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Electrical percolation in the presence of attractive interactions: An effective medium lattice approach applied to microemulsion systems

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Abstract

Within the framework of an effective medium approach and a mean-field approximation, we present a simple lattice model to treat electrical percolation in the presence of attractive interactions. We show that the percolation line depends on the magnitude of interactions. In 2 dimensions, the percolation line meets the binodal line at the critical point. A good qualitative agreement is observed with experimental results on a ternary AOT-based water-in-oil microemulsion system.

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The concept of percolation has been widely used in recent years to explain the transport properties of disordered systems. This concept plays a central role in

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numerous physical phenomena such as fluid invasion in porous media, vitreous transitions, amorphous semiconductors composite materials (insulator to conductor), dilute magnetic materials and communication [1–3]. For instance, when allowed to cross link, polymers can undergo gelation: a transition from liquid to solid during which these polymeric systems suffer dramatic modifications especially on their macroscopic viscoelastic behavior. De Gennes and Stauffer conjectured that the process of gelation could be described as a percolation transition [4,5]. For systems composed of particles dispersed entirely at random in a continuous medium, the percolation transition corresponds to the appearance of a cluster of infinite size. The probability that such a cluster would appear for a system of finite size, strongly increases when the volume fraction Φ of particles approaches the percolation threshold Φ_c . In a system of interacting objects, it is not only the volume fraction, which governs the existence of percolation, but also the interactions between objects, which involve correlation of positions. For instance, some microemulsion systems exhibit both an electrical percolation phenomenon whose concentration threshold depends strongly on temperature and a phase separation with a lower consolute critical point (Fig. 1) [6]. It is now widely admitted that the electrical percolation occurring in these systems is mediated by attractive interactions between microemulsion droplets also at the origin of phase separation [6–8]. One important theoretical question is therefore to predict analytically the relationship between the percolation threshold and interactions.

Understanding the percolation of interacting particles in a continuous medium presents at first two major difficulties. The first one is connected to the definition of

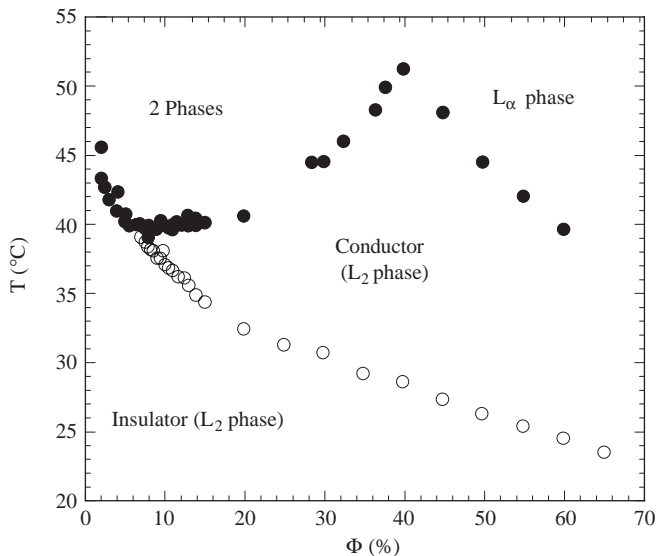


Fig. 1. Phase diagram of the microemulsion made of AOT, water and decane from [6] at a molar ratio $X = [\text{water}]/[\text{AOT}]$ equal to 40.8. The hydrodynamic diameter of droplet is 170 \AA . The open circles correspond to the electrical conductivity percolation line.

an interaction potential, which must be able to simulate a system close to reality and, as far as possible, treat the problem analytically. The second one is related to the definition of connectivity. Using an earlier work by Hill [9], Coniglio et al. [10] have proposed a method to study percolation in continuous media. These authors defined the pair connectivity function $P(r)$, which is related to the probability of finding two particles at distance r apart and belonging to the same cluster. $P(r)$ has a role comparable to that of the radial distribution function $g(r)$ in the classical theory of liquids [11]. In this approach, it follows that an equation of the Ornstein–Zernike type can be written and solved with conditions and approximations appropriate to the thermal problem (phase separation) and percolation. Several other models of percolation in continuous media have been proposed. Some analytical solutions have been derived using Percus–Yevick approximation for simple systems such as permeable sphere fluids [12] or adhesive sphere fluids [13–15]. There are also a few studies by Monte Carlo methods. In these simulations [16,17], two particles are considered to be connected if the distance between their center is less than a given value ℓ . Connectivity between particles on lattice can be easily defined in a natural way by assuming that two particles are connected if they sit on two adjoining sites. This method based on lattice cannot take into account the fine details of the interaction between particles. However, it is known that in complex systems, fine details of interactions are not so important since in most cases the interactions are averaged. Lattice approaches are particularly suited to compute transport properties in solutions of complex fluids. Indeed, surfactants in solutions form a large variety of mesophases such as bicontinuous microemulsions, sponge and lamellar phases, micelles, vesicles, etc. The description of thermodynamic properties of solutions of surfactant is a real challenge since the microstructures of these mesophases change with concentration and temperature. For instance, in some micellar systems the size and shape of micelles change with concentration [18]. The micelles, which are spherical at low surfactant concentration, become elongated and flexible as the concentration increases. In the last decade, Hamiltonians based on a lattice representation have been successfully introduced to describe the thermodynamics of complex fluids [19–24].

In this letter, we present a simple and tractable lattice model based on an effective medium approach and a mean-field approximation to describe the phase diagram and to treat electrical percolation in the presence of interactions. We show that the lattice approach introduced herein is particularly suited to predict the conductivity of microemulsion solutions where thermodynamical fluctuations play an important role.

Let us consider a hypercubic Flory–Huggins lattice in d dimensions with M sites. To each site k is associated an occupation number s_k whose possible value $+1$ or 0 tells us whether or not this site is occupied by a microemulsion droplet. In order to take into account the interaction energy Δ between two adjacent droplets, we define the Hamiltonian H of the system in the usual way:

$$-H = \Delta \sum_{\langle ij \rangle} s_i s_j + \mu \sum_{i=1}^M s_i, \quad (1)$$

where μ is the chemical potential of a microemulsion droplet, β the Boltzmann's factor and where the summation on $\langle ij \rangle$ is taken on nearest neighbor sites independently of the lattice dimensionality d .

In order to calculate the electrical conductivity σ at zero frequency of the microemulsion, we use an effective medium approach. The solution is divided into hypercubic cells. The cells are centered on the lattice sites and correspond to Voronoi's construction. If the site has an occupation number $s = 1$, it corresponds to a conducting microemulsion "hypercubic" droplet with a conductivity σ_1 . On the other hand, if the occupation number $s = 0$, it corresponds to an insulating continuous phase of conductivity σ_0 . This is shown in 2 dimensions in Fig. 2. In this approach the conductivity of the microemulsion droplet is modelled by an average conductivity $\bar{\sigma}_1$ taking into account the conductivity of both the water and the counterions coming from the ionic surfactant of the surfactant monomolecular layer. To model the thermodynamic fluctuations due to entropy and interactions between droplets, we consider an elementary volume v consisting of 2^d sites. In a mean-field approximation, we compute the probability $P_i(C_i)$ of all the possible thermodynamics configurations C_i of this elementary volume. Each microstate C_i has been weighted by its Boltzmann's factor $\exp(-H/k_B T)$, k_B being the Boltzmann's constant and T the temperature. Fig. 2 gives the probability $P_i(C_i)$ of each configuration C_i in two dimensions. The chemical potential μ is determined by the conservation of the number of microemulsion droplets, namely,

$$\frac{1}{2^d} \sum_{\{C_i\}} N_i(C_i) P_i(C_i) = \Phi, \quad (2)$$

where $N_i(C_i)$ is the number of sites being occupied for the configuration C_i of the volume v .

First let us recall that the electrical resistance of a homogeneous hypercube of size L is related to its conductivity $\bar{\sigma}$ by

$$R = \frac{L^{2-d}}{\bar{\sigma}}. \quad (3)$$

We then calculate the equivalent conductivity tensor of each configuration C_i . To do so, we use the assembly of equivalent resistors in series and in parallel as shown in Fig. 2 for 2 dimensions. The conductivity along x (respectively y) has been deduced by assuming the electric field to be directed along the x axis (respectively y axis). In this calculation we assume that no transverse current exists. The macroscopic conductivity tensor of the configuration is then computed by assuming an infinite periodic assembly of the same elementary cell. Because of the absence of broken symmetry in the direction transverse to the field, there is no current along this direction. The same argument holds if we try to calculate the local conductivity of the same configuration embedded in the continuous medium. Indeed, there must be a potential difference in the transverse direction to observe a transverse current between 2 sites of the considered 2^d sites configuration. In order to deduce this potential difference, one must know the configuration of the whole lattice. In a


















Configuration	Conductivity along x	Conductivity along y
(a) 	 $\sigma_x = \sigma_0$	 $\sigma_y = \sigma_0$
(b) 	 $\sigma_x = \frac{1}{2} \left(\sigma_0 + \frac{2\sigma_1\sigma_0}{\sigma_1 + \sigma_0} \right)$	 $\sigma_y = \frac{1}{2} \left(\sigma_0 + \frac{2\sigma_1\sigma_0}{\sigma_1 + \sigma_0} \right)$
(c) 	 $\sigma_x = \frac{1}{2} (\sigma_1 + \sigma_0)$	 $\sigma_y = 2 \frac{\sigma_1\sigma_0}{\sigma_1 + \sigma_0}$
(d) 	 $\sigma_x = 2 \frac{\sigma_1\sigma_0}{\sigma_1 + \sigma_0}$	 $\sigma_y = 2 \frac{\sigma_1\sigma_0}{\sigma_1 + \sigma_0}$
(e) 	 $\sigma_x = \frac{1}{2} \left(\sigma_1 + \frac{2\sigma_1\sigma_0}{\sigma_1 + \sigma_0} \right)$	 $\sigma_y = \frac{1}{2} \left(\sigma_1 + \frac{2\sigma_1\sigma_0}{\sigma_1 + \sigma_0} \right)$
(f) 	 $\sigma_x = \sigma_1$	 $\sigma_y = \sigma_1$

Fig. 2. Representation of the different possible thermodynamic configurations in 2 dimensions between one site and its nearest neighbors for a square lattice. Each thermodynamic configuration corresponds to a specific equivalent electric network made of an assembly of resistors in series and in parallel. The probabilities corresponding to each configuration are (a) $(1 - \Phi)^4 / \mathcal{F}$, (b) $4\Phi(1 - \Phi)^3 \exp(\beta\mu) / \mathcal{F}$, (c) $4\Phi^2(1 - \Phi)^2 \exp[\beta(2\mu + \Delta)] / \mathcal{F}$, (d) $2\Phi^2(1 - \Phi)^2 \exp(2\beta\mu) / \mathcal{F}$, (e) $4\Phi^3(1 - \Phi) \exp[\beta(3\mu + 2\Delta)] / \mathcal{F}$, (f) $\Phi^4 \exp[\beta(4\mu + 4\Delta)] / \mathcal{F}$. \mathcal{F} is the mean-field free energy per site.

mean-field approach, it is reasonable to neglect fluctuations in the transverse direction and therefore assume that the equipotential surfaces are orthogonal to the macroscopic electric field direction.

The conductivity of the solution is then estimated within the effective medium approximation by considering each configuration C_i as an independent chemical specie, and by taking its probability $P_i(C_i)$ for volume fraction. In this approach, the macroscopic polarization $P(\sigma)$ induced by an electrical field $\vec{E} = E\vec{u}_x$, where \vec{u}_x is the unit vector in the direction x , is given by

$$\sum_{\{C_i\}} P_i(C_i) \frac{\sigma_x(C_i) - \sigma}{\sigma_x(C_i) + (d - 1)\sigma} E\vec{u}_x = P(\sigma)\vec{u}_x, \tag{4}$$

where d is the dimension of space. $\sigma_x(C_i)$ is the conductivity of the C_i configuration in the x direction, and σ the conductivity of medium, of the field. Setting $P(\sigma) = 0$ allows us to deduce the value of the effective conductivity σ of the mixture.

Fig. 3 shows the evolution of the effective conductivity σ as a function of volume fraction Φ for different energies of interaction Δ . Numerical results are depicted in Fig. 3(a) whereas Fig. 3(b) gives the experimental evolution (from [6]) of the conductivity σ as a function of both Φ and the temperature T . When the conductivities of dispersed and continuous phases are very different, the conductivity of the mixture increases drastically in a small concentration range: this is referred in the literature as the electrical percolation phenomenon. Indeed, the conductivity function of concentration exhibits an inflexion point that permits a clear definition of the electrical percolation threshold. Below this concentration, the mixture behaves like an insulator, whereas above it, it becomes an electrical conductor. The percolation threshold depends on the energy of interaction Δ (Fig. 3). Attractive (i.e., repulsive) energies favor (inhibit) low percolation thresholds.

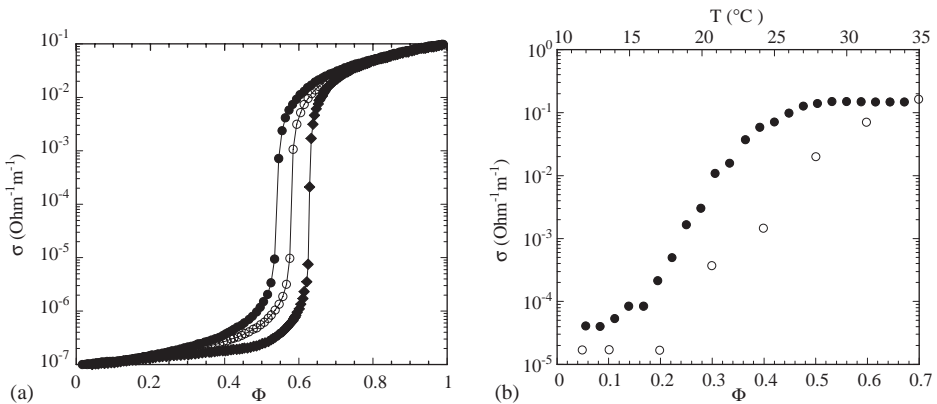


Fig. 3. (a) Evolution of the conductivity of a 2-D mixture as a function of the volume fraction of the solute for different values of the interaction energy Δ . The conductivity of the solute and the solvent are respectively 10^{-7} and $10^{-1} \Omega^{-1} \text{cm}^{-1}$. The lattice is a square. Diamonds, open circles and closed circles correspond respectively to $\Delta = -3k_B T$, $-k_B T$ and 0. (b) Experimental evolution of the conductivity (from Ref. [6]) as a function of both the temperature T (\bullet , $\Phi = 60\%$) and Φ (\circ , $T = 25^{\circ}\text{C}$). The system is identical to that of Fig. 1.

To deduce the phase diagram of the system, we have used the well-known mean-field free energy per site of a binary fluid starting from the Hamiltonian given by Eq. (5):

$$-\frac{\beta F(\Phi)}{M} = \Phi \ln(\Phi) + (1 - \Phi) \ln(1 - \Phi) + \frac{\beta z \Delta \Phi^2}{2}. \quad (5)$$

The spinodal line is given by equating the second derivative of F vs. Φ to zero, and the binodal line is computed by the common tangent method. The phase diagram deduced with these procedures is depicted in Fig. 4. In this phase diagram defined in the plane $(\Phi, \Delta/k_B T)$, three regions are clearly identified (see Fig. 4). For $\Delta < k_B T$ and not too high concentrations, the system is monophasic and insulator. At higher energies, the system undergoes a phase separation at low concentration or stays monophasic for higher concentrations but then becomes an electrical conductor. The lower point on the spinodal line corresponds to the critical point whose coordinates are $\Phi_c = 50\%$ (symmetrical mixture) and $\Delta_c = k_B T$. It is interesting to note that the percolation line meets the binodal line at the critical point. This theoretical phase diagram is qualitatively in remarkable agreement with the phase diagram of ionic ternary microemulsions obtained with sodium bis(2-ethylhexyl) sulfosuccinate (AOT) as a surfactant, and water with decane [7] (see Fig. 1), or glycerol with isooctane [25]. However, the model gives a much sharper change in conductivity with respect to Φ . We believe that this discrepancy results from the fact that our analysis is 2 dimensional and only takes into account four sites. A cluster analysis taking more than four sites would include more lattice configurations, each having different conductivity values intermediate between those of the solvent and of the dispersed

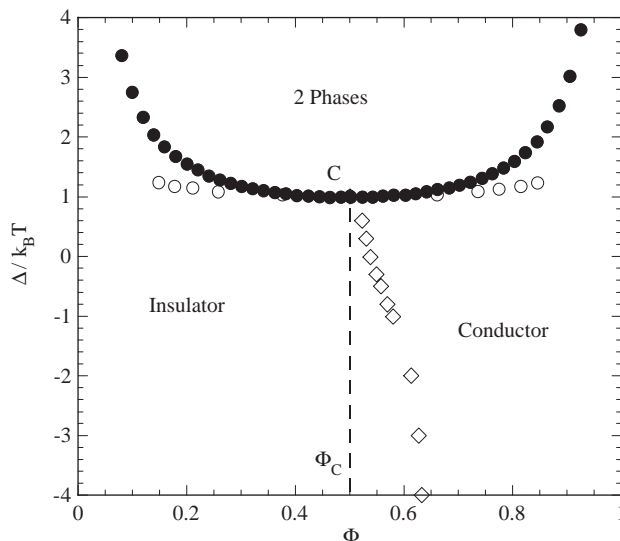


Fig. 4. Spinodal (●), binodal (○) and percolation (◇) lines in a 2-D mixture derived from our effective medium model in the mean-field approximation. Electrical conductivities are the same as in Fig. 3(a).

phase. As a consequence the change of conductivity versus Φ would likely be smoother.

At this point it has to be remarked that the critical volume fractions Φ_c of the above AOT-based micromulsion systems are about 10%, i.e. much lower than the theoretical values. In order to obtain a numerical value of Φ_c consistent with the experimental finding, it is necessary to take into account an effective volume fraction Φ_E due to the existence of an oil molecules shell of thickness δ around the microemulsion droplet. In this case, Φ_E is given by: $\Phi_E = \Phi(1 + \delta/\mathfrak{R})^d$, where \mathfrak{R} is the radius of the microemulsion droplet. With this model, the lattice model critical volume fraction occurring at $\Phi_E = 50\%$ is strongly lowered. In three dimensions, in order to obtain a value close to 10% the ratio $\delta/\mathfrak{R} \approx 0.7$. It has been found by neutron scattering [26] that the radius of the water core of the AOT–water–decane microemulsion droplet at a water/AOT molar ratio $X = 40.8$ is nearly 50 Å; on the other hand, dynamical light scattering data [27] provide a hydrodynamic radius of the order of 85 Å. So the above numerical value of δ/\mathfrak{R} is not unreasonable.

Taking into account such an insulating layer around the microemulsion droplet's core renormalizes the conductivity of the disperse phase (see Ref. [28]) according to Eq. (6):

$$\bar{\sigma}_1(\delta, \mathfrak{R}, \sigma_0, \sigma_1) = \frac{\delta}{\mathfrak{R}} \frac{\sigma_0}{1 + \delta/\mathfrak{R}} + \frac{\sigma_1 \sigma_0}{\sigma_0 + (\delta/\mathfrak{R})\sigma_1} . \quad (6)$$

Using the effective medium lattice model, we obtain a new conductivity for the solution which does not vary too much in all the volume fraction range; in other words, the electrical percolation phenomenon is inhibited. This result is not surprising since it is now well admitted that in microemulsion systems the percolation threshold is mediated by the opening of conducting channels between adjacent droplets [29–31].

In conclusion, we have shown that a simple model based on an effective medium approach can qualitatively describe the phase diagram and the electrical transport properties of microemulsion systems made of conducting droplets. We find that attractive interactions between droplets trigger the electrical percolation transition occurring in these systems. In good agreement with experimental data, our results show that the percolation line and the binodal lines intersect at the critical point. In principle, our model could be easily extended to study the frequency dependence of electrical properties (this could be done simply by using both capacitors and resistors). We believe that this simple effective medium lattice approach is well suited to study the zero frequency transport properties of solutions of complex fluids for which thermodynamical fluctuations are important.

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