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Dynamic percolation in microemulsions

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We study a model for dynamic percolation relevant to the electrical conductivity of water in oil microemulsions. The charge carriers reside on percolation cluster sites and can propagate by hopping between nearest-neighbor sites. The cluster sites also undergo diffusion, so that the clusters continuously rearrange themselves. The conductivity below the percolation threshold p_c is finite and, as $p \rightarrow p_c$, increases as $|p_c - p|^{-\tilde{s}}$ where $\tilde{s}$ differs from the static exponent s. In the neighborhood of p_c, the conductivity depends as a power law on the rate of cluster rearrangement.

A remarkable electrical conductivity transition has recently been observed in several water-in-oil microemulsion systems.[1-5] As the volume fraction of water p is increased towards a critical volume fraction p_c (which is a function of temperature and other parameters such as the surfactant concentration), a sharp increase of several orders of magnitude in the electrical conductivity occurs. There is considerable experimental[1-6] and theoretical [7-9] evidence that at low and intermediate water concentrations the microemulsions consist of globules of water in oil which undergo Brownian motion. In some systems, the globules also show attractive interactions.[7,8]

A percolation picture for the transition involves the formation of clusters of water globules which are sufficiently close to each other so that an efficient transfer of charge carriers between the globules can occur.[4,9] An alternative view is that the formation of a continuous connected water phase is responsible for the conductivity transition.[10] The experimental results, together with the present theoretical arguments, provide additional support in favor of the former view, at least for the systems studied in Refs. 1 and 2.

In a previous publication[9] we analyzed the volume fraction of water at which the transition occurs, and the effect of the interactions and temperature T on the transition. We showed how the location of the percolation threshold p_c depends on the strength of the attractive interactions. The system can go through a percolation transition when either the water fraction or T is varied. Since the location of p_c is a slowly varying function of T, we expect the exponents when the temperature is varied to be identical with those measured when the concentration of globules is varied.

In the usual static model consisting of a system of conducting regions randomly embedded in an insulating matrix, the conductivity vanishes below p_c of the conducting phase.[11] However, for microemulsions, the clusters continuously rearrange themselves because of Brownian motion, resulting in a finite conductivity for $p < p_c$. The charge carriers are not trapped in the finite clusters. A charge on a water globule can propagate by either hopping to a neighboring globule, or via the diffusion of the host globule. If the typical hopping time of the carriers between globules is much shorter than some characteristic time related to the motion of the globules, one expects a steep increase in the overall carrier diffusion as the concentration p approaches the critical concentration p_c. This is due to a transition from a regime of transport dominated by globular motion and cluster rearrangement to one dominated by the motion of charge carriers on a large connected cluster of globules.

Thus, in microemulsions there are two relevant time scales: (a) The characteristic time it takes for a cluster to rearrange itself, and (b) the time it takes for a diffusing charge carrier to visit all the sites in a typical finite percolation cluster. For percolation clusters,[12] this latter time is also the time for the mean-square displacement to be of the order of the cluster size. The ratio of these times determined whether the system is in a slow- or fast-rearrangement regime. This observation leads to the formulation of a scaling expression for the diffusion of a charge carrier below p_c. The main consequence of this scaling is that in the limit of slow cluster rearrangement, the conductivity increases as $|p_c - p|^{-\tilde{s}}$ as $p \rightarrow p_c$ (except for a small region around p_c). The exponent $\tilde{s}$ can be expressed in terms of static percolation exponents and it differs from the corresponding exponent s for the termite case.[13] The fact that $\tilde{s} > s$ is in agreement with experimental results in microemulsions[1,2,5,14] which find $\tilde{s} \simeq 1.2 \pm 0.05$ in three dimensions (3D) whereas $s \sim 0.6$–0.7. The other consequences of the cluster dynamics are (i) a "smearing" of the conductivity transition in a region around p_c and (ii) the ac conductivity of the dynamic system differs from the ac response of a static percolating system.

We consider a lattice with a fraction p of sites randomly occupied by cluster particles one of which hosts a charge. Each cluster particle performs a random walk on the lattice which is characterized by a jump rate T^{-1}; the charge performs a random walk only on the cluster sites with a jump rate of unity. The only interaction between the particles is the excluded volume. The unique feature here is that the clusters evolve and rearrange in time, so that neighboring configurations in the Markov chain are correlated.

Initially, one cluster particle hosts a charge, which can propagate in the system either by hopping to a nearest-neighbor cluster particle, if one exists, or being carried along if the host particle diffuses. Let T_R be the time for rearrangement of a typical cluster, e.g., for a large cluster to be broken up into two smaller ones, or for two clusters to fuse into a single larger one. This rearrangement may be considered a slow process if the time τ it takes the charge carrier to visit all the sites in a typical cluster is much smaller than T_R.

The corresponding characteristic time for $p \lesssim p_c$ is the time to explore a cluster of size ξ, $\tau \sim \xi^{2D_f/\tilde{d}}$. D_f is the fractal dimension, $\tilde{d}$ is the spectral exponent given by[12]

$\tilde{d}=2D_f\,\nu/(\mu+2\nu-\beta)$, μ is the conductivity exponent for $p>p_c$, ν is the correlation-length exponent, $\xi\sim|p-p_c|^{-\nu}$, and β is the exponent for the probability to be in the infinite cluster, $P(p)\sim(p-p_c)^{\beta}$ for $p>p_c$.[15] In a time τ, the charge carriers explore a region of size ξ; if $\tau \ll T_R$, the mean-square displacement for times comparable to T_R is of the order of $R_g^2\sim\xi^{2-\beta/\nu}\sim|p-p_c|^{-(2\nu-\beta)}$. Since the spectral dimension[12] $\tilde{d}<2$, the time for the mean-square displacement to be of the order of the mean cluster size is comparable to the time needed to visit all sites of the cluster once. Note that T_R represents an effective rearrangement time, which in principle depends on $|p-p_c|$. The rearrangement time of individual clusters may depend on the cluster size. Our assumption that T_R does not depend on $|p-p_c|$ means this dependence on the cluster size does not affect the global macroscopic diffusion.[16] Our numerical results, shown below, support this picture. Due to the cluster rearrangement, the motion of the charge carriers is diffusive for $t \gg T_R$ with a diffusion coefficient ($\tau \ll T_R$):

$$D(p-p_c)\sim\frac{R_g^2}{T_R}\sim\frac{1}{T_R}|p-p_c|^{-(2\nu-\beta)} \ . \tag{1}$$

If p is sufficiently close to p_c, or T_R is not very large, the rearrangment of the cluster will occur before the charge carrier visits all the particles in the cluster. The diffusion coefficient will then depend only weakly on the typical cluster size. This criterion defines the fast-rearrangement regime. For times $t \ll T_R$ the random walkers see the fractal nature of the static structure and the diffusion will be anomalous[12,17] with $\langle R^2(t)\rangle \sim t^{\tilde{d}/D_f}$.

One can use this analysis to generalize Eq. (1) into a complete scaling relation:[18]

$$D(p-p_c,\tau)=\frac{1}{T_R}|p-p_c|^{-(2\nu-\beta)}f\left(\frac{\tau}{T_R}\right) \ , \tag{2a}$$

$$f(x)=\begin{cases}1, & x \ll 1 \ ,\\ x^{-\tilde{d}(2\nu-\beta)/2\nu D_f}, & x>1 \ .\end{cases} \tag{2b}$$

Equation (2b) predicts that for p sufficiently close to p_c, D depends only on the p-independent rearrangement time as $D\sim(T_R)^{-\mu/(\mu+\tilde{s})}$ where $\tilde{s}=2\nu-\beta$.

To test the scaling hypothesis of Eq. (2) we have carried out numerical simulations and calculated the diffusion coefficient for the lattice model described above. The simulations were carried out on a 400×400 square lattice, where a fraction p of the sites are occupied by cluster particles. $N_w=1000$ "blind" random walkers[19] (representing the charge carriers) are placed randomly on occupied sites. The random walkers (RW's) do not interact with one another. A large number of independently diffusing RW's were chosen in order to achieve good statistics.

The two microscopic times in the simulation are (a) the time it takes each RW to attempt a move (this time is taken to be unity) and (b) the time it takes for each cluster particle in the system to attempt one move. In practice, we move each random walker m steps and then move a randomly selected fraction ϕ of cluster particles once. The ratio of these two microscopic times is $\gamma\equiv1/T=\phi/m$. The diffusion coefficient was determined from long runs, typically $(3\text{–}5)\times10^5$ RW steps, which was long enough to be in the diffusive regime where

$$R^2(t)\equiv\frac{1}{N_w}\sum_i[\mathbf{r}_i(t)-\mathbf{r}_i(0)]^2\sim Dt \ .$$

The smallest diffusion constant we could accurately measure was $D\sim3\times10^{-4}$, so that for the smaller values of γ, we could not go to as low a probability p as for larger γ. For each value of γ, we used several values of ϕ and m, to be convinced that the results for the diffusion coefficient of the random walker depended only on γ. This was true for small $\phi \ll 1$; however, for large $\phi\sim1$, D depends on both γ and m. For all of the data presented here, D depends only on γ.

A semilog plot of diffusion coefficient versus p is shown in Fig. 1. For values of $\gamma \gtrsim 10^{-2.5}$, there is a rather smooth transition at $p_c=0.59$, and the transition becomes steeper with decreasing γ. Although we have no numerical results for γ of order unity, it is quite obvious that the percolation threshold would not be reflected in the behavior of D. At p_c, $D\sim\gamma^{\rho}$ as predicted by Eq. (2), where $\rho=\mu/(\tilde{s}+\mu)$. The normalized diffusion coefficient $D(p-p_c)|p-p_c|^{\tilde{s}}/\gamma$ is plotted versus the scaling variable $|p-p_c|^{\mu+\tilde{s}}/\gamma$ in Fig. 2 for $\tilde{s}=s=1.28$ and $\tilde{s}=2.53$. Clearly the scaling relation $\tilde{s}=s$ does not fit the data. Figure 2 also shows that scaling is obeyed very well for $\tilde{s}=2\nu-\beta$, for which all the data collapse onto a single curve. Experimental results[1,2,5] for microemulsions in 3D find $\tilde{s}=1.2$, consistent with the result $\tilde{s}=2\nu-\beta=1.2$. While our 2D simulations determine $\tilde{s}=2.6\pm0.3$ with only moderate precision this is in good agreement with[15] $2\nu-\beta=2.53$. The possibility $\tilde{s}=s$ is definitely ruled out. The crossover from the slow rearrangement regime, where D changes as $|p-p_c|^{-(2\nu-\beta)}$ and depends linearly on γ, to the fast rearrangement regime, in which D depends on γ as a power law is clearly seen.

For the dynamic system studied here, the diffusion coeffi-

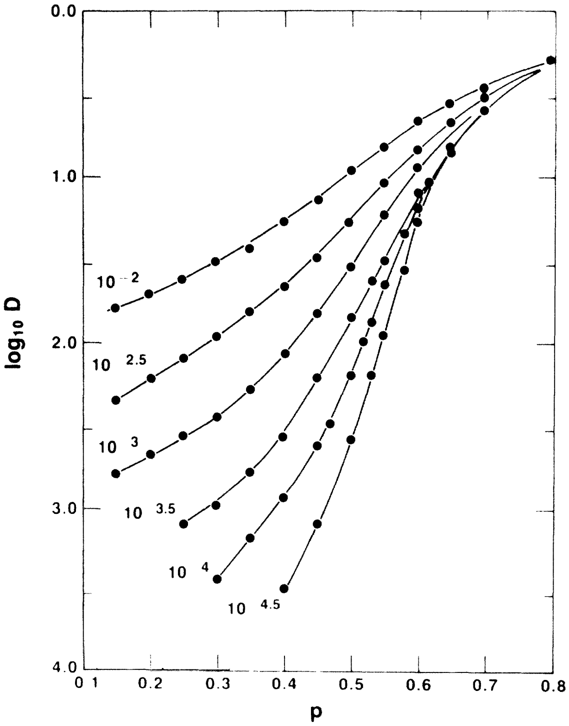

FIG. 1. Diffusion constant D in 2D vs the fraction p of occupied lattice sites for six values of γ, where γ is the ratio of the time for each random walker to attempt a move to the time for each cluster particle to attempt one move.

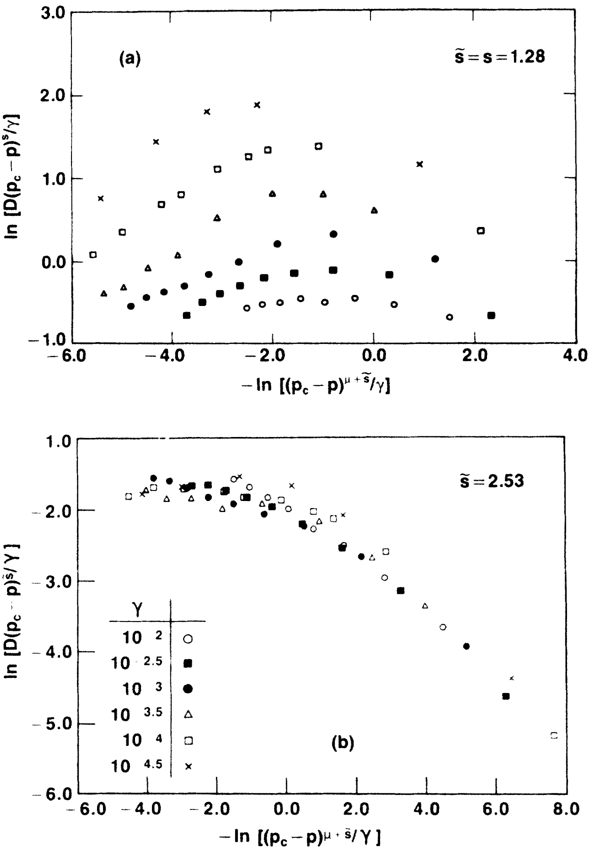

FIG. 2. Normalized diffusion coefficient from Fig. 1, plotted vs the scaled variable $|p-p_c|^{\tilde s+\mu}/\gamma$, with (a) $\tilde s = s = 1.28$ and (b) $\tilde s = 2\nu - \beta = 2.53$.

cient D and the conductivity Σ of the system are proportional to each other. In this respect, diffusion on dynamic percolation clusters differs from diffusion on static percolation system, where for $p > p_c$, $\Sigma = D|p-p_c|^{\beta}$, where $|p-p_c|^{\beta}$ is the probability that a site is in the infinite cluster. In the dynamic system above p_c, the distinction between the infinite cluster and the finite clusters becomes meaningless for times larger than T_R.

ac conductivity measurements[1,2] on microemulsions can provide information on the conductivity mechanism, due to the introduction of an extra time scale, the driving frequency ω. The scaling expression for the dc conductivity, including ω and τ is

$$\Sigma(p-p_c,T_R,\omega) = (p-p_c)^{-(2\nu-\beta)}\psi(\omega\tau,\tau/T_R) \ . \tag{3}$$

For $x/y \sim \omega T_R \ll 1$ the frequency does not play a significant role due to the rearrangement which takes place on times much shorter than ω^{-1}. Thus, $\psi(x \ll y) \sim (1/T_R)f(y)$ as given by Eq. (2b). For $\omega T_R \gg 1$ we expect $\Sigma(p-p_c,T_R,\omega)$ to be independent of T_R, with scaling similar to the dc case, save that the variable is $\omega\tau$.[17] These limits are obeyed for

$$\psi(x,y) = (\alpha x + \beta y) f(\alpha x + \beta y) \ , \tag{4}$$

where f is the scaling function defined in Eq. (2) and α,β are (possibly complex) constants of order unity. The scaling form of Eq. (4) can be heuristically demonstrated by invoking the Kubo relation for the frequency-dependent diffusion coefficient,

$$D(\omega,T_R) \propto \int \langle V(t)V(0)\rangle e^{-i\omega t}dt \ , \tag{5}$$

where $\langle V(t)V(0)\rangle$ is the velocity autocorrelation function of the charge. Assuming that the hopping of the charge and the breakup of the cluster are uncorrelated,

$$\langle V(t)V(0)\rangle = \langle V(t)V(0)\rangle_c e^{-t/T_R} \ , \tag{6}$$

where $\langle V(t)V(0)\rangle_c$ is the autocorrelation function for $T_R \to \infty$ and $\exp(-t/T_R)$ represents the probability that the cluster has not rearranged at time T_R. Writing $\langle V(t)V(0)\rangle_c$ in the scaling form we find

$$\langle V(t)V(0)\rangle_c \sim \frac{1}{\tau^2}\phi(t/\tau) \ . \tag{7}$$

Inserting Eq. (7) into (5) and comparing with (3), we see that

$$\Sigma(p-p_c,T_R) = \tau^{-1}\int \phi(y) e^{-\tau y/T_R} dy \ . \tag{8}$$

By comparison

$$D(p-p_c,T_R,\omega) = (T_R^{-1}+\omega)(p-p_c)^{-\tilde s} f(i\omega\tau + \tau T_R^{-1}) \ . \tag{9}$$

Because the conductivity is dominated by hopping, Σ and D are proportional by the Einstein relation. At $p = p_c$ we predict a frequency-independent conductivity for $\omega < 1/T_R$ followed by a power-law behavior with an exponent $\mu/(\tilde s + \mu)$ at higher frequencies. Recently this prediction has been confirmed by Bhattacharya *et al.*[1] and VanDijk.[2] The study of $\Sigma(\omega)$ near p_c can give information on the magnitude of T_R, which can be compared with other data such as that from inelastic light scattering[6] in order to understand the dynamics of microemulsions.

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[19] The random walkers are "blind" in the sense that they attempt to move to all neighboring sites with equal probability. If the site is occupied, the move is accepted, while if the site is unoccupied the random walker does not move.