

Complex Electrical Conductivity of Water-in-Oil Microemulsions

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The behavior of frequency-dependent electrical conductivity and permittivity close to the percolation threshold of a two-component system is interpreted in terms of formation of polydispersed fractal clusters. We derive an explicit form of the scaling function for the complex conductivity and its limit of validity. The measurements performed on two water-in-oil microemulsion systems are very well accounted for and show the expected scaling behavior. Stretched exponential behavior of the polarization correlation function is also obtained.

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The description of complex physical systems in terms of collections of independent clusters has a long history. It has been proposed in different forms to describe various physical situations, for example, systems close to critical points [1], kinetics of phase separation [2,3], and systems close to the glass transition [4]. More recently, such an approach has been associated with the problem of finding the appropriate mapping between a system under investigation and the corresponding percolation model [5]. The mapping requires the selection of the correct clusters (which can be formed by either random or correlated groups of elementary units) and of their size distribution. Interestingly enough, such a mapping depends not only on the physical system under study, but also on the physical quantity used to investigate the system. Recent examples of such a rich approach have been limited to the description of light scattering, both for the static scattered intensity in Ising critical systems [5] and for the decay of the time correlation function of the order parameter fluctuations near the demixion critical point in a microemulsion system [6]. These works have shown that the relevant percolation model associated with light scattering experiments is a random-bond correlated-site one [5].

In this Letter we use the independent cluster approach to describe a frequently measured physical quantity, namely, the frequency-dependent complex electrical conductivity in a two-component system, $\tilde{\sigma}(\omega) = \sigma(\omega) + i\omega\epsilon(\omega)$, where σ and ϵ are the measured conductivity and permittivity. We map this problem onto a random percolation problem in which clusters are formed by aggregates of monomers. We consider the case of a water-in-oil microemulsion, a two-component system in which the monomers are water droplets, coated by a monomolecular surfactant layer, immersed in an oil bath. In terms of temperature T and composition of the

dispersed phase ϕ , the occurrence of a percolation locus (T_p, ϕ_p) , and an associated anomalously large increase of electrical conductivity, has been noticed and studied since long ago, both experimentally [7–15] and theoretically [16–19], in microemulsion systems. The main theoretical results are the identification of charge migration on clusters as the percolation mechanism (stirred [7] or dynamic percolation [11]), the calculation of the relevant static and dynamic indices [11], and a scaling description of $\tilde{\sigma}$ [19]. From the experimental standpoint, the percolation indices have been measured and some of the scaling properties tested [13,14]. In particular, an extensive comparison between dielectric measurements in a five-component ionic microemulsion system, the Bruggeman theory [20], and the dynamic percolation model has been made by Clarkson [13].

We calculate $\tilde{\sigma}$ in a water-in-oil microemulsion through the following steps: (i) Assume that the microemulsion droplets, which interact through a short-range attractive potential, form clusters the size of which tends to diverge on approaching the percolation threshold. (ii) Calculate the conductivity and permittivity of a cluster by an effective medium approximation (EMA) [21], in order to have the correct dependence on the electrical parameters of the two components. (iii) Relate the relaxation amplitude and the relaxation time of a cluster to the physical mechanism of conduction by dynamic percolation on fractal clusters [7,11]. (iv) Use the scaling distribution of cluster sizes at percolation to account for the polydispersity of the aggregates. The results we obtain using a combination of the cluster model and EMA are the following: (i) the simultaneous description of the experimental data for $\sigma(\omega)$ and $\epsilon(\omega)$ at a quantitative level, using the known values of the electrical parameters of the components; (ii) the explicit formulation of a scaling function for $\tilde{\sigma}(\omega)$ and the

establishment of the limit of validity of scaling; (iii) the evidence for power-law and stretched exponential behaviors of the polarization time correlation function and the evaluation of their exponents. The latter two points are obtained for the first time.

We begin by writing down the contribution to the complex conductivity $\tilde{\sigma}_k$ of a cluster made of k spherical inclusions characterized by σ_B and ϵ_B , in a medium with σ_A and ϵ_A [21],

$$\tilde{\sigma}_k = \tilde{\sigma}_A(A_k \tilde{\sigma}_B + 2\tilde{\sigma}_A)/(\tilde{\sigma}_B + B_k \tilde{\sigma}_A), \quad (1)$$

where A_k and B_k are assumed to be independent of the dielectric parameters of the system and power-law functions of the cluster size, to be determined on the basis of the physics of the problem. Equation (1) is equivalent to a Debye relaxation function [22], $\tilde{\sigma}_k = i\omega\epsilon_A\Delta_k/(1 + i\omega\tau_k)$, with amplitude Δ_k and relaxation time τ_k given by

$$\Delta_k = \frac{(A_k B_k - 2)(\sigma_B \epsilon_A - \sigma_A \epsilon_B)^2}{\epsilon_A(\sigma_B + B_k \sigma_A)^2(\epsilon_B + B_k \epsilon_A)},$$

$$\tau_k = \frac{\epsilon_B + B_k \epsilon_A}{\sigma_B + B_k \sigma_A}. \quad (2)$$

Note that Δ_k and τ_k have a particularly simple form for conducting clusters in an ideal nonconducting medium (RC case, $\sigma_A \ll \omega\epsilon_A$, $\sigma_B \gg \omega\epsilon_B$): $\Delta_k^{RC} = A_k - 2/B_k$ and $\tau_k^{RC} = \epsilon_A B_k / \sigma_B$. These simple expressions allow a direct evaluation of the power-law behavior in k of A_k and B_k , via Δ_k^{RC} and τ_k^{RC} . The values of the scaling exponents are determined by the physical mechanism of conduction in the system. In the microemulsion case, the relaxation time is controlled by the diffusion of charged surfactant ions in the cluster [23]. Since the clusters are fractal objects, the relaxation time scales with k as $\tau_k^{RC} \approx (R_k^2)^{D/\tilde{d}}$, where D is the fractal dimension of the cluster and \tilde{d} is the spectral exponent [24]. On the other hand, the cluster polarization builds up in proportion to the cluster size [25]. The amplitude of the relaxation is thus proportional to the squared radius of gyration of the cluster, so it will scale with k as $k^{2/D}$. We then obtain

$$A_k = (A_1 - 2/B_1)k^{2/D} + 2/B_k, \quad B_k = B_1 k^{2/\tilde{d}}, \quad (3)$$

with A_1 and B_1 constants to be determined. B_1 is related to the relaxation time of a monomer, while A_1 is related to its polarization, as given by Eq. (2). This procedure is thus an application of the EMA [13], which guarantees the correct dependence on the electrical properties of the two materials, and in which the volume fraction dependence has been relaxed in favor of the appropriate scaling behavior in k .

For systems close to percolation the cluster size distribution is characterized by a power-law behavior with index τ and a cutoff cluster size k_c [26], i.e.,

$$p(k) = k^{1-\tau} e^{-k/k_c} / k_c^{2-\tau} \Gamma(2-\tau, k_c^{-1}), \quad (4)$$

where $\Gamma(a, x)$ is the incomplete gamma function. k_c diverges at the percolation threshold (T_P, ϕ_P) and is

related to the connectivity length $\xi \sim k_c^{1/D}$ [26]. The latter behaves as $\xi \sim \Delta p^{-\nu}$, where $\Delta p = |1 - \phi/\phi_P|$ at constant T as a function of ϕ or $\Delta p = |1 - T/T_P|$ at constant ϕ varying T . Then $\tilde{\sigma}$ is calculated as a sum of independent contributions $\tilde{\sigma}_k$ weighted with the distribution of Eq. (4). To lowest order in k_c^{-1} , we find

$$\tilde{\sigma}(\omega) = \sigma_u(1 + i\omega/\omega_B)k_c^{1-1/D-2/\tilde{d}}\tilde{\Phi}(\zeta, k_c), \quad (5)$$

where the constant $\sigma_u \equiv \sigma_B(3/D - 1)NA_1/B_1$ is a conductivity scale, N is the total number of monomers, $\omega_B \equiv \sigma_B/\epsilon_B$, $\omega_A \equiv \sigma_A/\epsilon_A$, and $\tilde{\Phi}(\zeta, k_c)$ is defined by

$$\tilde{\Phi}(\zeta, k_c) = \zeta \int_{k_c^{-1}}^{\infty} dz e^{-z} z^{-1/D} / (1 + \zeta z^{2/\tilde{d}}). \quad (6)$$

$\tilde{\Phi}$ is a complex function of the complex variable

$$\zeta \equiv B_1 \frac{\tilde{\sigma}_A}{\tilde{\sigma}_B} k_c^{2/\tilde{d}} = \frac{1 - \omega_B \tau_1}{\omega_A \tau_1 - 1} \frac{\omega_A + i\omega}{\omega_B + i\omega} k_c^{2/\tilde{d}}. \quad (7)$$

ζ involves four parameters, the cutoff cluster size k_c , which measures the distance from the percolation threshold, the monomer relaxation time τ_1 , and the two frequencies ω_B and ω_A referring to the electrical characteristics of the dispersed phase and the medium, respectively. In the RC limit $\omega_A \approx 0$ and $\omega_B = \infty$, so that $\zeta = i\omega\tau_1 k_c^{2/\tilde{d}}$.

Note that $\tilde{\Phi} \sim \zeta$ for small values of $|\zeta|$. For large values of $|\zeta|$, $\tilde{\Phi}$ has the asymptotic expansion $\tilde{\Phi} \sim \zeta^u$ when $|\zeta| \ll k_c^{2/\tilde{d}}$ and the constant limiting value $\tilde{\Phi} \approx k_c^{2u/\tilde{d}}$ when $|\zeta| \gg k_c^{2/\tilde{d}}$, with $u = \tilde{d}(1/D + 2/\tilde{d} - 1)/2 = 0.59$. Therefore $\tilde{\Phi}$ is a function of ζ only up to the point $\zeta \approx \zeta_c$ where the power law crosses over to a constant value. Hence below the crossover point ζ_c we get $\tilde{\Phi}(\zeta, k_c) \approx \tilde{\Phi}(\zeta, \infty)$, a true scaling function, in agreement with the scaling theory of conduction in disordered systems [11,16,19]. In the zero-frequency limit we recover the usual scaling behavior for the static conductivity σ_0 and permittivity ϵ_0 . In fact, when $|\zeta|$ is small $\sigma_0 \sim k_c^{1-1/D} \sim \Delta p^{-s}$ and $\epsilon_0 \sim k_c^{1-1/D} \sim \Delta p^{-s}$, where $s = \nu(D - 1) = 1.33$ [24]. For large $|\zeta|$ both σ_0 and ϵ_0 become constant because of the finite values of the parameters ω_A and ω_B , due to the finite conductivity of the oil phase and the finite permittivity of the droplets. At the percolation threshold $\tilde{\sigma}(\omega)$ can be evaluated as a Gauss hypergeometric function

$$\tilde{\sigma}(\omega) = \sigma_u \frac{1 + i\omega/\omega_B}{2/\tilde{d} - 1/D - 1} {}_2F_1\left(1, u; 1 + u; -\frac{\tilde{\sigma}_B}{B_1 \tilde{\sigma}_A}\right). \quad (8)$$

Data on complex conductivity can be transformed from frequency to time to give the normalized time autocorrelation function $C(t)$ of the polarization as the average of an exponential decay over a relaxation time distribution. In the RC case $C(t)$ is given by a power-law distribution of relaxation times, with a stretched exponential cutoff function depending on k_c , similar to the

Cole-Davidson distribution [21]. We stress that there are different time (or frequency) scales in a two-component mixture, fixed by the electrical properties of the two components (ω_A and ω_B) and by the distance from percolation. ω_A , ω_B , and k_c combine to determine the smallest τ_1 and the longest τ_{k_c} relaxation times in the system [see Eq. (2)]. $C(t)$ behaves as an exponential for $t \ll \tau_1$, as $1 - (\Gamma t)^\alpha$ for $\tau_1 \ll t \ll \tau_{k_c}$, and as a stretched exponential $\exp[-(\Gamma t)^\beta]$ when $t \gg \tau_{k_c}$, with inverse lifetimes Γ and exponents $\alpha = \tilde{d}(1 + 1/D)/2 = 0.39$ and $\beta = \tilde{d}/(\tilde{d} + 2) = 0.41$. Note that only in the RC case τ_{k_c} diverges at percolation. In the non-RC case the longest relaxation time is fixed by ω_A^{-1} . The existence of a maximum cutoff time in the non-RC case reflects the fact that the large cluster decay time becomes independent of the cluster size [Eq. (2)]. Loss of correlation of the cluster polarization arises from the finite probability for the charge carriers to leave the cluster and migrate in the low conducting oil phase.

In order to test the validity of the independent cluster model, we have performed measurements on two microemulsion systems, AOT-water-undecane and AOT-water-decane. The latter system has been studied extensively by small angle neutron scattering [27], and we have firm evidence that up to the percolation threshold the droplet structure of the microemulsion is well preserved and transition to a bicontinuous structure does not happen until far above the percolation threshold. Experiments were done as functions of volume fraction and temperature. The measurements span a wide range of frequencies, ranging from 10 kHz to a few GHz, using three different instruments, namely, two radio-wave impedance bridges and a time-domain reflectometer for the high-frequency part of the spectrum. Figures 1 and 2 show the results of some typical measurements and the fitting by the theoretical expressions derived from Eq. (5). The approach to percolation in these mixtures can be realized on increasing ϕ (Fig. 1) or T (Fig. 2). It is mirrored in the progressive change, with T or ϕ , of the slope of $\sigma(\omega)$ vs ω at intermediate frequencies and in the decrease of ω_{\max} , the frequency of the maximum of the imaginary part of $\tilde{\epsilon}$ indicated by the arrows, as well as in the increase of σ_0 and ϵ_0 . Figure 3 reports k_c , σ_0 , ϵ_0 , and ω_{\max} , scaled with the power-law amplitudes evaluated from Eq. (5), as a function of Δp . It shows that they follow the power laws $k_c \sim \Delta p^{-\nu D}$, $\sigma_0 \sim \Delta p^{-s}$, $\epsilon_0 \sim \Delta p^{-s}$, and $\omega_{\max} \sim \Delta p^{-(s+t)}$, where $t = \nu(1 - D + 2D/\tilde{d}) = 1.94$, with the accepted values of the indices [24,26]. In order to specify k_c along the thermodynamic path of approach to the percolation threshold, we use one parameter relating k_c to ξ .

The theoretical conductivity $\tilde{\sigma}(\omega)$ describes very well, and with the same set of parameters simultaneously, the ω dependence of σ and ϵ of the samples, as well as their limiting zero- and infinite-frequency values. It depends on the five parameters ω_A , ω_B , τ_1 , σ_u , and

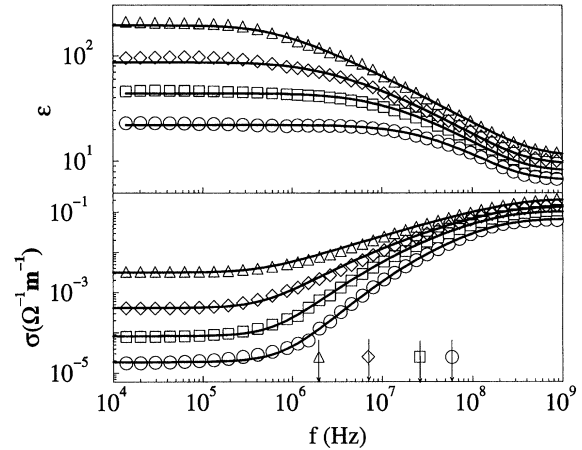


FIG. 1. The measured conductivity and relative permittivity in a water-AOT-decane microemulsion ($\phi_p = 0.38$) as a function of the frequency f for different values of ϕ : 0.24 (\circ), 0.28 (\square), 0.32 (\diamond), and 0.36 (\triangle), $T = 25^\circ\text{C}$ and $X = [\text{H}_2\text{O}]/[\text{AOT}] = 40.8$. The full lines are given by Eq. (5). Note the decrease of $f_{\max} = \omega_{\max}/2\pi$, shown for each set by the arrow, on approaching percolation.

k_c . τ_1 and σ_u can also be related to the amplitude and the characteristic time of the monomer relaxation, which in turn are connected to the electric parameters of the materials. We stress that these parameters are the minimal set one can use to describe completely at a quantitative level the dielectric behavior of a two-component system. We find $\omega_A \approx 0.1\text{--}0.5$ MHz and $\omega_B \approx 2\text{--}4$ GHz for both systems, and $\tau_1 \approx 200$ ps for the undecane system and ≈ 500 ps for the decane [28]. We note that the ratio between the two times is close to the ratio of the squared radius of the droplets in the two systems [29], suggesting that the relaxation time of the monomer is indeed related

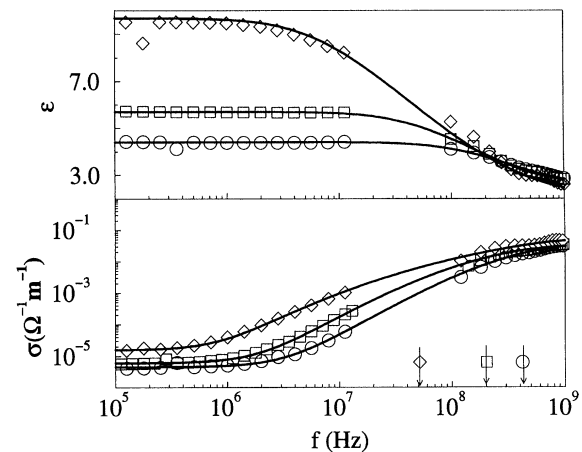


FIG. 2. Measured conductivity and relative permittivity in water-AOT-undecane ($T_p = 37^\circ\text{C}$) for different values of T , 22°C (\circ), 26°C (\square), and 30°C (\diamond), for $\phi = 0.15$ and $X = 30$. The full lines and the arrows have the same meaning as in Fig. 1.

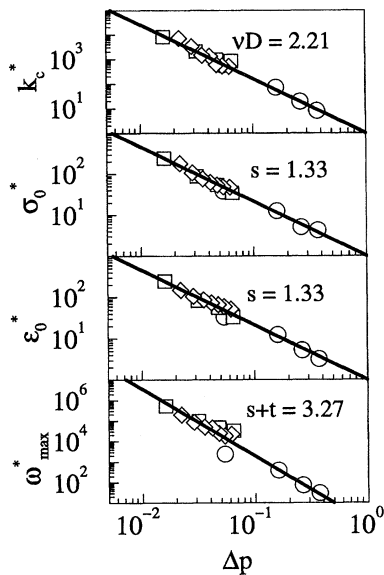


FIG. 3. Scaling plots for k_c^* , σ_0^* , ϵ_0^* , and ω_{\max}^* as a function of the reduced distance to the percolation threshold. The * indicates division by the power-law amplitudes calculated according to Eq. (5). The full lines are the power laws with the slopes reported for each plot. The \circ refer to the measurements of Fig. 1, the \square to a set of data taken on the same system at $X = 15$, $\phi = 0.20$, $T_p = 40^\circ\text{C}$ as a function of T and the \diamond to the data of Fig. 2.

to the diffusion of charge carriers in the droplet. In the end, we find that the k_c values obtained from the fit increase monotonically on approaching the transition from a few droplets far from percolation, to about 10^3 close to it. In conclusion, the theory as formulated above has been tested against several measurements, not entirely shown here [30], and satisfactory agreement has been obtained. A full comparison will be presented later.

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- [23] Surface conductivity has been invoked as a possible mechanism in similar systems [13]. We expect it to be relevant in microemulsions containing salt, where the concentration of counterions is significantly increased.
- [24] The fractal dimension D is defined through the dependence of the radius of gyration on the number of monomers in a cluster $R_k = R_1 k^{1/D}$, where R_1 is the monomer radius. The spectral exponent \tilde{d} is given by $2D\nu/(t + 2\nu - \beta)$, which involves the indices t for the conductivity above percolation, ν for the correlation length, and β for the probability to be in the infinite cluster. The indices obey the scaling relation $D = d - \beta/\nu$ for space dimension d . The accepted values are $D = 2.52$ and $\tilde{d} = 1.37$ for $d = 3$.
- [25] The amplitude Δ_k^{RC} is proportional to the average squared electric dipole moment due to charge fluctuations, which will be therefore proportional to the square of the radius of gyration of the cluster R_k^2 .
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- [28] These figures are close to the expected ratios σ/ϵ of oil and water plus surfactant droplets. In fact $\sigma_A \approx 10^{-6} \Omega^{-1} \text{m}^{-1}$, $\epsilon_A \approx 2$, and $\sigma_B \approx 10^{-2} \Omega^{-1} \text{m}^{-1}$, $\epsilon_B \approx 10^2$, and therefore we expect for the parameters $\omega_A \approx 100 \text{ kHz}$ and $\omega_B \approx 1 \text{ GHz}$. We also expect a slight dependence of ω_A and ω_B on ϕ and T , reflecting the trivial change of the electric properties of the materials.
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- [30] We have used Eq. (5) to fit data of different microemulsion systems [8,9,12] with a very good quality in all cases.