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Monte Carlo Simulation of the Formation of Layered Structures and Membranes by Amphiphiles

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Abstract. — We investigate a Larson-type model of a ternary mixture of nonionic amphiphiles, water and oil confined between walls or forming a membrane by performing Monte Carlo simulations on a cubic lattice. We compute the concentration profiles of water/oil and the distribution of the amphiphiles with varying temperatures and distance from a solid wall. For temperatures below the critical temperature for demixing of oil-water and amphiphiles on cubic lattices, we observe an oscillatory pattern in the distribution of the water/oil molecules. We also examine the stability of membranes both in an extended system and when confined between walls. Below the critical demixing temperature, double layer membranes are stable when there is no oil present. We find that single layers are stable only when between walls and if we start with a finite amphiphile concentration away from the membrane. At higher temperatures, we also observe the development of periodic layered structures for one type of amphiphile.

1. Introduction

Amphiphile molecules are constituted of two parts with opposite properties: a hydrophilic, water loving "head" and a hydrophobic hydrocarbon "tail". In dilute aqueous solutions and at ambient temperatures, the amphiphiles are disperse in water (monomeric), but as concentration increases, they aggregate into structures called micelles which shield the hydrocarbon tails from contact with water [1]. This hydrophobic "force" which leads to aggregation has been explained [1, 2] in terms of an entropic effect due to the structuring of water [3] around free surfactant molecules. Amphiphiles aggregate to avoid the ensuing decrease in water entropy. The repulsive force may be interpreted as an effective result of the interplay between energy and water entropy loss which drives aggregation, whose microscopic origin remains to be explained. For higher concentrations one can obtain several types of structures: hexagonally ordered cylinders, monolayers, bilayers or lamellae [4]. The structures obtained depend on the concentration of surfactant, on the external parameters (like temperature or pressure), the concentration of oil and water in the mixture. The thermodynamic behavior of these mixtures

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has been the subject of much study over the last few decades, and some progress has been made using lattice models. The simplest version of these models is the Widom model [5], which considers water, oil or amphiphiles occupying a bond on the lattice. Recently, more realistic models were also developed, introducing the length of the chains, the head repulsion (for ionic amphiphiles) and conformation energy of the amphiphiles [6–8].

For ternary mixtures confined between oil-soaked pores, using the simpler Widom model, Chowdury and Stauffer [9] obtained oscillation patterns in the distribution of the components of the mixture, namely, oil, water and amphiphiles. In this spirit, we considered a version of a model simulated by Larson [6] to investigate amphiphile-water-oil mixtures confined between (hydrophilic) walls.

Membranes are ubiquitous in nature and form the basis of almost all life forms. Using a similar model, Jan and Stauffer [7] were unable to construct stable membranes. Stable membranes must exist and with that in mind, we explore the behaviour and stability of single layer membranes in a ternary mixture and bilayer membranes in a binary mixture of with a finite concentration of chains surrounding the membrane. We also note the effects of walls on the behaviour of membranes.

2. The Model and Simulation

In the present model, an amphiphile molecule is represented by \( \ell_a \) connected particles and a water or oil molecule by a single particle on a cubic lattice of \( L \times L \times L_z \) sites. When the system is confined by walls \( L \) is the dimension of the wall and \( L_z \) the distance between walls. Each site may be occupied only once. We simulate two types of amphiphiles: in the first one the amphiphiles are constituted of a hydrophilic head with two sites (both “water-loving”), a liaison site (that plays a noninteraction role) and a hydrophobic tail \((\ell_a - 3 \text{ “oil-loving” particles})\); in the second type an amphiphile are symmetrically built, constituted of \( \ell_a/2 \) “water-loving” particles and \( \ell_a/2 \) “oil-loving” particles. The amphiphiles can fold in the lattice and the effect of the other chains is modelled by the amphiphiles constrained to slither along their length moving only to occupy neighbour sites (on the chain). The solvent is simulated by an Ising model, the amphiphiles by this reptation algorithm.

In order to simulate the hydrophilic and hydrophobic effects we assume water-water and oil-oil attractions and water-oil repulsions through the following energy:

\[
E = - \sum_{\langle ij \rangle} \varepsilon S_i S_j \quad (\varepsilon > 0).
\]

where the sum \( \langle ij \rangle \) is only over nearest neighbour sites. Water has spin +1 and oil a spin −1. Hydrophilia is thus identified with positive spin and hydrophobia with negative spins. All computations were performed for amphiphiles occupying 6 sites — the tail with 3 sites. The two types of amphiphiles we simulate have an Ising spin distribution along the chain given by type A +2,+1,0,−1,−1,−1 and type B +1,+1,0,−1,−1,−1. For the first type of amphiphile the two head molecules carry Ising spins +2 and +1, the tail molecules −1, for the second one the three head molecules carry Ising spins +1 and the tail −1. We define the temperature of the system in units of the energy interaction between sites

\[
t = k_B T/\varepsilon ,
\]

where \( k_B \) is the Boltzmann constant. As indicated in the sum, only nearest neighbour interactions are taken into account. We do not consider different types of conformational energy of the hydrocarbon chains as it has been considered in other simulations of this type of model [8].
Helical boundary conditions were adopted in one direction and the molecules cannot move in
or through the walls. The sites on the walls are occupied by either fixed water or fixed oil
molecules in order to simulate the hydrophilic or hydrophobic behaviour. In the three com-
ponent model, the number of amphiphilic molecules is fixed, while the number of water or oil molecules
can change by Glauber kinetics. A MC step corresponds to one trial move to change water to
oil (or oil to water) for all solvent sites by a Metropolis algorithm (i.e., a flip of an Ising spin)
and a trial move of all the amphiphilic molecules. In the two component model, the number of
amphiphilic, water or oil molecules remains fixed and a MC step consists of a trial move of all
amphiphilic molecules.

3. Walls and Oscillatory Behaviour

At the beginning of the simulation the amphiphilic molecules of type A are uniformly distributed
according a defined concentration and the rest of the lattice is occupied by water. The walls
are hydrophilic and remain that way for the whole of the simulation.

We initially performed computations for different distances between walls (all of these dis-
tances a few times the length of an amphiphilic molecule) and at a concentration of $\phi_a = 0.1$.
This means that one has a volume occupied by amphiphilic molecules given by

$$V_a = \phi_a \times \ell_a,$$  \hspace{1cm} (3)

where $\ell_a$ is the length of amphiphilic molecules (in our simulations $\ell_a = 6$). At the beginning
of the simulation water tends to accumulate near the walls. We observed that a peak of water
concentration forms half way between the walls but, for distances $L_z \leq 25$ this peak disappears
when the system reaches equilibrium.

However, for $L_z = 30$ we clearly observe that an intermediate peak in the water concentration
was formed half way between the walls, as one can see in Figure 1a, where we represent only
the sum of water (+1) and oil (−1) molecules, not the amphiphiles. There is a concentration of
water near the walls, while two minima of water concentration (maxima in oil concentration)
were formed on layers 7/8 and 23. A maximum in water concentration was seen to be stable
half way between the walls (layer 15). This result is the average of results obtained for a
simulation with 250,000 MC steps in a Paragon parallel computer using 136 processors (with
almost 3 h for each processor). Figure 1b shows the evolution of these points (for layers 8,
15 and 23, respectively). As one can see in this figure, these points seem to be stable. The
structure of water and oil molecules indicates that the amphiphiles are organized in a layered
structure, with the heads in contact with the maximum of water and tails in contact with oil.

In Figure 2 one can see the evolution of the simulations for different temperatures. For
temperature $t = 2.0$ discussed above, we observe that the system is near the equilibrium for
the 250,000 iterations. We made one simulation with 400,000 MC steps (black diamonds) and
it shows that the system could be considered close the equilibrium state for those simulation
with 250,000. In this figure it is possible to see that for a simulation with temperature $t = 1.4$
the system reaches the equilibrium quickly. However, for temperature $t = 2.5$ the system is very
far from equilibrium at 250,000 MC steps. The reason could be that this temperature is above
the critical temperature of demixing of amphiphiles and solvent in 3d ($t_c = 2.3$ for amphiphiles
with length 6) [7] and in this case the equilibrium was reached when the number of water and
oil molecules are almost the same (zero total magnetization). Figure 3a shows the last profiles
of water/oil concentrations obtained for simulations in $t = 2.5$. Though the system is far from
equilibrium, as we have pointed out above, it is clear that the intermediate maximum tends
to disappear. The minima are asymmetric, but one can see that the intermediate maximum
Fig. 1. — a) The water/oil concentration profiles for a ternary mixture confined by hydrophilic walls with amphiphiles of type A (see text). The size of the wall is \( L = 30 \), distance between walls \( L_z = 30 \), temperature \( t = 2.0 \) and concentration of amphiphiles \( \phi_a = 0.1 \). One can see that the intermediate maximum, as well as the two minima are stable. Five different configurations are shown: (\( \circ \)) = 210,000 MC steps, (\( \bullet \)) = 220,000; (\( \circ \)) = 230,000; (\( \square \)) = 240,000 and (\( \bigcirc \)) = 250,000. This figure represents the average of results obtained for 136 samples; b) MC evolution of the maximum and minima in the water/oil concentration shown in (a). Three layers are shown (\( \bullet \)) = layer 8; (\( \circ \)) = layer 15 and (\( \circ \)) = layer 23.

diminishes with the MC steps. Figure 3b show this tendency. There we have plotted the behavior of the water/oil concentration in layers 10, 17 and 21, and the water/oil concentration in layer 17 (black diamonds) diminishes faster than that in the others. These figures represent
the average of the results obtained for simulations performed in 110 processors. Thus, we can conjecture that in this case the intermediate maximum will disappear when the system reaches equilibrium, and it is not possible to affirm that any kind of layered structure will be formed. For very low temperature \( t = 1.4 \) we can observe a different profile in water/oil concentration. As shown in Figure 4a, in this case we have four maxima in the water concentration between the walls (two near the walls and two in the bulk). Three minima can be observed, though in this case we do not observe a symmetric profile: the intermediate one is weaker than other two. The figure is almost symmetrical. One could conjecture that this intermediate minimum is a fluctuation, but when we observe the evolution of the concentration in these layers (layer 5, 10, 15, 20 and 25), as shown in Figure 4b, it seems that these points are stable, and we have a layered structure in the middle filled by oil. This simulation was performed in 110 processors.

4. Membranes

We study both single and double layer membranes. For the single layer case we begin with a completely ordered layer of \( L \times L \) amphiphiles aligned with heads towards water and tails to oil between two equal regions of water and oil. The value of \( L \) used was \( L = 24 \). Simulations were performed at \( L = 48 \) but these did not produce qualitatively different results. We also put in a finite concentration of chains \( \phi'_a \) in a uniform distribution on either side of the membrane. This can be seen from the initial profile in Figure 5a. We do not consider concentrations of \( \phi'_a > 0.5 \). At such concentrations we expect complicated ordered phases which are not the purpose of this study. The volume occupied by amphiphile chains is then given by

\[
V_a = l_a(L^2 + \phi'_a)
\]
Fig 3. — a) The water/oil concentration profiles for the same ternary mixture shown in Figure 1 with the same parameters, except that now temperature $t = 25$. The system is far from equilibrium and the intermediate maximum tends to disappear. Five different configurations are shown: $\circ = 210,000$ MC steps, $(\bullet) = 220,000$, $(\diamond) = 230,000$, $(\square) = 240,000$ and $(\bigcirc) = 250,000$. This figure represents the average of results obtained for 110 samples; b) MC evolution of the maximum and minima in the water/oil concentration shown in a). Three layers are shown: $(\bullet) =$ layer 10, $(\diamond) =$ layer 17 and $(\bigcirc) =$ layer 21.

The height of our lattice was varied and values $L_z = 20, 40$ were mainly used. We performed simulations both with periodic boundary conditions to model an extended system, and with one hydrophobic and one hydrophilic wall to study the effects of confinement. There were
Fig. 4. — a) The water/oil concentration profiles for the same ternary mixture shown in Figure 1 with the same parameters, except that now temperature $t = 1.4$. Five different configurations have been plotted: (o) = 210,000 MC steps; (●) = 220,000; (◆) = 230,000; (□) = 240,000 and (○) = 250,000. One can see that the three minima and the two central maxima are stable. This figure represents the average of results obtained for 110 samples; b) MC evolution of the maxima and minima in the water/oil concentration shown in a). Five layers are shown: the maxima - (o) = layer 10 and (●) = layer 20; the minima - (◇) = layer 15; ( ▼ ) = layer 5 and ( ▼ ) = layer 25.

striking differences in the behaviour for the different types of amphiphile studied.

In the extended system, we found that for both types of amphiphiles the membrane was unstable for all values of concentration and at reasonably high temperatures ($t \geq 2.0$). In
Fig. 5. — a) The concentration profile of a single layer membrane, amphiphile type A at \( t = 2.5 \) with \( \phi_a' = 0.3 \), \( L = 24 \), \( L_z = 20 \) and periodic boundaries. Evaluated at (●) = the start; (□) = 50,000, (○) = 100,000 MC steps. Note the top hat structure of the initial membrane; b) The decay of the membrane for type A at \( t = 2.0 \) with \( L = 24 \), \( L_z = 20 \) with periodic boundaries. We plot the concentration of the layer at the edge of the membrane (layer 13) which gives a good measure of the rate of decay of the membrane. Comparison of (□), \( \phi_a' = 0.0 \), (○), \( \phi_a' = 0.1 \), (●), \( \phi_a' = 0.3 \), (○), \( \phi_a' = 0.5 \); c) Concentration profile of single layer type B at \( t = 2.5 \) with \( \phi_a' = 0.5 \), \( L = 24 \), \( L_z = 40 \) and periodic boundaries Evaluated at (○) = initial; (□) = 15,000, (○) = 90,000; (●) = 100,000 MC steps. Note the curves are provided as a guide.
Fig. 6. — a) Decay of monolayer, amphiphile type A at \( t = 2.0 \), with \( L = 24, L_z = 20 \) and walls. Comparison of (●) \( \phi_a' = 0.0 \); (□) \( \phi_a' = 0.1 \); (◇) \( \phi_a' = 0.5 \) showing progressive stabilisation; b) Concentration profile of single layer type A at \( t = 2.5 \) with \( \phi_a' = 0.5 \), \( L = 24, L_z = 20 \) and walls. Evaluated at (●) = initial membrane; (□) = 50,000; (◇) = 100,000 MC steps. Note depletion region and the monolayer membrane is stable, c) Concentration profile of single layer type B at \( t = 2.5 \) with \( \phi_a' = 0.5 \), \( L = 24, L_z = 40 \) and walls. Evaluated at (◇) = initial membrane; (□) = 15,000; (○) = 90,000, (●) = 100,000 MC steps. Again, note the curves are provided as a guide, d) A picture of a cut perpendicular to the walls to show layered structure for type B at \( t = 2.5 \) after 100,000 MC steps. We have \( \phi_a' = 0.5 \), \( L = 24, L_z = 20 \) and walls. (+) = water; (∼) = oil; (○) = head site; (●) = tail site.
Fig. 7. — a) Concentration profile of double layer membrane, amphiphile type A at $t = 2.0$ with $\phi'_a = 0.0$, $L = 24$, $L_z = 26$ and periodic boundaries. Evaluated at (●) initial membrane; (□) = 500,000; (○) = 1,000,000 MC steps; b) Decay of bilayer, amphiphile type A at $t = 2.0$, with $L = 24$, $L_z = 26$. We compare (●) $\phi'_a = 0.0$ walls; (□) $\phi'_a = 0.3$ periodic BC; (○) $\phi'_a = 0.3$ walls to see that there is no difference in behaviour.

Figure 5a, we see that there is a tendency for the membrane profile for amphiphile type A to steadily decay to a uniform distribution with background fluctuations. We performed 100,000 MC steps using 30 processors to get this graph. In Figure 5b we have plots of the evolution in time of a point on the profile corresponding to the “edge” of the membrane for type A at $t = 2.0$ and several values of $\phi'_a$. When this is horizontal we may consider the system to be in thermal
equilibrium. The rate of decay is seen to be slowed by the extra concentration of chains but we were unable to find any reasonable concentration of chains for which the membrane was stable. We may try to explain this by the fact that there is always a finite probability that oil (or water) molecules will diffuse to the other side of the membrane which would encourage amphiphiles to leave the membrane and form other structures such as micelles. As the concentration of chains around the membrane is increased there is also a diffusion of amphiphiles back into the membrane but this does not seem to be enough to stabilise it.

After 100,000 MC steps, and at a temperature \( t = 2.5 \), we found that for structure A, the membrane decayed to a homogenous distribution signifying formation of micelles as can be seen from Figure 5a. Conversely, for structure B, which was the one studied by Larson [6] (at \( t = 2.5 \), after 100,000 MC steps), we observed oscillations in the density profile of amphiphiles (see Fig. 5c) but the amplitude of oscillations decayed as we moved away from the original position of the membrane. With walls, we observed that for structure A the membrane was stabilised. From Figure 6a we see that at \( t = 2.0 \), as we increase \( \phi'_a \), the rate of decay is slowed until at \( \phi'_a = 0.5 \) it may be considered "stable" (the decay curve is horizontal from about 40,000 MC steps). For structure B, at \( t = 2.5 \), we observed strong oscillations generated by the walls which decayed as we approached the middle as is illustrated in Figure 6b. We used 64 processors for this simulation. It should be noted that the membrane was totally dissolved after 70,000 MC steps. We have a picture of one realisation showing this periodic structure shown in Figure 6c. We also studied a double membrane or bilayer in a binary mixture of water and amphiphile with no oil molecules. Here we begin the simulation with a regular array of two layers of \( L \times L \) amphiphiles arranged with heads outwards towards the water and tails inwards. The value of \( L \) used was \( L = 24 \). We also have an extra concentration \( \phi'_a \) of amphiphiles so that the total volume occupied by amphiphiles is

Fig. 8. — A picture of a stable bilayer membrane of type A after 100,000 MC steps at \( t = 2.0 \) with \( \phi'_a = 0.5 \), \( L = 24 \), \( L_z = 52 \) and periodic boundaries. (+) = water; (o) = liaison site; (*) = tail site; (O) = head site.
We either have periodic boundary conditions or hydrophilic walls. The height of the lattice was set at \( L_z = 26, 52 \).

In this situation one observes that for at at temperature of \( t = 2.0 \) bilayers are stable for both types of amphiphiles. We performed simulations up to 1,000,000 MC steps using 30
processors on type A and the profile remained stable. We show the profile at different times in Figure 7a. Since the bilayers are stable at this temperature, a finite concentration of chains outside the membrane does not qualitatively change the behaviour. We see this in Figure 7b and that there is no difference if walls or periodic boundary conditions are used. We illustrate by showing a slice through the middle of a membrane in Figure 8.

At a temperature of \( t = 2.5 \) the behaviour is quite different. We observed that both types of amphiphiles did not have stable bilayers though the rate of dissolution was much higher for type B than type A. To see the dissolution of bilayer of type A we had to go to 1,000,000 MC steps on 30 processors. We compare the unstable bilayer at \( t = 2.5 \) to the one at \( t = 2.0 \) in Figure 9a to show the striking difference. The presence of a finite concentration of amphiphiles outside the bilayer was seen to slow down the dissolution of the membrane. From Figure 9b it can be seen that an increase in \( \phi_a' \) progressively slows the decay of the membrane but does not stop it. We found that for \( (t = 3.0) \) there are no stable membranes for both the extended case and when walls are present. This was observed by Jan and Stauffer [7]. The presence of walls seems to have no effect in this case.

5. Conclusions

From these simulations we have obtained the formation of oscillatory correlations in the structure of amphiphiles in ternary mixture. We find that both walls or membranes can act as generators of oscillatory behaviour. In particular, we find that the nature of the structures created is quite heavily dependent on the type of amphiphiles. This shows clearly the advantages of using more realistic models of amphiphiles. In our study of membranes we found that monolayers were stable below the critical temperature \( t_c \) of demixing of amphiphiles and solvent but only when confined within walls and with an extra concentration of chains around the membrane. We have found that bilayers were stable below \( t_c \) but were unstable above it. We also find that the inclusion of a finite concentration of amphiphiles will slow down the dissolution of a bilayer at higher temperatures but that the membrane is still unstable.

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Note added in proof

In equations (3)-(5), a factor of \( \ell_a \) must be replaced by \( L^2 \times L_z \) so that equations (3)-(5) become \( V_a = \phi_a \times L^2 \times L_z \), \( V_a = L^2(\ell_a + \phi'_a L_z) \), \( V_a = L^2(2\ell_a + \phi'_a L_z) \), respectively.

Upon improvement of the algorithm and performing the simulations for much longer, it was found that the maxima in Figures 1a and 4a vanished but the bilayer membrane remained stable. Further results can be found in reference [10].
References


[10] Liverpool T.B. and Bernardes A.T., preprint