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Conductivity of a Three-Component "Reactive" Percolation Model

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We consider a new kind of percolation model in which sites can be occupied by two kinds of "atoms," A or B, or by "molecules" formed from A and B. Introducing plausible models for conductivity we find numerically that the total sample resistivity ρ can be a nonmonotonic function of the total concentration of free and bound A. These results are qualitatively consistent with recent experiments on solid mixtures of sodium and ammonia. We discuss other features of the model qualitatively.

In recent years, there has been widespread interest in applying simple percolation models[1] to account for a variety of phenomena as diverse as disease propagation, electrical conduction in amorphous solids, and tertiary recovery of oil from porous rock.[2] We recall that a simple percolation model is specified by a lattice, and a rule for inserting conductive nodes (site percolation) or bonds (bond percolation) on the lattice. Recently Zallen[3] has introduced "polychromatic" percolation models in which the sites can be occupied by more than two kinds (colors) of entities. In the present Letter we introduce a model corresponding to three "colors" in Zallen's terminology but with an added constraint on the concentrations which arises from the condition that two of the species interact chemically to form the third. In this new model we also present the first transport calculations made for any polychromatic model. The transport results are qualitatively similar to recent experimental results[4] on the conductivity of solid mixtures of sodium

and ammonia.

To describe the model, we consider two types of "atoms" A and B which can react via

$$A + B \rightleftarrows AB \tag{1}$$

to form "molecules" AB. For a fixed ratio of the total number of A's to the total number of B's, we then have N_A free A's, N_B free B's, and N_{AB} "molecules." We let N_s be the number of lattice sites and N the total number of "atoms" (free or in molecules). We define $X_A = N_A/N_s$, $X_B = N_B/N_s$, $X_{AB} = N_{AB}/N_s$, and $X = (N_A + N_{AB})/N$. Then X_A, X_B, and X_{AB} are fixed by the following conditions. First, the lattice is filled:

$$X_A + X_{AB} + X_B = 1. \tag{2}$$

Here there is one molecule per site. Secondly, Reaction (1) is characterized by equilibrium constant K:

$$X_A X_B = K X_{AB}. \tag{3}$$

Thirdly, X is fixed by experiment. Combining

the definition X with Eq. (2) one has

$$X = \frac{X_A + X_{AB}}{1 + X_{AB}} . \tag{4}$$

Solutions to Eqs. (2)–(4) are easilty obtained and are shown for a few values of K in Fig. 1. The results for $K = 0$ have a particularly simple interpretation: The minority species is only found in "molecules." The limit $K \to \infty$ corresponds to no "molecules," so that in the limit $K \to \infty$ we recover a simple percolation problem.

To complete the specification of the extended percolation model, we now specify a lattice. (In our numerical work we have used a three-dimensional simple-cubic lattice.) At each site we place a "free" A with probability X_A, a "molecule" with probability X_{AB}, and a "free" B with probability X_B.

With the resulting network one can pose questions concerning static critical properties which are natural analogs of the corresponding questions in the percolation problem.[1] For example we can study the probabilities $P_A(X)$, $P_B(X)$, and $P_{AB}(X)$ of infinite clusters of A, B, and AB, respectively; and $S_A(X)$, $S_B(X)$, and $S_{AB}(X)$, the mean-square cluster sizes of A, B, and AB, respectively. Because our primary interest was in the transport properties of the model, we confine ourselves in this preliminary report to some qualitative remarks on static critical properties: At $K = 0$ there will be four critical values of X, corresponding to values (with increasing X) of $X_{c,+}{}^{AB}$ at which $P_{AB}(X)$ becomes finite, $X_c{}^B$ at which P_B

goes to zero, $X_c{}^A$ at which P_A becomes finite, and $X_{c,-}{}^{AB}$ at which P_{AB} goes to zero again. These critical values of X for $K = 0$ are indicated in Fig. 1 for a simple-cubic lattice and one molecule per site. As K increases from zero these critical values of X can be seen to behave as follows: At a value K_1 of K, X, $X_c{}^B = X_c{}^A$. For the simple-cubic lattice with one molecule per site, we estimate $K_1 \simeq 0.24$. At a second value K_2 of K, $X_{c,+}{}^{AB} = X_c{}^A$ and $X_{c,-}{}^{AB} = X_c{}^B$; for the simple-cubic third value K_3 of K, $X_{c,+}{}^{AB}$. For $K > K_3$ there is no infinite molecular cluster ($K_3 = 0.381$ for the simple-cubic lattice). In Fig. 2, we show the phase diagram for the simple-cubic lattice (for which $x_c \simeq 0.31$) using a diagram of a type introduced by Zallen.[3]

To explore the conductive properties of this model we computed the conductivity numerically for a number of models for the nearest-neighbor conductances. We distinguish models for which the molecule at a site is regarded as isotropic for the purposes of modeling conduction from models in which the molecule is regarded as anisotropic. In the isotropic model we have just six nearest-neighbor conductive parameters. For a special case, the conductivity of this model can be determined from numerical results[5] on the simple percolation model without additional numerical computation. The special case is that for which $\sigma_{A-A} = 1.0$, $\sigma_{AB-AB} \neq 0$, $\sigma_{AB-B} = \sigma_{AB-A} = \sigma_{B-B} = \sigma_{A-B} = 0$. The conductivity of the system will in
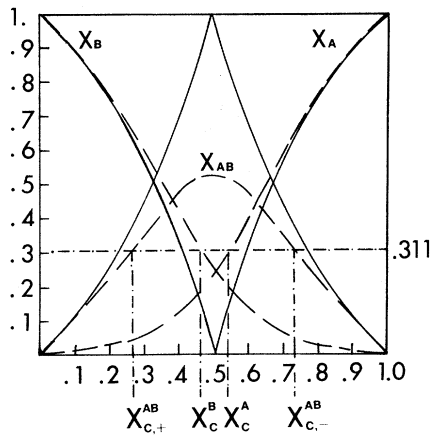

FIG. 1. Solutions to Eq. (2)–(4) for $K = 0$ (full lines) and $K = 0.1$ (dashed lines). Dash-dotted horizontal line is X_C for simple cubic lattice. $X_{C,\pm}{}^{AB}$, $X_C{}^{A,B}$ are defined in the text.
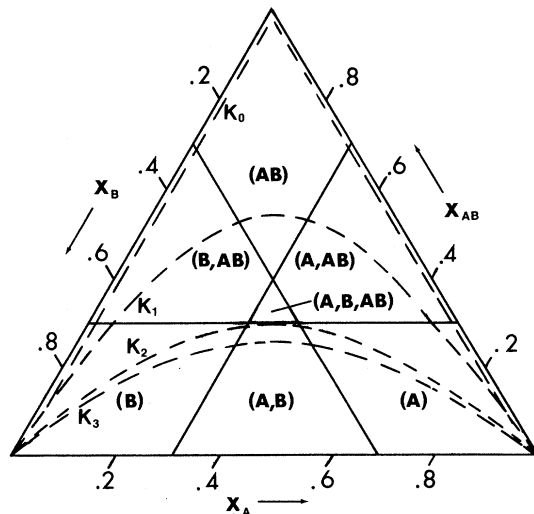

FIG. 2. Phase diagram for the model. Format is as in Ref. 3. Dotted lines show various K values: $K_0 = 0$, $K_1 = 0.1$, $K_2 = 0.381$, $K_3 = 0.5$.

this case be the sum of the conductivity of a simple percolation model with site concentration X_A and nearest-neighbor conductance 1 plus the conductance of another simple percolation model with site concentration X_{AB} and nearest-neighbor conductance σ_{AB-AB}. We thus get the result by scaling the numerical results of Kirkpatrick[5] as shown in Fig. 3 as the full line when $\sigma_{AB-AB} = 0.1$. One sees that the nonmonotonicity of ρ arises from the infinite cluster of "molecules" which produces a dip in ρ at $X = 0.5$. The dots in Fig. 3 show our numerical data for 10^3 sites for the same model. These results indicate that our numerical results are reliable to within about 10% in the worst cases. The numerical technique used is a standard iterative one. (In the numerical calculations we took the conductances σ_{A-B} $= \sigma_{AB-A} = \sigma_{AB-B} = \sigma_{B-B} = 0.001$ instead of zero.) Figure 4 shows that for finite values of K and σ_{AB-A}, the sharp structure in ρ seen in Fig. 3 is softened.

We have also studied two models in which the molecules are anisotropic, and one model in which there was $\frac{1}{2}$ molecule per site. All these other models, which will be described in more detail elsewhere, indicate that the dip structure in ρ versus X becomes sharper with decreasing coordination number.

Finally we comment on the comparison with the experiments in $Na_x(NH_3)_{1-x}$. The data from Ref. 4 appear in Fig. 5. Most of the qualitative features[6] appearing in the model calculation of Fig. 3 also appear in the experimental curve in Fig. 5. The positions of the maxima and the minima are very similar in the two curves. Remaining discrepancies may plausibly be due to uncertainties in relating the mole percent metal through the lattice invariant volume fraction to X for the simple-cubic lattice. Another good feature is that similar experiments[7] on $Na_x Ar_{1-x}$ show a monotonic ρ vs x curve as expected for our model if $K \to \infty$. On the other hand the relative magnitudes of the resistivities at $X = 1$, at the local maximum and at the minimum in $Na_x(NH_3)_{1-x}$ are not in good agreement: If we set $\rho_{min}/\rho (x = 1.0) \simeq 10^2$ as observed experimentally, then a calculation within the model gives $\rho_{max}/\rho (x = 1.0) \simeq 2.5 \times 10^2$ whereas
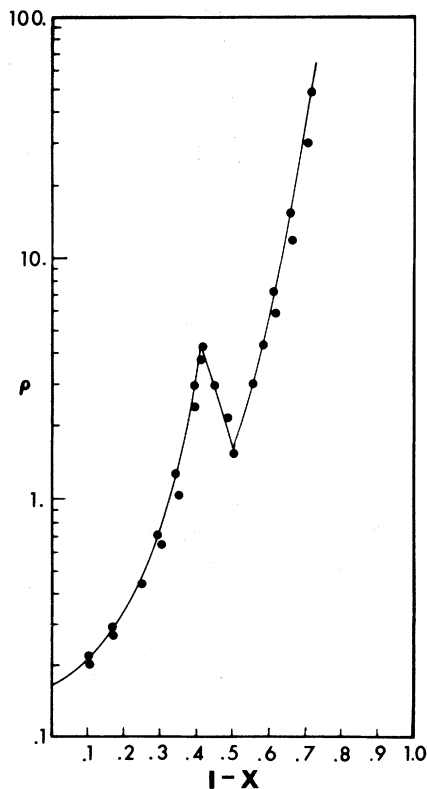

FIG. 3. Resistivity vs X for $K = 0$ and an isotropic conductive model. Units of ρ are arbitrary. See text for the significance of the dots and full line.
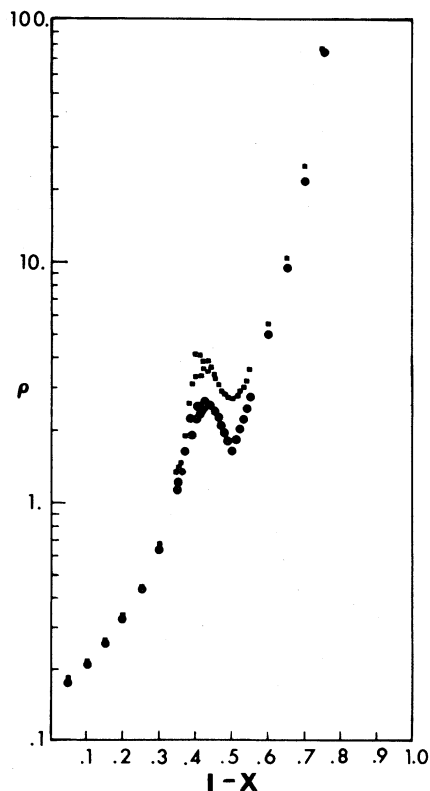

FIG. 4. Resistivity vs X for $K = 0.01$ (squares) and $\sigma_{AB-A} = 0.01$ (dots).
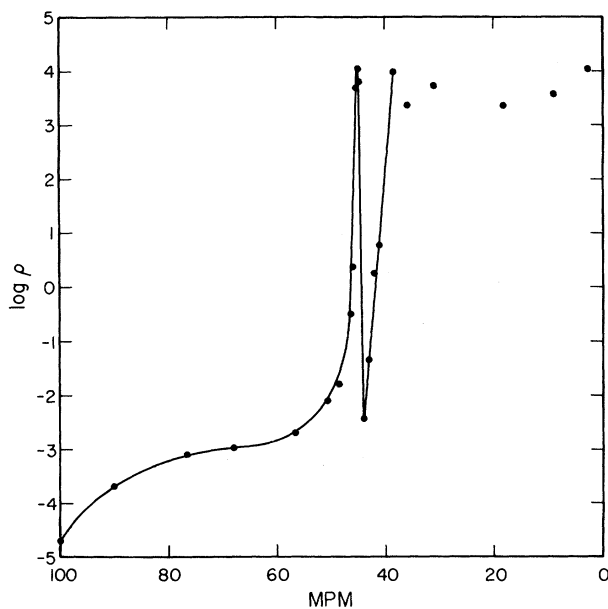
FIG. 5. Experimental data on resistivity ρ vs mole percent metal (MPM) for $Na_x(NH_3)_{1-x}$ from Ref. 4. Solid line is a guide to the eye.

the data apparently give $\rho_{max}/\rho(x=1.0) \gtrsim 6 \times 10^4$. We cannot account for this quantitive discrepancy at this time. We tentatively suggest that two factors may be entering it: Firstly, the experimental results for the ratios are very sensitive to small errors in the determination of X. Secondly, a simple-cubic lattic will certainly give a smaller ρ_{max} for $K=0$ than more open structures would give. This is evident from Fig. 1, bearing in mind[1] that X_c for a diamond structure is 0.425. Thus a model taking account of positional disorder and anisotropy in a way which reduced the effective coordination number below 6 would increase the ratio $\rho_{max}/\rho(X=1.0)$.

Comparing the model with the sodium-ammonia data raises the question of the physical identity of "molecules" in this case. We do not have a definite proposal in this regard but tentatively suggest the following. The reaction

$$Na + NH_3 \rightleftharpoons NaNH_2 + \tfrac{1}{2}H_2$$
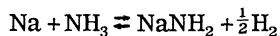
is known to occur[8] with a rate which is very sensitive to the presence of a wide variety of substances which act as catalysts. If suitable catalysts are present in the McNeal-Goldman experiment then we might identify AB with $NaNH_2$ (sodium amide). Unfortunately information on reaction rates and conductivity of $NaNH_2$ does not seem to be available for testing this suggestion. We note that the presence of H_2 in this case would reduce the effective coordination of the resulting lattice and therefore might enhance the local maximum in the resivitity as discussed in the preceding paragraph.

In summary we have introduced a new percolation model and made a preliminary exploration of its phase diagram and transport properties. The model appears to account qualitatively for recent data on resistivity in $Na_x(NH_3)_{1-x}$.

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