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Self-assembly of surfactant liquid crystalline phases by Monte Carlo simulation

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Three-dimensional microstructures of surfactant–water–oil systems self-assemble in a Monte Carlo lattice model, as shown here. The microstructures that form depend on the volume ratios of oil, water, and surfactant, and on the length of the surfactant, and on the ratio R of the length of the oil-loving to the water-loving portion. For $R = 1$ we find lamellar phases when the surfactant is mixed with equal amounts of oil and water. The lamellar spacing increases as the surfactant concentration is lowered. In the presence of water only, as the surfactant concentration is lowered the microstructure evolves from lamellar to broken lamellar to cylinders to spheroids. This progression is found to be independent of lattice size for lattices as large as $40 \times 40 \times 40$. For $R = 3$, the progression seems to be replaced by a progression from lamellae to regular bicontinuous structures to cylinders, although we are not yet confident that this latter progression is independent of lattice size effects. The Monte Carlo technique can be used to study a wide variety of interesting phenomena, from micelle size and shape transitions to packing transitions and phase behavior to interfacial properties in the presence of surfactant.

I. INTRODUCTION

The problem of predicting the microstructure of surfactant-containing fluids based on the shape and flexibility of the constituent molecules and the intermolecular forces between them is an outstanding problem towards which many theories—starting with that of Hartley[1] in 1935—have been directed.[2] Since these theories inevitably involve specification of allowed microstructures, we believe that *direct computer simulation of microstructure of self-assembly*, with no *a priori* limitations on which microstructures are to be allowed, will prove invaluable in testing and enhancing the theories. In such a computer technique, the molecules are allowed to self-select a microstructure based only on the molecular properties and intermolecular interactions. The simulations could serve as a test of the theories in a way not possible by experiment, since in the simulations the molecular and intermolecular properties can be adjusted or simplified at will, and the resulting microstructure can be examined in all detail.

A Monte Carlo lattice technique that can simulate microstructures of idealized surfactant–oil–water solutions was announced in an earlier publication.[3] In this technique, oil and water molecules occupy single sites on the square or cubic lattice and surfactant molecules occupy a sequence of adjacent sites. By "adjacent" we here mean nearest neighbor or diagonal nearest neighbor sites. Thus each site has eight adjacent sites on the square lattice, 26 on the cubic lattice. The diagonal interactions are nonconventional, but speed up computations by allowing kink type motions to occur with the interchange of a single pair of units. The diagonal interactions also partially suppress the bias that exists in a regular lattice along the directions in which two sites can be adjacent. 26 directions of adjacency is a better approximation to a continuum than is six, for example.

Starting at infinite temperature to randomize the molecular configuration, the system is slowly "cooled," and mi-

crostructures spontaneously self–assemble at low temperatures. In the previous paper we presented evidence for the appearance of lamellar, cylindrical, and spheroidal microstructures[3] for systems containing varying amounts of oil, water, and the surfactant H_4T_4 that contains four water-loving "head" units and four oil-loving "tail" units, and occupies eight sites on the lattice. We tentatively suggested for this system the schematic phase diagram depicted in Fig. 1.

II. SIMULATION RESULTS

In this paper, we present additional simulations that qualitatively support the phase diagram for the symmetric surfactant H_4T_4 depicted in Fig. 1, and show the effects of molecular asymmetry by presenting some simulation results for H_2T_6. The phase behavior depicted in Fig. 1—which is
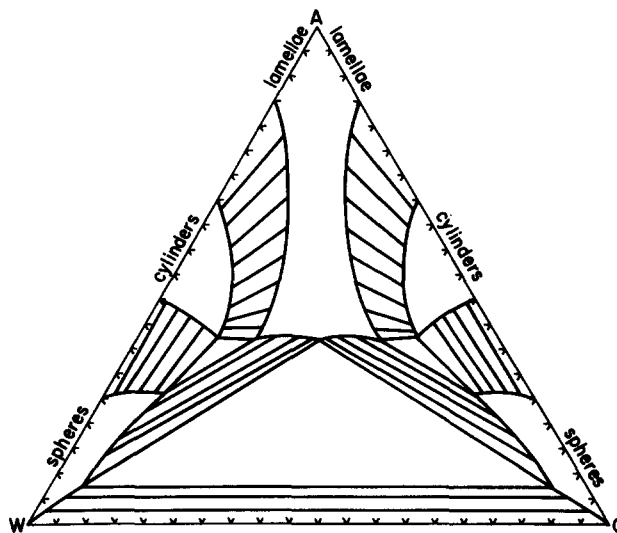

FIG. 1. Schematic phase diagram for H_4T_4 on the cubic lattice.

consistent with the results of the simulations reported here—is simpler than, but nevertheless bears many similarities to phase diagrams typical of real systems. A schematic summary of the phase behavior found in real surfactants is reproduced in Fig. 2 from Davis et al.[4]

The simulation method is described earlier. The shortest runs presented here required two days on an Alliant FX1 computer; the longest runs consumed five weeks of time on this machine. The compositions investigated can be grouped into two progressions. In progression I, the surfactant concentration C_A is systematically varied, holding the ratio of oil to water fixed at unity. Thus this progression runs down the center of the ternary diagram of Fig. 1. In progression II, the surfactant concentration is varied, with the oil concentration remaining at zero; this progression runs along the left side of the ternary diagram. Because of the symmetry of H_4T_4 and of the assumed intermolecular interactions, the microstructures along the right-hand side of the diagram for H_4T_4 are identical to those along the left-hand side.

The system is cooled from infinite temperature to inverse dimensionless temperature $w = 0.1538$ in steps tabulated in Table I. The critical value of w for oil and water to form a single phase is $w \approx 0.09$.

The numbers tabulated in Table I include failed attempts at movement. Progression I, which produces lamellar microstructures, requires fewer Monte Carlo steps than does progression II. The number of Monte Carlo steps required was determined empirically. Runs that are too short to equilibrate sufficiently produce irregular microstructures such as that depicted in Fig. 3. For the surfactants investigated here, runs of sufficient length always produced a well defined microstructure: either lamellae, interrupted lamellae, cylinders, or spheroids. The asymmetric surfactant produced a bicontinuous phase also. The large $30 \times 30 \times 30$ or $40 \times 40 \times 40$ systems require many more Monte Carlo steps than do the smaller lattices, both because the larger systems contain many more molecules, and because on the larger lattices molecules and structural information has to diffuse over larger distances. The quantity "T" in Table I, the number of Monte Carlo steps at $w = 0.1538$ for large lattices, is given case by case in Figs. 7, 14, and 15.

A. Symmetric surfactant H_4T_4

Figures 4–6 show the microstructures that develop on $20 \times 20 \times 20$ lattices for H_4T_4 in progression I; these microstructures contain equal amounts of oil and water. In these and most subsequent figures, two orthogonal slices of the system are shown. The system can be readily visualized by imagining that the two images shown are abutting faces of a cube. The dashed line in Fig. 3 and following figures demarks the volume actually simulated; the rest of the region is filled with periodic images of the simulated region. In Figs. 4–7, both tail and oil units are shown; in all other cases only
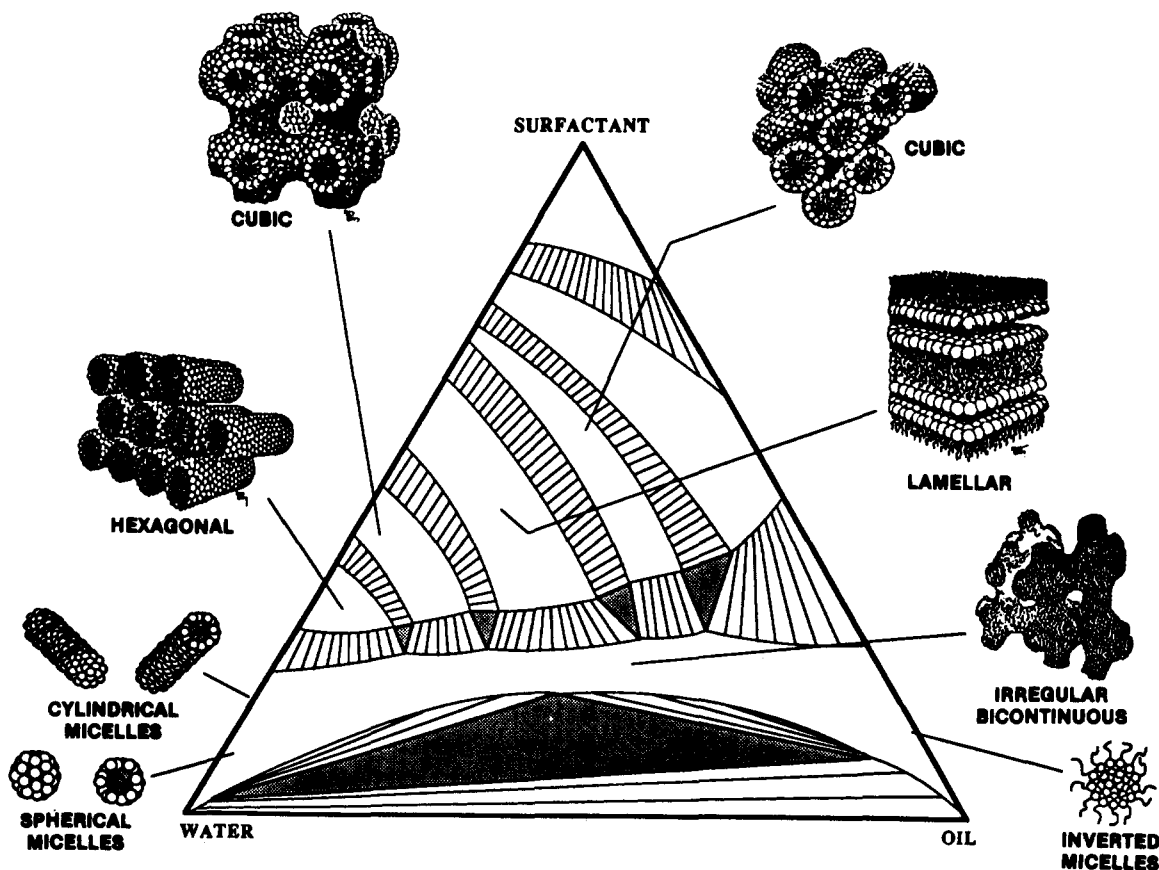

FIG. 2. Schematic diagram illustraing the phase behavior of real surfactant–oil–water systems. (from Davis et al., Ref. 4).
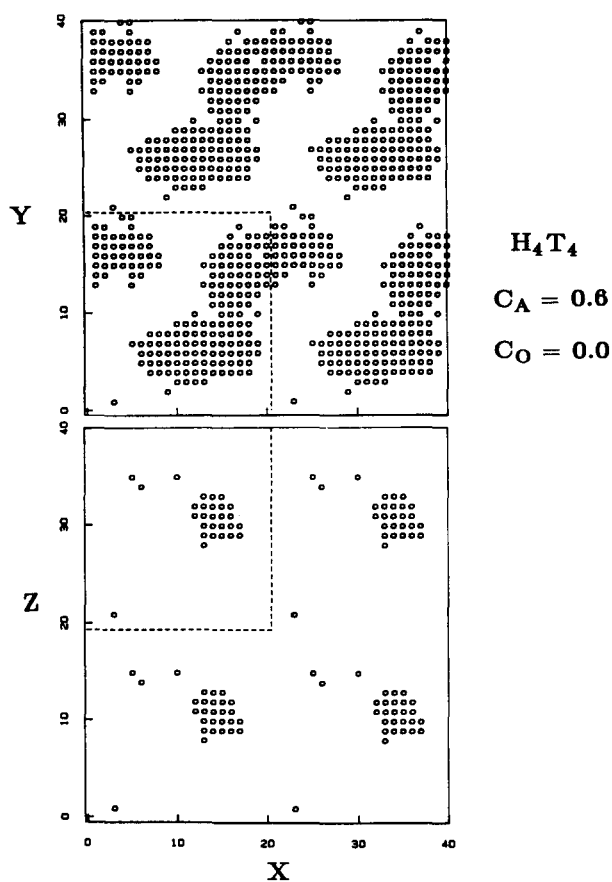
H_4T_4

$C_A = 0.6$

$C_O = 0.0$

FIG. 3. Perpendicular slices through $20 \times 20 \times 20$ lattice containing 60% H_4T_4, 0% oil, 40% water. Only the tail units are shown. For this system the run time was only 25% of that given in the third column of Table I. This was inadequate to obtain a regular structure. The result of a run four times as long as this is depicted in Fig. 10.

H_4T_4

$C_A = 0.8$

$C_O = 0.1$

FIG. 4. $20 \times 20 \times 20$ lattice containing 80% H_4T_4, 10% oil, 10% water. Tail units are designated by (O), oil units by (*).

the tail units are shown. By symmetry the microstructures in progression I must be invariant to interchange of oil for water and (simultaneously) heads for tails. The only known regular microstructures that possess such symmetry are lamellar and various bicontinuous structures. In the simulations we observe lamellar microstructures with the lamellar
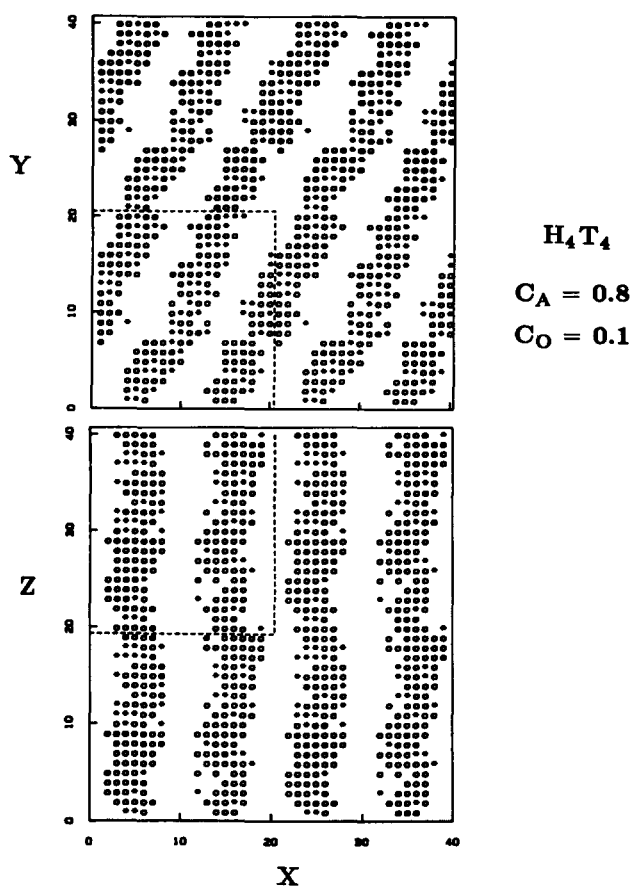
spacing increasing as the surfactant concentration drops from 80% to 30%. As reported earlier,[3] the pattern takes an orientation on the lattice that allows it to fit the desired periodicity into the given lattice size. We expect that if the surfactant concentration becomes low enough, the system will form three coexistent phases; see Fig. 1. Figure 7 shows,

TABLE I. Number of configurations sampled in each Monte Carlo run.

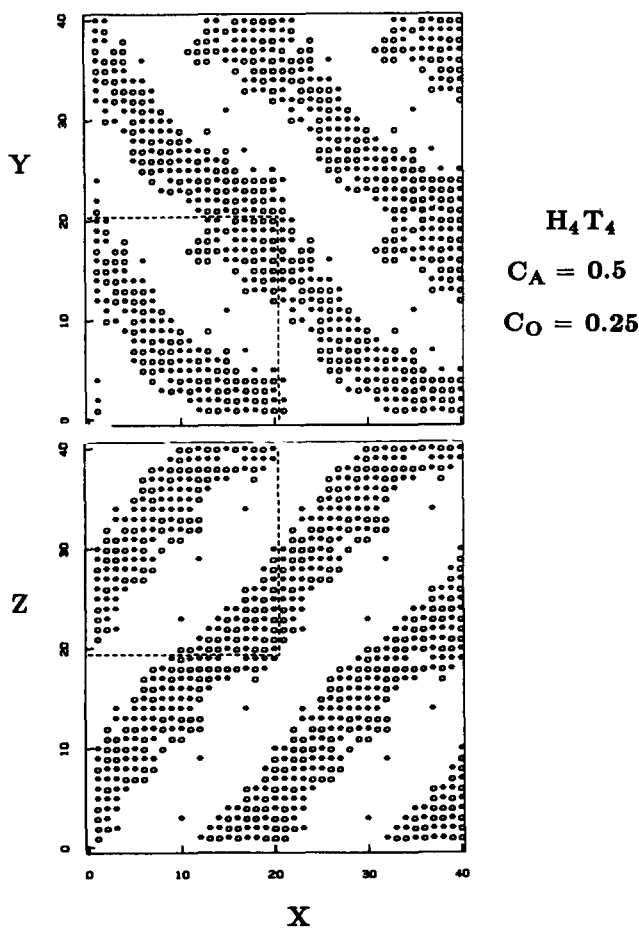|	$20 \times 20 \times 20$ lattices		
w	Progression I	Progression II	$30 \times 30 \times 30$ or $40 \times 40 \times 40$ lattices
0.0154			$0.10T$
0.0308	20 000 000	80 000 000	$0.10T$
0.0462			$0.10T$
0.0615	50 000 000	200 000 000	$0.10T$
0.0769			$0.25T$
0.0923	50 000 000	200 000 000	$0.25T$
0.1077			$0.5T$
0.1231	100 000 000	400 000 000	$0.5T$
0.1308			T
0.1385	200 000 000	800 000 000	T
0.1462			T
0.1538	200 000 000	800 000 000	T
total	620 000 000	2 480 000 000	$5.9T$

FIG. 5. $20 \times 20 \times 20$ lattice containing 50% H_4T_4, 25% oil, 25% water. Tail units are designated by (O), oil units by (*).

however, that lamellar structures are obtained when C_A is as low as 30%, even on a $30 \times 30 \times 30$ lattice.

It has been hypothesized that some surfactant systems ought to display irregular bicontinuous structures for oil/water ratios near unity when the surfactant concentration is reduced to values near those at which multiphases appear.[5] Lamellar phases in this region are to be expected when the surfactant-laden interface between water and oil domains of the microstructure is rigid and not susceptible to thermal distortions that would bend it enough to produce the curved surfaces required for bicontinuous structures. It is known empirically that the addition of "cosurfactants"—usually consisting of short surfactant or alcohol molecules—is required in surfactant–oil–water mixtures if undesirable high-viscosity liquid crystalline structures, such as the lamellar phase observed in our simulations, are to be avoided. In future simulations, it is hoped that we can compute bending energies of surfactant–laden interfaces, and examine the effects of added small amphiphiles such as H_1T_1.

Figures 8—13 show the microstructures of $20 \times 20 \times 20$ systems containing H_4T_4 and water with no oil (progression II). As the concentration of surfactant decreases, the microstructure evolves from broken lamellae at 80%–70% surfactant to arrays of cylinders at 60%–50% to arrays of spheroids at 40%–30% surfactant. The spacing of the broken lamellae at 80% surfactant concentration in progression II is
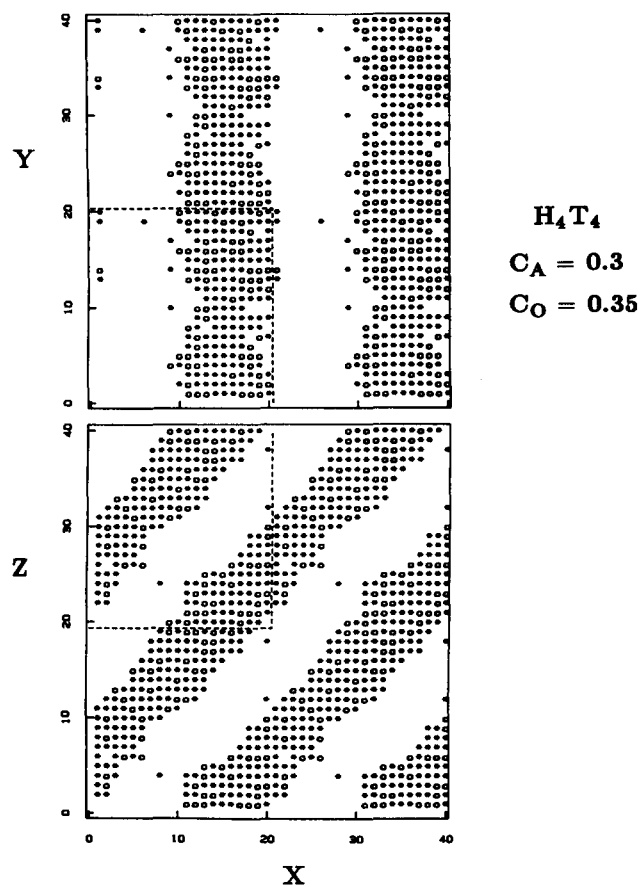

FIG. 6. $20 \times 20 \times 20$ lattice containing 30% H_4T_4, 35% oil, 35% water. Tail units are designated by (O), oil units by (*).
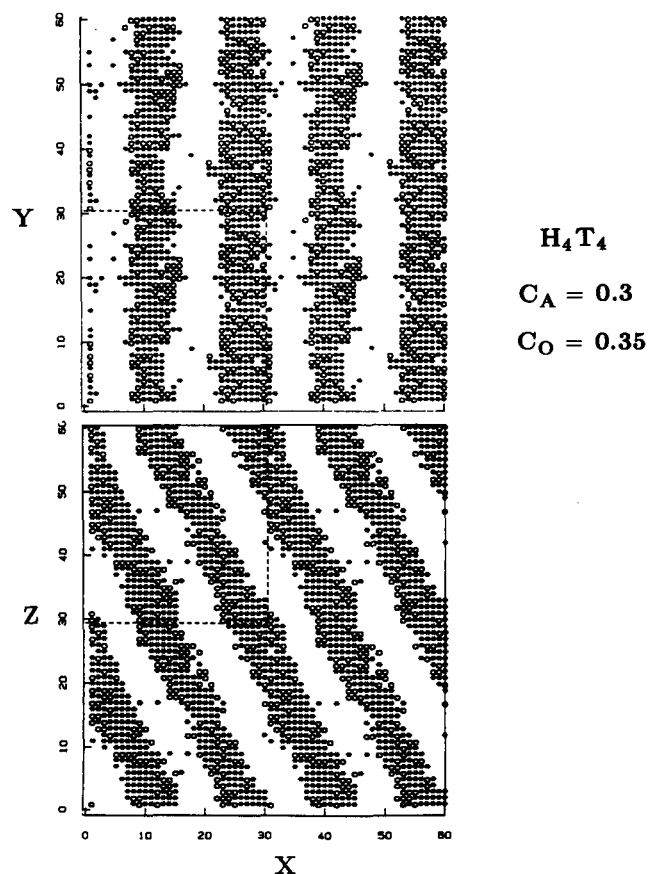

FIG. 7. $30 \times 30 \times 30$ lattice containing 30% H_4T_4, 35% oil, 35% water; T in Table I equals 0.8×10^9. Tail units are designated by (O), oil units by (*).

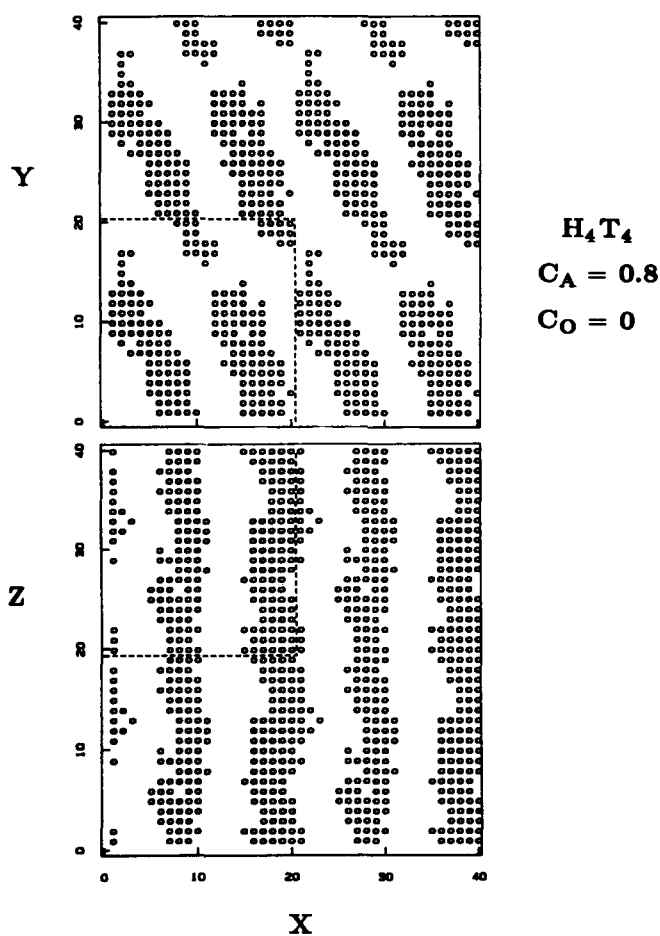H_4T_4

$C_A = 0.8$

$C_O = 0$

FIG. 8. $20 \times 20 \times 20$ lattice containing 80% H_4T_4, 0% oil, 20% water. This run was twice as long as the other runs of progression II for $20 \times 20 \times 20$ systems.

the same as that of the lamellae at 80% surfactant concentration in progression I; compare Figs. 4 and 8. As C_A decreases in progression II, the spacing increases between broken lamellae in Figs. 8 and 9, between cylinders in Figs. 10 and 11, and between spheres in Figs. 12 and 13. Although for the small systems studied here compromise structures such as the broken lamellae seen in Figs. 8 and 9 seem to be optimal, we suspect that bulk systems with surfactant concentrations in this range would form lamellae and cylinders in coexistence; this is indicated on Fig. 1. The preference for cylindrical microstructures at intermediate concentration is confirmed in Fig. 14, which shows the microstructure on $30 \times 30 \times 30$ lattice for 50% surfactant. In Fig. 10 the cylinders are oriented parallel to the Z axis of the lattice, while in Fig. 11 they are parallel to a diagonal of the ZX face of the lattice, consistent with the reduced concentration of surfactant, and consequent wider spacing of the cylinders in the latter. On the $30 \times 30 \times 30$ lattice of Fig. 14 they orient parallel to the diagonal of lattice cube itself. Thus in this latter case, to visualize the cylinders, we depict the YX face of the cube (Fig. 14, upper), and a cross section which is a plane perpendicular to the YZ face of the cube whose intersection with the YZ face is a diagonal of the YZ face (lower). Although one would expect hexagonal packing of cylinders in macroscopic systems, for the $20 \times 20 \times 20$ and $30 \times 30 \times 30$ lattices simulated here, the cylinders pack in asymmetric
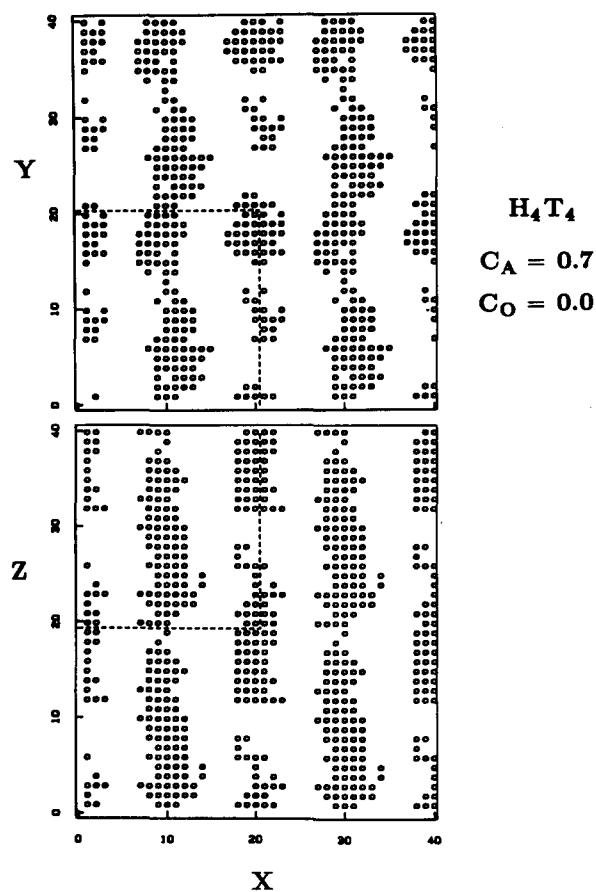

H_4T_4

$C_A = 0.7$

$C_O = 0.0$

FIG. 9. $20 \times 20 \times 20$ lattice containing 70% H_4T_4, 0% oil, 30% water.
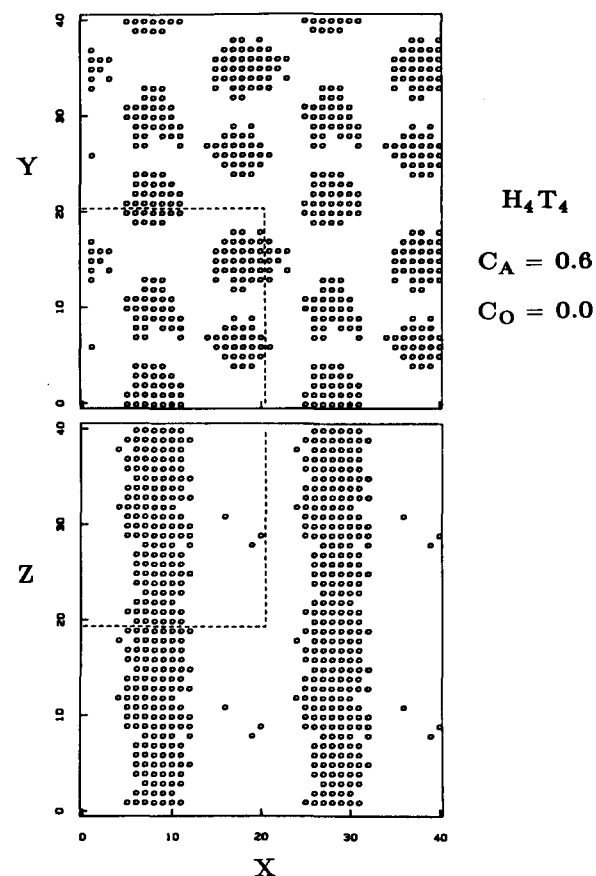

H_4T_4

$C_A = 0.6$

$C_O = 0.0$
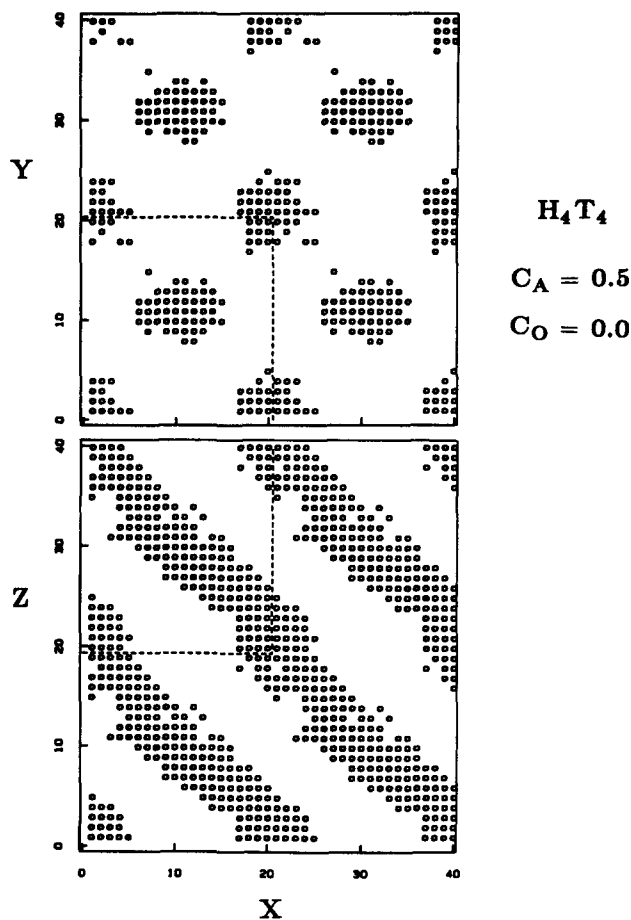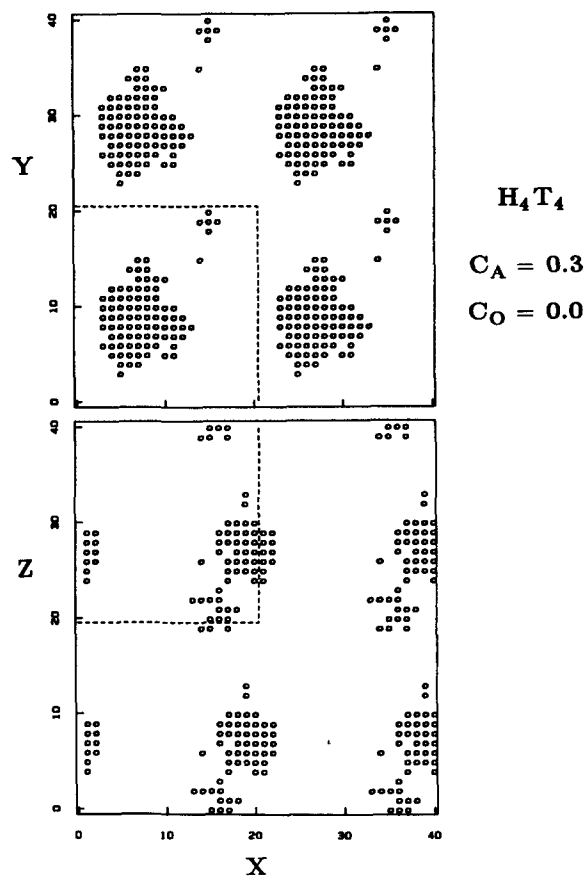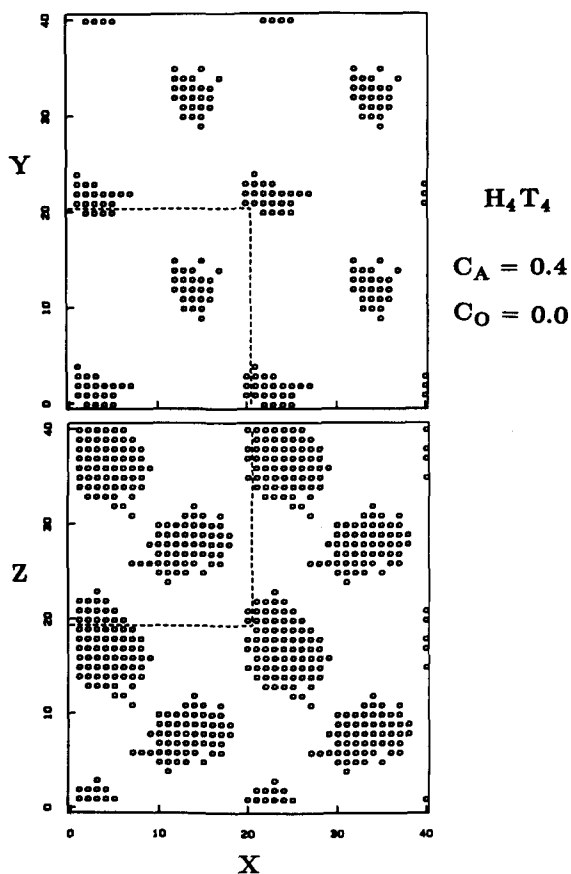
FIG. 10. $20 \times 20 \times 20$ lattice containing 60% H_4T_4, 0% oil, 40% water.

FIG. 11. 20×20×20 lattice contining 50% H₄T₄, 0% oil, 50% water.

FIG. 13. 20×20×20 lattice containing 30% H₄T₄, 0% oil, 70% water.

staggered arrays (Figs. 10 and 11) or in square arrays (Fig. 14). Apparently these lattices are too small to yield the packings that we expect for bulk systems. For low concentrations we obtain spheroids, not only on the 20×20×20 lattices of Figs. 12 and 13, but also on 30×30×30 and 40×40×40 lattices. On the 20×20×20 lattices the spheres pack in regular arrays, a face centered cubic (fcc) packing appears in Fig. 12 and body-centered cubic (bcc) in Fig. 13. These lattices are so small that they contain only one unit cell of the crystalline structure, and so one should not expect these symmetries to typify the bulk. Figure 15 shows that for larger 30×30×30 and 40×40×40 lattices, the 30% system forms positionally disordered spheres. It is not known whether these larger systems require longer runs to organize equilibrium crystal structures, or whether the disordered spheres of Fig. 15 represent the true equilibrium behavior of this system. Recent and forthcoming increases in computer power may allow runs long enough to resolve this uncertainty.

Within the volume of the 40×40×40 lattice in Fig. 15 there are 27 spheroidal micelles with aggregation numbers ranging from a low of 63 to a high of 113. The mean aggregation number is 88 and the standard deviation about this mean is 14. Thus the distribution of micelle sizes is relatively narrow. In addition to these micelles there are ten unaggregated singlet surfactant molecules and one dimer. There are no aggregates with sizes in the range 3–62. A more detailed study of the micelle distribution function of this and other systems is in progress.
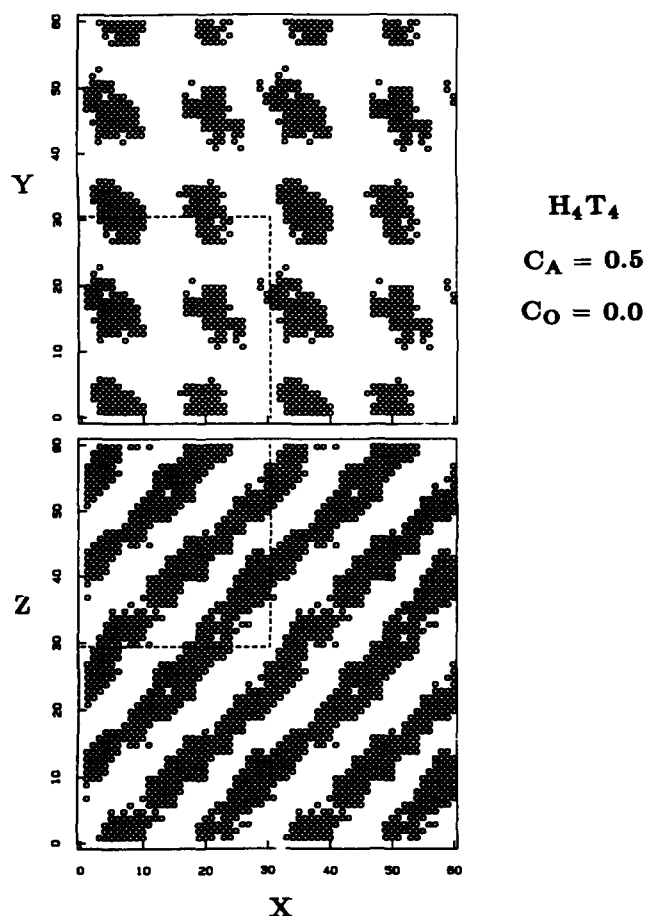

FIG. 12. 20×20×20 lattice containing 40% H₄T₄, 0% oil, 60% water.

FIG. 14. $30 \times 30 \times 30$ lattice containing 50% H_4T_4, 0% oil, 50% water; T in Table I equals 3.2×10^9. In this depiction the lower image is not a face of the cubic lattice, but is a diagonal slice defined by the condition $Z + Y = 61$.

FIG. 15. $40 \times 40 \times 40$ lattice containing 30% H_4T_4, 0% oil, 70% water; T in Table I equals 1.6×10^9.

Because lamellae are infinite in two directions, there are two angles through which a lamellar microstructure can rotate to fit on a finite three-dimensional lattice. Thus we believe that even with the small lattices considered here we have obtained lamellar crystalline order typical of the bulk. There is only one angle through which a cylindrical crystalline microstructure can rotate, so the correct symmetry is less likely to be obtained on small lattices. Unless the lattice size is by chance commensurate with the equilibrium size of the unit cell, spheroidal packings such as bcc or fcc cannot fit on a finite lattice without defects or distortions. Thus for these latter systems, simulations on very large lattices (perhaps $100 \times 100 \times 100$) will be required if one is to have any confidence that the crystal symmetry represents that of bulk material.

B. Asymmetric surfactant H_2T_6

The changes in microstructure from lamellar to cylindrical to spheroidal that occur as one decrease C_A in progression I are driven by volumetric constraints. Since the surfactant H_4T_4 is symmetric, it would prefer to reside at uncurved interfaces. As C_A is reduced however with the oil concentration held at zero, the oil-loving component (tails only) becomes more and more in the minority volumetrically. The system therefore chooses to pack the tails into confined cy-
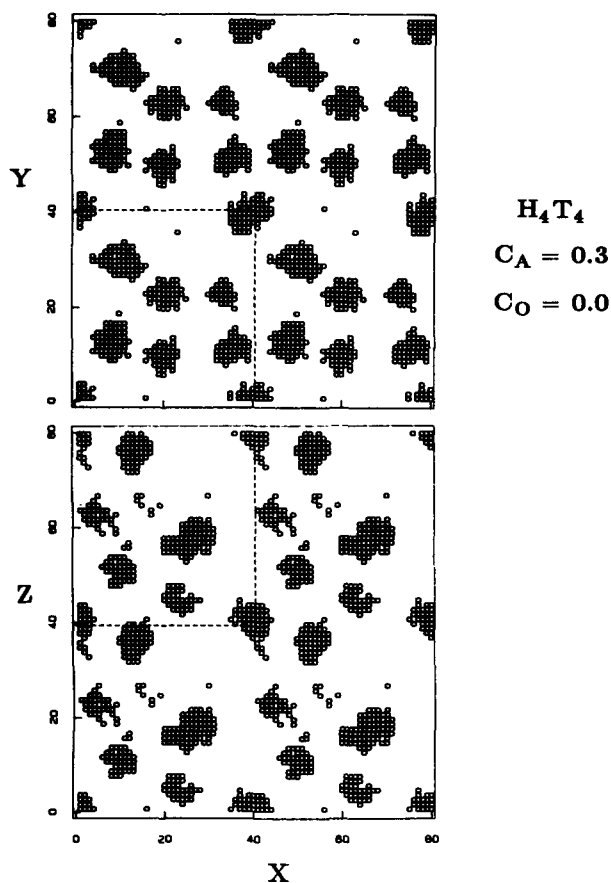
lindrical or spheroidal regions to make room for the majority water-loving material (heads and water). It is of interest to counter this tendency by mixing an asymmetric surfactant H_2T_6—that prefers to reside at interfaces curved towards the water-loving side—with water and no oil. For such mixtures, the volumetric constraints are opposed by the curvature tendencies inherent in the surfactant. Thus consider a system containing 20% H_2T_6 in water. Since for this surfactant the ratio R of the length of oil-loving portion to water-loving portion is 3, the volume of oil-loving material in this system is 15%—the same as a system containing 30% H_4T_4 in water. If the volumetric constraint controlled the microstructure, 20% H_2T_6 should then form spheroids, and look comparable to Fig. 12 or 13. The surfactant, however, does not want to reside at an interface curved toward the long tails. A compromise is struck, therefore, and the simulation produces a cylindrical morphology; see Fig. 16. Likewise 50% H_2T_6, which has volumetrically the same amount of oil-loving material as 75% of H_4T_4, forms lamellae in Fig. 17 instead of the broken lamellae formed by H_4T_4 in Figs. 8 and 9. A 40% concentration of H_2T_6 yields the most interesting microstructure of all. Figure 18 shows successive slices through this system arranged in a clockwise progression. It is bicontinuous and is topologically equivalent to the Schwarz surface depicted in Fig. 19. The system size here is too small for one to be at all confident that this result is
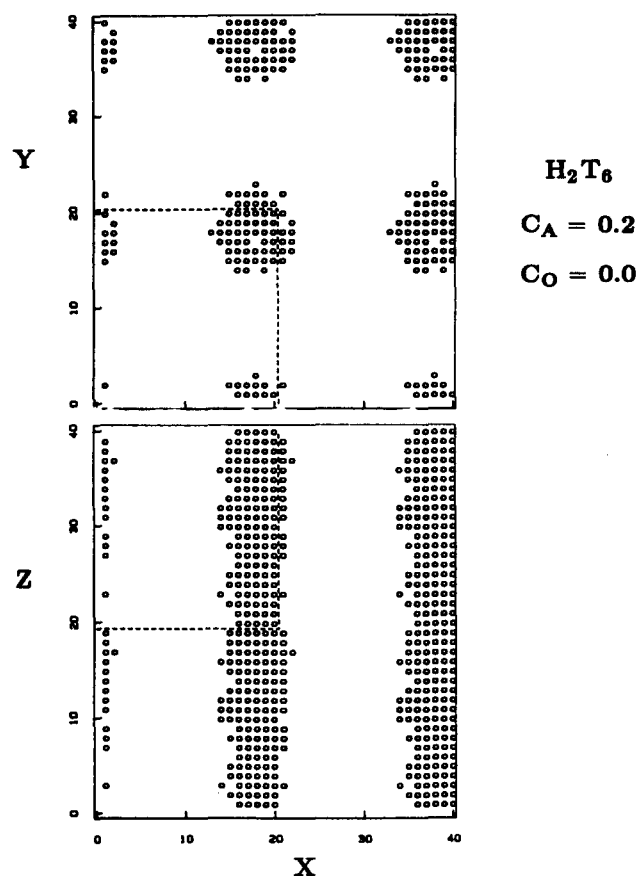
FIG. 16. $20 \times 20 \times 20$ lattice containing 20% H_2T_6, 0% oil, 80% water.

H_2T_6

$C_A = 0.2$

$C_O = 0.0$

FIG. 17. $20 \times 20 \times 20$ lattice containing 50% H_2T_6, 0% oil, 50% water.

H_2T_6

$C_A = 0.5$

$C_O = 0.0$

typical of the bulk: only one unit cell is generated on the $20 \times 20 \times 20$ lattice. On the $40 \times 40 \times 40$ lattice with T in Table I equal to 3.2×10^9, this system again yields a bicontinuous microstructure, but it is not a regular one. It does, however, show a cellular structure with a cell size that is comparable to that found on the $20 \times 20 \times 20$ lattice. This compositon on the $30 \times 30 \times 30$ lattice with $T = 3.2 \times 10^9$ gives a lamellar structure rather than bicontinuous, apparantly because the preferred cell size of the bicontinuous structure is not commensurate with the $30 \times 30 \times 30$ lattice. We believe that it is significant that regular bicontinuous structures appear only for the asymmetric H_2T_6 and are not generated by the symmetric surfactant H_4T_4, at the compositions investigated here. Scriven et al.[4,5] have speculated that bicontinuous microstructures might appear in surfactant-water mixtures.

Because of the small size of the lattices, any conclusions that we draw about liquid crystalline phase behavior must be somewhat tentative. However, it is noteworthy that the topology of the microstructure (spheres, cylinders, lamellae, or bicontinuous) obtained for $20 \times 20 \times 20$ lattices always persisted when larger lattices were considered. The regular crystal symmetries (fcc, bcc) seen on $20 \times 20 \times 20$ systems never persisted on the larger lattices, however. This could mean either that the regularity found on $20 \times 20 \times 20$ lattices is an artifact of the smallness of the lattice and the artificial constraint of the periodic boundary conditions, or that the big lattices would have shown regularity if only the runs had been longer. If, as we think likely, the former possibility is
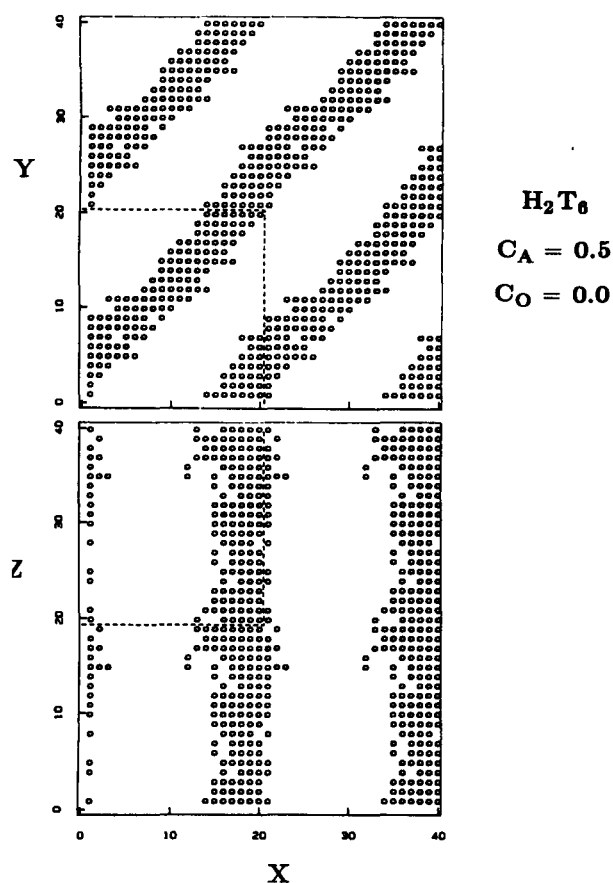
the correct one, then perhaps ordering transitions to regular symmetries occur in these systems at temperatures lower than those considered here.

III. PROSPECTS

There are many interesting issues that can be addressed by a computer technique of the kind presented here.

One can seek the minimum length that a symmetric amphiphile must be to form a given liquid crystalline microstructure as a function of temperature. Preliminary results indicate that at $w = 0.1538$ H_4T_4 is the shortest amphiphile that forms cylinders and H_3T_3 is the shortest that forms lamellae. H_2T_2 can be made to form lamellae if the inverse temperature w is increased to 0.20. The transition from a disordered phase to lamellae or any other ordered phase is first order. The thermodynamic properties of these transitions bear examination.

It will be worthwhile to examine the behavior at amphiphile concentrations above the critical micelle concentration but below the concentration at which any crystalline order appears. Indications from the results presented here are that H_4T_4 forms spheroids in this regime and H_2T_6 forms cylinders. It would be interesting to determine the ratio of the length of head group to the length of tail group at which the transition from spheres to cylinders in this concentration regime occurs.[6] Also, the distribution of micelle aggregation number in this regime would be worth exploring.
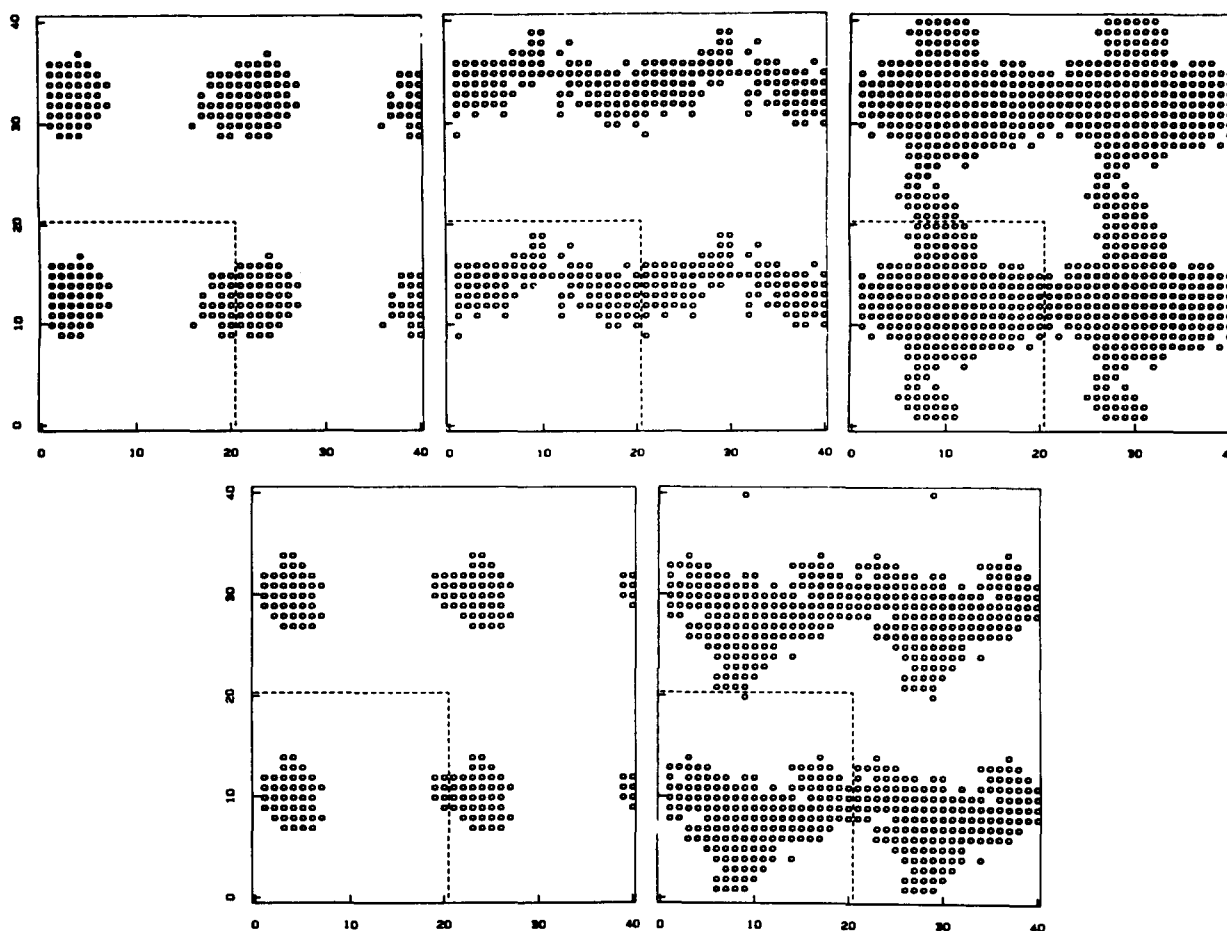
FIG. 18. Successive slices through a $20 \times 20 \times 20$ lattice containing 40% H_2T_6, 0% oil, 60% water. Every fourth layer of the lattice is shown above with the sucessive layers arranged in a clockwise progression.

It will be fascinating to study larger systems containing oil, water, surfactant, and possibly cosurfactant (such as H_1T_1) in regions of the phase diagram where one expects transitions to random bicontinuous phases of the kind postulated by Scriven[5] and modeled by Talmon and Prager,[7] Widom,[8] and others.[9] For symmetric surfactants, such transitions are most likely to occur at compositions just above the large three-phase triangle in Fig. 2.

As alluded to earlier, we would like to study the properties of single surfactant layers between oil and water regions. Special box shapes and boundary conditions can be imagined that would facilitate this computer study.[11] Interfacial tension and bending constants, and the effects on these of addition of "cosurfactants" such as H_1T_1, could hopefully be calculated.

In principle, the phase behavior of mixtures of surfactant, oil, and water can be calculated since we can both inspect the simulations visually for the presence of multiple phases, and can also compute free energies. In practice, this is very expensive computationally, since large systems are needed so that bulk quantities of all coexisting phases can be present simultaneously. Some preliminary work along this line was presented earlier,[3] however, and more is currently under way for H_1T_1. To compute phase behavior, a grand canonical ensemble[11] (where chemical potential rather than composition is fixed) is better than the canonical ensemble used in all simulations to date. The canonical ensemble is useful for computing interfacial tensions, however, as illustrated in Ref. 3.
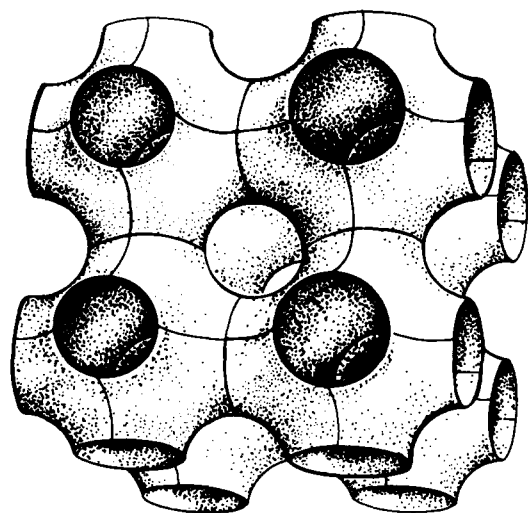

FIG. 19. Schwarz surface suggested as a model for regular bicontinuous structures of surfactant-containing phases (taken from Scriven, Ref. 5).

In this paper we have begun to probe the effects of surfactant asymmetry, that is asymmetry in the length of hydro-

philic and lyophilic parts. Asymmetry in the interactions, e.g., between head and tail vis a vis water and oil, are also well worth studying, since such asymmetries are characteristic of real systems. A small step in this direction was reported earlier.[10] One could also introduce longer range interactions than those considered here, although the artificiality of the lattice model would limit the significance of such an extension of the basic model. Of course, moving the simulation off the lattice into continuous space would be a major step towards realism, but would entail vastly more computational effort, if one is to remain true to the intention of allowing microstructure to self-assemble.

Finally, it may be possible to use this type of computer program to investigate the behavior of polymer amphiphiles such as block copolymers, or random copolymers.[12] There is a similarity between the microstructural transitions that occur for diblock polymeric amphiphiles and those for surfactant amphiphiles as we have earlier noted.[3] Of course, simulation of polymeric systems with molecular weight comparable to those used in typical experiments is currently out of the question.

The scope and diversity of the possibilities beckon new efforts and energies in this area.

ACKNOWLEDGMENTS

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