Percolation threshold for Bruggeman composites

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Using a simple phenomenological approach, we calculate the percolation threshold for Bruggeman composites having microgeometry of two kinds. Both kinds of composites consist of spheroids whose shape follows the Beta distribution. At the same time, the first one is a mixture of spheroids equally oriented along their revolution axis. In this case the percolation threshold is shown to be the same as for an assembly of equally oriented identical spheroids whose shape corresponds to the most probable shape of the distribution. For such composites the percolation threshold can vary between 0 and 1. The second one is a random mixture of the spheroids. In this case the percolation threshold is expressed in terms of the Gauss hypergeometric function; it is shown to vary between 0 and 1/3. The derived analytical results are supplemented with numerical calculations carried out for different values of the Beta distribution parameters.

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Percolation is important to develop a basic understanding of microgeometry- (morphology-) property relationships in heterogeneous materials (composites). In particular, the percolation threshold is an important parameter characterizing heterogeneous systems of various types. However, although the percolation theory is a well developed branch in the theory of the heterogeneous systems and critical phenomena, there is still a great deal to learn about relationship between the microgeometry of composites and the percolation threshold.

There are several approaches to describe the microgeometry of random composites. The advantages and disadvantages of various methods of composite media characterization are considered in the review [1]. We note that, among others, an approach based on the statistical correlation functions [2] appears to be quite useful and to have considerable promise. Many researchers employ computer simulation to describe percolation properties of various materials (see, e.g., [3–5]). Generally, many results of the percolation theory are derived using the simulation (see, e.g., [2,6–10] and references therein). Other techniques, such as network mapping and renormalization, are apparently of limited application. Anyway, consideration of size- and shape-distributed particle systems involves great difficulties. In this report, we develop a simple phenomenological approach allowing one to obtain analytical estimations for the percolation threshold of composites of a special type possessing the so-called Bruggeman microgeometry.

It is well known that percolation has a strong influence on transport. On the other hand, if the effective transport coefficients are wanted, for two-phase composites they can be expressed in terms of the spectral representation [11]. The latter signifies the microgeometry of the composites. In specific cases (for specific microgeometries) a number of effective medium theories exist for the effective transport coefficients. Here we deal with Bruggeman (symmetrical) composites. For such composites, all components (phases) are symmetrical in the statistical sense. This means that an interchange of any two phases results in the same type of composite but with interchanged volume fractions.

The Bruggeman composite is one in which each sphere (ellipsoid) is surrounded by a mixture of the two phases which has the effective value for the composite. To fill the space up, the spheres (ellipsoids) must have an infinite range in size. In the more general case, the ellipsoids are also shape distributed. In Ref. [12], an approach is proposed to describing such composites based on introducing shape-distribution functions. The main objective of this paper is to find the percolation threshold for the composites. So we refine on and supplement the previous work [12].

First of all, we remark that in two dimensions (2D) our problem has a trivial solution and the exact percolation threshold can be determined by a straightforward argument [13]. Indeed, as was noted above, the original system and "conjugate" system (obtained by interchanging the roles of conducting and insulating areas) are statistically equivalent. This means that if the conductor percolates at p_c, then the insulator percolates as its volume fraction is $1-p_c$. Because in 2D the percolation path of one phase blocks the percolation of the other; the point at which one phase first percolates and that at which the other phase last percolates are the same. It immediately follows that $p_c=1/2$ for Bruggeman composites in 2D.

Let us now consider the generalized Bruggeman equation in 3D. For equally oriented shape-distributed spheroids (ellipsoids of revolution), if the electric field is directed along the revolution axis, it is of the form [12]

$$\sum_i p_i \int_0^1 dL \frac{P(L)}{s_i + L} = 0, \qquad (1)$$

with the ith phase volume fraction p_i, the spheroid depolarization factor L corresponding to the direction of its revolution axis, a positive shape-distribution function $P(L)$, and the spectral variables $s_i=\sigma_{eff}/(\sigma_i-\sigma_{eff})$, where σ_i and σ_{eff} are the conductivities of the ith phase and the effective medium, respectively. Because each integral in Eq. (1) can be consid-

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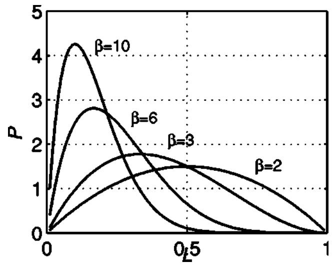

FIG. 1. General view of the Beta distribution (4) at $\alpha=2$.

ered as the averaged spheroid polarizability, this equation means that the total polarization along the revolution axis must vanish. In this case the two-phase composite undergoes percolation transition at the critical point $p_2 \equiv p = p_c$ if the equation

$$\int_0^1 dL\, P(L)G(L) = 0 \tag{2}$$

holds; here

$$G(L) = \frac{L - p_c}{L(L-1)}. \tag{3}$$

Generally, the integral equation (2) possesses many solutions. In other words, many functions exist which are orthogonal to the kernel $G(L)$ on [0, 1]. At the same time, it is clear that the form of the distribution function has a determining effect on the percolation properties of the composite. In the subsequent development, however, we restrict our attention to a Beta distribution case. So we take

$$P(L) = P_B(L) = CL^{\alpha-1}(1-L)^{\beta-1}, \tag{4}$$

where $C=\Gamma(\alpha+\beta)/\Gamma(\alpha)\Gamma(\beta)=1/B(\alpha,\beta)$ is the normalization constant, $\Gamma(\ )$ is the gamma function, and $B(\ )$ is the Beta function. Besides, we take here $\alpha>1$, $\beta>1$. There are several reasons for this choice. First of all, the Beta distribution is the simplest two-parameter distribution which seems to be physically feasible. Unlike the widely used steplike distribution [12,14–19], it is smooth. In a sense, the Beta distribution defined on [0,1] is of the same importance as the Gauss one defined on $[-\infty,+\infty]$. In addition, if $\alpha>1$, $\beta>1$ then the distribution has a peak; it is easy to check that it occurs at

$$L^* = \frac{\alpha-1}{\alpha+\beta-2}. \tag{5}$$

This means that a most probable shape exists for each phase. By varying the relationship between α and β, we can vary this shape over wide limits, from long needles to flat disks. At the same time, if $L\to 0$ or $L\to 1$ then $P(L)\to 0$. So infinitely long needles and infinitely thin disks are absent in the system under consideration. Mathematically, this allows one to determine the nontrivial percolation threshold for the generalized Bruggeman equation. As an illustration, general view of the Beta distribution for this case is presented in Fig. 1.

It was noted in our previous work [12] that the choice of the Beta distribution for Bruggeman composites does not yield a nontrivial percolation threshold. However, as we shall see below, this statement is not exactly correct, namely, if $\alpha>1$, $\beta>1$ then a nontrivial percolation threshold exists.

Let us substitute Eqs. (3) and (4) into Eq. (2). As a result, one has

$$\int_0^1 dL\, L^{\alpha-1}(1-L)^{\beta-2} = p_c\int_0^1 dL\, L^{\alpha-2}(1-L)^{\beta-2}. \tag{6}$$

This equation can be rewritten as [20]

$$B(\alpha,\beta-1) = p_c B(\alpha-1,\beta-1), \tag{7}$$

or as

$$\frac{\Gamma(\alpha)\Gamma(\beta-1)}{\Gamma(\alpha+\beta-1)} = p_c\frac{\Gamma(\alpha-1)\Gamma(\beta-1)}{\Gamma(\alpha+\beta-2)}. \tag{8}$$

Then, using the relationship $\Gamma(x+1)=x\Gamma(x)$, one obtains the needed equation for the percolation threshold,

$$p_c = (1+\gamma)^{-1} \tag{9}$$

where $\gamma=(\beta-1)/(\alpha-1)$. Comparing this with Eq. (5) we can see that

$$p_c = L^*. \tag{10}$$

It is worth mentioning that the same percolation threshold corresponds to the choice of the distribution function in the form of the Dirac delta function, $P(L)=P_\delta(L)=\delta(L-L^*)$ [12] and is in line with that obtained from different generalizations of the Bruggeman theory [21]. On the other hand, it is well known that when the variance of the Beta distribution tends to zero, the distribution, in its turn, tends to the Dirac delta function. This means that in contrast to the steplike distribution [12] allowance for the smearing of the delta function in this model does not change the percolation threshold. If $L^*\to 0$ then the spheroids degenerate into infinite parallel cylinders, and we obtain the trivial result $p_c \to 0$. If $L^*\to 1$ then the spheroids degenerate into parallel flat disks, the problem becomes one dimensional, and the percolation becomes impossible.

Consider now the case when the spheroids are randomly distributed. Then for the spheroids of a fixed shape the Bruggeman equation reads (see, e.g., [22])

$$\sum_i p_i \sum_{j=1}^{3}(s_i+L_j)^{-1} = 0 \tag{11}$$

where we have to take into account that $L_1=L, L_2=L_3=(1-L)/2$. If the spheroids are shape distributed, Eq. (11) should be rewritten as

$$\sum_i p_i \int dL\, P(L)\sum_{j=1}^{3}(s_i+L_j)^{-1} = 0. \tag{12}$$

It can easily be seen that in this case the kernel of Eq. (2) is

$$G(L) = \frac{p_c}{L} + \frac{5p_c-1}{1-L} - \frac{4(1-p_c)}{1+L}. \tag{13}$$

Substituting Eqs. (13) and (4) into Eq. (2), one has

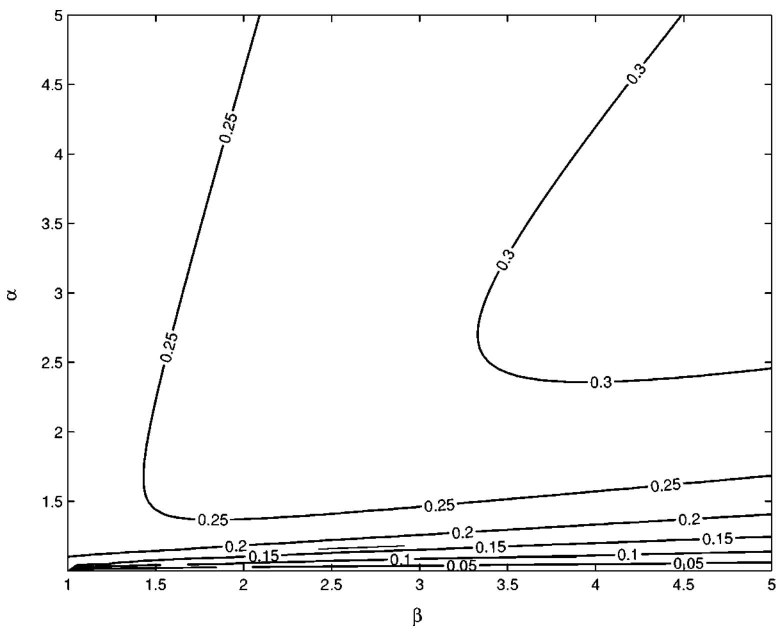

FIG. 2. Curves $p_c(\alpha,\beta)=$const computed according to Eq. (16).

$$p_c\frac{\alpha+\beta-1}{\alpha-1}B(\alpha,\beta)+(3p_c-1)\frac{\alpha+\beta-1}{\beta-1}B(\alpha,\beta) - 4(1-p_c)\int_0^1 dL\frac{L^{\alpha-1}(1-L)^{\beta-1}}{1+L}=0. \qquad (14)$$

Using the integral representation for the hypergeometric function ${}_2F_1$ [20], Eq. (14) may be rewritten as

$$p_c\frac{\alpha+\beta-1}{\alpha-1}+(3p_c-1)\frac{\alpha+\beta-1}{\beta-1} - 4(1-p_c){}_2F_1(\alpha,1;\alpha+\beta;-1)=0. \qquad (15)$$

This yields the chosen equation for the percolation threshold

$$p_c=\frac{\dfrac{\alpha+\beta-1}{\beta-1}+4{}_2F_1(\alpha,1;\alpha+\beta;-1)}{5\dfrac{\alpha+\beta-1}{\beta-1}+\dfrac{\alpha+\beta-1}{\alpha-1}+4{}_2F_1(\alpha,1;\alpha+\beta;-1)}. \qquad (16)$$

If the variance of the Beta distribution, $D(L)=\alpha\beta/(\alpha+\beta)^2(\alpha+\beta+1)$, tends to zero, then the distribution tends to the Dirac delta function. Thus, when $\alpha,\beta\rightarrow\infty$ we may write

$$P(L)=P_\delta(L)=\delta(L-L^*). \qquad (17)$$

Substituting Eqs. (17) and (13) into Eq. (2) gives after simple algebra the well known result (see, e.g., Ref. [22])

$$p_c\cong L\frac{5-3L}{1+9L}, \qquad (18)$$

where we have dropped the superscript near L. As is easy to see from Eq. (18), $p_c(L)$ peaks at $L=L_{\max}=1/3$; the peak value of the percolation threshold in this case is $p_c(L_{\max})=1/3$.

In Fig. 2, there are shown the isolines $f_c=$const calculated according to Eq. (16) as a function of α and β. One can see that, generally, the percolation threshold can vary between 0 and $1/3$. We note that most of the known 3D composites percolate within this range [12]. At the same time, two salient regions can be distinguished, $0<p_c<0.2$ and $0.2<p_c<1/3$. The first region is inherent in elongated spheroids, when $(\alpha-1)/(\beta-1)\ll 1$. The distinctive feature of this region is a monotonic decrease of the percolation threshold as $\beta\rightarrow\infty$ or $\alpha\rightarrow 1$. As to the second region, the dependence $p_c(\alpha)$ is nonmonotonic. We note also that if $\alpha\rightarrow\infty$ or $\beta\rightarrow\infty$ then the isolines approach the straight lines

$$\frac{\alpha-1}{\beta-1}=\frac{L_c}{1-L_c}, \qquad (19)$$

where

$$L_c=\frac{1}{6}[5-9p_c\pm\sqrt{(5-9p_c)^2-12p_c}] \qquad (20)$$

is a solution of the quadratic equation (18) (here the sign "+" corresponds to $\alpha\rightarrow\infty$ and the sign "−" corresponds to $\beta\rightarrow\infty$). Besides, if $\beta\rightarrow 1$ then $L_c\rightarrow 1$ (this corresponds to flat disks) and $p_c\rightarrow 0.2$.

Of course, it is vital to know for which composites the generalized Bruggeman equation (12) holds. We must admit that up to now this question is, generally, unclear and is, hence, open for further consideration. At the same time, Eq. (12) has, undoubtedly, a considerably wider area of applications than the much used classical Bruggeman equation. A simple example of a system of the first kind, evidently, is the flow of insoluble liquids or freezing of these liquids/melt flow. As to 3D isotropic composites, sandstones, for example, are formed from particles with a variety of shapes and sizes [23]. In ceramics processing and metallurgy, a wide range of materials are formed by sintering powders of polydisperse nonspherical particles [24]. Particular examples are conductor-insulator composites prepared by mixing and compressing initial fine powders [25] and by coprecipitation of solid solutions [26]. It is likely that many of these composites whose phases may be treated on an equal basis may be considered as Bruggeman-like ones.

Finally, it should be noted that, although a great body of percolation simulation data exists, a quantitative comparison of our results and the data is difficult due to the specificity of the Bruggeman microgeometry. Nevertheless, we hope that our theoretical results will prompt more simulation work.

In summary, we have considered the problem of finding the percolation threshold of two-phase Bruggeman-like composites of two kinds consisting of spheroids whose shape adheres to the Beta distribution. The first kind of distribution is an (anisotropic) system of parallel spheroids oriented along their revolution axis. We have shown that for such composites the percolation threshold does not depend on the dispersion of the distribution. It is determined by the position of the distribution mode only and can vary from 0 to 1. The second kind of composite is a system of randomly oriented spheroids. In this case the percolation threshold depends on the distribution dispersion and can vary from 0 to $1/3$. To illustrate the results obtained, the isolines $p_c=\text{const}$ are calculated as a function of the distribution parameters.

[1] R. Hilfer, Adv. Chem. Phys. **92**, 299 (1996).
[2] S. Torquato, *Random Heterogeneous Materials: Microstructure and Macroscopic Properties* (Springer, New York, 2002).
[3] P. Bentz, J. Am. Ceram. Soc. **80**, 3 (1997).
[4] E.J. Garboczi, P. Bentz, and N.S. Martys, in *Methods in the Physics of Porous Media*, edited by P. Wong (Academic, San Diego, 1999).
[5] E.J. Garboczi and P. Bentz, Annu. Rev. Comput. Phys. **7**, 85 (2000).
[6] D. Stauffer, Phys. Rep. **54**, 1 (1979).
[7] E.J. Garboczi, K.A. Snyder, J.F. Douglas, and M.F. Thorpe, Phys. Rev. E **52**, 819 (1995).
[8] A. Bunde and W. Dieterich, J. Electroceram. **5**, 81 (2000).
[9] L.A. Pugnaloni and B. Vericat, J. Chem. Phys. **110**, 4028 (1999).
[10] D. He, N.N. Ekere, and L. Cai, Phys. Rev. E **65**, 061304 (2002).
[11] K. Golden and G. Papanicolaou, Commun. Math. Phys. **90**, 473 (1983).
[12] A. V. Goncharenko, Phys. Rev. E **68**, 041108 (2003).
[13] R. Zallen and H. Scher, Phys. Rev. B **4**, 4471 (1971).
[14] A. V. Goncharenko, E.F. Venger, and S.N. Zavadskii, J. Opt. Soc. Am. B **13**, 2392 (1996).
[15] A. V. Goncharenko, Yu.G. Semenov, and E.F. Venger, J. Opt. Soc. Am. A **16**, 517 (1999).
[16] L. Gao, Phys. Lett. A **309**, 435 (2003).
[17] L. Gao and Z. Li, J. Phys.: Condens. Matter **15**, 4397 (2003).
[18] A. V. Goncharenko, Chem. Phys. Lett. **386**, 25 (2004).
[19] P. Xu and Z. Y. Li, Physica B **348**, 101 (2004).
[20] F. Oberhettinger, in *Handbook of Mathematical Functions with Formulas, Graphs and Mathematical Tables*, Natl. Bur. Stand. Appl. Math. Ser. No. 53, edited by M. Abramovitz and I.A. Stegun (U.S. GPO, Washington, DC, 1964).
[21] F. Brouers, J. Phys. C **19**, 7183 (1986).
[22] A.N. Lagarkov and A.K. Sarychev, Phys. Rev. B **53**, 6318 (1996).
[23] See, e.g., R.C. Selley, *Applied Sedimentology* (Academic, London, 1988).
[24] See, e.g., G.C. Kuczynski, D.P. Uskovic, H. Palmour III, and M.M. Ristic, *Sintering'85* (Plenum, New York, 1987).
[25] Y. Song, T. W. Noh, S.-I. Lee, and J.R. Gaines, Phys. Rev. B **33**, 904 (1986).
[26] T. W. Noh, Y. Song, S.-I. Lee, J.R. Gaines, H.D. Park, and E.R. Kreidler, Phys. Rev. B **33**, 3793 (1986).