structure and to illustrate better the hexagonal packing arrangement of the individual molecules. X-ray diffraction[5] has also shown the tendency for the molecules to arrange themselves into layers of this type.

Figure 1d is an interesting image of a sample dried from a benzene solution. This image was recorded with the sample under mineral oil, a commonly used technique of scanning tunnelling microscopy (STM) which often yields images with lower noise. There are several balls of the usual size in the company of a significantly larger ball, ~1.5 nm in diameter. This ball may be a larger fullerene such as $C_{180}$ or $C_{240}$, although this is highly speculative[7]. This is the only such image we have found amid many thousands of fullerene molecules. The other significant aspect of the image in Fig. 1d is that some of the smaller balls show ridges roughly 0.3–0.4 nm apart, whereas others reveal no features. Ridges have been observed in many instances, both with and without the oil present. Although these features might be produced by the carbon cage underlying the $\pi$-electron cloud of the fullerenes, they may instead be simply a consequence of surface contamination of the molecules.

Figures 1a–c are images of the surface of bulk, solid fullerite.

The individual fullerene molecules that produce the images are in contact with other fullerene molecules, not interacting directly with the gold substrate. The mechanism by which the current flow enables these images to be recorded is not entirely clear. There are, however, many examples in the literature where nominally insulating species produce excellent images[8]. One possibility is that the presence of the tunnelling tip perturbs the molecules in such a way that suitable electronic states become available for occupation. Another possibility is that the necessary electronic states may arise from the alteration of molecular orbitals due to the proximity of neighbouring molecules when in the solid state.

These images corroborate other evidence for the existence of the fullerenes and provide information about the structure of their solid phase. Other applications of STM to the fullerenes will probably use the spectroscopic and manipulative potential of STM to study individual molecules in detail. One problem to be overcome is that of getting an individual molecule to stay in place under the influence of the probing tip. STM experiments at low temperature and in vacuum are the next steps. □

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# Computer simulations of a water/oil interface in the presence of micelles

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AMPHIPHILIC molecules such as detergents or lipids, which contain a hydrophilic 'head' and a hydrophobic 'tail' are capable of forming a wide variety of complex structures, including micelles, vesicles, bilayers, monolayers and liquid crystalline structures. This property is essential in many biological processes and is exploited in industrial and domestic applications, but remains poorly understood at a molecular level. Here we present the results of computer simulations of a molecular model for an oil–water–surfactant system. Micelles form spontaneously in the water phase and a monolayer of surfactants forms at the oil/water interface. A depletion layer, containing only water, separates this monolayer from the micelles. The density profiles of the micelles and the water show pronounced oscillations, which result from packing constraints on the micelles near the interface. These oscillations in the water density profile furnish a possible explanation of the results of neutron reflectivity experiments on water–surfactant systems.

We performed molecular dynamics calculations on an oil–water–surfactant system. The model we used for this three-component system has two kinds of particle, which we label by the letters o and w respectively. An oil molecule consists of a single o particle and a water molecule consists of a single w particle. A surfactant molecule is a chain of two w particles followed by five o particles, each bound to its neighbour by a strong harmonic force. All particles interact by a Lennard–Jones potential $\phi(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6]$. The o–o and w–w inter-

action is truncated at $2.5\sigma$. The o–w interaction is truncated at $2^{1/6}\sigma$ to make this interaction completely repulsive. As a result, the oil and water do not mix and form a stable liquid/liquid interface[1,2]; the surfactant molecules are amphiphilic, one end is hydrophilic and dislikes oil, the other end likes oil and is hydrophobic[2,3]. Monte Carlo simulations on a related model have been reported[4,5].

We performed our simulations at constant temperature ($T = 1.0\varepsilon/k_B$) and volume on a network of 100 transputers using an efficient parallel-processing algorithm for molecular dynamics (K.E., P.A.J.H. and B.S., manuscript in preparation). The particles were initially placed on a face-centred-cubic lattice of size $30.4\sigma \times 30.4\sigma \times 60.8\sigma$. The density obtained was $\rho = 0.7\sigma^{-3}$, with 39,304 particles. Surfactants were introduced in a way that guarantees a spatially random distribution. All the remaining particles on one half of the lattice were water and on the other half oil. The surfactant concentration ranged from 1% to 3%. The system was equilibrated for at least 100,000 time steps ($\Delta t = 0.005(m\sigma/\varepsilon)^{1/2}$), and then run for at least another 100,000 time steps. Because we use periodic boundary conditions, there are two interfaces and both are depicted in the figures.

Figure 1 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 towards water). In the water phase, next to the monolayer, there is a depletion layer a few molecular diameters wide that contains almost no surfactant. 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. Lower surfactant concentrations yielded similar results.

Figure 2 shows a typical instantaneous arrangement of the surfactants. In the water phase the formation of micelles has occurred. In the oil phase the surfactants also tend to cluster, but clearly defined reversed micelles cannot be discerned. In addition, this figure clearly shows the depletion layer.

We base our explanation of these observations on the fact that structure in simple liquids[6], and even in some more complex systems such as liquid crystals[7], is largely determined by hard-core interactions. Imagining the micelles to be hard spheres[8]
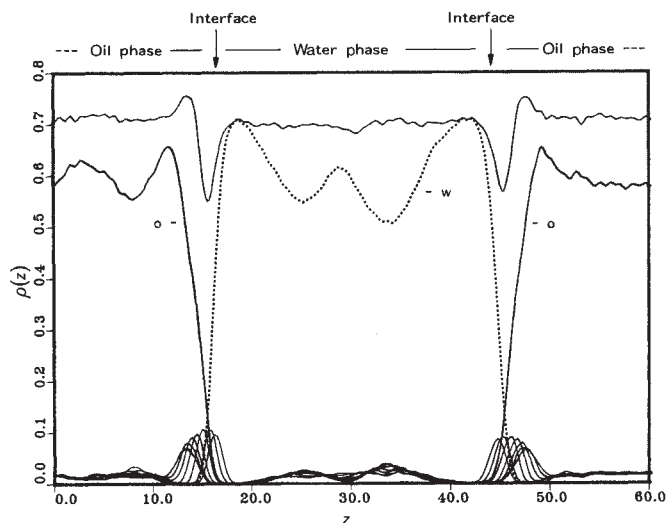
FIG. 1 Density profiles of the oil, water and surfactant particles. The green line gives the total density (oil, water and all surfactant segments). The dotted black line gives the density profile of the water particles, the solid black line of the oil particles. The blue lines give the density profiles of the two hydrophilic segments and the red 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.

and the monolayer to be a wall, the system is equivalent to a hard-sphere fluid confined between parallel plates. In such a system, packing constraints cause characteristic oscillations in the density profile[9]. Similarly, packing constraints on the micelles will cause oscillations in their distribution. As the total density in the water phase is constant (see Fig. 1), 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 there is only one interface, and the oscillations will be present in the neighbourhood of the interface.

If the interaction between the micelles and the monolayer was really the same as that between a hard sphere and a hard wall, then the first layer of micelles would be in contact with the monolayer and no depletion layer would be present. In our simulations, however, we observe a depletion layer, the width of which suggests a short-ranged repulsion between the micelles and the monolayer. Because the direct interactions between the heads of the surfactants are attractive in our model, this is somewhat surprising. This repulsive interaction is probably due to the water molecules between the micelles and the monolayer. Such an effective force between supramolecular structures caused by solvent molecules is often referred to as a solvation force[10].

Whereas previous theoretical work has been concerned mainly with either micelles[11] or with a monolayer[12], our model involves both and can therefore be used to help interpret recent specular neutron reflection experiments[13,14]. These experiments on the air/water interface of a solution containing ionic surfactants showed an 'unexpected' enhancement in the reflectivity of $D_2O$ above the critical micelle concentration, which has not been explained satisfactorily. The oscillations of the density profile



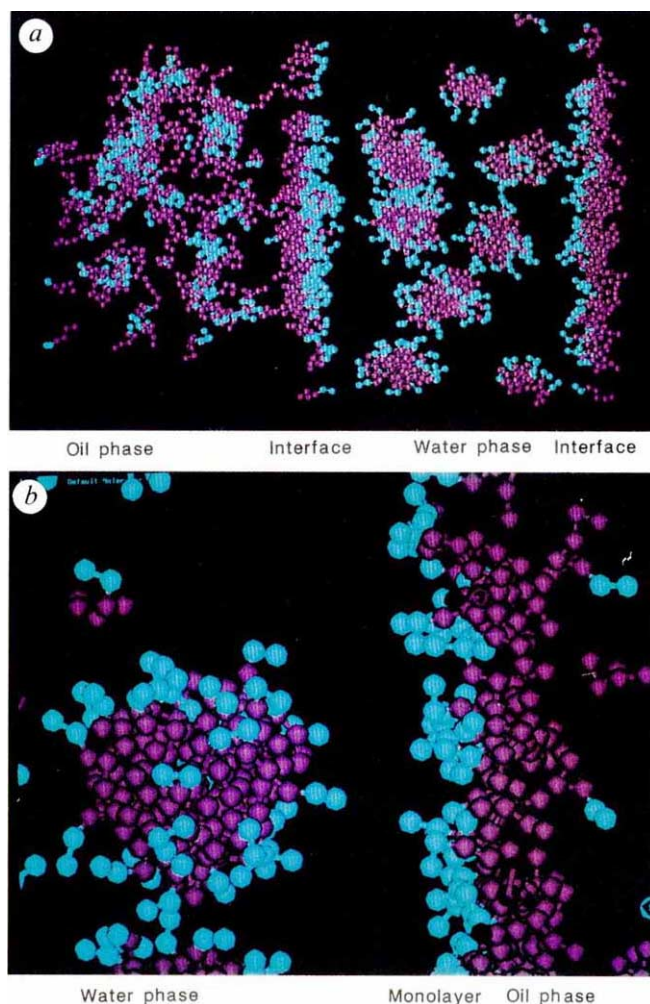FIG. 2 a, Typical example of a configuration of surfactants in an oil–water system. The hydrophilic segments are blue and the hydrophobic segments purple. For clarity the positions of the oil and water particles are not drawn. b, Close-up of one of the micelles close to the monolayer.

of water as observed in our simulations, however, should give rise to just such an enhancement of the reflectivity. The location of the maximum, which corresponds to the period of the oscillations, depends on the size of the micelle, which in turn depends on the type of surfactant. Indeed, these dependencies have been observed in the reflectivity experiments[14]. Lee et al.[14] have stated that an oscillating water density profile would explain the enhancement. They attribute the oscillations to a complicated layered structure of water and surfactant bilayers but our simulations indicate that these oscillations simply result from the packing constraints of micelles.

The depletion layer we have found may be of importance in understanding practical problems such as the rate of oil solubilization in micellar solutions. It is therefore of considerable practical importance to verify this layer experimentally. □

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