PHYSICAL REVIEW B VOLUME 35, NUMBER 16 1 JUNE 1987

Scher and Zallen criterion: Applicability to composite systems

I. Balberg
The Racah Institute of Physics, The Hebrew University, Jerusalem 91904, Israel

N. Binenbaum
RCA Laboratories, Princeton, New Jersey 08540
(Received 17 October 1986)

The application of the Scher and Zallen criterion to continuum systems, made of metallic particles of radius R_M and insulating particles of radius R_I, is examined in view of the many cases of its misuse. It is argued that in the $R_M \ll R_I$ limit an excluded-volume determination of the percolation threshold should be used. For the $R_M \approx R_I$ case the Scher and Zallen critical fractional volume is maintained in the continuum only when the particles are spherical and of equal size. In the more common case of $R_M \gg R_I$, a hard-core soft-skin particle model provides the best available description of the system.

Seventeen years ago Scher and Zallen[1] found that the occupied conducting-volume fraction needed for the onset of percolation shows a "remarkable insensitivity to lattice structure."[2] In three dimensions the Scher and Zallen (SZ) invariant was found to be 16% of the total volume. In the many works[3-8] which have applied this criterion, little attention has been given to the fact that this invariant was found for lattices composed of a disordered mixture of metallic spheres of radius R_M and insulating (or missing) spheres of radius R_I, such that $R_M = R_I$. Correspondingly, this criterion has been misused in many discussions where it was treated as a much more general invariant than it actually is. In particular, the above value has been compared with experimental results obtained on systems in which metallic (or conducting) particles were embedded in a continuous insulating matrix,[3,6] on systems made of metallic and insulating particles[4,7] for which $R_M \neq R_I$, and on systems where the conducting particles[7] or the insulating parts[5] cannot be approximated by a spherical shape. Two recent examples are typical. In one, the fact that the critical conducting-volume fraction ϕ_c was close to that of the SZ value was misinterpreted as indicating spherical conducting particles,[6] while in the other[7] the different experimental result was described as "near the theoretical value." In the corresponding systems the SZ conditions are not fulfilled and, thus, *a priori*, the SZ value is not to be expected. As we shall show below, the ϕ_c values obtained in these systems have very little to do with the SZ criterion; rather, they are associated with other, special, properties of the systems. We also note that the large deviations of the percolation threshold from the SZ value in granular metals[3,8] and systems of particle mixtures,[9,10] have not been explained thus far.

That the SZ value does not hold beyond lattice systems of equal size spheres (for which it was found) is apparent from the experimental results on three-dimensional composites which show fractional volumes as low[9] as 2% and as high[8] as 60%. Hence, if percolation thresholds are to be derived, one has to consider more details of the system with the hope of finding trends in the effect of the system parameters on these thresholds.[11-13] This paper presents an attempt to find such trends and to call attention to the limited applicability of the SZ criterion. In particular, we show that three regimes, defined by the R_M/R_I ratio, determine three different approaches for the evaluation of the critical fractional volumes. We further show that the use of the appropriate percolation approach can yield information regarding the transport mechanism in the corresponding composite. Finally, we suggest that existing phenomenological theories provide a good description of composites for the regimes where the SZ criterion is not applicable.

Let us start with the $R_M \ll R_I$ limit. In this case, the metal particles fill the nonspherical voids between the insulating particles in a situation that resembles a conducting liquid filling the pores in a sedimentary rock. Under these conditions, as we have shown recently,[11] the total pore space can be made as small as desired. Correspondingly for this limit (which is well described by the excluded volume theory[11,13]) the critical volume fraction of the conducting metal, ϕ_c, should be determined by considering a system of pores rather than a system of particles. This means that the shape of the metal particles or their size distribution are of little importance in the determination of the value of ϕ_c. Hence, values[11] of $\phi_c \approx 0$ should come as no surprise. *Indeed,* such low values of ϕ_c have been obtained[9] in composites where the $R_M \ll R_I$ condition prevails. In fact, these experimental results are the *best* confirmation of the situation expected in rocks[11] (Archie's Law) where a well-controlled experiment has not been carried out thus far. (The $\phi_c \approx 0$ results have been derived from a collection of electrical conductivity data on "similar" rocks[11] with different total pore volumes.) In contrast, the above-mentioned composites[9] provide a well-characterized system in which the metal content can be varied continuously. We note that the case of a conducting liquid in a system of overlapping spherical pores (rather than insulating spherical particles) belongs to the above group of systems and is the simplest case for which the excluded-volume theory[13] applies. Hence, in these "Vycor" glasslike systems[5] the value[11,13] of $\phi_c = 0.29$ rather than the SZ value[5] of $\phi_c = 0.16$ should be used.

The second group of systems to be considered is the group of mixtures of *touching* spheres for which $R_M = R_I$. Under these conditions the value of ϕ_c is expected to be close to the SZ value because the number of nearest neighbors in a random packing of spheres[10] is about the same as that of a bcc lattice for which the SZ criterion is fulfilled.

As the value of R_M is increased from $R_M < R_I$ to $R_M > R_I$ the value of ϕ_c should increase through the SZ value, monotonically. The effect of metal particle distribution is expected to increase the value of ϕ_c since (see below) the randomly positioned smaller metal particles can be "trapped" in voids between the larger insulating particles where they are unable to contribute to the conduction. Note that we may use the term "trapping" since the onset of percolation is at a much lower metal content, ϕ_c, than insulator content, $1-\phi_c$, and thus there will be more trappings of metal particles in an insulating environment than the reverse. This expectation is supported by the higher ϕ_c values which were obtained on experimental systems where such distributions of metal-sphere size do exist.[10] On the other hand, the deviation from sphericity has the opposite effect on ϕ_c. As to be expected intuitively[12] and as confirmed by computer simulations,[13,14] a lower connectivity is needed for the onset of percolation when the system is made of elongated particles (see below). However, this is true only if the orientations of these objects provide a random isotropic system. Under some preparation conditions of composities the elongated objects may line up[15] and thus the value of ϕ_c will increase.[11,13] We may conclude then that for systems of nonspherical particles a ϕ_c value lower than 0.16 is expected for the isotropic case while higher values are expected for the extreme anisotropic cases. In Ref. 7, where the system considered was made of elongated metallic particles, which have a size distribution, the threshold at $\phi_c = 0.21$ is the combined result of these two contradicting factors. Hence the proximity to the SZ value is quite accidental.

Let us turn now to the case of widest interest in the physics of composite materials, i.e., composites in which metallic particles are embedded in an insulating matrix. This case, which is less understood than the previous two, is well described by the $R_M \gg R_I$ limit. Here the conducting particles are placed randomly in space and the insulating matrix can be viewed as made of fine particles filling the pores between them. If there is no operative attraction between the conducting particles they will not touch each other since exact touching requires an infinite accuracy of positioning. Hence, the system will exhibit percolation only in the trivial limit of random close packing. The situation in the continuum is very different then from the situation found in the SZ case of lattices, where two nearest-neighbor spheres touch each other *automatically*. In fact, as will be argued below, this property rather than the "being-on-lattice" property is responsible for the SZ invariance. For spheres the (well-known[2]) corresponding fractional occupied volume in the continuum is 64%. We may conclude then that for a continuum system of spheres we should relate $\phi_c \rightarrow 0.0$ to the $R_M \ll R_I$ case, $\phi_c = 0.16$ to the $R_M \approx R_I$ case, and $\phi_c \rightarrow 0.64$ to the $R_M \gg R_I$ case.

We know, however, that most systems,[3,6,15] which seem to be described by the $R_M \gg R_I$ random close packed structure,[2] have ϕ_c values which are smaller than 0.64. Such a lower value can come about when adjacent spheres are forced to touch each other, or when two spheres can be considered touching or in physical contact, even though they are not touching geometrically. Geometrical contact can be provided, for example, by a "gravitational force" under which the essence of the automatic touching, which exists in the lattice (i.e., the SZ case), is restored. This suggests that in the presence of an external force the deviation of ϕ_c from the 0.16 value should be quite small. Indeed, computer simulations[16] of such a system yield a value of $\phi_c = 0.18$. On the other hand, if short-range-order attraction and repulsion are considered, a more complicated behavior of the percolation threshold takes place.[17] One notes of course that a long-range attraction will make the whole system collapse, and the problem at hand ceases to be a percolation problem.

In solid composites,[6,8,15] such forces do not seem to play any significant role and thus the particles can be assumed to be randomly distributed in the insulating matrix. Correspondingly, there must be a mechanism which enables electrical conduction between nontouching nearest neighbors. If the charge-transfer mechanism is of long range, the percolation threshold loses its meaning and thus only short-range charge-transfer cases should be considered. Such cases can be described by spherical particles, of hard core radius b, which have a soft (penetrable) skin (charge-transfer range) thickness, $a-b$. We do know already[17] that the percolation threshold will vary between $\phi_c = 0$ in the $b/a = 0$ case and $\phi_c = 0.64$ in the $b/a = 1$ case. Physical touching in composites (see examples below) corresponds, usually, to the case where b/a is smaller than, but close to, unity.[8,15]

In order to consider this (composites-most-common) regime we have carried out a Monte Carlo computation which yielded the critical concentration of particles of a given shape, N_c, as a function of b/a. In particular, we have followed the two effects which may cause deviations of ϕ_c from the results obtained for an ensemble of equal-size spheres. In our simulations, particles were implanted randomly in a unit cube. If the hard core of a new particle overlapped the hard core of any already existing particle it was discarded, while if only their soft skin overlapped they were considered in contact. This procedure[14,18] creates a homogeneous distribution of particles, as to be expected from an equilibrium situation,[17] from a good mixing of the metal particles[7,15] or from the random preferential locations in which new particles will grow.[6,8] To check our computation procedures we have compared our results with those obtained by Bug, Safran, Grest, and Webman,[17] using a different procedure and intended for another purpose. We found that their results, which were derived only for spheres, were exactly the same as ours. This becomes apparent when one notes that the dependence of N_c (or[17] $N_c 4\pi a^3/3$) on b/a can be easily translated to a dependence of $\phi_c = N_c 4\pi b^3/3$ on b/a. The corresponding results are shown by the "fixed a, $b = B_\mu$ spheres" curve in Fig. 1. Since, as pointed out above, there are no practical composites (in the $R_M \gg R_I$ limit) in which the metallic particles have an exact spherical shape or a single size, we studied the b/a dependence of ϕ_c for capped cylinders (length L, hard core radius b, skin $a-b$) as well as for variable-size spheres.[14] In the latter case we assumed a hard-core radius b which had a normal distribution (with a mean B_μ and a width σ) so that for a given B_μ the value of $a-b$ was kept constant. This corresponds, for example, to cases where the conduction mechanism depends only on the distance between the surfaces of the particles (e.g., tunneling). The results shown in Fig. 1 indicate clearly that for elongated particles (for the same b/a), lower ϕ_c values will be obtained, while if a distribution of particle sizes exists (small particles trapped in voids—see above), larger values of ϕ_c will be obtained. As for the soft-core limit ($b/a=0$) one obtains[11] that the larger the aspect ratio (e.g., L/b) of the particles the lower will be the percolation threshold N_c or ϕ_c. Further, if there is a length distribution of the L values one can account for the distribution by considering their average value as we have done for the soft-core limit.[13,14]

Let us now see what the present results teach us regarding three composites of interest. For carbon-black composites[15] where $\phi_c \approx 0.1$ the aspect ratio and the "structure"[15] of the particles determine the number of "contact" points between two adjacent particles. If we consider then the results of Fig. 1 as pertinent to some "average" particle which is approximated by a cylinder (of an aspect ratio L/b of 10) we may get an estimate for the average value of $2(a-b)$. Following the data in the literature[15] such an average particle is 1500 Å long and 150 Å wide. For $\phi_c \approx 0.1$ this yields, according to Fig. 1, an average of $2(a-b) \approx 100$ Å, which means that tunnelable distances (less than 100 Å) exist between adjacent particles. This conclusion is consistent with the fluctuation-induced tunneling mechanism suggested[19] for these composites. For various granular metals, in which nearly spherical particles of radii between 10 and 60 Å and corresponding ϕ_c values between 0.60 and 0.40 were found,[8] the lack of explanation for the deviation from the SZ value has been pointed out.[3] Such an explanation is provided now by the results of Fig. 1, since these results imply that for all granular metals $2(a-b)$ at the percolation threshold is than about 10 Å. We interpret these results as indicating that, close to the percolation threshold, contacts are established by the coalescence of particles. This interpretation is supported by the fact that the metal grain radius can be varied by a few Å due to sample annealing[8] (which means that particles are bridged by "necks" in the real material) and by the fact that the temperature dependence of the conductivity is changed from activated to metallic at the percolation threshold.[8,14] Hence, due to the absence of an "automatic contact" (see above) the large deviations from the SZ result is not surprising, and the present hard-core soft-core Monte Carlo model is a much more realistic description for the connectivity of the granular systems. The fact that a preliminary attempt to provide an analytical solution[20] for a system of spheres yielded results which are not too far from the Monte Carlo results indicates that liquidlike (hard-core soft-core) theory[20] (Percus-Yevick approximation) may be a promising approach for the description of this third ($R_M \gg R_I$) regime.

Another composite of interest is that of microcrystalline silicon in which crystalline clusters are embedded in an insulating hydrogenated amorphous silicon matrix. For this system it was found[6] that $\phi_c=0.16$ and $b=500$ Å. From Fig. 1 one finds that this implies a distance of $2(a-b) \approx 300$ Å if spherical particles are assumed.[6] Since such a distance is not in agreement with any reasonable charge transfer mechanism, and since no short-range attraction between the microcrystallites is known to exist, we must conclude from Fig. 1 that the particles are elongated (or most likely, have a disklike shape[11]). It is quite apparent, then, that the fact that the experimental ϕ_c equals the SZ result is quite accidental, and thus the conclusion regarding microcrystalline spherical clusters[6] is unfounded.

In conclusion, we have defined three regimes of percolation thresholds in the continuum, each of which has to be treated by a different approach. The well-known Scher and Zallen approach appears to be applicable only to the intermediate regime where the system provides geometrical contacts between its equal-size spherical particles. The other two regimes are better described by either excluded-volume or liquidlike empirical theories.

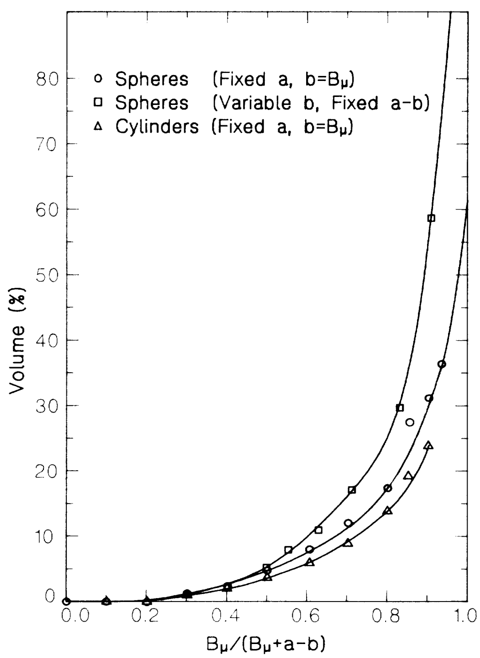

FIG. 1. The b/a dependence of the critical fractional volume occupied by the hard cores of the particles ϕ_c. For spheres, a was fixed (0.04 in sample's diameter units) and the b/a ratio was determined by the variation of $b \equiv B_\mu$. For the capped cylinders, the length L ($=0.15$) and the radius a ($=0.015$) were fixed and the b/a ratio was determined by the variation of $b \equiv B_\mu$. In the case of spheres with a distribution of radii, the soft-skin thickness, $a-b$, was fixed for a given value of the mean of the distribution of the hard cores B_μ. These results were derived for a normal distribution with a width of $\sigma=0.01$. Again, the different values of the B_μ/a ratio were obtained by the variation of B_μ.

[1]H. Scher and R. Zallen, J. Chem. Phys. **53**, 3759 (1970).
[2]R. Zallen, *The Physics of Amorphous Solids* (Wiley, New York, 1983).
[3]B. Abeles, H. L. Pinch, and J. I. Gittleman, Phys. Rev. Lett. **35**, 247 (1975).
[4]D. M. Grannan, J. C. Garland, and D. B. Tanner, Phys. Rev. Lett. **46**, 375 (1981).
[5]G. Baym, Physica A **96**, 131 (1979).
[6]R. Tsu, J. Gonzalez-Hernandes, S. S. Chao, S. C. Lee, and K. Tanaka, Appl. Phys. Lett. **40**, 534 (1982).
[7]D. A. Rudman, J. J. Calabese, and J. C. Garland, Phys. Rev. B **33**, 1456 (1986).
[8]B. Abeles, Appl. Solid State Sci. **6**, 1 (1976).
[9]G. E. Pike, in *Electrical Transport and Optical Properties of Inhomogeneous Media,* American Institute of Physics Conference Proceedings No. 40, edited by J. C. Garland and D. B. Tanner (AIP, New York, 1978), p. 366.
[10]H. Ottavi, J. Clerc, G. Giraud, J. Rossenq, E. Guyon, and C. D. Mitescu, in Ref. 9, p. 372.
[11]I. Balberg, Phys. Rev. B **33**, 3618 (1986), and references therein.
[12]R. Landauer, in Ref. 9, p. 2.
[13]I. Balberg, N. Binenbaum, and N. Wagner, Phys. Rev. Lett. **52**, 1465 (1984).
[14]I. Balberg and N. Binenbaum, Phys. Rev. A **35**, 5174 (1987).
[15]K. T. Chung, A. Sabo, and A. P. Pica, J. Appl. Phys. **53**, 6867 (1982); I. Balberg, N. Binenbaum, and S. Bozowski, Solid State Commun. **47**, 989 (1983); I. Balberg and J. Blanc, Phys. Rev. B **31**, 8295 (1985).
[16]M. J. Powell, Phys. Rev. B **20**, 4194 (1979).
[17]A. L. R. Bug, S. A. Safran, G. S. Grest, and I. Webman, Phys. Rev. Lett. **55**, 1896 (1985).
[18]G. E. Pike and C. H. Seager, Phys. Rev. B **10**, 1421 (1974).
[19]E. K. Sichel, J. I. Gittleman, and P. Sheng, Phys. Rev. B **18**, 5712 (1978).
[20]T. DeSimone, R. M. Stratt, and S. Demoulini, Phys. Rev. Lett. **56**, 1140 (1986).