Spin-1 aggregation model in one dimension

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We studied a simple model of aggregation in one dimension that resembles the self-assembly of amphiphiles in an aqueous solution. We mapped the water and amphiphilic molecules by Ising spin variables for $S=1$. The zero component of spin represents the water molecules, while the remaining components (± 1) account for the amphiphilic molecules. We defined an aggregate in one dimension by a set of spin components (± 1) placed between two zero spin components. There is no difference between up and down components of the spins inside the aggregates. In this way what really matters is the square of the spin component. The grand-canonical partition function and the probability of formation of different aggregate sizes were calculated by the transfer matrix method. We have shown that for any value of the chemical potential and temperature, the system does not exhibit the typical aggregate size distribution which is observed in micellar solutions at low concentrations. The distribution curve for the aggregate size does not show the minimum and the maximum as a function of the concentration which is the signature of the appearance of micelles. We can say that this one-dimensional model does not present any phase transition nor a transition from the micellar to nonmicellar state.

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I. INTRODUCTION

It is well known that one-dimensional systems with short-range interactions do not exhibit a phase transition from an ordered to disordered state [1]. In spite of this fact, short-range forces can give rise to the formation of islands containing a different number of particles at finite temperature. In this work we are concerned with the formation of a special type of aggregates, which we think can mimic the self-assembly of amphiphilic molecules in aqueous solutions [2–5]. Some recent models have been presented in the literature to describe the linear self-assembly of molecules. Henderson [6] considered as an example of chain forming amphiphilic solution, a mixture of solvent (A) and solute (B) with repulsive interactions between them, opposed to the interactions (AA) and (BB) considered attractive and of equal magnitude as that of the (AB) pair. He obtained an exact expression for the cluster distribution and showed that the model cannot display a phase transition. Duque and Tarazona [7] presented a simple one-dimensional model with molecular interactions favoring the formation of clusters with a defined optimal size. Their model is a system of hard rods of fixed length, moving along a line and with internal degrees of freedom. They found an exact solution that incorporates excluded volume effects and molecular attraction. They have shown that, at low molecular concentrations, the curve of the chemical potential against molecular density changes its slope at a given concentration. This could be interpreted as the equivalent to the CMC (critical micellar concentration), which is in qualitative agreement with real systems of amphiphilic molecules. Kolomeisky and Widom [8] also considered a one-dimensional lattice model for the hydrophobic attraction. In their model, the accomodation of the solute molecules in the lattice depends on the state of nearest-neighbor solvent molecules. The model was exactly solved in one dimension, and they found the condition of hydrophobicity at temperature T as a function of the interaction parameters of the model, and the number of possible states of the solvent molecules. The model we consider here consists of a linear array of sites, where each site is occupied by a variable with three possible values. One of these values (0) represents the solvent molecules, while the other two (± 1) are associated with the amphiphilic molecules. We use the spin 1 Ising model to describe the interactions between nearest neighbor sites, and we restrict the number of components equal to zero to a fixed value, that is, the number of solvent molecules determines the value of the concentration of the solution. We use the transfer matrix method to compute the grand-canonical partition function of the model, and to calculate the probability of finding an aggregate of a given size. We also performed Monte Carlo simulations on this model, and we have seen that the evolution of the system towards its equilibrium states is driven by two simultaneous stochastic processes. The dynamics processes that fit our model are the following: one that conserves the order parameter, of the exchange Kawasaki type [9], and the other, where the order parameter is not conserved, related to the single spin-flip Glauber kinetics [10]. We show that this model, albeit very simple, is capable of predicting a change in the slope of the curve of the free amphiphilic molecules against total concentration. We also show that the distribution curve for the aggregate sizes does not exhibit the local minimum and maximum characteristic of micellized systems [5]. For a typical system in its micellar state, the local minimum in the aggregate-size distribution curve lies always below the concentration of free amphiphiles, and it is different from zero. The local maximum in this curve, which appears for larger values of the aggregate size than that observed at the minimum, indicates the typical size of the micelles. This work is organized as follows. In Sec. II we present the model and the calculations. In Sec. III we describe the Monte Carlo simulations. In Sec. IV we present our results and conclusions.

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II. MODEL AND CALCULATIONS

We consider a lattice model to describe the aggregation of amphiphilic molecules in a solvent. The simplest model we can imagine is a linear array of sites, where each site is occupied by an amphiphilic or by a solute molecule. We choose to represent these molecules in the language of spins, and we make use of the spin 1 Ising model, with three possible components. In this way, to each solute molecule we associate the zero component of the spin, and the two other components (± 1) are attached to the amphiphilic molecules. For instance, the values (± 1) are related to the hydrophobic and hydrophilic properties of the amphiphilic molecules. If two nearest neighbor amphiphiles have the same value of the spin components, it can be thought that two hydrocarbon chains are touching each other in a real solution. On the other hand, two antiparallel spin components mimic the repulsion between the hydrophilic head and the hydrophobic chain of the amphiphile. We define an aggregate in one dimension by a set of spin components (± 1) placed between two zero spin components. There is no difference between an up and down component of the spin inside the aggregate, but the different orientations of spins can take into account the possible values of the aggregate energy. In order to simulate a fixed concentration in the real solution, in this model, the number of zero spin components is made constant. We define the following Hamiltonian model for the system:

$$\mathcal{H} = -J\sum_{i=1}^{L} S_i S_{i+1}, \tag{1}$$

where J represents the coupling constant between nearest neighbor spins, and L is the linear size of the lattice. By imposing periodic boundary conditions, we have $S_{L+1}=S_1$. The constraint of constant number of zero spin components can easily be handled by employing the formalism of the grand-canonical ensemble. The grand-partition function is expressed by the equation

$$\Xi = \sum_{N=0}^{L} e^{-\beta\mu N} Z, \tag{2}$$

where $\beta = 1/k_B T$, and k_B is the Boltzmann constant. μ is the chemical potential, $N=\Sigma_{i=1}^{L}(S_i)^2$ is the number of amphiphiles, and Z is the canonical partition function for a fixed N. The grand-partition function can also be written in the form

$$\Xi = \sum_{\{S_i\}} \prod_{i=1}^{L} R(S_i, S_{i+1}), \tag{3}$$

where $R(S_i,S_{i+1}) = e^{\beta J S_i S_{i+1} + (\beta\mu/2)(S_i)^2 + (\beta\mu/2)(S_{i+1})^2}$, are the elements of the 3×3 transfer matrix. Finally, in the thermodynamic limit, the grand-canonical potential density is

$$\Phi = -(\beta)^{-1}\ln(\lambda), \tag{4}$$

where λ is the largest eingenvalue of the transfer matrix that can be written as

$$\lambda = \frac{1}{2}\left[1 + \frac{a}{b} + ab + \sqrt{\left(1 - 2\frac{a}{b} - 2ab + \frac{a^2}{b^2} + 2a^2 + a^2b^2 + 8a\right)}\right], \tag{5}$$

and we defined $a=\exp(\beta\mu)$ and $b=\exp(\beta J)$.

In the next step we define the probability to find an aggregate of size n in the system. It is chosen as the sequence $(0 \pm 1 \pm 1 \pm 1 \cdots \pm 1 \pm 1\, 0)$, where we have n nonzero spin components between two zero components. Therefore, the probabilility is given by

$$\begin{aligned} P(S_k, S_{k+1}, \ldots, S_{k+n+1}, S_{k+n+2}/0, \pm 1, \ldots, \pm 1, 0) &= P(S) \\ &= \frac{1}{\Xi}\langle \delta_{S_k,0}(1-\delta_{S_{k+1},0})\cdots(1-\delta_{S_{k+n+1},0})\,\delta_{S_{k+n+2},0}\rangle \end{aligned} \tag{6}$$

where the brackets mean

$$\langle \varepsilon \rangle = \sum_{\{S_i\}} \prod_{i=1}^{L} \varepsilon e^{\beta J S_i S_{i+1} + (\beta\mu/2)(S_i)^2 + (\beta\mu/2)(S_{i+1})^2}, \tag{7}$$

and the $\delta_{S_k,0}$ are the delta's Kronecker. Defining $\delta_{S_k,0} = 1 - S_k^2$, and using the transfer matrix, we can write the equation

$$P(S) = \frac{1}{\Xi}\mathrm{Tr}[(U^{-1}RU)^{L-n-1}U^{-1}(\underline{1}-S^2)R\cdots R \times (\underline{1}-S^2)U], \tag{8}$$

where Tr means the trace of the matrix, U is the matrix that diagonalizes the transfer matrix R, $\underline{1}$ is the unity matrix and S is the matrix representation of the spin. This last equation can be used, after we take the thermodynamic limit $L\to\infty$, to find the distribution of the aggregate size as a function of temperature and the chemical potential. Also using the formalism of the transfer matrix we obtain, in the thermodynamic limit, the density of amphiphiles, that is given by

$$\rho = \frac{1}{4}\frac{(bc + ab^2 - b - 3a)(2b^2 + bc - b + a + ab^2)}{bc(ab^2 - a - b + b^2)}, \tag{9}$$

where

$$c = \sqrt{\left(1 - 2\frac{a}{b} - 2ab + \frac{a^2}{b^2} + 2a^2 + a^2b^2 + 8a\right)}.$$

III. MONTE CARLO SIMULATIONS

We have performed Monte Carlo simulations in order to understand the underlying mechanism that leads the system towards its equilibrium state. We used linear sizes up to $L = 10^4$ and we have taken into account periodic boundary

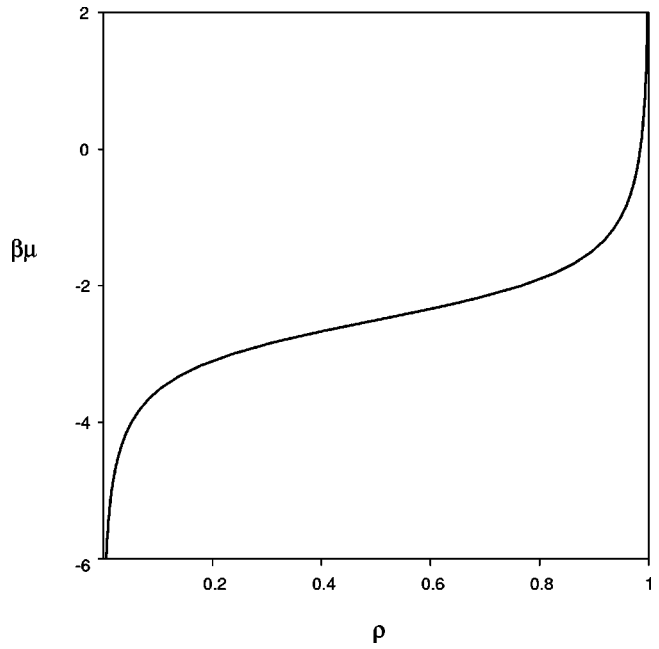

FIG. 1. Reduced chemical potential $\beta\mu$ versus total concentration ρ. This isotherm was obtained for $\beta J = 2.5$.

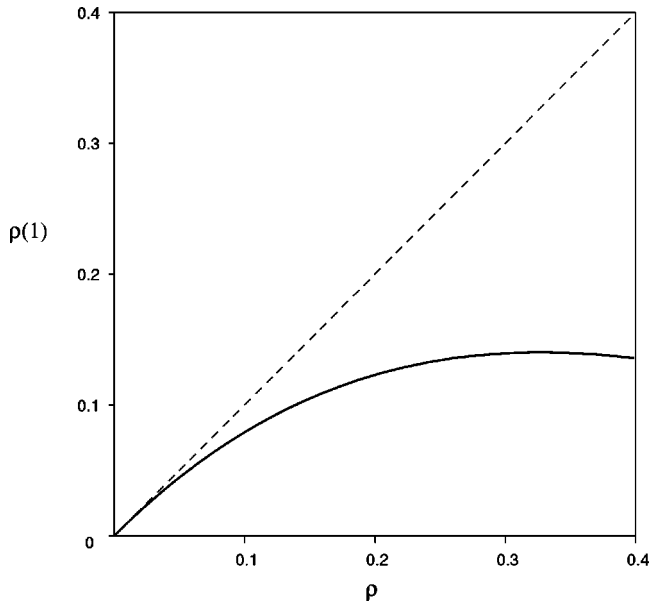

FIG. 2. Free amphiphile concentration as a function of total concentration for $\beta J = 0.5$. The dashed line indicates the ideal gas behavior.

conditions. We also used different initial random configurations to guarantee that the final equilibrium state is the same. First of all, we define the concentration by fixing the number of zero spin component in the system. The dynamics employed here is a mixture of two different stochastic processes [11]: one of them is the exchange Kawasaki process, where two nearest neighbor spins are exchanged accordingly with the Metropolis prescription [12]. For this dynamical process the order parameter is conserved, which in our case is equivalent to keep constant the concentration of the solution (the number of zero spin component is fixed). The other dynamical process used here is the single spin-flip Glauber kinetics where a given ± 1 spin is also flipped if it satisfies the Metropolis rule. This special Glauber mechanism changes the order parameter without changing the concentration. We follow the steps described below to find the equilibrium states of the system for given values of temperature, concentration and q, that gives the probability to perform the Kawasaki process in each step [the probability of choose the Glauber process is $(1-q)$]: we choose at random a site in the lattice, and a random number to select the process to apply. If the Kawasaki process is chosen, we select at random a nearest neighbor of the given site and we exchange them if they satisfies the requirements of Metropolis prescription. On the other hand, if the Glauber process is chosen, we only flip the given spin if it is nonzero and if it satisfies the Metropolis rule. To attain the equilibrium we need nearly 2×10^4 Monte Carlo steps (MCs), where each MCs represents L random trials to select a spin in the lattice. After thermalization we used 10^5 MCs to obtain the mean value of the aggregate size distribution.

IV. RESULTS AND CONCLUSIONS

We exhibit in Fig. 1 the plot of the isotherm of the reduced chemical potencial $(\beta\mu)$ as a function of the number density of amphiphiles (ρ). It is easy to see, that in the limit $\mu\to\infty$ the lattice is saturated by amphiphiles, and this corresponds, in our case, to the usual $S=1/2$ Ising model. In the regime of very small densities, we have almost isolated amphiphiles, and the behavior is that of the ideal gas, where $(\beta\mu)$ is a logarithmic function of the density. In Fig. 2, we show the density of isolated amphiphiles as a function of the total density for a fixed temperature. As to be expected, at very small densities, the slope of the curve is equal to 1. However, slightly increasing the total density, the slope of the curve in Fig. 2 decreases, and we can associate this fact with the appearance of small aggregates inside the solution. The plot of Fig. 2 resembles with the typical CMC curves observed in micellar systems. However, this is not sufficient to characterize these aggregates as being true micelles. It is well accepted in the literature of micellar systems [5] that, with the exception of CMC curves, to characterize a true micellar aggregate, it is necessary the presence of a local minimum and a local maximum in the distribution curve of aggregates. We already used this property to study the behavior of two- and three-dimensional diluted systems as a function of temperature [13,14]. We have shown in these works that the parameter that controls the micellization process is the difference in height between the maximum and the minimum of the distribution curve. This difference in height vanishes linearly with temperature in two dimensions, while it vanishes quadratically in three dimensions. In both cases we defined a temperature at which the difference in height becomes zero, and it represents a transition from the micellar to a nonmicellar state. We present in Fig. 3 the plot we obtain for the distribution curve of aggregate size n for the same temperature and concentration in the range of Fig. 2. As we can see, the distribution curve is monotonically decreasing with the aggregate size. Then, there is no typical aggregate, and the system does not exhibit a true micellar behavior. The behavior observed in Fig. 3 is qualitatively the same up to densities of 20%. For higher values of density, the curve exhibits a single local maximum, but never shows

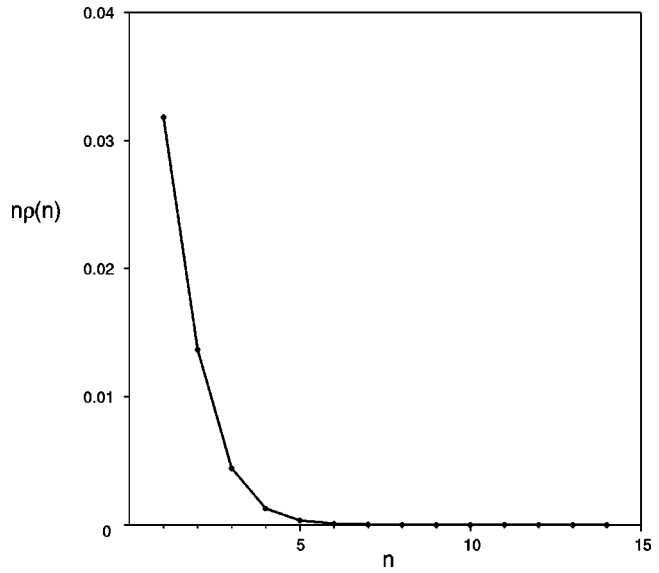

FIG. 3. Distribution function $n\rho(n)$ as a function of the size of the aggregates n for total concentration $\rho=5.5\%$ and $\beta J=2.5$. The lines serve to guide the eyes.

up the corresponding local minimum, as we can see in Fig. 4, for the particular value of density $\rho=50\%$. The general behavior observed in Figs. 3 and 4, can be obtained from Fig. 5, where we exhibit, for each aggregate size, the density of all molecules aggregated as a function of the total density. From this very simple one-dimensional model, we can conclude that it cannot support the existence of micelles. We also exhibit in Fig. 4 the distribution curve of aggregate sizes obtained through Monte Carlo simulations for $q=1/2$. For instance, in Fig. 6, choosing $q=0$, that is, only the Glauber dynamics is present, the distribution of aggregate sizes is exactly that random one that we generate at the beggining of the simulation. This is expected, because the Glauber process

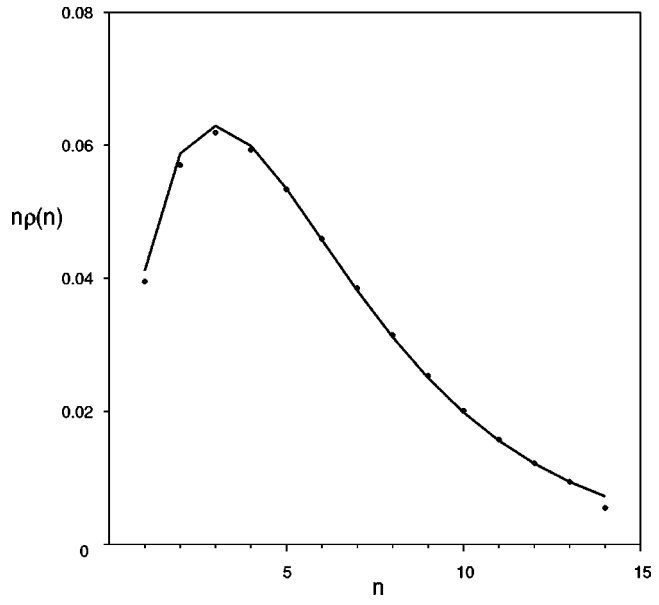

FIG. 4. Distribution function $n\rho(n)$ as a function of the size of the aggregates n for total concentration $\rho=50\%$ and $\beta J=2.5$. The line represents the exact solution and the small circles are the results of Monte Carlo simulation for $q=1/2$.

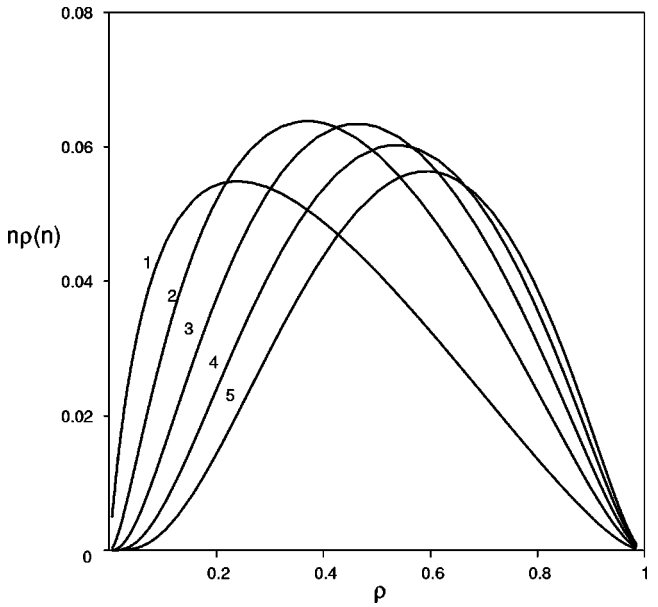

FIG. 5. Distribution function $n\rho(n)$ as a function of the total concentration ρ for different aggregate sizes, as indicated in the figure. We used $\beta J=2.5$.

cannot change the size of the aggregates at any time. The only effect here is to change the value of order parameter, which is reflected only in the energy of the aggregates. On the other hand, for $q=1$, that is, using only the exchange Kawasaki dynamics, the simulation results are still different from the exact values. This happens because with this dynamics, which conserves the order parameter, only a finite region of the phase space is explored. Finally, for any other value of q, the simulation curve and the exact one coincide for all aggregate sizes. This clearly indicates that both dy-

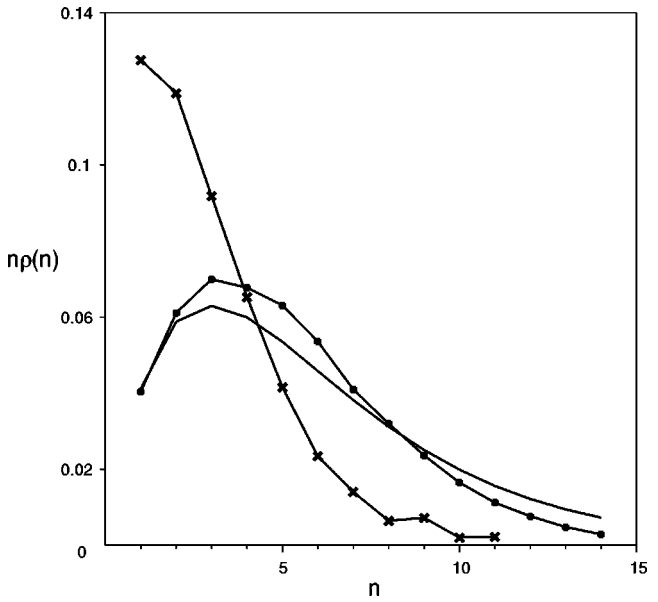

FIG. 6. Distribution function $n\rho(n)$ as a function of the size of the aggregates n for $\beta J=2.5$ and total concentration $\rho=50\%$. The full line is the exact result and the connected circles represent Monte Carlo simulation results for $q=1$ (pure Kawasaki dynamics). The connected crosses give Monte Carlo results for $q=0$ (pure Glauber dynamics).

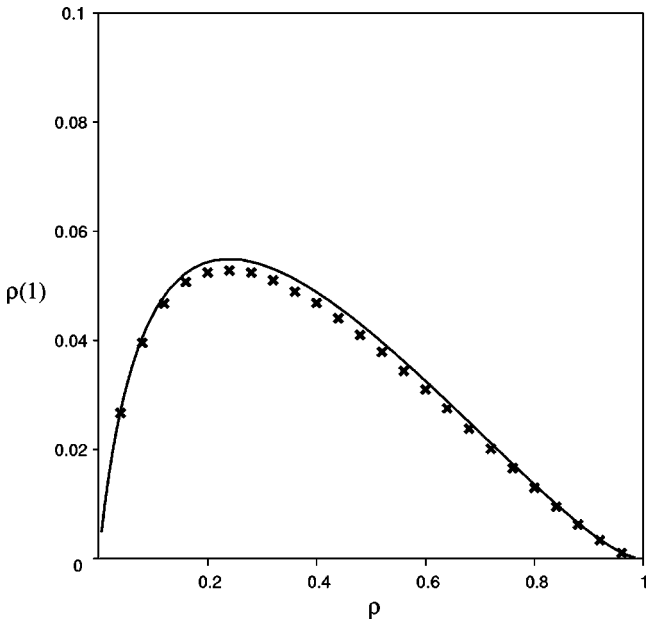

FIG. 7. Free amphiphile concentration as a function of total concentration for $\beta J = 2.5$. The full line is the exact result and crosses represent the Monte Carlo results for $q = 1/2$.

namical processes are essential to describe the evolution of the system towards the equilibrium states. Figure 7 displays the agreement between simulation and the exact results for the density of free amphiphiles as a function of total concentration. In conclusion, we have presented a simple one-dimensional model of aggregation of amphiphiles to understand the process of micellization. The model was mapped onto a spin $S = 1$ Ising model where the density of the solution was associated to the number of zero spin components. We were able to solve it exactly to obtain the densities of aggregate sizes as a function of total density, temperature, and the chemical potential. We also performed Monte Carlo simulations on this model and we demonstrated that the equilibrium states can only be attained through a combination of Glauber and Kawasaki dynamical processes. The model exhibits some characteristics similar to that of micellar systems, but the aggregate-size distribution curve does not show up the minimum and maximum that must be present in a micellized system. Although in Fig. 4 we observe a local maximum, we cannot say that this behavior caracterizes a true micellar system. The presence of the minimum in the distribution curve, below the free amphiphile concentration, is necessary. The disappearance of this minimum would lead to the coalescence of the two relaxation processes involved in the kinetics of micellization: the fast process, which accounts for the exchange of monomeric surfactants between micelles and solution, and the slow process, attributed to the micelle formation breakdown [15]. The model does not present any phase transition, and the transition from the micellar to nonmicellar state is absent.

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