Equilibrium States of Self-Assembly Systems: Monte Carlo Simulations

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We investigated the equilibrium states of the self-assembly of amphiphilic molecules in water. The amphiphiles are represented by chains of the type H_1T_4, where H is the hydrophilic part of the molecule and T is its hydrophobic portion formed by four monomers. We have performed Monte Carlo simulations on a two-dimensional lattice, in which each water molecule occupies a single site, and the amphiphiles occupy five sites of the lattice. We have determined the aggregate distribution curves for the system at low concentration and fixed temperature. We have shown that the criterion to determine the equilibrium states of the system, based on the stabilization of energy curves as a function of the simulation time, is not reliable. The best way to ensure that the equilibrium state was reached was to follow the route to equilibrium of all aggregate sizes of the system.

The purpose of this work is to present some studies concerning the equilibrium states of the dilute solutions of amphiphiles in water. Depending on temperature and concentration of the amphiphilic molecules, formation of molecular aggregates, called micelles,[1-3] is observed. According to Wennerstrom and Lindman,[4] the micelle formation is characterized by a well-defined critical micelle concentration and by a minimum and a maximum in the distribution curve of the aggregates. The difference between the concentrations at the maximum and the minimum decreases with temperature as we approach the transition temperature of the micellar to non-micellar regimes.[5,6] In the nonmicellar state, the curve of the aggregation number is a monotonically decreasing function of the aggregate size.

In this work, we consider Monte Carlo simulations on a lattice to describe the equilibrium states of a dilute solution of amphiphiles. In our lattice model, the amphiphilic molecules are represented by five monomers and are described by the formula H_1T_4. Here, H denotes the head group of the molecule, which loves water, and T is its hydrophobic part, which avoids direct contact with water. These chain molecules are placed on a square lattice, each monomer occupying a single site of the lattice, while the remaining lattice sites are filled with water molecules, each one per site. In our model, only nearest-neighbor interactions between sites are taken into account. We chose to simulate this model due to its simplicity and because it exhibits some of the qualitative features of the micellar agregates. Larson[7-10] pioneered the Monte Carlo calculations of these systems for a wide range of concentrations, including in some cases oil molecules, finding ternary phase diagrams. Since then, many other studies have appeared in the literature, exploring the low concentration behavior of these systems.[11-14]

In this study, the interaction between nearest-neighbor monomers of the type H–T and H–H are repulsive, and we take for these interactions the value ϵ, where $\epsilon > 0$. The interaction between nearest-neighbor monomers belonging to two different hydrocarbon chains (T–T) is attractive, and the

same happens for the interaction between a water molecule and the polar head of the amphiphiles. The attributed value for the attractive interactions is $-\epsilon$. For simplicity, we have assumed that all the interactions have the same absolute value. In our calculations, temperature is simply scaled by the factor ϵ. In general, to have a micellized state, it is required that the interactions among hydrophilic groups (heads and waters) be more attractive than the interactions between hydrophilic groups and hydrophobic tails. In the present calculations, we have also explicitly considered that T–T interactions are attractive. Because our amphiphilic molecules are small (the polar head is a single monomer and the hydrocarbon tail contains four monomers), we discarded chain twisting and considered only chain reptation movements.[7] We also arbitrarily added an amount of energy, ϵ, to each bending of a chain molecule. This choice for the value of the bending energy favors a more straight conformation of the molecules and measures the effect of chain stiffness.[15,16] The idea to take this bending energy in our system is to allow the presence of larger aggregates; otherwise, because our amphiphilic molecules are very short, we would have a very small polydispersity.

An essential step in the study of the micellar systems is to ensure the system is in equilibrium so that its thermodynamic properties can be calculated. The general procedure adopted in the course of the simulations is to follow the evolution of the total energy of the system. The equilibrium is achieved when the total energy fluctuates around some constant mean value. We will show next that this is not a reliable criterion. Although the energy appears to be stabilized, the aggregate size distribution curve is still evolving in time.

The following steps were considered in our Monte Carlo simulations: First, we randomly distribute the amphiphiles on the lattice, and then we fill the remaining lattice sites with water molecules. We have performed the simulations on a square lattice of linear size $L = 200$, and periodic boundary conditions were assumed. The concentration of amphiphiles was fixed at the value 4%, and two different temperatures were considered. Then, after we generated a random initial distribution of amphiphilic molecules on the lattice, we attempted to change

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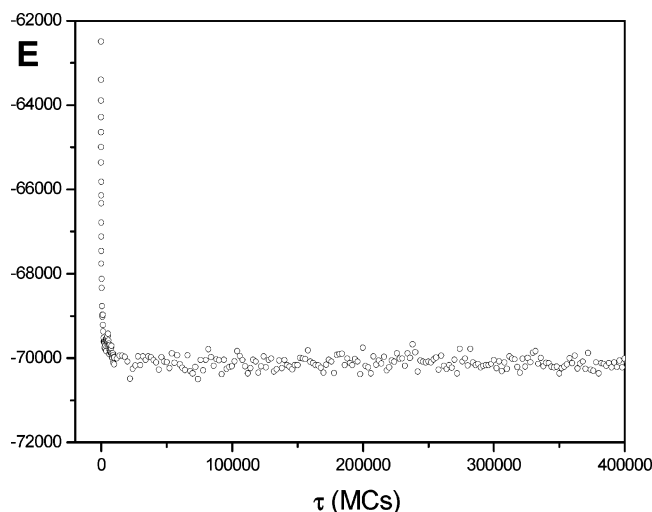*J. Phys. Chem. B, Vol. 111, No. 20, 2007* **5649**

Figure 1. Plot of the total energy of the system as a function of time, measured in units of Monte Carlo steps, for the reduced temperature $t = (k_B T/\epsilon) = 2.20$.

the energy of the system by moving the chain molecules in order to reach the equilibrium state. We have employed the Metropolis[17] algorithm to accept or reject the reptation movements of the molecules. The time was measured in units of Monte Carlo steps (MCs), which means two complete runs over all the amphiphilic molecules. During the course of the simulations, we monitored the size and the number of clusters. A cluster is considered a micellar aggregate only when a hydrocarbon chain has at least one first neighbor contact with another hydrocarbon chain.

We computed at each instant of time, the concentration (number density) of aggregates of size n by the equation

$$X_n = \frac{N_n}{N^2} \tag{1}$$

where N_n is the number of aggregates containing n amphiphiles. In this way, the total concentration is given by $X_t = \sum_{n=1}^{\infty} nX_n$.

We determined the energy and the distribution curve of the aggregates as a function of time. We exhibit in Figure 1 a plot of the total energy of the system as a function of time, measured in units of Monte Carlo steps. This curve was obtained for a reduced temperature $t = (k_B T/\epsilon) = 2.20$, for which the system is in a micellized state. Looking at this Figure, we could accept that just after 50 000 MCs, the system entered into the equilibrium state. This criterion is clearly qualitative rather than quantitative. Zaldivar and Larson[18] considered this type of problem, and instead of simulating at a fixed temperature, they started with the system at an infinite temperature, which is equivalent to take $\epsilon = 0$. Then, by increasing the parameter ϵ in controllable steps, they reached the desired temperature. The temperature was afterward reduced in six steps from infinite to the selected temperature, where they performed their thermodynamic calculations. Typical simulations take a total of 10^9-10^{10} Monte Carlo steps.

Our approach to probe the equilibrium states is somewhat different. We chose to simulate the system at a same fixed temperature, starting from a random distribution of molecules on the lattice. We recorded at each Monte Carlo step the energy and the aggregate size distribution curves. In Figure 2, we exhibit typical plots of the aggregate size distribution curve at different times of observation. We have considered averages over 300 samples to draw these curves. For instance, when $\tau =$
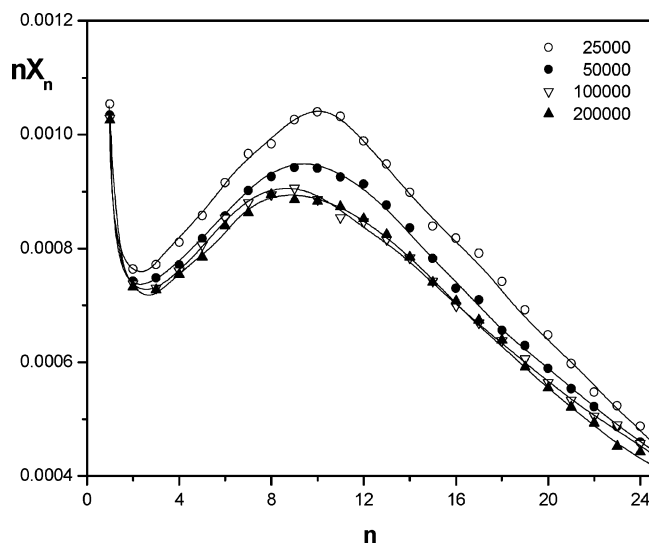

Figure 2. Distribution function, nX_n, versus size of the aggregates, n, at different times of observation, as indicated in the figure. The temperature is $t = (k_B T/\epsilon) = 2.20$, and the lines are guides to the eye.
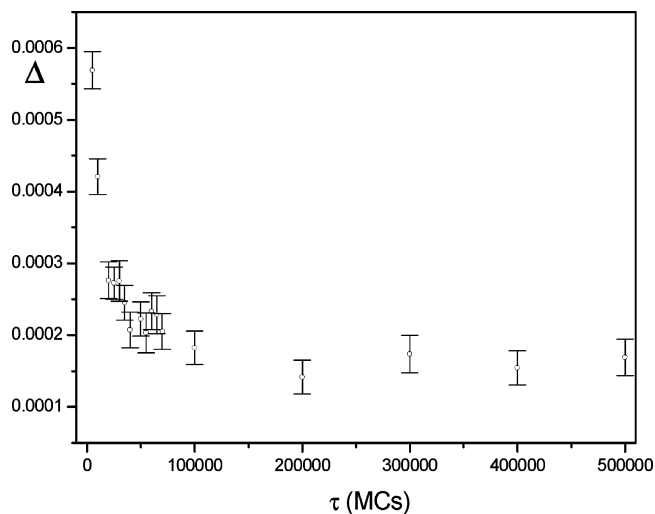

Figure 3. Plot of the parameter Δ as a function of time for the temperature $t = (k_B T/\epsilon) = 2.20$. Δ is the difference in height between the local maximum and minimum of the aggregate size distribution curve.

50 000, it is clear from Figure 2 that we are very distant from the equilibrium state. For this temperature, the stabilization of these curves occurs only for times longer than 2×10^5. In Figure 3, we also measured the difference in concentration between the local maximum and the minimum of the aggregate size distribution curve as a function of time. A nonzero value of the parameter Δ characterizes a micellized state,[5,6] and we see again that a stable value is reached for times longer than 2×10^5. Although the aggregate size distribution curve displays the typical local maximum and minimum already at a time as early as $\tau = 5 \times 10^3$, the parameter Δ attains its equilibrium value only at a later time, which is two orders larger than this time. Therefore, a criterion that is based solely on the stabilization of the energy to define the equilibrium state of micellar solutions is not trustworthy. A more detailed description based on the temporal evolution of the concentration of the aggregate sizes gives a more reliable method to ensure that the equilibrium state was, indeed, attained.

A more dramatic situation can be seen in Figures 4 and 5. Figure 4 shows the evolution of the energy for the same system
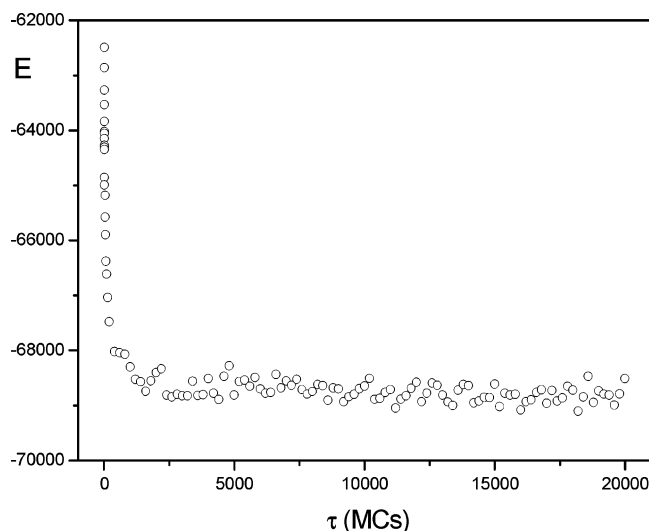
Figure 4. Plot of the total energy of the system as a function of time, measured in units of Monte Carlo steps, for the reduced temperature $t = (k_B T/\epsilon) = 2.50$.
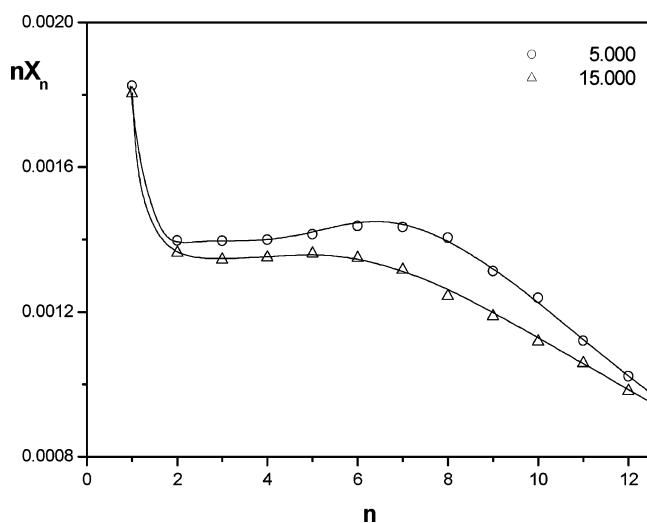

Figure 5. Distribution function, nX_n, versus size of the aggregates, n, at two different times of observation, as indicated in the Figure. The temperature is $t = (k_B T/\epsilon) = 2.50$, and the lines are guides to the eye.

at a higher temperature, $t = 2.50$. Now, for the time $\tau = 5 \times 10^3$, the system appears to have reached equilibrium, and Figure 5 indicates that at this time, the aggregate size distribution curve still displays the signature of a micellized system with its typical local maximum and minimum, for which the parameter Δ is different from zero. However, if we wait for a longer time, this

structure disappears, and for a time as large as $\tau = 10^5$, the distribution curve becomes monotonically decreasing, which is typical of a nonmicellized state. Then, if thermodynamic measurements were performed at the earliest times, when the energy appears to indicate the equilibrium, the results would lead us to wrong conclusions.

In summary, we have studied the equilibrium states of micellar aggregates through Monte Carlo simulations. We have recorded the energy and the distribution curve for the concentration of the aggregates as a function of time. We have shown that the criterion based on the stabilization of energy is not always sufficient to ensure the equilibrium. A more detailed description based on the time evolution of the concentration of the aggregate sizes is more powerful in predicting the correct equilibrium states. The time to stabilize the micelle size distribution is much longer than that for the energy. Only after the stabilization of the size distribution is the thermodynamical equilibrium really reached and we can start computing the thermodynamical properties of the system.

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