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Out-of-plane phase segregation and in-plane clustering in a binary mixture of amphiphiles at the air-water interface

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We have carried out extensive Monte Carlo simulations of a microscopic lattice model of a binary mixture of amphiphilic molecules, of two different lengths, in a system where water is separated from the air above it by a sharp well-defined interface. We have demonstrated an entropy-driven phase segregation in a direction perpendicular to the air-water interface when the initial total surface density of the amphiphiles is sufficiently high. We have also investigated (a) the conformations of the amphiphiles, (b) the distribution of the sizes of the clusters of monomers belonging to the long amphiphiles as well as of those belonging to the short amphiphiles in planes parallel to the interface, (c) the effects of varying the lengths, total concentration, and the ratio of the numbers of the two types of the amphiphilic molecules as well as those of varying the strength of the intermonomer interactions and temperature. We have critically examined the interpretations of some recent experimental results in the light of our observations. [S1063-651X(97)02607-X]

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I. INTRODUCTION

Amphiphilic molecules, e.g., soap and phospholipid molecules, are known to form various types of self-assemblies; micelles, vesicles, etc. are some typical examples of such supermolecular aggregates. Self-assemblies of binary mixtures have received attention in recent years [1–4]. Phase segregation of amphiphiles in bilayers is also an active area of research. We are interested in binary mixtures of amphiphiles in water and at an air-water interface.

In a recent paper [5] one of the authors has introduced a microscopic lattice model of a system which contains water, air, and a binary mixture of long-chain and short-chain amphiphilic molecules where water is separated from the air above it by a sharp well-defined interface. By carrying out Monte Carlo (MC) simulation, it was demonstrated that a novel vertical phase segregation of the two types of amphiphiles takes place provided the total surface density of the amphiphiles is sufficiently high. It was also argued that this phase segregation phenomenon is *entropy* driven, i.e., this phenomenon is accompanied by a gain of the conformational entropy of the amphiphilic chain molecules. The aim of this paper is to study this phase segregation phenomenon in detail and to elucidate further the physical mechanism by carrying out a series of computer experiments.

In the earlier preliminary report [5] only the concentration profiles of the heads (and monomers), belonging to the long and short amphiphiles, in the vertical direction (i.e., in the direction perpendicular to the air-water interface) were computed. In this paper we also compute several quantities to characterize the detailed conformations of both types of amphiphiles. Moreover, in Ref. [5] the two types of amphiphiles were assumed to be *chemically* identical; no distinction was made between the two components except the length of their hydrophobic chains, which were kept fixed at two values and no systematic study was carried out by varying the chain lengths. Furthermore, in that preliminary report [5] only equal initial surface densities of the two components of the binary mixture of amphiphiles were considered. In this paper we report the results of our detailed investigations of the effects of varying (a) the lengths of the long and short amphiphiles, (b) the ratio of the initial surface densities of the two components, (c) the strength of the intermonomer interactions, and (d) temperature.

We shall also critically examine the implications of our observations so far as the interpretations of experimental data are concerned. We shall compare the phenomena observed in our computer simulation with some similar phenomena in grafted polymers and compare the underlying physical mechanisms in the two cases.

The model and the characteristic quantities of interest are defined in Secs. II and III, respectively. The concentration profiles of chemically identical amphiphiles of two different lengths are presented in Sec. IV. The in-plane clustering of the amphiphile monomers are studied in Sec. V. Conformations of the amphiphiles are investigated in Sec. VI. Results for chemically different amphiphiles are summarized in Sec. VII. In Sec. VIII, we compare our results with laboratory experiments and binary mixture of grafted polymers. Finally, in Sec. IX, we present a summary of our results.

II. THE MODEL

The model developed in Ref. [5] is based on the Larson model of microemulsions [6,7]. Some modifications and generalizations of the Larson model have been made in recent years [8–10]. The system is modeled as a simple cubic lattice of size $L_x \times L_y \times L_z$ where the horizontal air-water inter-

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face is parallel to the XY plane and the *vertically downward* direction is chosen as the $+Z$ axis.

Each lattice site is occupied by a classical Ising spin; each Ising spin is allowed to take only two values, namely, $+1$ and -1. If the ith lattice site is occupied by water it is represented by $S_i=1$ whereas if it is occupied by air (or, empty) it is represented by $S_i=-1$, S_i being the classical Ising spin at the ith site. Each amphiphile, denoted by the symbol H_mT_n, consists of a string of m head units and n tail units; each of these units occupies a lattice site and the distance between any two successive units is precisely one lattice spacing. If a lattice site, say the jth is occupied by a head unit the corresponding value of the jth Ising spin (S_j) is assumed to be $+1$ whereas $S_j=-1$ if the jth site is occupied by a tail unit. The total length of each of the amphiphiles is $L_a=m+n$. We shall refer to each unit of an amphiphile, regardless of whether it is a part of the head or tail, as a *monomer*.

Since we are studying a binary mixture of the amphiphiles, let us represent them by the two symbols $H_{m_\ell}T_{n_\ell}$ and $H_{m_s}T_{n_s}$ for the long and short amphiphiles, respectively, so that the length of the long amphiphiles is $L_\ell=m_\ell+n_\ell$ and that of the short amphiphiles is $L_s=m_s+n_s$. All our investigations in Ref. [5] as well as in this paper have been carried out for a fixed value of $m_\ell=m_s=2$. In our preliminary report, we had chosen $n_\ell=15$ and $n_s=5$. In this paper we shall study the effects of varying n_ℓ and n_s.

The intermolecular interactions are taken into account through the interaction between the corresponding pair of Ising spins. Two spins interact provided the spins are located on the nearest-neighbor sites on the lattice; the interactions are attractive if both the spins are in identical states and repulsive otherwise. Thus the Hamiltonian for the system is given by the standard form for an Ising spin system with only nearest-neighbor interaction:

$$\mathcal{H}=-J\sum_{\langle ij\rangle} S_iS_j. \tag{1}$$

We measure the temperature of the system in the units in which the monomer-monomer interaction $J=1.0$ and the Boltzmann constant $k_B=1.0$. In this paper we shall also study systematically the effects of varying the temperature of the system.

Notice that the monomers of the same chain as well as different chains are not allowed to occupy the same lattice site; this represents a hard-core intrachain as well as interchain repulsion for chain separations smaller than one lattice spacing. Moreover, at any nonvanishing temperature, during the out-of-line thermal fluctuations of the chains, the hard-core repulsion leads to steric repulsion between the chains. Furthermore, in the present formulation, there are no potential energies associated with the torsion of isolated amphiphiles in water.

Since both types of amphiphiles are represented by the Ising spin variables, the amphiphiles may be regarded as *chemically* identical if the strength of the interaction J is also assumed to be identical for both types of amphiphiles. However, chemically different types of amphiphiles can be modeled by taking different values of the interactions J_{LL}, J_{SS}, and J_{LS}, where J_{LL} is the interaction between two monomers both belonging to the long amphiphiles, J_{SS} is that between two monomers both belonging to short amphiphiles, while J_{LS} is that between two monomers one of which belongs to a long amphiphile and the other to a short amphiphile.

In our model here, chemically different amphiphiles can be described by first associating a "strength" C_i with the ith site ($i=1,2,\ldots,N$). If the ith site is occupied by water or air, then $C_i=1$, whereas $C_i=C_\ell$ (>0) if the ith site is occupied by a monomer belonging to a long amphiphile, while $C_i=C_s$ (>0) if the ith site is occupied by a monomer belonging to a short amphiphile. In this case, the Hamiltonian for the system is given by

$$H=-J\sum_{\langle ij\rangle} C_iC_jS_iS_j. \tag{2}$$

In our preliminary report we had considered only chemically identical amphiphiles of different lengths. In this paper we shall also study binary mixtures of amphiphiles which differ not only in their length but also chemically.

In each of the computer experiments, the initial state is constructed in such a way that air occupies the upper part while water occupies the lower part of the lattice. We begin with a mixture of N_ℓ long amphiphiles and N_s short amphiphiles; the heads of all the amphiphiles were initially put randomly on the sites in a horizontal lattice plane immediately below the air-water interface in a lattice of size $L_x\times L_y\times L_z$ and each of the amphiphiles was fully extended in the vertical direction. In this paper we shall study the effect of varying the ratio $R_d=N_\ell/N_s$. The system is then equilibrated at temperature T using the following dynamics: during the updating of the states of the system in our MC simulation, air and water molecules were not allowed to exchange position as dispersion of air and water inside each other is not possible in our model.

The moves allowed for the amphiphiles in our model are as follows [10]: (i) *Reptation*: This move effectively mimics the reptilelike slithering of the amphiphile along its own contour by one lattice spacing, and hence the name. (ii) *Spontaneous chain-buckling*: a portion in the middle of the chain is allowed to buckle spontaneously. (iii) Kink movement: A kink formed by the buckling or reptation can move to a new position. (iv) Lateral diffusion at the surface: those amphiphiles whose heads are located no deeper than the molecular layer at the interface are allowed to move laterally where one of the four possible directions is chosen randomly and each of the units of the amphiphile is moved in that direction by one lattice constant. Each of these moves is possible only if the new positions are not occupied by any other amphiphile.

We follow the standard "Metropolis algorithm": each of the above-mentioned moves takes place certainly if $\Delta E<0$ and with a probability proportional to $\exp(-\Delta E/T)$ if $\Delta E\geqslant 0$, where ΔE is the change in energy that would be caused by the proposed move of the amphiphile under consideration. Each amphiphile is allowed to try each of the

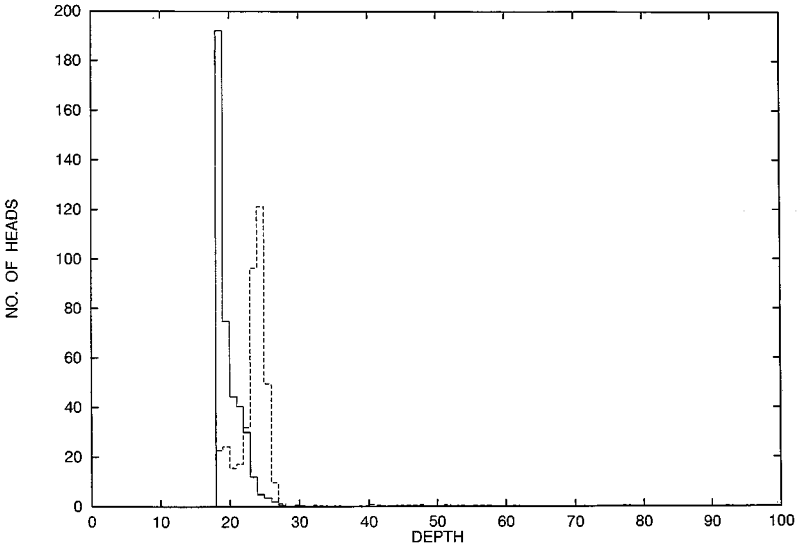

FIG. 1. The equilibrium concentration profile of the hydrophilic heads perpendicular to the air-water interface. The system consists of 30×30×100 lattice sites and contains a mixture of 405 long amphiphiles of length 17 and 405 short amphiphiles of length 7 equilibrated at temperature $T=2.5$. The solid lines correspond to the long amphiphiles whereas the dashed lines correspond to the short amphiphiles.

above-mentioned moves once during each MC step. Time is measured in units of the MC steps per molecule.

The largest systems simulated were 60×60×100. However, the data for smaller systems, e.g., 30×30×100, do not differ significantly from those for these large systems. Therefore most of the production runs were made for 30×30×100 systems. The data were averaged over a sufficient number of different initial configurations; typically ten configurations were found to be adequate.

III. DEFINITIONS OF CHARACTERISTIC QUANTITIES OF INTEREST

Now we define all the quantities we intend to compute for these models through MC simulation. We compute all these characteristic quantities for the long amphiphiles and the short amphiphiles separately.

The gross features of the spatial organization of the constituent molecules can be expressed through the equilibrium profiles of concentrations of the amphiphiles in the Z direction, i.e., in the direction perpendicular to the air-water interface. So far as the concentration profiles of the amphiphiles are concerned, one can calculate two different quantities: at each layer one can count the number of monomers or one can count just the number of hydrophilic *heads* in that layer.

It is straightforward to see that at any nonvanishing temperature, the amphiphiles cannot remain fully extended. One of the quantities that characterizes the average size of the amphiphiles is their average radius of gyration (R_g) which is defined by

$$R_g=\left[\frac{1}{N_aL_a}\sum_{j=1}^{N_a}\sum_{i=1}^{L_a}\{R_i(j)-R_{\text{c.m.}}(j)\}^2\right]^{1/2}, \tag{3}$$

$$R_{\text{c.m.}}=\frac{1}{L_a}\sum_{i=1}^{L_a}R_i,$$

where $R_i(j)$ is the position of ith monomer of the jth amphiphile and $R_{\text{c.m.}}$ is the corresponding center of mass of a single amphiphile. The symbol $[\cdots]$ shows the ensemble averaging over different configurations. The symbols L_a and

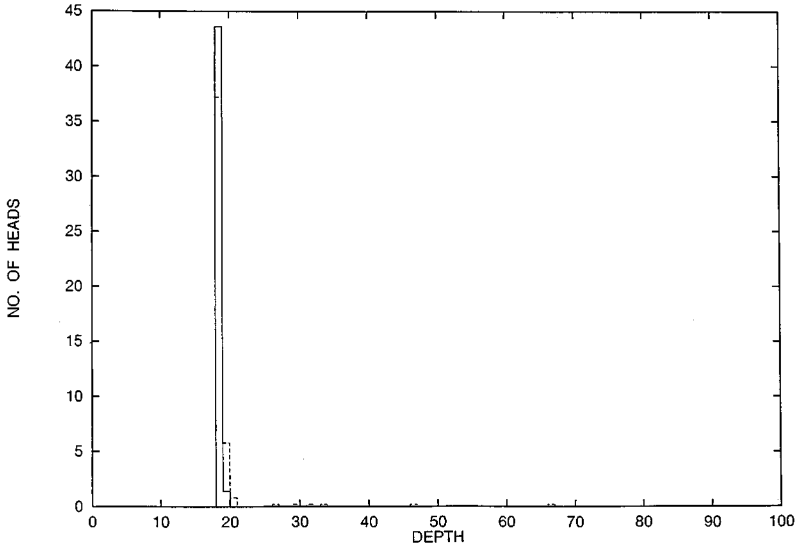

FIG. 2. Same as in Fig. 1 except that there are 45 amphiphiles of each type, instead of 405.

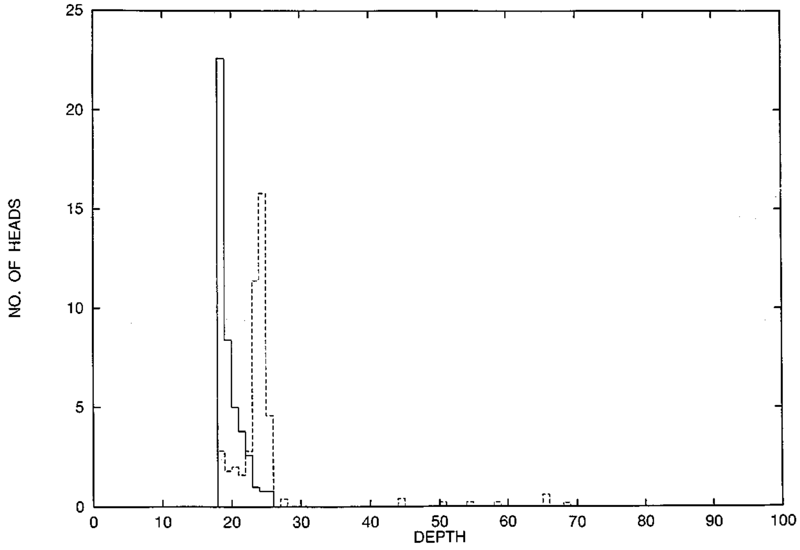

FIG. 3. Same as in Fig. 2 except that the size of the lattice is 10×10×100.

N_a denote, respectively, the length and the number of the amphiphiles of the particular species under consideration; for the computation of the radius of gyration of the long amphiphiles we take $L_a = L_\ell$, $N_a = N_\ell$ and for that of the short amphiphiles we take $L_a = L_s$, $N_a = N_s$.

Next, we introduce a measure of the average projection of the amphiphiles on the Z axis at a given instant of time t as follows: we calculate $\Delta Z(t)$, the difference of the instantaneous values of the z coordinates of the highest and the lowest monomers (i.e., the monomers with the largest and the smallest values of z coordinates), on each amphiphile and average it over all the amphiphiles of the same species present in the system thereby getting $\langle \Delta Z(t) \rangle$. The data are, then, averaged over a sufficiently large number of runs thereby getting the configurationally averaged value $[\langle \Delta Z(t) \rangle]$. In order to get more detailed information on the distribution of vertical extent of the amphiphiles we simultaneously also calculate $P(\Delta Z)$, the fraction of the amphiphiles with vertical extent ΔZ at equilibrium.

Another related quantity of interest is $[\langle R_z(t) \rangle]$, the average instantaneous projection of the vector $\vec{R}(t)$ on the Z axis where $\vec{R}(t)$ for a given amphiphile is the vector *from* the first monomer on its head *to* the last monomer on its tail. Note that, in equilibrium, the first monomer on the head and the last monomer on the tail of an amphiphile do not necessarily have the largest and smallest z coordinates. Therefore, in general, $[\langle R_z \rangle]$ is smaller than $[\langle \Delta Z \rangle]$. Moreover, ΔZ is always positive whereas, in general, for amphiphiles in water [11], $R_z(t)$ can be both positive and negative. Therefore at every temperature T the equilibrium value of $[\langle R_z(t) \rangle]$ has been used as the order parameter for measuring the *average orientational order* (Ψ) exhibited by the "head-to-tail" vectors at the temperature T.

Detailed information on the orientation of the individual *bonds* between the monomers of the amphiphiles is contained in the so-called "bond orientational order parameter," defined as

$$\Phi(p) = (1/N_a) \sum_{i=1}^{N_a} [3 \langle (z_{i,p+1} - z_{i,p})^2 \rangle - 1]/2 \quad (p = 1, \ldots, L_a - 1), \tag{4}$$

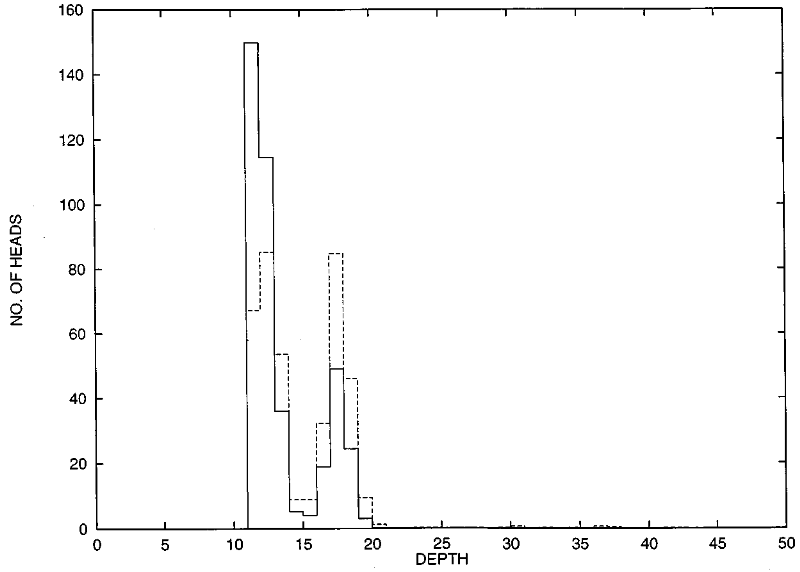

FIG. 4. Same as in Fig. 1 except that the lengths of the long and the short amphiphiles are 17 and 13, respectively.

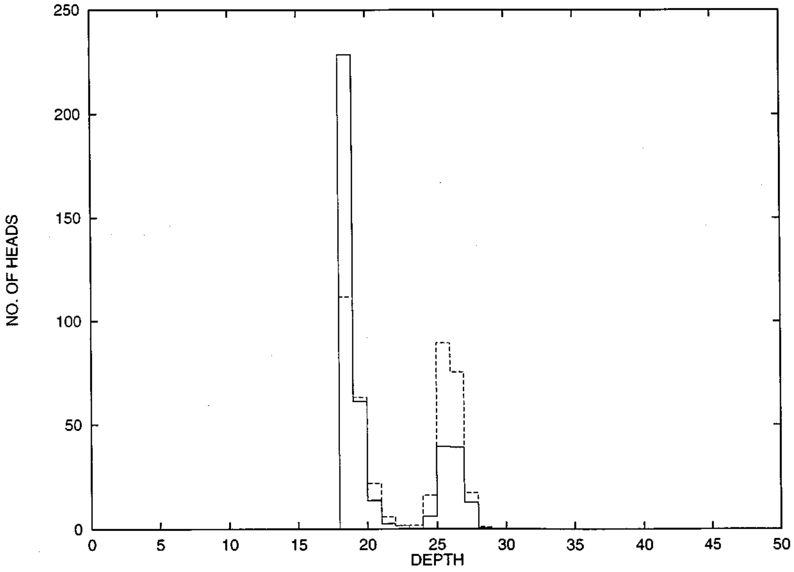

FIG. 5. Same as in Fig. 1 except that the lengths of the long and the short amphiphiles are 10 and 7, respectively.

where $i=1,2,\ldots,N_a$ ($N_a=N_\ell$ for the long amphiphiles and $N_a=N_s$ for the short amphiphiles) refer to the amphiphiles and $z_{i,p}$ refers to the z coordinate of the pth monomer on the ith amphiphile. Thus, $z_{i,p+1}-z_{i,p}$ is the difference in the heights of the two end points of the pth bond connecting the pth and $(p+1)$th monomers of the ith amphiphile. For example, $\Phi(p)=-0.5$ describes a situation where the pth bond, on the average, lies in a plane parallel to the air-water interface whereas $\Phi(p)=1$ corresponds to a vertical pth bond. The factors 3 in the numerator and 2 in the denominator in Eq. (4) have been chosen so that $\Phi(p)=0$ in the case of complete randomness in the orientation of the corresponding bond.

IV. CONCENTRATION PROFILES FOR CHEMICALLY IDENTICAL AMPHIPHILES OF DIFFERENT LENGTHS

First, we briefly summarize the main results of Ref. [5]. We begin with a mixture of 405 long amphiphiles and 405 short amphiphiles, i.e., $N_\ell=405=N_s$ and the size of the lattice is 30×30×100. The system was equilibrated at a temperature $T=2.5$ using the dynamics described in Sec. II. The concentration profile of the hydrophilic heads of the long as well as the short amphiphiles are shown in Fig. 1. The two profiles are clearly shifted with respect to each other, thereby establishing a vertical phase segregation of the long and the short amphiphiles. We shall refer to this computer experiment as the *first* experiment.

Next we carry out further experiments to establish the physical reason for this phase segregation. We reduce the concentrations of both types of amphiphiles by a factor of 9, but keeping the relative concentration ratio of the two types 1:1, as before, without changing the size of the system. In other words, we now repeat the first experiment with 45 long amphiphiles and 45 short amphiphiles in a system of size 30×30×100 at $T=2.5$. Interestingly, unlike Fig. 1, no vertical phase segregation is now observed in the equilibrium profiles plotted in Fig. 2. We refer to this experiment as the *second* experiment.

Note that the crucial difference between the first and the

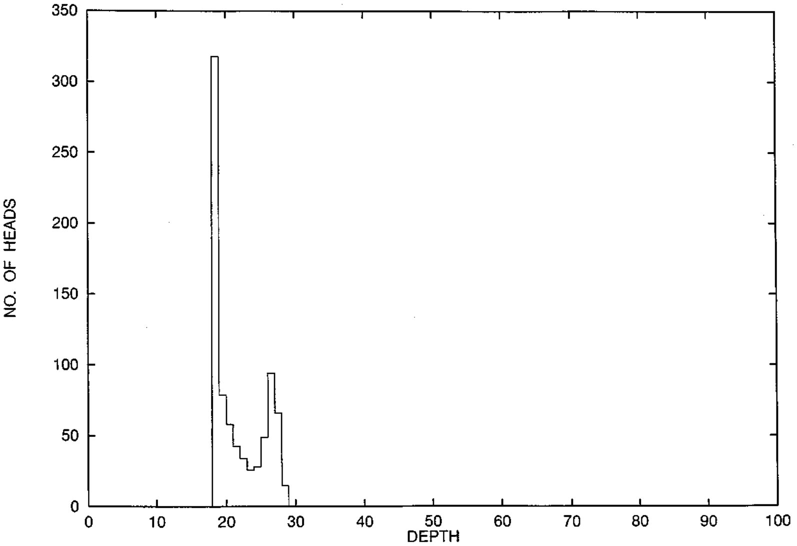

FIG. 6. The equilibrium concentration profile of the hydrophilic heads perpendicular to the air-water interface. The system consists of 30×30×100 lattice sites and contains 810 amphiphiles each of length 17. The system has been equilibrated at temperature $T=2.5$.

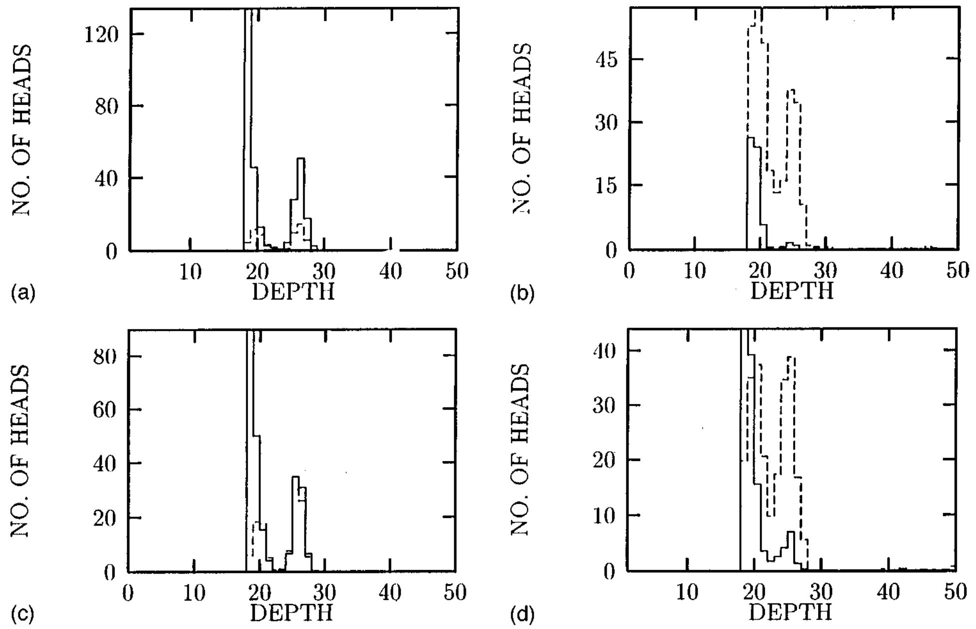

FIG. 7. The equilibrium concentration profile of the hydrophilic heads at $T=2.5$ perpendicular to the air-water interface in a system consisting of $20\times 20\times 100$ lattice sites. The numbers of long and short amphiphiles are, respectively, 300 and 60 in (a), 60 and 300 in (b), 240 and 120 in (c), 120 and 240 in (d); the continuous line corresponds to the long amphiphiles and the dashed line corresponds to the short amphiphiles.

second experiments lies in the different initial surface densities of the amphiphiles; the total number of amphiphiles in the first experiment is 810 whereas that in the second experiment is 90, although the total number of sites available in the plane immediately below the air-water interface is 900 in both the experiments. In other words, the initial surface density of the amphiphiles in the first experiment is 90% whereas that in the second experiment is only 10%. Does it imply that the vertical phase segregation observed in the first experiment occurs only if the surface density of the amphiphiles is sufficiently high (i.e., the interfacial area per amphiphile in the initial state is sufficiently small)? In order to check this possibility we carry out our *third* experiment.

In the third experiment we keep the number of amphiphiles of both varieties fixed at 45 but the lattice size is taken to be $10\times 10\times 100$. Thus the number of amphiphiles of both types in this experiment are identical to those in the second experiment while the initial surface density of the amphiphiles in this experiment is identical to that in the first experiment. In the third experiment we observe a vertical phase segregation (see Fig. 3) which is very similar to that observed earlier in the first experiment. Thus we conclude that the vertical phase segregation takes place only if the initial *surface density* of the amphiphiles is sufficiently high. In the next few subsections we shall present results of all the new computer experiments we have carried out to elucidate various aspects of this phenomenon.

A. Dependence on the lengths of the hydrophobic chains

In this subsection we shall examine the effects of varying the lengths n_ℓ and n_s of the hydrophobic chains by keeping

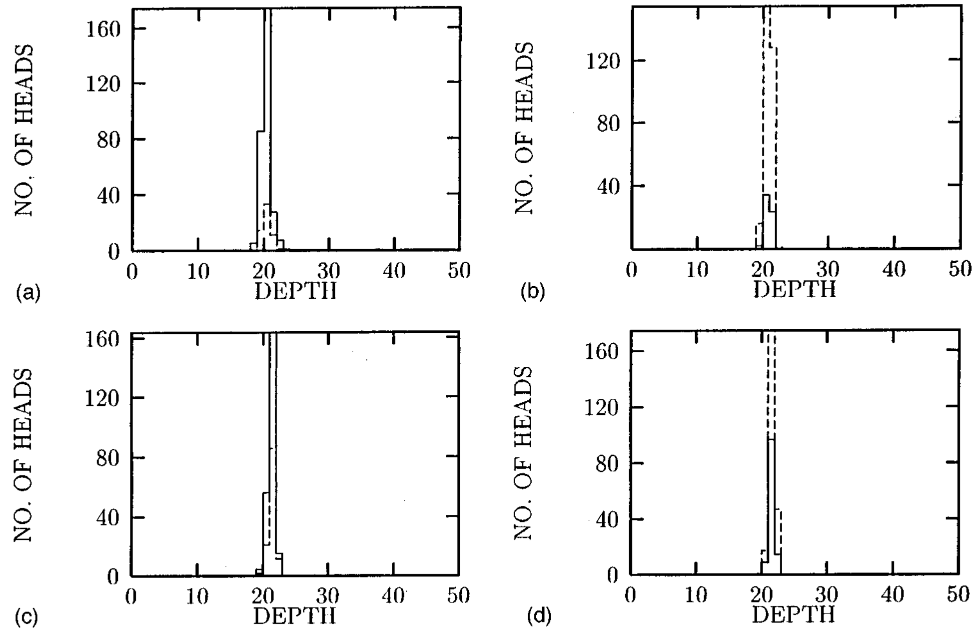

FIG. 8. Same as in Fig. 7, except that the temperature of the system is $T=1.0$.

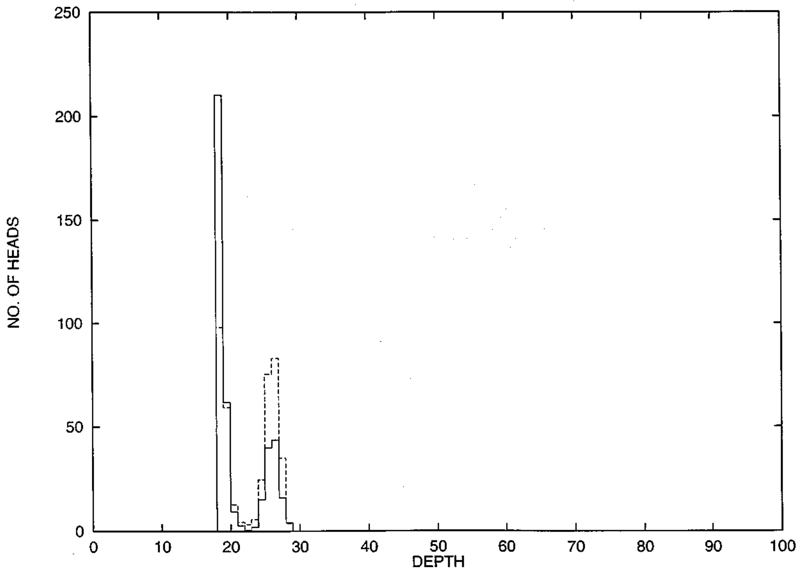

FIG. 9. Same as in Fig. 4, except that the bending stiffness of each of the amphiphiles is $B=2$ in contrast to $B=0$ in Fig. 4.

the size of the heads of both types of amphiphiles fixed at $m_{\ell}=m_s=2$ in a binary mixture of equal numbers of the two types of amphiphiles.

We have repeated the *first* experiment with amphiphiles of lengths 17 and 13, instead of 17 and 7. The vertical phase segregation observed in this experiment (see Fig. 4) is qualitatively very similar to that observed in the first experiment. However, the phase segregation is not as complete as it was in Fig. 1. Similarly, again repeating the first experiment with amphiphiles of lengths 10 and 7 we observed vertical phase segregation of the long and short amphiphiles, as before (Fig. 5). Thus in a binary mixture of equal numbers of chemically identical amphiphiles of two different lengths, the phase segregation is more complete when the longer amphiphiles are very long and the shorter amphiphiles are very short.

Since in this section we are considering chemically identical amphiphiles, a binary mixture of 405 long amphiphiles and 405 short amphiphiles reduces to a system of 810 effectively identical amphiphiles in the limit of vanishing length difference. Even in such a situation, a fraction of the amphiphiles are forced out of the monolayer in the equilibrium state provided the amphiphiles are sufficiently long (Fig. 6).

B. Dependence on the ratio of the initial surface densities of the two components

In the results reported in our earlier report, and in all the results presented so far in this paper, we have taken equal initial surface densities of the long and short amphiphiles. In this subsection we study the effects of varying the ratio of the initial surface densities of the two types of amphiphiles. Since in all our earlier computer experiments we did not find any significant difference in the results (when appropriately normalized) for lattices of cross section 30×30 and 20×20, all the experiments to be discussed in this subsection have been carried out for 20×20×100 lattices. Moreover,

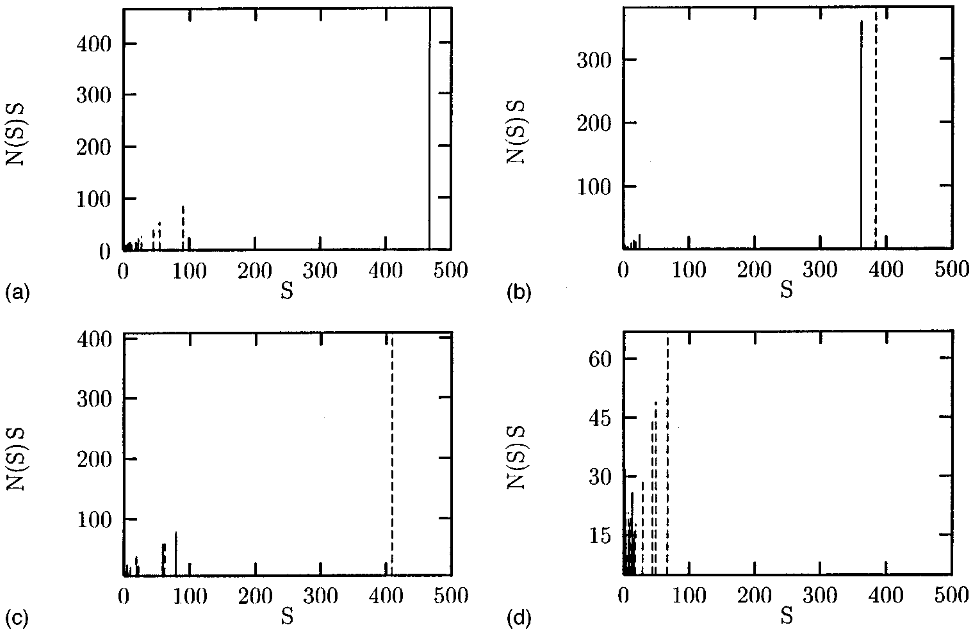

FIG. 10. The distribution of the sizes of the clusters formed by the monomers belonging to the long and the short amphiphiles in the layers (a) 20, (b) 21, (c) 22, and (d) 23, respectively. The values of all the parameters are identical to those in Fig. 1. The continuous and the dashed lines correspond to the long and short amphiphiles, respectively.

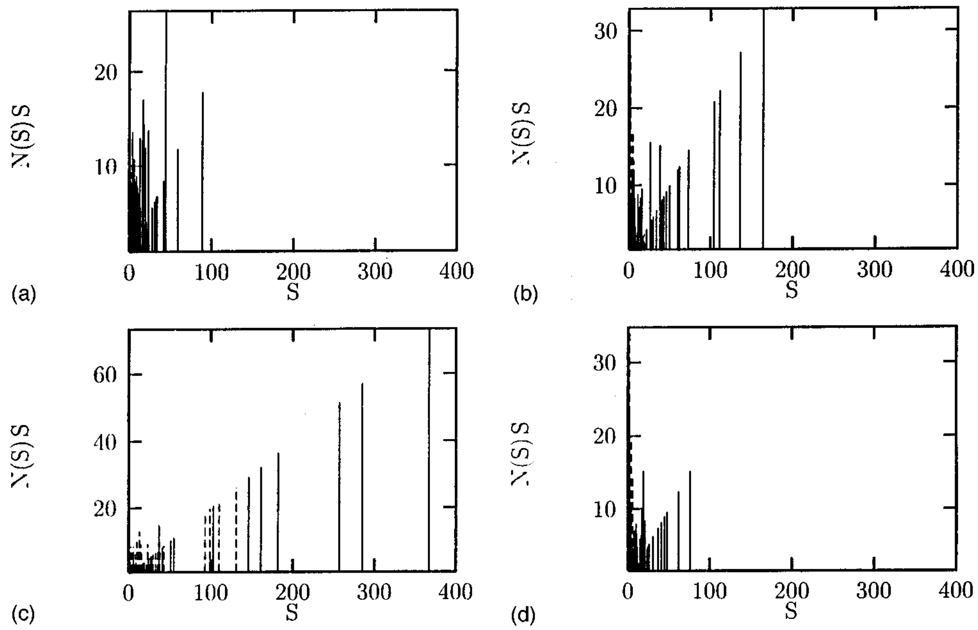

FIG. 11. Same as in Fig. 10, except that the number of both the long and short amphiphiles is 90 and (a), (b), (c), and (d) correspond to the layers 14, 15, 16, and 17, respectively.

since the extent of unmixing is largest for the amphiphiles of lengths 17 and 7, the computer experiments in this subsection have been carried out with lengths 17 and 7 of the long and the short amphiphiles, respectively.

The concentration profiles of the hydrophilic heads of both the long and short amphiphiles are shown in Figs. 7(a)–7(d) for four different ratios of the initial surface densities of the two types of amphiphiles. If the ratio R_d is small [Figs. 7(b)–7(d)] very few of the longer amphiphiles have to be sterically expelled from the long-rich layers. With the increase of ratio R_d, not only does the population of shorter amphiphiles in the long-rich layers decrease, but an increasingly larger number of the longer amphiphiles are sterically expelled.

C. Dependence on the temperature

The values of the parameters in Figs. 8(a)–8(d) are identical to those in Figs. 7(a)–7(d) except that the temperature in Fig. 8 is $T=1.0$ in contrast to $T=2.5$ in Fig. 7. No vertical phase segregation takes place at the lower of the two temperatures. Clearly, temperature plays a crucial role in driving the out-of-plane phase segregation phenomenon. This is consistent with our interpretation that the phase segregation of the long and the short amphiphiles is *entropy* driven; at low temperatures the likelihood of spontaneous buckling of the chains is very small and hence the steric interaction is suppressed.

D. Effect of bending stiffness of the amphiphiles

Because of the discreteness of the lattice, only bends of 90° of an amphiphile at a lattice site are possible. Every bend of an amphiphile is assumed to cost an energy B. In Fig. 9 we show the equilibrium concentration profile for a mixture of 405 amphiphiles of length 17 and an equal number of amphiphiles of length 13 in a $30\times30\times100$ system, where each bending of the amphiphiles of either variety costs an

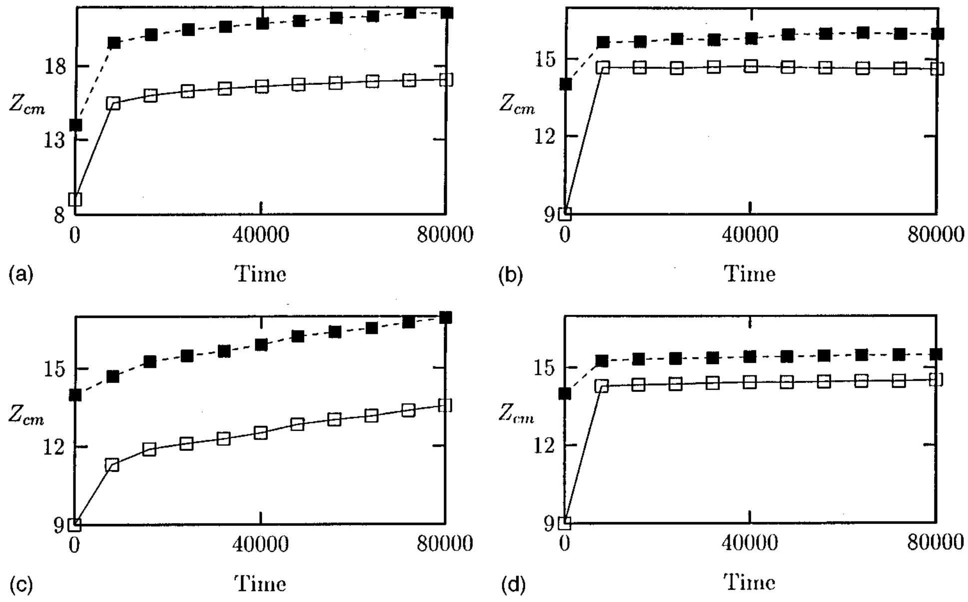

FIG. 12. The Z component of center of mass ($Z_{\mathrm{c.m.}}$) of the amphiphiles averaged over all the amphiphiles is plotted against MC steps; (a) $N_{\ell}=N_s=405$ and $T=2.5$, (b) $N_{\ell}=N_s=45$ and $T=2.5$, (c) $N_{\ell}=N_s=405$ and $T=1.0$, (d) $N_{\ell}=N_s=45$ and $T=1.0$. The continuous line and white square correspond to the long amphiphiles and the dashed line and black square correspond to the short amphiphiles.

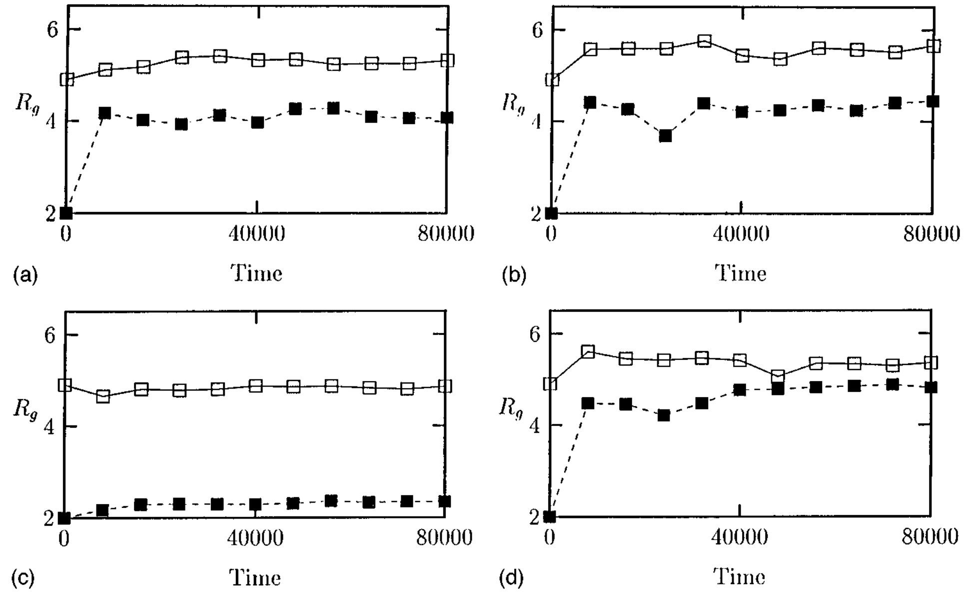

FIG. 13. The averaged radius of gyration (R_g) of the amphiphiles plotted against MC steps; (a) $N_\ell=N_s=405$ and $T=2.5$, (b) $N_\ell=N_s=45$ and $T=2.5$, (c) $N_\ell=N_s=405$ and $T=1.0$, (d) $N_\ell=N_s=45$ and $T=1.0$. The continuous line and white square correspond to the long amphiphiles and the dashed line and black square correspond to the short amphiphiles.

energy of $B=2$ in the units of J. Clearly, there is no significant difference between the profile in Fig. 9 and the corresponding profile for $B=0$ shown in Fig. 4. Thus bending stiffness of the amphiphiles does not have a significant effect on this phase segregation phenomenon unless B is very large; in the limit of $B\rightarrow\infty$ a total of $L_x\times L_y$ amphiphiles can be accommodated in the monolayer at the air-water interface irrespective of the lengths of each of the individual amphiphiles because each amphiphile remains straight and fully extended in this limit. In other words, the extent of unmixing keeps decreasing as the value of B keeps increasing far beyond J.

V. IN-PLANE CLUSTERING OF THE AMPHIPHILE MONOMERS

So far we have focused our attention on the concentration profiles of the amphiphiles in a direction perpendicular to the air-water interface. How are the monomers belonging to the long and short amphiphiles arranged in each of the planes parallel to the interface? In order to answer this question we have computed the distributions of the sizes of the clusters formed by the monomers belonging to the long and short amphiphiles in each of the lattice planes. A cluster of monomers belonging to long (short) amphiphiles in a given plane is defined as the set of those nearest-neighbor lattice sites which are occupied by monomers belonging to long (short) amphiphiles only [12].

We have analyzed the equilibrium state of a $30\times30\times100$ lattice containing 405 long and 405 short amphiphiles. Let $N(S)$ be the number of clusters of size S in a given lattice plane. The quantity $N(S)S$ is plotted against S in each of Figs. 10(a)–10(d); the continuous lines correspond to the long amphiphiles whereas the dashed lines correspond to the short amphiphiles. Clearly, as we move from the top of the system across long-rich layers to short-rich layers (and eventually deeper inside water), the nature of the clustering changes. In the 20th layer [Fig. 10(a)] the monomers belong-

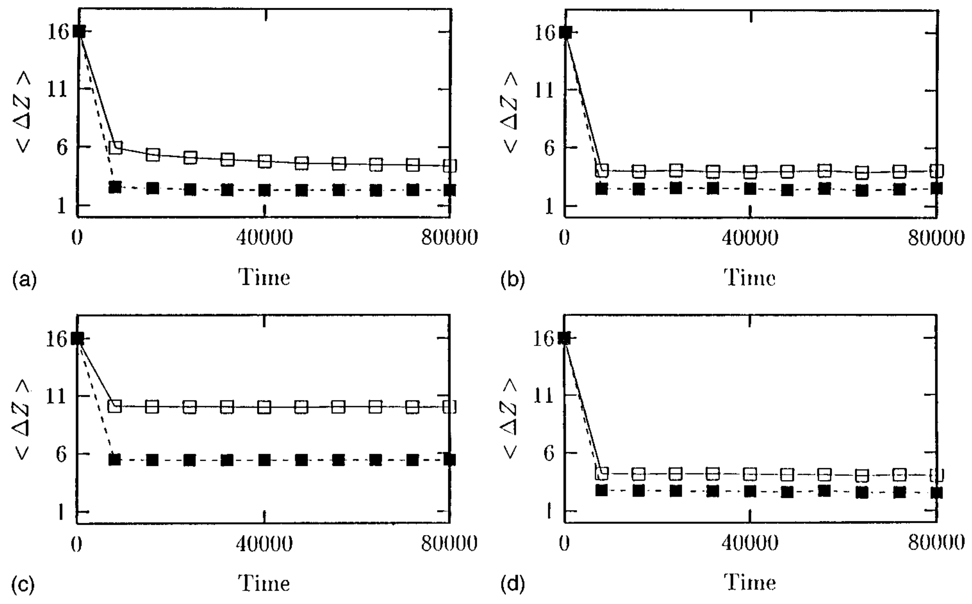

FIG. 14. The average vertical extension $\langle\Delta Z\rangle$ plotted against MC steps and the parameters and notations for (a)–(d) correspond to those in Fig. 13.

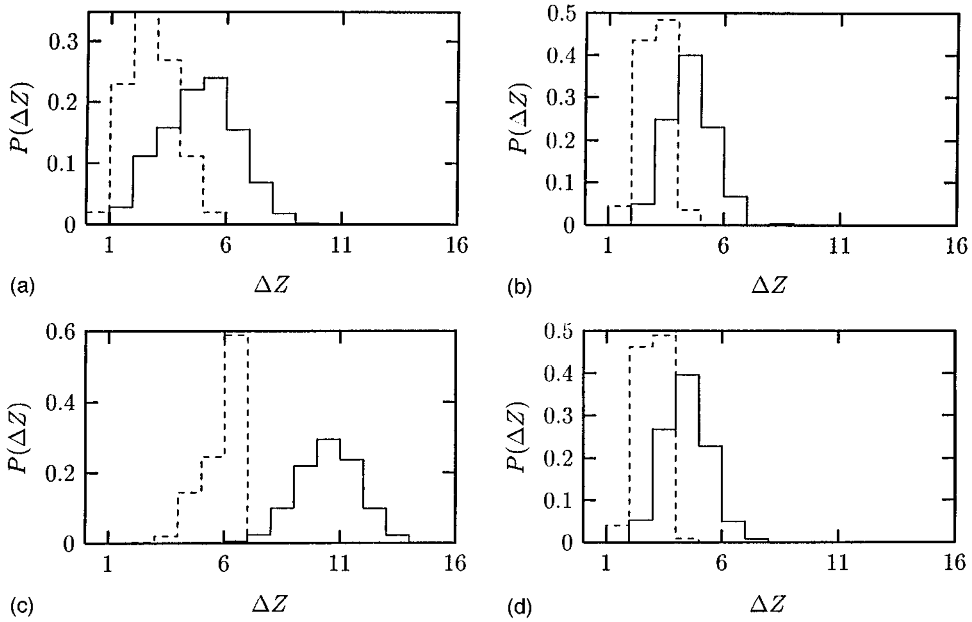

FIG. 15. The probablity distribution of the vertical extensions $P(\Delta Z)$. The parameter values and the notations for (a)–(d) are the same as in Fig. 13.

ing to long amphiphiles form a single large cluster coexisting with a distribution of smaller clusters of monomers belonging to short amphiphiles. The size of the largest cluster formed by the monomers belonging to short amphiphiles in layer 21 is larger than the largest cluster formed by the monomers belonging to the long amphiphiles [Fig. 10(b)]. As we move to layer 22 we find that the clusters of the monomers of long amphiphiles are much smaller than in the preceding layer [Fig. 10(c)]. Beyond this layer even the size of the clusters of monomers of short amphiphiles rapidly decreases as we move deeper into water [Fig. 10(d)].

This behavior is in sharp contrast with the corresponding cluster size distributions when the initial surface density of the amphiphiles is small. We have repeated the computation with 90 long and 90 short amphiphiles keeping all the other parameters identical to those in Fig. 10. Since no phase segregation takes place in this case, almost all the monomers are confined to layers at and above the air-water interface. $N(S)S$ in layers 14–17 are shown, respectively, in Figs. 11(a)–11(d); the largest cluster in each of these layers consists of monomers belonging to the longer amphiphiles.

Liverpool and Bernardes [13] investigated the in-plane clustering of amphiphiles at the oil-water interface in a lattice model based on a Larson-type prescription for modeling the ternary system. An oil-water interface was constructed in the initial configuration where the lower half of the system was occupied by water (just as in our model) whereas the upper half was occupied by oil (instead of air) and the amphiphiles were uniformly distributed over the entire system. As the system began evolving with time, the amphiphiles moved quickly to the interface, forming clusters. However, since the molecules of oil and water were allowed to exchange positions, the planar interface itself was subsequently destroyed spontaneously. On the other hand, the air-water interface in our model is stable, as air and water are not allowed to exchange their positions.

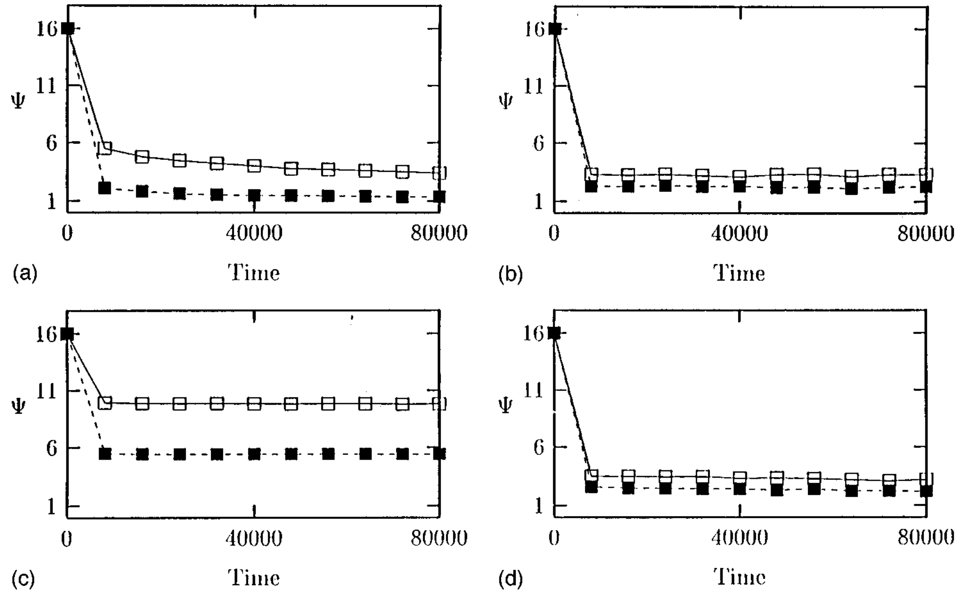

FIG. 16. Average orientational order parameter Ψ for different temperatures and surface densities of amphiphiles. The parameter values and notations for (a)–(d) are the same as in Fig. 13.

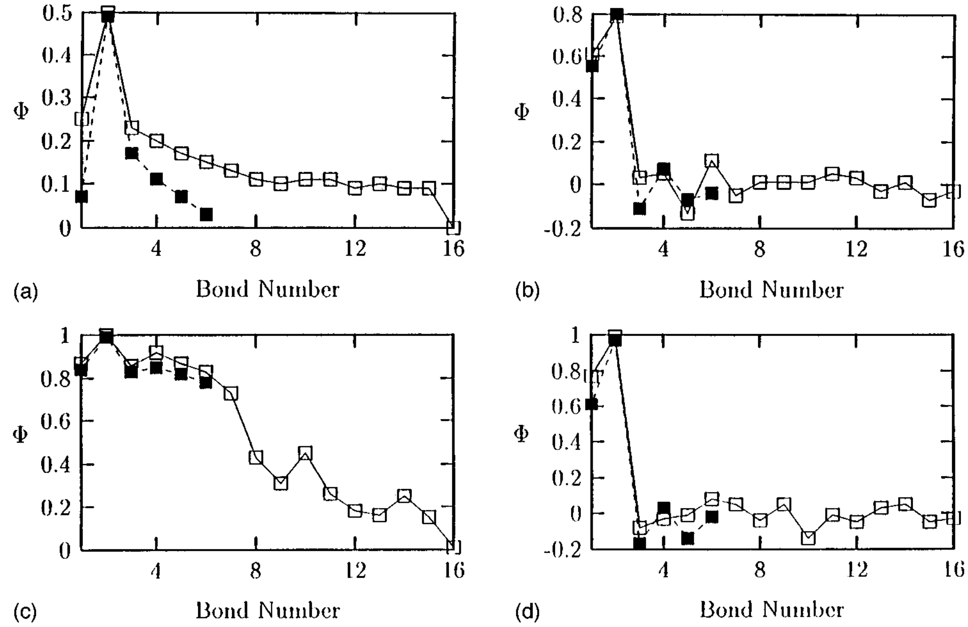

FIG. 17. Average bond order parameter Φ as a function of bond number. The parameter values and the notations for (a)–(d) are the same as in Fig. 13.

VI. CONFORMATION OF AMPHIPHILES

Variations of the Z components of the position of the center of mass, $Z_{\mathrm{c.m.}}$, of the amphiphiles with time are shown in Fig. 12; the positions are measured from a reference plane in the air. The corresponding radius of gyration of the amphiphiles is plotted in Fig. 13. Figures 13(a) and 13(c) both correspond to a high density for which vertical phase segregation was observed (see Figs. 1 and 3). On the other hand, Figs. 13(b) and 13(d) both correspond to a low density for which no vertical phase segregation was exhibited (see Fig. 2).

In all four Figs. 13(a)–13(d), the center of mass of the long amphiphiles lies at a higher level, as expected. Moreover, comparing Fig. 12(a) with 12(c) and 12(b) with 12(d), we find that at higher temperatures the equilibration is much quicker. Furthermore, at higher temperatures, the center of mass of the long amphiphiles lies at a significantly lower level compared to that at lower temperatures; this is a consequence of the ''crumpling'' of the amphiphiles caused by the increase of temperature. The most interesting observation is that there is significantly larger lowering of the center of mass of the short amphiphiles in Fig. 12(a) as compared to that in Fig. 12(c); thermal crumpling alone is inadequate to explain such large lowering of the center of mass. This is consistent with our earlier observation of the vertical phase segregation and the interpretation in terms of entropically induced steric repulsion.

Since at low densities both the long and short amphiphiles get enough space to access all possible conformations, no significant ''swelling'' takes place by increasing the temperature from $T=1.0$ to $T=2.5$. In contrast, at high densities, the radius of gyration of the short amphiphiles at $T=2.5$ is almost double that at $T=1.0$ (see Fig. 13).

In Fig. 14 we plot the average vertical extension $[\langle \Delta Z\rangle]$ of the amphiphiles as a function of time for different temperature and for different surface densities of amphiphiles. The corresponding distribution of the *vertical extensions* $P(\Delta Z)$ of the amphiphiles for different values of surface densities and temperatures are shown in Fig. 15. At low densities, there is practically no change in $[\langle \Delta Z\rangle]$ [see Figs. 14(b) and 14(d)] as well as in $P(\Delta Z)$ of amphiphiles of both types when the temperature is increased from $T=1.0$ to $T=2.5$. At high densities, the data for $[\langle \Delta Z\rangle]$ of the amphiphiles at $T=2.5$ are almost identical to those observed at low densities. In contrast, both the long and short amphiphiles remain much more extended (i.e., $[\langle \Delta Z\rangle]$ is much larger) at the same high density when the temperature is $T=1.0$.

Figure 16 shows the variation of the average orientational order parameter Ψ with concentration and temperature. At low densities, there is practically no variation in Ψ by decreasing the temperature from $T=2.5$ to $T=1.0$. On the other hand, at higher concentrations, significant increase in the orientational ordering takes place by decreasing the temperature. A higher value of Ψ indicates a higher position of the hydrophilic head compared to the location of the tip of the hydrophobic tail.

The bond-orientational order parameters Φ_p of the amphiphiles are plotted against the bond number p in Fig. 17, where p is counted from the head. It demonstrates that, when the concentration is high, the bonds near the hydrophilic head are more likely to be oriented vertically than in any other direction; the closer this bond is to the head, the stronger this tendency is. Even for high densities at low temperatures [Fig. 17(c)] the last bond is equally likely to be oriented in any of the six allowed directions.

VII. CHEMICALLY DIFFERENT AMPHIPHILES

The strengths of the intermonomer interactions were varied by varying C_{ℓ} and C_s. When $C_{\ell}=10=C_s$ both the long and short amphiphiles spontaneously entered into water [see Fig. 18(a)]. However, when $C_{\ell}=10$ and $C_s=1$ the longer amphiphiles move deeper into water, although both varieties move into water [Fig. 18(b)]. On the other hand, when $C_s=10$ and $C_{\ell}=1$ it is the shorter amphiphiles which move deeper into the water [Fig. 18(c)].

VIII. PHYSICAL MECHANISM, COMPARISON WITH EXPERIMENTS, AND SIMILAR PHENOMENA IN OTHER SYSTEMS

Why are the majority of the short amphiphiles in the binary mixture so selectively pushed out of the original monolayer? The answer to this question is very closely related to the physical mechanism that leads to the phenomenon of vertical phase seperation. If the surface density is high, the tails of the amphiphiles encounter stronger steric repulsion. If the short chains move down by a few molecular layers, that leaves more empty space for the unconstrained movement of the tails of the neighboring long amphiphiles. The same would not be possible if the long amphiphiles, instead of the short ones, were selectively pushed into water by the same amount. It has been argued earlier in a different context [14] that the short amphiphiles, by placing themselves in between long amphiphiles, create more space for the movement of the long amphiphiles.

Recently, Rosilio *et al.* [15] have carried out laboratory experiments on the miscibility of monolayers of dimyristoylphosphatidycholine (DMPC) and poly(ethylene oxide) lipids (PEO lipids) at the air-water interface. They assumed the additivity rule

$$A_{\mathrm{mixture}} = x_1 A_1 + x_2 A_2, \tag{5}$$

where A_{mixture} corresponds to the mean molecular area per molecule of the mixture, x_1 and $x_2 = 1 - x_1$ are the mole fractions of components 1 and 2, respectively, and A_1 and A_2 are the molecular areas of pure components 1 and 2 at the same given surface pressure. From their analysis they concluded that ''the addition of PEO lipid to DMPC produced mixed films in which molecules of both components occupied larger surface areas compared to those of their pure films.'' This observation can now be interpreted to be a consequence of a vertical phase segregation of the same type as that observed in our computer simulation. Since the amphiphiles in the binary mixture are distributed over several molecular layers the surface area per molecule in a mixture is much more than the area of the air-water interface. This interpretation is also consistent with the experimental observation that the apparent increase in the surface area per amphiphile is ''more pronounced at high PEO lipid surface concentrations in the mixtures.'' In fact, we expect the entropic effect driving this phase segregation to be stronger in the experiment of Rosilio *et al.* [15] than in our computer simulation because our simulations have been carried out on single-chain amphiphiles whereas the lipids are known to be double-chain amphiphiles.

Entropy-driven phase separation has been observed recently in a wide variety of systems [17,18]. Very recently it has been demonstrated through computer simulations [16] that entropy-driven phase separation is possible in polymer blends characterized by vanishing Flory χ where $\chi \propto 2\epsilon_{12} - \epsilon_{11} - \epsilon_{22}$, ϵ_{ij} being the energy of interaction between two nearest-neighbor segments of type i and j.

The moves allowed for the amphiphilic molecules in our algorithm are related to similar moves introduced earlier in the context of polymers [19]; the ''kink'' move in our algorithm is identical to the ''normal-bead motion'' in Ref. [19]. Moreover, the ''spontaneous chain buckling'' in our model not only generates new ''buckles'' or enhances the hump of existing buckles but also leads to the ''crankshaft motion'' [19] of existing buckles.

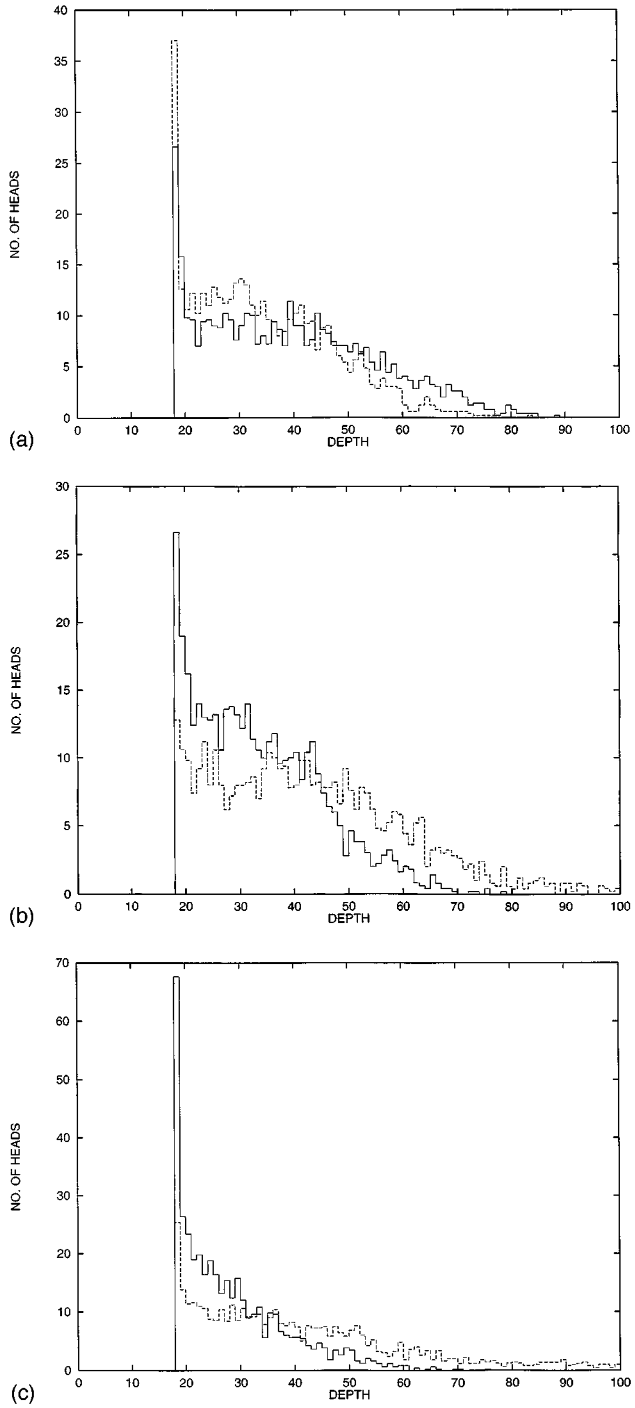

FIG. 18. The equilibrium concentration profile of the hydrophilic heads at $T = 2.5$ perpendicular to the air-water interface in a system consisting of $30 \times 30 \times 100$ lattice sites. The number of both long and short amphiphiles is 405; (a) $C_\ell = C_s = 10$, (b) $C_\ell = 10$ and $C_s = 1$, (c) $C_\ell = 1$ and $C_s = 10$. The continuous line corresponds to the long amphiphiles and the dashed line corresponds to the short amphiphiles.

The systems studied in this paper have some similarities to binary mixtures of polymer chains grafted on solid surfaces [20,21]. A direct comparison of such polymer brushes with our results would require a study of a mixture of grafted polymers of two drastically different lengths when the surface coverage is very high and the temperature is not too low.

IX. SUMMARY AND CONCLUSION

In this paper we have investigated the out-of-plane phase segregation of the amphiphiles in a binary mixture at the air-water interface. We have also studied the nature of the in-plane clustering of the monomers belonging to the long and the short amphiphiles. The entropy-driven phase segregation can be observed in laboratory experiments with chemically identical amphiphiles of two different lengths. For complete unmixing of the two components the long amphiphiles should be as long as possible and the difference in the lengths of the two types of the amphiphiles should also be large.

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