Percolation in a lattice model of a microemulsion

C. M. McCallum

Department of Chemistry, University of the Pacific, 3601 Pacific Avenue, Stockton, California 95211

J. R. Gunn

Department of Chemistry, Université de Montréal, Case Postale 6128, succursale A, Montréal, Québec, Canada H3C 3J7

(Received 3 May 1995; revised manuscript received 19 August 1996)

In this paper we investigate the properties of a three-component, three-dimensional lattice model of self-assembly in the context of percolation. The percolating regions in the three-component phase-diagram are mapped out and the different kind of percolating regions are discussed. The growth and scaling of clusters leading to percolation are investigated and the scaling exponents β and γ are determined to be 0.373 and 1.79, respectively, which are identical to the noninteracting three-dimensional percolation exponents. Finally, percolation in the lattice model is discussed in terms of micelle and microemulsion structure, as defined by size and spectroscopic methods. [S1063-651X(96)12411-9]

PACS number(s): 82.70.Kj, 64.60.Ak, 83.70.Hq

Percolation is a branch of statistical physics that has applications in many diverse fields, including conductivity [1,2], diffusion [3], and even studies of forest fires [4]. Lattice models are particularly useful for studying percolation, as the critical concentration can be well-characterized by using the regularity of the lattice. There are well-defined scaling relations for clusters of sites near the percolation transition and these relations seem to be universal [5].

Percolation and cluster growth have recently been studied for lattice models having interactions, such as the Ising model [6,7] and Potts model [8,9]. As a general rule, while interactions get stronger, the number of components increase or the dimensionality increases in a given system, the percolation concentration, p_c for a given component decreases for all percolation systems [10].

We investigated percolation and cluster growth in a three-component lattice model of microemulsion with the Hamiltonian [11]

$$\mathcal{H} = \frac{1}{2} \sum_{\mathbf{n},\mathbf{n}'} \left[c_1 \sigma_\mathbf{n} \Delta\mathbf{n} \cdot \mathbf{s}_{\mathbf{n}'} + c_2 \sigma_\mathbf{n}^2 (\Delta\mathbf{n} \cdot \mathbf{s}_{\mathbf{n}'})^2 + c_3 \sigma_\mathbf{n} \sigma_{\mathbf{n}'} \right.$$
$$\left. + c_4 \sigma_\mathbf{n}^2 \sigma_{\mathbf{n}'}^2 \right] - \sum_\mathbf{n} (\alpha \sigma_\mathbf{n}^2 + \omega_\mathbf{n}). \tag{1}$$

Our motivation is to investigate the microscopic structure of clusters as they build up into micelles and microemulsion and also to determine if there is a connection between percolation in this model and the equilibrium properties. We describe the microemulsion system using an oil-water-amphiphile model. (This is a Potts-Heisenberg system, where the Ising variables are allowed to take on three values.) The Hamiltonian used for the following percolation investigations is a nearest-neighbor sum: the c_k are coupling constants, the σ_n are the discrete variables at site $\mathbf{n}$, $\Delta_\mathbf{n}$ is the lattice difference vector, and $\mathbf{s}_\mathbf{n} = (1 - \sigma^2)\mathbf{S}_\mathbf{n}$ is the unit vector orientation at the amphiphile sites; $\mathbf{S}_\mathbf{n}$ is a three-dimensional vector spin.

This general model has been the basis for many studies of amphiphilic systems. The vector variable is used to represent the directionality of an amphiphile. The number and type of terms are the minimum needed to see interesting phases, that is, lamellar, crystalline, and disordered. In general, more complex terms can be added in order to model more complex phases, but since percolation is most clearly illustrated in the microemulsion (disordered) phase, this simple set of terms suffices. It is not merely a decorated Ising lattice; it is a hybrid model constructed from Ising- and Heisenberg-like spin variables.

The parameters were chosen so that oil and water have inversion symmetry and so that a continuous pathway between the oil and water and microemulsion phases is created. We use the parameters $c_1 = 5$, $c_2 = 3/2$, $c_3 = -3/4$, and $c_4 = -1/3$, which were shown to have this property in Ref. [11]. There are no equilibrium phase transitions across this oil-water single-phase channel in the phase diagram. This particular choice of parameters includes a microemulsion phase over a large area of temperature or composition (Fig. 1).

Metropolis Monte Carlo simulations were used in this study. Both canonical and grand canonical simulations utilizing periodic boundary conditions were used, with the canonical simulations used to collect cluster statistics. The trial moves consisted of single changes in the discrete variable (grand-canonical runs) or pairwise exchanges (canonical cases). The continuous spins were updated separately [11]. For these series of simulations, system size was generally held at $24 \times 24 \times 24$ and the number of Monte Carlo lattice passes was typically 35 000, including at least 20 000 equilibration lattice passes. A lattice pass is defined as one attempted Ising spin flip for every site on the lattice, together with 10–20 continuous spin updates. Some simulations were run with $32 \times 32 \times 32$ or $40 \times 40 \times 40$ system sizes and longer run times in order to give a rough check of finite-size effects, though no dedicated finite-size scaling study [12,13] was done.

A series of simulations was run in order to determine the percolation thresholds of the system, as well as the microstructure of the clusters as they grew to percolating size. The percolation thresholds investigated included amphiphile per-
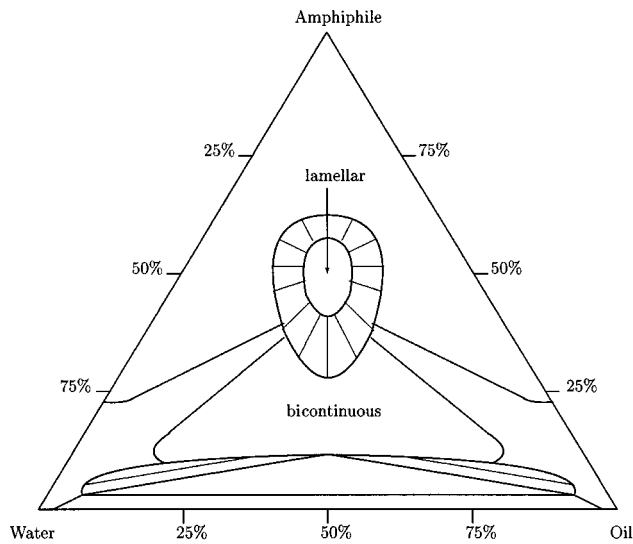
FIG. 1. Percolation phase diagram: three-component composition diagram for the lattice model of microemulsion. Upper solid lines correspond to amphiphile percolating in oil or water; lower solid lines correspond to the bicontinuous percolation region.

colating in an oil-water background and water-amphiphile clusters percolating in oil. That is, clusters were defined as consisting of either amphiphile in oil or amphiphile plus water in oil. This distinction is necessary, as the results may be somewhat different.

At the percolation threshold, for a particular species, the second moment of the distribution of noninfinite clusters, defined by

$$S = \sum_s w_s s, \qquad (2)$$

where

$$w_s = \frac{n_s s}{\sum_s n_s s} \qquad (3)$$

and n_s is the number of clusters of size s, diverges in an infinite system. Just above p_c and for any higher concentration p, the amount of clustering sites contained in the infinite cluster as a fraction of the total volume of the infinite cluster

$$P = \sum_s [n_s(p_c) - n_s(p)]s \qquad (4)$$

becomes nonzero. This is defined as the strength P of the infinite cluster. Exactly at p_c, P is zero in an infinite system. We also used the percolation fraction F, defined as that fraction of configurations stored by the simulation that contain clusters that connect to themselves across the periodic boundary in at least one dimension. A plot of F versus p shows a very rapid increase at the transition; in an infinite system it would appear as a step function. With these measures, the percolation threshold can be accurately determined. The percolation phase diagram is presented in Fig. 1. Included in the diagram are the two-phase and ordered-phase

areas determined in Ref. [11]. The percolation lines for different system sizes did not deviate more than a few percent. As the percolation lines move towards two-phase and structured regions, such as the lamellar or microemulsion region, determination of p_c becomes difficult, if not impossible due to the large-scale fluctuations near phase transitions. Thus, in the lower part of the microemulsion percolation region, phase separation competes with uniform percolation, and the two-dimensional lamellar structure serves to prevent three-dimensional percolation near the middle of the phase diagram.

The areas between the microemulsion and the amphiphile percolation phases can be identified as complex ordered regions. For example, consider the region of the phase diagram where oil is the solvent and water or amphiphile is the solute. Here the water and amphiphile were found to percolate when considered together as constituting a cluster, but not singly. That is, no separately continuous water or amphiphile channels were found. In experimentally observed mixtures, cylindrical micelles are often seen in this region, and while these structures are difficult to categorize in the lattice model, some evidence as to their existence was found. The ratios of the calculated moments of inertia of the cluster sizes were approximately 2.5:2.1:1. With information such as this, we conclude that on a trajectory from this region to the microemulsion region, the connected amphiphile-surrounded water tubes gradually lengthen and bend into channels, until the water percolates throughout the oil. That no drastic change in structure occurs is shown by the ratios of the principal moments of the large noninfinite clusters (sizes near l^2) as the threshold is crossed, although there seems to be some effect. Both amphiphile clusters and water clusters show monotonic growing or shrinking of the ratios of the principal moments. But, although the sizes of the clusters change, the relative shapes do not. The average principle moments of the clusters near size l^2 decrease sharply at p_c, while the ratio I_1/I_2 remains monotonic. A trajectory that increases the amphiphile concentration seems to cause the clusters to become connected together through the amphiphile layers on the outer portion of the clusters.

The microemulsion region was found to be bicontinuous only in the oil and water components. Other studies define microemulsion with either bi- or tricontinuity [14]. Nowhere in our phase diagram was a stable tricontinuous phase found; we use the bicontinuous definition. The area where a tricontinuous phase may have been expected is where the two sets of percolation lines meet, but this occurs in the lamellar or two-phase region and that structured phase seemingly exerts too strong an influence on the configurations to observe a tricontinuous phase. It should be noted experimental studies show percolation behavior in microemulsions beginning at about 7% by volume amphiphile [15]. This does not necessarily mean that the amphiphile is percolating in the microemulsion, only that the oil and/or water species are, since the diffusion and conductivity measurements are made on the oil and water phases.

We have investigated the scaling behavior of the clusters generated by the lattice model of microemulsion and how these results compare with other lattice models. The scaling assumption for clusters of size s at a concentration p is

$$n_s(p) = s^{-\tau}\mathcal{F}((p-p_c)s^{\sigma}), \qquad (5)$$

where the function $\mathcal{F}$ is specific to a particular model, but the exponents τ and σ are universal. The exponent σ can be assumed from three-dimensional models or determined by the relations between the other scaling exponents [16]: $\beta = (\tau-2)/\sigma$ and $\gamma = (3-\tau)/\sigma$. The exponents β and γ are defined through the relations $S \propto |p-p_c|^{-\gamma}$ and $P \propto (p-p_c)^{\beta}$. P is the strength of the infinite cluster, defined in Eq. (4), and S is the second moment of the finite cluster distribution, defined by Eqs. (2) and (3).

The scaling assumption needs to be validated in two regions: at p near and away from p_c. At $p=p_c$, we have $n_s \approx s^{-\tau}$ and thus the exponent τ may be determined from a regression. At p away from p_c, the ratio

$$\nu_s(p) = \frac{n_s(p)}{n_s(p_c)} = \mathcal{F}((p-p_c)s^{\sigma}) \qquad (6)$$

is plotted as $\mathcal{F}(z)$ versus $z = |p-p_c|s^{\sigma}$ and the different data will fall along the same curve. Identical curves were obtained whether or not the amphiphile concentration varied. The value $\sigma = 0.48$ for three-dimensional noninteracting percolation was used for these plots. We believe this is valid; the effects of an incorrect σ are clearly seen as spreading of the individual points about the predicted curve versus mere scatter of data away from the "correct" value.

A plot of the distribution of second moments gives two sets of points, corresponding to those clusters above and below the transition. The post-transition clusters are smaller than those below. This is the opposite of the behavior for noninteracting percolation clusters. Exactly why this is is unknown; it may be a "critical-micelle-concentration-like" effect due to interactions. The threshold can be determined to a high degree of accuracy by adjusting p_c until the two slopes γ are parallel. In the same way, β can be determined accurately. A scaling exponent plot is presented in Fig. 2. Notice that although the data appear to be scattered, the values of slopes drawn through each set of points are very close. The values we obtain, $\beta = 0.373$ and $\gamma = 1.79$, are in agreement with the values of 0.4 and 1.80 tabulated for three-dimensional noninteracting percolation.

The apparent composition of the clusters was considered carefully. Should a cluster be defined to consist of only amphiphile *or* water in oil? Or should a cluster be defined to consist of both water and amphiphile, as in a micelle? Noninteracting polychromatic percolation is simpler, as the multicomponent problem can be broken into two species: one or more percolating species, or solute, and all the other species as the solvent. Introducing interactions into a model of course changes this. If three species A, W, and O are considered, and A is the solvent (that is, considered to be the species in excess) with $p = W + O$, there are then two possibilities. For a given concentration p, one or both of W and O may percolate in a given region, and this percolation may or may not be dependent upon different concentrations W and O. In other words, percolation may or may not depend simply on p, but also on the composition of p. If this were the case, it would manifest itself in different exponents β and γ for different components of p. In our case, we find more statistical error for a trajectory where two species vary in
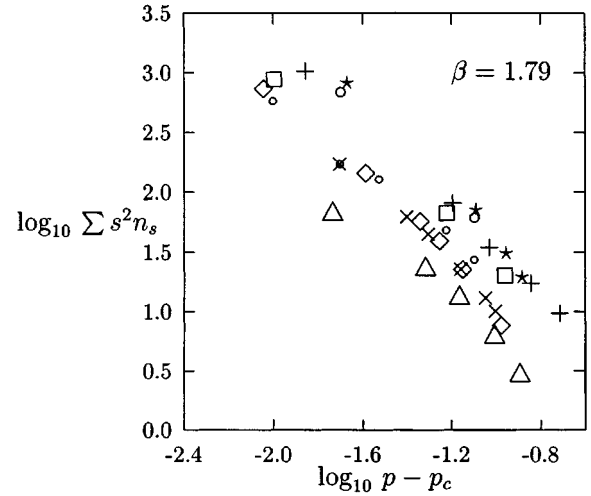

FIG. 2. log-log plot of the second moments of noninfinite clusters. The upper points correspond to clusters above p_c, while the lower points are below p_c. Note that this is the inverse of second-moment results for random percolation. Different symbols correspond to differing trajectories. Squares represent results where both amphiphile and water concentrations were varied in an oil solvent; the other symbols represent trajectories where only the amphiphile concentrations were varied.

concentration, but the data still fit the scaling assumption well; our values for β and γ were not significantly different for the differing trajectories. This bears some consideration, as it implies that the cluster growth is the same no matter what the composition of the clusters. The composition does seem to affect exactly *where* percolation happens, that is, at what concentration p percolation happens: The percolation lines do not vary greatly from a constant p_w/p_a value of about 0.7. This would seem to indicate a constant micelle size and microemulsion developing from the increasing number of micelles bumping into each other. The data in Fig. 2 show points from two composition cases, that is, holding the
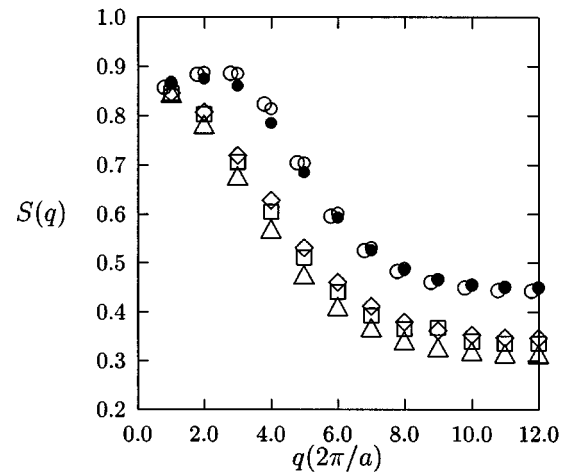

FIG. 3. Scattering function $S(k)$ from simulations. Triangles are below, squares are very near, and diamonds are above the percolation concentration p_c at a 10% amphiphile concentration. The circles correspond to three concentrations p for a 20% amphiphile concentration.

water species constant and also varying both ''solute'' species. Points from all trajectories were used to obtain the values for the exponents.

Is it possible to somehow define the microemulsion region of the phase diagram through the percolation thresholds? Some independent measure of what constitutes a microemulsion is needed, and though there is no definitive answer, there is some general agreement. Previous models [17,18] and experimental results [19] have used the Fourier transform $S(k)$ of the correlation function $g(r)$ as evidence of a microemulsion phase. Specifically, the existence of a peak at nonzero k, giving rise to two characteristic length scales, is generally accepted as microemulsion signature. We investigated the possible correlation between the emergence of a peak in the $S(k)$ and the onset of percolation. A discrete Fourier transform of the site-site correlation function $\langle \rho_i(0)\rho_i(\mathbf{n})\rangle$ for the water sites was calculated by averaging over the lattice directions. This assumption of spherical symmetry ignores any lattice effects, but has been shown to give satisfactory results [11]. The $S(k)$ were calculated at two concentrations of amphiphile across the percolation threshold in order to determine whether the nonzero peak is a pure concentration effect or a percolation effect. At amphiphile concentration of 10%, there was no peak for $k>0$. At amphiphile concentration of 20%, a peak emerges, but it only coincides generally with the percolation threshold and no certain conclusions can be drawn about any possible correlations. See Figure 3. These results were obtained from a $32\times32\times32$ lattice in order to not severely limit the domain sizes of the oil and water regions.

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