Dispersed Ionic Conductors and Percolation Theory

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We suggest that ionic conductors containing a dispersed insulating phase are suitable materials for investigating static and kinetic aspects of percolation. We develop a lattice model for the two-phase mixture with special emphasis on the role of an enhanced interface conductivity. By using two-dimensional Monte Carlo simulations we show that our model correctly describes the distinct conduction properties of those materials, and in addition displays the critical behavior of both random-superconducting and random-resistor networks at two different critical concentrations.

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Ionic conductors like LiI or AgI show an enhanced conductivity after addition of small particles of an insulating second phase, e.g., of Al_2O_3.[1,2] Enhancements up to two orders of magnitude have been reported, initiating considerable practical interest in these materials as suitable electrolytes in solid-state batteries. Physically, it is widely accepted that the overall effect is a result of an enhanced conductivity along the interface between the conducting matrix and the dispersant particles, possibly through the formation of space-charge layers.[3]

In this Letter we suggest that materials of that type are unique examples for studying various aspects of percolation.[4] Our concern is the charateristic dependence of the overall conductivity σ on composition, as observed through experiment. The conductivity shows a marked initial increase with dispersant concentration p, followed by a rapid drop,[1,2] which seems to extrapolate to zero at some threshold concentration. We construct a lattice model which incorporates the effect of an enhanced interface conductivity and investigate the conductivity by Monte Carlo simulations. Our results correctly describe the main features of the measured function $\sigma(p)$. A detailed analysis shows that our model may display the critical properties of both a random resistor network[5-9] and a random superconducting network[5,6,9-12] near certain threshold concentrations p_c and $1-p_c$, respectively.

In our quantitative study, we start from a two-dimensional square lattice and generate our two-phase mixture by producing random occupation of unit squares with probability p. Representative examples are shown in Fig. 1 for a few values of concentration p. The sides of the squares are called bonds and have three different conductances. Consider a given bond and its two adjacent squares. If both squares are occupied, the conductance is zero; if only one of them is occupied the conductance is taken as σ_A, the interface conductance. Finally, if none of them is occupied, the conductance is σ_B. In this way we model the conductance properties of a composite system containing a fraction p of insulating phase in a conducting matrix, with the special feature of a modified interface conductivity.

Let us now assume that $\sigma_A >> \sigma_B$ and discuss the qualitative behavior of the conductivity as expected from Figs. 1(a)-1(c). For small p there are preferred paths connecting the surface of isolated clusters, giving rise to a certain enhancement of the current flow. A pronounced increase of the conductivity is expected for the situation shown in Fig. 1(b), where a macroscopic path consisting only of σ_A bonds is formed for the first time. In two dimensions, this onset of "interface percolation" precisely coincides with the threshold p_c' for percolation of next-nearest-neighbor clusters. In the square lattice, $p_c'=1-p_c$, where $p_c \simeq 0.593$ is the threshold for nearest-neighbor percolation.[4] On increase of p, the conductivity will first go further up. However, beyond the threshold $p_c''=1-p_c'$ for percolation of next-nearest-neighbor clusters of the conducting material (which equals p_c here), we have $\sigma=0$ [see Fig. 1(c)]. Thus, the enhancement mechanism destroys itself shortly after becoming most effective.

Now we turn to the quantitative analysis of the conductivity σ, which we achieve by mapping our resistor model on a random walk. The walker jumps between sites which are the end points of the bonds, with hopping rates $\tau_A^{-1} \propto \sigma_A$, $\tau_B^{-1} \propto \sigma_B$, and $\tau_0^{-1}=0$, corresponding to the three types of bonds introduced above. In order to deal with hopping rates τ_A^{-1} and τ_B^{-1} with an order-of-magnitude difference, we follow a method of Ref. 11, recently developed for diffusion in random composite media.[13] Here we use the following rules. Initially, the walker is either on sites belonging to the conducting matrix or on ones belonging to the inter-

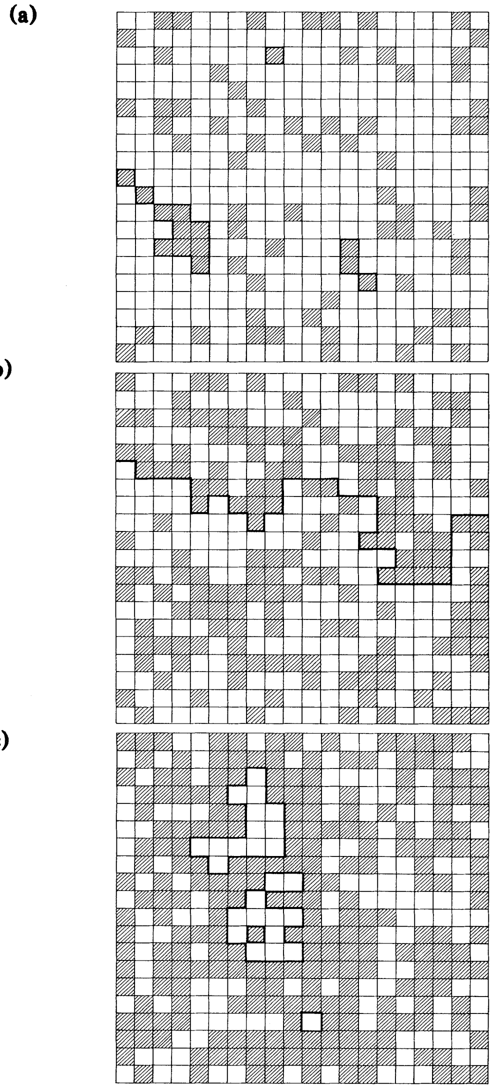

FIG. 1. Graphs of our two-phase mixture for three concentrations p of the insulating phase. Shaded clusters correspond to the dispersed phase. Some of the paths involving only highly conducting σ_A bonds are marked by dark lines. (a) $p=0.2$, dilute systems; (b) $p=0.407$, onset of interface percolation at $p_c'=1-p_c$; (c) $p=0.593$, disruption of conducting paths at $p_c''=p_c$.

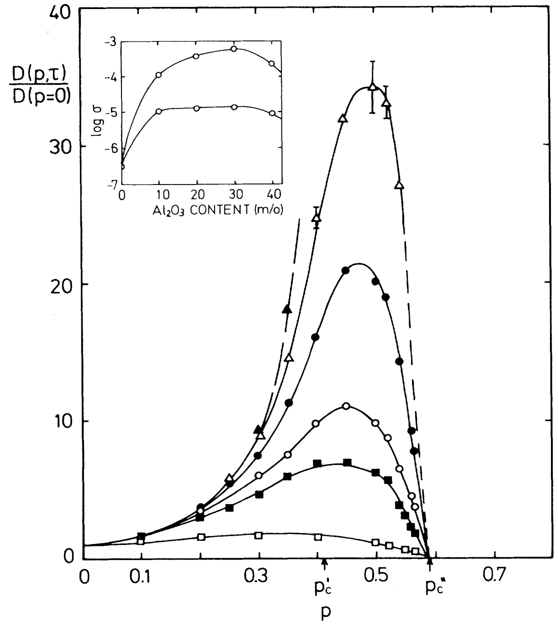

FIG. 2. Diffusion constant as a function of p for different ratios $\tau=\sigma_A/\sigma_B$ between interface and bulk conductance. Open square, $\tau=1$; filled square, 10; open circle, 20; filled circle, 50; open triangle, 100; and filled triangle, 200. Error bars of simulation data for $\tau=100$ are indicated. The inset shows experimental results on a logarithmic scale for the conductivity in units of Ω^{-1} cm^{-2} for AgI-Al_2O_3 mixtures, the upper and lower curve corresponding to undried and dried Al_2O_3, respectively (after Ref. 2, reprinted by permission of the publisher, The Electrochemical Society, Inc.).

face. Within the conducting matrix the walker proceeds at random in any direction with one step per unit of time. Once the walker has arrived at an interface site it chooses at random one of the four possible directions, which corresponds either to an insulating bond, to a σ_A bond, or to a σ_B bond. Then with probability 0, 1, or $\tau^{-1}=\tau_A/\tau_B \leq 1$, respectively, the walker will step along the attempted direction. For steps along the interface, time will not be counted. Thus, the walker will spend about τ steps in the interface within one unit of time, which corresponds to the desired enhancement of the interface diffusion by a factor of τ.

We calculated the mean square displacement $\langle r^2(t)\rangle$ of the walker as a function of time t by using the Monte Carlo method. Our simulations were carried out on a square lattice of size 500×500. To obtain $\langle r^2(t)\rangle$ we averaged over typically 2×10^3 initial configurations, consisting of 200 random lattice configurations with ten walks on each lattice. The asymptotic regime of the walk, where $\langle r^2(t)\rangle \simeq Dt$, was reached at about 10^3 time steps for $p<0.5$. For larger concentrations, in the neighborhood of p_c'', sometimes more than 10^6 time steps were needed. In this way we determined the diffusion constant D, which is proportional to the conductivity σ according to the Nernst-Einstein relation.[11]

Results for different values of τ are summarized in Fig. 2. The qualitative features of our curves are in close agreement with the measured dependence of the conductivity on the content of insulating material. Extrapolation of our data shows that a value of $\tau\sim500$ would be needed to produce a maximum conductivity enhancement of two orders of magnitude. Such an enhancement can be reasonably accounted for by a

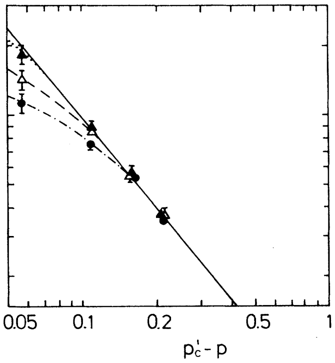

FIG. 3. Logarithmic plot of the diffusion constant vs $p_c'-p$, where $p_c'=1-p_c$, for $\tau=50$ (filled circle), 100 (open triangle), and 200 (filled triangle). The straight line corresponds to the exponent $s=1.3$.

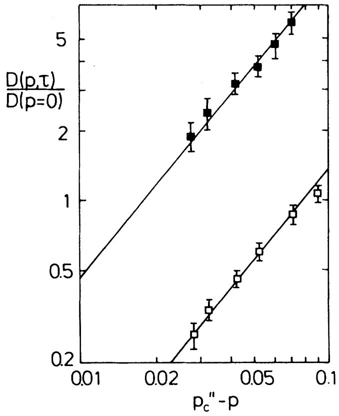

FIG. 4. Logarithmic plot of the diffusion constant vs $p_c''-p$, for $\tau=1$ (open square) and $\tau=10$ (filled square). The straight line corresponds to the exponent $\mu=1.3$.

space-charge-layer model, where the increased interface conductivity is attributed to an excess of defects at the interface.[3] It is well known[1,2] that the measured ratio $\sigma(p,\tau)/\sigma(0)$ depends on the detailed conditions of sample preparation, in particular on the water content of the Al_2O_3 phase. Changing the water content therefore offers the intriguing possibility of varying our parameter τ experimentally.

Keeping this point in mind we now analyze our results in more detail. First we note that for p well below p_c' the diffusion constant $D(p,\tau)$ saturates rapidly for larger τ. The following interpretation is obvious. If τ is such that after τ moves the walker will leave the surface of a cluster of insulating component at any site with nearly the same probability, then a further increase of τ would no longer be advantageous, i.e., σ saturates. The limiting function $D(p,\infty)$, which diverges at p_c', corresponds to a "superconducting" interface. It should therefore display the characteristic critical behavior observed in a random superconducting network near the percolation threshold.[9–12]

To test this we have plotted D vs $\epsilon'=p_c'-p$ for different τ up to our largest value $\tau=200$ (see Fig. 3). For large τ and small ϵ' our data tend to assume a power-law divergence,

$$D\sim(p_c'-p)^{-s}, \tag{1}$$

where s is compatible with the accepted exponent[4] $s\simeq1.3$. We have also confirmed that close to p_c', $D(p,\tau)$ satisfies the scaling relation[11]

$$D(p,\tau)=\tau^{u}H(\epsilon'\tau^{\phi}), \tag{2}$$

where $\phi=u/s$ and $u=0.5$ in two dimensions.[6] Within our numerical accuracy the normalized scaling function $h(x)\equiv H(x)/H(0)$ coincides with the corresponding scaling function found for two-component mixtures.[11] This indicates that our system near p_c' belongs to the same universality class as usual two-component systems near p_c.

In the vicinity of the percolation threshold p_c'' the blocking effect becomes dominant. Then the diffusion constant tends to zero. Figure 4 shows that our data, for fixed τ, are consistent with the well-known power law

$$D\sim(p_c''-p)^{\mu},\quad \mu=s, \tag{3}$$

which describes the critical behavior of the diffusion constant in random resistor networks.[5–9]

In summary, we have shown that ionic conductors containing a dispersed insulating phase are good candidates to investigate the predictions of kinetic percolation theory in a real system. Although we have considered a two-dimensional system here, we expect the essential physics to remain unchanged in three dimensions. In three dimensions, the percolation of clusters of cubes having one corner in common must be considered and we expect the critical indices μ and s to change to $\mu\simeq2.0$ and $s\simeq0.7$.[4] These exponents should be detectable in dispersed ionic conductors and, in addition, the interesting phenomenon of anomalous diffusion[7–12] in both the random resistor and the random superconducting network might become experimentally accessible.

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