energy and Pressure.mov

Left: velocity 5 μm/s; radii 30 μm, 31 μm (Stable)
Middle: velocity 3 μm/s; radii 30 μm, 31 μm (Coalescent on retraction)
Right: velocity 25 μm/s; radii 34 μm, 27 μm (Coalescent on approach)

The Left and Middle frames show results from the same drop pair.

The bottom row of three frames shows the calculated drop profiles corresponding to the top row up until the time of coalescence, for the middle and right cases.

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