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Structure of a Water/Oil Interface In the Presence of Micelles: A Computer Simulation Study

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In this article we present the results of computer simulations on a simple oil/water/surfactant system. These simulations show surprisingly rich structural detail. A monolayer of surfactants is formed at the oil/water interface, and in the water phase spontaneous micellization has occurred. A depletion layer, containing only water, separates the monolayer from the micelles. The density profile of the micelles oscillates close to the interface. It is suggested that these oscillations provide an explanation of the results of neutron reflectivity experiments on water-surfactant systems. Furthermore, the structure of the formed micelles has been studied in detail and compared with experimental data and some theories.

1. Introduction

Amphiphilic molecules such as surfactants, lipids, or detergents have an affinity for both water and oil. The polar head of the molecule is hydrophilic, while the hydrocarbon chain is responsible for the affinity for oil. This makes it for amphiphiles favorable to adsorb at an oil/water interface and causes a reduction of the bare oil/water interfacial tension. Because of this property, surfactants are used in practical applications such as detergency and tertiary oil recovery. In these applications the systems are usually complex.¹ Besides oil/water/surfactants, salts and co-surfactants are utilized as well. Various types of surfactants are used. Furthermore, oil is generally a mixture of many hydrocarbons. It is obvious that it is nearly impossible to make a (tractable) molecular model containing all these features.

Progress can be made by considering simplified models. Of course, the extent of simplification depends on the details of what one is interested in. An experimental observation is that many different oil/water/surfactant systems have similar properties, such as a characteristic pattern of phase transitions,² low interfacial tensions compared to the normal oil/water interfacial tension, and the formation of various structures like micelles, vesicles, bilayers, and liquid crystalline structures.¹ A natural question to ask is, what features of the oil/water/surfactant system are essential for the behavior observed experimentally?

Widom and co-workers were among the first to ask this question.³⁻⁵ Two simple observations constituted their starting point: oil and water do not mix, and a surfactant is a molecule that looks like an oil molecule from one end and like water from the other. Using these ingredients, they constructed a lattice model that predicted three-phase equilibria and ultralow surface tensions. Since then, various other lattice models have appeared in the literature⁶⁻¹² which are reviewed in ref 13. These lattice models predict a very large number of phases.¹⁴ However, it is now known

that a number of these phases are directly related to the use of a lattice and would not exist in a continuum version of those models.¹³

A continuum model has been developed by Telo da Gama and Gubbins.¹⁵ This model uses the same (simple) ingredients as the Widom-Wheeler model. Compared to lattice models, the statistical mechanical techniques to study continuum models are far less developed.

In this article we present (section 2) a continuum oil/water/surfactant model, which was constructed in the spirit of the Widom and Telo da Gama models. Oil and water molecules are modeled with Lennard-Jones potentials. Surfactants consist of oil and water-like particles connected with harmonic springs. In refs 15 and 16 it is shown that by using this model a stable liquid/liquid interface can be formed and the influence of surfactants on the surface properties can be studied. In refs 17 and 18 this model is used to study the effects of the chain length on the interfacial tension. A similar model is considered by Stillinger,¹⁹ who used a simple field theory to study the aggregation in amphiphile solutions. Monte Carlo lattice simulations on a related model have been reported in refs 20 and 21.

The model that was used in the present simulations is a drastic simplification of real oil/water/surfactant systems. Of course, using the molecular dynamics or Monte Carlo technique, it is possible to study realistic models of specific experimental systems including all the atomic details. Such simulations have been performed²²⁻³¹ and provide a wealth of information. However,

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such "realistic" simulations require so much computer time that it is, at present, impossible to perform systematic studies.

O'Connell and co-workers^{23,24,30,31} studied the structure of a micelle by confining the surfactants in a sphere and connecting the heads with a force to the surface of this sphere. This force models the water. Their predictions of the distribution of the tail segments showed good agreement with small-angle neutron scattering data. In this model, the number of surfactants in a micelle and the radius of the hydrocarbon core of the micelle are chosen a priori, rather than "measured" in the course of a simulation.

The effect of water is explicitly taken into account in refs 25, 27, and 28. Watanabe et al.^{27,28} simulated a sodium octanoate micelle in an aqueous solution for 0.2 ns. The micelle was stable over the length of the simulation.

With these realistic models a simulation of the time evolution of such a system during 0.2 ns requires a sizable amount of computer time. Yet, 0.2 ns turns out to be too short to observe the spontaneous formation of micelles. Therefore, in these studies, the micelle is constructed a priori and the behavior of these "postulated" micelles is studied. An obvious question is whether it is possible to study the spontaneous formation of micelles within our simple model.

Pioneer Monte Carlo simulations on micelles in lattice models have been reported in refs 32 and 33.

In the simulations described in refs 16 and 17 by us, ordered structures such as micelles could not be discerned. The simulations of refs 16 and 17 were performed on relatively small systems (500–1000 particles). It turns out that these systems are too small to accommodate the ordered structures of interest.

In this article simulations on much larger systems (39 000 particles) are described, which were run on a parallel computer. (Computational details are given in section 3.) These simulations show the spontaneous formation of micelles in the water phase in addition to the formation of a monolayer of surfactants at the interface. The results of these simulations are compared (section 4.1) with recent specular neutron reflectivity experiments.^{34,35} The latter experiments on the air/water interface showed an "unexpected" enhancement of water (D₂O) reflectivity that could not be explained satisfactorily. The results of our simulations provide a possible explanation of this enhancement.

The structure of our model micelles is discussed in detail in section 4.3.

Some preliminary results of these simulations have been published in ref 36.

2. The Model

In our model, which is based on an early model of Telo da Gama and Gubbins,¹⁵ we assume the existence of two types of particles: o particles which are "oil-like" and w particles which are "water-like". These two types of particles are used to model three types of molecules, namely oil molecules, water molecules, and surfactant molecules. An oil molecule consists of a single o particle, and a water molecule consists of a single w particle. A surfactant molecule is made up of one or more o particles and one or more w particles; these are joined together by harmonic potentials

$$U_{ij} = \frac{1}{2}k(|\mathbf{r}_i - \mathbf{r}_j| - \sigma)^2 \quad (1)$$

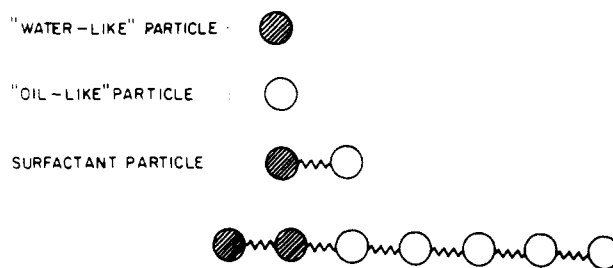


Figure 1. Schematic drawing of the oil/water/surfactant model.

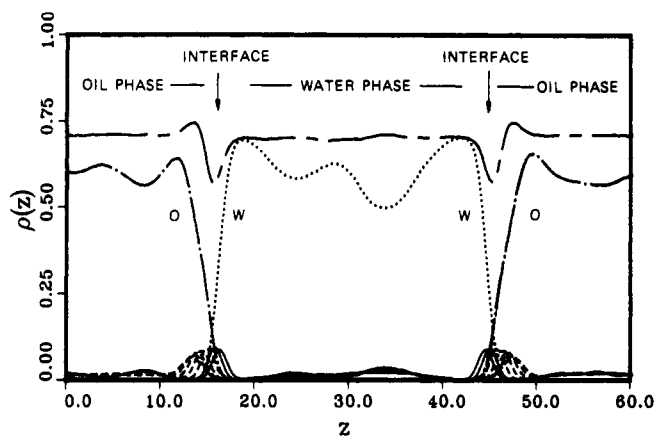


Figure 2. Density profiles of the oil, water, and surfactant particles for a 3% surfactant solution. The chain-dashed line gives the total density (oil + water + all surfactant segments). The dotted line gives the density profile of the water particles and the chain-dotted line of the profile of the oil particles. The solid lines give the density profiles of the two hydrophilic segments and the dashed lines the profiles of the five hydrophobic segments of the surfactant. The density is defined as the number of particles or segments per unit volume.

in which r_i is the position of particle i and σ is the length parameter of the Lennard-Jones potential (see eq 2) and where the value of the force constant (k) is made sufficiently large that at any instant 98% of the connected units have lengths that are within 2% of the average value σ .

The two types of particles interact with truncated and shifted Lennard-Jones potentials with energy parameter ϵ_{ij} , distance parameter σ_{ij} , and the cutoff radius R_{ij}^c

$$\Phi_{ij} = \begin{cases} \phi_{ij}(r) - \phi_{ij}(R_{ij}^c) & r \leq R_{ij}^c \\ 0 & r > R_{ij}^c \end{cases} \quad (2)$$

and

$$\phi_{ij}(r) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r} \right)^{12} - \left(\frac{\sigma_{ij}}{r} \right)^6 \right] \quad (3)$$

where i, j indicate the type of atom (w or o) and r is the distance between the atoms.

Of course, the use of a Lennard-Jones type potential is a drastic simplification. Therefore, we have not tried to optimize the Lennard-Jones parameters for the various interactions. We have assumed that for all interactions $\epsilon_{ij} = \epsilon$ and $\sigma_{ij} = \sigma$. In order to make the o-o and w-w interactions different from the w-o interaction, the truncation of the potential (R_{ij}^c) is made depending on the type of interaction. The w-w and o-o interaction is truncated at $R_{ij}^c = 2.5\sigma$ and the o-w interaction at $R_{ij}^c = 2^{1/6}\sigma$, which makes the latter interaction completely repulsive.

As a result it turns out that, at a temperature $T = 1.0\epsilon/k_B$, the oil and water do not mix and form a stable liquid-liquid interface.¹⁶ The surfactant molecules are of amphiphilic nature; one end is hydrophilic (and dislikes oil) the other end (likes oil and is) hydrophobic.

In most of the simulations described in this article we have used a surfactant with a hydrophilic part consisting of two w particles

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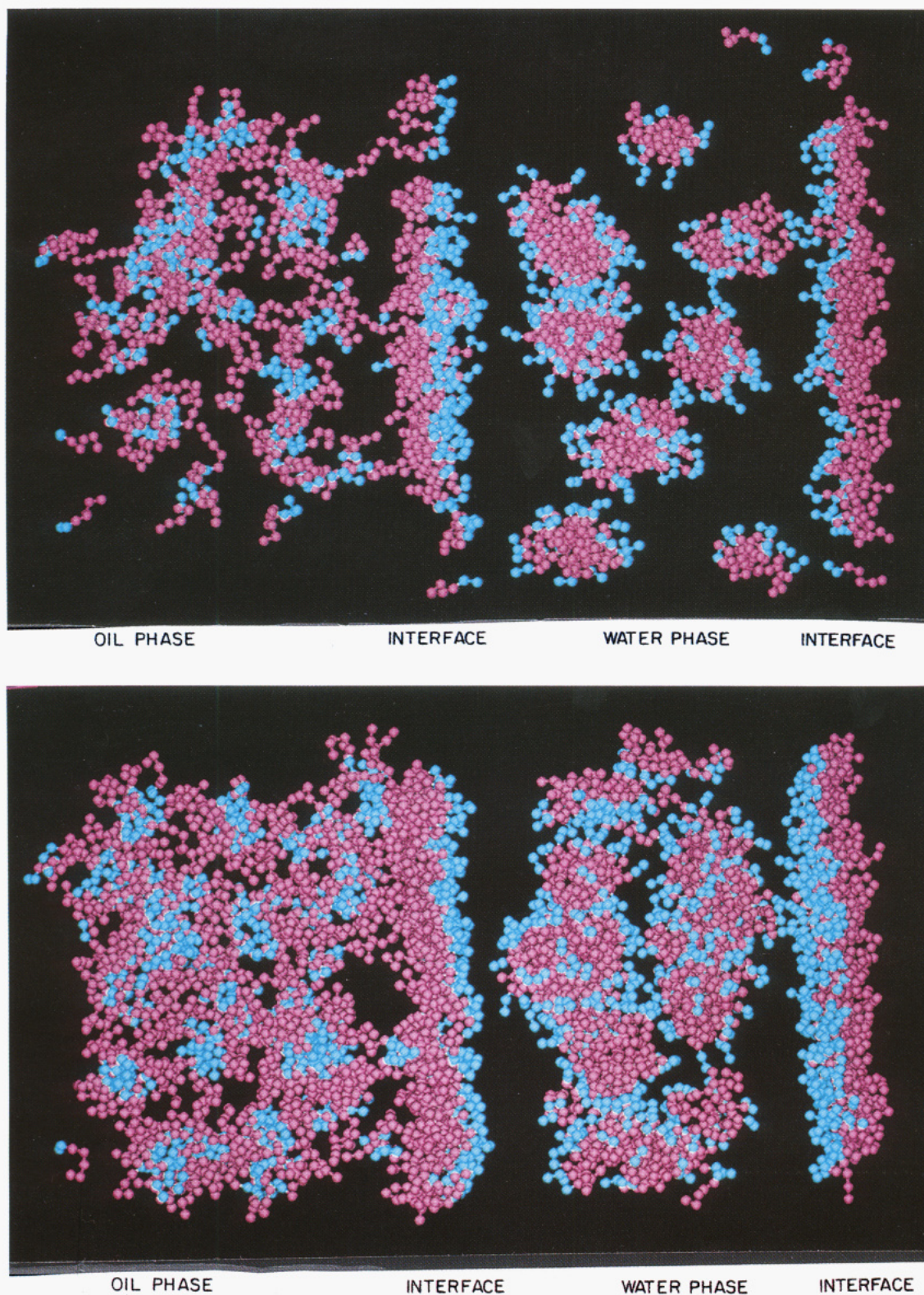


Figure 3. Typical examples of a configuration of surfactants in an oil/water system for (a, top) 1.5% surfactants and (b, bottom) 3.0% surfactants. The hydrophilic segments are blue and the hydrophobic segments red. For clarity, the positions of the oil and water particles are not drawn.

and a linear hydrophobic chain with five σ particles. For comparison, some simulations were performed with the dumbbell surfactants (see Figure 1).

3. Computational Details

The simulations were performed at constant temperature ($T = 1.0\epsilon/k_B$) and volume. The temperature was kept constant by scaling the velocities every 200th time step. Periodic boundary conditions are imposed in all three directions.

Initially, a number of particles were placed on an fcc lattice with size $30.4\sigma \times 30.4\sigma \times 60.8\sigma$. The density obtained in this instance was $\rho = 0.7\sigma^{-3}$, with 39 304 particles. The simulations were performed on a network of 100 transputers using a parallel molecular dynamics algorithm.³⁷ The equations of motion were solved by using Verlet's integration scheme.³⁸ Tests showed that a time step of length $\Delta t = 0.005\tau_0$ ($\tau_0 = \sigma(m/\epsilon)^{1/2}$) was appro-

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priate. On this parallel computer one time step takes approximately 2.8 s.

Surfactants were introduced in the following way. First a randomly chosen particle on the fcc lattice was connected with one of its randomly chosen neighbors. Then the latter was connected again to one of its neighbors. This procedure was repeated until the desired number of surfactants with the desired length was formed. This initialization guarantees a spatially random distribution of surfactants. All the remaining particles in half of the periodic box were water and in the other half oil. The surfactant concentration ranged from 0.75% to 3%. The system was equilibrated for at least 100 000 time steps ($\Delta t = 0.005\tau_0$), followed by a production run of at least another 100 000 time steps.

4. Results and Discussion

4.1. Structure of the Oil/Water Interface. Density Profiles.

Figure 2 shows density profiles for a surfactant concentration of 3%. The surfactants are preferentially adsorbed at the interface as a monolayer. The segment distribution reflects the expected orientational ordering (hydrophilic heads toward water). In the water phase, next to the monolayer, a depletion layer is observed. This is a layer of water of a few molecular diameters that contains almost no surfactants. The density profile of the water shows pronounced oscillations. The density profile of the oil phase also shows some oscillations, but these are much less significant. Simulations of systems with lower surfactant concentrations yielded similar results.

Snapshots. Typical examples of the instantaneous arrangement of the surfactants are shown in Figure 3. In the water phase micelles have formed spontaneously. For the 3% surfactant concentration Figure 3b suggests big aggregates. However, this is an artifact of the graphical representation. All surfactants are projected on the x,z plane; therefore, differences in the position in the y direction cannot be distinguished anymore.

Figure 4 shows a projection on the x,y plane of one of the monolayers as seen from the water side. This figure shows only those surfactants that are part of the monolayer. Note that no ordering of the monolayer in this plane can be observed. If we also project with this monolayer the surfactants in the water phase close to this monolayer, we obtain Figure 4b. This figure clearly demonstrates that also at the high concentration of surfactants well-defined micelles can be observed.

The depletion layer is clearly visible in Figure 3 for both concentrations.

Figure 5 shows a snapshot from a simulation with dumbbell surfactants (1.5% surfactant concentration). In this simulation the formation of micelles could not be observed.

Discussion. A possible explanation of these observations is the following. We recall that the structure of simple liquids³⁹ and even of some more complex systems such as liquid crystals⁴⁰ is largely due to hard-core interactions. Imagine a micelle to be a hard sphere and the monolayer to be a wall. The system is then equivalent to a hard-sphere fluid confined between two parallel plates. In such a system packing constraints are known⁴¹ to cause characteristic oscillations in the density profile. Similarly, packing constraints on the micelles cause oscillations in the micelles' distribution. Since the total density in the water phase is constant (see Figure 2), the water molecules will fill the remaining space and thus the water density will oscillate, with a period of the order of the diameter of the micelle. In a real system we have only one interface, and the oscillations will be present in the neighborhood of the interface.

The observed width of the depletion layer suggests a short-ranged repulsion between the monolayer and the micelles. Since in our model the direct interactions between the heads of the surfactants are attractive, this is somewhat surprising. Strong

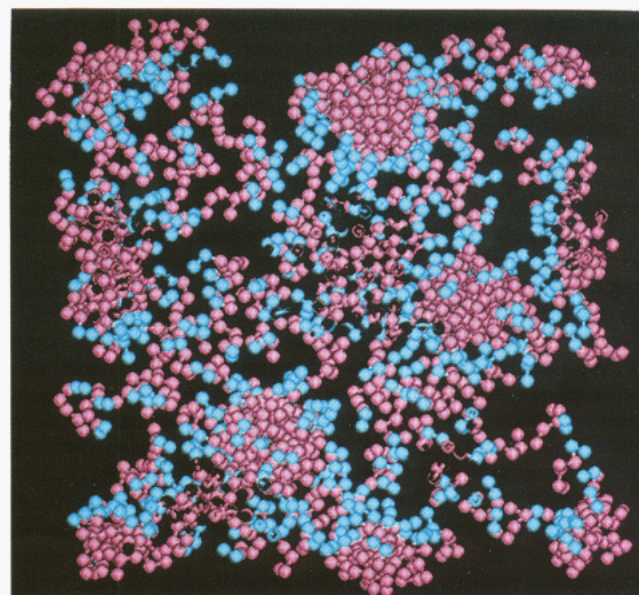
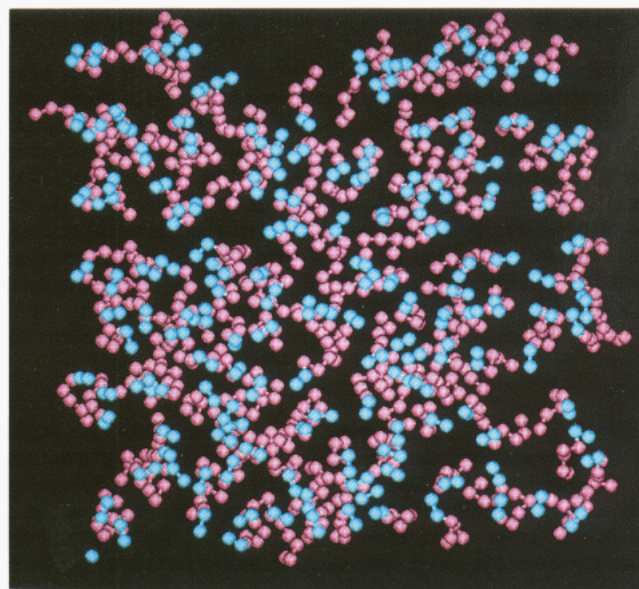


Figure 4. Projection of the surfactants on the x,y plane. In (a, top) only the surfactants in the monolayer at the interface are drawn. In (b, bottom) the surfactants in the water phase close to the monolayer are drawn as well. See also the caption to Figure 3.

repulsive short-ranged forces have been measured between bilayers and other amphiphilic surfaces in water.⁴²⁻⁴⁸ Several mechanisms have been proposed to explain this repulsion. One possible explanation is that repulsive forces arise whenever the surfaces have a strong affinity for water. These forces are commonly referred to as "hydration" or "solvation" forces.⁴⁹⁻⁵¹ Another explanation which has appeared in the literature is that the repulsion may be caused by thermal undulations of the bilayers.⁵²⁻⁵⁴ Recently,

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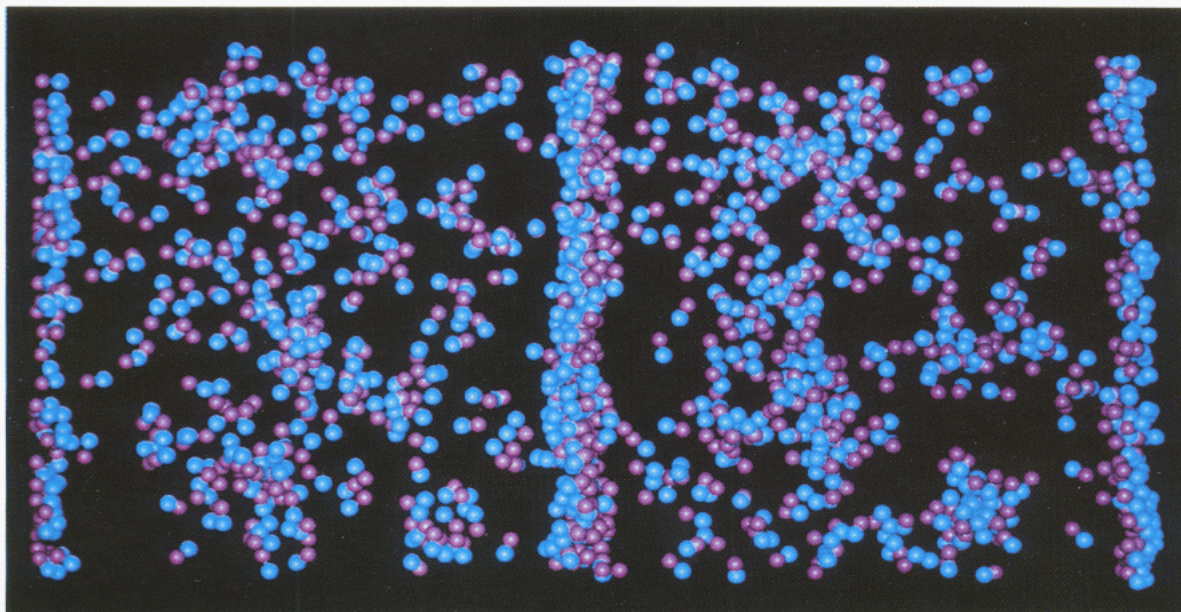


Figure 5. Typical configuration of dumbbell surfactants in an oil/water/surfactant system. The concentration of surfactants was 1.5%. See also the caption to Figure 3.

Israelachvili and Wennerström⁵⁵ have suggested that thermally excited protrusions of, for example, head groups or isolated chains are responsible for the repulsion. These authors refer to these forces as "steric" or "protrusion" force.

In our simulations the interface was very stable. Therefore, it is unlikely that the repulsive force between the micelles and the monolayer can be attributed to an undulation force. In fact, the surface tension in this particular system appears to be too high (see below) to expect a strongly fluctuating interface.⁵⁶

We could not observe any protrusions either. It can be expected that protrusions have a much larger effect on layered structures than on micellar structures. This is so because the probability that a protrusion from the monolayer touches a micelle is much smaller than the corresponding probability for a bilayer system. However, our simulations are probably too short to be able to observe these types of fluctuations. It is therefore much more likely that in our simulation the repulsive force is due to the water molecules between the micelles and the monolayer and can be taken as an indication of a solvation force.

It would therefore be interesting to "measure" this force. This can be done by freezing the micelle and calculating the force that is necessary to keep the micelle at a given position from the interface. When differences would be observed when the monolayer is frozen as well, this would give some information on the relative importance of possible fluctuations of the monolayer. Furthermore, comparison of the magnitude of the force with experimental data could give some indication of whether in real systems protrusion forces or undulation forces are dominating these solvation forces.

Structure of the Interface. A novel aspect of the present work is that the interface as well as the micelles is described with one model, whereas previous theoretical work has been mainly con-

cerned with either isolated micelles²⁷ or a monolayer.⁵⁷ It is therefore interesting to compare our simulations with experimental data on a real system of micelles near an interface. Recently, specular neutron reflection experiments were performed on the air/water interface of solutions containing ionic surfactants^{34,35,58} or nonionic surfactants.⁵⁸ The experiments reveal an "unexpected" enhancement in the reflectivity of D₂O once the surfactant concentration exceeds the critical micelle concentration. This enhancement has not yet been explained satisfactorily. It is therefore interesting to note that the oscillations of the density profile of water as observed in our simulations should give rise to just such an enhancement of the reflectivity. The location of the maximum, which is a measure of the period of the density oscillations, depends on the size of the micelle, which in turn depends on the type of surfactant. Indeed, such a dependency has been observed in the reflectivity experiments.³⁵ It would be interesting to test our hypothesis experimentally by adding deuterated oil to the solution. The oil molecules will dissolve in the interior of the micelles. This results in an oscillating density profile of the oil close to the interface. This should give rise to an enhancement of the reflectivity as well.

Lee et al.³⁵ have stated that an oscillating water density profile would explain the enhancement. They attribute these oscillations to a complicated layered structure of water and surfactant bilayers. Our simulations suggest, however, that these oscillations simply result from the packing of micelles near an interface.

Recently, Gompper and Schick⁵⁹ have studied the structural and interfacial properties of amphiphilic systems using a Ginzburg-Landau free energy. Gompper and Schick observed oscillating density profiles at an oil/microemulsion interface. Important is that these oscillations are only observed on the microemulsion side and *not* on the oil side. Furthermore, their model predicts a water-rich layer at the oil/microemulsion interface. Such a nonmonotonic density profile has also been obtained by Dawson⁶⁰ in a lattice model.

Although Gompper and Schick have considered a microemulsion, while we do not have a microemulsion, the similarities are striking. In our simulation we also find an enhancement of water near the interface, the depletion layer, and oscillating water density profiles. In the model of Gompper and Schick the os-

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(56) Such a strongly oscillating interface can be observed in a simulation with a high concentration of surfactants. For example, we have performed a simulation with 10% surfactants with one head and one tail segment. The surface tension in this system was zero. The density profiles showed a broad surfactant peak at the interface. However, the peaks of the o segment of the surfactant completely overlapped with the peak of the w segment. This suggests that at the interface no ordering occurred. However, inspection of a snapshot showed that the ordering was smeared out because of large fluctuations of the interface. This could indicate the formation of a microemulsion.

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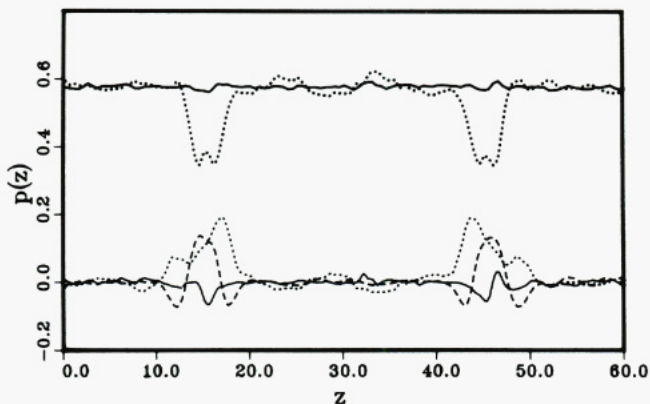


Figure 6. Normal and tangential components of the pressure tensor as a function of the distance from the interface (z). The upper curves give the normal component (solid line) and the tangential component (dotted line). The lower curves give the various contributions to $p_n - p_t$, the solid line gives the surfactant-surfactant contribution, the dashed line gives the surfactant-water/oil contribution, and the dotted line gives the water and oil contribution. The concentration of surfactants was 3%.

TABLE I: Interfacial Tension ($\gamma^* = \gamma\sigma^2/\epsilon$) as a Function of the Total Surfactant Concentration (c_s)^a

c_s , %	γ
0.00	1.7 ₁
0.75	1.22 ₁₈
1.5	1.05 ₁₃
3.0	0.84 ₁₅

^aThe subscript gives the accuracy of the last decimals.

TABLE II: Cluster Size Distribution in the Water Phase (Using Criterion 1) and in the Oil Phase (Using Criterion 2) for Various Concentrations of Surfactants^a

N_s	F_w	F_o	N_s	F_w	F_o
1.5% Surfactants					
1	1	15	16-20	1	
2-5	3	8	21-25	1	
6-10	2	12	26-35	3	
11-15	1	2	36 ⁺		
3.0% Surfactants					
1		5	21-25	1	2
2-5		4	26-30	1	2
6-10		5	31-35	2	
11-15		8	36-45	2	
16-20	1	3	45 ⁺	2	

^a N_s is the average number of surfactants in a cluster; F is the average number of clusters with this size. The averages are based on four samples which span 50 000 time steps.

oscillations arise from the interactions that cause the amphiphile to interact strongly with both the oil and water and not from packing constraints as suggested in this work. It would therefore be of interest to make a more detailed study on the relation of the two models.

4.2. Interfacial Tension. In a homogeneous system at equilibrium the thermodynamic pressure is constant and equal in all directions. For an inhomogeneous system hydrodynamic equilibrium requires that the component of the pressure tensor normal to the interface be constant throughout the system. The components tangential to the interface can vary in the interfacial region but must be equal to the normal component in the bulk liquids.

For an inhomogeneous fluid there is no unambiguous way for calculating the normal (p_n) and tangential (p_t) components of the pressure tensor.⁶¹⁻⁶³ Here we have used the Kirkwood-Buff convention.⁶⁴ The system is divided into N_{sl} equal slabs parallel

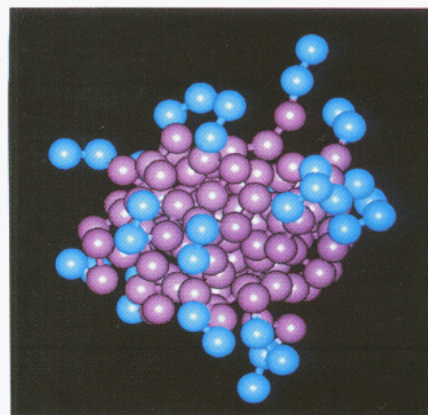


Figure 7. Snapshot of one micelle (1.5% surfactants). See also the caption to Figure 3.

to the x,y plane. The local normal ($p_n(k)$) and tangential ($p_t(k)$) components of the pressure tensor are given by⁶⁵

$$p_n(k) = T\langle\rho(k)\rangle - \frac{1}{V_{sl}} \left\langle \sum_{(i,j)}^{(k)} \frac{z_{ij}^2}{r_{ij}} \Phi'(r_{ij}) \right\rangle \quad (4)$$

and

$$p_t(k) = T\langle\rho(k)\rangle - \frac{1}{2V_{sl}} \left\langle \sum_{(i,j)}^{(k)} \frac{x_{ij}^2 + y_{ij}^2}{r_{ij}} \Phi'(r_{ij}) \right\rangle \quad (5)$$

where $\langle\rho(k)\rangle$ is the average density in slab k , $V_{sl} = L_x L_y L_z / N_{sl}$ is the volume of a slab, $\Phi'(r)$ is the derivative of the intermolecular potential, and $\langle \rangle$ denotes an ensemble average. $\sum_{(i,j)}^{(k)}$ means that the summation runs over all pairs of particles i,j for which the slab k (partially) contains the line which connects the particles i and j . A slab k gets a contribution $1/N_0$ from a given pair (i,j) , where N_0 is the total number of slabs which intersect this line.

In Figure 6 the normal and tangential components of the pressure tensor (eqs 4 and 5) and $p_n - p_t$ are shown as a function of the distance from the interface. The normal component is constant. The tangential component varies in the interfacial region but is equal to the normal component in the bulk. Interesting to note is that for a 3% solution the tangential component in the water phase shows oscillations. This is also an indication that the system is not homogeneous close to the interface. In the oil phase such oscillations cannot be observed.

It can be shown that the definition of the interfacial tension (γ) is free from ambiguities.⁶³ The interfacial tension can be calculated by integrating the difference of the normal and tangential components of the pressure tensor across the interface. In the case of our system with two interfaces, γ reads

$$\gamma = \frac{1}{2} \int_0^{L_z} dz (p_n(z) - p_t(z)) \quad (6)$$

Comparison of the normal component of the pressure tensor for 0.75% and 3.0% shows that as the concentration of surfactants increases, the pressure of the system decreases. In order to make a comparison with experimental results, which are normally obtained at constant pressure, it would be interesting to extend our algorithm in order to be able to simulate at constant normal pressure instead of constant volume.

The interfacial tension as a function of the total surfactant concentration is given in Table I. The interfacial tensions in these simulations are not very low. Comparison of the density profiles of these simulations (Figure 2) with for example the density profiles of the dumbbell surfactants Figure 2 in ref 16 shows that the concentration of surfactants at the interface is relatively low.

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This could indicate that the interface is not completely equilibrated yet. This could be due to the formation of micelles, since its extremely slow decomposition (on the time scale of a molecular dynamics simulation) does not allow the surfactants to reach, and saturate, the interface.

4.3. Micelles. The snapshots (Figure 3) show that during the simulations micelles have been formed. In this section we study the structure of the micelles in more detail. In ref 66 a review of recent experimental and theoretical work on the structure of micelles is given.

The role of hydrogen bonding in promoting amphiphilic self-assembly is still a much-debated question. For a long time it was the general belief that aggregation is driven by the release of "structured" water from around the hydrocarbon chains.⁶⁷ Reexamination of thermodynamic data showed that even at high temperatures, where the unique structural properties of water are almost completely negligible, aggregation can occur. Furthermore, micelle formation has also been observed in other liquids such as hydrazine,^{68,69} ethylammonium nitrate,⁷⁰⁻⁷² formamide,^{73,74} and various glycols.⁷⁵ Striking is that all these liquids can form hydrogen bonds. This observation motivated Beesly et al.⁷⁶ to study the formation of micelles in non-hydrogen bonding polar fluids. They observed that in 3-methylsyrone no self-aggregation of surfactants occurs. From this observation they concluded that, for cooperative interaction between amphiphilic molecules, hydrogen bonding is essential. Our simulations, however, strongly suggest that micelles can occur in fluids that do not form hydrogen bonds!

4.3.1. Definition of a Micelle. To arrive at a practical definition of a micelle, we first should specify a criterion to decide whether a given surfactant belongs to a cluster. One possible definition would be to identify a micelle as a cluster of surfactants whose tails are in contact with each other. In a reverse micelle the heads are in contact. In order to distinguish between these two types, two criteria have been used.

Let us define a radius R_{cl} and assign to each pair of particles (i, j) a Boolean variable $acc(i, j)$. If the distance between two particles i, j is less than R_{cl} and $acc(i, j)$ holds, then two particles belong to the same cluster. (Notice that the reverse is not true.) $acc(i, j)$ was true when i and j were both (criterion 1, for ordinary micelles) an o particle of a surfactant chain and (criterion 2, for reversed micelles) a w particle of a surfactant chain; for all other pairs (i, j) $acc(i, j)$ was false. Of course, particles that belong to the same surfactant belong to the same cluster. We have set $R_{cl} = 1.4\sigma$. The results are not sensitive to the exact value of R_{cl} .

For several configurations we have determined the number of clusters and the number of surfactants in the clusters. The results are shown in Table II. It turns out that once a cluster is formed it is stable for a large number of time steps. However, during the simulation we could observe that occasionally a surfactant left or entered a micelle and that two clusters fused. It would be interesting to study the dynamics of these processes.

4.3.2. Micellar Structure. We have chosen one of the micelles in the water phase (see Figure 7) of the 1.5% surfactant solution and studied the structure of this micelle in detail. This was done by performing a simulation in which the positions of the surfactants in this micelle were stored every 100th time step. We have

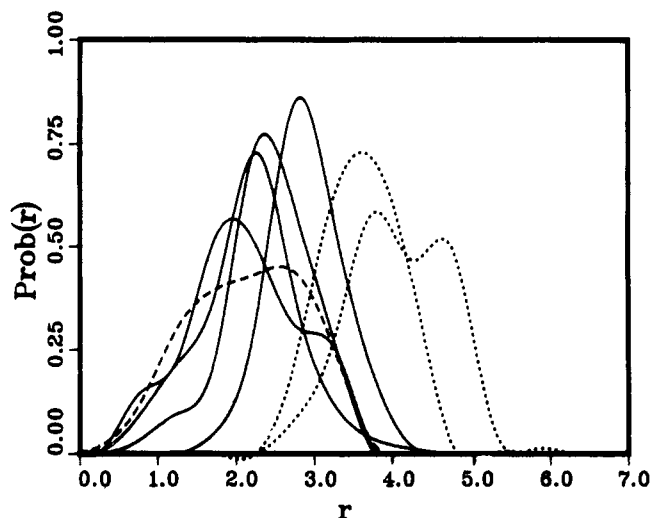


Figure 8. Probability distributions of the segments of the surfactants in a micelle measured with respect to the center of mass. The dotted lines are the distributions of the two w particles of the surfactant, the solid lines of the four following o particles, and the dashed line of the last o particle of the surfactant chain.

continued this simulation for 43 000 time steps. At the end of this simulation it was tested whether this micelle still contained the same particles as when the simulation was started. This micelle contained 20 surfactant particles. Our first attempt to study a micelle failed, because the chosen micelle fell apart during the simulation.

Segment Distribution. In Figure 8 the probability distributions of the surfactant segments are shown. Comparison with the distributions obtained by O'Connell and co-workers^{23,24,30,31} and by Watanabe et al.^{27,28} shows that all three studies yield nearly identical results. In fact, Szleifer et al.^{77,78} showed that the internal structure of the micelle is not very sensitive to details of the potential of the surfactant chain. For example, Szleifer et al. showed that there is no quantitative difference in the probability distribution between a "real" chain (with a trans/gauche energy difference of 500 cal/mol) and a "flexible" chain (difference of 0 cal/mol).^{77,78} In our model the surfactant is effectively a free chain while the surfactants in the simulations of O'Connell et al. and Watanabe et al. are "real" chains. The observed similarities confirm the statement of Szleifer et al. that the internal energy of the chains plays only a secondary role.

Szleifer et al.⁷⁷⁻⁸⁰ have shown that the position of the end segment depends on whether the micelle is rough or compact. In a compact micelle, i.e. one in which the total density profile of the o segments is approximated with a step function, Szleifer et al. show that the distribution of the end segments shows a peak near the interface (see Figure 7 in ref 77). For a rough micelle, i.e. one in which the total density profile goes gradually to zero at the interface, this peak occurs at intermediate distance between the interface and the center of the micelle (see Figure 7 in ref 77). Figure 8 shows that in our model the peak is in the middle, indicating a rough micelle; also the density profiles (see Figure 9) indicate that the micelle surface is rough. This is in good agreement with small-angle neutron scattering experiments,⁸¹ which show a similar distribution of end segments.

Density Profiles. In Figure 9 the density of the surfactant segments and water with respect to the center of mass of the micelle is shown. We have included only those molecules which

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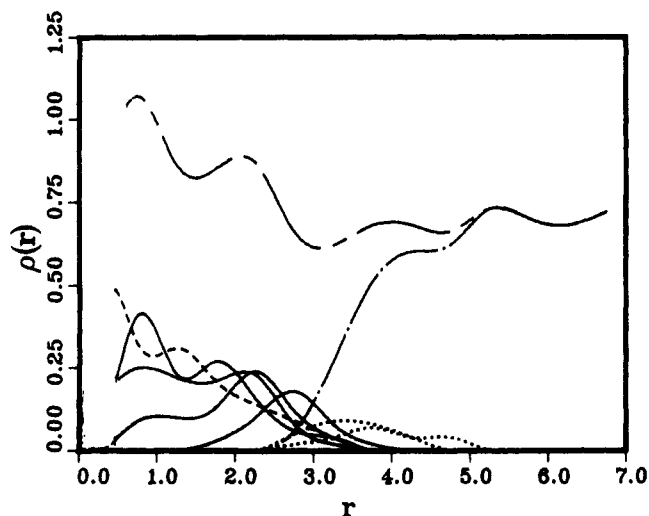


Figure 9. Density of the segments of the surfactants and water in a micelle measured with respect to the center of mass. The dotted lines are the distributions of the two water particles of the surfactant, the solid lines of the four following surfactant segments, and the dashed line of the last surfactant segment. The chain-dotted line gives the density of the water molecules. The chain-dotted line gives the total density (water plus all surfactant segments).

are within a radius of 7σ from the center of mass of the micelle. We have not found any oil inside the micelle. This density profile shows that the water penetration is small. All segments of the chain have approximately equal probability to be in contact with the water. (Only the first surfactant segment next to the hydrophilic heads has a significantly higher probability.) This is in perfect agreement with the experiments of Menger et al.⁸² These authors observed that the kinetics of the oxidation of a double bond in the surfactant with a hydrophilic reagent was not very sensitive to the position of this bond in the surfactant chain. From these experimental results Menger et al.⁸³ concluded that the water penetration inside a micelle is significant. The simulations show, however, that even for a micelle without water penetration, the probability of water contact is approximately equal for all chain segments.

Casal⁸⁴ studied the water penetration into the interior of a micelle using probe molecules. These studies suggest that although water can penetrate into a micelle, the central core of a micelle contains no water. This is in good agreement with our results. Figure 9 shows that in our case the radius of the core in which no water can be found is approximately 2.5σ .

The total segment density in the core of the micelle appears to be higher than in the bulk. This is in disagreement with the simulations reported in refs 25, 27, and 28 and may be due to the different models that have been used. In the theory of Szeifer et al. it is assumed that in the "hydrocarbon core" of the micelle the density is liquidlike and equal to the density of the oil. This assumption is not supported by these results.

Order Parameters. In Table III the average angle between two neighboring bonds in a surfactant is given. In a real surfactant this bond is fixed and approximately 110° . Note that by the addition of another spring between segments $k-1$ and $k+1$ we can fix this angle to any value.

The C-H bond order parameter can be measured experimentally by using NMR techniques. The C-H bond order parameter (S_{CH}) is determined by the angle between the normal to the interface and the bisectrix of the H-C-H angle. This parameter measures the alignment with the bonds in the chain with respect to the interface and contains therefore some information about the conformational statistics. In our model we have not taken the H atoms into account explicitly. Therefore, we cannot calculate this bond order parameter directly, but we can calculate

TABLE III: Average Angles between Three Segments in a Micelle and the Bond Order Parameter $S_{k-1,k+1}$ and S_{CH} ^a

	angle, deg	$S_{k-1,k+1}$	S_{CH}	S_{Exp}
1-2-3	112	0.32	-0.16	-0.20
2-3-4	111	0.43	-0.22	-0.20
3-4-5	99	0.08	-0.04	-0.14
4-5-6	93	-0.04	0.02	-0.12
5-6-7	95	-0.12	0.06	-0.02

^aThe segments (labeled k) are numbered from 1 to 7, where 1 is the first water particle and 7 is the last water particle of a surfactant. For comparison, some typical experimental data are shown in the tables.⁸⁶ Note that these experimental data have been obtained for larger surfactants.

the bond order parameter ($S_{k-1,k+1}$) defined by the angle between the vector spanned by the segments k and $k+1$ ($r_{k-1,k+1}$) and the vector between segment k and the center of mass of the micelle. When H atoms would be present it is reasonable to assume that these would be located in the plane that is perpendicular to $r_{k-1,k+1}$ and that contains the segment k . Thus $S_{k-1,k+1}$ is similar to S_{mol} , which measures the alignment of a vector perpendicular to the C-H-H plane. For tetrahedral molecules $S_{mol} = -2S_{CH}$.⁸⁵

The bond order parameters are given in Table III. The order parameter shows that the heads are more aligned compared to the tail segments. Although the same trend is observed experimentally,⁸⁶ the order parameter for the end segments is smaller than observed experimentally.

5. Concluding Remarks

In this article a simple oil/water/surfactant model is presented. The model contains only the most obvious elements: oil and water do not mix, and a surfactant is an amphiphilic molecule. Computer simulations of this model revealed rich structural detail. This detail is sufficient to qualitatively reproduce a number of experimental observations.

For sufficiently large systems, we could observe the formation of micelles. To our knowledge this is the first simulation that shows the spontaneous formation of micelles. An important aspect is that in our model hydrogen bonds are not present. Yet micelles are observed. This strongly suggests that self-assembly in surfactant systems does not require the presence of hydrogen bonds.

Simulations of the oil/water interface in the presence of micelles showed pronounced oscillations of the density profile of water and micelles in the water phase, which result from the packing constraints of the micelles. These oscillations provide a possible explanation of recent neutron reflectivity experiments.^{34,35}

Furthermore, our model predicts a depletion layer, a layer of water containing no surfactants, between the monolayer and the micelles. The presence of this layer suggests that there is a short-ranged force between the monolayer and the micelle. In our simulation this force is probably a solvation force. Additional simulations are required to measure this force.

One might speculate that such a depletion layer is of importance to the understanding of practical problems such as the rate of oil solubilization in micellar solutions. It would therefore be of considerable practical importance to verify this experimentally.

Besides the fact that our model clearly shows two-phase coexistence between an oil-rich and a water-rich phase, almost nothing is known on the rest of the phase diagram produced by our model. It would be of interest to determine the phase diagram and see whether this model also produces three-phase equilibria or other types of surfactant assemblies.

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