

## Surfaces of percolation systems in lattice problems

P. S. Grinchuk\* and O. S. Rabinovich

A.V. Luikov Heat and Mass Transfer Institute, National Academy of Sciences of Belarus, 15 Petrus Brovka Street, Minsk 220072, Belarus

(Received 1 November 2002; published 8 April 2003)

The internal and external surface area of a percolation cluster along with a full surface area of whole percolation system are investigated both analytically and numerically. Numerical simulation is performed by a Monte Carlo method for site and bond problems on square and simple cubic lattices. It is shown that both the external and full surface areas of a percolation cluster as well as the full surface area of the whole percolation system have maxima for a certain share of occupied sites (for the site problem) or permeable bonds (for a bond problem). On the basis of a probabilistic approach, analytical expressions are obtained which relate the surface area of percolation cluster to its density. The last value has been studied in more details at present that allows to analyze the behavior of the above-mentioned surface for various lattices. Two particular technological processes are discussed where the surface area of a percolation cluster plays an important part: generation of electric current in a fuel cell and self-propagating high-temperature synthesis in heterogeneous condensed systems.

DOI: 10.1103/PhysRevE.67.046103

PACS number(s): 64.60.Ak, 02.50.-r

## I. INTRODUCTION

For a large number of physical and chemical processes, a surface area of participating components plays an important role. Its magnitude is essential in heat and mass exchange processes, many chemical reactions, etc. The components or phases involved in such processes can have either determinate or random structure. This work is dedicated to the consideration of the latter case. The percolation theory [1,2] is one of the models giving an adequate description of geometric properties of disordered systems. The main feature of such systems is related to a possibility of a geometric phase transition, i.e., the formation of an infinite (percolation) cluster (further PC). Below we consider two examples of systems in which the surface area of the PC plays an essential role.

The first example of such systems is a fuel cell whose important part is a porous electrode [3]. One of the main problems in the theory of porous electrodes consists of the determination of conditions when all the participants of an electrochemical process [reactants, ions, electric current (electrons), catalyst] will be brought together on an internal surface of the electrode, and the useful and waste products of the reactions be removed. At the same time, it is important that the electrochemical process be extended on a macroscopic distance as compared with a microscopic characteristic size of the porous medium. However, a restriction exists which is connected with slow fuel (gas) transport to the electrode surface through an electrolyte. This restriction is related to the diffusion mechanism of the transport of gas molecules in a liquid. At the same time, it is well known that in an individual pore the most of electric current is generated in the area of meniscus where the electrolyte film is already sufficiently thin for gas diffusion but its electric resistance is still small (Fig. 1). Therefore, in order to get large current it is desirable to have a large number of such meniscus [the so-called “three-phase” borders: gas(hydrogen)-electrolyte-

electrode] per unit volume. Here it is necessary to take into account the following circumstance: the electric circuit must be closed on ionic component of the current. It means that inside the electrode there should exist a connected system of electrolyte-filled pores, i.e., the percolation cluster. It is this cluster which plays a key role in the current generation. If the electrolyte droplets insulated on all sides (the finite clusters) are present in the electrode, they will not contribute to the total current generation by the fuel cell because therein the current on ionic component will be open circuit. In this situation all the “useful” electrochemical reactions will proceed most intensively near the above-mentioned three-phase border. It means that the electrochemical reactivity (i.e., the generated current) will be proportional to the mentioned interface area. In its turn, the useful three-phase interface area will be proportional to the *external* surface area of the PC

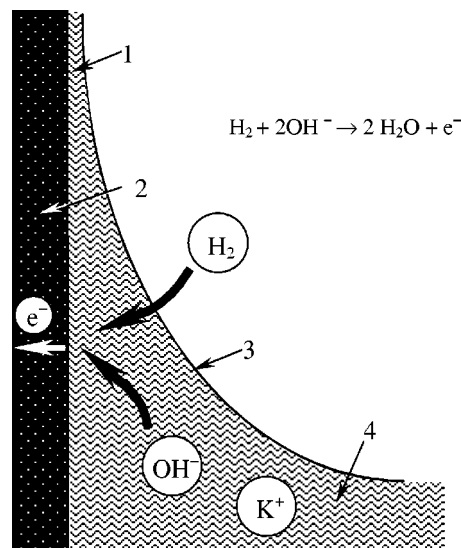


FIG. 1. To the problem of electricity generation in a fuel cell on the “three-phase” boundary: hydrogen-electrolyte-electrode. 1, a film of electrolyte; 2, electrode; 3, meniscus of the liquid; 4, electrolyte.

\*Email address: gps@hmti.ac.by

which constitutes the contact surface of two percolation clusters composed of liquid-filled and gas-filled pores. The first cluster provides circuit closing on the ionic component of current and the second cluster allows a continuous supply of the gaseous component to the reaction domain. Thus, only the external surface of PC will participate in a continuous process of current generation. So, if there is a gas “bubble” inside a PC then the surface of such a bubble, which is an internal surface of the PC in this case, ceases to take part in the current generation after a certain time because the gaseous component needed for electrochemical reactions is not delivered to that domain. Thus, in the given case the following optimization problem appears: it is necessary to find such degree of saturation of a porous electrode by the electrolyte when the external surface area of the percolation cluster is maximal. It is pertinent to note that the problem of the liquid distribution inside a porous body can be reduced to the bond problem of the percolation theory [4,5].

As the second example, let us consider self-propagating high-temperature synthesis (SHS) in a heterogeneous condensed system (a mixture of powders), which is one of the most efficient cost-effective methods for producing inorganic compounds, in particular, intermetallics [6]. Recently, in studying the combustion in heterogeneous systems a number of phenomena has been observed which can be explained only taking into account the random structure of such systems [7–10]. Therefore, we shall discuss the influence of geometric randomness on the combustion processes in heterogeneous systems.

In combustion reactions (except exothermal decomposition of certain compounds), typically a fuel and an oxidizer participate which must be premixed on the molecular level to provide the conditions for the reaction to proceed. If the fuel and oxidizer are in a gaseous state, then in many cases it is possible to premix them before the reaction begins. If the components are in condensed state, then such premixing is practically impossible. In this case, during interaction the contact interface of the reactants become important. In mixtures composed of nonmelting particles (for example, Ta-C and some intermetallic systems [11]) the interaction between the reactants proceeds via solid-phase diffusion. Therefore, in such systems for proceeding of the reaction in an arbitrary particle of one component a mechanical contact of the latter with at least one particle of the second component is needed. For propagation of the reaction on the macroscopic distance (as compared to the size of an individual particle), the existence of two PC's formed by the particles of both the first and the second kind is necessary. In this case, the conversion of components is maximal when the contact surface area of two clusters is maximal. We will point out that this surface by definition coincides with the external surface of a percolation cluster.

For a monodisperse mixture of powders, geometric randomness can be modeled by a classical site problem of the percolation theory. At that, a mixture of powders *A* and *B* is associated with a spatial lattice, each site of which is occupied either by particle of sort *A* with probability *p* or by particle of sort *B* with probability  $(1-p)$ . Here *p* is a numerical fraction of particles *A* in the mixture which can be

connected to a volumetric fraction of these particles with the help of Scher-Zallen construction [12].

Then the problem of optimization of SHS in heterogeneous condensed systems is formulated as follows: it is necessary to find a concentration of initial components in a mixture for which the corresponding interfacial area and, accordingly, the degree of conversion will be maximal. It is important to note that when we consider an external surface of a PC, its extremum for one of the PC's can be reached only in the range of the particle concentrations, where a PC of particles of the other sort can exist. The stipulated condition is satisfied if  $p_c \leq p_m \leq 1 - p_c$ , where  $p_m$  is the point in which the surface area of PC is maximal,  $p_c$  is a percolation threshold. From this inequality, a condition for the percolation threshold on a modeling lattice is derived:  $p_c \leq 0.5$ . In a two-dimensional case this condition is met only for a triangular lattice (in the site problem) and for a square lattice (in the bond problem) and only in one point, viz., in the percolation threshold ( $p_c = 0.5$  [13]). In a three-dimensional case this condition is satisfied for all regular lattices.

We should outline some circumstances which indirectly confirm an important role of the interfacial area in SHS. As is noted in a number of experimental works [14–16], in many heterogeneous condensed systems full conversion of components in SHS processes does not occur. One of a reasons for this is the statistical inhomogeneity of such mixtures. So, even for very good intermixing of initial components taken in a stoichiometric ratio, not each of the particles will have in its neighborhood a particle of another kind. It is impossible to obtain a system in which particles of different kinds will be located, for example, in the chess order. Powder particles of one kind in mixtures with other particles always exhibit a tendency to clusterization. Therefore, after intermixing some of them will not have the particles of other kind among the nearest neighbors, i.e., the interfacial area (the contact surface area) of the reactants will be considerably less than the theoretically possible one for the case of regular (chess) packing. The deficient content of one component in the reaction zone results in the retardation of the reaction with the increase of the conversion degree and finally only in a partial conversion of initial components into the product in SHS processes [17]. We will give special attention to one more experimental fact. As is known, SHS can be performed only in a certain concentration range [14,18]. If the concentration of one component is lower than a certain threshold then it is not possible at all to initiate SHS. On one hand, this is stipulated by diminution of the reaction exothermicity with decreasing the content of one of the reactant. But on the other hand, this effect can also be attributed to the diminution of the contact surface area between the reactants, which becomes critical for small concentrations of one of them [14]. Moreover, a possible reason for this effect can be the absence of the PC formed by the particles of the deficient component, which may be necessary for the reaction propagation over the whole system.

It should be noted that a somewhat similar problem referring to powder sintering was considered in Ref. [19] using the percolation theory methods. However, there is a principal difference between the sintering of powders and the process

of self-propagating high-temperature synthesis. The sintering process is isothermal, i.e., the powder mixture is heated by an external source and is for during several hours at a constant high temperature. Unlike this process, during SHS an exothermic chemical reaction (for example,  $\text{Ni} + \text{Al} \rightarrow \text{NiAl}$ ) is initiated at one of the borders of a system. The heat released due to the reaction in ignited particles initiates the reaction in their neighborhood, thus making possible self-propagation of the reaction wave over the system.

Thus, the purpose of this work is the investigation of interfacial areas in two-component heterogeneous systems on the basis of percolation models. The surface of a percolation cluster and finite clusters was studied in a number of works [20–26] both numerically and analytically. A comprehensive review of this problem is given in Sec. 6.4 of Ref. [1]. However, a distinctive feature of most works is a study of such surfaces in the neighborhood of percolation threshold. In our work, the surface of a percolation cluster will be considered over a wide range of  $p$ , from  $p_c$  up to 1, and our results in the neighborhood of percolation threshold will be compared with the results of other authors.

## II. ANALYTICAL INVESTIGATION OF THE SURFACE OF A PERCOLATION CLUSTER

### A. Site problem

Let us consider a spatial lattice and assume that a certain liquid can flow from one site to the other along the pipes which are hereinafter named bonds. Defining stochastic elements of this system in different ways we obtain a site problem or a bond problem of the percolation theory. So, in the site problem for spreading of a liquid over the lattice all bonds are permeable for the liquid, and the sites are either closed or open for the liquid with a definite probability. In the bond problem, all the sites are permeable for the liquid but a certain part of bonds is considered broken. In these problems it is supposed that elements with different properties (occupied or unoccupied sites, permeable or impermeable bonds) are distributed *absolutely chaotically* over the lattice and, therefore, a probability that an arbitrary element has a definite property, is equal to a share of such elements in the lattice and *does not depend* on the properties of neighboring elements. From the supposition about the randomness of distribution it follows that each site (bond) in the lattice is occupied with an equal probability  $p$  and is unoccupied with probability  $(1-p)$ . Here  $p$  is a share of occupied sites (permeable bonds) in the lattice.

As a measure of the surface area of any cluster of a percolation system, two parameters are traditionally used perimeter or energy [27]. So, for the site problem the perimeter of a cluster is a number of unoccupied sites of the lattice which do not belong to the cluster but are separated from its sites by only one bond. The energy is determined as a number of adjacent sites (number of pairs), one of which is occupied (belongs to a cluster) and the other is unoccupied.

Let us show that the surface area of the PC has extremal behavior in the site problem. We consider a regular  $d$ -dimensional lattice with coordination number  $z$  and the share of occupied sites  $p$ . Let a PC appears on the lattice and

share of sites belonging to it is equal to  $P_\infty(p)$ . This value is also the probability that an arbitrary site belongs to the PC.

Let us consider a complex of conditions at the fulfillment of which an arbitrary site of the lattice can belong to the *full perimeter* of the PC. Firstly, the considered site should be unoccupied [probability  $(1-p)$ ] and, secondly, among its  $z$  neighbors at least one site should belong to PC. Let us speak that on arbitrary site an event  $\Omega_j$  occurs if *any*  $j$  from  $z$  sites in the neighborhood of the considered site belong to PC (probability  $[P_\infty(p)]^j z! / [j!(z-j)!]$ , where  $z! / [j!(z-j)!]$  is a number of combinations of  $j$  sites chosen from  $z$ ), and  $(z-j)$  of remaining sites are either unoccupied or belong to any finite cluster (probability  $[1 - P_\infty(p)]^{z-j}$ ). We can also multiply the probability of elementary events related to an individual site due to the above mentioned suggestion about absolute randomness of their distribution over the lattice. Then probability of the occurrence of event  $\Omega_j$  is determined by the following expression:

$$P(\Omega_j) = \frac{z!}{j!(z-j)!} P_\infty(p)^j [1 - P_\infty(p)]^{z-j}. \quad (1)$$

The site belongs to the perimeter of a PC (event  $A$ ) if (i) it is not occupied and (ii) any of events  $\Omega_j$  for  $j$  from 1 up to  $z$  occurs on it. As events  $\Omega_j$  are pairwise incompatible then conditional probability  $P(A/\Omega_j) = 1$ . Using the formula of total probability and taking into account the obtained relations, we can write the following expression:

$$\begin{aligned} S_\infty(p) &= (1-p) \sum_{j=1}^z P(\Omega_j) P(A/\Omega_j) \\ &= (1-p) \sum_{j=1}^z \frac{z!}{j!(z-j)!} P_\infty(p)^j [1 - P_\infty(p)]^{z-j} \\ &= (1-p) \{1 - [1 - P_\infty(p)]^z\} \end{aligned} \quad (2)$$

for the perimeter of PC per lattice site. It is significant that the obtained expression is valid for arbitrary natural  $z$ . The application of the probabilistic approach in this case is justified by the fact that the number of lattice sites over which averaging of the parameters is performed is macroscopically large.

It should be noted that in Ref. [1] it is shown that the perimeter  $t_s$  of a large *finite* cluster is defined by the expression

$$t_s = \frac{1-p}{p} s + A s^\zeta, \quad (3)$$

where  $s$  is a number of sites in a cluster and  $A$  is a parameter which is independent of  $s$ . Here  $\zeta > 0$ , and  $A$  vanishes at  $p = p_c$ . In Refs. [20,21] this perimeter was investigated near a percolation threshold for  $d=2$  using the Monte-Carlo method. In agreement with theoretical predictions the relation  $t_s \approx s(1-p_c)/p_c$  was obtained.

From Eq. (2) obtained in the present work it follows that close to a percolation threshold ( $p \rightarrow p_c$ ), where the magnitude of  $P_\infty(p)$  is small, the PC perimeter is determined by an expression

$$S_\infty(p) \approx z(1-p)P_\infty(p). \quad (4)$$

As can be seen, the expressions for the perimeter of a large finite cluster (3) and for the PC perimeter (4) close to a percolation threshold have a similar form, but at the same time some difference between them exists. It consists in non-coincidence of one of the factors in these expressions ( $1/p$  for finite clusters and  $z$  for percolation cluster). An approximate expression for the percolation threshold  $p_c$  versus the space dimension  $d$  and the coordination number of lattice  $z$  was obtained in Ref. [28]. For the site problem it is the following:  $p_c = p_0[(d-1)(z-1)]^{-a}$ , and for  $d=2$   $a = 0.3601$  and  $p_0 = 0.8889$ , but for  $3 \leq d \leq 6$   $a = 0.6160$  and  $p_0 = 1.2868$ . As can be seen, the magnitudes  $1/p$  and  $z$  are not equal to one another in the neighborhood of a percolation threshold, and accordingly, the surfaces of large finite clusters and PC behave differently. The reason for the difference between expressions for the perimeter of a large finite cluster [Eq. (3)] and the PC perimeter [Eq. (4)] lies in following: our result [Eqs. (2) and (4)] was obtained for a percolation cluster in the limit of an infinitely large system, while expression (3) was obtained for a *finite* cluster of a large size, which is generally not equivalent to the percolation cluster. In particular, Eq. (3) was obtained with the use of expressions  $n_{st} = g_{st}p^s(1-p)^t$  and  $n_s \propto \exp(-Cs^z)(n_s = \sum_t n_{st})$  for an average number of  $s$  clusters having  $t$  perimeter sites each. It is questionable whether expressions for the percolation cluster can be used.

For the energy of PC,  $E_\infty(p)$ , a relationship similar to Eq. (2) can be obtained. A difference from the case when the perimeter was considered is the following: when event  $\Omega_j$  occurs, then the energy in the given site is equal to  $j$ , while the contribution of any event  $\Omega_j$  to the perimeter is equal to 1.

Then for PC energy in the site problem, we have

$$E_\infty(p) = (1-p) \sum_{j=1}^z j \frac{z!}{j!(z-j)!} P_\infty(p)^j [1 - P_\infty(p)]^{z-j} = z(1-p)P_\infty(p). \quad (5)$$

We should note that the full energy of a percolation cluster was investigated numerically both for  $d=2$  [29,30] and for  $d=3$  [31] with the result  $\langle E \rangle \propto s$ . As can be seen, the obtained relationship (5) agrees perfectly with this result.

In the limit of an infinitely large system the density of PC tends to zero at  $p \rightarrow p_c + 0$ . Therefore, in the percolation threshold the surface area (perimeter, energy) of PC will be equal to zero. For  $p=1$  all sites of the lattice belong to the PC, therefore the PC surface area in this point is also equal to zero. Since the density of PC is a continuous function in the interval  $[p_c, 1]$  and differentiable in the interval  $(p_c, 1)$ , then from Eqs. (2) and (5) it follows that the surface area (perimeter, energy) of PC is also a continuous and differentiable

function in these intervals. Thus, for a perimeter (energy) of PC, the conditions of the Rolle theorem are fulfilled: it is continuous in  $[p_c, 1]$ , differentiable in  $(p_c, 1)$ , and  $S_\infty(p_c) = S_\infty(1)$ . Therefore, there is a certain point in the given interval in which the derivative of function  $S_\infty(p)$  will vanish. This point is a point of a maximum owing to the fact that the given function is non-negative.

The formulas for a perimeter and energy of the whole system can be obtained in an analogous manner. For this purpose, in the derivation of Eqs. (2) and (5) it is necessary to replace  $P_\infty(p)$  with  $p$ , i.e., to require that at occurrence of event  $\Omega_j$  the appropriate sites can belong to both PC and any finite cluster. Then, we have

$$S_{tot}(p) = (1-p)[1 - (1-p)^z], \quad (6)$$

$$E_{tot}(p) = z(1-p)p. \quad (7)$$

From Eqs. (6) and (7) it follows that the full perimeter and energy also have an extremum. In this case, a maximum of the full energy for *anyone* the lattice is reached in point  $p_m = 0.5$ . At the same time, the maximum of a full perimeter is reached in the point  $p_m = 1 - [1/(z+1)]^{1/z}$ , i.e., it depends on the lattice type (for  $z=3$   $p_m = 0.37, 4 - 0.33, 6 - 0.28$ ). The results of our numerical simulation have confirmed this conclusion.

Within the framework of the proposed approach it is also possible to obtain formulas for the external perimeter and energy of PC. An arbitrary site belongs to the external perimeter of PC if (i) it belongs to the PC of unoccupied sites [with probability  $P'_\infty(p)$ , where  $P'_\infty(p) \equiv P_\infty(1-p)$  is the density of PC at the share of occupied sites equal to  $(1-p)$ ] and (ii) any of the above defined events  $\Omega_j$  has occurred on it. Then, using an analogy with Eq. (2) for an external perimeter  $S_\infty^{(ext)}(p)$  and external energy  $E_\infty^{(ext)}(p)$  of PC, we obtain the following expressions:

$$S_\infty^{(ext)}(p) = P'_\infty(p) \sum_{j=1}^z \frac{z!}{j!(z-j)!} P_\infty(p)^j [1 - P_\infty(p)]^{z-j} = P'_\infty(p) \{1 - [1 - P_\infty(p)]^z\}, \quad (8)$$

$$E_\infty^{(ext)}(p) = zP'_\infty(p)P_\infty(p). \quad (9)$$

In the limit  $p \rightarrow 1$ , we have  $P'_\infty(p) = 0$ . Therefore, from Eqs. (8) and (9) it follows that in this limit the PC has only internal surface. Equations (2) and (5) in the considered limit pass into Eqs. (6) and (7), correspondingly, owing to relation  $P_\infty(p) \approx p$ . It means that for a large share of occupied sites the surface of the whole percolation systems and the PC surface almost coincide. These conclusions also perfectly agree with the results of our numerical experiment.

### B. Bond problem

For this problem, we investigate only the PC perimeter. Let us note that in this case, an impermeable bond which connects two sites belonging to the same cluster is counted twice in the perimeter of this cluster [4].

Let us consider a regular lattice of bonds with coordination number  $z$ , the share of permeable bonds being  $p$ . In order to avoid counting the same impermeable bond many times in calculating the PC perimeter, it is necessary to consider an arbitrary site of the lattice and find probabilities of elementary events for this site similarly to the case of the site problem. A bond adjacent to an arbitrary site of a lattice belongs to the full perimeter of PC if (i) it is impermeable, and (ii) at least one of the bonds adherent to the same site belongs to the PC. Let us note that in the bond problem all the bonds adherent to the given site and not belonging to the PC are impermeable by definition. Let us speak that event  $\bar{\Omega}_j$  occurs on an arbitrary site if (i) any  $j$  of  $z$  the bonds adherent to the given site are impermeable (probability  $[(1-p)]^j z! / [j!(z-j)!]$ , where  $z! / [j!(z-j)!]$  is the number of combinations of  $j$  bonds chosen from  $z$ ), and (ii)  $(z-j)$  of remaining bonds belong to PC (probability  $[P_\infty^{(b)}(p)]^{z-j}$ ). The bond belongs to the PC perimeter (event  $B$ ) if (i) it is impermeable and (ii) any of events  $\bar{\Omega}_j$  for  $j$  from 1 to  $z-1$  has occurred on a site to which the given bond adjoins. The contribution of event  $\bar{\Omega}_j$  to the perimeter of the percolation cluster on the considered site is equal to  $j$ . Taking into account that in the lattice composed of  $N$  bonds there is  $2N/z$  sites, for average full perimeter of PC per one lattice bond we have

$$\begin{aligned} S_\infty^{(b)}(p) &= \frac{1}{N} \frac{2N}{z} \sum_{j=1}^{z-1} j \frac{z!}{j!(z-j)!} [P_\infty^{(b)}(p)]^{z-j} (1-p)^j \\ &= 2(1-p) \{ [1-p + P_\infty^{(b)}(p)]^{z-1} - (1-p)^{z-1} \}. \end{aligned} \quad (10)$$

Here  $P_\infty^{(b)}(p)$  is a connectivity function, or a share of bonds belonging to PC [4]

The existence of a maximum of the PC perimeter in the interval  $(p_c, 1)$  is proved in a way similar to the site problem.

The total perimeter of the percolation system calculated per one bond, which includes both the perimeter of PC and that of all finite clusters, can be found for the bond problem, as well as for the site problem, by replacing  $P_\infty^{(b)}(p)$  for  $p$ :

$$S_{tot}^{(b)}(p) = 2(1-p)(1 - [1-p]^{z-1}). \quad (11)$$

Let us note that in Ref. [4] an expression for the total perimeter of a percolation system for the bond problem was obtained which coincides with relationship (11).

An expression for the external perimeter of PC can be obtained in the same manner as Eq. (8) was derived for the site problem. It should be remembered that if an impermeable bond belonging to a PC of impermeable bonds adjoins a certain site then by definition all other impermeable bonds contiguous to this site belong to the given PC. Then for the external perimeter of the PC, we have

$$\begin{aligned} S_\infty^{(b,ext)}(p) &= 2P_\infty'^{(b)}(p) \{ [P_\infty^{(b)}(p) + P_\infty^{(b)}(p)]^{z-1} \\ &\quad - [P_\infty'^{(b)}(p)]^{z-1} \}, \end{aligned} \quad (12)$$

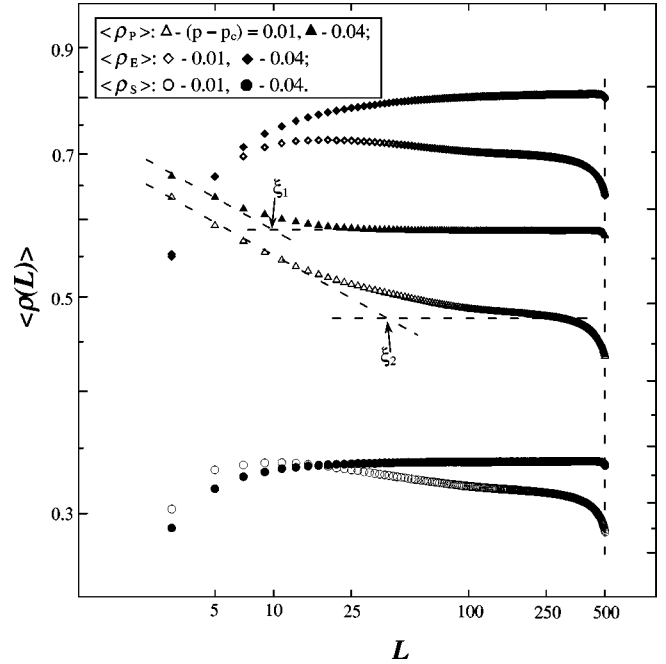


FIG. 2. Average density of a percolation cluster  $\langle \rho_p \rangle$ , its “energy”  $\langle \rho_E \rangle$  and perimeter  $\langle \rho_S \rangle$  vs the size  $L$  of averaging area for the site problem on a square lattice  $501 \times 501$  ( $p_c \approx 0.593$ , log-log scale).  $\xi_1$  and  $\xi_2$  are the correlation lengths for corresponding shares of occupied sites.

where  $P_\infty'^{(b)}(p) \equiv P_\infty^{(b)}(1-p)$ . In the limit  $p \rightarrow 1$ , the surfaces behave in the same manner as in the site problem: Eq. (12) vanishes and Eq. (10) passes into Eq. (11).

### III. NUMERICAL EXPERIMENT

As is known, the percolation cluster is a fractal object on lengths smaller than the correlation length  $\xi$  [1,32]. At numerical simulation this fact can play an essential role. In classical work [33] for the site problem on a square lattice the density of PC was investigated  $\rho(L)$ , i.e., ratio of the number of sites of the PC located in a rectangular area of a size  $L$  to the total number of sites in the given area. It was shown that  $\rho(L)$  strongly depends on a relation between  $L$  and  $\xi$ . If  $L < \xi$ , then the number of sites belonging to the PC grows as  $L^D$  ( $D$  is the fractal dimension of PC), and the surface area (volume) grows, naturally, as  $L^d$  ( $d$  is the topological dimensionality of space). Inasmuch as  $D < d$ , in the given area the density of PC decreases with increasing  $L$ . On lengths larger than the correlation length PC behaves itself as a homogeneous object, and its density in this area is constant. It is important that this value of density corresponds to an infinitely large system. And, finally, if a distance from the boundaries of the considered area to the edge of the lattice is below the correlation length then  $\rho(L)$  begins decreasing with increasing  $L$ . In more detail it is described in Ref. [33].

In the numerical experiment, we used a similar method for investigating the PC surface. It turns out that in the most interesting region  $L > \xi$ , the perimeter and energy of PC do not depend on  $L$  as well (Fig. 2). The position of this plateau was assumed to be a value of a corresponding measure of the

surface area in the experiment. A distinction was observed only for the region  $L < \xi$ , wherein the density of the perimeter and energy were increasing with raising  $L$ . We suppose that in this case a superposition of several effects takes place. At first, the fractality of the PC exerts influence on the densities of the surface measures. Secondly, an unoccupied site, which inside the “old” region did not belong to the PC surface, in a “new” enlarged area can have a neighbor belonging to the PC. For small  $L$  this effect can give a noticeable contribution to the growth of the density of the perimeter and energy of PC. We should note that the mentioned augmentation of the density should not be identified with any cluster and its fractal dimension since all unoccupied sites inside a hypercube with side  $L$  do not necessarily belong to the same cluster composed of unoccupied sites.

For calculating the surface measures (perimeter and energy) for a PC we have chosen the following way. The lattice of a reasonably large size ( $501 \times 501$  for two-dimensional problems and  $151 \times 151 \times 151$  for a three-dimensional case) was filled at a given share  $p$  of occupied sites (permeable bonds) with the help of a standard procedure [34]. For each site (bond) of the lattice a pseudorandom number  $\zeta$  uniformly distributed in interval  $[0,1]$  was generated. If this number  $\zeta \leq p$ , the corresponding site was considered as occupied and in the opposite case it was treated as unoccupied. Then a percolation cluster connecting the left and right borders of the lattice was sought and labeled if found. For determining an external surface of the PC composed of occupied sites, a PC of unoccupied sites was also sought and labeled if the latter existed. Further on, in corresponding areas of the lattice a number of unoccupied sites neighboring to the sites belonging to the PC was counted. For improving the accuracy of numerical simulation we took into account only those lattices, for which a share of occupied sites differed from the given value of  $p$  by less than 0.0001. For each  $p$  value, in each of the four problems investigated here we accumulated  $(5-10) \times 10^3$  histories that allowed us to obtain the accuracy of up to 0.001. The total central processing unit time on a dual-processor Pentium III computer with 800 MHz processors was about 2000 h.

#### IV. RESULTS AND DISCUSSION

The site problem was investigated numerically on square ( $z=4$ ) and simple cubic ( $z=6$ ) lattices. The results of simulation are presented in Figs. 3 and 4, and Table I. In compliance with predictions made in Sec. II, both the surface area of PC and the total surface area of the system have an extremum for a certain share of occupied sites. At that, the position of a maximum and its absolute magnitude essentially depend on the choice of a measure of the surface area (perimeter or energy) (Table I). Since for the site problem on a square lattice the percolation threshold is  $p_c = 0.59274621 > 0.5$  [35], then the full surface of PC in this case is internal (Fig. 3). For a simple cubic lattice, the percolation threshold is  $p_c = 0.3116080 < 0.5$  [36,37], therefore in this case the PC has both internal and external surfaces (Fig. 4). In the region where the maximum of the external surface area of PC is reached, the internal surface area is negligible. It is interest-

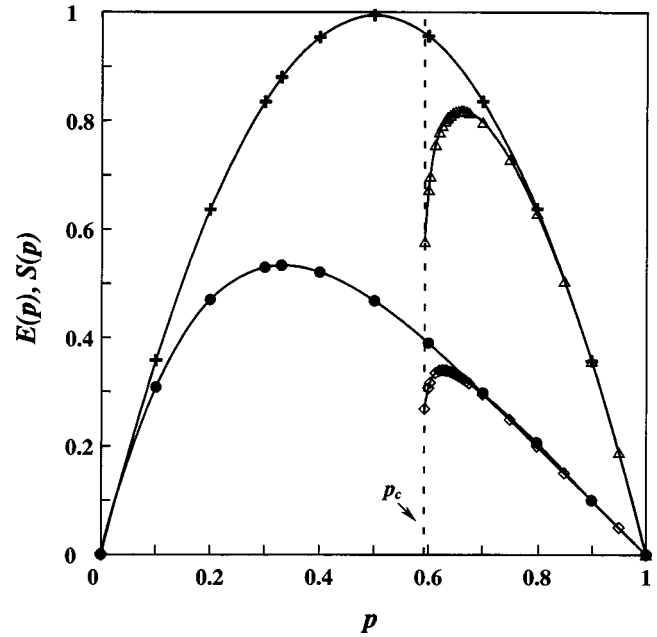


FIG. 3. The perimeter  $S(p)$  and energy  $E(p)$  of a percolation cluster vs a share of occupied sites  $p$  for the site problem on a square lattice  $501 \times 501$ :  $\diamond$ —full perimeter of the percolation cluster,  $\bullet$ —perimeter of the whole system;  $\triangle$ —full energy of the percolation cluster,  $+$ —energy of the whole system.

ing to note that in a three-dimensional case the internal surface area of PC also has a maximum which is reached in point  $1 - p_c$ .

To check the accuracy of numerical simulation, we have calculated the fractal dimension of a PC for the two-

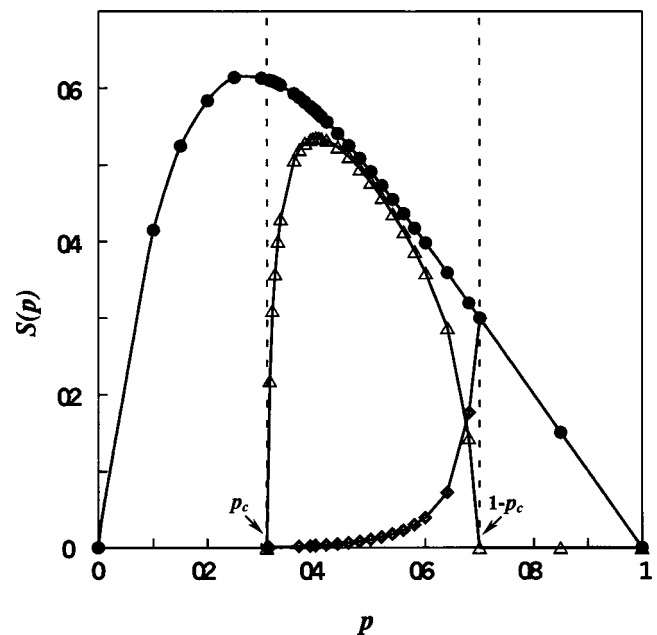


FIG. 4. The perimeter  $S(p)$  of the percolation cluster vs a share of occupied sites  $p$  for the site problem on a simple cubic lattice  $151 \times 151 \times 151$ :  $\triangle$ —external perimeter of PC,  $\diamond$ —internal perimeter of PC,  $\bullet$ —perimeter of the whole system.

TABLE I. The full  $S_\infty$  and external  $S_\infty^{(ext)}$  perimeter and energy ( $E_\infty, E_\infty^{(ext)}$ ) of PC for the *site problem*: points of maximum  $p_m$  and the magnitudes in these points.

	Square lattice ( $d=2$ )		Simple cubic lattice ( $d=3$ )	
	$p_m$	Magnitude	$p_m$	Magnitude
$S_\infty$	$0.625 \pm 0.001$	$0.3397 \pm 0.0001$	$0.406 \pm 0.001$	$0.538 \pm 0.001$
$S_\infty^{(ext)}$			$0.402 \pm 0.001$	$0.535 \pm 0.001$
$E_\infty$	$0.660 \pm 0.001$	$0.819 \pm 0.003$	$0.538 \pm 0.001$	$1.42 \pm 0.01$
$E_\infty^{(ext)}$			$0.501 \pm 0.001$	$1.35 \pm 0.01$

dimensional problem. We have used the angle of inclination of the density curve for the PC in the case  $L < \xi$ . The value  $D = 1.889 \pm 0.004$  was obtained, which is in agreement with the exact result  $D = \frac{91}{48} = 1.8958 \dots$  [32].

The bond problem was investigated both on square and simple cubic lattices. The results of simulation are presented in Figs. 5 and 6, and Table II. The qualitative behavior of surfaces in this case is the same as in the site problem. A difference appears only in particular numerical values.

Verification of the equations obtained in this work was performed for all of the four problems. For this purpose, the density of PC was calculated numerically for sets  $\{p_i\}$  and  $\{1-p_i\}$  and after that the numerical data were substituted into corresponding equations. A discrepancy between thus calculated perimeters (energies) and the same values obtained immediately in numerical experiments was less than 10%. Figure 6 presents the comparison of the perimeters obtained by these two methods on a simple cubic lattice for the bond problem. As can be seen from this figure, a maximal discrepancy occurs close to the percolation threshold where the scaling effects reveal themselves most significantly.

To elucidate the role of scaling effects, similar simulation

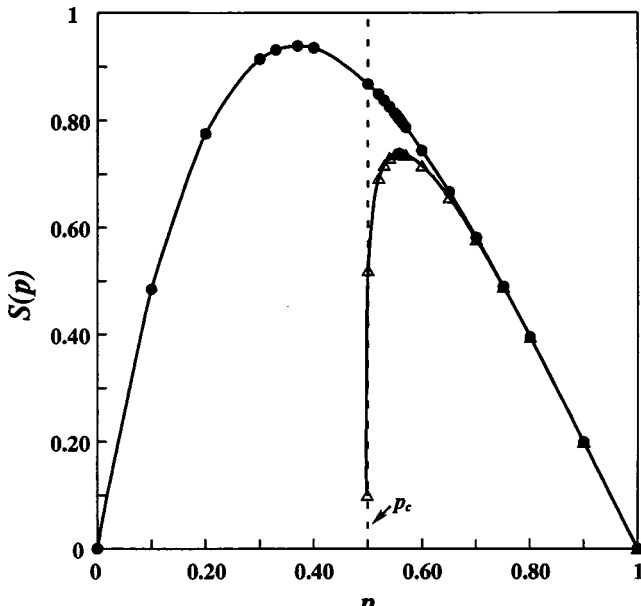


FIG. 5. The perimeter  $S(p)$  of PC vs a share of permeable bonds  $p$  for the bond problem on a square lattice  $501 \times 501$ :  $\Delta$ —full perimeter of PC,  $\bullet$ —perimeter of the whole system.

for two- and three-dimensional systems having the size of  $101 \times 101$  and  $51 \times 51 \times 51$ , correspondingly, was performed. For each point,  $(10-20) \times 10^3$  histories were treated. A general tendency in behaviors of surface areas was observed: far from the percolation threshold all measures of a percolation cluster surface did not change (within the limits of an experimental error) as compared with systems of a larger size. At the same time, in the neighborhood of a percolation threshold the considered measures of the surface decreased by 0.5 to 4% for two-dimensional systems and by 0.5 to 2% for three-dimensional systems. It means that the above-mentioned divergence between the direct numerical simulation and the calculations based on equations obtained in this work may be only partially related to the scaling effects. The second reason of the considered divergence is that in the neighborhood of the percolation threshold, a plateau whose position is used for determining the surface measures (Fig. 2) becomes more diffuse and indistinct thus adding inaccuracy to the experimental results. We can expect that this diver-

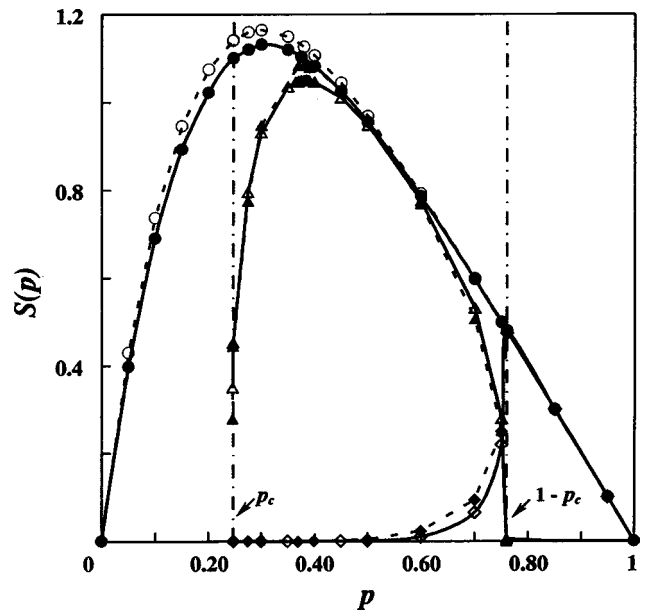


FIG. 6. The perimeter  $S(p)$  of PC vs a share of permeable bonds  $p$  for the bond problem on a simple cubic lattice  $151 \times 151 \times 151$  according to the numerical experiment:  $\Delta$ —external perimeter of PC,  $\diamond$ —internal perimeter of PC,  $\bullet$ —perimeter of the whole system. Dashed lines are the same parameters calculated by Eqs. (10)–(12) using the results of numerical simulation for the PC density  $P_\infty^{(b)}(p)$ .

TABLE II. The full  $S_{\infty}^{(b)}$  and external  $S_{\infty}^{(b,ext)}$  perimeter of PC for *bond problem*: points of maximum  $p_m$  and the magnitude of perimeter in these points.

	Square lattice ( $d=2$ )		Simple cubic lattice ( $d=3$ )	
	$p_m$	Magnitude	$p_m$	Magnitude
$S_{\infty}^{(b)}$	$0.558 \pm 0.001$	$0.737 \pm 0.001$	$0.382 \pm 0.001$	$1.050 \pm 0.002$
$S_{\infty}^{(b,ext)}$			$0.382 \pm 0.001$	$1.050 \pm 0.002$

gence will decrease with increasing the system size.

We will note that one more possible cause of theory and numerical simulations divergence arises owing to ignoring of small correlations in the occupation status of neighboring parts of the infinite cluster. If we look at all clusters then results like Eq. (6) or Eq. (11) are exact since each site is independent of the other sites. If however, we require that the sites are part of the infinite cluster then this requirement causes some correlations, which make results like Eq. (1) valid only approximately. These correlations can be more easily understood if we look at the probability that a site of the infinite cluster is surrounded by  $j$  other sites of the infinite cluster. An approach similar to expression (1) is not exact in this case since  $j=0$  is impossible. The requirement that the central site belongs to the infinite cluster puts to zero the probability that it has no neighbors from that infinite cluster. The other probabilities, for  $j=1$  to  $z$ , are then also modified since their sum must be equal unity. If we consider now the probability that an empty site is surrounded by  $j$  sites from the infinite cluster then again the occupation probabilities of the  $z$  neighbors are no longer statistically independent of each other since it is required that they belong to

the infinite cluster. Only now the correlations are more hidden than in the above simpler example.

## V. CONCLUSION

Thus, theoretical and numerical investigation of the surface areas of percolation systems has been performed, which has revealed an interesting phenomenon: an extremal behavior of the external and full surface areas of the percolation cluster. Similar behavior was observed also for the full surface area of the percolation system. The results of research allow us to make a conclusion that the developed analytical approach is valid for the description of various surfaces in percolation systems. The obtained analytical relationships can also be used for describing corresponding surface areas of percolation systems on lattices different from those investigated in the given work. For this purpose, is only necessary to know the density of a percolation cluster as a function of a share of occupied sites (permeable bonds) on the lattice. The latter value has been investigated in much detail [5,38–42].

Two examples of particular systems were considered, viz., a fuel cell and a heterogeneous condensed system (a mixture of powders), wherein the effect revealed in this work can be used for the optimization of important technological processes: generation of electric current and self-propagating high-temperature synthesis of refractory compounds or composites, correspondingly.

## ACKNOWLEDGMENTS

This work was supported in part by the Belarusian Republican Fund for Fundamental Research (Grant Nos. T00-171 and T02P-031).

- 
- [1] D. Stauffer and A. Aharony, *Introduction to Percolation Theory*, 2nd ed. (Taylor and Francis, London, 1995).
  - [2] M. Sahimi, *Applications of Percolation Theory* (Taylor and Francis, London, 1994).
  - [3] E.U. Justi and A.V. Winsel, *Fuel Cell* (Franz Steiner Verlag, Weisbaden, 1962).
  - [4] L.I. Kheifets and A.V. Neimark, *Multiphase Processes in Porous Media* (Khimiya, Moscow, 1982), p. 98 (in Russian).
  - [5] A.V. Neimark, Zh. Tekh. Fiz. **56**, 2235 (1986) [Sov. Phys. Tech. Phys. **56**, 2235 (1986)].
  - [6] *Carbide, Nitride and Boride Materials Synthesis and Processing*, edited by A.W. Weimer (Chapman and Hall, London, 1997); A.G. Merzhanov, *Combustion Processes and Materials Synthesis* (ISMAN, Chernogolovka, 1998) (in Russian).
  - [7] H. Tephany, J. Nahmias, and J.A.M.S. Duarte, Physica A **242**, 57 (1997).
  - [8] N. Provatas *et al.*, Phys. Rev. E **51**, 4232 (1995).
  - [9] A.S. Mukasyan, A.S. Rogachev, and A. Varma, Chem. Eng. Sci. **54**, 3357 (1999).
  - [10] A. Varma, A.S. Mukasyan, and S. Hwang, Chem. Eng. Sci. **56**, 1459 (2001).
  - [11] L.G. Voroshnin, B.M. Khusid, and B.B. Khina, J. Eng. Phys. **55**, 822 (1988).
  - [12] H. Scher and R. Zallen, J. Chem. Phys. **53**, 3759 (1970).
  - [13] B.I. Shklovskii and A.L. Efros, *Electronic Properties of Doped Semiconductors* (Springer-Verlag, Heidelberg, 1984).
  - [14] T.F. Grigor'eva *et al.*, Dokl. Chem. **369**, 285 (1999).
  - [15] S.W. Jo *et al.*, Acta Mater. **44**, 4317 (1996).
  - [16] T. El-Raghy and M.W. Barsoum, J. Am. Ceram. Soc. **82**, 2849 (1999).
  - [17] V.I. Itin, Yu.S. Naiborodenko, and A.D. Bratchikov, Combust., Explos. Shock Waves **37**, 429 (2001).
  - [18] G.A. Nersisyan *et al.*, Combust., Explos. Shock Waves **37**, 423 (2001).
  - [19] G.A. Kohring, Physica A **295**, 1 (1993).
  - [20] P.L. Leath, Phys. Rev. B **14**, 5046 (1976).
  - [21] P.L. Leath and G.R. Reich, J. Phys. C **11**, 4017 (1978).
  - [22] H. Saleur and B. Duplantier, Phys. Rev. Lett. **58**, 2325 (1987).
  - [23] J.F. Gouyet and S. Havlin, J. Phys. A **21**, 1921 (1988).
  - [24] R.M. Ziff, Phys. Rev. Lett. **56**, 545 (1986).
  - [25] M. Aizenman, B. Duplantier, and A. Aharony, Phys. Rev. Lett. **83**, 1359 (1999).
  - [26] Q. Cao and P. Wong, J. Phys. A **25**, L69 (1992).
  - [27] *Monte Carlo Methods in Statistical Physics*, edited by K. Binder (Springer-Verlag, Berlin, 1979).
  - [28] S. Galam and A. Mauger, Phys. Rev. E **53**, 2177 (1996).



- [29] C. Domb and E. Stoll, *J. Phys. A* **10**, 1141 (1976).  
[30] C. Domb, T. Schneider, and E. Stoll, *J. Phys. A* **8**, L90 (1975).  
[31] A. Sur *et al.*, *J. Stat. Phys.* **15**, 345 (1977).  
[32] J. Feder, *Fractals* (Plenum Press, New York, 1988).  
[33] A. Kapitulnik *et al.*, *J. Phys. A* **16**, L269 (1983).  
[34] A.L. Efros, *Physics and Geometry of Disorder* (Nauka, Moscow, 1982), p. 54.  
[35] M.E.J. Newman and R.M. Ziff, *Phys. Rev. Lett.* **85**, 4104 (2000).  
[36] C.D. Lorenz and R.M. Ziff, *J. Phys. A* **31**, 8147 (1998).  
[37] H.G. Ballesteros *et al.*, *J. Phys. A* **32**, 1 (1999).  
[38] A.K. Sarychev, A.P. Vinogradoff, and A.M. Karimov, *J. Phys. C* **18**, L105 (1985).  
[39] H.L. Fish, J.M. Hammersley, and D.J. Welsh, *Phys. Rev.* **126**, 949 (1962).  
[40] D.S. Gaunt and M.F. Sykes, *J. Phys. A* **16**, 783 (1983).  
[41] J. Blease, J.W. Essam, and C.M. Place, *J. Phys. C* **11**, 4009 (1978).  
[42] M.F. Sykes, D.S. Gaunt, and J.W. Essam, *J. Phys. A* **9**, L43 (1976); M.F. Sykes, D.S. Gaunt, and M. Glen, *ibid.* **9**, 725 (1976); M.F. Sykes, M. Glen, and D.S. Gaunt, *ibid.* **7**, L105 (1974).