Percolation in a system of polydispersed particles

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Percolation on planar lattices in a binary system of similarly sized particles was investigated experimentally. It was found that the percolation threshold of the system increases linearly with the number of large particles. For a particle size ratio of order 10 or more, the behavior of the system is practically asymptotic. Percolation was studied analytically in binary and polydispersed systems of spherical (circular) particles with greatly varying sizes. It is shown for the first time that virtually complete, percolation-free filling of space with the remaining unfilled pores forming a fractal structure is possible.

1. INTRODUCTION

It is convenient to describe percolation for a system of identical nodes by an equivalent system of spherical (circular) particles. Irrespective of the type of packing (lattice), the so-called Scher–Zallen invariant holds for the relative fraction of a space of dimension d occupied by particles: $\theta_c = 0.45 \pm 0.02$ ($d = 2$) and $\theta_c = 0.15 \pm 0.01$ ($d = 3$). For $\theta \geqslant \theta_c$ the particles form a percolation cluster (PC). A percolation cluster is also called an infinite cluster, since it contains chains which permeate the entire space. For continuous problems, the percolation thresholds are close to lattice thresholds:[1,2] $\theta_c = 0.50$ ($d = 2$) and $\theta_c = 0.15 \pm 0.02$ ($d = 3$). In this connection, there arises the question of the fundamental possibility of filling a space with relative fraction exceeding θ_c without forming macroscopic clusters.

In the present paper we consider percolation in binary and polydispersed systems of spherical (circular) particles with very different sizes. It is shown, for the first time, that percolation-free filling in the limit $\theta \to 1$ with the remaining unfilled pores forming a fractal structure is possible. Percolation was investigated experimentally for a binary system on planar lattices of particles with close sizes. It was found that the percolation threshold of the system increases linearly with the number of large particles. For particle size ratio of the order of 10 and higher the behavior of the system is practically asymptotic.

2. BINARY SYSTEM

We consider percolation in a binary system of particles with very disparate sizes (asymptotic system). As the space is gradually filled with large particles below the percolation threshold, i.e., with relative fraction of the space occupied by the particles $\theta \leqslant \theta_c$, small particles, occupying a volume of at most $\theta_c(1-\theta)$, can be arranged in the remaining unfilled volume without percolation clusters forming. Therefore, the percolation threshold for a binary system of particles with greatly varying sizes is given by the expression

$$\theta_b = \theta_c + A_b \theta, \qquad (1)$$

where $A_b = 1 - \theta_c$.

Thus for an asymptotic system the percolation threshold is a linear function of the number of large particles.

The behavior of the system for an arbitrary ratio of particle sizes cannot be traced analytically. Let the ratio of the particle sizes be $\mu = R_1/R_2$. If $\mu = 0$, then the expression (1) for the percolation threshold holds. If $\mu = 1$, the system becomes degenerate and the percolation threshold is equal to θ_c.

In order to study the behavior of a binary system for intermediate ratios (i.e.,) for $R_1 \sim R_2$, we employed the Monte Carlo method, implemented on planar lattices according to the standard method of searching for percolation.[2] Percolation (the problem of nodes) in trigonal and tetragonal lattices was investigated. The number of nodes was not less than 20 736 in all experiments.

The experiment was performed as follows. Let an empty lattice with step L be filled in a random manner by large particles with radius $R_2 = (2k+1)L/2$, where $k = 1, 2, 3,\ldots$, up to a relative fraction x_2 of occupied nodes. Percolation arose in the system of large particles for x_2 greater than $x_{2c} = 0.6$ in the tetragonal lattice and $x_{2c} = 0.5$ in the trigonal lattice; this agrees with known results.[2] For values below the percolation threshold $x_2 < x_{2c}$, a definite number of small particles with radius $R_1 = R_2/(2k+1)$ was added in a random fashion. The choice of the radii of the small particles was dictated by the requirement that the lattices be commensurate. The percolation threshold in the binary system was determined by gradually increasing the fraction x_1 of nodes occupied by small particles. Ten experiments were performed and the results were averaged.

Figure 1 shows as a function of x_2 and for different val-

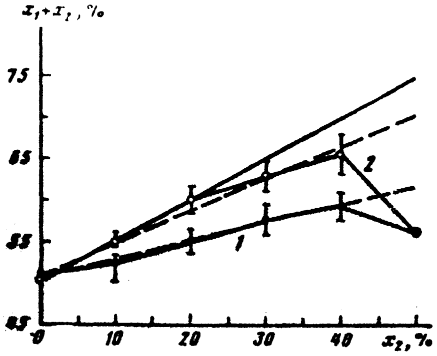

FIG. 1. Percolation threshold of a binary system on a trigonal lattice with $\mu = 1/3$ (*1*) and 1/7 (*2*).

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ues of μ the total value of the fraction of nodes $x_1 + x_2$ which are occupied by particles such that percolation arises in the binary system (on a trigonal lattice). As expected, near the percolation threshold with respect to large particles, $x_2 \to x_{2c}$, the percolation threshold of the binary system fluctuates strongly. In all experiments, however, the percolation threshold of the binary system is a linear function x_2 in both the trigonal and tetragonal lattices: $x_b = x_{1c} + a(\mu)x_2$. This dependence is observed for all x_2 with the exception of threshold regions satisfying the condition $(x_{2c} - x_2)/x_{2c} < 0.1$, where fluctuations are large. As the parameter μ decreases the characteristics of the system approach the limit of strongly differing particle sizes, where the percolation threshold is given by Eq. (1). Therefore the θ_2 dependence of the percolation threshold of a binary system with arbitrary particle sizes can be given by a formula analogous to Eq. (1):

$$\theta_b=\theta_c+A_b(\mu)\theta_2. \tag{2}$$

The coefficient $A_b(\mu) = a(\mu)(1 - \theta_c)/(1 - \theta_c/f)$, where f is the packing density, has the limiting values $A_b(0) = A_b$ and $A_b(1) = 0$. The study of percolation in continuous systems[2] shows that for particles with very close sizes, i.e., for $(1 - \mu) \ll 1$ we have $A_b(\mu) \approx 0$. For μ in the interval $0 < \mu < 1$ the values of the coefficient $A_b(\mu)$ are found by analyzing the experimental data.

The parameter $A_b(\mu)$ as a function of the particle size ratio μ in the experiments on the trigonal and tetragonal lattices is shown in Fig. 2. The behavior of the binary system is virtually asymptotic already for $\mu \leqslant 0.1$: within the limits of error it satisfies $A_b(\mu) \approx A_b$. The rapid passage to the asymptotic limit is probably connected with the fact that the smallness parameter is the ratio not of the particle radii, but rather the particle areas (volumes), i.e., μ^2. For particle size ratios $\mu \geqslant 0.1$ the coefficient $A_b(\mu)$ depends on the type of packing (lattice). The asymptotic regime is reached more quickly in the tetragonal lattice than the trigonal lattice. Thus the invariance of the percolation threshold with respect to the fraction of the occupied space breaks down here. We were not able to follow the behavior of the system in the limit $\mu \to 1$ on the lattices. In the experiment $\mu_{max} = 1/3$. It could be assumed that, until at least one small particle occupies the pores between the large particles we have $A_b(\mu) \approx 0$. For a tetragonal lattice this value of A_b corresponds to $\mu = 0.414$, which cannot be checked experimentally, since it is greater than μ_{max}. For the trigonal lattice, however, $\mu = 0.155$, and for this reason there are at least two experiments which do not confirm our assumption. The coefficient $A_b(\mu)$ is different from zero for large values of μ because a percolation cluster forms significantly earlier than close packing of particles is achieved. Correspondingly, the remaining pores are significantly larger than in the case of close packing.

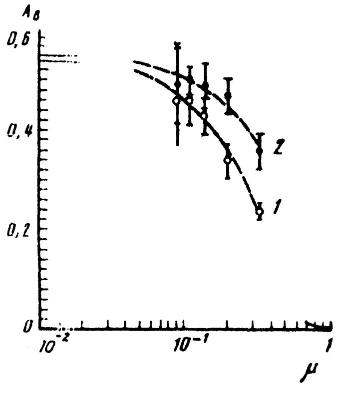

FIG. 2. $A_b(\mu)$ as a function of the particle size ratio $\mu = R_1/R_2$ in experiments on trigonal (*1*) and tetragonal (*2*) lattices.

3. POLYDISPERSED SYSTEM

The limit of greatly varying particle sizes can be naturally extended to polydispersed systems. If the particle radii satisfy the condition $R_1 \ll R_2 \ll ... \ll R_N$, then the percolation threshold is found by solving the recurrence equation

$$\theta_n=\theta_c+(1-\theta_c)\theta_{n-1}, \tag{3}$$

where $n = 2, 3,..., N$ and $\theta_1 = \theta$. The equation (3) for $N \gg 1$ has the asymptotic solution

$$\theta_N=1-(1-\theta)\exp[-\theta_c(N-1)], \tag{4}$$

which can be used to estimate the percolation threshold.

The geometric structure of the system formed when the space is filled with polydispersed particles is fractal. In addition, it differs significantly from the structure of ordinary percolation clusters consisting of monodispersed particles. It is well known that on small scales the geometric structure of percolation clusters is determined by the fractal dimension $D = (d - \beta/\nu)$, where d is the dimension of the space and β and ν are critical exponents.[3] It is the system of particles and not the remaining unfilled volume of the space that is fractal.

When the space is filled by a system of polydispersed particles the situation changes qualitatively: The remaining pore space is fractal. We shall clarify this for the example of a fractal set with dimension less than unity. We take a segment of unit length and divide it into three parts. We discard the central part, and we divide the remaining two segments into three parts, once again discarding the central part. If this process is continued long enough, we obtain a fractal set (Cantor dust) with dimension $D = \ln 2/\ln 3$ (Ref. 4). Now, examine the filling of the space with polydispersed particles. First we arrange the largest particles, making sure that the filling does not exceed the percolation threshold $\theta \leqslant \theta_c$. After this, we arrange the next fraction of the particles, whose size is $1/\mu$ times smaller than the preceeding particles, $R_n/R_{n+1} = 1/\mu$, in the remaining pores. We continue filling the space with the next fractions, and we set the fraction of the volume occupied by particles in the pores equal to θ. In this manner the space can be practically completely filled without formation of macroscopic clusters of touching particles. In contrast to the particle distribution, the pore distribution is described by a fractal set with similarity dimension equal to the Hausdorf–Besikovich dimension

$$D=d+\ln(1-\theta)/\ln(1/\mu).$$

This is the analog of Cantor dust for a space of dimension d. The values $d = 1$, $\theta = 1/3$, and $1/\mu = 3$ correspond to Cantor's construction.

4. CONCLUSIONS

The continuous limit can be obtained by decreasing the period of the regular lattice. This explains the closeness of the percolation threshold for the lattice and continuous problems. However this is not the only possible passage to the limit. One possible path is to fill gradually the space with increasingly smaller particles. The results obtained in this paper indicate that the percolation threshold can be significantly increased in the process.

Percolation-free filling of space, exceeding the percolation thresholds of monodispersed systems, is already possible for a binary system. A space can be filled practically completely by a system of polydispersed particles without infinite clusters forming. This circumstance could be of practical value in optimal-packing problems, for example, for arranging microelectronic elements on a two-dimensional substrate or fixing dangerous substances in the volume of a matrix material.

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