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Molecular-dynamics simulations of amphiphilic molecules at a liquid-liquid interface

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In this paper we present molecular-dynamics simulations for a simple liquid-liquid-amphiphile model system. We have determined the density profiles and the influence of the amphiphilic particles on the interfacial tension of the liquid-liquid interface. The amphiphilic particles distribute preferentially to the interface. The addition of a small amount of these surface-active particles gives rise to a substantial decrease of the interfacial tension.

For many years amphiphilic compounds (surfactants or blends of surfactants) have been used to lower the interfacial tension of an oil-water interface. Since such oil-water-surfactant systems are encountered in many practical situations, such as use of detergents, tertiary oil recovery, etc., they have been the subject of extensive experimental studies. However, owing to their complicated nature, they have far less often been the subject of theoretical work.[1,2] Therefore computer simulations of simple model systems may provide insight into the specific microscopic mechanisms of the behavior of these systems.

In this paper we report on simulations of a simple model liquid-liquid-amphiphile system, in which we have tried to incorporate, albeit crudely, some of the characteristics of a real oil-water-surfactant system. This is as far as we know the first report on a molecular-dynamics calculation which demonstrates that the interfacial tension can be reduced by the addition of amphiphilic compounds. Previous simulations of amphiphilic systems have concerned the internal structure of a micelle[3,4] and a Monte Carlo calculation on a lattice.[5]

Our model system contains two liquid layers of 256 particles A and 256 particles B placed at the center of a periodic box of size $7.15\sigma \times 7.15\sigma \times 14.30\sigma$ (Fig. 1), where σ is the unit of length. The particles are assumed to interact via a shifted Lennard-Jones (6-12) potential,

$$V_{ij}(r)=\begin{cases}4\varepsilon[(\sigma/r)^{12}-(\sigma/r)^{6}]-V(R_{ij}^{c})\,, & r\le R_{ij}^{c}\\ 0, \quad r>R_{ij}^{c}\,, & \end{cases} \tag{1}$$

where r is the distance between particles i and j.

For the A-A and B-B interactions the potential is truncated at

$$R_{AA}^{c}=R_{BB}^{c}=2.5\sigma\ .$$

For the A-B interactions, only the repulsive part of the Lennard-Jones potential is considered:

$$R_{AB}^{c}=2^{1/6}\sigma\ .$$

An amphiphilic particle (C) is defined as a particle A connected via a harmonic force to a particle B,

$$U_{A,B}^{H}=\tfrac{1}{2}k(\,|\,r_A-r_B\,|\,-\sigma)^2\ , \tag{2}$$

where the value of the force constant is made sufficiently large such that 98% of the connected units have a momentary length within 2% of the average value σ.

All the simulations have been performed at a reduced temperature $T^{*}=1.0kT/\varepsilon$ and a reduced overall density $\rho^{*}=0.7\rho\sigma^{3}$. We have kept the total number of particles constant in such a way that each amphiphile replaces one particle A and one particle B. Note that owing to the symmetry of the model the two liquid layers have identical properties.

We have calculated the surface tension γ by integrating the difference of the normal $[p_N(z)]$ and tangential $[p_T(z)]$ pressure tensor components across the system.[6] In the case of our system with two interfaces, γ reads,

$$\gamma=\tfrac{1}{2}\int_{0}^{L_z}dz\,[p_N(z)-p_T(z)]\ , \tag{3}$$

where L_z is the height of the box (Fig. 1).

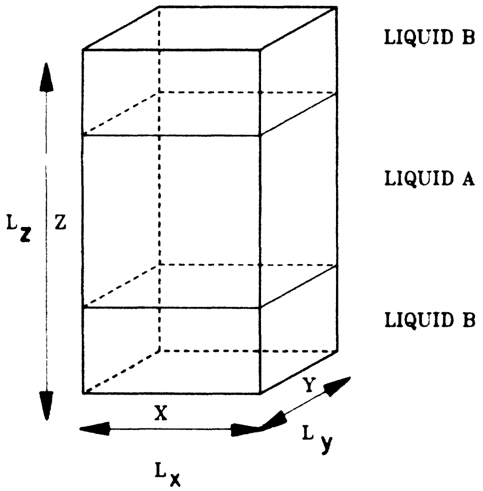

FIG. 1. Schematic drawing of the liquid-liquid interfaces: $L_x=L_y=7.15\sigma$, $L_z=14.30\sigma$.

In order to save computing time and to ensure an equal distribution of the amphiphiles between the two interfaces, the amphiphiles were placed initially close to (but not at) the interfaces. Comparison of this initialization with one in which the amphiphiles were placed randomly in the two liquids showed no significant variation in the final results.

We have allowed 2×10^4 time steps [$\Delta t=0.007\tau_0$, $\tau_0=\sigma(m/\varepsilon)^{1/2}$] for equilibration, which was sufficient to obtain stable density profiles and constant total energy. After equilibration we measured the density profiles and the components of the pressure tensor, and stored the positions of the amphiphilic particles every twentieth time step on magnetic tape for further analysis. In order estimate the statistical reliability we divided the simulations into subruns of 4×10^4 time steps. The standard deviation of the values for the surface tension was calculated from these subruns. One total run took from 10 to 20 subruns.

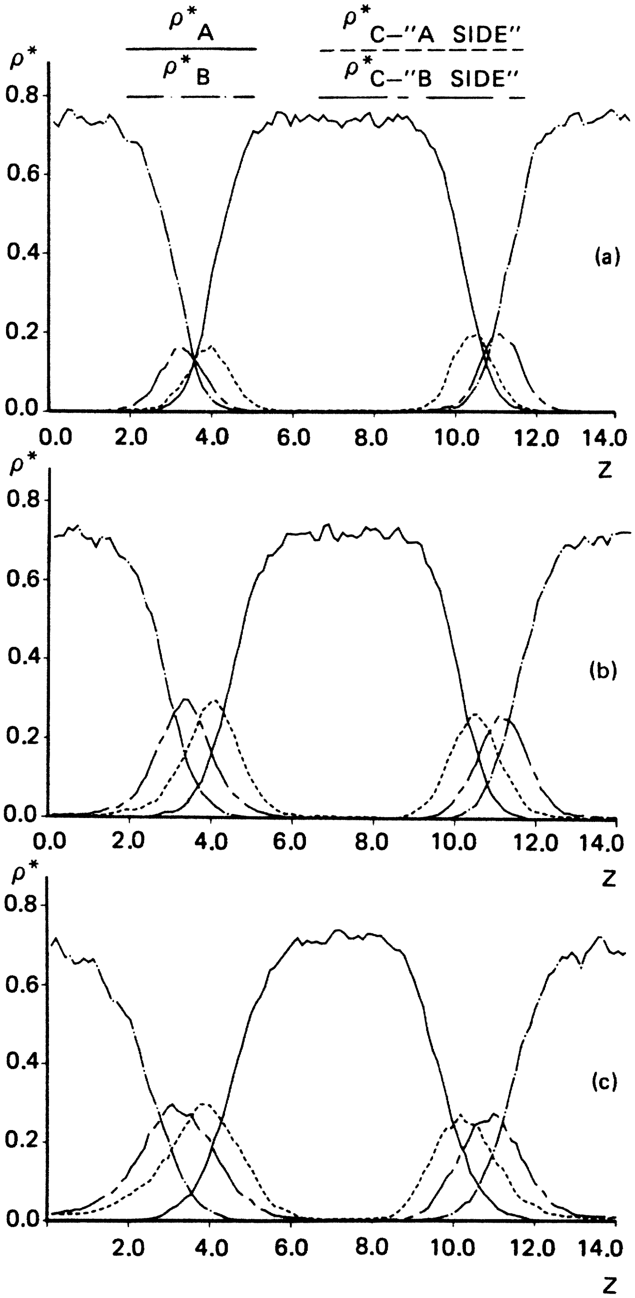

FIG. 2. Density profiles of compounds A, B, and C as a function of the height z. In order to demonstrate the ordering of the amphiphiles (C), the density profiles of the "A side" and "B side" of the amphiphiles are drawn separately. The total number of amphiphiles is (a) $N_C=24$, (b) $N_C=48$, (c) $N_C=64$.

In Figs. 2(a)–2(c) we have plotted a series of density profiles for different numbers of amphiphilic particles. These plots demonstrate that the amphiphiles distribute preferentially to the interface. As the concentration of component C is increased, the interface broadens to accommodate the amphiphilic particles. Detailed inspection of the density profiles of the amphiphiles shows that some particles diffuse from one interface to the other. This can be clearly seen in the snapshots of the positions of the amphiphiles, which are given in Fig. 3.

The projection of the positions on the plane $z=0$ [Fig. 3(c)] shows no specific ordering, while the projection on the plane $y=0$ [Fig. 3(b)] demonstrates that the amphiphiles are aligned. The "A side" of a C particle is pointed towards the A-rich layer. This alignment is quantified by the order parameter[7] S,

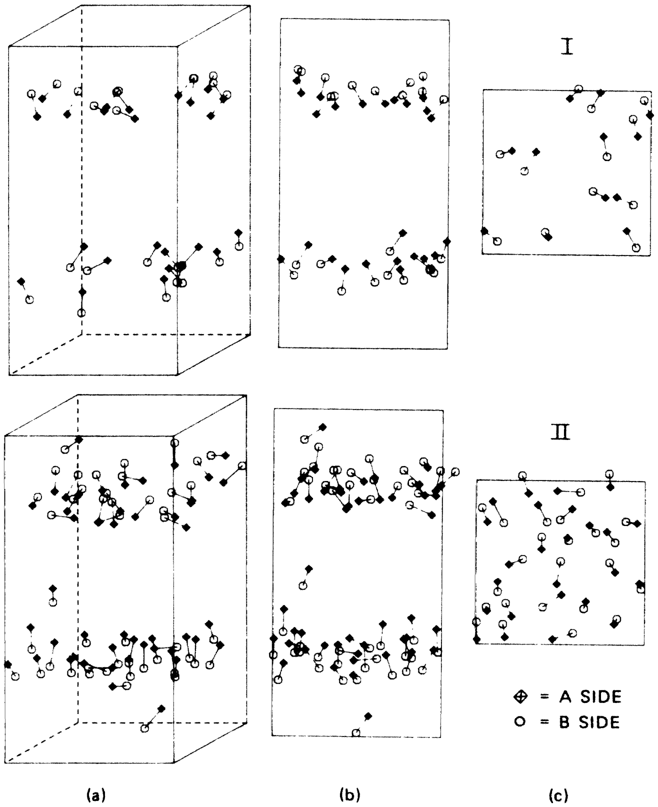

FIG. 3. Snapshot of the positions of the amphiphiles. (Note that the positions of particles A and B of the bulk liquids are not drawn.) In (a) a perspective view is given, in (b) a projection on the front plane, and in (c) a projection of the lower layer on the bottom plane. The total number of amphiphiles is 24 (I) and 48 (II).

$$S = \tfrac{1}{2}\langle (3\cos^2\theta - 1)\rangle \ , \tag{4}$$

where θ is the angle of the amphiphile with the normal to the interface. When all the particles are aligned parallel to the surface, $S=-\frac{1}{2}$; when they are all perpendicular to the surface, $S=1$. Typical values of the order parameter in the interfacial region were $S=0.30\pm0.03$ ($N_c=16$). We have found a slight tendency for the order parameter to decrease as the number of amphiphilic particles was increased. On account of the steric hindrance of the amphiphilic particles on the interface we would expect an increase of the order parameter; however, the density profile (Fig. 2) demonstrates that as the number of amphiphiles is increased, not only does the height of the peak increase but the peak also broadens. This broadening probably causes the decrease of the order parameter.

The influence of the concentration of the amphiphilic compounds on the interfacial tension is presented in Fig. 4. The reduction in γ is proportional to the number of particles C. We were not able to extend this study to a larger number of amphiphiles due to the small size of our system and the significant broadening of the interfacial region as the number of amphiphiles is increased (cf. Fig. 3). In this paper we have demonstrated that computer simulations can be used to study the behavior of model water-oil-surfactant systems.

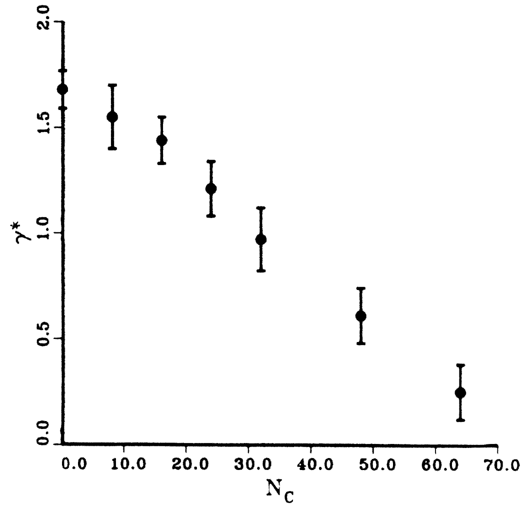

FIG. 4. The reduced surface tension $\gamma^*=\gamma\sigma^2\varepsilon^{-1}$ of the liquid-liquid interface as a function of total number of amphiphiles (N_C).

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