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Particle-size effect on the percolation and conductivity of dispersed ionic conductors: A random sequential packing model

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The particle-size effect on the percolation and conductivity of ionic conductors containing a dispersed second phase is investigated on the generalized random resistor networks model. A random sequential packing model different from the one used by Roman and Yussouff is proposed, and by computer simulations we find that there is a maximum critical particle size above which the second critical concentration p_c'' at which the conductor-insulator transition takes place, will disappear. The first critical concentration p_c' at which the interface percolation transition occurs may also disappear above the critical particle size. The particle-size effect on the conductivity property of the present model is studied with a powerful and efficient Y-∇ transformation algorithm, and the numerical results are in good agreement with experiment results and previous conclusion.

I. INTRODUCTION

Dispersed ionic conductors form a class of composite materials with intriguing conductance properties. As observed by Liang,[1] addition of a dispersed insulating component to an ionic conductor can increase the overall conductivity by two or three orders of magnitude. This peculiar behavior results from an increased conductivity along the interface between the conducting matrix and the insulating fine particles.[2–6] Because of such distinct interfacial properties, dispersed ionic conductors can be regarded as three-component systems. Bunde, Dieterich, and Roman[2] have proposed a random resistor network (RRN) model which consists of nonconducting, normally conducting, and highly conducting bonds. They start from a two-dimensional square lattice and generate their two-phase mixture by producing random occupation of unit squares with probability p, which is the concentration of the dispersed insulating phase. The sides of the squares are called bonds and have three different conductances. They consider a given bond and its two adjacent squares. If both squares are occupied, the bond is called insulating bond and the conductance $\sigma_C=0$. If only one of them is occupied the bond is called interface bond (highly conducting bond) and the conductance is σ_A. Finally if none of them is occupied, the bond is taken as a normally conducting bond with conductance σ_B. The resistor model is mapped in the conventional way on a random walk,[7] which in turn is solved by means of Monte Carlo simulations. They show that their model correctly describes the distinct conduction properties of those materials and in addition it displays the critical behavior of both random-superconductor and random resistor networks[8,9] at two different critical concentrations, and they conclude[2–5] that ionic conductors containing a dispersed insulating phase are good candidates to investigate the predictions of static and kinetic percolation theory in a real system. Later, in order to explain the experimentally observed particle-size effect[6] for the whole range of concentrations of the insulating particles for such composite materials, Roman and Yussouff[6] generalize the random resistor network model by introducing an additional parameter s called the particle size, so the size of elementary insulating clusters can be varied. For more details of this model, we refer the reader to Ref. 6. Monte Carlo calculations[6] on the generalized RRN for two-dimensional systems are reported for square as well as rodlike particles of different size. It is found[6] that the corresponding critical concentrations p_c' and p_c'', respectively, for interface percolation and the conductor insulator transition, strongly depend on the size and shape of the dispersed particles, and the simulation results for the diffusion constant as a function of the particle size are in good overall agreement with the experimentally observed particle-size effects.

In this paper we will propose a random sequential packing (RSP) model that is different from the one in Ref. 6, and discuss the particle-size effect on the percolational behavior as well as conductivity property of the present model. We explore directly the percolation behavior[10] which is characterized by percolation susceptibility χ, and by the percolation probability $p_s(p)$ that a "spanning cluster" occurs on a $L\times L$ finite size for each particle size s. We will show that there is a maximum critical particle size s_c above which the second percolating threshold p_c'' for the conductor-insulator transition disappears, and the first percolating threshold p_c' for the interface percolation transition may also disappear. The particle-size effect on the conductivity property of the present model is studied with a recently proposed Y-∇ transformation[20] algorithm which is more efficient than the previous method.[2–7] The particle-size effect on the conductivity property of the present model obtained by Y-∇ transformation is in good agreement with that of Roman and Yussouff.[6]

The paper is organized as follows. In Sec. II we will present our RSP model, and in Sec. III we will study the percolation behavior as well as the conductivity property of the present model through computer simulations, and compare the present model with the one in Ref. 6. Our discussion will be presented in Sec. IV.

II. RANDOM SEQUENTIAL PACKING MODEL

The random sequential packing problem has been mainly studied in continuum or lattice space.[11–13] The random sequential packing in square cellular structures has been studied by Nakamura.[14–18] Nakamura[17] finds that the maximum critical percolation length α_c (3 units length) of the packed squares is presented for the insulator-metal transition to take place on the random sequential packing textures if the random sequential patterns are formed by filling metallic squares with integer length α on the insulator substrate divided into square unit cells. When $\alpha > \alpha_c$, no insulator-to-metal transition occurs even at the saturation coverage where no more squares can be filled without any overlap.

We employ the algorithm used by Nakamura[18] to generate the "patterns." We follow Ref. 1 and model the pure ionic conductors to be the matrix with length L and L^2 unit meshes of unit square. A square insulator with length s and s^2 unit cells is deposited on the meshes of the matrix at random one by one without any overlap but permitting contact. The depositions are repeated, searching places where no overlaps occur, and they are continued until the concentration of the insulating particle ($p = ns^2/L^2$, n is the total number of insulating particles) reaches a fixed value or a square with length s cannot be placed without any overlap. The computerized procedures are the following:

(1) Assign numbers from 1 to 100 at random to every unit cell of the matrix.

(2) Find out the unit cells with number i ($1 < i < 100$) and register their places.

(3) Selected at random one place from the registration and deposit an insulator square with length s, setting one of the corners to the selected place. As a mark of the deposited square, all the numbers of the cells in the square are changed from the originally assigned numbers to 1000 (for example). If the square overlaps a cell with the number 1000 in the course of deposition, the deposition is ceased. Delete the selected place from the registration whether the deposition is executed or not. Continue this operation until the concentration of the insulating particles reaches a fixed value or all the places are deleted from the registration (the concentration in this case is the saturation concentration).

(4) Complete operation (2) and (3) for every i from 1 to 100.

The RSP problem studied by Nakamura[15–18] is also useful for studying the particle-size effect on the percolation properties of the present model. The connection between the RSP problem in Ref. 17 and the present RSP model is very simple, and from the results of Ref. 17 leads to the conclusion that there is a critical size ($s=4$) at and above which no percolation transition could possibly occur for the present model.

Note that the present model is different than the one in Ref. 6, and both percolating thresholds cannot be expected to be identical. In the model of Ref. 6, although not stated explicitly, squares are not distributed completely at random, but a "local relaxation" is allowed when a new square is attempted to be created in a position where it overlaps with the previously deposited squares.

After a pattern has been generalized, both the percolation properties and conductivity properties can be obtained, respectively, by the standard percolation theory[10] and electric circuit theory, as we now proceed to demonstrate.

III. NUMERICAL RESULTS

A. Percolation behavior

As pointed by percolation theory, the percolation behavior is characterized by percolation susceptibility χ, the probability $p_s(p)$ that a "spanning cluster" occurs in the system, and the percolation probability $p_\infty(p)$ (the probability that an occupied site is part of the percolating cluster). Here we only present the results of the percolation susceptibility χ and $p_s(p)$. The percolation susceptibility χ is defined as

$$\chi = \sum_{l=1}^{\infty}{}' \, l^2 n_l(p), \tag{1}$$

where $n_l(p)$ is the number of clusters which contain l occupied sites. The prime means that the largest cluster is omitted from the summation. Since there exist two critical concentrations p_c' and p_c'', the definition of cluster is very different for these two critical concentrations. p_c' is related to the interface bonds only and defines the lowest concentration where an infinite network of interface bonds or highly conducting bonds develops. Two sites belong to the same cluster if there is a highly conducting bonds connecting them. We call such clusters "interface cluster," which will be used in Eq. (1) to calculated χ^i. The concentration p_c'' is the threshold concentration for disrupting the conducting paths and defines the percolation where all normal and interface bonds get disrupted. The cluster must be defined in the following way: two sites belong to the same cluster if there is a normal or interface bond connecting them. The critical concentration p_c'' at which the conductor-insulator transition takes place is linked to such clusters. We will call such clusters "metal-insulator (MI) clusters," which will be used in Eq. (1) to calculate χ^{mi}.

We employ Monte Carlo computer simulation procedures for the square lattice with $(L+1)$ sites on its edge, where L ranges from 20 to 120, so that there are L^2 unit squares in the square lattices. Periodic boundary conditions are used, so that the lattice is in reality a torus. We say that a given finite $L \times L$ system "spans" if there is a cluster which surrounds the hole in the torus. The amount of data generalized for each value of p ranges from 2000 realizations at $L=20$ and $L=60$, to 1000 realizations at $L=120$. We use the label algorithm of Hoshen and Kopelman[22] to identify all clusters in a given configuration.

In Fig. 1. we have shown the interface percolation susceptibility χ^i as a function of the concentration p of insulating particles for different particle size s. Some interesting features appear in Fig. 1. For $s=1$, $s=2$, and $s=3$, two peaks develop as the concentration p increases. For $s=4$, as the concentration increases, the interface percolation susceptibility increases and has a maximum value at its saturation concentration ($p=0.646$).[15] The concentration dependences of χ^i for $s=1$, $s=2$, and $s=3$ are very different from that of

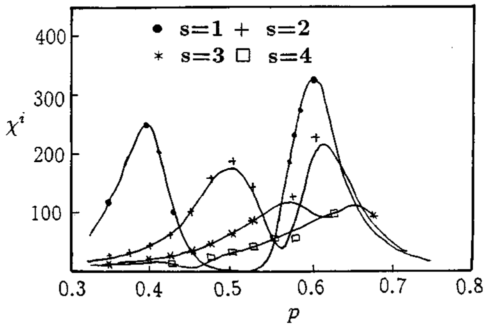

FIG. 1. The interface percolation susceptibility χ^i as a function of the concentration p of the insulating particles for different particle size s, $L=120$.

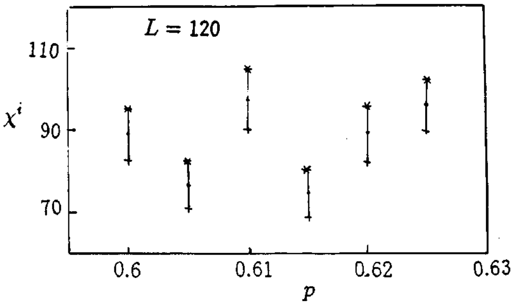

FIG. 2. The interface percolation susceptibility χ^i near the saturation fraction of the insulating particle for $s=4$.

$s=4$. Such a result implies that the interface percolation behavior for $s=1$, $s=2$, and $s=3$ may also have different characteristics from that of $s=4$. For $s=1$, $s=2$, and $s=3$, when the concentration p of the insulating phase is very small, the number of the interface bonds is also very small, and only some nonpercolating small interface clusters exist, therefore the interface percolation susceptibility χ^i is very small. As the concentration p increases, more and more normal bonds become the interface bonds and the interface clusters become larger and larger, so the percolation susceptibility χ^i will increase. At the interface percolation threshold p'_c, the percolation susceptibility χ^i will obtain the maximum value. By further increasing the concentration p, the percolating cluster will become larger and larger and the percolation susceptibility will decrease because in calculating the percolation susceptibility the largest cluster is omitted from the summation in Eq. (1). When the interface cluster becomes the largest one, the percolation susceptibility become the minimum in Fig. 1. The dependence of the interface percolation susceptibility χ^i on concentration p around p'_c is as the same as the percolation susceptibility for the bond percolation problem on the square lattice.[19] However, the second peak seems to be an unexpected result and is quite different from the bond percolation problem near p_c on the square lattice.[19] In conventional percolation problems,[10] such as bond percolation on the square lattice,[19] when the concentration p of the bonds is becoming larger, the percolating cluster is also becoming larger. When $p=1$, the percolating cluster dominates the whole lattice, so the percolation susceptibility is exactly 0. However, for the present model, when the interface percolation cluster becomes the largest one (corresponds to the minimum of percolation susceptibility in Fig. 1), the further increase of the concentration p of the insulating phase will disrupt the interface percolation cluster and some nonpercolating of local interface clusters will be generated. This corresponds to the second increase of the interface percolation susceptibility. By further increasing p, the nonpercolating clusters will become larger, and the contribution of these clusters to the percolation susceptibility will increase until χ^i gets its second maximum value. When one further increases the concentration p, these nonpercolating clusters will become small and χ^i will decrease. When p approaches its saturation concentration, the interface percolating susceptibility will obtain its second minimum value. It is not surprising that the second peaks are larger than ($s=1$, $s=2$) or comparable to ($s=3$) that of first peak. This is because the first peak corresponds to the formation of the percolating cluster, and the contribution of this percolating cluster to χ^i is omitted in Eq. (1), while the second peak corresponds to some nonpercolating clusters, and the largest cluster in this case is still nonpercolating and the ignorance of the contribution of this cluster to χ^i in Eq. (1) will have relative small effect on the final result. For $s=4$ a very different phenomenon occurs. As the concentration p increases, more and more normal conducting bonds become the interface bonds and the nonpercolating interface clusters become larger and larger. Finally when the concentration p approaches the jamming coverage, the interface cluster becomes the largest one and may also become a percolating cluster accidently. So for $s=4$, we cannot give a definite answer whether the interface percolation occurs. However, if the interface percolation takes places, the concentration p'_c must be equal to the saturation fraction.

In Fig. 2 we present the results of the interface susceptibility χ^i near the saturation fraction. We find that the fluctuation of χ^i is very large and there is not a definite tendency as p increases as shown in Fig. 1. Our result in Fig. 2 is in agreement with that of Nakamura:[17] for $s=4$ even at the saturation concentration, the pattern is usually made of the nonpercolating clusters, and the largest cluster and the second largest cluster are separated (see Fig. 2 in Ref. 17). There is no reason to believe that the largest cluster is becoming larger and larger as the concentration approaches the saturation fraction, so the interface percolation susceptibility χ^i cannot be expected to increase monotonically as p approaches the saturation fraction. This is very different from those of $s=1$, $s=2$, and $s=3$ where the infinite interface cluster forms, and the interface percolation susceptibility χ^i will decrease monotonically as p approaches the saturation fraction. So for $s=4$ by a detailed calculation near the saturation fraction, we can definitely conclude that no interface percolation transition occurs for the present model in a 120×120 lattice. We do not know whether this conclusion may also hold in the thermodynamic limit, and we have not performed numerical simulations for larger lattice size because of limited computer power. However, we hope further investigation may be carried out along this line.

The estimates of p'_c are listed in Table I. The value of p'_c is obtained by locating the concentration p at which the first peak develops. Note that the second peak in Fig. 1 has no physical meaning, and the corresponding concentration

TABLE I. Percolation thresholds of dispersed ionic conductor for the present RSP model. (a): from $\chi^{i}(p_c')$ or $\chi^{mi}(p_c'')$. (b): from $p_s^{i}(p_c')$ or $p_s^{mi}(p_c'')$. (c): from Ref. 6.

s	p_c'			p_c''		
Method	a	b	c	a	b	c
1	0.400±0.01	0.415±0.02	0.407±0.01	0.600±0.01	0.595±0.02	0.593±0.01
2	0.500±0.02	0.525±0.03	0.510±0.01	0.610±0.01	0.601±0.03	0.590±0.01
3	0.575±0.01	0.590±0.02		0.640±0.02	0.625±0.03	
4	?0.646	?0.646	0.580±0.02	?0.646	none	0.610±0.02

cannot be used to define the critical concentration for the metal-insulator transition, because such a transition is linked not only to the interface bonds, but also to the normally conducting bonds.

Numerical results of interface $p_s^{i}(p)$ that a "spanning cluster" made of interface bonds occurs in a finite lattice size for different particle size s are presented in Fig. 3. In the lower concentration region, the insulating particles are dispersed in the normal bonds, and the number of interface bonds is very small so the probability that a "interface spanning cluster" occurs in the system is very small. As the concentration increases, more and more normal bonds become the interface bonds and the interface clusters become larger, so $p_s^{i}(p)$ increases. As p further increases, one of the interface clusters becomes the interface percolating cluster, and the interface percolating cluster becomes larger and larger [$p_s^{i}(p)$ still increases], and finally the interface percolating cluster disrupts itself and divides into several small clusters, so $p_s^{i}(p)$ will decrease. Before the interface percolating cluster disrupts itself, $p_s^{i}(p)$ will approach its maximum value. We can see from Fig. 3 that as the lattice size increases, the maximum value of $p_s^{i}(p)$ will also increase.

For $s=1$ even a 60×60 lattice can make it possible for $p_s^{i}=1$. However, as the particle size increases, the maximum value of $p_s^{i}(p)$ will decrease for the same lattice sizes. For $s=2$ even in a 120×120 lattice the $p_s^{i}(p)$ cannot approach 1. The dramatic difference between $s=4$ and $s<4$ can be easily seen in Fig. 3. For $s=4$, $p_s^{i}(p)$ always increases as p increases. When p approaches its saturation concentration (this saturation concentration is lattice size dependent[15]), $p_s^{i}(p)$ approaches its maximum value. Figure 3(d) corresponds to the parts of Figs. 3(a)–3(c) in the lower concentration region. Here again one cannot be sure whether the interface percolation still occurs for $s=4$ in the thermodynamic limit. One possibility is that in the thermodynamic limit the interface percolation may also occur at the saturation concentration accidently. We also see from Figs. 3(a)–3(d) that for a given lattice size (for example $L=100$), when the particle size increases, $p_s^{i}(p)$ will decrease: for $s=3$ $p_s^{i}(p)$ will always be 0 at any concentration for $L=20$; for $s=4$, $p_s^{i}(p)=0$ even in a 60×60 lattice.

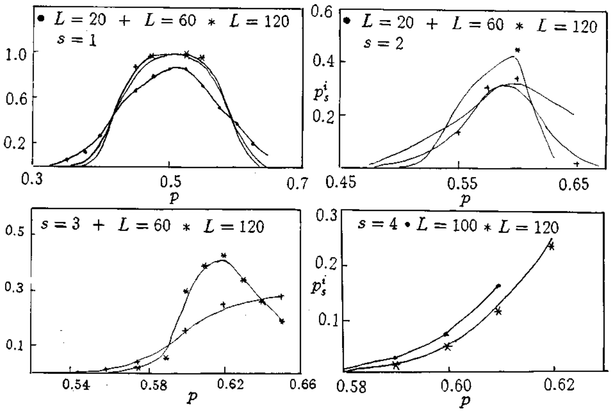

FIG. 3. The interface spanning probability $p_s^{i}(p)$ as a function of the concentration p of the insulating particle for different lattice sizes. (a) $s=1$; (b) $s=2$; (c) $s=3$; (d) $s=4$.

Our results of $p_s^{i}(p)$ are very different from those of Ref. 6. Previous studies show that for every particle size the $p_s^{i}(p)$ may obtain the value 1/2 even for $L<100$. Our results show that for $s=1$, this is correct, and for $s=2,3,4$, this is incorrect. Previous results may be true in the thermodynamic limit.

The interface percolation threshold p_c' is obtained as the common intersection point of the curves. For $s=2$ we use the intersection point generated by larger lattice sizes. Our results of p_c' are also listed in Table I. Since the maximum value of $p_s^{i}<1$ for $s=2$ and $s=3$ for the lattice sizes we have used in this paper fluctuates, we think the resultant accuracy in our values of p_c' for $s=2$ and $s=3$ is correspondingly lower.

Numerical results of the metal-insulator percolation susceptibility χ^{mi} for different particle sizes are presented in Fig. 4. Here again the percolation susceptibilities χ^{mi} for $s=1$, $s=2$, and $s=3$ are different from that of $s=4$. In the lower concentration region, the infinite cluster definitely exists in the system (note here the cluster is defined by both interface bonds and normal bonds). As the concentration increases, some normal bonds become insulating bonds and the MI percolation cluster become smaller. At the critical concentration p_c'', the metal-insulator percolation cluster disrupts itself and divides into several small clusters; this corresponds

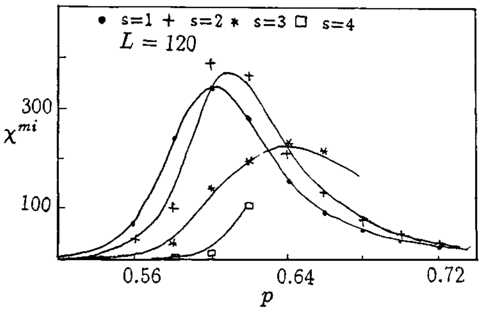

FIG. 4. The metal-insulator percolation susceptibility χ^{mi} as a function of the concentration p of the insulating particles for different particle size s, $L=120$.

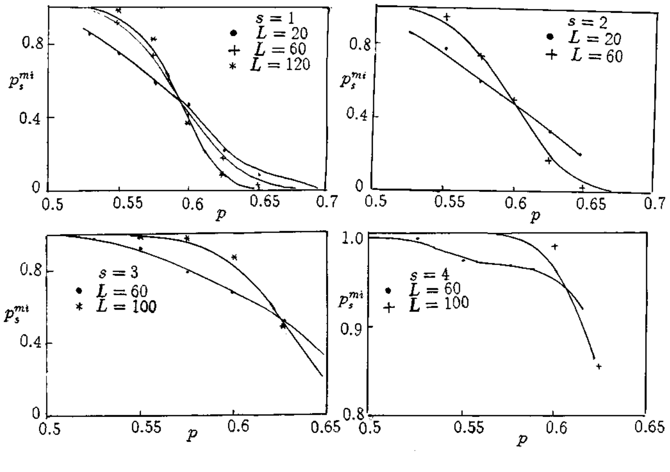

FIG. 5. The metal-insulator spanning probability $p_s^{mi}(p)$ as a function of the concentration p of the insulating particle for different lattice sizes. (a) $s=1$; (b) $s=2$; (c) $s=3$; (d) $s=4$.

to the peaks in Fig. 4. As the concentration further increases, the local clusters become smaller and smaller, and χ^{mi} will decrease. Finally all bonds in the system become the insulator bonds and χ^{mi} obtains the minimum value. For $s=4$ the percolation susceptibility χ^{mi} will always increase as the concentration p increases. If the metal-insulator transition occurs for $s=4$, the transition must occur at the saturation concentration. So from Fig. 4(d) we can only conclude that for $s=4$ if the metal-insulator transition occurs, the critical concentration must be equal to the saturation concentration. However, numerical results of p_s^{mi} presented next will rule out this possibility.

Numerical results of $p_s^{mi}(p)$ that a "spanning cluster" made of interface bonds or normal bonds in a finite lattice size for different particle size s are presented in Fig. 5. In the lower concentration region, although the number of interface bonds is very small, the metal-insulator percolating cluster exists definitely in the system since the metal-insulator transition is linked not only to interface bonds but also to normal bonds. As the concentration p of the insulating particle increases, some normal bonds become interface bonds and insulator bonds, so the percolating cluster becomes smaller. By further increasing the concentration p, there will be different consequences for the cases $s=1$, $s=2$, and $s=3$ and the case $s=4$. For $s=1$, $s=2$, and $s=3$, the percolating cluster becomes smaller and smaller and may be divided into several small clusters when the concentration approaches the critical concentration p_c''. However, for $s=4$ the percolating cluster does become smaller and smaller and before it is divided into several clusters, the concentration already approaches the saturation concentration. So the metal-insulator percolating cluster still exists even at the saturation concentration and the metal-insulator transition definitely disappears for $s=4$.

The percolation thresholds p_c' and p_c'' are listed in Table I and comparisons are made with previous estimates.[6] Methods (a) and (b) indicate that the percolation thresholds are determined by the percolation susceptibility for $L=120$ and the spanning probability p_s for $L\leqslant 120$, respectively. Finite-size scaling arguments have been used to determine the percolation thresholds by Roman and Yussouff.[6] But our estimates of percolation thresholds are less accurate than the previous estimates because our results are obtained only on some small lattice sizes and finite-size scaling has not been used to determine the percolation thresholds in the infinite lattice size. So the results listed in Table I should be regarded as preliminary results.

For $s=1$ the present model reduces to the model in Ref. 6 and both percolating thresholds are expected to be identical. The results for $s=1$ listed in Table I indeed support this conclusion. For $s\geqslant 2$ the present model is different than the one in Ref. 6 and both percolating thresholds cannot be expected to be identical. For $s=2$, the discrepancy for p_c' between method (a) and (b) is somewhat large, and we are unable to arrive at a definite conclusion whether the percolating threshold p_c' of the present model is different from that of the model in Ref. 6. However, comparing p_c'' with previous estimates, we conclude that for $s=2$ the percolating thresholds p_c'' of the present model are larger than p_c' of previous models. As s increases, the differences between the percolating thresholds of the present model and those of previous models also increase. For $s=4$, Roman and Yussouff[7] predict the existence of the percolation transition at p_c' and p_c'' for their model. However, for the present model, no percolating transition possibly occurs. The second percolating threshold p_c'' will disappear definitely from the data presented in Fig. 5. We are unable to arrive at a definite conclusion of whether the first percolating threshold p_c' still occurs for the present model because our simulations are performed on some relatively small lattice sizes. However, the difference between the present model and the previous one still can be examined by comparing the percolating thresholds: if there exists a percolation transition at p_c' for the present model, then the percolating threshold p_c' must be equal to the saturation concentration of the RSP model discussed by Nakamura.[17] For $s=4$ the saturation concentration is 0.646 ± 0.01,[15] while the percolating threshold $p_c''=0.610\pm 0.02$ for previous models. The percolating thresholds for $s=3$ have not been studied in Ref. 6 and a comparison cannot be made. In Table I we use the question mark "?" to denote that whether the percolation transition occurs in this case cannot be determined by the present study. As mentioned above, if the percolation transition occurs for $s=4$, then the percolation threshold p_c' must be equal to the saturation concentration in the RSP model discussed by Nakamura, so we also list in Table I the percolating transition at which the percolating transition possibly occurs.

B. Conductivity behavior

In this section we want to discuss the particle-size effect on the conductivity behavior of the dispersed conductors. Previous studies[2–6] have mapped the three-resistor model on a random walk.[7] The mean-square displacement of the walker as a function of time t was calculated by using the Monte Carlo method.[2–6] For large time t the mean-square displacement of the walker is proportional to Dt, D being the diffusion constant, which is proportional to the conductivity according to the Nerst-Einstein relation.[7] One drawback of this algorithm[7] is that in order to obtain the correct diffusion constant, the asymptotic regime of the walker, where the mean-square displacement of the walker is proportional to

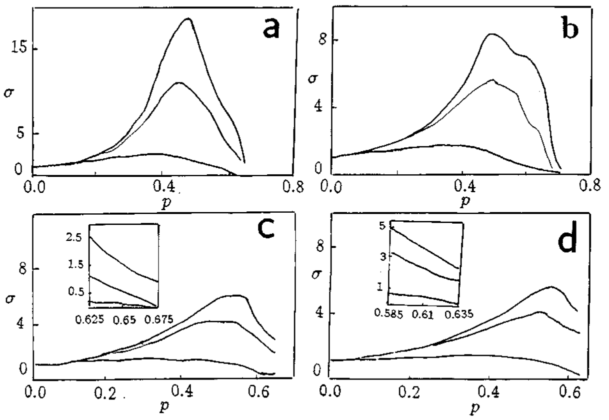

FIG. 6. The effective conductance σ as a function of concentration p for different values of $\tau=\sigma_A/\sigma_B$ (from bottom to top τ are 10, 100, and 200). The inset shows the effective conductance near the saturation concentration in a 100×100 network. (a) $s=1$; (b) $s=2$; (c) $s=3$; (d) $s=4$.

Dt, must be reached. It usually takes the walker 10^3 for $p<p_c'$ and 10^4–10^5 for $p<p_c''$ to reach the asymptotic regime.[2] Here we deal with this problem from a different point of view and use the Frank and Lobb algorithm[20] to calculate the effective conductivity for samples of size 60×60. In this method one can exactly calculated the equivalent conductance of a square network of arbitrary size, using a sequence of network reductions familiar to electrical engineers, known as Y-∇ transformations. The propagation starts from the square in the first column and first row. After each propagation, one square is deleted. The Y-∇ algorithm is then used to delete successively all the other squares in the first column. Once the first column is deleted, the propagation algorithm comes to the next column. After approximately $L^3/3$ propagation on a $L\times L$ network, the whole network is reduced to just a single conductor which gives the effective conductance of the whole network. It has been shown[20] that this algorithm is highly efficient for reducing a large square network to a single effective conductance. This algorithm has been shown to work efficiently not only for problems involving the conductivity but also for calculating the critical current of a normal-metal–superconductor composite. The same algorithm has been used successfully to simulate far-infrared absorption in a two-dimensional normal-metal–superconductor composite.[21] We carried out our simulations on 60×60 networks. For each concentration p the results were averaged over 100 realizations.

In Fig. 6, we have shown the effective conductivity σ as a function of the concentration p of the insulating particles for different values of $\tau=\sigma_A/\sigma_B$. Although the present model is different from the one in Ref. 6, both percolating thresholds cannot be expected to be identical, however, we are surprised to find that the result of the effective conductance of the present model is in good agreement with the diffusion constant $D(p)$ reported earlier.[6] As a by-product, we also calculated the effective conductance σ for $s=3$, which has not been studied previously.[6] As the particle size varies from $s=1$ to $s=4$, for constant τ, the peak height of σ decreases and the peak position moves to a higher concentration. This can be understood by noting that the corresponding fraction of highly conducting bonds decreases with s. The differences between our results and those of Ref. 6 are that the effective conductivities at higher concentrations can also be calculated by our method while previous methods can only extrapolate the results in the low-concentration region to the higher-concentration region because of the limitation of their method. The particle-size effect on the effective conductivity in the higher-concentration region can easily be seen from Fig. 6(a) to Fig. 6(d). In Figs. 6(a) and 6(b), the effective conductance can approach zero for different τ even in a 60×60 lattice. This corresponds to the case where not only normal bonds but also interface bonds are disrupted and there is not a connected path formed by the normal or interface bonds. In Figs. 6(c) and 6(d) the effective conductances approach finite values even at the saturation coverage in a 60×60 lattice; this corresponds to the case where the interface and normal bonds still form a connected path in a 60×60 lattice. That the effective conductance of $s=3$ approaches finite value even at the saturation fraction, seems to be contradictory to the percolation properties of the present model. For $s=3$ the prediction of the percolation property of the present model shows that the metal-insulator transition will occur at the concentration which is definitely smaller than the saturation fraction. So at the saturation fraction the composite will be an insulator and the effective conductance of the composite will be exactly zero. This is because numerical results presented in Fig. 6 are performed on a relative smaller lattice size (60×60). The finite lattice size effect[23] on the effective conductance can be seen from the insets of Figs. 6(c) and 6(d), where numerical simulations are performed in a 100×100 lattice near the saturation fraction. The effective conductance of $s=3$ for $\tau=10$ and 100 will approach zero as p approaches the saturation concentration from below. The effective conductance for $\tau=200$ does not approach zero when p approaches the saturation fraction, however, the effective conductance will decrease as lattice size increases. If one performs a simulation on a larger lattice, the effective conductance will finally approach zero as p approaches the saturation concentration. For $s=4$ although the increase of the lattice size can decrease the effective conductance, the effective conductance in a 100×100 lattice for $\tau=10$ cannot approach zero. This effect cannot be accounted for the finite lattice size. A numerical simulation on a large lattice (200×200) is performed, and the effective conductance still approach nonzero value. This implies that for $s=4$ the metal-insulator transition cannot occur which is in agreement with our previous discussions by exploring directly the percolation behavior numerically.

The effect of the particle size on the conductivity is clearly seen in Fig. 7 where for a fixed value of $\tau=100$, we have plotted the effective conductivity σ 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). Here we choose the same parameters as the previous study[6] in order to see whether the present model will bring out different conductivity behavior from the one in Ref. 6. The conductivities for $s=3$ and $s=5$ are also presented in Fig. 7 which have not been studied previously. Our results are in very good agreement with the results obtained by the Monte Carlo method.[6]

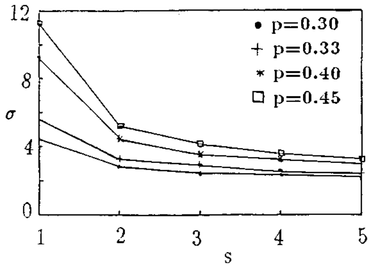

FIG. 7. The effective conductivity σ as a function of particle s for fixed $\tau=100$ and different concentrations (from bottom to top the concentrations are 0.30, 0.33, 0.40 and 0.46).

IV. DISCUSSION AND CONCLUSIONS

In this paper we have considered a random-resistor model for studying particle-size effects on the conductivity of mixtures of insulating particles dispersed in a conducting matrix, a subject which is of both theoretical and practical interest. We have proposed a random sequential packing model, which is different from the one in Ref. 6, and we find that both percolating thresholds of the present model are different from those of previous estimates, and for the RSP of squares, there is a critical size ($s=4$) at and above which no percolating transition possibly occurs. Particle-size effect on the conductivity property of the present RSP model is investigated with a powerful and efficient Y-∇ transformation algorithm, and to our surprise the numerical results of the present RSP model are in good agreement with previous study.[6]

There are some possibilities for future investigations of the present RSP model. Whether the present RSP model belongs to the university class of two-dimensional lattice percolation still requires further study. However, the present RSP model does not change the transport exponents $s(t)$, and the transport exponents still take the universal values. This is because previous studies[24–28] have predicted that the transport critical exponent can be nonuniversal for percolating networks with an anomalous distribution of bond strengths, arising naturally in continuum models,[26–28] such as the random-void models, where circular or spherical holes are randomly placed in a uniform transport medium. For the present RSP model, the normal bonds have finite conductivity, and the increase of the particle size does not lead to the singularity of the distribution of the conductance; therefore the present RSP model cannot be expected to change the transport exponents.

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