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Computer Simulations of Surfactants

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ABSTRACT. This Chapter is a review of the computer simulations of surfactant systems. The focus is on monolayers and on micelles as relatively simple examples of surfactant self assemblies. During the last decade simulations of monolayers have progressed to a level of sophistication where they can be used to interpret experimental data and even suggest new experiments. The computer simulation of micelles is much less advanced. We demonstrate that simulations of micelles are much more difficult than those of the corresponding monolayers, and we present some very simple models that are able to describe a micellar solution.

1. Introduction

Amphiphilic molecules such as surfactants, lipids, or fatty acids 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. At the oil/water interface these molecules can locate their hydrophobic chains in the oil phase and allow the polar head to be in the water phase. This situation is energetically more favourable than complete solution in either phase. The tendency for these surface-active agents to adsorb causes a reduction of the bare oil/water interfacial tension. Because of this property, surfactants are used in applications such as detergency and tertiary oil recovery [1].

The complexity of these systems makes it impossible to study surfactant systems with the same level of detail that would be used in a simulation of a simple liquid. It is therefore essential to make simplifications. As we will see, making a simplification is a subjective matter which reflects the interests of the individual researcher. For example, if we are interested in the chain conformations in a micelle, it is important to take into account the details of the intramolecular potentials of the molecules. Simulations with such realistic potentials are limited to times of the order of nanoseconds:

too short to observe surfactants leaving or entering a micelle. For realistic models, the observations are limited to the shortest time scale, e.g. the movements of surfactants within a micelle. If we choose to model a surfactant with a more idealized potential, the (effective) time span of the simulations is much larger, and it is possible to observe surfactants entering or leaving a micelle. However, since all the atomic details are lost, direct comparison with experimental data is impossible.

In this Chapter we focus on two examples of surfactant self assemblies: surfactant monolayers and micelles. This is a small selection out of the vast number of different assemblies that form in surfactant systems. For simulations that have been performed on bilayers (of importance in biological systems, since a bilayer is a simple model of a membrane) we refer the reader to the various review articles (for example, Refs. [2, 3]).

2. Surfactant monolayers

2.1. LANGMUIR MONOLAYERS

There is now a history of 100 years of experimental work [4] on Langmuir films. Langmuir films are monolayers of amphiphilic molecules on the water surface. These monolayers are studied by measuring their surface pressure-area isotherms. These experiments gave evidence for the existence of three phases: a gas phase, liquid phase, and solid phase of the monolayer. Some of the later experiments suggested that even more phases existed [5, 6], but these results were controversial because of the possible presence of impurities. It is only recently that these additional phases have been confirmed using novel experimental techniques [7–9]. Nowadays it is even possible to make direct observation of domains of the various phases characterized by different tilt directions of the chains (see for example Ref. [10]). At present considerable effort is being spent in identifying the various phases [11]. One can expect that simulations will contribute to the characterization of these phases. As a result, monolayers are an attractive area of research, and several simulation studies of these systems have been reported.

One of the first simulations of a 'realistic' model of a monolayer was reported by Kox *et al.* [12]. The model surfactants were chains of seven sites. The water was modeled as an external field that constrained the head groups to move in a plane. The interactions between the tail segments consisted of a short-ranged repulsion, and a Lennard-Jones potential was used for the interactions between the head groups. Springs were used to fix the distance between neighbouring carbon sites (C) and the angle between the C-C bonds. These simulations showed evidence for a liquid-gas phase transition. These early simulations were not sophisticated enough to observe other phase transitions.

The controversy about the existence of the LE (liquid-expanded) and LC (liquid-condensed) phases inspired several groups to study Langmuir monolayers using more detailed models [13, 14]. The models of these simulations are based on the pioneering work of van der Ploeg and Berendsen on bilayers [15]. The surfactants are represented with a pseudo-atom model, i.e. the methylene, the methyl, and head groups are treated as one atom. The water substrate is modelled with an external field so that the head groups cannot evaporate from the surface. These simulations yield information on the structure of the monolayers and the chain conformations. The differences between the models used by the various groups are small.

At high surface density and low temperatures, various solid-solid phase transitions can occur. For example, Lin *et al.* [16] used X-ray-diffraction to study a monolayer of heneicosanic acid ($\text{CH}_3(\text{CH}_2)_{19}\text{COOH}$) and observed first-order transitions between different lattice structures, and continuum transitions between phases characterized by different tilts of the molecules. Computer simulations at these high surface concentrations were performed by Karaborni and Toxvaerd [17, 18]. At these conditions, it is questionable whether a united-atom approach is sufficiently accurate [19, 20] (for more information on the importance of explicit hydrogen atoms see Ref. [21]). Karaborni and Toxvaerd used an anisotropic united-atom model to represent the interactions of the alkane backbone. This anisotropic potential is introduced to model the effects of the hydrogens. In Refs. [22, 23] it is shown that, at high densities, these anisotropic potentials give a significantly better equation of state than the united-atom model for alkanes. Furthermore, repulsive dipolar interactions were used to model the interactions between the head groups. The water was modelled using an external potential. This external potential was such that the chains could penetrate in the water phase. The simulations of this model of surfactants with 15 C segments showed two distinct phase transitions in the dense monolayer region. A transition between a liquid and solid was observed, and at higher densities a solid-solid transition. This solid-solid transition was characterized by a change from an all-trans conformation to conformations of the chains with kink defects. Interestingly, the solid-liquid transition was not observed when the simulations were repeated with a united-atom model.

Most of the previous results were for monolayers of hydrogenated fatty acids ($\text{CH}_3(\text{CH}_2)_n\text{COOH}$). To study the relative importance of the various intermolecular interactions, experiments have been performed in which the H-atoms are replaced by the larger F-atoms [24]. These fluorocarbon chains are much stiffer than their hydrogenated counterparts. Furthermore, for the fluorocarbon chains the head group is smaller than the backbone of the chain, while for the hydrogenated chains the head group is larger. Whether a computer simulation can predict the subtle difference between these systems is an important test for the credibility of these methods. In fact, Rice and

co-workers [25, 26] have shown that computer simulations can describe most of the experimental observations in these systems. The study in Ref. [26] predicts that the monolayer exhibits a phase in which the molecules tilt towards their nearest neighbours or towards their next-nearest neighbours depending on whether the chain length is odd or even. It is interesting to see whether these predictions will be verified by experiments in the near future.

2.2. LANGMUIR-BLODGETT FILMS

Monolayers that form at the air/water interface can be transferred to a solid substrate by dipping the substrate into the water. Depending on whether the substrate is hydrophobic or hydrophilic, the heads or the tails of the surfactants attach to the surface, respectively. When the substrate is dipped into the solution again, a second layer will attach. This procedure can be repeated, and films with over 1000 layers can be produced with this technique.

Most computer simulations have been performed on a single-layer Langmuir-Blodgett film [20, 27]. In a real system, there is a clear difference between water as a substrate (Langmuir monolayer) and a solid substrate (Langmuir-Blodgett film). In most simulations, however, both water and a solid substrate are modelled with an external potential that constrains the head groups to a plane. This makes a distinction between the two types of monolayers somewhat arbitrary. In fact, the distinction depends mainly on the experimental systems the authors chose to compare their results with. Many of the simulations discussed in the previous section could also be discussed in this section, and vice versa.

Cardini *et al.* [28] were the first to present computer simulations of a surfactant monolayer with the term "Langmuir-Blodgett film" in the title. The model used by Cardini *et al.* is identical to the one used by Bareman *et al.* [13] for a Langmuir monolayer (see the previous section), i.e. united atoms, no explicit head group, and the substrate modeled with an external field. The simulations yielded information on the structure of a relatively dense monolayer of arachidic acid ($\text{CH}_3(\text{CH}_2)_{18}\text{COOH}$). A more realistic model was introduced by Moller *et al.* [20]. The head group was explicitly taken into account (but the interactions between the head groups was modelled with a Lennard-Jones potential instead of a more realistic dipolar interaction). Furthermore, a detailed comparison was made between the united-atom model for the CH_2 backbone and a model in which the hydrogens were taken into account explicitly. The simulations of Moller *et al.* predict a transition of the tilt of the molecules, depending on the temperature. In the united-atom model such a transition could not be observed.

2.3. SELF-ASSEMBLED MONOLAYERS

Monolayers of surfactants on a gold or silica surface can form spontaneously by self assembly of the surfactant molecules from solution [29]. The structure of these monolayers is found to depend on the face of the gold crystal used, and the nature of the head groups of the surfactant. By altering the chain terminal group, the characteristics of the monolayer can be manipulated.

Detailed molecular dynamics simulations on these systems have been performed by Hautman and Klein [30–32]. The model used in these simulations is similar to the one used in the simulations of the Langmuir films (see section 2.1). The main difference is that the head group is now chemically bound to the substrate, and the underlying structure of the substrate will influence the structure of the monolayer. At present, the detailed nature of this bond is unknown, and different models are studied. The first study [30] used an artificially large, hard core for the S-S interactions to model the gold crystal lattice. Subsequent studies [32] used a corrugation potential. The lattice structure of the substrate does not necessarily correspond to the optimal structure for the head groups. This source of frustration leads to many interesting phenomena. For example, Hautman *et al.* [32] studied the structure of the exposed surface for various head groups; in particular the systems with $X = -CH_3$, $-OH$, and $-C \equiv N$ were studied. As might be expected, the surface of the $-CH_3$ terminated layer does not differ much from that of an ordinary Langmuir monolayer. The $-OH$ surface, however, shows a disordered (glass-like) one-dimensional network of hydrogen bonds. For the $-C \equiv N$ surface, a ferroelectric structure is observed that is incommensurate with the gold lattice. The wetting properties have also been studied in Ref. [33].

Siepmann and McDonald [34] studied the behaviour of binary mixtures of alkyl thiols with different chain lengths. These simulations were made possible by the use of special Monte Carlo techniques (details of these techniques can be found in Chapter 4). Siepmann and McDonald observed segregation in mixtures of C_{10} and C_{20} chains.

The simulations on self-assembled monolayers are already at such a level of sophistication that they provide a molecular explanation of the experimentally observed phenomena.

2.4. THE OIL/WATER INTERFACE

The oil/water interface is important in many applications. In these systems, surfactants are often used to reduce the interfacial tension. From an industrial point of view, one is interested in the relationship between the structure and properties of these surfactants. These structure-property relationships can be obtained from experiments on surfactants in which the

chemical structure is changed systematically [35]. Smit and co-workers [36, 37] developed a highly idealized model, based on that of Telo da Gama and Gubbins [38], to study the behaviour of surfactant molecules at the oil/water interface. In this work, Smit and co-workers tried to eliminate all molecular details. As a result oil, water, and surfactants were modeled with simple Lennard-Jones potentials using the same ϵ and σ for all interactions. Only the truncation of the potential depends on the type of interaction. Surfactants are constructed by connecting oil and water segments with harmonic springs. Using such an approach, it is impossible to obtain detailed molecular information, but the effects of tail length or branching on the efficiency of a surfactant in reducing the surface tension is predicted [37, 39].

3. Micelles

When surfactants are added to water they will form a monolayer at the water surface. The properties of such a layer have been discussed in section 2. A further increase of the surfactant concentration saturates the interface and the surfactants aggregate in the bulk. In these micelles, the surfactants point their hydrophilic head towards the water phase, and their hydrophobic tails form the interior of the micelle. The importance of these structures does not need any further discussion when we realize that it would be impossible to wash our hands with soap if micelles did not exist.

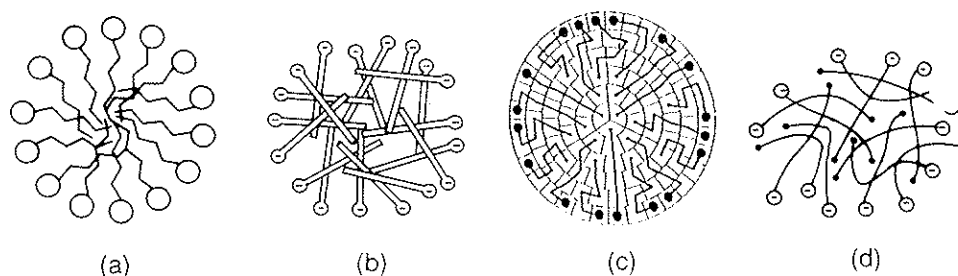


Fig. 1. Various views of a micelle based on Refs. (a) [40], (b) [41], (c) [42], and (d) [43].

Compared to our knowledge at a molecular level of the structure of a monolayer, our understanding of a micelle is still very poor (see Fig. 1 for a historic evolution of the structure of a micelle). Elementary questions are

still unanswered. To what extent does water penetrate into the core of a micelle [44]? What is the nature of the hydrocarbon/water interface [45]? What type of interactions are essential for the formation of micelles [46]? In fact, there are still qualitative differences of opinion on how a micelle might look.

From a computer simulation point of view, micelles are extremely difficult to study. The problem becomes clear if we consider the time scales that are involved in a micellar solution. These have been experimentally estimated. It takes from between 10^{-8} s to 10^{-6} s for a surfactant to enter or leave a micelle, the fusion of two micelles occurs in a time span of between 10^{-5} s and 10^{-3} s, and the lifetime of a micelle is estimated at between 10^{-2} s and [47]. If we recall that a computer simulation with realistic potentials is limited to several nanoseconds, it is obvious that drastic assumptions have to be made to study micelles. If one wishes to use a realistic model, it is necessary to construct the micelle at the beginning of the simulation and study its evolution. With more idealized models, it turns out that one can actually observe the self assembly of micelles.

3.1. ISOLATED MICELLES

Computer simulations of micelles have been pioneered by Pratt and co-workers [48-50]. In these studies, a simple lattice model was proposed in which the surfactant chain can occupy the sites of a diamond lattice. The energy parameters are chosen so that the tail-tail interactions are attractive and the head-head interactions repulsive. In contrast with the conventional notion that a micelle is a spherical structure with the head groups localized on the outside of a sphere, these simulations showed that fluctuations in shape and size lead to a more irregular picture of the micelle. This irregularity is also present in the more recent studies of more realistic models.

The first molecular dynamics simulations of a micelle containing 'realistic' surfactants were performed by Haile and O'Connell [51]. In this study a dodecyl surfactant was modelled with a united-atom representation of the carbon chain (similar to the model of Ref. [15]) and the head group is modelled as an external potential that fixes the carbon chain to lie inside a sphere. The volume of this sphere was chosen so that the density of the core of the micelle corresponds to that of liquid butane. These simulations yield results on the conformations of chains in the micelle. However, these results are biased by the underlying assumption that the micelle can not fluctuate in size, and that the head groups are constrained to fixed points on the surface of a sphere. In view of the results of Pratt and co-workers, these assumptions may not be valid. In subsequent work, by Wood *et al.* [52], the surfactants were allowed to move on the surface of the sphere, but were still constrained by a harmonic spring to the outer layers of the sphere.

The results of these simulations were similar to those of the earlier work. This work was extended by Karaborni and O'Connell [53, 54]. Their model of water allowed the surfactants to move everywhere, but the tails have to cross an energy barrier to enter the water phase, and the head groups a barrier to enter the core of the micelle. Since the external fields are spherically symmetric, only small fluctuations in size and shape were observed in this model.

The effect of water is explicitly taken into account in Refs. [55–57]. In addition, these simulations start with a postulated micellar structure. Watanabe *et al.* [56, 57] simulated a sodium octanoate micelle in an aqueous solution for 0.2 ns. They show that the micelle was stable over the length of the simulation. Considering the time scales of the simulations compared to t^* relevant experimental time scales, it is impossible to be certain that such a micelle is thermodynamically stable.

If we compare the simulations of monolayers with those of micelles, it is evident that the latter are much more difficult. In a micelle, the interface between the hydrocarbons in the core of the micelle and the water is ill defined. This implies that the modelling of the water using an external field will be less successful. Furthermore, a micellar solution is characterized by its micelle size distribution [58], i.e. there is not one micelle that determines all properties, and we can expect that, on the experimental time scale, fluctuations in micelle size will be important. With these realistic models, a simulation of the time evolution of such a system over 0.2 ns requires a sizable amount of computer time. Since, 0.2 ns is too short to observe surfactants leaving or entering a micelle, these simulations are necessarily focused on the configurations of the surfactant chains in a micelle. Unfortunately, experimental information is scarce and is not specific enough to allow direct comparison with simulation, a problem already encountered with the monolayers.

Smit and co-workers [39, 59, 60] studied micelles with a coarse-grained model (see section 2.4). In this case, all molecular details are lost, but a much longer time scale can be studied. In Ref. [61] the simulations were started with a random distribution of surfactants in a water/oil system. It was observed that a monolayer was formed at the oil/water interface and that micelles were formed in the bulk. A snapshot of the system is shown in Fig. 2. Despite the simplicity of the model, the simulations required a large amount of computer time and were performed on a parallel computer [62]. Unfortunately, the number of micelles was too small to determine the micelle size distribution from these simulations. Such a distribution was obtained in subsequent work using a slightly different model [60]. In these simulations (equilibrium) dynamical processes such as the inclusion of single surfactants into micelles, the elimination of single surfactants from the micelles, the fusion of two micelles, and the slow breakdown of a micelle, were observed.

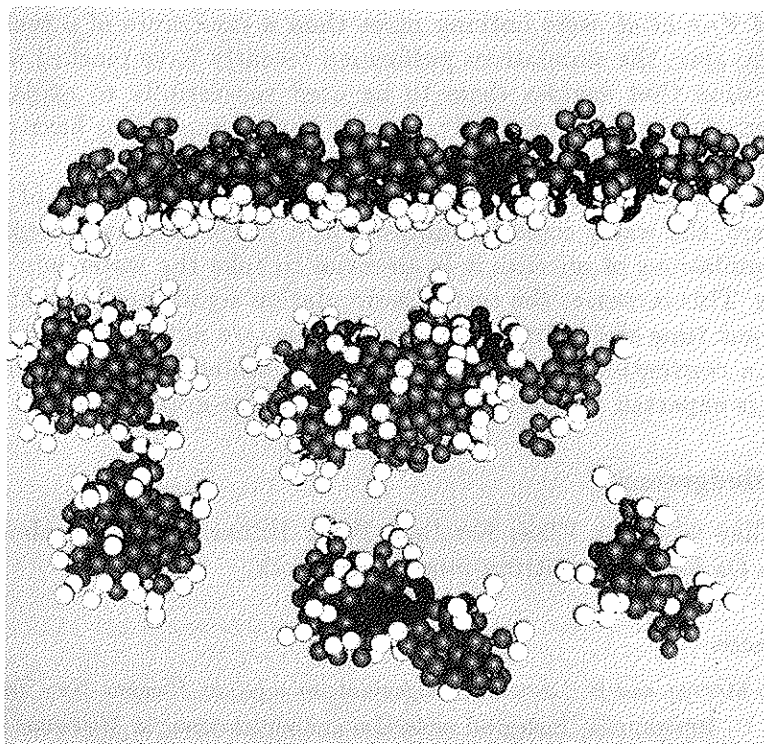


Fig. 2. A typical example of a configuration of surfactant molecules in an oil/water system for 1.5% surfactants. The snapshot shows only the surfactants at one of the monolayers and the surfactants in the water phase. For clarity, the surfactants in the oil phase and the oil and water particles are not shown. The hydrophilic segments are light grey and the hydrophobic segments dark. The surfactants have a head of two hydrophilic w particles and a tail of five hydrophobic o particles (h_2t_5).

This is an encouraging observation, since the experimental time scale for these processes spans more than 6 decades. These results suggest that it is possible to perform systematic studies of dynamical processes in micellar solutions. The first interesting results in this direction have been reported by Karaborni *et al.* [63]. Karaborni *et al.* used a similar oil/water/surfactant model to study the oil solubilization in surfactant solutions. On the basis of their molecular dynamics results they identified three different mechanisms of oil solubilization.

4. Concluding remarks

Looking back at a decade of computer simulations of monolayers, one can only conclude that the progress has been enormous. While the first simu-

lations of Kox *et al.* were nothing more than a caricature of a real surfactant monolayer, the simulations performed recently have reached a level of sophistication that enables them to be used successfully to explain some experimental data. Encouragingly, some of these simulations have provided interesting suggestions for new experiments.

Simulations of micelles are far less advanced. In simulations of aqueous monolayers, the water could be modeled as a static external potential, but in the simulations of micelles it is essential to take the water into account explicitly. This increases the cost of a simulation significantly. Furthermore, the relevant time scales for realistic potentials, are not, at present, accessible with a conventional molecular dynamics simulation. As a consequence, progress is expected to come from the more coarse-grained models.

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