Conductivity of a system of metallic particles dispersed in an insulating medium

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The variation of the conductivity of metal-particle–insulator systems with the volume percent of metal is explained in terms of an "effective medium" theory.

Recently, Bueche[1] suggested a polymer model to explain the transition from insulating to metallic behavior of a system of metal spheres embedded randomly in an insulating medium. This topic is important because it is an easily characterized system and bears a strong relation to the processes thought to underly the variation of conductivity in amorphous semiconducting alloys and other microscopically random systems. Bueche's model compares favorably with the observed large variation in conductivity; its two major shortcomings are a very steep slope in the transition region and a discontinuity in the slope of conductivity versus metal volume percent.

We suggest here an alternative, though similar, model which removes the aforementioned discontinuity and lessens the steepness of the slope somewhat. We also point out that the treatment of the system near the insulating and metallic limits needs a more detailed approach than the sort of macroscopic averaging so far adopted.

For purposes of illustration, we take the insulator to be a continuous medium and the metal to be in the form of spherical particles. These restrictions permit evaluation of a simple example, but the model can be used to accomodate various experimental configurations. We know that spherical particles form a variety of lattices; we choose here a simple cubic lattic. As more and more metal is introduced, the lattice sites become occupied in a random fashion. With each lattice site can be associated a conductivity, σ_i, whose value depends on whether the site is occupied by metal or insulator. In this way we arrive at a network of conductances. The probability, p, that a site is occupied by metal in this picture is v_m/f, where v_m is the volume fraction of metal and f is the packing fraction, equal to 0.52 for a simple cubic lattice. A network such as this can be described[2] by replacing each conductance by an average conductance $\bar{\sigma}$. This average conductance is arrived at in the following way. Assume that all conductances are the average, $\bar{\sigma}$. Now let just one conductance be changed back to its true value, σ_i, and examine the voltage difference between V_i, the voltage across σ_i, and the voltage across $\bar{\sigma}$ far from σ_i, $\bar{V}$. To calculate this difference we note first that the conductance looking into adjacent nodes of a network of conductances $\bar{\sigma}$ is $\frac{1}{2}z\bar{\sigma}$, where z is the coordination number of the lattice. Now we fix our attention on one such pair of nodes and consider the conductance across it, replacing the rest of the network by a conductance σ_n. If the current flowing into the lattice is i, the voltage drop across the node is, when all conductances equal $\bar{\sigma}$,

$$V = i/(\sigma_n + \bar{\sigma}) = \bar{V}. \tag{1}$$

Therefore, $\sigma_n = (\frac{1}{2}z - 1)\bar{\sigma}$. When $\bar{\sigma}$ is replaced by σ_i, the voltage drop becomes

$$V_i = i/(\sigma_n + \sigma_i) = \bar{V}(\sigma_n + \bar{\sigma})/(\sigma_n + \sigma_i). \tag{2}$$

Substituting for σ_n we have,

$$V_i - \bar{V} = \bar{V}(\sigma_i - \bar{\sigma})/[\sigma_i + (\tfrac{1}{2}z - 1)\bar{\sigma}]. \tag{3}$$

By the definition of $\bar{\sigma}$, as all conductances are replaced by their original values, $V_i - \bar{V}$ should average to zero. Thus, if $p(\sigma)$ is the probability distribution of conductances σ, we have, for a cubic network,

$$\int d\sigma\, p(\sigma)(\sigma - \bar{\sigma})/(\sigma + 2\bar{\sigma}) = 0. \tag{4}$$

If $p(\sigma)$ is a binary distribution, σ_m is the metallic conductivity, and σ_α is the insulator conductivity, Eq. (4) becomes

$$\frac{(v_m/f)(\sigma_m - \bar{\sigma})}{\sigma_m + 2\bar{\sigma}} + \frac{(1 - v_m/f)(\sigma_\alpha - \bar{\sigma})}{\sigma_\alpha + 2\bar{\sigma}} = 0. \tag{5}$$

This is a quadratic equation for $\bar{\sigma}$, with the root given by

$$4\bar{\sigma} = \sigma'_\alpha + \sigma'_m + [(\sigma'_\alpha + \sigma'_m)^2 + 8\sigma_\alpha\sigma_m]^{1/2}, \tag{6}$$

where

$$\sigma'_\alpha = (2 - 3v_m/f)\,\sigma_\alpha,$$

and

$$\sigma'_m = (3v_m/f - 1)\,\sigma_m.$$

The conductivity resulting from (6) is shown in Fig. 1, as is the result of Bueche. The conditions are that the ratio of the metallic conductivity, σ_m, to that of the insulator, σ_α, is 10^8, and the plot is of $\log(\sigma_\alpha/\bar{\sigma})$ vs v_m. Al-

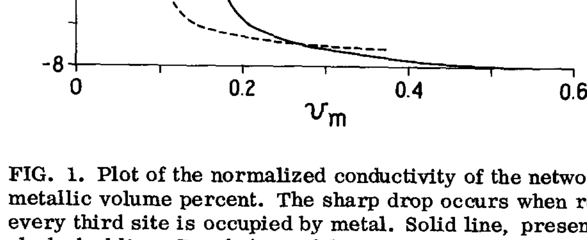

FIG. 1. Plot of the normalized conductivity of the network vs metallic volume percent. The sharp drop occurs when roughly every third site is occupied by metal. Solid line, present model; dashed line, Bueche's model.

though it is hard to discern from the figure, the present model has a slope (in the coordinates of the graph) some 30 times less steep than the model of Bueche. In fact, Bueche's model is somewhat similar to the present one in that it also is an averaging model. He considers only those metallic particles which form a connected chain through the whole sample. He uses a polymer theory to obtain the condition for this. He then forms an average conductance between the number of such chains and the remaining matrix. One result of this approach is that there is no increase in conductivity until a chain of the same length as the sample is formed, which accounts for the slope discontinuity exhibited in Fig. 1. An interesting aspect of both theories and of experiment is that in a certain region $\bar{\sigma}$ is extremely sensitive to v_m. Thus, for example, application of pressure could cause large changes of conductivity.

The experimental results,[3] which deal mainly with spheres of micron size, are quite similar to the solid line in Fig. 1 save in the region where the conductivity is slowly varying. A two-dimensional experiment by Last and Thouless[4] shows similar discrepancies. It is obvious that, in order to obtain meaningful comparisons with theory, quite carefully controlled experiments are necessary. But such experiments could prove exceedingly useful in determining the relevance of percolation theory[2] to the calculation of the conductivity in the regions where the metal particles first form small connected, but tortuous, chains in the material, and where there are no longer any continuous chains of the insulator.

Another shortcoming of Bueche's model is that it ignores all metal particles not in a continuous chain. It is worthy of note that measurements of the ac conductivity can throw some light on the degree of clustering by comparing the measurements with a Maxwell-Wagner-Sillars sort of theory.

As the number of nearest neighbors increases, both curves in Fig. 1 shift to the left. When a variety of different-sized spheres is taken into account, the packing fraction, which reflects the number of nearest neighbors, will increase. These two effects can explain some of the additional details of the experimental results to date. They are susceptible of inclusion in the model via the distribution function, $p(\sigma)$, and via the lattice coordination number, z.

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