Mesoscale Self-Assembly: Capillary Interactions When Positive and Negative Menisci Have Similar Amplitudes

Daniel B. Wolfe, Aaron Snead, Chengde Mao, Ned B. Bowden, and George M. Whitesides*

Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge, Massachusetts 02138

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This paper describes the two-dimensional self-assembly of hexagonal plates at the interface between perfluorodecalin and water. The plates were prepared with five different permutations of hydrophobic and hydrophilic faces. The shapes and amplitudes of the menisci that form on the faces of the plates determine the magnitude of the lateral capillary forces through which they interact. The amplitudes of the menisci also influence—through their out-of-plane components—the position and orientation of the plate relative to the plane of the liquid−liquid interface. In these experiments, the plates were made of poly(dimethylsiloxane) (PDMS) (ρ = 1.05 g/cm^3) containing aluminum oxide (ρ = 4.00 g/cm^3); this dopant adjusted the density of the plates, the extent to which they sank into the liquid−liquid interface, and thus the structure of their menisci. The plates studied had densities of 1.05 to 1.86 g/cm^3. This work complements previous papers (Bowden, N.; Choi I. S.; Grzybowski, B. A.; Whitesides, G. M. *J. Am. Chem. Soc.* **1999**, *121*, 5373. Bowden, N.; Oliver, S. R. J.; Whitesides, G. M. *J. Phys. Chem. B* **2000**, *104*, 2714.) that examined the assembly of hexagonal plates with densities at the extremes of the range studied. By following the structures of the aggregates formed at intermediate densities, it is possible to observe the way in which the self-assembling system transitions from an aggregate of one structure to that of another. The results from these studies are relevant to the design of micrometer-sized plates capable of self-assembly.

Introduction

This paper extends our studies of the self-assembly of millimeter-sized hexagonal plates floating at the interface between two immiscible liquids[1,2]—one hydrophobic and one hydrophilic—to include the assemblies that form when the amplitude of the positive (+) menisci (those that rise above the mean plane of the interface) at the edges of the plates and the negative (−) menisci (those that sink below the mean plane of the interface) are approximately equal. The amplitudes and the signs of the menisci are determined by the density of the plates and the properties of their edges (Figure 1). We formed the assemblies at the interface of H_2O (ρ = 1.00 g/cm^3) and perfluorodecalin (PFD; ρ = 1.91 g/cm^3). The plates were fabricated of poly(dimethylsiloxane) (PDMS; ρ = 1.05 g/cm^3) containing alumina powder (Al_2O_3; ρ = 4.00 g/cm^3). We controlled the extent to which the hexagonal plates sank into the interface by adding alumina to adjust their density within the range spanning those of the two liquids or by changing the density of the aqueous phase.

This work had three motivations. First, we wished to study the aggregation of the millimeter-sized hexagonal plates under conditions such that the system could be used as a model system to identify designs of micrometer-sized plates that should aggregate into ordered structures. In small (micrometer-sized) plates, the ratio of buoyancy forces to capillary forces is smaller (by a factor of ~10^4)[3] than that for millimeter-sized plates of the same density. These small plates thus behave substantially differently than millimeter-sized plates.[4] For micrometer-sized plates, the position of the plate relative to the plane of the liquid−liquid interface is dictated by the vertical capillary forces generated by the menisci and is relatively independent of the density of the solid or liquid components of the system. *Competition* between the vertical capillary forces is thus required for menisci to form on the faces of the micrometer-sized plates. This fact constrains the useful configurations of these plates to those with both hydrophilic and hydrophobic faces. The information learned from the studies described in this paper of millimeter-sized plates having both (+) and (−) menisci should extend to the assemblies of micrometer-sized plates with the same configurations of menisci and aid in the identification of patterns of hydrophobic and hydrophilic faces on micrometer-sized plates that will aggregate into well-ordered structures. Second, we wished to understand self-assembly under conditions in which both (+) and (−) menisci were important in determining the interactions between plates to design plates that self-assembled in predictable ways in other regimes of densities than those studied previously. Our studies of self-assembly based on capillary interactions have been restricted to conditions in which the amplitudes of the (+) and the (−) menisci were substantially different, and interactions involving only one type of meniscus dominated self-assembly.[1,2] These studies have provided a solid understanding of the capillary interactions and the types of assemblies that result from interactions among either (+) or (−) menisci but have not rationalized the more complicated assemblies that form when both (+) and (−) menisci contribute to self-assembly. Third, we wished to use these data to determine the most

* To whom correspondence may be addressed: telephone, (617) 495 9430; fax, (617) 495 9857; e-mail, gwhitesides@gmwgroup.harvard.edu.

(1) Bowden, N.; Choi, I. S.; Grzybowski, B. A.; Whitesides, G. M. *J. Am. Chem. Soc.* **1999**, *121*, 5373−5391.

(2) Bowden, N.; Oliver, S. R. J.; Whitesides, G. M. *J. Phys. Chem. B* **2000**, *104*, 2714−2724.

(3) The magnitude of the buoyancy forces scales with the volume of the plates. The volume of a 10-mm-sized plate is roughly 10^4 larger than that of a 100-μm-sized plate. (See ref 2.)

(4) Bowden, N.; Arias, F.; Deng, T.; Whitesides, G. M. *Langmuir* **2001**, *17*, 1757−1765.

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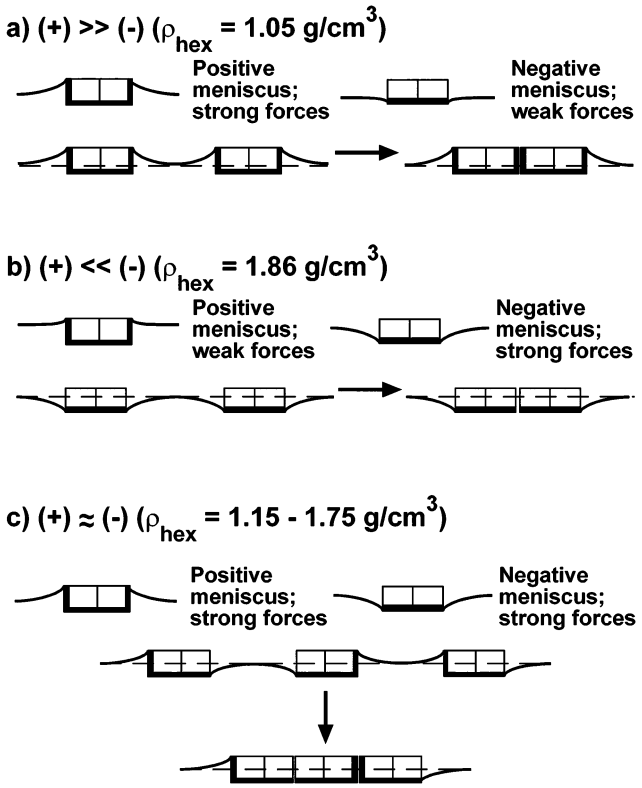


Figure 1. Diagram sketching the cross-sectional shape of the menisci as a function of placement of the hexagonal plate with respect to the liquid−liquid interface. (a) The hexagonal plates of low density have large (+) menisci and are attracted by capillary interactions between these (+) menisci. (b) The hexagonal plates of high density have large (−) menisci and interact through them. (c) When the amplitudes of (+) menisci and (−) menisci are equal, the situation is more complicated: the hexagonal plates interact by capillary interactions involving both types of menisci. The thick lines and dark faces signify the hydrophobic faces; the thin lines signify the hydrophilic faces. The dashed lines correspond to the level of the PFD/H_2O interface in the absence of perturbations by the hexagonal plates.

favorable conditions for the assembly of hexagonal plates into more complex, ordered systems.

Figure 2 shows the contours (qualitatively) of the (+) and the (−) menisci along the edges of a millimeter-sized hexagonal plate with alternating hydrophobic and hydrophilic edges. For simple geometries (e.g., infinite slabs) these contours can be described by the Laplace equation; we do not have analytical solutions for the more complex hexagonal plates.[5−9] The interaction of the menisci on the faces of separate plates results in the attraction between the plates. As the plates move along the interface toward each other, the area of the fluid−fluid interface decreases; this movement decreases the surface free energy of the interface and lowers the energy of the system.[6,8,10] We refer to the forces acting on plates at the interface as "capillary forces".[1,2,4,8,10,11] The plates aggregate based on a simple rule, "like menisci attract, and unlike menisci repel".[1,2]

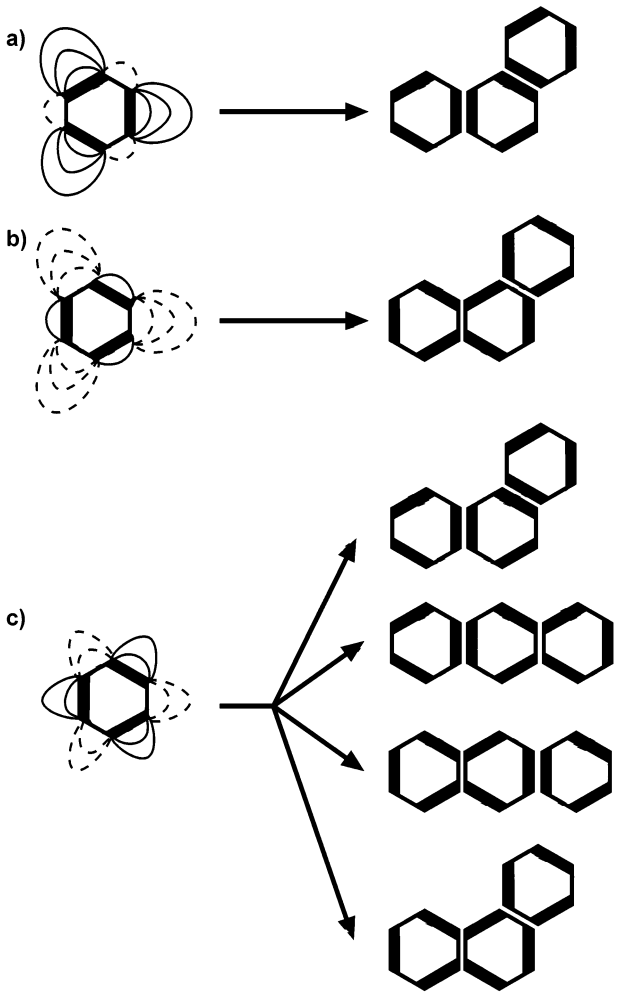


Figure 2. Contours of menisci for a hexagonal plate with its faces composed of an alternating hydrophobic−hydrophilic configuration. The solid lines correspond to (+) menisci and the dashed lines correspond to (−) menisci. These contours are a topographic representation of the menisci and are estimated by observation (by eye). (a) Contours of menisci for a hexagon of low density ($\rho = 1.05$ g/cm^3) and an example of the expected pathway of assembly. (b) Contours of menisci for a hexagon of high density ($\rho = 1.86$ g/cm^3) and an example of the expected pathway of assembly. (c) Contours of menisci for a hexagon with equal (+) and (−) menisci, and examples of possible pathways for assembly.

The objective of this work was to study the assembly of hexagonal plates as a function of relative amplitudes of both (+) and (−) menisci to answer three questions: (1) At what value of the density (or over what range of values) does aggregation shift from assembly through (+) menisci to assembly through (−) menisci? (2) What are the structures that form when forces due to (+) menisci are comparable to those due to (−) menisci, and how do these structures compare to those observed when forces due to (+) menisci are much greater than those due to (−) menisci (or *vice versa*)? (3) Does the extent of order in the assemblies change as a function of the amplitude of the menisci?

Experimental Section

The details of the fabrication of the hexagonal plates have been described previously.[1,2,4] The primary difference between this procedure and our previous work was the amount of alumina powder (<10 μm; $\rho_{Al_2O_3} = 4.00$ g/cm^3) added to the PDMS to achieve densities between 1.05 g/cm^3—the density of PDMS—and 1.86

(5) Paunov, V. N.; Kralchevsky, P. A.; Denkov, N. D.; Nagayama, K. *J. Colloid Interface Sci.* **1993**, *157*, 100−112.
(6) Kralchevsky, P. A.; Paunov, V. N.; Denkov, N. D.; Ivanov, I. B.; Nagayama, K. *J. Colloid Interface Sci.* **1993**, *155*, 420−437.
(7) Kralchevsky, P. A.; Nagayama, K. *Langmuir* **1994**, *10*, 23−36.
(8) Gao, C. *Appl. Phys. Lett.* **1997**, *71*, 1801−1803.
(9) Fortes, M. A. *Can. J. Chem.* **1982**, *60*, 2889−2895.
(10) Chan, D. Y. C.; Henry, J. D., Jr.; White, L. R. *J. Colloid Interface Sci.* **1981**, *79*, 410−418.
(11) Grzybowski, B. A.; Bowden, N.; Arias, F.; Yang, H.; Whitesides, G. M. *J. Phys. Chem. B* **2001**, *105*, 404−412.

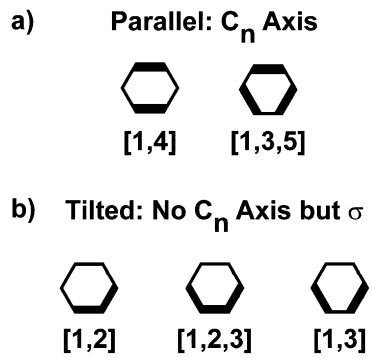


Figure 3. The configurations of hydrophobic and hydrophilic faces of the hexagonal plates studied. "Parallel" means the plates float with their horizontal surfaces parallel to the mean plane of the liquid−liquid interface; "tilted" means just that.

g/cm^3— the maximum density of the hexagonal plates studied.[12] We used a dark permanent marker to make stripes on the top of the hexagonal plates to denote the location of the hydrophobic faces. The markings were limited to the top to avoid changing the wettability of their faces. The surface of PDMS is hydrophobic. We exposed the PDMS to an oxygen plasma (5 min on a Harrick PDC-23G) to make the surface hydrophilic. We made hexagonal plates with specific combinations of hydrophobic and hydrophilic faces by protecting the hydrophobic faces from the oxygen plasma with a layer of undoped PDMS; the procedure has been described previously.[2]

The hexagonal plates were placed manually at the interface of H_2O and PFD in a crystallization dish (diameter 14.5 cm) and were agitated on an orbital shaker (r_g = 13 mm) at a fixed frequency of rotation ($\omega = \sim 1.2$ s^{-1});[13] the experiments were conducted as described previously.[1,2] Each assembly was made up of approximately 80 hexagonal plates of one density. The tilt angles for the nonsymmetrical, hexagonal plates were measured at the interface by methods described in the Supporting Information.

Results and Discussion

We chose to use hexagonal plates with the configurations of hydrophobic and hydrophilic faces shown in Figure 3 as a representative subset of the 14 combinations that are possible.[1,2] This work uses the same convention of labeling used in our previous papers.[1,2,4,14] We chose two hexagonal plates with a center of symmetry about an axis perpendicular to the plane of the plate; the [1,4] configuration has C_2 symmetry and the [1,3,5] configuration has C_3 symmetry. The plates with a C_n axis of symmetry float with their planes parallel to the mean plane of the interface. Plates without a C_n axis of symmetry tilt relative to the mean plane of the interface (see Table 1 in the Supporting Information).[1,2]

Analysis of the Data. The results presented in Figures5−12 are representative of the aggregates formed with hexagonal plates of densities within the region of values stated in the respective discussion. The graphs in each of these figures plot the percentage of hydrophobic-hydrophobic (++), hydrophilic−hydrophilic (− −), and mixed (+−) capillary interactions in the aggregates versus the density of the hexagonal plates. The percentages were obtained by visually counting the number of occurrences of each type of interaction and then dividing each value by the total number of interactions counted (eq 1). We define the (+−) capillary bonds as shown in Figure 4 and identify them as one of two classes of bonding: mismatches and vertices. Each datum is from one experiment at each value of density studied.

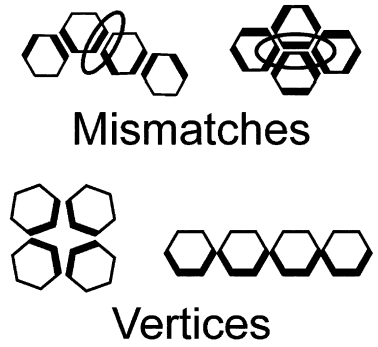


Figure 4. Diagram of the types of interactions that are defined as a mixture of capillary bonds (+−). The ovals highlight the mismatches within the structures.

$$\%_{(++)} = \frac{\sum(++)}{\sum((++) + (- -) + (+ -))} \times 100 \qquad (1)$$

The data for the (++) and (− −) interactions were fit using a sigmoidal equation. We chose to use a sigmoid because we expected the percentages of each type of interaction to reflect a kind of equilibrium and to vary smoothly across the spectrum of densities studied. The fit for the (+−) data was calculated as $\%_{(+-)} = 100\% - \%_{(++)} - \%_{(- -)}$. We conducted at least five runs for each configuration of faces and for each density of the hexagonal plates. We used these data to calculate the standard deviation for each type of interaction at each value of the density of the plates. The error bars on the graphs correspond to the standard deviation calculated for each datum.

The plots of the (++) and (− −) interactions have been separated from the plot of the (+−) interactions for the [1,3,5] hexagonal plates in parts g and h of Figure 5 to demonstrate clearly the method we used and to illustrate the quality of the data. These experiments show qualitative trends but are not such that they will support detailed quantitative analysis. The plots for the remaining configurations have been overlaid to save space.

Each run of a single configuration of the hexagonal plates, with densities at either extreme of the range studied, reproducibly aggregated into similar final structures. Hexagonal plates having densities in the middle of the region studied gave a range of structures. We consistently observed more structures at densities in the middle of the range than at the extremes. It would be necessary to use more vigorous agitation to distinguish kinetic and steady-state structures in these intermediate densities. Experimental details prevent vigorous agitation: agitation beyond $\omega = 1.4$ s^{-1} caused drops of PFD to detach and rest at the liquid−liquid interface; these drops disrupt the menisci and prevent assembly by capillary forces.

Table 1 summarizes the assemblies observed for each configuration of hydrophobic and hydrophilic faces of the hexagonal plates over the range of densities studied.

(12) The alumina did not substantially change the surface properties of the hexagonal plates. The contact angle of PFD under water on Al_2O_3-doped PDMS was measured to be ~30° higher than undoped PDMS at the maximum loading of Al_2O_3. This small difference in wetting did not appear to have an effect on the assemblies observed in our previous studies. (See ref 2.)

(13) We chose a fixed frequency of rotation for our studies because the initial results obtained from experiments with $\omega < 1.2$ s^{-1} yielded less ordered and less reproducible results than those carried out at higher rates of agitation.

(14) The hydrophobic faces are labeled as numbers in square brackets. For example, a [1,2] hexagonal plate has two adjacent hydrophobic faces and four hydrophilic faces. A [1,3,5] hexagonal plate has alternating hydrophobic and hydrophilic faces.

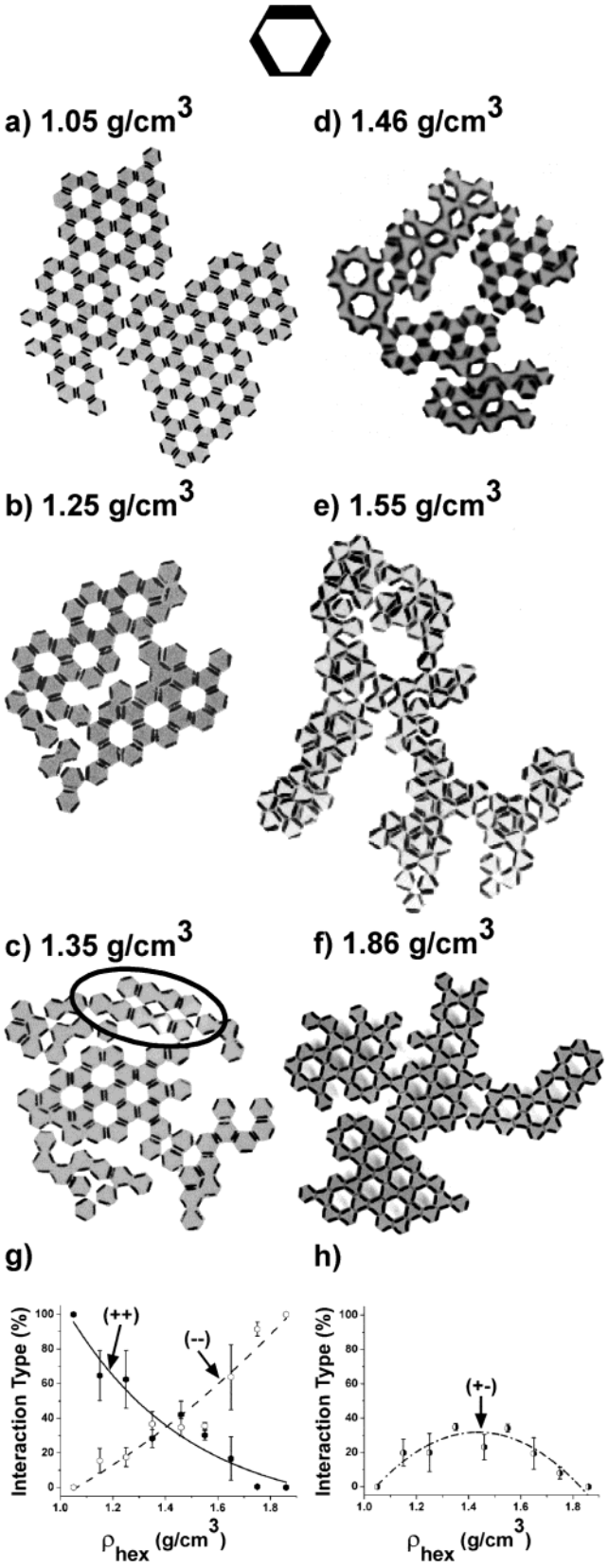


Figure 5. (a−f) Representative set of assemblies of [1,3,5] hexagonal plates. The density of the hexagonal plates is given in each figure. The circle in (c) highlights two lines formed in the assembly. (g and h) Plots of the percentage of the type of interaction versus the density of the hexagonal plates.

Hexagonal Plates with C_n Symmetry: [1,3,5] and [1,4] Hexagons (Figures 5 and 6). The hexagonal plates with C_n symmetry assembled into aggregates with the

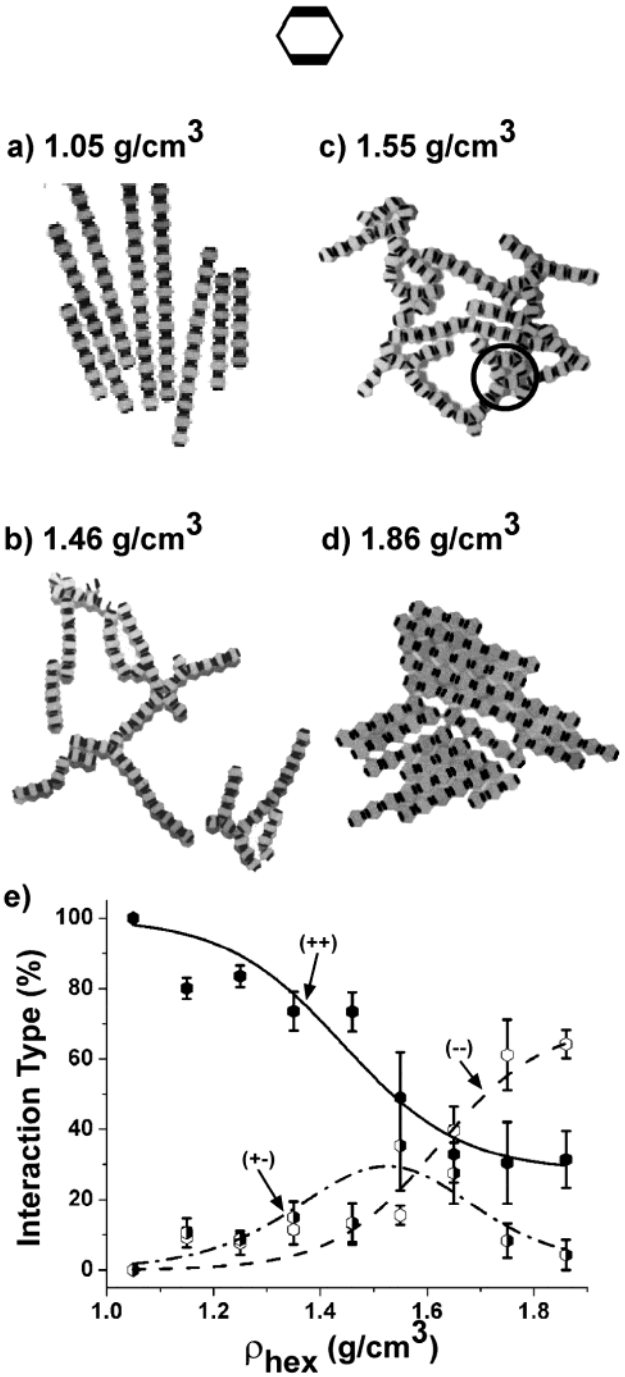


Figure 6. (a−d) Representative set of assemblies of [1,4] hexagonal plates. The density of the hexagonal plates is given in each figure. The circle in (c) highlights a trimer and tetramer formed in the assembly. (e) Plot of the percentage of the type of interaction versus the density of the hexagonal plates.

expected configurations. Ordered assemblies dominated at both extremes of the range of densities studied, and mixtures of structures were observed at intermediate densities. We attribute the fact that the density ($\rho_{\text{crossover}}$) of the plates at the crossover point between different types of bonding—i.e., the value of the density at which $\%_{(++)} \approx \%_{(- -)}$—is larger than the average of the densities of the two liquid phases ($\rho_{H_2O} = 1.00$; $\rho_{PFD} = 1.91$; $\rho_{avg} = 1.46$) to buoyancy forces. It is necessary, in this model, for the vertical capillary forces that pull the plate into the interface to be equal to the sum of the opposing vertical capillary *and* the buoyancy forces that push the plate out of the interface for the amplitude of the (+) menisci to

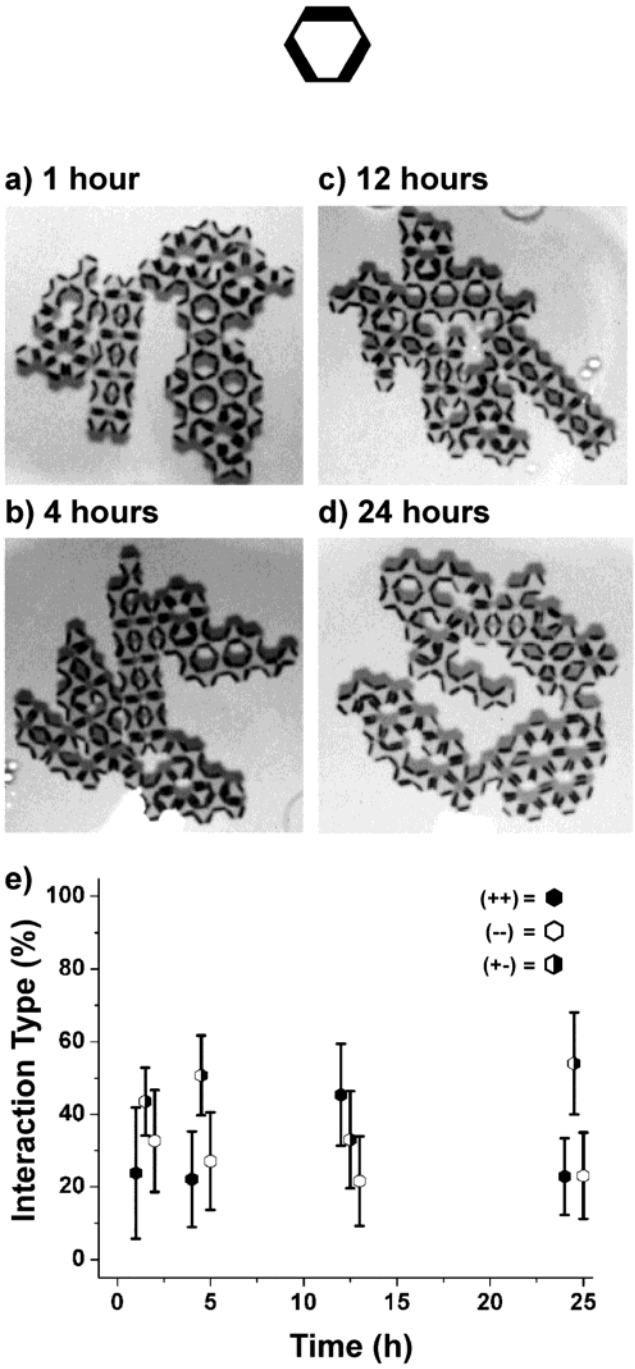


Figure 7. (a−d) Representative set of the assembly of [1,3,5] hexagonal plates with densities of 1.46 g/cm^3 agitated over 24 h. The length of time the assembly was agitated is given in each figure. (e) Plot of the percentage of the type of interaction versus time. For clarity, the data for the (− −) and (+−) interactions have been offset horizontally by 0.5 and 1 h, respectively.

equal that of the (−) menisci. This fact requires the density of the hexagonal plate to be slightly greater than that of ρ_{avg} for the amplitudes of the menisci to be equal in magnitude.

We believe an additional contributor to the location of the crossover point is the decrease in the vertical capillary forces that occurs when three or more plates are "bonded". This effect results from the fact that when the faces of the plates come into contact with one another, the menisci that were pinned on the bonded faces are eliminated. When three or more plates interact, the ratio of positive menisci to plates decreases. This change reduces the vertical

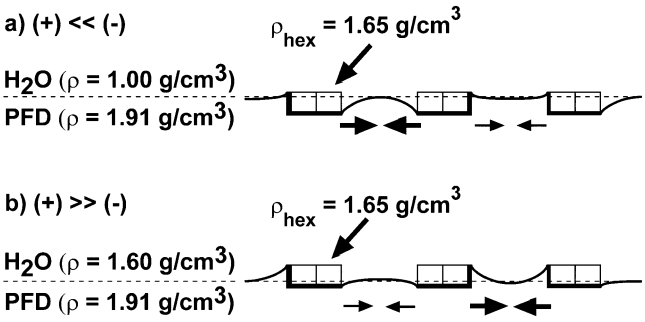


Figure 8. Contours of menisci for a hexagonal plate ($\rho = 1.65$ g/cm^3) at the interface of (a) pure water and PFD and (b) water doped with WO_4^{2-} and PFD. The arrows indicate the direction and the relative strength of the interactions between the menisci.

capillary force and results in the formation of larger menisci on the faces of the aggregated plates than those that are not aggregated. Higher densities than ρ_{avg} are, therefore, required for (− −) bonding to dominate the assemblies.

[1,3,5] Hexagonal Plates. We predicted, and observed, the formation of lines by the [1,3,5] hexagonal plates (Figure 5c). This configuration of the plate has hydrophobic and hydrophilic faces that are on opposite sides; thus, lines may form when (++) and (− −) bonds are allowed in the same assembly. The [1,3,5] plates underwent a more gradual transition from all (++) bonding to all (− −) bonding than the [1,4] plates (Figures 5g,h and 6e). This difference may be due to the fact that the number of possible configurations for the aggregate in which both (+) and (−) menisci can interact favorably is larger for the [1,3,5] plates than for the [1,4] plates.

Are Aggregates Kinetic or Steady-State Structures? We examined the distribution of capillary bonds in the assemblies of [1,3,5] hexagonal plates with a density of 1.46 g/cm^3 over 24 h with continuous agitation (Figure 7). There was no significant change after $t = 24$ h. This result suggested that we reached a steady-state (and perhaps minimum energy) structure in less than 1 h and that although the detailed structure of the aggregate pattern may change after that time, the percentages of the types of interactions do not change significantly.

Effect of Changing the Density of the Aqueous Phase. We also carried out experiments in which we held the density of the plates constant and changed the density of the aqueous phase.[15] In these experiments, we examined the assemblies formed by [1,3,5] hexagonal plates with a constant density of 1.65 g/cm^3 floating at the interface between an aqueous solution of sodium metatungstate and PFD; the density of the aqueous phase was adjusted from 1.00 to 1.60 g/cm^3.[16] This experiment was analogous to those described previously, in that the density of the aqueous layer affected the position of the plate at the interface of the two liquids, and hence affected the amplitudes of the (+) and the (−) menisci (Figure 8). These results (Figure 9) are similar to those shown in Figure 5.

Persistent Disorder in the Aggregates of the [1,4] Plates. The [1,4] hexagonal plates have a configuration of hydrophobic and hydrophilic faces that theoretically permit them to assemble into a close-packed lattice at intermediate values of density. We did not, however, observe the formation of a close-packed lattice by the [1,4]

(15) The experimental setup of the system was the same as that of the experiments involving the solid hexagonal plates.

(16) Mao, C.; Thalladi, V. R.; Wolfe, D. B.; Whitesides, S.; Whitesides, G. M. *J. Am. Chem. Soc.* **2002**, *124*, 14508−14509.

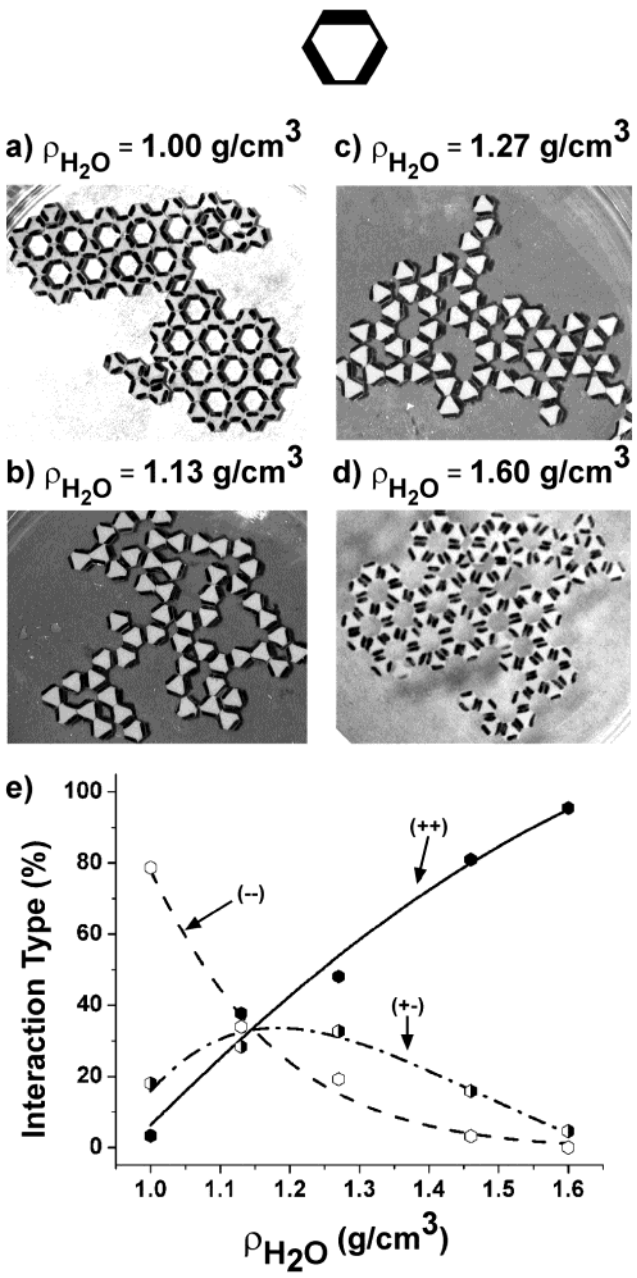


Figure 9. (a−d) Representative set of assemblies of [1,3,5] hexagonal plates ($\rho = 1.65$ g/cm^3) at the interface between PFD and an aqueous phase of varying density. The density of the aqueous phase is given in each figure. (e) Plot of the percentage of the interaction type versus the density of the aqueous phase. We did not perform a statistical analysis to obtain error bars for this experiment.

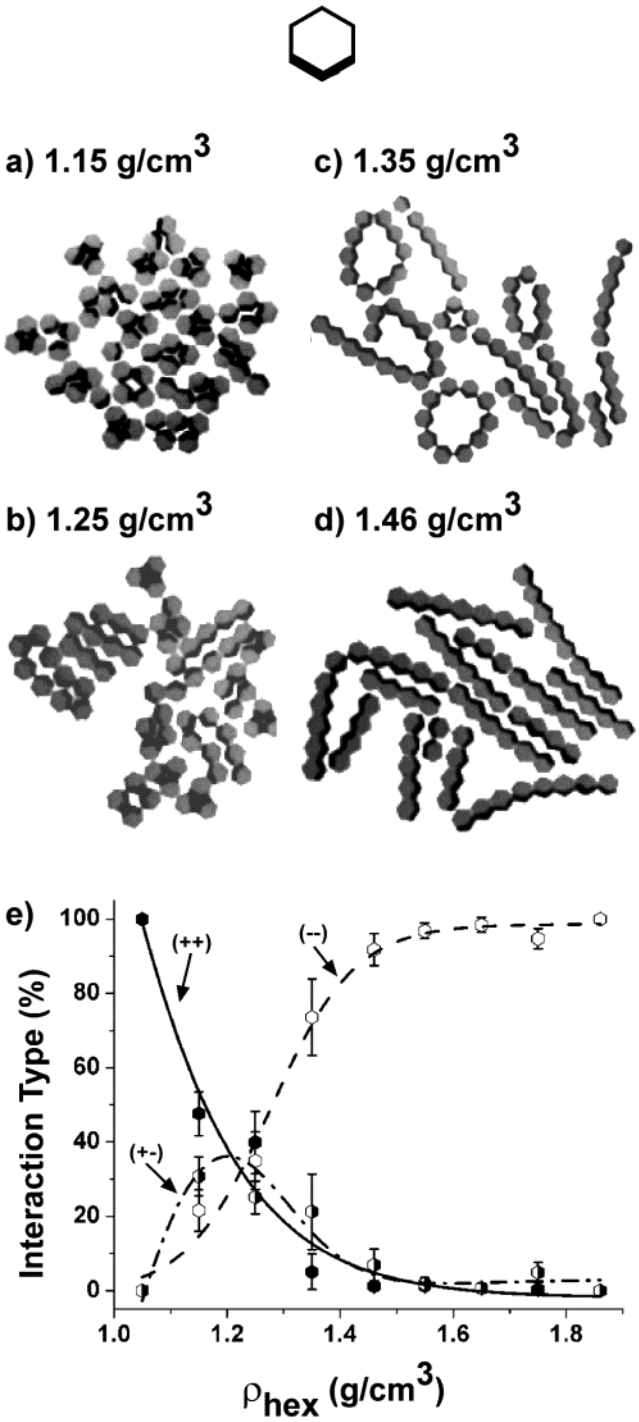


Figure 10. (a−d) Representative set of assemblies of [1,2] hexagonal plates. The density of the hexagonal plates is given in each figure. (e) Plot of the percentage of the type of interaction versus the density of the hexagonal plates.

plates with densities below 1.86 g/cm^3. Instead, the plates aggregated into disordered structures that included trimers and tetramers formed by interactions through the vertices of the plates (Figure 6c).

Hexagons without C_n Symmetry: [1,2], [1,3], and [1,2,3] Hexagonal Plates (Figures 10−12). The smallest value of $\rho_{crossover}$ ($\rho_{crossover[1,2]} = 1.15$ g/cm^3; $\rho_{crossover[1,3]} = 1.25$ g/cm^3; $\rho_{crossover[1,2,3]} = 1.35$ g/cm^3) for all of these configurations occurred at a value below that of ρ_{avg}. We suggest two possible origins of the difference between ρ_{avg} and $\rho_{crossover}$. First, the tilt of the hexagonal plate about the plane of the interface reduces the magnitude of the vertical component of the buoyancy forces that pushed the plate out of the interface. This factor only accounts for a small decrease (∼5%) in the vertical component of the contributing forces, since the maximum angle of tilt was ∼16°. Second, the tilt of the hexagonal plate allows a face or vertex to be completely buried in the interface. The amplitudes of the menisci decrease as the faces become buried in either liquid. The amplitudes of the positive menisci for the tilted hexagonal plates of low density (1.05 g/cm^3) are, therefore, smaller than those for the non-tilted hexagonal plates of the same density.

[1,2] Hexagonal Plates. The value of $\rho_{crossover}$ for these plates was the lowest among those studied. The vertical components of the capillary forces tilted these plates sharply with respect to the plane of the interface. This tilt

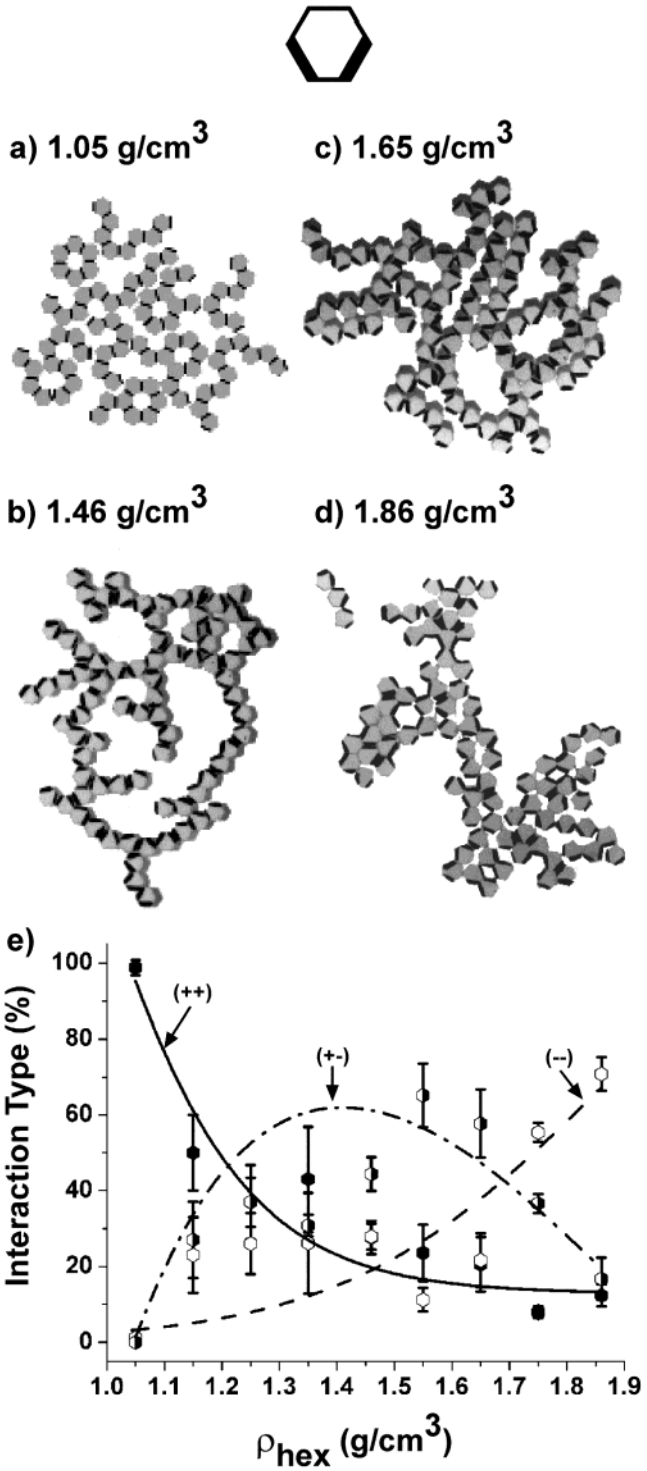


Figure 11. (a−d) Representative set of assemblies of [1,3] hexagonal plates. The density of the hexagonal plates is given in each figure. (e) Plot of the percentage of the type of interaction versus the density of the hexagonal plates.

significantly decreased the area of the hydrophobic faces that was in the water layer. The magnitudes of the positive menisci for the low-density, [1,2] hexagonal plates were thus the smallest of all the plates studied.

[1,2,3] Hexagonal Plates. The [1,2,3] hexagonal plates were the only configuration that showed a well-defined structure (lines of plates joined at their vertices) at intermediate densities. Bonding at the vertices was favored because both the positive and the negative menisci could interact simultaneously. The [1,2,3] configuration was one that we also studied using micrometer-sized

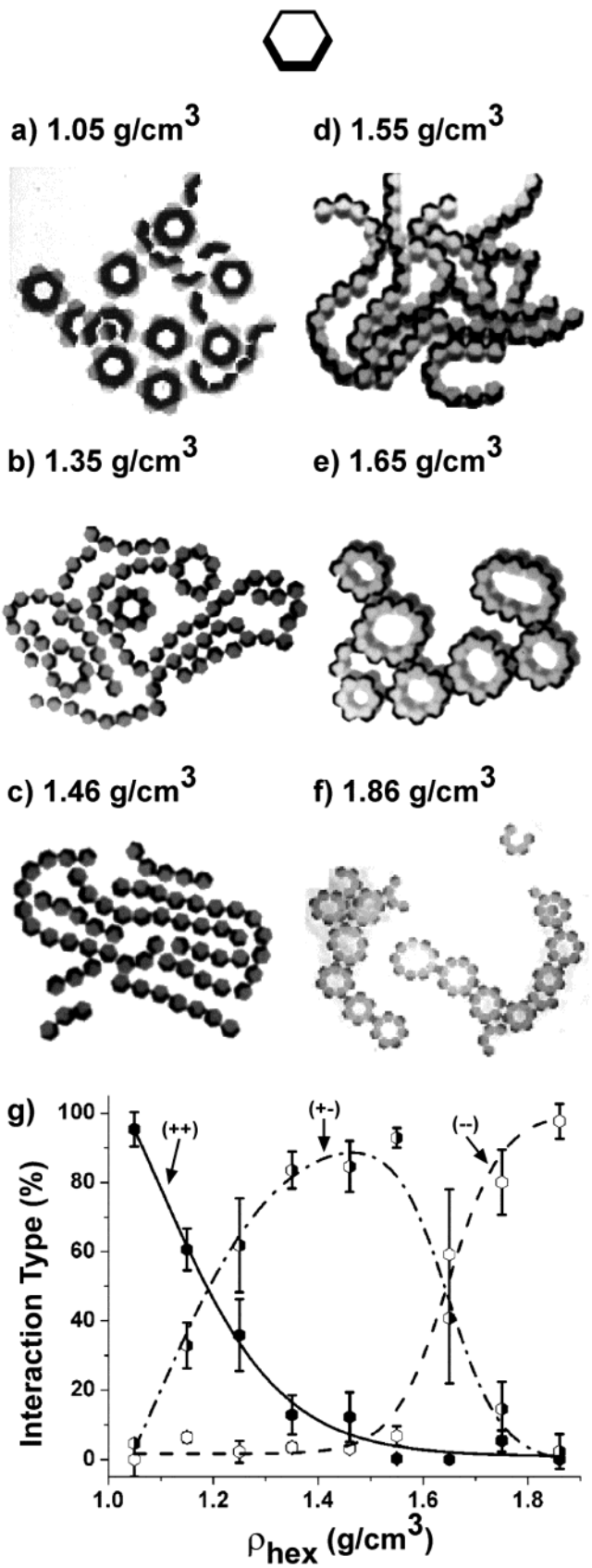
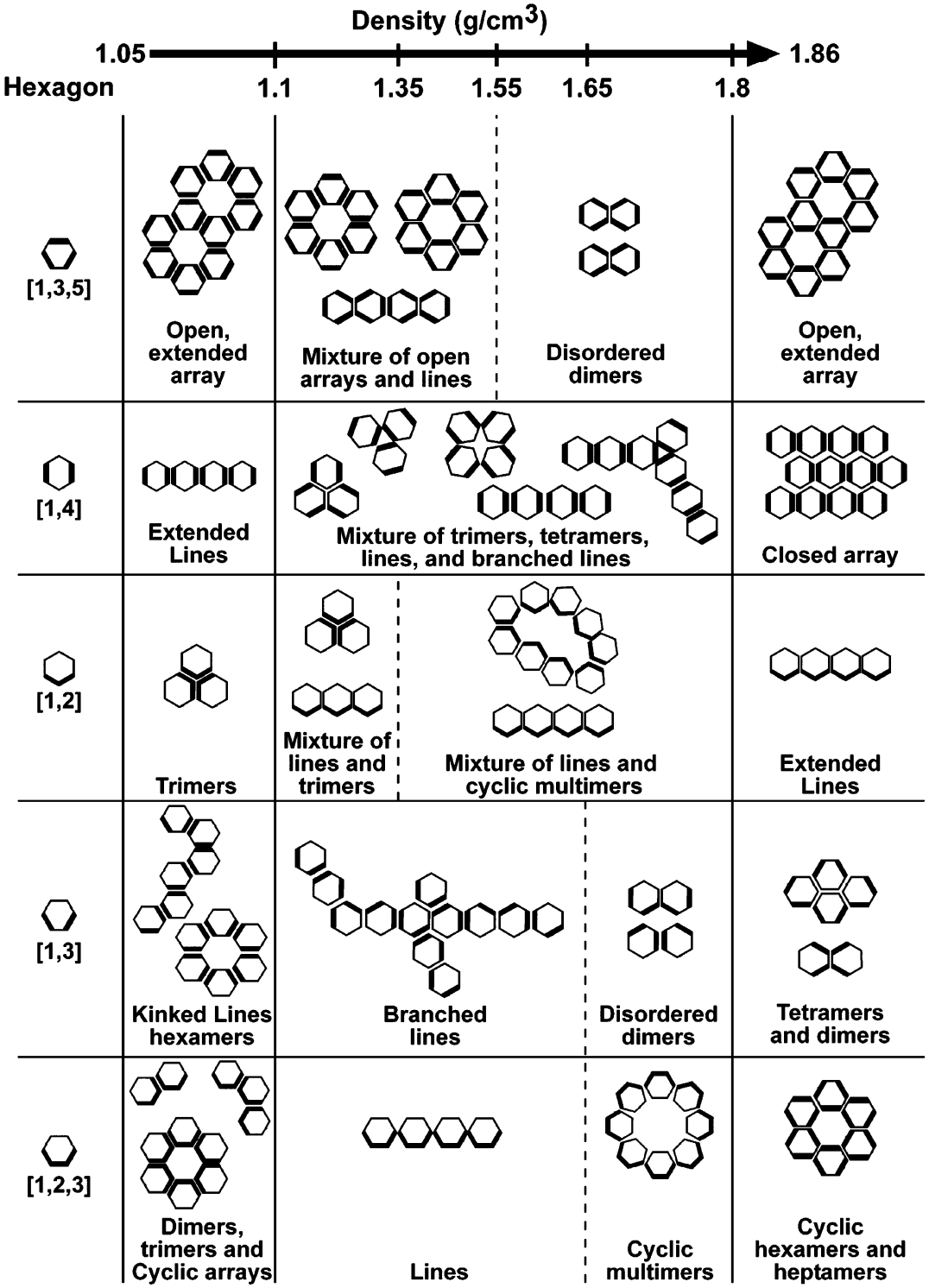


Figure 12. (a−f) Representative set of assemblies of [1,2,3] hexagonal plates. The density of the hexagonal plates is given in each figure. (g) Plot of the percentage of the type of interaction versus the density of the hexagonal plates.

hexagonal plates.[4] The structures that were observed with millimeter-sized plates of densities between 1.35 and 1.55 g/cm^3 were similar to those observed for the micrometer-

Table 1. Summary of the Structures Observed as a Function of the Density of the Hexagonal Plates



sized plates. Bonding through the vertices of the plates was preferred, and lines dominated the assemblies.

We hypothesize (but have not yet proved) that the behavior of millimeter-sized plates with densities in the intermediate range, and with competing (+) and (−) menisci, predicts the behavior of micrometer-sized plates with the same configuration of hydrophobic and hydrophilic faces. The assemblies formed from millimeter-sized plates with competing (−) and (+) menisci did not aggregate into ordered lattices for any of the configurations studied; we infer that disordered structures will also result for the corresponding micrometer-sized plates. We also suggest that adjusting the density of micrometer-sized plates will not succeed in generating ordered structures in which either (+) or (−) menisci dominate, because the vertical components of the capillary forces are greater by a factor of $\sim 10^4$ than the buoyancy and gravitational forces.[3] Different strategies are therefore required to obtain ordered assemblies of micrometer-sized plates.

Alternative Configurations and Shapes Yield Ordered Structures. An example of a configuration that should lead to ordered arrays of both millimeter- and micrometer-sized plates is an open plate with external faces hydrophilic and internal faces hydrophobic (or *vice*

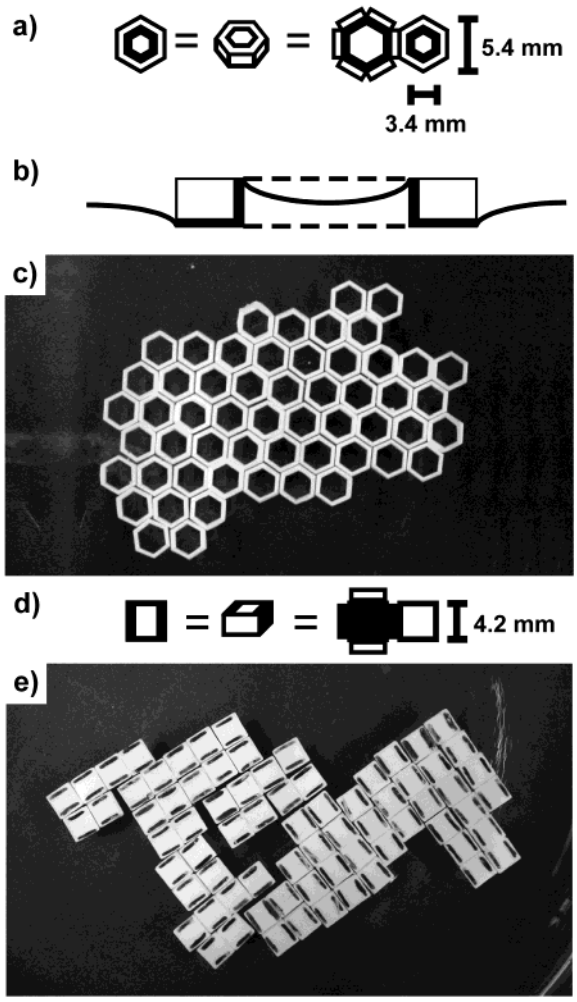


Figure 13. (a) Schematic diagram of an open hexagonal plate with hydrophilic external faces and hydrophobic internal faces. (b) Cross section of the plate depicted in (a) at the PFD/water interface. (c) Representative assembly of the plates described in (a). (d) Schematic diagram of [1,3] square plates. (e) Representative assembly of the plates described in (d). All of the plates used in these assemblies have densities of 1.46 g/cm^3. The dimensions of each plate are shown in the schematic diagrams.

versa: Figure 13a). This configuration has roughly equal lengths of (+) and (−) menisci and will be pulled into the interface even when buoyancy is unimportant (Figure 13b). It presents, however, one type of meniscus to the other plates and therefore should self-assemble cleanly. Millimeter-sized plates with this shape and configuration of hydrophobic and hydrophilic faces, and with densities of 1.46 g/cm^3, aggregated (as predicted) into a close-packed array (Figure 13c).[17]

We also investigated the assembly of millimeter-sized square plates; this shape can also form a close-packed lattice. We fabricated [1,3] square plates with densities of 1.46 g/cm^3 and assembled them in the same manner as the previous experiments (Figure 13d,e).[18] The plates assembled through both their hydrophobic and hydrophilic faces to form small rafts made up of 8−15 plates; these plates were separated from one another during the agitation but aggregated into larger mosaics in the absence of agitation.[19]

Conclusions

The construction of complex systems by self-assembly requires the ability to predict the outcome of the process of assembly. This work implies that for most configurations of (+) and (−) menisci, the most ordered structures result when one or the other meniscus dominates the interactions between plates. The formation of ordered close-packed lattices required new designs (Figure 13).

We believe that this work should enable millimeter-sized plates having densities approximately the average of the two immiscible fluid phases, and supported at the interface between these plates, to be used to predict the behavior of micrometer-sized plates. Since the millimeter-sized plates are easy to fabricate and manipulate, this correspondence permits the facile screening of configurations and shapes for plates and may allow the identification of those that will aggregate at the micrometer scale.

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Supporting Information Available: Tilt angles for the hexagonal plates of a given density. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) The fabrication of the open hexagonal plates with internal faces functionalized hydrophobic and external faces functionalized hydrophilic is described in the Supporting Information.

(18) The [1,3] square plates were fabricated the same way as the hexagonal plates except a square brass rod was used to make the original molds. See refs 1, 2, and 10 for a description of details.

(19) Some slight mismatches were observed after the agitation was stopped. These mismatches resulted from the fact that the magnitudes of the centripetal force and the inertia of the plate were much larger than those of the repulsive forces from the mismatched menisci. Slight agitation of the system easily broke up these mismatches but did not disturb the bonds formed through matched menisci.