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Monte Carlo Simulation of Spatio-Temporal Organization of Amphiphiles in Water and Air-Water Interface

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Abstract. — Following the Larson prescription for modelling amphiphilic molecules in ternary microemulsions, we develop a microscopic lattice model for a pseudo-ternary system consisting of amphiphiles, water and air, where water is separated from the air above by a sharp well-defined interface. We investigate, through extensive Monte Carlo (MC) computer simulation, the dependence of the spatio-temporal organization of the amphiphiles in this model complex fluid in various regimes of amphiphile concentration, temperature and the length of the hydrophobic tails of the amphiphiles. We also study the average orientational order, the average vertical extension and the distribution of the vertical extensions of the amphiphiles, for several different values of their concentration and chain length, over a wide range of temperature. We compare our results with the corresponding results of laboratory experiments.

1. Introduction

Amphiphilic molecules consist of a “hydrophilic head” and a “hydrophobic tail”; the polar head likes to be in contact with water whereas the hydrocarbon chains constituting the tail tend to minimize their contact with water [1, 2]. The spatio-temporal organization of amphiphilic molecules in water as well as that in ternary mixtures of water, oil and surfactant amphiphiles has become a frontier area of interdisciplinary research involving physical, chemical and biological sciences as well as industry. These problems have been studied extensively in recent years using the techniques of statistical physics (see Ref. [3-13] for reviews). Roughly speaking, three different theoretical approaches have been followed so far; the phenomenological Ginzburg-Landau approach, the theories based of elasticity of the membranes formed by the amphiphiles (see [14-21] for reviews) and the microscopic theories [22, 23]. The microscopic models, in turn, are of two types. In the continuum models the molecules are located in a continuous d-dimensional space and, usually, one studies the spatio-temporal organization of the molecules through Molecular Dynamic (MD) simulation assuming specific types of inter-molecular interactions [22]. On the other hand, in the microscopic lattice models [23] the

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molecules occupy positions on a discrete lattice and the spatio-temporal organization is usually investigated through Monte Carlo (MC) simulation [24].

Because of the hydrophobicity of the tails the amphiphiles self-assemble in such a way as to minimize the contact between the tails and water; the nature of the self-assemblies, of course, depend on the temperature, concentration, etc. Super-molecular aggregates, such as micelles, vesicles, etc. are typical example of such self-assemblies. In ternary systems the amphiphiles form a monolayer at the interface between water and the third component in such a way that the heads are in contact with water but the tails are oriented towards the third component (for example, the third component is oil in case of microemulsions). Because of these special property of assembling at the interface and water surfaces, amphiphiles are often referred to as surfactants, an abbreviation for "surface active agent". In this paper we investigate the spatio-temporal organization of the amphiphiles in a system where water is separated from air above it by the air-water interface. Although, at first sight, it may appear to be a ternary system, it is more appropriate to call it a pseudo-ternary system because, unlike the true ternary systems like ternary microemulsions, air and water do not disperse in each other in our model. The structure of the amphiphilic monolayers at the air-water interface has been investigated in recent years by novel experimental techniques and some theoretical studies have also been made [25–33].

The microscopic lattice model, which we propose in this paper for the air-water-amphiphile system, is a slightly modified version of a lattice model developed by Larson [34–36] originally in the context of ternary microemulsions. The self-assembling of amphiphiles in bulk water and in ternary systems consisting of amphiphile, water and oil have been studied before [37–41]. In this paper we investigate the interplay of bulk and the air-water interface. Carrying out extensive MC simulation of this model we have computed several quantities characterizing various aspects of the spatial organization of the amphiphiles as a function of time starting from well defined initial states. The variation of these quantities with a) the temperature, b) tail length have been studied systematically in three different regimes of concentrations occupied by the amphiphiles, namely, i) low surface-density ii) intermediate and high surface-densities. The equilibrium properties of the system have been extracted from its time-dependent properties in the long-time limit \( t \rightarrow \infty \).

The paper is organized as follows: the model is defined and compared with earlier models in Section 2. The characteristic quantities of our interest are defined in Section 3. The data for low surface densities are presented and analyzed in Subsection 4.1 while those for intermediate and high surface densities are presented and analyzed in Subsection 4.2. The relative importance of the depth of the water column and the area of the air-water interface are demonstrated in Subsection 4.3. A brief summary of the results is given in Section 5 where we also make some concluding remarks.

2. The Model

Our model is based on the Larson model of microemulsions [34–36]. Some modifications and generalizations of the Larson model have been made in recent years [37–41]. We begin by summarizing the general features of this model; specific differences between the original version and the various later versions will be mentioned later.

The physical system in three dimensions is modelled as a simple cubic lattice of size \( L_x \times L_y \times L_z \). Each lattice site is occupied by a classical Ising spin; each Ising spin has only two possible allowed values, namely, +1 and −1. If the \( i \)-th lattice site is occupied by water it is represented by \( S_i = 1 \) whereas if it is occupied by oil it is represented by \( S_i = -1 \); \( S_i \) being the classical Ising spin at the \( i \)-th site. Each amphiphile, denoted by the symbol \( H_m T_n \),
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 \( j \)-th, is occupied by a head unit the corresponding value of the \( j \)-th Ising spin \( (S_j) \) is assumed to be +1 whereas \( S_j = -1 \) if the \( j \)-th site is occupied by a tail unit. The total length of each of the amphiphiles is \( \ell = m + n \). We shall refer to each unit of an amphiphile, regardless of whether it is a part of the head or tail, as a monomer.

The inter-molecular interactions are taken into account through the "exchange" interaction between the corresponding pair of Ising spins. The interaction between a pair of spins is assumed to be independent of the relative orientation of the amphiphiles even when one or both of the interacting sites happen to be occupied by a monomer of the same or different amphiphiles. So far as the MC algorithm is concerned, a molecule of water is allowed to exchange position with a molecule of oil in the same manner in which standard Kawasaki spin-exchange is carried out. The two different moves allowed for the amphiphiles will be explained later, as these are also included in our model for the air-water-amphiphile system.

In some later versions of this model the amphiphiles have been denoted by \( H_mN_pT_n \) where \( p \) number of 0's are put in between the head and the tail regions as neutral or liason sites. In such situations, the total length of each of the amphiphiles is \( \ell = m + p + n \). In some other versions, the tail and/or head has been assigned spin values of -2 and 2, while the absolute values of the spins associated with all the other remaining monomers of the amphiphiles are unity. The latter modification has been done to break the symmetry between interactions involving head units and interactions involving tail units. Moreover, head-head repulsions have also been considered to model ionic surfactants. However, we shall restrict our attention only to the simplest form of amphiphiles (i.e., \( p = 0 \)), where no extra fictitious charge is associated with any unit of the amphiphiles.

Now we describe our model. First of all, \( S_i = -1 \) is interpreted to represent air instead of oil. Moreover, air and water were not allowed to exchange position as dispersions of air and water inside each other is not possible. Besides, the initial states are always constructed in such a way that air occupies the upper part while water occupies the lower part of the lattice. By convention, we chose the \( Z \)-axis of our coordinate system along the vertical direction so that the air-water interface is parallel to the \( XY \)-plane. We have carried out the computations for amphiphiles of two different lengths, namely, \( \ell = 7 \) and \( \ell = 17 \). However, while varying the length of the amphiphiles, represented by \( H_mT_n \), we have always kept the head size \( m \) fixed at the value \( m = 2 \) and changed only the tail size \( n \) from 5 to 15. The motivation for choosing the value \( \ell = 7 \) was to have a size identical to that in the MD simulation of a very similar model [22, 42]. The choice of the other size, namely, \( \ell = 17 \) was motivated by the same size used in the earlier MC simulations of different models by Stettin, Mögel and co-workers [43, 44]. It is worth mentioning that the actual number of carbon atoms in the short amphiphiles is less than 10 and that in the long amphiphiles is more than 20. Therefore, our choice of the two values of \( \ell \) should be regarded as quite realistic.

A pair of spins is assumed to interact mutually through positive "exchange" interaction (ferromagnetic in the terminology of magnetism) provided the spins are located on the nearest-neighbour sites on the lattice. Although interactions between farther-neighbour spin pairs have also been included in an earlier work [34] on microemulsions, we do not allow such interactions as to achieve simplicity without sacrificing any essential feature of the problem.

The moves allowed for the amphiphiles in our model are as follows:

i) reptation: reptation of an amphiphile takes place when either of the two end-monomers moves to a neighbouring lattice site, the second monomer from that moved end side moves to the site occupied earlier by the end-monomer, the third monomer from the same end
moves to the earlier position of the second monomer..., and so on. Thus, this move effectively mimics the reptile-like slithering of the amphiphile along its own contour by one lattice spacing, and hence the name. If both before and after the reptation move the amphiphile finds itself completely immersed inside water, then the water molecule, which was earlier at the position taken over by the amphiphile, moves to the vacant position left behind by the moved amphiphile. However, if the two ends of the amphiphile before or/and after the reptation move happen to be in two different media, i.e., air and water, then the molecules of air and water at the two ends are not allowed to exchange their positions, as this would lead to dispersion of air/water and water/air. Therefore, in such situations we imagine that, depending on the move, the molecules of air and water can either move in to occupy vacant positions or move out to make room for a monomer of the amphiphile. Thus, although the total number of amphiphiles in our model system is strictly conserved, those of air and water are not conserved. Thus, our algorithm mimics situations where both the air and water columns are semi-infinite in the $Z$-direction.

ii) *Spontaneous chain–buckling*: a portion in the middle of the chain is allowed to buckle in a manner explained in the preceding paper by Liverpool and Bernardes [41]. Dispersion of air/water and water/air are avoided by the same trick as mentioned above in the context of reptation.

iii) *Kink movement*: a kink formed by buckling or reptation can move to a new position in various different ways, as explained in the preceding paper by Liverpool and Bernardes [41]; some of these moves of the kinks are equivalent to simple rotations of the amphiphile along $X$-, or $Y$-, or $Z$-axis. Again, the formation of any dispersion of air/water and water/air are avoided by the trick mentioned above (the algorithms for the moves (ii) and (iii) were developed by Liverpool and Bernardes [41] originally in the context of ternary microemulsions).

iv) *Lateral diffusion at the interface*: 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 provided each of the new sites were occupied by water or air before. Thus, if an amphiphile performs only such motions at each successive time step, each of its elements would be, effectively, carrying out a two dimensional random walk in a horizontal plane parallel to the $XY$ plane, i.e., parallel to the interface. To my knowledge, this move has not been taken into account in any previous MC work on the lattice models of the Larson type.

We measure the temperature of the system in the unit in which the “exchange” interaction $J = 10$ and the Boltzmann constant $k_B = 1.0$. We follow the standard Metropolis algorithm; each of the above mentioned moves takes place with a probability proportional to $\exp(-\Delta E/T)$, where $\Delta E$ 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 above mentioned moves once during each MC step. However, unlike the algorithm for microemulsions, molecules of air and water are not allowed to interchange their positions. During any particular move of an amphiphile, if the site(s) left vacant by the move happens to be below the air-water interface it is imagined that water molecule(s) supplied from the sides take up that vacant position. Time is measured in the units of the MC steps per molecule.

Notice that because the monomers of the same chain as well as of different chains are not allowed to occupy the same lattice site, there is a hard-core intra-chain as well as inter-chain
repulsion whenever the chain separations are smaller than one lattice spacing. On the other hand since the tails of each amphiphile consist of a string of Ising spins in the $-1$ state there is an attractive inter-chain interactions if the chains are on the nearest-neighbour sites of the lattice. Tails of amphiphiles separated by distances larger than a single lattice spacing do not interact directly with each other. Moreover, at any non-vanishing temperature the chain conformations fluctuate around their fully extended linear conformation; during such out-of-line thermal fluctuations of the chains the hard-core repulsion leads to steric repulsion between the chains. Moreover, in the present formulation, there are no potential energies associated with the bending and torsion of an isolated amphiphiles in water. But, we plan to extend our model to include these extra energies in a future publication.

Let us now compare this model with some other related models. Widom and Wheeler [45,46] made a key observation: in a microemulsion the “water-loving” head of a surfactant can be regarded as “water-like” and the “water-hating” tail can be modelled as “oil-like”. Therefore, if the sites occupied by a water molecule correspond to $+1$ value for the Ising spin at these sites, those spins at sites occupied by the “water-like” head should also have the value $+1$. Similarly, the spins on sites occupied by oil molecules as well as “oil-like” tail of the amphiphiles should have the same value $-1$.

Larson model [34] also shares this special feature — the amphiphiles are assumed to consist of “water-like” heads and “oil-like” tails. However, in contrast to all the earlier lattice models, the head of the amphiphiles in this model consist of $H_m$ units and the tail consists of $T_n$ units, where both $m$ and $n$ can be larger than unity. The advantage of modelling amphiphiles through Larson prescription is that the various possible chain conformations are modelled more realistically and this enables us to incorporate the steric interactions of the amphiphiles explicitly.

The lattice models of Stettin, Mögel and co-workers [43,44] included the detailed conformations of amphiphiles as long as 17 lattice constants, but in their simulations all molecular configurations that would place tail segments inside water were forbidden, thereby presuming the amphiphiles to be completely insoluble in water. Similarly, MC simulations by Pratt and co-workers [47,48] focussed attention on the thermal and structural aspects of micelles, in particular. On the other hand, our model is more realistic in the sense that the actual solubility of the amphiphiles is an output, rather than input, in our calculation. In other words, the computer experiment demonstrates, rather than assume, under what circumstances the amphiphiles remain more or less confined to the interface.

Our model amphiphiles captures some the generic features of real amphiphilic molecules and do not incorporate the specific details as to the number and sequence of the CH₂, CH₃ and COOH groups in any particular amphiphilic molecule. Consequently, our model accounts for some of the general features of the systems under consideration. On the other hand, the detailed molecular structures and conformations have been included in the MD simulations almost from the beginning more than a decade ago, but all the authors before Smit et al. [22,42] forced the amphiphiles to remain confined to the air-water interface by construction of the model. The model simulated by Smit et al. [22,42,49] is based on a continuum counterpart of the Widom’s lattice model proposed earlier by Telo da Gama and Gubbin [50]. While the earlier MD simulations were concerned mainly with either micelles or with a monolayer, Smit et al. demonstrated the spontaneous formation of both of these self-assembly simultaneously in the same system.

There is a close similarity between our model and the model studied by Smit et al.. The latter model consists of two kinds of particles, which Smit et al. labelled by the letters O and W. An oil molecule consists of a single O particle, a water molecule consists of a single W particle. An amphiphile was assumed to consist of a chain of two W particles followed by five
O particles, each bound to its neighbors by a strong harmonic force. The W and O particles are the analogues of +1 and −1 values of the Ising spins in the Larson model as well as in our model. The number of head units and the number of tail units of the amphiphiles in the model of Smit et al. are identical to those of amphiphiles of length \( \ell = 7 \) units in our model. However, unlike the model of Smit et al., the inter-monomer separation along the chain of each amphiphile remains rigidly fixed to one lattice spacing in our model. In other words, in our model, the bonds between the successive monomers of the amphiphiles are neither stretchable nor compressible at all.

In the model of Smit et al. [22, 42, 49] the W-W, O-O and O-W interactions were each appropriately truncated Lennard-Jones potentials so that the O-W interaction was completely repulsive to make oil and water immiscible. Similarly, in our model positive values of \( J \) makes the air-water interaction completely repulsive. The surfactant nature of the amphiphiles is captured in the model of Smit et al. by the fact that the W-end of the amphiphiles are “water-like” and the O-end are “oil-like”. Similarly, in our model, the +1 end of the amphiphiles are “water-like” while the −1 ends are “air-like”.

The relative advantages and disadvantages of MC and MD methods of computer simulation are well known [51]. While MD monitors the real time evolution of the system, equilibration is often difficult to achieve within the available computer time. On the other hand, MC is a stochastic algorithm that measures time in the units of MC steps per particle. But, equilibration of the system is easier to achieve by this method. However, because of the underlying discrete lattice, the finer details of the organization on atomic scales, e.g., the shapes of the amphiphilic aggregates, should not be taken too seriously. Therefore, our work here should be regarded as complimentary to the earlier MD works.

3. Definitions of Characteristic Quantities of Interest

Now we define all the quantities we intend to compute for this model through MC simulation. The gross features of the spatio-temporal organization of the constituent molecules can be expressed through the time-dependent profiles of concentrations of air, water and amphiphiles in the Z-direction. Thus, \( N(z, t) \) is the number of amphiphilic molecules at a height \( z \), measured from the bottom, at a time \( t \). So far as the concentration profiles for the amphiphiles are concerned, one can calculate two different quantities: at each layer one can count the number of monomers constituting the amphiphiles or one can count just the number of amphiphilic heads in that layer.

While computing the profile for the monomers of the amphiphiles, one just counts the total number of amphiphiles in a given molecular layer; one, however, does not keep track of the position of the picked up monomers on the respective amphiphiles. In other words, two monomers located on the same molecular layer may be the \( i \)-th and \( j \)-th monomers of the respective amphiphiles to which they belong. An even more detailed information on the profiles of the monomers of the amphiphiles can be obtained if one calculates the quantity [52] \( P_k(x) \), the probability of finding the \( k \)-th monomer of an amphiphile at a distance \( x \) from the interface.

It is a well known fact that if, at a given temperature, the concentration of the solute exceeds the solubility limit corresponding to that temperature, the excess solute separates out. If there is any surface available for precipitation, the excess solute get preferably deposited onto it. However, the same amount of solute may be smaller than the solubility limit at a higher temperature and, therefore, the solute may be made soluble simply by raising the temperature. In earlier papers [37–41], most often the concentration of the amphiphiles has been varied at a fixed temperature to study the problem of solubility. On the other hand, in this paper, we
study variation of solubility with temperature keeping the number of amphiphiles fixed.

The air-water interface provides a surface for deposition of the excess amphiphiles above the solubility limit. If the number of amphiphiles is small and the interfacial area between air and water is large all these excess amphiphiles form just a single monolayer at the interface. As the solubility is expected to be higher at a higher temperature, an increasing number of these amphiphiles are also expected to move into water with increasing temperature.

The heads of those amphiphiles, which are insoluble in water and are located at the air-water interface, usually occupy sites in the two horizontal lattice planes just below the interface. From the profile we can find out the total number of the monomers of the amphiphiles \( N_w \) below the second horizontal lattice plane inside water in equilibrium. We define the ratio \( N_w/(N \ell) \) as a direct measure of the solubility of the amphiphiles in water at the given temperature. Note that interpreting \( N_w/\ell \) as the number of amphiphiles inside water the ratio may be regarded as that between the number of amphiphilic molecules inside water and the total number of amphiphiles. The reason for following this definition of solubility is that this definition is independent of the values of \( L_x \) and \( L_y \), provided the initial surface density of the amphiphiles is kept constant.

It is well known from experiments that, for every type of amphiphilic molecules, there exists a characteristic temperature, called the Krafft point, where the solubility of the amphiphiles in water increases very sharply with increasing temperature [53]. We shall investigate if this empirical fact is reproduced by our model.

It is straightforward to see that at any non-vanishing temperature, the tails of the amphiphiles cannot remain fully extended because of the thermal fluctuations. Intuitively, it is expected that the higher is the temperature the more tortuous is the contour of the tails of each of the amphiphiles. Therefore, for all \( T > 0 \), the average height of an amphiphile from its uppermost point to the lowermost would be less than its full length. We introduce a measure of the average vertical extent of the amphiphiles at a given instant of time \( t \) as follows: we calculate the difference of the instantaneous values of the \( z \)-coordinates of the highest and the lowest points \( \Delta Z(t) \) on each amphiphile and average it over all the amphiphiles present in the system thereby obtaining \( < \Delta Z(t) > \). The data are, then, averaged over a sufficiently large number of runs thereby getting the configurationally-averaged value \( < \Delta Z(t) > \).

In order to get a more detailed quantitative information on the vertical extent of the amphiphiles we also compute the distribution \( \{N(\Delta Z(t))\} \) at successive intervals of time starting from the same initial state as used in the computation of \( < \Delta Z(t) > ; N(\Delta Z(t)) \) being the number of amphiphiles with a given value of \( \Delta Z(t) \) at time \( t \).

While carrying out the averaging over the amphiphiles to calculate \( < \Delta Z(t) > \) we had included not only the surfactants at the air-water interface but also those dispersed inside water. Although the surfactants at the interface are oriented with their head dipped into water and tails wagging in the air the orientations of those dispersed in water need not be identical. In order to investigate if the majority of the amphiphiles are oriented preferentially in any particular direction we have computed another quantity related to \( < \Delta Z(t) > \). Here, instead of measuring the magnitude of the separation between the head and the tail, we measure the \( z \)-component, \( R_z(t) \), of the head–to–tail vector \( \mathbf{R}(t) \) and get \( < R_z(t) > \) by averaging \( R_z(t) \) over all the amphiphiles and different runs. Note that for each individual amphiphile, \( \Delta Z(t) \) is always non-negative whereas \( R_z(t) \) can also be negative.

At every temperature \( T \) the equilibrium value of \( < R_z(t) > \) can be used as the order parameter for measuring the average orientational order exhibited by the amphiphiles at the temperature \( T \). This order parameter should not be confused with that for amphiphiles confined within a single monolayer because in our calculation of \( < R_z(t) > \) all the amphiphiles in the system are included. Therefore, \( \Psi(t) = < R_z(t) > \) is a measure of the average in-
stantaneous orientational order of the amphiphiles in the entire system rather than that of only those at the interface. One can also compute separately the amount of average instantaneous orientational order, within the amphiphilic monolayer at the air-water interface. Since the number of molecules at the interface itself is a fluctuating quantity, we compute [54] the following quantity: \( \Psi_1(t) = [(1/N_i(t)) \sum R_i^2(t)] \), where the summation runs from \( i = 1 \) to \( i = N_i(t), N_i(t) \) being the number of amphiphiles at the interface at time \( t \).

A more detailed information can be obtained by calculating the orientational order of each individual amphiphile separately, i.e., by computing \( [R_i^p(t)] \) for the \( n \)-th amphiphile [52].

Detailed information on the orientation of the individual bonds between the monomers of the amphiphiles is contained in the so-called "bond order parameter" [43,44], defined as

\[
b(p) = (1/N) \sum_i (3 < (z_{i,p+1} - z_{i,p})^2 > -1)/2
\]

where \( z_{i,p} \) is the \( Z \)-coordinate of the \( p \)-th monomer on the \( i \)-th amphiphile. Thus, \( z_{i,p+1} - z_{i,p}, (p = 1, ..., \ell - 1) \), refers to the height difference between the two ends of the \( p \)-th bond connecting the \( p \)-th and the \( p + 1 \)-th monomers on \( i \)-th amphiphile. For example, \( b(p) = -0.5 \) describes a situation where the \( p \)-th bond lies in a plane parallel to the air-water interface whereas \( b(p) = 1 \) corresponds a vertical \( p \)-th bond. Results on these, together with \( [R_i^p(t)] \), will be published elsewhere [54].

We define the term concentration as follows: if the total number of amphiphiles in the system is \( N \), then the concentration \( \phi_a \) of the amphiphiles is given by

\[
\phi_a = (N \times \ell)/(L^2 \times L_z)
\]

Thus, concentration refers actually to the total number of monomers of the amphiphiles per unit volume.

4. Results and Discussion

4.1. Low Surface-Density of Amphiphiles — We measure the surface density of the amphiphiles by the ratio of total number of amphiphiles in the system and the number of lattice sites in any cross section, parallel to the \( XY \) plane, of the lattice. Thus, by the term "low surface-density" we mean large interfacial area per amphiphile in the initial state. For the purpose of illustrating the various physical phenomena in the regime, we chose a specific value \( L^2/20 \) for the total number of the amphiphiles. The choice was guided by the following considerations: the longest amphiphilic molecules in our work has the length of 17 lattice spacings in the fully extended state and all the data were generated for an interfacial area of \( L^2 = 30 \times 30 \). Therefore, all the \( L^2/20 \) molecules can, in principle, organize themselves in such a way as not to have significant mutual interaction among themselves.

In this section we first present the concentration profiles of the amphiphilic molecules. All the amphiphiles are initially distributed uniformly over the interface only; there are no amphiphiles inside water in the initial state. Thus, in this computer experiment we are investigating if the monolayer thus prepared remains stable.

At each temperature, the choice of \( L_z \), particularly the depth of the water column, is crucially important. In order to demonstrate how strongly the data can be affected by the finite-depth effect, if the depth is not chosen judiciously, we demonstrate the effect of the finite-depth on the concentration profile of the monomers and the heads of the amphiphiles in Figures 1a.b, respectively. Therefore, for each set of values of \( \ell, surface-density \) of the amphiphiles and \( T \), the depth of the water column was chosen, through trial and error, to be sufficiently large.
Fig. 1 — a) A demonstration of the finite-depth effect. The number of amphiphile monomers in equilibrium are plotted against the depth of the molecular layer, measured from the top of the system. The two curves correspond to two different systems, both at the same temperature $T = 50$ and both contain the same total number of amphiphiles, $N = 45$. The length $\ell = 7$ of the amphiphiles is also same in both. The horizontal cross-sectional area of the two systems are also identical, namely, $30 \times 30$. But, the depth of the system corresponding to the full curve is $L_z = 30$ whereas that of the system corresponding to the dashed curve is $L_z = 100$. Each data point has been obtained by averaging over five runs. b) Same as Figure 1a, except that only the number of the amphiphilic heads have been plotted against the depth of the molecular layer.
so that the data do not suffer from any spurious finite-depth effects. More specifically, the higher is the temperature, the higher is the possibility for the amphiphiles to move into the water and, hence, the larger was the chosen corresponding value of $L_z$.

In Figure 2 we show the concentration profile of the monomers of the amphiphiles of length $\ell = 7$ at times $t = 0$, $t = 10^4$ and $t = 10^5$, respectively, at the temperature $T = 1.0$.

The corresponding concentration profiles for only the amphiphilic heads at the three different times are indistinguishable from each other. The data presented in Figure 2 establish that the amphiphilic monolayer at the air-water interface is stable. Besides, because of low initial surface-density of the amphiphiles, the tails find enough space to form wiggles and kinks caused by thermal fluctuations; this is reflected in the existence of a maximum in the profiles for long times in Figure 2.

The profiles of the monomers of the amphiphile at a somewhat higher temperature, $T = 4.0$, are presented in Figure 3 at the same three times as in Figure 2, namely, $t = 0$, $t = 10^4$ and $t = 10^5$.

It is clear that, in thermal equilibrium, although a large number of the amphiphiles remain at the air-water interface forming an amphiphilic monolayer, the remaining amphiphiles are dispersed inside water maintaining an approximately uniform distribution of amphiphiles over the molecular layers. During their time evolution at this relatively higher temperature, starting from fully extended conformation, the chains not only tend to coil-up quickly but also simultaneously tend to move into water; this gives rise to the accumulation of a large number of monomers at, and closely around, the interface in the initial stages. But, then, as a fraction
of the amphiphiles succeeds in moving into water and overcrowding is resisted by mutual steric repulsion between the chains, the number of monomers of the amphiphiles at, and around, the interface also decreases until the system reaches equilibrium. The solubility of the amphiphiles extracted from the profiles will be presented a little later in this section.

It is the hydrophobicity of the chain which makes an amphiphile poorly soluble in water. Naturally, the next question we addressed is: how does the solubility of the amphiphiles depend on the length of the hydrocarbon chain? In order to answer this question we have repeated the calculation of the concentration profiles with longer chains ($\ell = 17$) at several temperatures from $T = 1.0$ and $T = 4.0$ all for the same total number of amphiphiles, namely, $N = L^2/20$. The equilibrium concentration profiles of the monomers of the amphiphiles for $\ell = 17$ for two different temperatures, namely, $T = 1.0$ and $T = 4.0$ are shown in Figure 4. The higher maximum at the higher temperature arises from the fact that at a higher temperature the amphiphiles are more coiled up than at a lower temperature. Also note that some amphiphiles have moved into water at $T = 4.0$ whereas none entered at $T = 1.0$; this is also seen in the profile of only the heads of the amphiphiles (not shown).

We have calculated the solubility of the amphiphiles in equilibrium as a function of temperatures using the equilibrium concentration profiles. The solubilities, at a fixed surface-density of amphiphiles, for both $\ell = 7$ and $\ell = 17$ have been plotted against temperature in Figure 5. For a given $\ell$, the qualitative trend of variation of solubility with temperature is consistent with that observed experimentally [53]. Moreover, at a given $T$, the longer is the chain the lower is the solubility of the amphiphile in water. This is in qualitative agreement with the earlier MC studies of the bulk systems [37-40] as well as with the experimentally observed trend of variation of solubility with the chain length of amphiphiles in water.

The average orientational order parameter and the average vertical extension at a few different temperatures are plotted against time in Figure 6 for $\ell = 7$ and in Figure 7 for $\ell = 17$. Note that, at low temperatures, the equilibrium value of the orientational order parameter is almost identical to the average vertical extension; the slight difference arises from the fact
Fig. 4. — The equilibrium concentration profile of the monomers of the amphiphilic molecules at $T = 10$ (full curve) and $T = 4.0$ (dashed curve) in a system whose size is $30 \times 30 \times 100$ and the length of the amphiphiles is $\ell = 17$ while the total number of amphiphiles is the same as in Figures 2 and 3, namely, $N = 45$. The number of the amphiphile monomers are plotted against the depth of the molecular layer, measured from the top of the system. Each data point has been obtained by averaging over five runs.

Fig. 5. — The solubility of the amphiphiles are plotted as a function of temperature for amphiles of length $\ell = 7$ (full curve) and $\ell = 17$ (dashed curve).

that the last monomer of the amphiphiles at the tail end need not always also be located at the highest. However, at higher temperatures there is significant difference between the two because the amphiphiles dissolved in water at these higher temperatures need not be oriented
Fig 6 — The average orientational order parameter and the average vertical extension of the amphiphiles are plotted as functions of time (measured in the units of MCS per molecule), starting from a state in which all the amphiphiles were fully extended, with heads down, at the air-water interface. The upper pair of curves correspond to $T = 1.0$ whereas the lower pair correspond to $T = 4.0$; the lower curve of each pair represents the order parameter while the upper curve of each pair represents the vertical extension. Each data point has been obtained by averaging over five runs. The length of the amphiphiles is $\ell = 7$

in the same direction as those at the interface.

A typical distribution of the vertical extensions of the amphiphiles with $\ell = 17$ at $T = 4.0$ is presented in Figure 8 in the form of a histogram.

4.2. Intermediate and High Surface-Densities of Amphiphiles. — We have carried out computer experiments in those regimes of surface-density of amphiphiles where there is substantial interaction among the amphiphiles. Two typical values of the total number of amphiphiles are $L^2/2$ and $L^2$. Note that the maximum initial surface density corresponds to a total number $N = L^2$ of the amphiphiles.

The equilibration of the system is very time consuming computer experiment in this regime. We carried out two separate sets of computer experiments: i) in the first, we began with an initial state in which all the amphiphiles were regularly distributed at the air-water interface, just as we did in the case of the low- surface density; ii) in the second, the amphiphiles were initially distributed randomly in the bulk of water and our aim was to watch how the amphiphilic monolayer formed at the air-water interface and if micellar aggregates also formed simulataneously inside water. In principle, the true equilibrium state should be independent of whether the initial state was constructed in the manner (i) or (ii) above. The structure of the concentration profiles observed in experiments of type (i) are very similar to those observed in the low surface-density regime and, hence, appear quite reasonable.

Let us now present the results of the computer experiments of type (ii). For all temperatures $T \geq 2.5$ we observed that the equilibrium profiles were almost identical to those obtained through computer experiments of type (i) at the same temperature (Fig. 9). However, even after 10 million MC steps, the profiles obtained in the two types of experiments at $T = 1.0$
Fig 7. — Same as in Figure 6, except that the length of the amphiphiles is $\ell = 17$.

Fig. 8. — The distribution of the vertical extensions of the amphiphiles of length $\ell = 17$ in equilibrium at a temperature $T = 4.0$.

were quite different (Fig. 10); there were still many more amphiphiles inside water in the experiment of type (ii) than in experiment of type (i). Surprisingly, in experiments of type (ii) the number of amphiphiles at the interface, after 10 million MC steps, at $T = 2.5$ was much larger than that at $T = 1.0$. This strongly suggests that the system could not be equilibrated through experiments of type (ii) at low-temperatures because of entaglements of the chains of the amphiphiles during their upward motion towards the interface.

We have also simulated the system for highest possible surface-density, namely, $L^2$ am-
Fig. 9. — The profiles of the monomers of amphiphiles of length $\ell = 7$ after ten million MCS per particle (solid lines) obtained at $T = 2.5$ starting from initial states where the amphiphiles were distributed randomly inside the bulk of water. The profiles shown by the dashed lines were obtained after $10^5$ MCS per molecule, starting from initial states where all the amphiphiles were put at the air-water interface in the fully extended conformations. Both the profiles correspond to the same system size of $30 \times 30 \times 100$ and same total number of amphiphiles, namely, 450.

Fig. 10. — Same as in Figure 9, except that the temperature was $T = 1.0$. Each amphiphile, each of length $\ell = 7$, was put initially at the interface. The profiles of the heads of the amphiphiles after 1 million time steps at $T = 1.0$ are shown in Figure 11, together with the corresponding initial profile. Interestingly, about half of the heads have moved in by one layer into the water. This is a consequence of the steric repulsion among the amphiphilic chains on
Fig. 11 — The profile of the heads of the amphiphiles in a $30 \times 30 \times 100$ system containing 900 amphiphiles, each of length $\ell = 7$, after one million MCS per molecule at $T = 1.0$. The corresponding initial profile is shown by the dashed lines. The number of amphiphile monomers up to a depth of 30 molecular layers are shown to clearly show the redistribution of the amphiphiles over two layers; there were no monomers of amphiphiles in molecular layers deeper than the deepest shown here.

The overcrowded interface. Energy loss results from the increase in the number of monomers in water. However, the sterically-induced exclusion of some monomers from the original monolayers leads to a gain of entropy. A balance between the energy loss and entropy gain decides how many amphiphiles should move into water and how far deep. A similar mechanism has been shown to result in a sterically-induced vertical phase separation of long-chain and short-chain amphiphiles in a binary mixture [55].

One of the questions that we have not addressed so far in this section is whether or not super-molecular aggregates are formed by those amphiphiles which are inside the bulk of water. We investigate this aspect of the problem systematically in the next section.

4.3. SUPER-MOLECULAR AGGREGATES OF AMPHIPHILES. — First we investigate the effect of varying $L_z$ keeping $L$ fixed. We begin with 400 amphiphiles initially distributed randomly over a lattice of size $20 \times 20 \times 60$ at a temperature $T = 2.5$. Note that the number of amphiphiles is exactly equal to the cross sectional area, which consists of 400 lattice sites. A typical instantaneous profile of the heads of the amphiphiles in equilibrium is shown in Figure 12. The form of the profile itself strongly suggests the possibility of the existence of super-molecular aggregates of amphiphiles inside water. Indeed, a cluster analysis revealed that, corresponding to the profile shown in Figure 12, there is a cluster of 77 amphiphiles and a few other aggregates of sizes smaller than 10, in addition to the cluster formed by the amphiphiles at the air-water interface.

In the next experiments, we reduce $L_z$ from 60 to 30. Of course, this can be done in two distinct ways: a) by keeping the total concentration of the amphiphiles unaltered, and b) by keeping the total number of the amphiphiles unaltered. In case (a) the number of amphiphiles is, therefore, 200 whereas in case (b) the total number of amphiphiles is 400. The temperature of the system is $T = 2.5$, as before. But now, unlike in Figure 12, no large aggregate appears
in case (a) as the total number of amphiphiles is only half of the total number of sites on any XY cross section of the lattice. But, in case (b), for example, a large aggregate of 140 amphiphiles, in addition to another cluster formed by the amphiphiles at the interface, was detected in a typical instantaneous state in equilibrium. Note that, in the case (b), the total number of amphiphiles is exactly equal to the total available sites at the interfacial layer.

These three computer experiments demonstrate that in the presence of air-water interface, whose size is not negligibly small compared to the volume of water, the concentration alone cannot determine the nature of aggregation of the amphiphiles and their location.

In the next set of experiment, we explored the effect of widening of the cross sectional area of the system without altering the depth. We have already mentioned about the experiment with 400 amphiphiles in a system of size $20 \times 20 \times 30$ at a temperature $T = 2.5$. Now we increase $L$ from 20 to 30 without changing $L_z$. Just, as before, we do one experiment with 400 amphiphiles, the same as was done for $20 \times 20 \times 30$. In another experiment we use 900 amphiphiles to keep the concentration equal to that in the earlier experiment for $20 \times 20 \times 30$ system. As expected intuitively, only one or two small aggregates were observed in case of 400 amphiphiles as the number of available sites at an XY cross section at the interface is now more than twice the total number of amphiphiles. On the other hand, large clusters, other than the cluster formed at the interface, formed in the computer experiment with 900 amphiphiles. Thus, we conclude that the formation of aggregates inside water is less likely if the air-water interface is large enough to accomodate all the amphiphiles and the water column is not deep enough.

Finally, we ask if it is possible to have a bilayer in equilibrium simulataneously with the monolayer at the air-water interface? In all the computer experiments, where we started from random initial positions of the amphiphiles, we never obtained any bilayer inside the bulk of water. Then, we tried to determine if a configuration consisting of coexisting bilayer (inside water) and monolayer (at the interface) can remain stable and, if so, for how long. In the latter experiment, there are $L^2$ amphiphiles initially distributed uniformly to form a monolayer at the
The profile of the monomers of the amphiphiles in a $30 \times 30 \times 100$ system at two different temperatures, after ten million MCS per molecule, initially, 900 amphiphiles formed a monolayer at the air-water interface while another 1800 amphiphiles formed a bilayer inside water at a distance of 50 layers from the bottom of the monolayer. The solid lines correspond to $T = 2.5$ whereas the dashed lines correspond to $T = 1.0$.

air-water interface. But, now, in addition, there are also $2 \times L^2$ amphiphiles forming a bilayer inside water at a distance of much more than $l$ from the interface. We now ask if the bilayer is stable against thermal fluctuations. If not, how do the amphiphiles constituting the bilayer reorganize themselves? The concentration profiles of the amphiphiles at this two temperatures after 10 million MC steps are shown in Figure 13. At $T = 1.0$ the bilayer survives till 10 million MC steps but at $T = 2.5$ it breaks and gives rise to some smaller aggregates inside water.

It is well known that the structures of self-assemblies observed in MC simulation of complex fluid systems on lattices are sometimes artefacts of the underlying lattice structure rather than intrinsic properties of the system. Therefore, we do not examine here the detailed shape of the self-assemblies formed by the amphiphiles.

Our data convincingly demonstrate that, for fixed $L$, $L_z$ at a fixed temperature $T$, as the concentration of the amphiphiles increases, more and more amphiphiles move from the air-water interface into water becoming part of aggregates. However, because of the prohibitively large amount of CPU time required for equilibration at low temperatures, we have not attempted any systematic study of the variation of the critical micellar concentration with temperature, chain length, etc. Besides, such investigations have already been carried out earlier [37-41] in the context of oil-water-surfactant systems where equilibration happens to be quicker.

5. Summary and Conclusion

In this paper we have developed a microscopic model for amphphilic molecules in water in the presence of a sharp interface separating water from the air above it. Through MC computer simulation of this model, we have studied the spatio-temporal organization of amphiphiles in this system.
In particular, we have shown that i) with the increase of temperature, the solubility of the amphiphiles in water increases sharply over a narrow range of temperature; ii) the longer is the hydrophobic tail the lower is the solubility; iii) if an amphiphilic monolayer is constructed at the air-water interface with very small interfacial area available per amphiphile, then a fraction of the amphiphiles is pushed out of the monolayer into the water by a few molecular layers because of the strong steric repulsions between the tails. In this case, the loss of energy is compensated by the gain of entropy; iv) although the monolayer at the air-water interface is stable, no such stable bilayer was formed inside water in equilibrium, except at very low temperatures where equilibration could not be guaranteed within the time of observation in our computer experiments; v) when the surface to volume ratio of the water is not negligibly small the nature of self-assembling of the amphiphiles depends not only on the concentration of the amphiphiles but also on the depth of the water column and the area of the air-water interface.

The approached followed in this paper is quite general. Depending on the physical situation, it can be easily extended a) to incorporate longer range interactions among the amphiphiles, b) vary the ratio of the sizes of the head and tail units, c) to mixtures of amphiphiles of different sizes and interactions, d) amphiphiles with two hydrophobic chains, etc. We hope this approach will become an alternative route to our theoretical understanding of the physical phenomena in surfactant-containing complex fluids.

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