Modeling of Menisci and Capillary Forces from the Millimeter to the Micrometer Size Range

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This paper examines lateral capillary interactions between millimeter- and sub-millimeter-sized objects floating at the interface between perfluorodecalin (PFD) and water. It describes methods—both experimental and computational—that allow the shape of the interface to be described for various geometries of the interacting objects. From these shapes, it derives the energy profiles characterizing the lateral capillary interactions. This work also demonstrates a new experimental method of imaging and studying menisci, and of studying capillary interactions between objects.

Introduction

We are using capillary forces as the basis of a system for the self-assembly of 0.1 to 10 mm-sized objects into ordered arrays.1–3 One overreaching objective of the work is to abstract concepts from molecular chemistry—especially concepts of bonding—and to develop them as the basis for a system of assembly of meso-scale objects. That is, we wish to give molecule-like properties to macroscopic objects.

The components of our system—small, polygonal polymeric plates with edge faces patterned to be hydrophobic or hydrophilic—float at the interface between two immiscible liquids, typically perfluorodecalin (PFD) and water. Self-assembly is caused by interactions between the menisci on these faces: that is, by capillarity.4,5 The contours of the menisci determine the direction and magnitude of the lateral capillary forces, and thus dominate the physics of the system. These contours are, however, difficult to model and to measure experimentally. The Laplace equation that describes the shapes of the menisci is not readily solved analytically, even for simple geometries, and certainly not for some of the shapes of interest in this work.6–9 The purpose of this paper is to describe methods for modeling the contours of the menisci by a Finite Element Method (FEM),10 to measure the contours experimentally, and to calculate the energy of interaction between objects at a fluid/fluid interface.

The self-assembly of objects represents an extension of the concepts of molecular self-assembly11–14 to the mesoscopic scale. Molecular self-assembly is important in chemistry and biology as a process that forms ordered arrays and structures—crystals, coordination compounds, proteins, nucleic acids—through noncovalent forces. In mesoscale self-assembly (MESA), nanometer-to-centimeter-scale objects assemble into ordered arrays through interactions—especially capillary interactions—that are, at least in principle, reversible. Capillary interactions have been used extensively in self-assembly by Denkov15,16 (two-dimensional colloidal crystals), Nagayama17 (crystalline arrays of proteins), Rothemund18 (millimeter-scale Penrose tiles), and others.

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interfacial free energies. We wished to find methods both to calculate and to measure the shape of the menisci.

This paper has four parts: (i) We describe the solutions of the Laplace equation for a simple case of two interacting, infinitely long faces of identical or opposite surface polarities. From these solutions, we derive energy profiles describing the interactions between such faces at various distances between them. (ii) We describe an experimental method for determining the contours of the menisci for objects with sizes in the range of millimeters to tens of micrometers. (iii) We present the results of Finite Element Modeling (FEM) of the shapes of the menisci along the faces of objects with finite lengths. We compare these shapes with the experimental contours, and explore how the contours of the menisci scale with the size of the objects. (iv) We construct interaction potentials for pairs of objects of finite sizes (here, hexagonal plates).

Results and Discussion

Analytical Solutions of the Laplace Equation for Two Infinitely Long Faces. One of the few geometries for which the Laplace equation can be solved analytically is that of two infinitely long faces of either identical (hydrophobic—hydrophobic or hydrophilic—hydrophilic) or different (hydrophobic—hydrophilic) wettability. The solutions of the Laplace equation for these simple cases provide a basis for establishing how the capillary and gravitational energies contribute to the energy of interaction, and for studying how the contours of the menisci change as two faces are brought into proximity; they can guide thinking about more complex geometries, where the Laplace equation cannot be solved analytically.

The nonlinear, one-dimensional form of Laplace equation is given in eq 1:

$$\frac{d^2h}{dx^2} = \frac{\Delta \rho gh - \Delta P_0}{\gamma}$$

Here, $\gamma$ (J m$^{-2}$) is the interfacial free energy of the PFD/H$_2$O interface, $h$ (m) is the height of the meniscus at point $x$, $\Delta \rho$ (kg m$^{-3}$) is the difference in density between the PFD and water, $g$ (m s$^{-2}$) is the acceleration due to gravity, and $\Delta P_0$ (Pa) is the difference in pressure across the interface (a value that is zero for open systems). The values for the parameters for the system with PFD and water are as follows: $\gamma = 0.05$ J m$^{-2}$, $\Delta \rho = \rho_{\text{PFD}} - \rho_{\text{water}} = 1910$ kg m$^{-3} - 1000$ kg m$^{-3} = 910$ kg m$^{-3}$, and $g = 9.81$ m s$^{-2}$. For contact angles, $\theta$ (°), between 55° and 125°, the Laplace equation can be linearized, and with $\Delta P_0 = 0$ it simplifies to $d^2h/dx^2 = (h/x_c)^2$, where $x_c = (\gamma/\Delta \rho g)^{1/2}$ is the so-called critical length ($x_c \approx 2.4$ mm for PFD/water interface).

The boundary conditions used to solve the Laplace equation for two interacting, infinitely long, parallel, hydrophobic faces are (i) the menisci are pinned at the top of the faces, $h(x = r, x = -r) = t$, and (ii) the slope of the meniscus halfway between the faces is zero, $d[h/dx]_{x=0} = 0$ (Figure 2). To satisfy the first boundary condition, the thickness of the objects must be smaller than the maximum height that the PFD reaches in wetting the faces ($\approx 1.4$ mm); in our experiments $t \approx 1.2$ mm. Equation 2 gives the solution to the Laplace equation for two interacting hydrophobic faces:

$$h(x) = t \cosh(x/x_c)/\cosh(r/x_c)$$

From this equation, the energy of the system can be calculated. The total energy, $E'(t)$ (J), is given by the sum of the capillary, $E'_C(t)$, and gravitational, $E'_G(t)$, energy terms (the prime denotes absolute energies; energies corrected for the reference state do not have primes). The capillary energy is proportional to the area of the interface, $E'_C = \gamma A(t)$, and the gravitational energy is $E'_G = \Delta \rho g s \rho_{\text{PFD}} - \rho_{\text{water}} = 1910$ kg m$^{-3} - 1000$ kg m$^{-3} = 910$ kg m$^{-3}$, and $g = 9.81$ m s$^{-2}$. For contact angles, $\theta$ (°), between 55° and 125°, the Laplace equation can be linearized, and with $\Delta P_0 = 0$ it simplifies to $d^2h/dx^2 = (h/x_c)^2$, where $x_c = (\gamma/\Delta \rho g)^{1/2}$ is the so-called critical length ($x_c \approx 2.4$ mm for PFD/water interface).

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The equations describing the interaction of two negative menisci (i.e., menisci on hydrophilic faces) depressed by \( t' \) below the level of the interface can be obtained from (2) and (4) by a simple symmetry argument. Because a positive meniscus rising by \( t = t' \) above the level of the interface is symmetric (with respect to the plane of the interface) to a negative meniscus depressed by \( t' \), the capillary energy of a pair of negative menisci is given by (2), and the gravitational energy is the opposite of (4). As the result, the total energy of interaction between two negative menisci on infinite faces (Figure 3b, right) does not decrease monotonically with decreasing separation, but rather shows a minimum at separation \( 2x_c \), and then increases to \( \sim 0 \) at zero separation. Also, at short separations, the absolute value of energy is roughly only a half of that for two positive menisci. Therefore, we expect the interactions between negative menisci to be weaker than between positive menisci.

The boundary conditions used to solve the Laplace equation for a hydrophobic face with a meniscus of height \( t_1 \) (m) interacting with a hydrophilic face with a meniscus of height \( t_2 \) (m) are that the menisci are pinned at the edges of the faces, \( h(x = -r) = t_2, h(x = r) = t_1 \). Here, we assume that the objects are thinner (in the vertical direction) than the maximum heights of the menisci on the faces. The solution to the contours of the menisci is given by eq 5:

\[
h(x) = \left\{ \begin{array}{ll} 
 e^{x/k_c} (t_1 - t_2 e^{2x/k_c}) + \\
 e^{-x/k_c} (t_2 - t_1 e^{2x/k_c}) \end{array} \right\} / (e^{x/k_c} - e^{-3x/k_c}) 
\] (5)

The graphs of \( E_G \) and \( E_C \) versus separation (Figure 4) show that the capillary energy is always positive, and that the gravitational energy is nonpositive (equal to zero for \( t_1 = t_2 \), and negative otherwise). Since the absolute value of \( E_G \) is smaller than \( E_C \), the total energy is always positive. Therefore, the interaction between a positive and a negative meniscus is repulsive.

**Finite Element Modeling (FEM).** The solutions for interacting infinite faces capture the essential features of lateral capillary interactions, but are clearly insufficient to give quantitative predictions for self-assembling systems of more complex

**Figure 3.** The graphs in (a) give the total, capillary, and gravitational energies for two positive (left) and two negative (right) menisci on infinitely long faces as a function of the separation between the faces. The positive menisci rise 1.2 mm above the level of the PFD/H\(_2\)O interface, and the negative menisci descend 1.2 mm below the level of the interface. The curves in (b) give the total energies for three different values of elevation (depression) of the menisci above (below) the level of the interface.

**Figure 4.** The capillary, gravitational, and total energies of interaction of a positive meniscus interacting with a negative meniscus on infinitely long faces; the positive meniscus rises \( t_1 = 1.2 \) mm above the level of the interface, and the negative meniscus is depressed by \( t_2 = 0 \) mm – 1.2 mm with respect to the level of the interface.
geometries (for instance, the hexagons). In the absence of analytical solutions for such geometries, we resorted to numerical methods, and used a Finite Element Modeling (FEM) software package called Surface Evolver (here, referred to simply as Evolver\textsuperscript{25}). The program allows liquid surfaces (or interfaces between liquids) of arbitrary geometries to be defined; surface properties (i.e., wettabilities) of the walls enclosing the liquids can also be specified. Evolver reports total energies (that is, the sum of capillary, gravitational, and constraint energies), and surface areas of the liquid surface (or liquid—liquid interface).

(i) Measured and Calculated Contours of the Menisci along Faces of Millimeter-Sized Objects. We measured and calculated the contours of the menisci along the hydrophobic faces for [1,4] and [1,2,3,4,5,6] hexagons that were 5.4 mm in diameter (2.75 mm wide on a face). The numbers in parentheses refer to the location of the hydrophobic faces; the [1,4] hexagon has two edges on opposite sides of the hexagon (and the bottom hexagonal face) that are hydrophobic and the [1,2,3,4,5,6] hexagon has every face (including top and bottom hexagonal faces) hydrophobic. We choose these hexagons for two reasons. (i) They had a symmetric distribution of vertical capillary forces and floated parallel to the PFD/H\textsubscript{2}O interface. (ii) The [1,4] hexagon displayed the contours of menisci on an isolated hydrophobic face and the [1,2,3,4,5,6] hexagon showed the contours of menisci on adjacent hydrophobic faces.

Experimental Measurements of the Shape of Menisci. We found it challenging to image the menisci at an unperturbed PFD/H\textsubscript{2}O interface. We unsuccessfully tried three optical methods: (i) in Nomarski-mode spectroscopy, the optical depth was too small to produce images of \textasciitilde1 mm-thick objects, (ii) a method based on monitoring the reflection of a laser beam from the interface suffered from low accuracy and low signal-to-noise ratio, (iii) diffraction-based designs, in which the interface was used as a “mirror” had very low resolution. All mechanical measurements (e.g., variation of profilometry) disrupted the interface. Ultimately, we settled on a method in which we first solidified the aqueous layer by adding gelatin to it, and then made replicas of the interface by casting and curing a UV-curable polymer (NOA) against the gelatin. These replicas were easy to handle and could be made of millimeter- and sub-millimeter-sized objects; they were easy to image using both optical and SEM microscopies.

First, we verified that the NOA replica faithfully reproduced the patterns imprinted in gelatin. To this end, we fabricated a replica of a poly(dimethylsiloxane) (PDMS) stamp with micron-sized features in gelatin (Figure 5). The gelatin was removed from the PDMS, blown dry with N\textsubscript{2}, and NOA was cured on its surface. The gelatin was removed with warm water, and the NOA replica was inspected by optical and confocal microscopies. The NOA replica was a copy of the PDMS stamp. From this result we conclude that we can reliably transfer a bas-relief pattern using gelatin.

Second, we quantified the differences between the menisci at the PFD/water and PFD/water—gelatin interfaces. We found that the decay length (\(x_c = h(x)/h(x = \text{face}) = 1/e\)) for menisci at the PFD/H\textsubscript{2}O interface was 1.2 mm, while that for menisci replicated in gelatin is slightly lower (1.1 mm). This change in decay length is not surprising, since gelatin lowers the interfacial free energy of the PFD/water interface.\textsuperscript{3}

The measured and calculated contours of the positive menisci on the [1,4] and [1,2,3,4,5,6] hexagons were similar (Figures 6 and 7). FEM reproduces several key aspects of the contours of the menisci. (i) The menisci do not wet the entire face of the hexagons; instead, they dewet from the edges and from sharp corners.\textsuperscript{26} Dewetting is more pronounced on the [1,4] hexagons than on the [1,2,3,4,5,6] hexagons. (ii) The value for the measured decay length was 1.1 mm (and 1.2 mm at the interface without gelatin) and the calculated value was 1.4 mm. (iii) The measured and calculated contours of the menisci can be overlaid; the contours are similar along the edges of the menisci. From these observations, we conclude that for millimeter-sized objects FEM calculations reproduce the measured menisci sufficiently accurately that we can use them to guide our analysis.

(ii) The Decay Lengths of the Menisci Scale with the Size of the Objects. One aspect of the menisci that could easily be compared is the value for the decay length as the width of the face is varied. The Laplace equation predicts a decay length of 2.4 mm for an infinitely long face. For a face of finite length, we expect the decay length to differ from this value because of the edge effects. As the width of the hydrophobic face decreases, the ratio of perimeter length to surface area becomes larger and edge effects more important. We, therefore, expect the decay...
length of the menisci to deviate (in fact, to decrease) from that for an infinitely long slab.

We had four experimental values for the decay length of the menisci: on a hydrophobic face 180 µm wide, the decay length was 70 µm (measured on an NOA replica); on a hydrophobic patch 1.6 mm wide, the decay length was 0.7 mm (measured on an NOA replica); on a hydrophobic face 2.7 mm wide the decay length was 1.2 mm (measured at the PFD/H2O interface); on a hydrophobic face 16 cm wide, the decay length was 1.7 mm (measured at the PFD/H2O interface). The value for the decay lengths on the menisci that were modeled by the FEM agreed with the trends of the measured menisci (Figure 8). The FEM could not reliably model the contours of objects that were less than a few millimeters wide (the triangulation of the surface was not sufficiently precise). The decay length for the 2.7 mm wide face was modeled well using FEM (1.4 mm). The decay lengths for wider faces approached the experimental value of 2.4 mm, albeit more rapidly than in experiment.

(iii) Modeling the Contours of the Menisci on Sub-Millimeter-Sized Objects. We wished to determine whether the menisci on sub-millimeter-sized objects were similar to those on millimeter-sized objects. Specifically, we wished to know how the contours and decay lengths of the menisci scaled as the dimensions of the objects were changed. Two positive menisci were measured by the gelatin method on hexagonal faces: (i) a meniscus on a 180 µm wide hydrophobic patch on a 300 µm wide face, (ii) a meniscus on a 1.6 mm wide hydrophobic patch on a 2.7 mm wide face; this meniscus was also modeled using FEM.

Figure 6. The contours of the menisci on the [1,4] hexagons. The (a) measured and (b) modeled side views of the menisci. The front views of the (c) measured and (d) modeled menisci.

Figure 7. The contours of the menisci on the [1,2,3,4,5,6] hexagons. The (a) measured and (b) modeled side views of the menisci from a face that is 0.6 mm thick. The (c) measured and (d) modeled front views of the menisci on the same faces. Notice PFD dewetting from the faces near the corners.

Figure 8. The dependence of the decay lengths of the FEM-modeled menisci on the 1.2 mm thick [1,2,3,4,5,6] hexagons as a function of face width of these hexagons.

Figure 9 shows the contours of these menisci. The decay lengths were 70 µm (on the 180 µm hydrophobic patch), 700 µm (on the 1.6 mm hydrophobic patch measured experimentally), and 750 µm (on the 1.6 mm hydrophobic patch modeled...
by the FEM). The ratio of the decay length to the width of the face was approximately 0.4 for all three hexagons (the ratio for the decay length—1.2 mm—from a 2.7 mm wide hydrophobic face was also 0.4).

We make two observations from these measurements: (i) the menisci on the sub-millimeter-sized objects are indistinguishable (up to a scale factor) from those on millimeter-sized objects; in other words, the menisci scale linearly with the size of the objects. (ii) The capillary forces per unit length of the interacting faces are constant for millimeter- and sub-millimeter-sized objects; the capillary forces scale linearly with the size of the objects.

(iv) The Energy of Interaction between Two Menisci from FEM. We calculated the energy of interaction for two hexagons that are 5.4 mm in diameter and 2.4 mm thick, half recessed into PFD. We modeled the energy of interaction for two [1,2,3,4,5,6] hexagons; two [0] hexagons ([0] hexagons have all hydrophilic faces), and for a [1,2,3,4,5,6] hexagon interacting with a [0] hexagon. The hexagons are initially at a separation of 20 mm, with the closest faces between the hexagons parallel to one another. They are moved toward one another until they come into contact; the capillary and gravitational energies are determined for the system (Figure 10).

The system of two interacting [1,2,3,4,5,6] hexagons has an energy profile similar to that of a pair of positive menisci on infinite faces. There are three interesting aspects of this energy profile: (i) The total energy is always decreasing. (ii) The gravitational energy at a maximum and slightly positive at a separation of ~3 mm. (iii) The capillary energy contributes

Figure 9. The contours of the front and side views of the menisci on a 1.6 mm wide hydrophobic patch on a 2.7 mm wide face; (a) is a schematic diagram indicating hydrophobic and hydrophilic regions on the face; (b) and (e) are optical micrographs; (c) and (f) are the modeled surfaces. The SEM image of a 180 μm hydrophobic patch on a 300 μm wide face is given in (d).

Figure 10. The capillary, gravitational, and total energies modeled by FEM for two interacting menisci on (a) two [1,2,3,4,5,6] hexagons, (b) two [0] hexagons, and (c) a [1,2,3,4,5,6] hexagon interacting with a [0] hexagon. The maximum rise for a positive meniscus, and the maximum depression of a negative meniscus were set at 1.2 mm. The faces of the hexagons were 2.75 mm wide. The inserts in (a) and (b) show aggregates formed by [1,2,3,4,5,6] and by [0] hexagons, respectively.
roughly three times as much to the total energy as the gravitational energy at short separations. We note that our interpretation of FEM results at very short separations (notably, when the faces are in contact), is still incomplete—indeed, the hexagons do not come into contact, but rather leave a thin layer of liquid between them (cf., the insert in Figure 10a). We do not attempt to explain this behavior here. We include the energies at zero separation only to show that, in principle, they continue the trends calculated for larger separations.

The energetics of interaction between two [0] hexagons is qualitatively similar to that of two negative menisci on infinite faces. The capillary energy decreases monotonically with decreasing distance; the gravitational energy is negative at large separations, and positive at short separations. The profile of the capillary energy is the same as (and the profile of the gravitational energy is the negative of) that for two interacting [1,2,3,4,5,6] hexagons (the menisci on [0] hexagons and the menisci on [1,2,3,4,5,6] hexagons are symmetric to each other with respect to the plane of the interface). The total energy has a minimum at \( \sim 3 \) mm and, the energies at short separations are less favorable (less negative) than for two interacting [1,2,3,4,5,6] hexagons. On the basis of these results, we expect the aggregates of [0] hexagons to be less stable than those of [1,2,3,4,5,6] hexagons. This prediction is validated by experiment (see inserts in Figure 10): the [1,2,3,4,5,6] hexagons form stable, close-packed arrays, while [0] hexagons result in loosely held (stable, but dissociated under agitation), less-ordered aggregates.

The interaction between a [1,2,3,4,5,6] hexagon and a [0] hexagon is repulsive at all separations (Figure 10c). The capillary energy is at a maximum at a separation of 2 mm, and decreases at shorter separations. The gravitational energy is negative and has a minimum at a separation of 4 mm; it becomes positive at shorter separations. Note that the gravitational energy is not zero, as it was for two infinite faces of analogous surface properties and equal thicknesses. The complicated form of energy profiles results from dewetting of the faces at short distances (Figure 11c). When the hexagons are close to each other, the interface reduces the energetic cost of high surface curvature by dewetting from the faces (we assume that the objects cannot tilt with respect to the interface; for free-floating objects this assumption is incorrect\(^1\), but holds for objects that have solid support below them\(^{15-17}\). As the result, the capillary energy decreases, but so does the area of the faces covered by the energetically favorable phase (that is, PFD dewets from hydrophobic faces, and water dewets from hydrophilic faces). The decrease in the wetted area on the faces results in nonzero values of gravitational energies\(^2\) (cf., Figure 4).

**Scaling to Smaller Sizes.** Since the menisci scale linearly with the size of the objects down to sub-millimeter range (\( \sim 500 \) \( \mu m \) in diameter), the energy profiles for sub-millimeter objects can be derived from those for millimeter-size objects by appropriate scaling. For smaller sizes, however, the situation is more complicated: gravitational effects in small objects are insignificant, and capillarity dominates the physics of the problem. For instance, a small [1,2,3,4,5,6] hexagon is completely drawn into the interface by the capillary forces (Figure 12), so that (unlike its millimeter-size analog) it does not form any menisci. A way to form menisci on small objects appears to be that of competing hydrophobic and hydrophilic faces against one another. Thus, a small [1,3,5] hexagon does form menisci. The theoretical analysis of capillary phenomena in systems of small floating particles would therefore require taking into account the variations in their elevation (or depression) with respect to the interface. On the other hand, menisci on small objects that are supported by a solid substrate\(^{15-17}\) might well be described by the methods outlined in this paper.

**Conclusions**

This work includes experimental and computational methods to determine the contours of the menisci for millimeter- and sub-millimeter-scale hexagonal plates floating at a PFD/water interface. Finite Element Modeling seems to be a reliable tool for predicting the shapes of the menisci, and for quantifying the lateral capillary interactions.

The FEM method (i) allows constructing energy profiles for geometries of floating objects for which the Laplace equation is not soluble analytically, and (ii) accounts for the effects that are usually not included in the analytical solutions for simple geometries (e.g., partial dewetting of the faces of hexagonal plates). The results we derived for parallel, infinite faces can give a qualitative understanding of capillary interactions in simple MESA systems (e.g., for interacting [1,2,3,4,5,6] hexagons), but they might be misleading (if not altogether wrong), when more complex assemblies are considered (cf., the energy profiles for a [0] hexagon interacting with a [1,2,3,4,5,6] hexagon). The flexibility of the FEM method makes it suitable to study such assemblies.

Our experimental results establish that the shapes of the menisci scale linearly with size down to submillimeter range. This observation makes it possible to derive energy profiles for small interacting particles by appropriate scaling of the energy profiles for large pieces. It also means that MESA systems at
millimeter and submillimeter scales should show qualitatively similar behaviors. On the other hand, we do not expect our calculations to apply to objects and phenomena on the micrometer (or smaller) scales, where the macroscopic description seems to be incomplete—even in the assemblies of millimeter-sized objects, some small-scale effects are not accounted for by our method (e.g., the effect of hexagons forming arrays, but not coming into full contact). Sinking of small objects with respect to the interface is another phenomenon not accounted for by our calculations.

This study supports the understanding of capillary interactions required for “rational design” of MESA systems based on capillarity. An interesting and so far unexplored result from the work is the existence of minima and maxima in the calculated energy profiles (Figure 10). The existence of these extrema suggests possibilities of designing—by selectively tuning either the capillary or gravitational components of energy—systems in which objects will assemble at a distance (at a minimum of energy), or will have to overcome an energy barrier (an energy maximum) to come into contact. The strategy of “competing” capillary and gravitational energies may lead to new types of assemblies that would have practical implications (e.g., open lattices for diffractive elements or long-wave band gap materials).

Experimental Section

Measurement of the Contours of the Menisci. The millimeter-sized objects (hexagonal plates ~1.4 mm high and ~5.4 mm on a diagonal, with selected patterns of hydrophobic and hydrophilic edges) were fabricated according to procedures described previously. They were placed at the PFD/H2O interface using tweezers (30 mL of PFD and 30 mL of H2O in a cylindrical container 6.5 cm in diameter). The dish was placed in a cold room at 4 °C. Water containing gelatin (gelatin type A from porcine skin, 300 bloom, purchased from Sigma) at a concentration of 9 g of gelatin per 100 mL of water was heated to 90 °C to dissolve the gelatin. Approximately 30 mL of the water/gelatin was slowly added to the container with the objects and the gelatin was allowed to gel at room temperature for 3 h. The solid gelatin gel was manually removed and was blown dry with N2 for 10 s. A UV-curable prepolymer (Norland Optical Adhesive 68; NOA) was poured onto the gelatin. The NOA was cured under UV light for 1 h, and the gelatin was removed from the NOA under warm water. The NOA was a replica of the PFD layer and the menisci.

The micrometer-sized objects were fabricated according to procedures outlined in other work. The contours of the menisci were cast into gelatin and NOA using the same methods as the millimeter-sized objects.

The Finite Element Program Used to Model the Contours of the Menisci. The FEM program “Surface Evolver” was obtained from a public domain (www.geometry.umn.edu/software/download/evolver.html) of the Geometry Center at the University of Minnesota. In this program, the surface is modeled as a union of triangles. After the geometry of the problem is specified in an input datafile, Evolver evolves the surface toward the minimal energy by the steepest descent method. Evolver can handle an arbitrary topology of the liquid surface, and allows calculation of gravitational and capillary energies.

The geometries of hexagonal (one or two) plates floating at an interface were coded in the input file. The extent of the interface was made large enough (25 hexagon diameters) that the boundary effects were minimized. Boundary conditions (limits and continuity), and parameters describing the system (sizes of the plates [5.4 mm in diameter], separation between the hexagons [1–20 mm], density of the fluids [PFD, 1910 kg m⁻³ ; H2O, 1000 kg m⁻³] and surface tension of the PFD/water interface [0.05 J m⁻²]) were specified.

The surface properties of the PDMS edge faces (hydrophobicity or hydrophilicity) were calibrated by the following procedure: (i) a long, thin slab (10 cm high and 20 cm × 5 mm in cross section) with all faces identical (hydrophobic or hydrophilic) and perpendicular to the PFD/water interface was coded into the program; (ii) a value of the parameter specifying surface properties of the faces (in Evolver, called tension, T [dimensionless]) was chosen (0.73), and the liquid surface was minimized; (iii) the extent of vertical rise or depression of the interface along the longer face of the rectangle was compared to the experimental value measured for a PDMS slab of the same dimensions (1.4 mm rise for hydrophobic faces, and 1.4 mm depression for hydrophilic faces); (iv) the parameter specifying the surface properties was adjusted, and steps (ii) and (iii) were repeated until the rise (or depression) of the interface matched the experimental value. The optimized values of T for hydrophobic and hydrophilic faces were subsequently used in other calculations.

Surfaces were triangulated until the average size of a facet (a triangle) was ~0.05 mm². To ensure proper convergence during minimization, triangles of area less than 0.005 mm² were deleted. Each surface was minimized until the variation in energy from step to step was less than 10⁻¹² J. Gravitational energy and surface area of the interface were stored during minimization. All calculations were performed on an Octane 1000 UNIX station. A full minimization of a surface required ~2 h of CPU time.

Capillary energies were calculated from the surface areas reported by Evolver by multiplying them by the value of the surface tension of the PFD/water interface. Gravitational energies were obtained by subtracting capillary energies from the total energies reported by the program.

Supporting Information Available: A template of Evolver input file for modeling a pair of interaction hexagons is included in the Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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References and Notes

(10) For background reading on FEM, see: Hughes, J. R. The Finite Element Methodol. Linear Static and Dynamic Finite Analysis; Prentice


(21) For the physical properties of PDMS, see: Publication No. 10-177-87, Dow Corning, Midland, MI.


(24) In calculating the gravitational energy, we assume that the level of the interface far from the interacting objects is constant for all separations \( r \) of the objects. This assumption is justified if the extent of the interface \((\sim r_{ref})\) is large compared to \( r \); if the level of the liquid between the interacting faces changes by \( \Delta h \), the level of the interface moves only by \(-\Delta h(r/2r_{ref})\) changing the gravitational energy of the system by \(-\Delta g \Delta h^2/(\pi^2 r_{ref}r^2) - 2\). For \( r_{ref} \gg r \), this contribution to the gravitational energy of the system is negligible.

(25) Surface Evolver was developed by K. Brakke; for a review, see Brakke, K. Exp. Math. 1992, 1, 141–152. Evolver is available free of charge from a public domain (www.geom.umn.edu/software/download/evolver.html) of the Geometry Center at the University of Minnesota.


(27) The gravitational energy reported by Evolver includes the energy of wetting of the PDMS faces—if the wetting of the faces is constant while the hexagons are brought into contact (as for positive–positive or negative–negative interactions), this energy does not change with respect to the reference state, and Evolver’s gravitational energy has its true meaning. If, however, the wetted area on the faces changes, the changes in gravitational energy reflect both the true gravitational effects, and the dewetting effects.