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Alternative Approach to Percolation in Microemulsions

Munir S. Skaf¹ and George Stell

Chemistry Department

State University of New York At Stony Brook

Stony Brook, NY 11794, U.S.A

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Abstract

An approach to study correlated percolation in lattice models of microemulsions is presented. Mean-field-like equations for the percolation locus for each of the molecular species are obtained, whose only input are the structure functions of the microemulsion model. Using a spin-1 Hamiltonian introduced by Schick and collaborators as a model for microemulsions, we find that the water percolation threshold increases as the surfactant becomes more lipophilic. This is in qualitative agreement with the behavior found in real microemulsions as salt is added to the system.

¹Present address: Chemistry Department, Colorado State University, Fort Collins, CO 80523, U.S.A

Ternary mixtures of oil, water and amphiphile exhibit interesting structural properties due to the amphiphile's tendency of being localized at the water-oil internal interfaces. In particular, the underlying structure of the thermodynamically disordered phase is highly dependent on the system's temperature and composition as well as on the surfactant's ability to solubilize oil and water and its hydrophilic-lipophilic (HL) balance (see, for instance, references [1] and [2]). At small water-to-oil concentration ratios the microemulsion's structure appears to consist of surfactant-coated water droplets dispersed in a continuum oil-rich phase. This is the so called water-in-oil (W/O) microemulsion. Such microemulsions have been extensively reported in the literature to present sudden increases of several orders of magnitude in their electrical conductivity as well as sharp variations in their dielectric behavior and viscosity when either the temperature or the volume fraction of the dispersed phase reaches a certain threshold value [3,4,5,6,7]. These phenomena have been associated with a percolative transition of the (surfactant-coated) water globules and have been investigated by means of phenomenological theories, either analytically or via computer simulations (see the review article by S. Safran *et al.* in reference [8]). The microemulsion in these studies is modeled by a one-component fluid of hard-spheres, representing the water globules, interacting with one another via an additional attractive potential. Despite the relative success of such phenomenological theories in determining some static and dynamical percolation properties of W/O-microemulsions, an understanding of their clustering properties in terms of a model for the molecular interactions between the components of the mixture is still lacking. Therefore, questions

such as the effects of the molecular interactions (e.g. the amphiphilic strength), salinity, composition and structural changes, upon the microemulsion's clustering properties remain to be addressed. A first step toward a microscopic theory for percolation phenomena in microemulsions has been recently proposed by Blossey and Schick [9] who determine correlated site percolation threshold lines of a two-component lattice model displaying a closed loop phase diagram. However, like phenomenological models their two-component lattice model cannot address, for instance, the effects of the amphiphilic interactions on the percolative properties of microemulsions.

We report here a novel approach to study percolation in microemulsion systems. Unlike phenomenological theories, the present framework assumes no *a priori* structure for the microemulsion, but rather assumes that the correlations between particles and hence the thermodynamic and structural properties of the mixture stem from the microscopic interactions of a (lattice) Hamiltonian model for microemulsions. References [10,11,12,13] are examples of such models (see also [2]). The clustering or percolative properties are obtained via an extension to multi-component mixtures of the Kikuchi's original tagging trick to study correlated percolation in the ordinary lattice-gas[14].

Consider the disordered phase of a 3-component microemulsion model, where the three species of particles are mixed in a homogeneous, isotropic state. We are interested in determining the critical locus of percolation for each molecular species, where a cluster of species α (α =water, oil or surfactant) is defined in a geometrical way. Two particles of the same species are connected if they occupy nearest-neighbor sites on the lattice. Particles of different species

do not belong to the same cluster, so that we can investigate clustering of each species, one at a time. In order to find the concentration threshold for a given molecular species α we must also notice that the particles are distributed over the lattice according to a given Hamiltonian, from which the thermodynamics and the correlations between particles are to be derived. There will be many clusters of a given species α . To each of these clusters we randomly associate a $+$ or a $-$ tag. In the present context these tags are mathematical devices labeling each cluster; they do not affect the energy of the system and therefore have no influence upon its thermal properties. From our definition of connectivity, it follows that clusters with different tags are not in contact with each other, otherwise both would be forming a single, larger cluster, having a single tag. Kikuchi's tagging trick is based on the following theorems, which are satisfied in the model we consider here [14]:

Uniqueness: In a homogeneous, isotropic mixture of particles for which connectivity of a given molecular species is defined, there cannot exist more than one infinite cluster of that particular species.

Tag Symmetry: In the most probable distribution of clusters of a given species

$$N_n^+ = N_n^- \quad \text{for } n < \infty ,$$

where N_n^\pm is the number of \pm clusters of size n (size of a cluster is the number of connected particles in the cluster).

In view of these two theorems it is clear how to define a percolation order parameter. Let us divide the particles of species α into three categories. Those

belonging to finite + clusters, those belonging to finite - clusters, and those belonging to an infinite, + cluster, with fractions ρ_f^+ , ρ_f^- and ρ_∞^+ , respectively. The total number densities of \pm -tagged α particles are

$$\begin{aligned}\rho^+ &= \rho_f^+ + \rho_\infty^+ \\ \rho^- &= \rho_f^-.\end{aligned}\tag{1}$$

By the symmetry theorem $\rho_f^+ = \rho_f^-$, therefore

$$\xi \equiv \rho^+ - \rho^- = \rho_\infty^+\tag{2}$$

is the concentration of particles α belonging to an infinitely extending (isotropic) cluster. That is, ξ is the percolation order parameter for species α , it is non-zero when the species α percolates and zero otherwise.

There are two distributions to be determined in this problem. The distribution of the three species of (untagged) particles, which is assumed to be known according to the Hamiltonian of the mixture, and the distribution of tags over the particles of species α . The most probable distribution of + and - tags among this species is found by maximizing the entropy of the tagged system since neighboring α -particles are connected with probability one. Furthermore, configurations of nearest-neighbor pairs $\alpha^+ - \alpha^-$ are not allowed since all α 's in a cluster have the same tag. Percolation occurs when the concentrations of α^+ and α^- are not equal. The entropy of the system, with the α species tagged, is approximated in our work here in the pair approximation of the Kikuchi's cluster variational method[15]. We have a ternary mixture of species W , O and S (W =water, O =oil, S =surfactant). Let us investigate

clustering of the surfactant, so the S -molecules are tagged with either a + or a - tag. The concentrations are denoted ρ , with $\rho^S = \rho^+ + \rho^-$, and are subject to the constraint $\rho^W + \rho^O + \rho^S = 1$. Let Y_{ij} be the fractions of nearest-neighbor pairs of particles i and j with multiplicity ω_{ij} (e.g., Y_{WS+} is the fraction of nearest-neighbor pairs of water and (+)-tagged surfactant particles, while Y^{++} refers to pairs of nearest-neighbor surfactant particles tagged with a +. These configurations have multiplicities 2 and 1 respectively). The pair configurations are also subject to the constraint $\sum_{ij} \omega_{ij} Y_{ij} = 1$. The entropy per particle in the pair approximation is given by

$$\mathcal{S} = (2d - 1) \sum_i \mathcal{L}(\rho^i) - d \sum_{ij} \omega_{ij} \mathcal{L}(Y_{ij}) , \quad (3)$$

where $\mathcal{L}(x) \equiv x \ln x$. We find

$$\begin{aligned} \mathcal{S} = & (2d - 1) \left[\rho^W \ln \rho^W + \rho^O \ln \rho^O + \rho^+ \ln \rho^+ + \rho^- \ln \rho^- \right] \\ & - d \left[Y_{WW} \ln Y_{WW} + Y_{OO} \ln Y_{OO} + 2Y_{WO} \ln Y_{WO} \right. \\ & + 2Y_{WS+} \ln Y_{WS+} + 2Y_{OS+} \ln Y_{OS+} \\ & + 2Y_{WS-} \ln Y_{WS-} + 2Y_{OS-} \ln Y_{OS-} \\ & \left. + Y^{++} \ln Y^{++} + Y^{--} \ln Y^{--} \right] . \end{aligned} \quad (4)$$

The fractions ρ and Y are geometrically related to each other. The fractions of water and oil molecules are respectively given by

$$\begin{aligned} \rho^W &= Y_{WW} + Y_{WO} + Y_{WS+} + Y_{WS-} , \\ \rho^O &= Y_{OO} + Y_{WO} + Y_{OS+} + Y_{OS-} . \end{aligned} \quad (5)$$

Similarly, the total fraction of tagged surfactant molecules are

$$\rho^+ = Y_{WS+} + Y_{OS+} + Y^{++} ,$$

$$\rho^- = Y_{WS-} + Y_{OS-} + Y^{--} . \quad (6)$$

Adding equations (6) we obtain the total surfactant concentration

$$\rho^S = Y_{WS} + Y_{OS} + Y^{++} + Y^{--} , \quad (7)$$

where

$$\begin{aligned} Y_{WS} &= Y_{WS+} + Y_{WS-} , \\ Y_{OS} &= Y_{OS+} + Y_{OS-} . \end{aligned} \quad (8)$$

The quantities $Y_{WW}, Y_{OO}, Y_{SS}, Y_{WO}, Y_{WS}$ and Y_{OS} are all obtained from the ensemble distribution dictated by the Hamiltonian model. The percolation order parameter is obtained by subtracting equations (6)

$$\xi \equiv \rho^+ - \rho^- = \xi_W + \xi_O + Y^{++} - Y^{--} , \quad (9)$$

where

$$\xi_W \equiv Y_{WS+} - Y_{WS-} \text{ and } \xi_O \equiv Y_{OS+} - Y_{OS-} . \quad (10)$$

The natural independent variables for the percolation transition are ξ, ξ_W and ξ_O . Solving equations (6)-(10) for the tagged unknowns, we obtain

$$\begin{aligned} \rho^\pm &= (\rho^S \pm \xi)/2 , \\ Y_{WS^\pm} &= (Y_{WS} \pm \xi_W)/2 , \\ Y_{OS^\pm} &= (Y_{OS} \pm \xi_O)/2 , \\ Y^{++} &= [(\rho^S - Y_{WS} - Y_{OS}) + (\xi - \xi_W - \xi_O)]/2 , \\ Y^{--} &= [(\rho^S - Y_{WS} - Y_{OS}) - (\xi - \xi_W - \xi_O)]/2 . \end{aligned} \quad (11)$$

These equations are substituted into (4) and the resulting entropy is then maximized with respect to the variables ξ , ξ_W and ξ_O . The extremum condition on the entropy with respect to ξ gives

$$(2d - 1) \ln \frac{\rho^S + \xi}{\rho^S - \xi} - d \ln \frac{Y^{++}}{Y^{--}} = 0 . \quad (12)$$

Let us define an auxiliary variable t by

$$t \equiv \frac{1}{4d} \ln \frac{\rho^S + \xi}{\rho^S - \xi} , \quad (13)$$

such that $t = 0$ at the percolation criticality (i.e. when $\xi = 0$). We have then

$$\xi = \rho^S \tanh(2dt) . \quad (14)$$

Similarly, the extrema with respect to ξ_W and ξ_O give

$$\begin{aligned} \xi_W &= Y_{WS} \tanh[(2d - 1)t] , \\ \xi_O &= Y_{OS} \tanh[(2d - 1)t] . \end{aligned} \quad (15)$$

From equations (11), (12) and (13) we obtain

$$Y^{++} - Y^{--} = (\rho^S - Y_{WS} - Y_{OS}) \tanh[2(2d - 1)t] . \quad (16)$$

Using equations (14), (15) and (16) we can rewrite equation (9) as

$$\begin{aligned} \rho^S \tanh(2dt) &= (Y_{WS} + Y_{OS}) \tanh[(2d - 1)t] \\ &+ (\rho^S - Y_{WS} - Y_{OS}) \tanh[2(2d - 1)t] . \end{aligned} \quad (17)$$

As criticality is approached (i.e. as $t \rightarrow 0$), we may expand both sides of this equation. The line of percolation threshold for the surfactant species is then given by the solution of

$$\rho^S = \frac{2d - 1}{2d - 2} (Y_{WS} + Y_{OS}) . \quad (18)$$

Similarly, one obtains the threshold lines for water and oil

$$\begin{aligned}\rho^W &= \frac{2d-1}{2d-2}(Y_{WO} + Y_{WS}) , \\ \rho^O &= \frac{2d-1}{2d-2}(Y_{WO} + Y_{OS}) .\end{aligned}\quad (19)$$

It should be noticed that the same expressions for the thresholds would have been obtained had we assigned tags to all the three species (e.g. species S tagged $+$ or $-$, species W tagged o or $*$, species O tagged \dagger or \ddagger), where, according to our discussion above, one must avoid the pair configurations $W^o - W^*$, $O^\dagger - O^\ddagger$ and $S^+ - S^-$.

In a lattice of coordination number z , Y_{ij} is given by

$$Y_{ij} = \lim_{N \rightarrow \infty} \frac{1}{zN} \sum_{\mathbf{r}} \sum_{\delta}^z \langle \rho^i(\mathbf{r}) \rho^j(\mathbf{r} + \delta) \rangle , \quad (20)$$

where the sum in δ goes over all nearest neighbors of site \mathbf{r} and $\langle \dots \rangle$ means thermodynamic average. Fourier expanding the local densities $\rho^j(\mathbf{r})$ around their respective equilibrium values in the disordered phase,

$$\rho^j(\mathbf{r}) = \rho_o^j + \sum_{\mathbf{k} \neq 0} \rho^j(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{r}} , \quad (21)$$

and using the relation $\lim_{N \rightarrow \infty} \frac{1}{N} \sum_{\mathbf{k}} \dots = \int_{BZ} \frac{d^d k}{(2\pi)^d} \dots$, we obtain

$$Y_{ij} = \rho_o^i \rho_o^j + \frac{1}{d} \int_{BZ} \frac{d^d k}{(2\pi)^d} \lambda(\mathbf{k}) S_{ij}(\mathbf{k}) . \quad (22)$$

(BZ stands for Brillouin Zone.) Here S_{ij} is the structure function given by

$$S_{ij}(\mathbf{k}) = \langle \rho^i(\mathbf{k}) \rho^j(-\mathbf{k}) \rangle , \quad (23)$$

and $\lambda(\mathbf{k}) = \sum_{i=1}^d \cos(k_i)$, with k_i the i^{th} cartesian component on the vector \mathbf{k} .

Using equation (22) and the relations

$$\begin{aligned} S_{WO} + S_{WS} &= -S_{WW} \quad , \\ S_{WO} + S_{OS} &= -S_{OO} \quad , \\ S_{WS} + S_{OS} &= -S_{SS} \end{aligned} \quad (24)$$

in equations (18) and (19), we obtain the following equation for the percolation density threshold of a given species α

$$(\rho^\alpha)^2 - \frac{1}{2d-1} \rho^\alpha + G_{\alpha\alpha}(T, \{\rho\}) = 0 \quad , \quad \alpha = W, O, S, \quad (25)$$

where

$$G_{\alpha\alpha}(T, \{\rho\}) = \frac{1}{d} \int_{-\pi}^{\pi} \frac{d^d k}{(2\pi)^d} \lambda(\mathbf{k}) S_{\alpha\alpha}(\mathbf{k}) \quad . \quad (26)$$

In the limit of high temperatures, where the particle correlations are vanishingly small, we obtain a mean-field *random site* percolation threshold

$$\rho^\alpha \stackrel{T \rightarrow \infty}{=} \frac{1}{2d-1} \quad . \quad (27)$$

At finite temperatures, equation (25) must be solved numerically. Furthermore, this equation yields meaningful approximated values for the thresholds for any temperature as long as the system is in a disordered, isotropic thermodynamic state.

In Fig.1 we show the percolation threshold for water clusters as function of the coupling C defined in the spin-1 model due to Schick and collaborators. The structure function S_{WW} for this model is calculated in reference[16]. The

system is in the disordered phase with parameters $K/J = 0.5$ and $L/J = -4.0$ held at temperature $T/J = 5.0$. The concentration ratio $w = \rho^W/\rho^S$ is fixed at $w = 4.0$ and the coordinate axis, ϕ , measures the concentrations of water plus surfactant ($\phi = \rho^W + \rho^S$) at (percolation) criticality for water clusters. The coupling C is a measure of the difference between the interactions of the surfactant with oil and water in Schick's model. When $C < 0$ the amphiphile dissolves better in water than in oil, while for $C > 0$ the reverse is true. Thus, by increasing the value of C one can mimic the effect of adding salt to a system where the surfactant is ionic. Our results show that water clusters percolate at higher thresholds as the surfactant becomes more lipophilic (hydrophobic). This is in qualitative agreement with experimental results on water + AOT + undecane, where ϕ was found to increase with salinity[6].

In conclusion, we have introduced a novel approach to study site-correlated percolation phenomena in lattice models of microemulsions, which is able to address questions related to the effects of molecular interactions upon the clustering properties of these systems. The formalism is quite general in the sense that it is applicable to any ternary mixture of particles, in particular to any 3-state model for microemulsions. (Binary mixtures of water and surfactant can be readily treated also.) Equation (25) requires only the knowledge of the structure functions, which can be easily calculated for a variety of microemulsion models within a local mean field approximation. A generalized theory to treat site-bond correlated percolation in microscopic models of microemulsions[17] will be published elsewhere[18].

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Figure Caption

Figure 1. Percolation threshold line for water particles as function of the coupling C in the disordered phase of the model proposed by Schick and collaborators. The system is at $T/J = 5.0$ with $w = \rho^W/\rho^S = 4.0$ and coupling energies $K/J = 0.5$ and $L/J = -4.0$.

