Correlated clustering in microemulsion models

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Abstract. The well known Potts Hamiltonian formalism for the general study of site–bond correlated percolation in lattice spin models is introduced for the first time in the context of microscopic theories of microemulsions. The approach is sufficiently general to be used in connection with any lattice model of microemulsions. Within a mean-field approximation, we obtain equations for the percolation thresholds, average cluster size and cluster size distribution for each of the molecular species of the mixture, which require only the knowledge of the structure functions of the model and an adopted bond activation probability. The theory is applied to a spin-1 model for microemulsions.

1. General formalism

Water-in-oil microemulsions can exhibit sharp variation in dielectric behaviour, viscosity and (most spectacularly) in electrical conductivity, upon appropriate variation of either the droplet volume fraction, temperature or salinity of the microemulsion system. Such phenomena has been extensively reported in the literature [1–5] and can be associated with a percolative transition of the water globules (swollen micelles) which are dispersed in an oil rich phase. At the percolation threshold the electrical transport regime is dominated by the motion of charge carriers on large, (electrically) connected clusters of water droplets.

In general the micellar Brownian motion of the water droplets, with an attendant continuous rearrangement of the clusters, appears to smear the percolation transition around the threshold [6], thus affecting the value of the critical exponent at the onset of the transition. Below the threshold the (low-frequency) conductivity has a power-law behaviour of the form [1–3] $\sigma(T < T_p) \sim (T_p - T)^{-s}$ with $s \approx 1.2$, which is larger than the static percolation exponent $s' \approx 0.7$. Above the threshold, when the system is percolating, dynamical effects are substantially reduced and the conductivity grows as a power-law $\sigma(T > T_p) \sim (T - T_p)^t$ with $t \approx 1.8$, which agrees with the static exponent for the metal–insulator problem [7]. The thresholds, on the other hand, experience little or no effect from the dynamical correlations between clusters and, therefore, are appropriately described by the static (frequency independent) percolation problem [6]. Both the percolation thresholds and the values of the critical exponents (dynamic percolation) have been successfully determined by phenomenological theories, either analytically or via computer simulations [3, 6]. The model system in these studies consists essentially of a one-component fluid of hard

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spheres, representing the water globules, interacting with each other via a square-well attractive potential [8] or via a more realistic Yukawa tail [3]. The inter-droplet interaction, which presumably arises from the surfactant monolayer coating each water droplet, accounts for the thermal phase separation as well as for the small values of the droplet volume fractions at the percolation transition. The values of the thresholds are also affected by other quantities, besides temperature, related to the adopted definition of connectivity, e.g. the radius of the conductivity shell [6, 8] or the strength and range of the bond activation probability [3, 9].

The aim of this work is to present an entirely different approach to the general study of correlated site–bond percolation in microemulsions, starting from microscopic lattice models of surfactant mixtures. In this treatment the thermodynamic and structural properties of the system are all derived from the microemulsion model, whereas connectedness or clustering properties such as percolation thresholds, cluster size distribution and many other quantities of interest, are all obtained via a generating function defined from a suitably chosen q-state Potts Hamiltonian coupled to the microemulsion model. The formalism is identical to the one employed in the celebrated approach to the gelation transition developed by Coniglio, Stanley and Klein [10] and subsequently studied by many authors [11–13]. In the present paper the particles are thermally correlated according to the microemulsion Hamiltonian instead of the Ising or Potts models [10, 13]. Besides its novelty in the context of microemulsions, this treatment is expected to answer questions that are difficult to address with phenomenological theories such as the effect of structure, composition, interparticle interactions (including the amphiphilic strength) and salinity, among others, on the clustering properties of microemulsions. Another important aspect of this approach is the fact that there is freedom of choice for the bond activation probability. The strength and range of the active bonds can be carefully chosen, for instance, to mimic the effect of the charge hopping process between clusters, or prescribed in such a way as to tune the percolation transition to be in synchrony with thermodynamic criticality [3, 10]. In a recent work Blossey and Schick [14] use a formalism due to Murata [15] to determine the correlated site percolation threshold lines of a two-component lattice model which displays a closed loop phase diagram. They find a rapid variation of the thresholds with temperature below the lower critical point similar to that observed in water-in-oil microemulsion systems [3]. Despite some similarities, their approach differs from ours in two important aspects. First, they study a correlated site percolation problem where the clusters consist of particles in contact, whereas in our approach there is freedom of choice for the bond activation probability. The second and most important difference is the fact that Blossey and Schick use a two-component lattice model which mimics the lower miscibility gap found in microemulsions, but cannot be considered a microscopic model for mixtures of water, oil and surfactant over a wide range of composition, temperature and interparticle interaction strengths. Consequently, as pointed out by Blossey and Schick, their approach cannot address, for instance, the effects of amphiphilic interactions on the percolation thresholds of microemulsions.

The three molecular species are distributed over the lattice according to the Boltzmann factors for the microemulsion Hamiltonian (sometimes referred to as the 'thermal' Hamiltonian) and, therefore are thermally correlated. Each cluster is formed by a maximal set of particles connected by 'active' bonds with a prescribed probability p. Thus, there may be a 'thermal' bond between two particles, say nearest-neighbours, which contributes to the energy of the system, but does not necessarily imply that

the particles belong to the same cluster, unless this bond is active. In addition to the site occupancy variables of the 'thermal' Hamiltonian, there is a Potts variable ν_i on every site of the lattice assuming values $\nu_i = 1, 2, \ldots, q$. One can show [13, 28] that the cluster statistics, and therefore the percolation problem, is determined by the following dilute Potts Hamiltonian

$$\mathcal{H} = \mathcal{H}_m\{n_i\} - \sum_{i,j}^{N} \sum_{\alpha,\beta} W_{\alpha\beta}^{ij} (\delta_{\nu_i\nu_j} - 1) n_i^\alpha n_j^\beta - \sum_i^N \sum_\alpha H_\alpha (\delta_{\nu_i 1} - 1) n_i^\alpha. \tag{1}$$

Here $\mathcal{H}_m\{n_i\}$ is the microemulsion Hamiltonian which depends on the site occupancy variables n_i^a, n_i^b and n_i^c representing water, oil and surfactant respectively. A number of such models have been proposed and studied in the literature over recent years [16–27]. The sums in α and β are over these three molecular species. The $\delta_{\nu_i\nu_j}$ is a Kronecker delta, which is 1 if sites i and j are in the same Potts state and zero otherwise. H_α are ghost fields for species α and are conjugate variables to the $\nu = 1$ Potts state. The quantities $W_{\alpha\beta}^{ij}$ are connectivity functions, the precise form of which depend on the details of the model. For instance, if only conventional clusters (i.e. clusters made of a single species α) are to be considered, we set

$$W_{\alpha\beta}^{ij} = W_\alpha^{ij} \delta_{\alpha\beta}. \tag{2}$$

Furthermore, if only nearest-neighbour sites are to be considered (directly) connected we have

$$W_\alpha^{ij} = \begin{cases} W_\alpha & \text{if } i \text{ and } j \text{ are NN} \\ 0 & \text{otherwise.} \end{cases} \tag{3}$$

In the following we shall consider only conventional clusters, so that equation (2) holds. (Clusters made of connected pairs of different species can be considered in the same fashion. See references [29] and the review article by J Halley in reference [11]). In addition we seek clustering of one particular species, denoted α. The partition function is given by the configurational sums of the occupancy and Potts variables

$$\mathcal{Z} = \sum_{\{n_i\}} \exp\left(-\beta \mathcal{H}_m\{n_i\}\right)$$

$$\times \sum_{\{\nu_i\}} \exp\left\{\beta \sum_{i,j} W_\alpha^{ij}(\delta_{\nu_i\nu_j} - 1) n_i^\alpha n_j^\alpha + \beta H_\alpha \sum_i (\delta_{\nu_i 1} - 1) n_i^\alpha\right\}. \tag{4}$$

Let us elaborate on the sum over the Potts configurations $\{\nu_i\}$. Given a particle configuration $\{n_i\}$ we distinguish two complementary sets: set $\Theta\{n_i\}$ of all sites occupied by particles of species α, and set $\overline{\Theta}\{n_i\}$, which is the set of sites in the configuration $\{n_i\}$ not occupied by α particles. For every site in $\overline{\Theta}\{n_i\}$ we pick up a term $\sum_{\nu_i=1}^q = q$ in equation (4), therefore the elements of $\overline{\Theta}\{n_i\}$ contribute a term $q^{\sum_i (1-n_i^\alpha)}$ for every configuration $\{n_i\}$. The partition function becomes

$$\mathcal{Z} = \sum_{\{n_i\}} \exp(-\beta \mathcal{H}_m) \mathcal{Z}_\mathcal{L}\{n_i\} \, q^{\sum_i (1-n_i^\alpha)} \tag{5}$$

where $\mathcal{Z}_{\mathcal{L}}\{n_i\}$ is the partition function of the q-state Potts model defined on the sublattice $\mathcal{L}$ consisting of those sites occupied by particles of species α in the configuration $\{n_i\}$. The set of vertices in this sublattice is $\Theta\{n_i\}$. The set of bonds (as defined by the couplings W_α^{ij}) in this sublattice is denoted $\mathcal{B}\{n_i\}$. After some manipulations it can be shown that

$$\mathcal{Z}_{\mathcal{L}}\{n_i\} = \sum_{\mathcal{C}\subseteq\mathcal{B}} p_{ij}^{|c|}\,(1-p_{ij})^{|d|}\prod_r \left[(q-1)\,e^{-\beta H_\alpha N_r}+1\right] \qquad (6)$$

where

$$p_{ij} = 1 - \exp(-\beta W_\alpha^{ij}). \qquad (7)$$

Here $\mathcal{C}$ is a subset of $\mathcal{B}\{n_i\}$ and $\mathcal{D}$ its complementary (i.e. $\mathcal{D}=\mathcal{B}\{n_i\}-\mathcal{C}$); $|c|$ denotes the number of bonds in $\mathcal{C}$, and $|d|$ is the number of bonds in $\mathcal{D}$; r labels the clusters in the subset $\mathcal{C}$ and N_r is the number of α particles in the rth cluster. The sum runs over all subsets $\mathcal{C}$. Notice that equation (5) reduces to the (purely) 'thermal' partition function in the limit $q=1$ since

$$\sum_{\mathcal{C}\subseteq\mathcal{B}\{n_i\}} p^{|c|}(1-p)^{|d|} = 1 \qquad (8)$$

for every molecular configuration $\{n_i\}$.

Equations (5), (6) and (7) yield the cluster statistics through the function $\mathcal{A}(\{W_\alpha\},H_\alpha)$ defined by

$$\mathcal{A}(\{W_\alpha\},H_\alpha) = \lim_{N\to\infty}\frac{\mathrm{d}\ln\mathcal{Z}}{\mathrm{d}q}\bigg|_{q=1} \qquad (9)$$

which gives

$$\mathcal{A}(\{W_\alpha\},H_\alpha) = 1 - \rho^\alpha + \sum_{t=1}\langle\!\langle n_t^{cl}\rangle\!\rangle e^{-\beta H_\alpha t} \qquad (10)$$

where ρ^α is the concentration of species α ($\rho^\alpha \equiv N^{-1}\sum_i\langle n_i^\alpha\rangle$) and

$$\langle\!\langle\cdots\rangle\!\rangle \equiv \frac{1}{\mathcal{Z}(q=1)}\sum_{\{n_i\}}e^{-\beta\mathcal{H}_\bullet}\sum_{\mathcal{C}\subseteq\mathcal{B}\{n_i\}} p_{ij}^{|c|}\,(1-p_{ij})^{|d|}\cdots \qquad (11)$$

defines the statistical average of any cluster related quantity. $\langle\!\langle n_t^{cl}\rangle\!\rangle$ is the average number of clusters of t particles per site. The sum in t extends to infinity for $H_\alpha>0$, however, only finite clusters contribute. Several quantities of interest are derived from equation (10); the average number of clusters per site is given by

$$\langle\!\langle n^{cl}\rangle\!\rangle = \mathcal{A}(\{W_\alpha\},0) - 1 + \rho^\alpha. \qquad (12)$$

Species α belongs to a cluster of t particles is given by

$$P_t = \frac{t}{\rho^\alpha}\langle\!\langle n_t^{cl}\rangle\!\rangle. \qquad (13)$$

The percolation probability is therefore

$$\mathcal{P} = 1 - \sum_{t=1}^{\prime} P_t \tag{14}$$

where the prime restricts the summation to finite clusters. It is convenient to define a generating function $\Gamma(\{W_\alpha\}, H_\alpha)$ through the first derivative of $\mathcal{A}$ with respect to βH_α

$$\Gamma(\{W_\alpha\}, H_\alpha) \equiv -\frac{1}{\rho^\alpha} \frac{\partial \mathcal{A}}{\partial \beta H_\alpha} = \sum_{t=1} P_t e^{-\beta H_\alpha t}. \tag{15}$$

The moments of the cluster distribution are then

$$\mu_m \equiv \sum_{t=1}^{\prime} t^m P_t = (-1)^m \frac{\partial^m \Gamma}{\partial (\beta H_\alpha)^m}\bigg|_{H_\alpha=0}. \tag{16}$$

The mean cluster size is given by

$$S = \mu_1 / \mu_0. \tag{17}$$

The pair connectedness, which gives the probability that two α particles located on sites i and j lie within the same cluster, can be defined by introducing an inhomogeneous field at each site

$$g_\alpha^c(i,j) = \frac{\partial^2 \mathcal{A}}{\partial \beta H_\alpha^i \, \partial \beta H_\alpha^j}\bigg|_{H_\alpha^i = H_\alpha^j = 0}. \tag{18}$$

2. Mean-field theory

In the following we describe a mean-field treatment for the Hamiltonian defined in equation (1) in order to obtain an approximate generating function for the percolation problem. The thermodynamic properties of the microemulsion model are assumed known in this approximation, such that only the Potts part of the Hamiltonian (1) is of concern. It is convenient to introduce the following 'spin' representation for the Potts variables [30]. At each site i the Potts variable ν_i assumes one of the q values $\nu_i = 1, 2, \ldots, q$. Let us define a complex variable σ_i which takes on the values $\sigma_i = 1, w, w^2, \ldots, w^{q-1}$, i.e. there is a unique correspondence between the variables ν_i and σ_i given by

$$\sigma_i = w^{\nu_i - 1} \tag{19}$$

where $w = \exp(2\pi i/q)$ is a qth-root of unity in the complex plane. The w therefore satisfies the equation $z^q - 1 = 0$, which can be written as

$$(z - 1)(1 + z + \cdots + z^{q-1}) = 0. \tag{20}$$

It is easy to show that

$$\delta_{\sigma\sigma'} = \delta_{\nu\nu'} = \frac{1}{q} \sum_{k=1}^{q} \sigma^k \sigma'^{q-k}. \tag{21}$$

In this representation the Hamiltonian (1) is written as

$$\mathcal{H} = \mathcal{H}_m - \frac{1}{q} \sum_{i,j} W_\alpha^{ij} \, n_i^\alpha \, n_j^\alpha \left[1 - q + \sum_{k=1}^{q-1} \sigma_i^k \sigma_j^{q-k} \right]$$

$$- \frac{1}{q} H_\alpha \sum_i n_i^\alpha \left[1 - q + \sum_{k=1}^{q-1} \sigma_i^k \right] \tag{22}$$

where we have used the fact that $\sigma^k = 1$ for $k = 0$ or $k = q$. The (local) fraction of particles of species α in the lth Potts state is defined by $\rho_i^\alpha f_i^l$, where

$$f_i^l = \langle \delta_{\nu_i l} \rangle = \langle \delta_{\sigma_i w^{l-1}} \rangle \qquad l = 1, 2, \ldots, q.$$

Using equations (19) and (21) we obtain

$$f_i^l = q^{-1} + q^{-1} \sum_{k=1}^{q-1} \langle \sigma_i^k \rangle w^{q-(l-1)k}. \tag{24}$$

The quantity $\langle \sigma_i \rangle$ is the local order parameter for the Potts states, which is written as

$$\langle \sigma_i \rangle = R_i \, e^{i\theta_i} \tag{25}$$

where θ_i indicates into which of the available states the order parameter at site i has fallen. The $R_i \in [0,1]$ indicates the corresponding amplitude. The σ_i lies on the unitary circle, and so does σ_i^k. Therefore

$$\langle \sigma_i^k \rangle = R_i \, e^{ik\theta_i}. \tag{26}$$

Since the field H_α couples to the $\nu = 1$ Potts state (i.e. zero phase), we may set $\theta_i = 0$. The local fraction of Potts states distributed over the sites occupied by species α is then

$$f_i^l = \begin{cases} q^{-1}[1 + (q-1)R_i] & \text{if } l = 1 \\ q^{-1}(1 - R_i) & \text{if } l = 2, 3, \ldots, q. \end{cases} \tag{27}$$

The energy functional in this approximation becomes

$$\overline{\mathcal{H}} = \overline{\mathcal{H}}_m - \sum_{i,j} W_\alpha^{ij} \rho_i^\alpha \rho_j^\alpha (1 - q^{-1})(R_i R_j - 1) - H_\alpha \sum_i \rho_i^\alpha (1 - q^{-1})(R_i - 1). \tag{28}$$

The mean-field entropy is given by

$$S = -\sum_i \left[\sum_{\beta \neq \alpha} \rho_i^\beta \ln \rho_i^\beta + \sum_{l=1}^q \rho_i^\alpha f_i^l \ln(\rho_i^\alpha f_i^l) \right] \tag{29}$$

where β here represents the particle species other than α. With f_i^l given by equation (27), we obtain for the mean-field free energy functional

$$\mathcal{F} = \mathcal{F}_m - (1 - q^{-1}) \sum_{i,j} W_\alpha^{ij} \rho_i^\alpha \rho_j^\alpha (R_i R_j - 1) - (1 - q^{-1}) H_\alpha \sum_i \rho_i^\alpha (R_i - 1)$$
$$+ q^{-1} T \sum_i \rho_i^\alpha \{ [1 + (q-1)R_i] \ln[1 + (q-1)R_i]$$
$$+ (q-1)(1 - R_i) \ln(1 - R_i) - q \ln q \} \tag{30}$$

where $\mathcal{F}_m$ is the mean-field free energy of the microemulsion model. In the limit $q \to 1$ equation (30) reduces to $\mathcal{F}_m$, whose minimization yields the thermodynamic and structural properties of the model. According to the discussion above, the clustering properties are obtained from the derivative of (30) with respect to q at the point $q = 1$.

In the following we consider a uniform (translational invariant) Potts order parameter R, keeping, however, the positional dependence on the particle densities. From equations (9) and (30) we obtain

$$N A(\{W_\alpha\}, H_\alpha) = (1 - R^2) \sum_{i,j} \beta W_\alpha^{ij} \rho_i^\alpha \rho_j^\alpha + (1 - R)\beta H_\alpha \sum_i \rho_i^\alpha$$
$$+ (1 - R)[\ln(1 - R) - 1] \sum_i \rho_i^\alpha. \tag{31}$$

Upon expansion of ρ_i^α in Fourier space around the value which minimizes the microemulsion free energy, equation (31) can be written as

$$A(\{W_\alpha\}, H_\alpha) = \beta(1 - R^2) \left[(\rho^\alpha)^2 \lambda_W(0) + \int_{BZ} \frac{d^d k}{(2\pi)^d} \lambda_W(k) S_{\alpha\alpha}(k) \right]$$
$$+ (1 - R)\rho^\alpha [\beta H_\alpha + \ln(1 - R) - 1] \tag{32}$$

where ρ^α is the concentration of α particles which minimizes the microemulsion free energy and

$$\lambda_W(k) = \sum_{i,j} W_\alpha^{ij} e^{ik \cdot (i-j)}. \tag{33}$$

$S_{\alpha\alpha}(k)$ is the structure function for species α defined by

$$S_{\alpha\alpha}(k) = \langle \rho^\alpha(k) \rho^\alpha(-k) \rangle. \tag{34}$$

Therefore, given a definition for connectivity between particles of a certain species α (through the couplings W_α^{ij}) and the structure function for any microemulsion

model, we find the clustering properties of interest. For instance, the percolation locus is found by minimization of equation (32), which gives

$$R = 1 - \exp\left\{-\beta H_\alpha - 2R\beta\rho^\alpha \lambda_W(0) - \frac{2R\beta}{\rho^\alpha} G_{\alpha\alpha}^W\right\} \qquad (35)$$

where

$$G_{\alpha\alpha}^W(T, \{\rho\}) = \int_{BZ} \frac{d^d k}{(2\pi)^d} \lambda_W(k) S_{\alpha\alpha}(k). \qquad (36)$$

(The temperature and composition dependence is explicitly shown for clarity). As the percolation criticality is approached $(R \to 0)$ at $H_\alpha = 0$, we may expand the right-hand side of equation (35), and the density threshold for species α is then given by the solution of

$$(\rho^\alpha)^2 - \frac{1}{2\beta\lambda_W(0)}\rho^\alpha - \frac{1}{\lambda_W(0)} G_{\alpha\alpha}^W(T, \{\rho\}) = 0. \qquad (37)$$

The generating function Γ is obtained from equations (15) and (31) as

$$\Gamma(\{W_\alpha\}, H_\alpha) = -\frac{1}{\rho^\alpha}\frac{\partial \mathcal{A}}{\beta H_\alpha} = 1 - R. \qquad (38)$$

Using equation (35), the function Γ satisfies

$$\Gamma = \exp(X\Gamma) \exp(-X - \beta H_\alpha) \qquad (39)$$

where

$$X = 2\beta\rho^\alpha \lambda_W(0) + 2\beta\frac{1}{\rho^\alpha} G_{\alpha\alpha}^W. \qquad (40)$$

Equation (39) can be solved in the following way. Differentiating both sides of (39) with respect to βH_α, we obtain the relation $\Gamma' = (X\Gamma' - 1)\Gamma$. Substituting for Γ in the form of equation (15) and matching the coefficients, we obtain the solution

$$\Gamma(\{W_\alpha\}, H_\alpha) = \sum_t \frac{(tX)^{t-1}}{t!} e^{-tX} e^{-\beta H_\alpha t}. \qquad (41)$$

Therefore, we find that the cluster size distribution is given by

$$P_t = \frac{(tX)^{t-1}}{t!} e^{-tX}. \qquad (42)$$

3. Percolation lines for water-in-oil microemulsions

In this section we apply our formalism to determine the water percolation thresholds of a water-in-oil microemulsion system. The microemulsion model we use here is the spin-1 Hamiltonian introduced by Schick and Shih [22] in which a three-body interaction term favors configurations where the surfactant particles sit between water and oil molecules. The phase diagram and the structural properties of this model have been investigated within a mean-field approximation [23]. In our calculations we used the set of parameters, $T/J = 5.0$, $K/J = 0.5$, $L/J = -3.0$, and $C/J = 0.3$, which was chosen such that the resulting phase diagram presents a continuous pathway between the water-rich and oil-rich corners of the composition triangle in the presence of a lamellar phase. The ternary phase diagram, at a constant temperature, is then similar to the one studied by Gunn and Dawson [31] who performed Monte Carlo simulations to investigate clustering properties of a lattice model for microemulsions.

We are interested in determining the percolation threshold for water molecules as a function of the surfactant concentration at a fixed temperature. For simplicity we consider connectivity only between nearest-neighbour water molecules with a connectedness probability p. Thus, using equations (7) and (33), equation (37) becomes

$$(\rho^{\mathrm{w}})^2 - x_{\mathrm{p}}\, \rho^{\mathrm{w}} - \int_{\mathrm{BZ}} \frac{\mathrm{d}^3 k}{(2\pi)^3}\, S_{\mathrm{ww}}(k)\, \cos k_x = 0 \qquad (43)$$

with $x_{\mathrm{p}} = -[12\,\ln(1-p)]^{-1}$. The structure functions $S_{\mathrm{ww}}(k)$ for this model, at the mean-field level, are given in [23]. The numerical results from equation (43) for $p = 1.0$ and $p = 0.8$ are shown in table 1 for surfactant concentrations between 0.12 and 0.22. The case where $p = 1.0$ corresponds to a connectivity with certainty [9], i.e. two nearest-neighbour water particles belong to the same cluster. In this case the percolation threshold depends solely on the structure of the system in this approximation. From table 1 one observes that the threshold line ($p = 1.0$) occurs at small concentrations of water ($\rho^{\mathrm{w}} \approx 0.1$) for this range of surfactant concentration. Along the threshold line with $p = 1.0$ the concentration of water increases slightly with ρ^{s}, reaching a maximum at about $\rho^{\mathrm{s}} = 0.17$, and then decreases as the surfactant concentration is increased still further. This is consistent with the fact that addition of surfactant tends to structure the system. Above a certain surfactant concentration, which depends on the ratio $\rho^{\mathrm{w}}/\rho^{\mathrm{o}}$, the disordered fluid structures itself with the surfactant sitting mostly on the water–oil interfaces, making it possible for the water particles to percolate at lower (water) concentrations as the amount of surfactant increases in the system. In fact, the water–water structure function S_{ww} develops its chatacteristic peak at non-zero values of k at $\rho^{\mathrm{s}} \approx 0.18$ for ρ^{w} in the vicinity of 0.13. For $p < 1$ one has a connectivity in probability [9], i.e. two neighbouring water particles do not necessarily belong to the same cluster. In this case it is necessary higher concentrations of water to reach a percolation threshold. This is well borne out by the results shown in table 1. For $p = 0.8$ one also notices that the threshold values of ρ^{w} decreases with increasing surfactant concentration as we have discussed.

4. Summary

In this work we have described how a well known technique to determine cluster statistics in lattice spin systems can be used to obtain clustering properties of

Table 1. Loci of percolation transitions for water species.

	ρ^s	0.12	0.14	0.16	0.18	0.20	0.22
$p = 1.0$	ρ^w	0.078	0.098	0.102	0.100	0.096	0.090
$p = 0.8$	ρ^w	0.178	0.170	0.162	0.154	0.146	0.139

Hamiltonian models for microemulsions. The formalism presented here is a microscopic one, which enables the study of the effects of the molecular interactions, composition and structure upon the percolative properties of any three-state, lattice model of microemulsions. Much in the same spirit of the work by Coniglio *et al* [10], connectivity between particles here does not necessarily imply that the particles occupy nearest-neighbour positions and vice-versa; there is freedom of choice for the activation of bonds, which may be chosen according to a particular clustering process one wishes to model. The theory has been applied to a simple model of surfactant mixtures whose phase diagram and structural properties have been published in the literature. The behaviour of the percolation threshold for water cluster as function of ρ^s is consistent with the fact that the surfactant structures the fluid. In a separate work [32] we have applied a similar, but less general approach to investigate the behaviour of the water percolation threshold in a model microemulsion as the surfactant is made more hydrophobic. A systematic study of several microemulsion models that includes further quantitative implementation of the formalism given here is currently underway.

Acknowledgments

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