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Particle-size effect on the conductivity of dispersed ionic conductors

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A random-resistor model proposed recently for dispersed ionic conductors is generalized to study the effect of dispersed particle size on the conductivity of such composites. Monte Carlo calculations for two-dimensional systems are reported for square as well as rodlike particles of different size. It is found that the corresponding critical concentrations p_c' and p_c'', for interface percolation and the conductor-insulator transition, respectively, strongly depend on the size and shape of the dispersed particles. The generalized model thus offers the possibility of studying a variety of physical situations which are relevant to experiments.

Enhancement of the conductivity of ionic conductors by the addition of small insulating particles[1-4] has been established experimentally and the recently proposed random-resistor-network (RRN) model[5-7] (hereafter referred to as model I) was successful in providing an explanation for it. In particular, the existence of two critical concentrations of the insulating phase, namely, $p=p_c'$ for the onset of enhanced conductivity and $p=p_c''$ for the conductor-insulator transition, could be understood in terms of percolation thresholds. However, the experimentally observed[2,3] particle-size effects have not been explained so far for the whole range of concentrations of the insulating particles. It is the purpose of this paper to generalize the RRN model and present results on the particle-size effects in dispersed ionic conductors.

The basic physical picture of conduction in mixtures of a solid ionic conductor, such as LiI with fine particles of an insulator such as Al_2O_3 dispersed in it, is in terms of charge accumulation on the surface of the insulating particles. This in turn implies an enhanced interfacial conductivity. The RRN[5,6] model assumes the existence of three types of resistors: (a) insulating resistors representing the lack of conduction through the insulating particles, (b) highly conducting resistors representing the enhanced interfacial conductivity, and (c) normally conducting resistors representing the conduction in the pure ionic conductor. Thus, one has (a) and (b) types of resistors in a matrix of normally conducting resistors. This is then mapped onto the problem of a random walk on a lattice with three types of bonds (hopping rates), and the diffusion constant is calculated by means of Monte Carlo simulations. The reason for doing this is that one can find, in principle, the "numerically" exact solution of the problem. The result of the simulations shows that the enhanced conductivity starts at a critical concentration of the dispersed particles corresponding to the onset of percolation of the highly conducting bonds. However, as the concentration p increases, one encounters the second critical concentration where the conducting bonds start forming closed loops inside the system and the conductivity drops drastically, leading to the conductor-insulator transition.

In two dimensions, one considers a square lattice in which an insulating particle is represented by a randomly

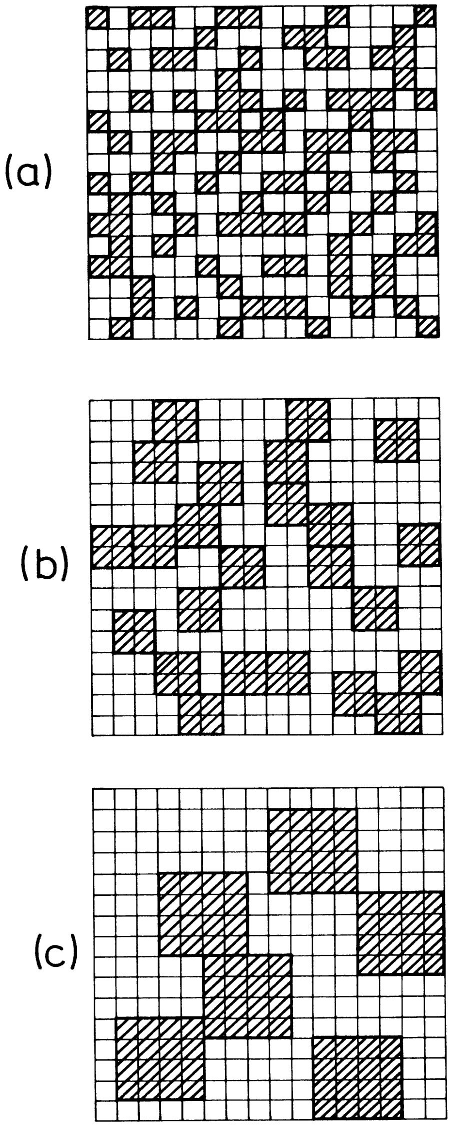

FIG. 1. Generalized random-resistor-network model for the concentration $p=0.375$ with particle sizes (a) $s=1$, (b) $s=2$, and (c) $s=4$.

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occupied unit square with the occupation probability p. This is shown in Fig. 1(a). The hopping rate associated with a bond of the lattice depends upon the occupation of both the adjacent squares. When both the squares are occupied, the hopping rate is zero and when both the squares are empty, the hopping rate is taken to be unity, representing normal conduction of the pure ionic conductor. Finally, when only one of the squares is occupied, the hopping rate is taken as $\tau \gg 1$ corresponding to the high interfacial conductivity. The generalization of this model is illustrated in Figs. 1(b) and 1(c). We introduce an additional parameter s called the particle-size parameter. For $s=1$, the earlier RRN model is obtained as in Fig. 1(a). For $s=2$ and 4, one has bigger squares representing larger particles (the area of the particles is proportional to s^2). The concentration of the particles is now a function of s given by

$$p = ns^2/L^2 \ , \tag{1}$$

where n is the total number of insulating particles and L is the length of the lattice. It is important to note that this generalized model is not a trivial extension of the original RRN model.[5,6] The new concentration of different bonds is no longer known exactly as for model I (Ref. 6) and the new percolation thresholds that arise cannot be related to values already known in the literature. Moreover, a careful inspection of Figs. 1(b) and 1(c) indicates that the general model ($s > 1$) cannot be reduced to model I by a simple rescaling of distance, and, therefore, constitutes a new model in itself.

In order to determine quantitatively the diffusion constant $D(p)$, we use the following rules[6] for the random walk: (i) The probability Π_δ that the walker takes a step from a given site to one of its z nearest neighbors in the direction δ is proportional to the hopping rate τ_δ^{-1} in that direction (admissible values of τ_δ^{-1} are 0, 1, and τ). Since $\sum_{\delta=1}^{z} \Pi_\delta = 1$ we have

$$\Pi_\delta = \tau_\delta^{-1} \Big/ \sum_{\delta=1}^{z} \tau_\delta^{-1} \ . \tag{2}$$

(ii) The total elapsed time t after N_1 steps along normal bonds and N_2 steps along the highly conducting bonds, is given by

$$t = N_1 + N_2 \tau^{-1} \ . \tag{3}$$

(iii) For large times t, the mean-square displacement of the walker $\langle r^2(t) \rangle$ is proportional to $D(p)t$, and $D(p)$ is proportional to the conductivity by the Nernst-Einstein relation. We have performed Monte Carlo simulations on a square lattice of size 500×500 and used periodic boundary conditions. To obtain $D(p)$ we calculated $r^2(t)$ for $t \sim 10^4$ and averaged it over typically 500 configurations.

The generalization of the RRN model described above is suitable for understanding the hitherto unexplained particle-size effects observed experimentally[2,3] in dispersed ionic conductors. Our results from Monte Carlo simulations show a similar effect. In Fig. 2, we have shown the diffusion constant $D(p)$ as a function of the concentration p for different values of τ. As the particle size varies from $s=1$ [Fig. 2(a)] to $s=4$ [Fig. 2(c)], the peak height of $D(p)$ for constant τ decreases and the peak position moves to higher concentrations. The fact that $D(p)$, for fixed p, decreases with increasing s, can be understood by noting that the corresponding fraction of highly conducting bonds decreases with s [compare Figs. 1(a)–1(c)]. One also expects a shift in the position of the maximum since the threshold for interface percolation p_c' occurs at higher concentrations when the particle size in-

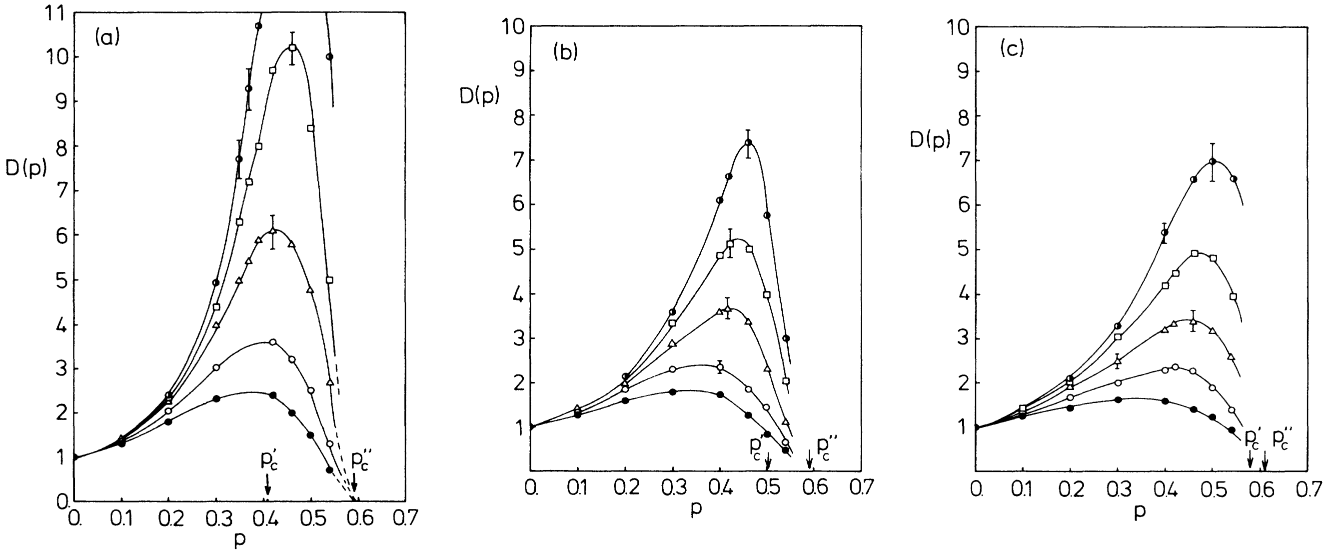

FIG. 2. Diffusion constant $D(p)$ as a function of concentration p for different values of τ [(●) 10, (○) 20, (△) 50, (□) 100, (◑) 200] with particle sizes (a) $s=1$, (b) $s=2$, and (c) $s=4$. The arrows show the values of p_c' and p_c''. A few error bars are indicated. The lines are a guide to the eye.

TABLE I. Percolation thresholds for the RRN model of dispersed ionic conductors.

s	p_c'	p_c''
	(a) Square particles	
1	0.407	0.593
2	0.51 ± 0.01	0.59 ± 0.01
4	0.58 ± 0.02	0.61 ± 0.02
	(b) Rodlike particles	
4	0.41 ± 0.01	0.45 ± 0.01
8	0.36 ± 0.02	0.38 ± 0.02

creases, while the second threshold remains almost unchanged by increasing s. We have determined values of p_c' and p_c'' by means of a standard method used in percolation calculations.[8] We explain it briefly here. The idea is to study the probability $P(p,L)$ that a lattice of linear size L percolates at concentration p. This function has a characteristic smooth step shape which becomes more pronounced by larger L. By definition one can take the value of p at which $P(p,L)=\frac{1}{2}$ to correspond to the critical value $p_c(L)$ for a given L. In the limit $L \rightarrow \infty$ one obtains the asymptotic value p_c for infinite systems. In practice the problem reduces to determine whether a cluster percolates or not for a given L and to perform an average over several configurations. We have worked with $L \leqq 100$ and averaged over about 1000 configurations. Our values of p_c' and p_c'' are listed in Table I. Since the fluctuations of the percolative properties in a finite system near the critical points are stronger, the larger the particle size, the resultant accuracy in our values of p_c', p_c'' for larger s is correspondingly lower.

The effect of the particle size is clearly seen in Fig. 3 where for a fixed value of $\tau = 100$, we have plotted the diffusion constant $D(p)$ as a function of the particle size s. The different curves are for different concentrations ($p = 0.46$, 0.40, 0.33, and 0.30). In order to perform a quantitative comparison with experiments one should note that different values of τ in our model correspond to different temperatures[6] in the experiment. Our results can be compared with those of Ref. 2 (inset in Fig. 3); the qualitative agreement is very good.

A further support for our model is obtained from the experimental results on the conductivity of $CuCl(Al_2O_3)$ as a function of Al_2O_3 particle size.[3] In such compounds a rapid drop is first observed in the conductivity σ for fixed temperature, as the size of Al_2O_3 particles increases. Later, σ tends to saturate for larger sizes.

A very interesting situation arises when one has (randomly oriented) rodlike particles of different sizes. The critical concentration p_c' for the onset of high conductivity does not change appreciably with increasing length l of the rods, but the second threshold p_c'' (see Table I) for conductor-insulator transition decreases rapidly as l in-

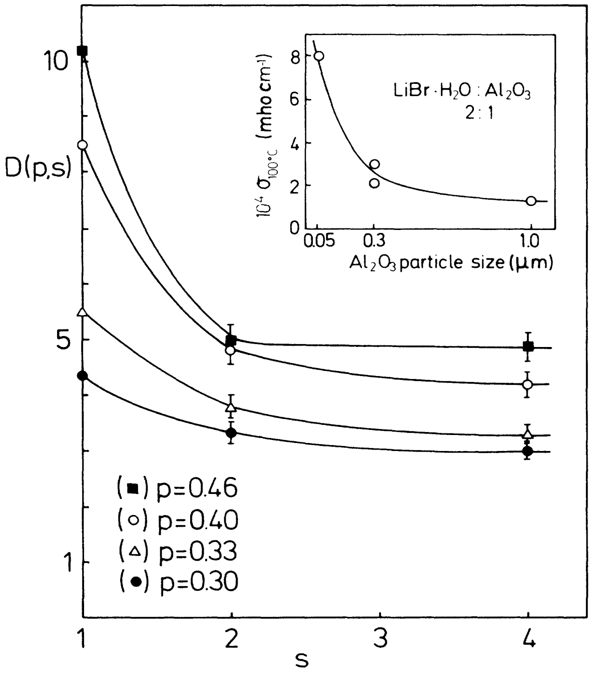

FIG. 3. Diffusion constant $D(p)$ as a function of particle size s for fixed $\tau = 100$ and different concentrations. The inset shows the experimental results (Ref. 2) for the conductivity of $LiBr \cdot H_2O$-Al_2O_3 system as a function of Al_2O_3 particle size. A few error bars are shown. The lines are drawn as a guide.

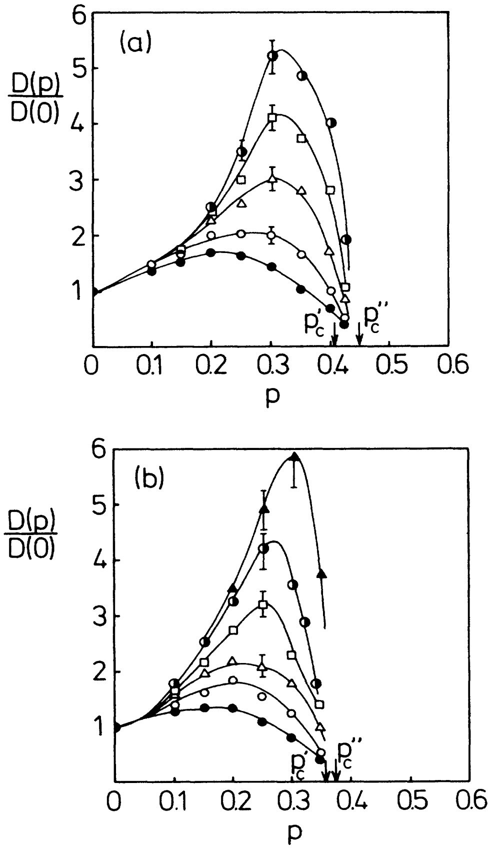

FIG. 4. Same as in Fig. 2 for rodlike particles as a function of particle size (a) $l = 4$ and (b) $l = 8$, for different values of τ [(●) 10, (○) 20, (△) 50, (□) 100, (◑) 200 and (▲) 500].

creases. This is physically reasonable because the longer the rods, the easier it is for them to form closed loops and destroy conducting paths. Clearly, in the case of rods, a more realistic model would be the continuous percolation analog. In the latter, the rods can assume any possible orientation without the restriction imposed by the lattice. Furthermore, the problem of continuum percolation of rods has been extensively studied in the past and the analytic dependence of the percolation threshold on particle anisotropy is known in some cases.[9] We proceed now with the discussion of our results on rods. In Fig. 4, we have shown the values of $D(p)$ as a function of the concentration, for various values of τ for $l=4$ [Fig. 4(a)] and $l=8$ [Fig. 4(b)]. This behavior of $D(p)$ is similar to that displayed by the conductivity[10] of AgI (fly ash) and one may expect that a similar mechanism as for long rods in two dimensions is playing a role in such compounds. Thus, our calculations provide a simple framework for understanding the particle-size effects in dispersed ionic conductors.

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