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Quantitative determination of the percolation threshold in waterless microemulsions

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This paper presents and discusses the problem of quantitative determination of the percolation threshold on the basis of interactions within microemulsions. The model recently developed by J. Xu and G. Stell [J. Chem. Phys. **89**, 1101 (1988)] was applied in the case of waterless microemulsions. The fit obtained is quantitatively highly satisfactory despite the approximation used to determine interactions from the cloud-point curve.

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INTRODUCTION

The concept of percolation has been widely used over the last few years to explain the transport properties of disordered systems. 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 should appear is, for a system of finite size, all the greater as the density ϕ of the particles approaches the threshold ϕ_c. In systems of interacting objects it is not only the density ϕ which governs the existence of percolation, but also the interactions between objects, which involve correlations of positions. This can cause the system to percolate, in other words to present a cluster of infinite size, even for relatively low densities. A current theoretical problem concerns the prediction of the relationship between percolation threshold and interactions. In this paper we present experimental results which show that for very clearly defined systems it is indeed possible to achieve a satisfactory quantitative interpretation of the position of the percolation thresholds.

BRIEF SUMMARY OF THE PROBLEM

Understanding the percolation of particles interacting in a continuous medium presents at first sight two major difficulties. The first is connected to the definition of an interaction potential which must be able both to simulate a system close to reality and, as far as possible, to treat the problem analytically. The second difficulty is linked to the definition of the notion of connectedness. For the study of percolation in lattices, this second difficulty is in fact not a difficulty at all, since any two particles are necessarily connected if they belong to two adjoining sites in the lattice. However, the situation is much more problematic for percolation in continuous media. A method able to deal with this case was developed by Coniglio, De Angelis, and Forlani [1] using earlier work [2] by Hill. It is based on the pair connectedness function $P(r)$, related to the probability of finding two particles at distance r apart belonging to the same cluster. Two particles are considered as belonging to the same cluster either if there is a direct bond between them or if they are connected by means of other intermediate particles. The $P(r)$ function has a role comparable to that of the radial distribution function $g(r)$ in the classical theory of liquids. At a point of thermodynamic equilibrium, an equation of the Ornstein-Zernike type can be written and solved with conditions and approximations appropriate to the problem, whether it is a thermal problem (gas-liquid coexistence curve) or a percolation problem.

A certain number of models of percolation in continuous media have been proposed. Some [3–8] yield results obtained by Monte Carlo methods; others provide analytical solutions. For some simple systems analytical solutions to the problem of percolation have been obtained using the Percus-Yevick approximation. This is the case, for example, of adhesive sphere fluids [9] and permeable sphere fluids [10]. In the Percus-Yevick approximation, the Ornstein-Zernike equation has been solved numerically for an interacting fluid by means of the following well of potential [11]: $U(r)=+\infty$ if $r<\sigma$, $U(r)=-\varepsilon$ if $\sigma<r<\lambda\sigma$, and $U(r)=0$ if $r>\lambda\sigma$. In this model, two spheres of diameter σ are considered to be connected if their centers are less than $\lambda\sigma(\lambda>1)$ apart. The quantity ε represents the depth of the well of potential. This model gives identical results to a previous model [12,13] within the limit $\varepsilon=0$. It is observed that when the distance of interaction increases, the density (or the number of particles per unit volume) at the percolation threshold decreases. A similar study was carried out by Monte Carlo simulations [4]. For a potential defined in a similar way, $U(r)=-\varepsilon$ if $\sigma<r<\lambda\sigma$, connectedness is processed more generally in this latter work. In these simulations, two particles are considered to be connected if their centers are less than $\delta\sigma$ apart, δ being a parameter unrelated to λ. When $\lambda=\delta$, the model proposed by Safran, Webman, and Grest [4] is identical to those of Netemeyer and Glandt [11] and De Simone, Demoulini, and Stratt [12,13]. If the results of these three last models are compared within the limit $\varepsilon=0$ (where the degree of attraction is zero) it is observed that there is good agreement between the results they yield, even if the values given by Safran, Webman, and Grest [4] are apparently slightly lower than those given by the other two methods.

The model fluids we have just mentioned, which can be resolved analytically, are too particular to represent a real fluid, even a simple one. The well of potential model possessing both attractive and repulsive interaction would be more realistic. There is a model fluid, that of Yukawa, which presents the advantage of giving a realistic representation of a real fluid, as well as enabling analytical calculation. The interaction potential is defined as follows:

$$\beta U(r)=\begin{cases}\infty & \text{for } x<1\\ -\sum_{i=1}^{N} k_i \exp[-z_i(x-1)]/x & \text{for } x>1\ ,\end{cases}$$

in which $\beta=1/(k_B T)$ where k_B is the Boltzmann constant, T is the absolute temperature, and $x=r/d$, where r is the distance between two particles and d is the diameter of the hard sphere. The quantities k_i and z_i are Yukawa's parameters and correspond, respectively, to the intensity and the range of the interaction. The more terms introduced into the interaction model, the closer the model fluid will be to reality.

It is possible to find real systems corresponding to a dispersion of spheres in a continuum, where the spheres interact, and the system presents a percolation transition. These are certain microemulsions and more particularly ternary microemulsions obtained with sodium bis(2-ethylhexyl) sulfosuccinate (AOT) as a surfactant. The reader may wish to consult a recent article [14] on the behavior of electrical conductivity, dielectric relaxation, and viscosity of these systems as a function of various parameters (volume fraction in dispersed phase, temperature, salinity, chemical composition, etc.). For these systems, the percolation model developed by Xu and Stell [15] for a Yukawa fluid at $N=1$ has already been applied [16,17] to the case of a ternary water-AOT-decane microemulsion. In this study we present results obtained with a system of a completely different nature, the waterless microemulsion glycerol-AOT-isooctane, which presents the phenomenon of percolation [18]. We show that since these two systems share the same structural description (here dispersion of spheres in dynamic movement within a continuum [19]), there is indeed a general description of the interpretation of the position of percolation thresholds.

XU AND STELL'S MODELS

General considerations

The pair connectedness function $h^+(r)$ plays a central role in the study of the formation of clusters. $h^+(r)$ is proportional to the probability of finding two particles at a distance r from each other and belonging to the same cluster. The mean number of particles belonging to the cluster is therefore given by

$$S=1+4\pi\rho\int_0^\infty r^2 h^+(r)dr\ , \tag{1}$$

in which ρ is the density, i.e., the number of particles per unit volume, such that the volume fraction of spheres of density ρ and diameter d is $\phi=(\pi\rho/6)d^3$. The percolation transition corresponds to the divergence of S, because that is the point where a cluster of infinite size appears. The function $h^+(r)$ satisfies the Ornstein-Zernike equation

$$h^+(r)=c^+(r)+\rho\int c^+(r')h^+(|\mathbf{r}-\mathbf{r}'|)d\mathbf{r}'\ ,$$

in which $\int d\mathbf{r}'$ is a notation for the integral of volume throughout three-dimensional space. One could also write $h^+(r)=c^+(r)+\rho c^+(r)\circ h^+(r)$ in which the symbol $\circ$ represents the three-dimensional convolution. The function $c^+(r)$ is the direct correlation function.

To solve both the thermal and percolation problems, it is necessary to make approximations. Among the best-known approximations, that of Percus-Yevick has already been used. For the thermal problem of the Yukawa liquid, Xu and Stell [15] used the mean spherical approximation (MSA), which gives rise to the following conditions: $h(r)=-1$ if $r<d$, $c(r)=k(e^{-z(r/d-1)})/(r/d)$ if $r>d$. Taking account of these conditions it was possible to solve the Ornstein-Zernike equation for a Yukawa fluid with N components [20]. The calculations are long and fastidious; the reader will find a complete account of the intermediate results in a recent paper by Saidi [21], which reviews a large number of studies carried out on this question [12,14,15,20–24].

Thermal problem

All the previous studies show that the Yukawa fluid presents a gas-liquid-type transition. Solution of the thermal problem provides among other data the points at which compressibility becomes infinite and thus the coexistence curve, or spinodal curve, can be obtained. As the interaction has an intensity ke^z, which would appear to be *a priori* dependent on the temperature T, and on the basis of knowledge of the range of interaction z, one can obtain the ϕ corresponding to the coexistence curve. The pair T,ϕ obtained thereby defines a point on the spinodal. This curve has been defined as being

$$k\phi=\frac{z^2}{6(z+2)^2}\left[\frac{\sigma-\gamma y}{(\sigma-\gamma)y}\right]U_0\ , \tag{2}$$

with

$$\sigma=\frac{1}{2z}\left[\frac{z-2}{z+2}+e^{-z}\right],\quad \gamma=\frac{1}{2z}\left[\frac{z^2+2z-4}{4+2z-z^2}+e^{-z}\right],$$

$$y=\frac{4+2z-z^2}{2(2+z)}\frac{U_0}{U_1},\quad U_0=\tfrac{1}{2}[p+(p^2+z^2p)^{1/2}]\ ,$$

$$U_1=(2-\sqrt{p}\,)U_0-\Gamma\ ,$$

where

$$p=\left[\frac{1+2\phi}{1-\phi}\right]^2,\quad \Gamma=\tfrac{1}{4}z^2\sqrt{p}\ .$$

When z is fixed, when $\phi\rightarrow 0$, Eq. (2) can be simplified to $k\phi=F(z)$. Figures 1(a) and 1(b) represent the coexistence curves for two values of Yukawa's parameter z, which characterizes the range of the interaction [respectively, $z=1.8$ for Fig. 1(a) and $z=7.5$ for Fig. 1(b)]. The parameter τ which is involved in the figures serves for the percolation problem and will be introduced below.

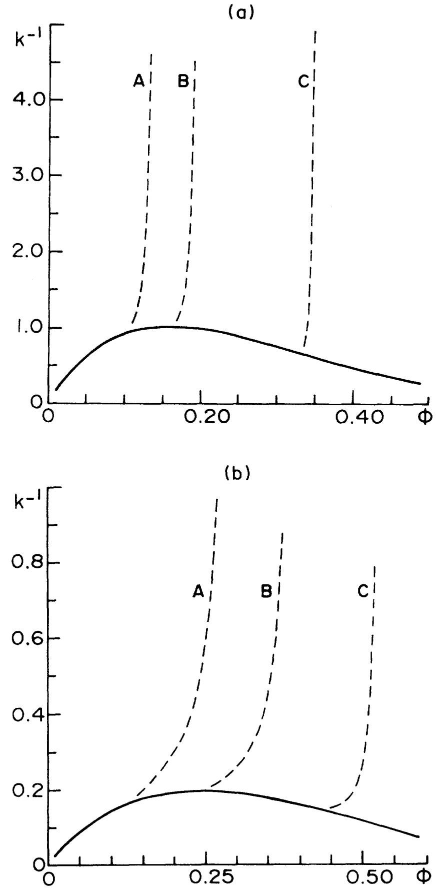

FIG. 1. Spinodal line (——) and percolation line (— — —) calculated using two values of Yukawa's parameter z for the first Xu and Stell model [15]. (a) $z=1.8$ and $\tau=0.7061$ (A), $\tau=0.7907$ (B), $\tau=0.9134$ (C); (b) $z=7.5$ and $\tau=0.8722$ (A), $\tau=0.9315$ (B), $\tau=0.9702$ (C).

Percolation problem

Two models have been developed [15]. The first involves a parameter D such that if two particles of diameter d have their centers less than D apart, they are automatically connected. One assumes $\tau=d/D$ and one defines $H(r)=1$ if $\tau<r/D<1$ and $H(r)=0$ if $r/D>1$, in which $H(r)$ is the probability of finding two particles at a distance r from each other (distance between their centers) and directly connected. Hence they show [15] that Eq. (1) may be rewritten in the form

$$S=\left[1-2\pi\rho\int_0^D Q(r)dr\right]^{-2} . \tag{3}$$

One introduces the function $Q(r)$, which obeys

$$rg(r)=-\frac{dQ(r)}{dr}+2\pi\rho\int_0^D g(|r-s|)(r-s)Q(s)ds , \tag{4}$$

in which $g(r)$, the radial distribution function, is determined on the basis of the study of the thermal problem. Solving Eq. (4) gives $Q(r)$ and this equation has an analytical solution if $\frac{1}{2}<\tau<1$, a result which had already been verified [12]. Obtaining $Q(r)$ is complicated, but the percolation threshold can then be obtained easily by writing that the mean size S of the clusters diverges at the threshold, in other words that $2\pi\rho_c\int_0^D Q(r)dr=1$, in which ρ_c represents the critical density.

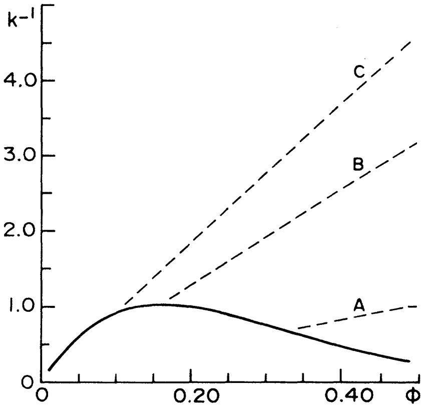

FIG. 2. Spinodal line (——) and percolation line (— — —) for the second Xu and Stell model [15]. $z=1.8$ (A) $\lambda=0.1248$, (B) $\lambda=0.3868$, (C) $\lambda=0.5611$.

In the second model the function $H(r)$ is defined in more general terms. It represents the probability that two particles located at a distance r apart should be connected when they no longer have any interaction with any other particle, in other words when the density tends towards zero. We have $0\leq H(r)\leq 1$ but otherwise $H(r)$ is random. One might for example envisage that $H(r)$ is the probability that two particles separated by a distance r can exchange electrical charges. It is in this sense that the second model seems likely to prove more satisfactory for microemulsions. With $c(r)=k(e^{-z(r/d-1)}r/d)$, Xu and Stell [15] found the percolation threshold to be at $k^{-1}=\lambda\phi/F(z)$ in which λ is an adjustable parameter and $F(z)$ is the limit for the right-hand member of Eq. (2) when ϕ tends towards zero. Since $F(z)$ is constant at fixed z, the place for the percolation thresholds is, for each value of λ, a straight line which in the k^{-1}-ϕ plane passes through the point $\phi=0$. Figure 2 provides an example of the results obtained [15] for different values of λ, z being fixed.

APPLICATION TO THE CASE OF MICROEMULSIONS

In the case of microemulsions with AOT, a demixing phenomenon is observed for a given volume fraction when temperature is increased. To make the above theory [15] applicable to these systems, it is necessary to introduce explicitly the variations $k(T)$ of the intensity of the interactions with temperature.

Water-AOT-decane microemulsions [16,17]

The authors assumed $ke^{z}=k_0+k_1T+k_2T^2$ in which k_0, k_1, and k_2 are empirical coefficients determined to

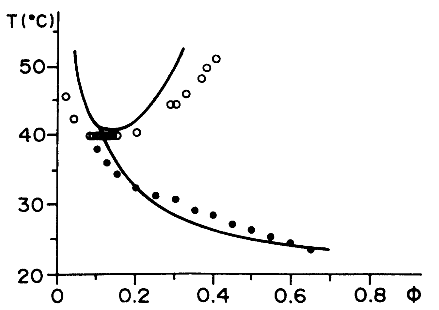

FIG. 3. Water-AOT-decane system; $n=40.8$. The experimentally determinated demixing curve (○) and percolation line (●) obtained by Cametti *et al.* [16], compared to the computed spinodal line and percolation locus for the second Xu and Stell model [15].

adjust neutron-scattering results. If T is in °C, one has $k_0=-0.329$ (we should indicate here that there was a typographical error in the original article), $k_1=0.013$, and $k_2=2.124\times10^{-4}$ for the molecular ratio $n=[H_2O]/[AOT]=40.8$ with a range of interaction $z=0.73$ [16]. In these conditions the authors observe an excellent fit between the experimental results for the $\phi_c(T)$ percolation threshold line and the predictions of the second Xu and Stell model. Figure 3 represents the spinodal curve calculated on the basis of this model, the experimental demixing curve, and the experimental and calculated percolation threshold lines. The agreement is extremely satisfactory. The reduction of the threshold with T had been previously discussed by us [25] from a qualitative point of view based on a model [3,4] and taking account of the fact that the interaction distance and the intensity of interaction increase with temperature as light-scattering experiments have shown [26]. But the above result [16] on water-AOT-decane microemulsions is the first satisfactory quantitative prediction of the percolation threshold line of a real microemulsion. Recently [17], supposing that the cloud-point curve is similar to the spinodal line, they succeed also to calculate the percolation line without the knowledge of the neutron-scattering results. They fitted simultaneously both the spinodal and the percolation line. This hypothesis, postulated independently at the same time by us [21,27], will be discussed in detail below, in the case of waterless microemulsions. But in our case we will show that it is necessary to fit only the spinodal curve in order to obtain the percolation line.

Waterless glycerol-AOT-isooctane microemulsions

This system presents a monophase domain at 25°C and it can be observed that the maximum value of the molecular ratio [glycerol]/[AOT] is slightly higher than 4. If a microemulsion of molecular ratio $n=4$ and a given volume fraction ϕ is heated it presents a demixing phenomenon for a certain temperature T_d. Figures 4(a) and 4(b) represent in the T-ϕ and $1/T-\phi$ planes the demixing curve and the locus of the previously determined percolation thresholds [14,18,28]. It will be noted that the results obtained are comparable to those observed for systems with water, in other words a reduction of the threshold as temperature increases [14,16,29].

For this system we have no previous data concerning the intensity of interactions. We therefore determined approximately the function $k(T)$ on the basis of the above theory [15] assuming that the spinodal is identical with the demixing curve [17,21,27]. On Fig. 4 we have represented the experimental points. As ϕ_d is known it is possible, for a given z, to calculate k using Eq. [2]. However, if z is not carefully selected, the function $k(T)$ is not univocal as regards temperature. Numerical analysis has shown us that if $z=0.435$ the resultant $k(T)$ curve is

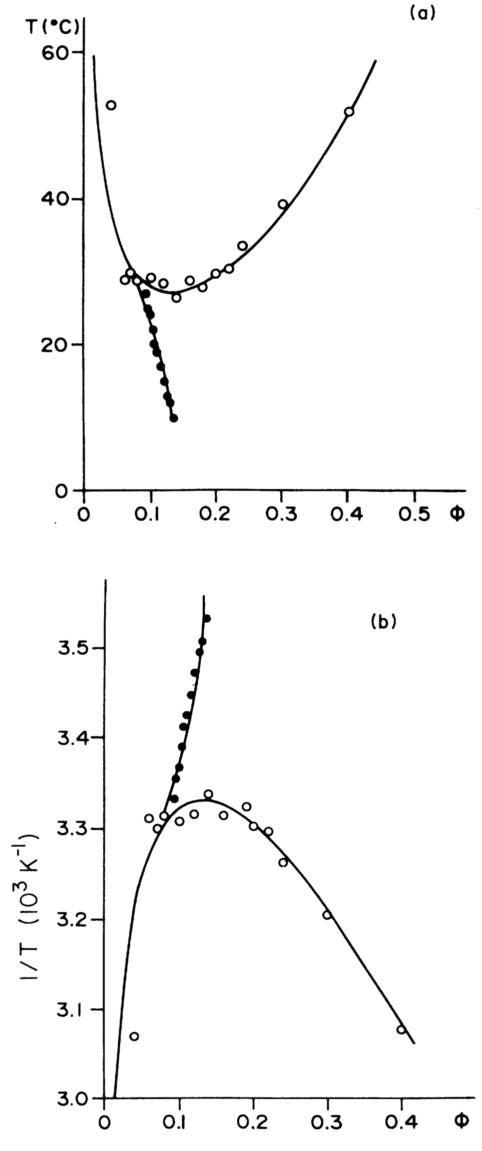

FIG. 4. Glycerol-AOT-isooctane system; $n=4$. The experimentally determinated demixing curve (○) and percolation line (●) compared to the computed spinodal line and percolation locus for the second model. (a) T-ϕ diagram; (b) T^{-1}-ϕ diagram.

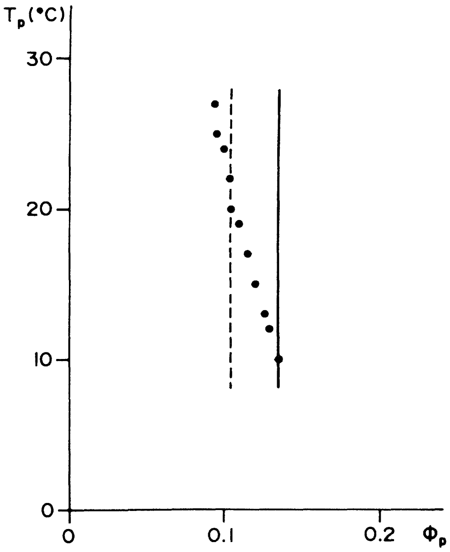

FIG. 5. Glycerol-AOT-iso-octane system; $n=4$. (●) experimental percolation threshold and percolation line computed for the first model. $\tau=0.650$ (— — —) and $\tau=0.7094$ (——).

univocal. This curve can be represented by the arc of a parabola and we obtained $k(T)=a_0+a_1T+a_2T^2$ with $a_0=8.982\,599\times10^{-2}$, $a_1=-3.909\,196\times10^{-3}$, and $a_2=1.482\,685\times10^{-4}$, when T is expressed in °C. Figures 4(a) and 4(b) represent the demixing curve calculated in this way. The values obtained for interaction in the case of the waterless microemulsions studied here can be compared with those for the system with water: water-AOT-decane [16]. The interaction potential appears to have a greater range for waterless systems since $z_{\text{glycerol}}=0.435$ whereas $z_{\text{water}}=0.73$. As regards the intensity of the interaction, this increases more quickly with increasing temperature in the case of the system with water. It should be recalled, however, that the molecular ratio in the glycerol-AOT-isooctane system, which is 4, is smaller than those used for the water-AOT-decane system, which are 30, 40.8, and 50.

For the locus of the percolation thresholds we used this interaction estimate to apply Xu and Stell's theory [15]. Their first model does not allow experimental results to be taken into account. This is because whatever the value of τ between $\frac{1}{2}$ and 1, one obtains a curve which falls rapidly in the T_p-ϕ_p plane (in which T_p is the percolation temperature and ϕ_p is the percolation threshold). Figure 5 represents the threshold line calculated for this model with two different values of τ. This can usefully be compared with Fig. 1 in which the percolation line is also a rapidly falling straight line.

As was also observed for systems with water [16,17], the second model provides a better representation of the experimental results. Knowing the experimental values of T_p and ϕ_p, we determined the best value of τ, which, taking account of the function $k(T)$ minimizes the deviations between experimental and calculated values. It can be seen that for $\lambda=0.579$, with the $k(T)$ function and z determined with the help of the thermal problem, a satisfactory fit is obtained for the locus of percolation thresholds. The calculated threshold line is indicated on Fig. 4.

CONCLUSION

It is satisfying to observe that despite the approximations made to calculate the interactions the values of the percolation thresholds are determined with a fair degree of accuracy. It is very surprising that despite the empirical nature of the hypothesis (assuming that the spinodal and the demixing curve would be identical), there was such a good quantitative fit between experimental and calculated values, but, in any case, it is interesting to know that a satisfactory theoretical model can, in certain conditions, calculate quantitatively the value of thresholds and thus complete the link between the threshold value and interactions within the system. It should be stressed that, as we mentioned above, the microemulsions presented here naturally correspond to a dispersion of spheres in Brownian movement in a continuum. These systems are therefore well adapted to the requirements of testing the theory presented.

We now have a complete description of the percolation phenomenon, the properties of these systems obeying scaling laws with specific exponents (the reader could consult a recent review [14]). To continue further research into the prediction of these thresholds, we now need to develop a theory able to calculate the value of interactions, but this is a subject that goes well beyond the scope of this paper.

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