Controlling 3D Percolation Threshold of Conductor-Insulator Composites by Changing the Granular Size of Insulators

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For a binary distribution of insulating particle sizes, we estimate the percolation threshold on a cubic lattice (3D). This work extends our previous investigation of a similar size distribution model in two dimensions (2D) where we found a drastic (~13%) reduction in the percolation threshold (Shida et al. Materials Transactions Vol. 51, No. 6). For three-dimensional cases, the result is qualitatively similar to the corresponding two-dimensional cases: we found a significant decrease in the percolation threshold compared to the monodisperse case.

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1. Introduction

The percolation model is a simple and powerful theoretical tool that significantly contributes to our understanding of the various physical phenomena related to the properties of disordered systems. Recently, a number of interesting modifications related to additional correlations between sites have been introduced into this simple model, thus drawing increased attention. In our previous works, we proposed a new type of two-dimensional (2D) site percolation model based on a Monte Carlo approach, where particles of two different sizes (unit size particles A and enlarged particles B) were randomly placed on a lattice. The presence of particle B apparently increased the probability of neighboring lattice sites to be occupied. Despite this “correlation”, when size distributions were limited to conducting particles, the percolation threshold $p_c$ did not significantly deviate from the threshold for the conventional 2D percolation model without particle size distribution. Similar results were obtained for a 2D triangular lattice, and other authors reported results that essentially agree with ours. However, when unoccupied sites are regarded as insulating particles and their size distribution is considered (that is, when the probabilities of unoccupied neighboring sites are correlated), the percolation threshold is drastically reduced. We next focused on a similar problem concerning the magnitude of electronic conductivity on a three-dimensional (3D) lattice, which can be modeled and evaluated by a random resistor network model and the Kirchhoff equation. The results suggest that, in the 3D case, binary distributions in the size of the (conducting) particles may strongly affect the percolation phenomena. Such analyses of percolation have numerous real-world applications in material design because the simple theoretical model of percolation (i.e., considering only whether neighboring sites are connected) accurately explains the characteristics of composite materials. This success, in turn, means that the limits of composite materials imposed by percolation transition can be a very fundamental limit, as demonstrated by the concept of a universality class, which suggests that the percolation limit is strongly restricted by the dimensionality of materials. Therefore, the percolation characteristics of bulk (3D) and film (2D) composite materials and their dependence on modulations in randomness should differ greatly. Therefore, cases in different dimensions merit detailed and independent research, even if their modes of correlation are similar.

Although many interesting results have been reported for 2D off-lattice systems, most studies did not properly treat the excluded volume effect between particles (e.g., permeable ellipse models). In the present report, we not only treat the complete excluded volume effect but also the situation in which insulating particles have size distributions. We believe that when applied to a more realistic dimensionality (i.e., 3D), the impact of the excluded volume effect between particles on modulated percolation problems is too large to neglect. More precisely, enlarged insulating particles may “push” the smaller conducting particles with the net effect of forcing the conducting particles into modulated spatial distributions (which may more efficiently conduct electricity), as observed in the 2D case. There also are important results from 3D experiments using enlarged insulating particles, but they have been carried out under control of average particle size, not under precise control of the size distribution of the insulator particles. Therefore, we report herein the results of a large-scale computational percolation experiment on systems of 3D impermeable particles and discuss the effect of size modulation on the basic percolation phenomena in terms of connectivity. Size modulation is performed in a basic but never explored manner, namely by using a binary size distribution of “insulating” particles. The more complicated size distributions such as simultaneous combinations of more than two-particle-size distributions for both conducting and insulating particles are beyond the scope of this report.

2. Methods

We studied the site percolation model on $L \times L \times L$ cubic lattices, with some insulating particles (total volume fraction of the insulating particles is $1 - p$) being larger than others, whereas all conducting particles are of unit size (the total volume fraction of conducting particles is $p$). In particular, we considered three different particle sizes: $1 \times 1 \times 1$, $2 \times 2 \times 2$ and $3 \times 3 \times 3$. Particle size is denoted by $X$...
(X = 1, 2, 3), and we deal with mixtures of X = 1, 2 or X = 1, 3 (see Fig. 1). Random particle configurations are basically generated in the same way as for similar systems. First, depending on p, X, L, and the volume fraction θ of the enlarged particles with respect to all insulating particles, the numbers of particles with unit size and enlarged size are calculated. Then, to determine the positions of the enlarged particles, non-overlapping X³ cubes with the required number and size are randomly and successively placed on the lattice via a simple trial-and-error algorithm. Next, all unoccupied lattice sites are distributed into insulating or conducting sites of unit size particles. This simple scheme essentially samples all possible configurations for a given combination of particle number and type. The main difficulty with this scheme is the decrease in efficiency for large θ; it becomes increasingly difficult to find an unoccupied site to host an enlarged particle when many such particles are already in the system. However, this problem of sampling efficiency is found to be severe only when 70% or more of the insulating particles are 3 x 3 x 3, where 1 - p > 0.790.

A much more efficient algorithm exists to generate sample configurations for percolation problems. A well-known example is the method proposed by Newman and Ziff8) that basically successively adds conducting sites to the system until the giant connected component finally appears in the system. This method is quite efficient because updating and maintaining cluster information after each site addition is relatively easy and a series of operations always yields a percolating configuration. However, for our purposes, this method presents a very simple problem: it is difficult to successively add conducting particles when θ is constant or equivalently, while preserving space for the given number of X > 1 insulating sites. To make particle size distributions coexist with the method of Newman and Ziff, we must devise a new algorithm and restructuring the entire experiment, that is beyond the scope of this report.

For a given condition, we repeat this procedure for 2000–10,000 different random particle configurations and finally perform standard cluster analysis to list all connected clusters of conducting sites in each configuration. For each condition introduced below, we simulate lattice sizes L = 64–256 (when L = 256, sample number is reduced to 2000 due to the limit of computational resources). The simulated range of p is set so that p_c, which is roughly estimated as the number of preliminary simulations with fewer samples, is confined within the range. Next, we perform a number of full-scale simulations to sweep the range of p over an interval of 0.002. To determine p_c more precisely for later analysis, shorter intervals are desirable but are not absolutely necessary. In fact, the interval 0.002 is the shortest we can afford given our computational resources.

The volume fraction ratio of the enlarged particles θ is, as introduced above, an important controlled parameter of our simulation. We performed four different series of simulations using θ = 0.1, 0.3, 0.5 and 0.7. For example, when X = 1 and X = 2 particles are mixed with θ = 0.3, their volume fraction ratio and number ratio are 7:3 and 30:70, respectively. Because of the difficulties of sampling when θ is large (as discussed in our previous report), we use θ ≤ 0.7. A stronger restriction (θ ≤ 0.5) is used when X = 3 particle are used with L = 64, 128.

The output of these calculations is the mean finite cluster size S(L,p) defined as the summation over all clusters except the largest:

\[ S(L, p) = \sum_s s^2 n_s(p), \]  

where \( n_s(p) \) is the average number of clusters with size s. In short, the peak of the finite cluster provides an estimate of p_c for the percolation, although better precision is possible by finite scaling analysis.
3. Results

Figure 2 shows the mean size of finite connected clusters as a function of density of conducting particles. The peaks in the plot give the percolation threshold \( p_c \). The results clearly show that the location \( p_c \) of the percolation threshold is strongly affected by enlarged insulating particles. As in the cases of all 2D and 3D percolation systems that we have tested with particle size distributions, the general percolation behavior (indicated by the peak profile) is unaffected by correlations induced by enlarged particles. Each condition shows four peaks with different heights and steepness that are an increasing function of four different lattice sizes \( L = 256 \) shows the highest and steepest plots). As intuitively expected, the greater the fraction of enlarged particles in the system, the lower \( p_c \) becomes and no special transition in the trend is observed in the parameter region investigated. This result shows that the introduction of enlarged insulating particles strongly reduces \( p_c \) for 3D cases as well as for the same type of correlations in 2D cases. The relationship between the size of enlarged insulating particles and the magnitude of the reduction in \( p_c \) is also consistent with our intuitive expectation; \( 3 \times 3 \times 3 \) insulating particles reduce \( p_c \) more than \( 2 \times 2 \times 2 \) particles. This trend is also consistent with our previous result\(^4\) for similar 2D systems.

We now discuss in detail how the magnitude of the reduction in \( p_c \) depends on the number of enlarged particles. For 3D conducting particles that vary in size, as we have reported before,\(^{19}\) the amount by which \( p_c \) is reduced is proportional to the volume fraction of enlarged conducting particles, also denoted as \( \theta \), and the limiting value for \( \theta \to 1.0 \) is curiously close to the midpoint of the values for the simple cubic (\( p_c = 0.311 \)) and hcp lattices\(^{20}\) (\( p_c = 0.199 \)).

Figure 3 shows the percolation threshold as a function of the fraction of enlarged insulating particles. Although the amount by which \( p_c \) is reduced still seems to be roughly proportional to the fraction of large particles, the quantitative dependence is slightly more complicated and nonlinear than expected. The reduction in \( p_c \) becomes progressively stronger as \( \theta \) increases and the limiting value for \( \theta \to 1.0 \) is clearly smaller than that observed for enlarged conducting particles. In short, enlarged insulating particles more strongly reduce \( p_c \) than enlarged conducting particles. In addition, note that the coefficient of proportionality and the limiting value of \( 2 \times 2 \times 2 \) and \( 3 \times 3 \times 3 \) insulating particles seem to differ. Moreover, \( 3 \times 3 \times 3 \) insulating particles reduce \( p_c \) more strongly, although this might be related to the system size being not large enough compared with the size of enlarged particles.

4. Discussion

In the conventional percolation model, the spatial arrangement of occupied (conducting) and unoccupied (insulating) sites is totally random and independent. As a result of this randomness, a rather strict mathematical limit spontaneously appears in the clustering characteristics of the conducting particles. However, recently there have been many proposals to break this complete randomness and analyze extended
percolation problems with some correlations between sites. In the present work, such a correlation is generated by assuming a simple binary distribution of the insulating particle size. Although the model and the correlation used here are very simple (which means that achieving the same correlation in a real material is also straightforward), the results of the present study are certainly important because it proves that in 3D percolation problems, spatial correlations between insulating sites have a stronger influence than spatial correlations between conducting sites. Moreover, the results presented here are further proof of the possibility of improving electronic conduction for a given amount of conductor material just by modulating the particle size distribution of the conducting particles. We have shown that the total volume fraction of conducting particles may be reduced by about 30% (note that this figure is 15% for 3D conductors) without causing significant damage to the conductance in the material. Note that although it is desirable to minimize $p_c$ via this method, this has not yet been attempted because of the limit of the mixture ratio of enlarged particles imposed by the sampling efficiency.

5. Conclusion

We report the results of a series of computer simulations of site percolation over a 3D cubic lattice with insulating particles that follow a given size distribution. Introducing this type of correlation into the percolation system does not change the general percolation behavior, but the transition point $p_c$ is notably decreased. In fact, compared to various types of correlations we have studied in our previous simulations, we observe in this work the strongest reduction in $p_c$. We find that the critical density decreases by 30% when 70% of the insulating sites are occupied by enlarged particles, and this value may be even lower beyond the range of correlation parameters investigated herein. The experimental reproduction of the situations simulated here requires precise control of the size distributions of conducting and insulating particles, but should be possible by means of methods already developed and utilized in a related work.\cite{21}

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REFERENCES