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COMPUTER SIMULATIONS OF SURFACTANT SELF ASSEMBLY

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A simple oil/water/surfactant model is used to study the self-assembly of surfactants. The model contains only the most obvious elements: oil and water do not mix, and a surfactant is an amphiphilic molecule, i.e. one side of the molecule likes oil but dislikes water, the other side likes water but dislikes oil. Computer simulations on large oil/water/surfactant systems were performed on a network of 400 transputers using a parallel molecular dynamics algorithm. The simulations yield a complete micellar size distribution function. Furthermore, we observe (equilibrium) dynamical processes such as the entering of single surfactants into micelles, single surfactants leaving micelles, the fusion of two micelles, and the slow breakdown of a micelle.

1. Introduction

The dynamics of self-assembled surfactant structures is of importance in a variety of processes ranging from the transport of molecules through cell membranes to the removal of stains in a washing machine. Even in the simplest assemblies, micelles in water, the time scales of dynamical processes vary from 10^{-8} to 10^{-2} sec.[1]

Over the last years, several computer simulation studies on systems containing surfactants have been reported.[2–9] Most of the molecular dynamics simulations[5–9] use "realistic" models of surfactants to study the structure of an aggregate. With these realistic potentials, simulations can be performed that span several nano seconds. This is too short to study the collective behaviour of *several* assemblies. An alternative approach, using simplified models, shows the spontaneous formation of monolayers, micelles[10], and also a membrane.[11] Here we show that with these models it is possible to observe in a computer simulations the dynamics that is observed experimentally.

2. Oil/Water/Surfactant Model

In our model, two simple observations[12] constituted our starting point: oil and water do not mix, and a surfactant is an amphiphilic molecule, i.e., a molecule of which one side is hydrophilic and dislikes oil and the other side is hydrophobic and likes oil.

We assume the existence of four types of particles: o particles, w particles, h particles, and t particles. These 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 t particles and one or more h particles; these are joined by harmonic potentials. The four types of particles interact with truncated and shifted Lennard-Jones potentials with energy parameter ϵ_{ij}, distance parameter σ_{ij}, and the cut-off radius R_{ij}^c. We have assumed that for all interactions $\epsilon_{ij} = \epsilon$ and $\sigma_{ij} = \sigma$. In order to make the interactions different, 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. Furthermore, we have used for the t particles the same interactions as for the o particles. For some surfactants the h-h interaction is truncated at $R_{ij}^c = 2.5\sigma$, for others $R_{ij}^c = 2^{1/6}\sigma$. With this model it is simple to mimic changes in the chemical structure. For example, addition of oil-like particles to the tail allows us to study the influence of increasing the tail length[13] or branching of a surfactant.[14]

3. Parallel molecular dynamics

To simulate large systems of particles for a large number of time steps, we have developed an efficient parallel molecular dynamics algorithm. We discuss some aspects of the implementation.

Molecular dynamics is suited for being done on parallel computers since the computations are the same for many particles. There are two main techniques to exploit parallelism, viz. particle parallelism and geometric parallelism.

When particle parallelism is used a fixed set of particles is assigned to a processor and these particles remain on this processor during the entire simulation.[15,16] Continually, each processor calculates forces and the new positions for its particles. Since the distribution of particles remains unchanged during the simulation, it is straightforward to determine the assignments such that the workload is evenly distributed. The communication overhead can, however, become severe, since in order to evaluate the Lennard-Jones potentials it is necessary for each processor to communicate with all others to determine whether any two particles interact.

Geometric parallelism does not suffer from this particular disadvantage. It assigns space, not particles, to processors.[17–19] During the computation, a processor calculates the trajectories of all particles it finds in its space. Because of the movement of the particles, some particles may enter a processor's space, others may leave. For this reason, processors continually need to redistribute the particles to make sure that each one has the right subset. Geometric parallelism can also efficiently be applied for evaluating multi-particle potentials such as bending and torsion potentials as is shown in.[17]

The short range nature of the Lennard-Jones potential can be turned into a real advantage for geometric parallelism. Since the interactions in our model do not exceed distances larger than 2.5σ, it is not necessary to exchange information over long distances. This consideration has led to the well-known 'linked-list' method in

ρ	#particles	Cray X-MP	36 T800	400 T800
0.5	2916	0.11	0.48	0.10
0.7	4000	0.19	0.79	0.14
0.9	5324	0.32	1.47	0.23
1.0	6912	0.48	1.84	0.36
0.7	19652	1.05	-	0.41
0.7	32000	-	-	0.68
0.7	39304	2.05	-	0.86

Table 1: Comparison of execution times (seconds per iteration). ρ is the reduced density.

which the simulation box is divided into a number of cells. These cells are assigned to a processor such that particles only interact with particles in the same cell or cells nearby (see ref. [20]). Furthermore, in our implementation we have used a combination of the neighbor list and linked list[21] (see ref. [17] for details). The resulting algorithm scales linearly with the number of particles.

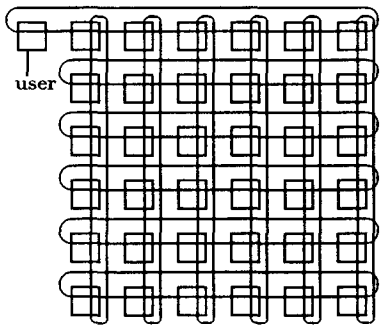

Fig 1: A toroidal network of $6*6$ processors, each square represents one transputer which is linked to four neighbors.

In table 1 we present timing results of simulations done on a Cray X-MP (single processor), 36 and 400 T800 Transputers (see Fig. 1). We should note that the FORTRAN implementation for the Cray is fully vectorized. The timing results show that molecular dynamics simulations can benefit greatly from parallel computing, both in time and in cost. Already for small numbers of particles a parallel machine can compete with a supercomputer as a Cray, but its real power is shown at large numbers of particles.

4. Results of the simulations

4.1. *Oil/water/surfactants*

The most simple surfactant that we can study with our model is a dumbbell sur-

factant (h_1t_1). We have performed simulations with a system of 512 particles. The computational aspects of these simulations are described in detail in refs. [22, 14]. The surface tension as a function of the number of surfactants on the interfacial tension is shown in Fig. 2. The reduction in γ is proportional to the number of surfactant particles. These results show that our simple oil/water/surfactant model captures some features of real system. We could not observe, however, the formation of micelles in these small systems.

Simulations on a large oil/water/surfactant system (39,304 particles) does show the formation of micelles. A typical example of the instantaneous arrangement of the surfactants is shown in Fig. 3. In the water phase micelles have formed spontaneously. For comparison, a simulation of dumbbell surfactants at the same concentration with the same system size was performed. In this simulation the formation of micelles could not be observed.

4.2. *Micelle formation*

In the previous section we have studied the formation of micelles at $T = 1.0\epsilon/k_B$. It turned out that at these conditions the the dynamics is so slow that it takes a large number of time steps for determining a micelle size distribution. In order to enhance the dynamics, we have studied our system at a higher temperature ($T = 2.2\epsilon/k_B$). The simulations were performed with $(h)_3ht_5$ surfactants (a branched head) with repulsive interactions between the h segments. The total number of particles were 32,000. For more computational details see ref. [24].

A solution containing micelles can be described quantitatively by the size distribution of aggregates[25]. We can determine this distribution by counting the clusters at regular intervals. The distribution as obtained from our simulations is shown in Fig. 4. In order to test whether equilibrium has been reached, we prepared a system with an entirely different initial condition at a much lower temperature. At this condition *all* surfactants were in aggregates. The temperature was then increased to $T = 2.2\epsilon/k_B$ and after equilibration the obtained micellar distribution function was indistinguishable from the one obtained starting from a completely random distribution of surfactants (Fig. 4).

The cluster distribution function shown in Fig. 4 has an optimal cluster size of 22 to 23 surfactants. We observe micelles with sizes ranging from 15 to 30 surfactants, indicating a significant polydispersity. An important aspect is that in the distribution function we observed a maximum, and a minimum between the (proper) micelles and the oligomers. Such a shape of the distribution function has been predicted by various mass-action models[26] and is one of the basic assumptions in the theory of the dynamics of micelle formation.[1] These results demonstrate that a simple molecular surfactant/water model gives rise to such a distribution and therefore confirms the basic assumptions of these theories. In future work we will study the shape of the micellar distribution function as a function of the temperature and surfactant structure in detail.

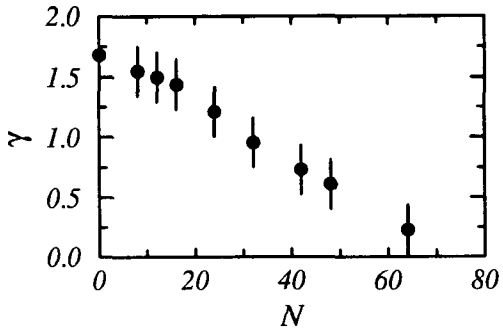

Fig 2: Surface tension γ as a function of the total number of surfactants N.

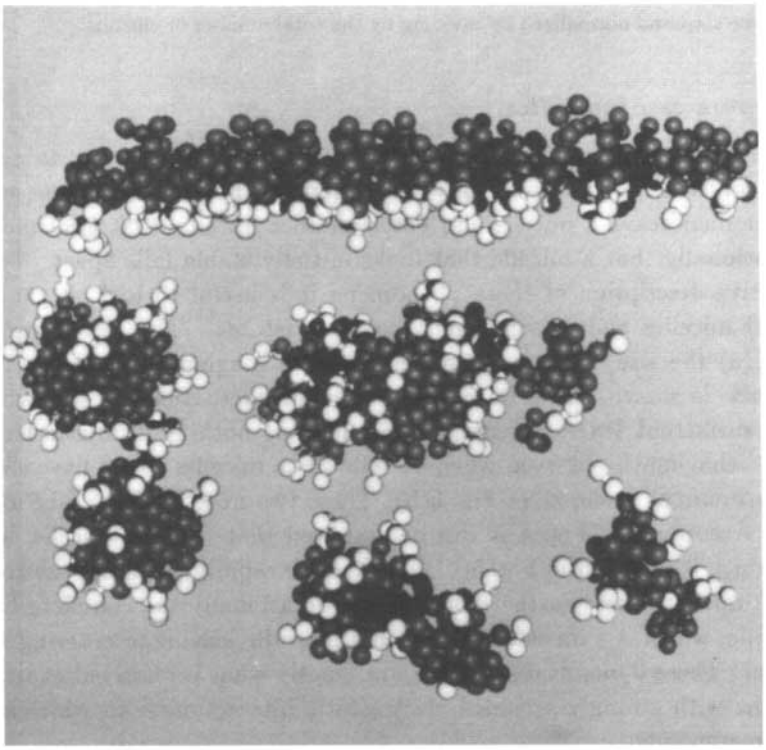

Fig 3: Typical example of a configuration of surfactants in an oil/water system for 1.5% surfactants. The snapshot shows only the surfactants at one of the monolayers and the surfactants in the water phase. For clarity, the surfactants in the oil phase and the oil and water particles are not shown. The 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).

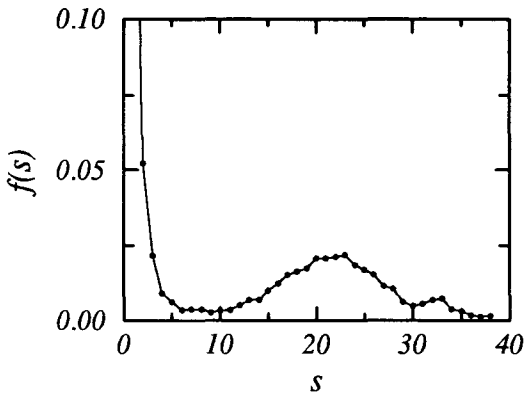

Fig 4: The micellar size distribution function $f(s)$. s is the number of surfactants in an aggregate. The figure has been obtained by averaging over approximately 200 configurations taken every 4000^{th} time step and normalized by dividing by the total number of clusters.

4.3. *Dynamics of micelles*

Having established that our model shows the same behaviour as an equilibrium micellar solution, we can now study the dynamics. In our simulations we observe that monomers leave a micelle and enter another micelle, that two micelles fuse, and occasionally that a micelle that looks initially stable falls apart. To obtain a quantitative description of these phenomena it is useful to look at the evolution of typical micelles and of some individual surfactants. This is shown in Fig. 5. In Fig. 5(a) the size evolution of a micelle, with roughly an optimum number of surfactants, is shown. This micelle shows small fluctuations in size when an individual surfactant leaves or enters a micelle, but nothing dramatic happens. A different behaviour is observed when we follow two micelles which have a size which is not optimum as is shown in Fig. 5(b). These two micelles fuse and form one big micelle. According to Fig. 4 it can be expected that this big micelle is not very stable, which is reflected in Fig. 5(b) since its size rapidly decreases towards a more optimum micellar size. Furthermore, we see occasionally the complete breakdown of a micelle, which is a much slower process than the leaving or entering of a single surfactant. These dynamical processes are exactly what is observed experimentally in systems with strongly screened electrostatic interactions,[1] to which our model closely corresponds.

5. Concluding remarks

We have presented a simple oil/water/surfactant model and this model to study various properties of surfactants. If we use a sufficiently large system our model predicts the formation of micelles.

The molecular interactions that play an essential role in promoting surfactant self-assembly are still the subject of debate. Beesly *et al*[27]. studied the formation of micelles in non hydrogen-bonding polar fluids. From these experiments they

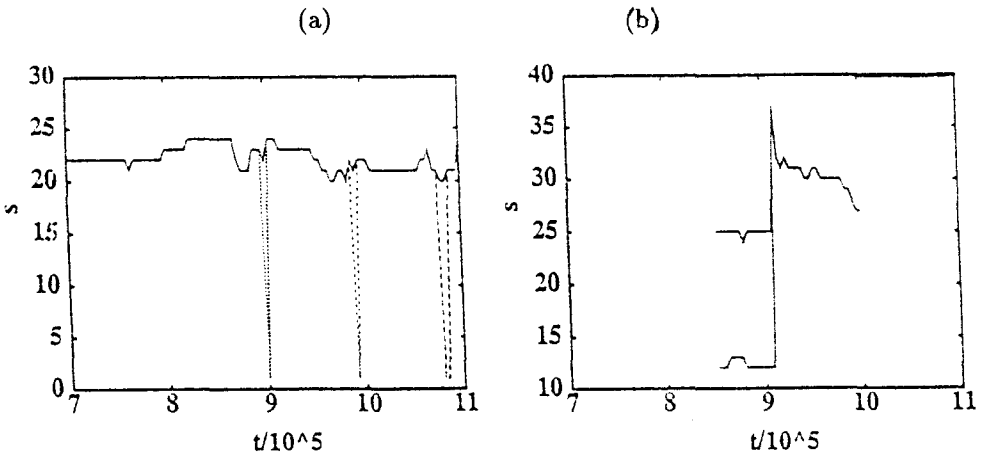

Fig 5: Evolution of micelles; the full line shows the total number of surfactants (s) in these micelles as a function of time t (in a particular time interval). In figure (a) the micelle shows small size fluctuations around its average value, caused by the entering or leaving of a single surfactant. The broken lines show the evolution of three single surfactants belonging to this micelle. Figure (b) shows the fusion of two aggregates into one large micelle (note that the origin has been shifted).

concluded that for cooperative interaction between amphiphilic molecules, hydrogen bonding is essential. In our model there are no explicit hydrogen bonds. This suggests that hydrogen bonds are *not* essential for the formation of micelles.

At various points in our simulations we observed a very slow dynamics. This can lead to very long equilibration times. A possible way to avoid these difficulties is to use a Monte Carlo method in which surfactants are inserted in random positions in the system. In an ordinary Monte Carlo method this will result in a prohibitively low acceptance rate. Frenkel *et al.* have shown that by using special techniques to grow a chain it is possible to insert chains at these conditions with a reasonable acceptance rate[28]. This development shows that it will be possible to use these configurational biased Monte Carlo methods for these systems.

One of the remarkable results of our simulations is that we can observe the dynamics of micelles. The typical time scale of these dynamical processes has been determined experimentally. For example, it has been observed that the time scale for individual surfactants to leave a micelle is $10^{-8} - 10^{-6}$ s and the typical life time of a micelle is of the order of $10^{-3} - 10^{-1}$ s. These time scales are clearly (far) out of the range accessible by simulations on realistic models, where the maximum simulation time is of the order of $10^{-9}s$. This allows us to use molecular dynamics to study dynamical processes that are of importance in biological and industrial applications. An interesting new development is reported in ref. [29]. Karaborni *et al.* used a similar oil/water/surfactant model to study the oil solubilisation in surfactant solutions. On the basis of their molecular dynamics results they identified three different mechanisms of oil solubilisation.

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