

## GENERALIZED PERCOLATION THEORY FOR THE ANALYSIS OF THE STRUCTURE AND PROPERTIES OF POROUS AND COMPOSITE MATERIALS

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UDC 621.762:5:539.32

*Expressions are obtained for calculating percolation characteristics of heterogeneous systems with the use of refined auxiliary relations in the entire range of their porosity (concentration of a disperse phase).*

To determine characteristics and describe the structure and properties of porous or composite materials use is usually made of models based on regular or random packings of monodisperse particles [1]. However, in so doing, percolation effects occurring in porous systems are often not taken into account, which is not always permissible (for instance, in the analysis of the porous structure of powder materials by the methods of water-air and mercury porometry). Problems described in percolation theory are solved, as a rule, by means of numerical experiments using concrete network models with a specified coordination number. This complicates the use of the obtained results for the analysis of the structure and properties of heterogeneous materials, since it is important to know the parameters of a structure with changing porosity, i.e., with variable coordination numbers of the particles constituting powder systems. In [2, 3] analytical expressions that are sufficiently convenient in practice are obtained for percolation characteristics of networks modeling powder systems. Below we describe these expressions as employed for calculating percolation characteristics of heterogeneous systems with the use of refined auxiliary relations in the entire range of their porosity (concentration of a disperse phase).

For the problem of bonds and nodes correlations of the percolation threshold  $a_{cr.b(n)}$  and the coordination number  $Z$  or the packing porosity  $\Pi$  [ $a_{cr.b} = 1.5/Z$  and  $a_{cr.n} = 0.15/(1-\Pi)$ ] are known that have an error of 5–10% for numerical calculations for regular networks. A higher accuracy may be achieved by using the least-squares method:

$$a_{cr.b(n)} = A_{b(n)}/Z + B_{b(n)}, \quad (1)$$

where  $A_b = 1.59$ ,  $A_n = 1.359$ ,  $B_b = -0.017$ ,  $B_n = 0.08$ .

In order to obtain expressions for heterogeneous systems, it is necessary to use general principles of the dependence of the behavior of the percolation characteristics on the share of the conductive bonds or nodes and the coordination number of model networks:

1. Percolation thresholds on a model network in problems of bonds and nodes are described by a single linear relation (independent of its coordination number).

2. The expression for the percolation probability (the bonding function)  $q_b(Q_n)$  of heterogeneous systems in terms of the share of the conductive bonds (nodes) in the generalized coordinates  $Za - B_{b(n)}$  does not depend on the coordination number of the model network.

3. The ratio of the percolation thresholds (the difference between unity and the thresholds) to the roots of the equations (the difference between unity and these roots) obtained by the self-consistent field method in the problem of bonds (nodes) is a constant.

4. The dependence of the conductance of the network  $\sigma_b$  on the generalized share of the conductive bonds  $[Z(a - B_b)]$  in the entire porosity range differs only by the scale relative to  $[(1 - B_b)Z - A_b]$ .

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Institute of Engineering Thermophysics, Academy of Sciences of the Ukraine, Kiev. Translated from *Inzhenerno-Fizicheskii Zhurnal*, Vol. 66, No. 3, pp. 348-352, March, 1994. Original article submitted October 27, 1992.

5. The dependence of the conductance of the network  $\sigma_n$  on the share of the conductive nodes in the generalized coordinates  $(a - a_{cr.n}) / (1 - a_{cr.n})$  in the entire porosity range does not depend on the coordination number  $Z$  of the network.

On the basis of the first two principles we obtain an auxiliary value of the share of the conductive bonds (nodes)  $a_{a.b(n)}$  for calculation of the percolation probability and the bonding function of heterogeneous systems. For this, we use simple cubic packing ( $Z = 6$ ) and equate  $A_{b(n)}$  for  $Z$  and  $Z = 6$ :

$$a_{a.b(n)} = Z [a - B_{b(n)}] / 6 + B_{b(n)}. \quad (2)$$

The last three principles follow from an analysis of the expression for the conductance of three-dimensional heterogeneous systems in the problem of bonds (nodes) obtained by the self-consistent field method at  $a \rightarrow 1$  (it corresponds to relations tangent at the point  $a = 1$  to those obtained from numerical experiments). Thus, for three-dimensional systems we have

$$\sigma_n(a) = 1 - (2Z - 2)(1 - a) / (Z - 2), \quad (3)$$

$$\sigma_b(a) = (a - 2/Z) / (1 - 2/Z). \quad (3a)$$

Equating  $\sigma$  in expressions (3), (3a) to zero, we obtain the corresponding values of  $a(\sigma_{n.(b)} = 0)$ :

$$a(\sigma_n = 0) = 1 - (Z - 2) / (2Z - 2), \quad (4)$$

$$a(\sigma_b = 0) = 2/Z. \quad (4a)$$

In [3] it is shown that the relation

$$[a(\sigma_n = 0) - a_{cr.n}] / (1 - a_{cr.n}) = 0.43 + 0.01, \quad (5)$$

i.e., the dependence of the conductance on the coordination number, is determined by the quantity  $1 - a_{cr.n}$ .

Substituting  $a(\delta_n = 0)$  from (5) into (4), we arrive at

$$a_{cr.n} = 1 - (7/4)(Z - 2) / (2Z - 2). \quad (6)$$

From expression (6) we obtain  $a_{cr.n}$  values for regular packings that coincide within 5% with known values obtained from numerical experiments [1].

The generalized value of  $a_{a.n1}$  (corresponding to simple cubic packing) is determined from the relation

$$(a - a_{cr.n}) / (1 - a_{cr.n}) = (1 - a_{a.n1}) / (1 - a_{cr.n, Z=6}).$$

From the last expression and (6) we obtain

$$a_{a.n1} = 0.307 - 0.693(a - a_{cr.n}) / (1 - a_{cr.n}), \quad (7)$$

where  $a_{cr.n}$  is determined by (1) or (6).

Equating the ratio  $[(a - B_b)Z - A_b] / [(1 - B_b)Z - A_b]$  for arbitrary  $Z$  and for  $Z = 6$  and using the values of  $A_b$  and  $B_b$  determined earlier, we obtain the generalized  $a_{a.b1}$  for calculation of the conductance of a powder system in the problem of bonds:

$$a_{a.b1} = 0.248 + 0.752Z [(a + 0.017)Z - 1.59] / (1.017Z - 1.59). \quad (8)$$

Figures 1 and 2 show the dependences of the conductance of three-dimensional systems in the problems of bonds and nodes in the generalized coordinates.

Based on the foregoing and [2, 3], the percolation characteristics of three-dimensional systems may be written in the following form:

$$\left. \begin{matrix} q_b(a) \\ Q_n(a) \end{matrix} \right\} = (t_{b(n)} + 1 - 1/a_{a,b(n)}) / (t_{b(n)} + a_{a,b(n)} - 1); \quad (9)$$

$$Q_b(a) = a q_b(a), \quad q_n(a) = a Q_n(a); \quad (10)$$

$$\sigma_{b(n)}(a) = K_{b(n)} (0.5 l_{b(n)} / a_{a,b(n)} + 1) / [1 + (a_{a,n(n)} - a_{cr,n(n), Z=6})^{-1}]; \quad (11)$$

$$l_{a,b(n)} = [1 - a_{a,b(n)} q_{b(n)}(a_{a,b(n)})] l_{b(n)} / [1 + a_{a,b(n)} q_{b(n)}(a_{a,b(n)}) (l_{b(n)} - 1)]; \quad (12)$$

$$t_b = 4a_{a,b} [1 + (3a_{a,b} + 4a_{a,b}^3 + a_{a,b}^4) / (1 - a_{a,b})^3 + 34a_{a,b}^4 (1 + 3a_{a,b})]; \quad (13)$$

$$t_n = t_n(a) = t_b(a_{a,b} = 0.713a_{a,n}); \quad (14)$$

$$l_{b,bl} = 4a_{a,b,1} [1 + (6a_{a,b,1} + 9a_{a,b,1}^2 + 29a_{a,b,1}^3) / (1 - a_{a,b,1})^3 + 139a_{a,b,1}^4 (1 + 6a_{a,b,1})]; \quad (15)$$

$$l_{n,bl} = l_{n,bl}(a) = l_b(a_{a,bl} = 0.713a_{a,n,1}), \quad (16)$$

where  $K_b = 7/3$ ;  $K_n = 2.443$ , and  $a_{a,b(n)}$  and  $a_{a,b(n)1}$  are calculated using expressions (2), (9), and (7), respectively.

It should be noted that the last summands in (13) and (15) are refined, as compared to [3], by taking into account, for the degree of filling of the planes of a model cubic network, the auxiliary bonds with the initial node of the four first-order nodes (via 5 bonds) for six variants and the eight second-order nodes (via 6 bonds) for sixteen variants.

The expressions for calculation of the percolation characteristics of two-dimensional systems may be generalized analogously.

To adopt the described procedure for practice applications, it is necessary to relate the coordination number of model networks to the porosity  $\Pi$  of analyzed materials by using its dependence on the averages of the coordination number of the particles (network) and the radius of interparticle contacts  $d_c$  (it may be assumed equal to zero in some cases) for two- ( $\Pi_2$ ) and three-dimensional ( $\Pi_3$ ) media

$$1 - \Pi_2 = \pi / [Z (1 - 2h_2/D) \tan(\pi/Z)], \quad (17)$$

$$1 - \Pi_3 = (Z - 2)^2 / [8 (Z^2 - 0.6Z - 1.76) (0.5 - h_3/D)^3], \quad (18)$$

where  $h_2 = h_0 - 0.25D^2 [\arcsin(d_c/D) + (d_c/D)(1 - 2h_0/D)/d_c]$ ;  $h_3 = h_0 - 4h_0^2(1.5D^2 - h_0)/(3d_c^2)$ ;  $h_0 = [D - (D^2 - d_c^2)^{0.5}] / 2$ ,  $D$  is the mean diameter of the particles constituting the porous system.

As an example, we consider a method for correcting the integral dependence of the distribution of the volume of the pores with respect to their neck sizes obtained by mercury or gas-liquid porometry (by gas-aided displacement of a liquid from a sample saturated with it)  $\sum_{r_{max,f}}^i V_i(r_i)$ .

Since the problem considered pertains to the bonding problem, we write the share of the pores filled with mercury (or freed of a liquid by a gas) in terms of the corresponding porosity:

$$a_i = \left( \Pi - \sum_1^i \Delta \Pi_{i,f} \right) / \Pi, \quad \Pi = \sum_1^n \Delta \Pi_{i,f}(r_{eq,i}),$$

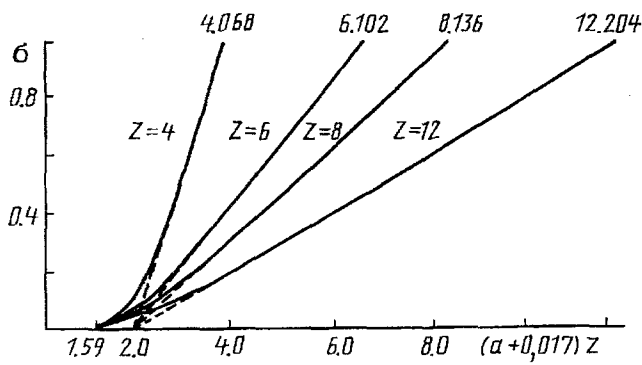


Fig. 1. Conductance in the problem of bonds versus the share of the conductive bonds in generalized coordinates.

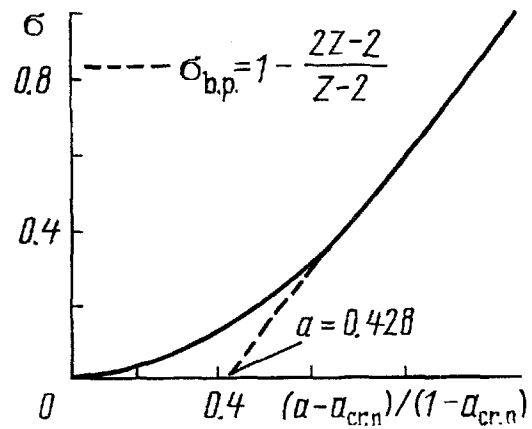


Fig. 2. Conductance in the problem of nodes versus the share of the conductive nodes in generalized coordinates.

$$\Pi_{i,f} = \Pi - \sum_1^i \Delta \Pi_{i,f}(r_{eq,i}),$$

where  $r = 2\gamma \cos \theta/P$ ,  $P$  is the pressure of mercury (a gas) in the  $i$ -th stage of the pressure rise.

An algorithm of correction is as follows:

1. The coordination number  $Z$  of the model network is determined by the porosity,  $\Pi_1$  the size of interparticle contacts  $d_c$ , and expression (18).
2. The values of the bonding function  $Q_{bi}[(a = (\Pi - \Pi_{i,f})/\Pi)]$  are calculated using expressions (9), (10), (13), and (2).
3. For all values the share of the blocked pores  $\Delta a = a - Q_{bi}(a)$  is calculated.
4. The porosity taken over blocked pores  $\Delta_{i,bl} = \Pi(1 - \Delta a_i)$  is calculated.
5. Using  $\Pi_{i,f}$  and  $\Delta \Pi_{i,bl}$  values, the corrected porosity  $\Pi_i$  is calculated:  $\Pi_i = \Pi_{i,f} - \Delta \Pi_{i,bl}$ .

Since at  $Q_i \rightarrow a_i$ ,  $a_i \rightarrow 1$ , the share of the blocked pores gradually decreases to zero with decrease in their size. However, for the portion of the coarsest particles corresponding to the percolation threshold (it makes up almost the one-fourth of the total porosity for a porosity of the material of about 50%) it may only be said that the pores have a size larger than  $r_{eq,i}$ . It is pertinent to note that the widely accepted method of determination of the maximum pore sizes of permeable materials by emergence of the first bubbles of a gas passing through a material saturated with a liquid (see, e.g., [4]) cannot be considered accurate. Indeed, displacement of a liquid out of a material begins only at a gas pressure corresponding to the percolation threshold, i.e., to pores whose radius is considerable smaller than the maximum one.

From the aforesaid it follows that it is desirable to use the methods of mercury and gas-liquid porometry in combination with stereologic studies of porous materials.

In conclusion, a generalized percolation theory is proposed that allows calculation of the percolation characteristics of permeable materials in a wide range of their porosity.

## REFERENCES

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