

## Theory of Porous Electrodes: The Percolation and a Calculation of Percolation Lines

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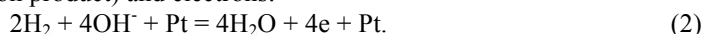
**Abstract** – The basis for a theory of porous electrodes is the percolation problem. Its solution would make it possible to answer the question of how effectively the structure of a porous electrode is used for ensuring the occurrence of electrochemical processes on its inner surface, for bringing together all its participants (reagents, ions, electrons, catalyst particles), and for removing the formed products. For the solution of this problem, it is necessary that both the elements of the structure of a porous electrode and the substances filling it should be connected. In the case of hydrophobized electrodes, these are exemplified by a mixture of agglomerated grains of polytetrafluoroethylene and catalyst, the gaseous reagent entering the electrons, and the electrolyte. In this publication, we describe a general method intended for the calculation of thresholds and lines of percolation and present particular estimates for an important class of lattices modeling porous media – rectangular: plane, square lattice, three-dimensional cubic, and their analogues in space of any number of measurements.

### INTRODUCTION

A practically important section of theoretical electrochemistry is the theory of porous electrodes. Porous electrodes of one modification or another are present in chemical power sources, fuel cells, electrolyzing cells, batteries, and devices for conducting electrosyntheses. The principal problem of this practically important section consists in the determination of conditions under which one can bring together on a sufficiently developed inner specific surface of a porous electrode (PE) all participants of the electrochemical process, such as reagents  $\sum r$ , supplied or removed ions, supplied or removed electrical current (electrons,  $e$ ), catalyst ( $c$ ), and remove the formed useful and side products of the electrochemical reaction  $\sum p$ . Thus, on the inner surface of a porous electrode, conditions must be ensured for occurrence of the process



A particular example of realization of relationship (1) may be the burning of gaseous hydrogen on platinum (catalyst) with the formation of water (reaction product) and electrons:



The occurrence of process (2) is not easy to realize even on a smooth surface of a platinum electrode because of the fact that gaseous hydrogen is poorly soluble in an aqueous solution of an electrolyte and its supply to the platinum surface wetted by a liquid is complicated. It is even more difficult to conduct process (1) on a porous electrode. It must be designed so as, first, to make the entire inner surface of pores available to the electrochemical process as much as possible (it is obvious that pores of size  $\sim 10^{-10}$  m are incapable of making any contribution in the occurrence of the electrochemical reaction and into the processes of the transfer of substances) and, secondly, to ensure technically acceptable magnitudes of the electrochemical activity  $I$ , i.e. sufficiently high current densities (for example, in electrochemical power sources) and large values of yields of target processes (in electrolyzing cells and installations for conducting electrosyntheses). To estimate the electrochemical activity, one can make use of the formula

$$I = j S \Delta, \quad (3)$$

where  $j$  is the current density of process (1) at the inner surface area of a porous electrode;  $S$  is the specific inner surface area of a porous electrode which is inversely proportional to the average radius of pores  $r$  or the average diameter of particles constituting a porous medium, i.e.

$$S \approx 1/r; \quad (4)$$

and  $\Delta$  is the PE thickness. The smallness  $j$  in formula (3) may be compensated by large values of  $S$ . For example, in formula (4),  $S = 10^7 \text{ cm}^{-1}$  at  $r = 1 \text{ nm}$ . However, the compensation is possible under the unavoidable condition that the electrochemical process (1) should spread to macroscopic, as compared with microscopic characteristic dimensions of a porous medium, distances, i.e. over the entire thickness of a porous electrode. The fulfillment of the last requirement is the principal difficulty facing the creators of effectively operating porous electrodes. It is necessary to organize special channels in porous electrodes for the supply and removal of all participants in process (1). The necessity to solve this problem both theoretically and practically was clearly comprehended for the first time when creating hydrophilic porous electrodes for hydrogen-oxygen fuel cells [1]. It was necessary to make sure that a gas reagent (hydrogen or oxygen), using electrolyte-free pores  $10^{-6}$  m in size, could reach the rear surface of PE starting from its front surface and overcoming a path of several millimeters. This was attained by creating an excess pressure difference between the gas phase and the liquid phase in specially arranged biporous electrodes that had both small pores, intended for the electrolyte supply, and large gas pores, intended for the gas supply. It was established both theoretically and experimentally that the aggregate of large pores available to the gas become a channel for the gas supply over the entire thickness of the electrode only after reaching a critical number of such pores, when the pores concerned could form a unified, connected with one another, network of large pores. The question of the channels intended for the supply of all participants in the electrochemical process (1) into the electrode pores became even more acute upon going from hydrophilic to hydrophobized porous electrodes. The latter include electrodes of various designs suitable for electrochemical power sources that make use of both gas reagents [2-10] and liquid electrochemically active substances difficultly soluble in aqueous electrolyte solutions, for example, petrol [11, 12]. The hydrophobized electrodes prepared from a mixture of a hydrophilic metal-catalyst and a hydrophobizing agent (polytetrafluoroethylene) managed to successfully operate only at an optimum weight ratio between hydrophilic and hydrophobic components. The hydrophobic component did the same for the gas reagent of the liquid reagent difficultly soluble in electrolyte. Specific features inherent in hydrophobized and hydrophilic porous electrodes were thoroughly analyzed in papers and reviews [13-21]. In very promising porous electrodes with solid polymer electrolytes that

appeared in the last decades [22, 23], which were used first chiefly for the water electrolysis, the principal problem became that of creating a channel for the supply into the electrochemical reaction zone of electrons moving along infinitely long chains of agglomerates in contact with one another. The agglomerates in question comprised microscopic particles of a catalyst (commonly, platinum black, whose amount in a porous electrode must be, naturally, as minimum as possible). Specific features pertaining to the operation of such a system are considered theoretically in [24-27].

Quite recently, for the cases where the porous space in a porous electrode happens to be lacking an electrolyte solution (water electrolyzing cells), it has been proposed to make porous electrodes hydrophilic [28-30]. This measure increases the effective ionic conductivity and makes it possible, in some cases, to substantially improve characteristics of porous electrodes.

In all examples of porous electrodes of various types and designs presented above, the efforts of an electrochemist-theorist must be directed towards solving the problem of percolation: to revealing the conditions under which a bond emerges sufficient for the realization of a normal progress of electrochemical processes (1), i.e. a bond between elements that had been separated before, such as hydrophilic or hydrophobic pores and particles of the catalyst, hydrophobizing agent, hydrophilizing agent, or solid polymer electrolyte. This is a problem of a structural, topological, and probabilistic nature important for the entire of porous electrodes. This is also the problem that will be the subject under study in the present publication. The essence of the percolation problem is as follows [31-35]. Consider a regular infinite lattice depicted in Figs. 1a-1c. Its basic elements are sites and bonds that connect neighboring sites. Let an arbitrarily selected lattice site (penetrable for a liquid) be wetted with a liquid. Suppose that elements of the lattice are only partially penetrable for a liquid, specifically, bonds – with the probability  $\gamma$ , and sites – with the probability  $\omega$ . Under these conditions, it is necessary to calculate the probability  $P(\gamma, \omega)$  that the liquid, while moving from one site to another or from one bond to another via sites and bonds that are penetrable for the liquid and are in contact with one another, wets an infinite number of sites and bonds (the liquid will be capable of traveling to an infinite distance from the site which is the source of the liquid). This probability is called the percolation probability. Obviously, with low probabilities  $\gamma$  and  $\omega$ , the liquid will be capable of percolating only to a finite distance, because its path will be blocked by sites and bonds impenetrable for it. In this region of probabilities  $\gamma$  and  $\omega$ , the probability  $P(\gamma, \omega)$  is identically equal to zero. However, probabilities  $\gamma$  and  $\omega$  may reach critical values fitting the  $\gamma$  vs.  $\omega$  curve which is called a percolation line. Once these values are reached, the liquid will be capable of percolating to an infinite distance. Under these conditions, the percolation probability  $P(\gamma, \omega)$  becomes other than zero in the regions  $\gamma > \gamma_c$  and  $\omega > \omega_c$ .

The problem of the determination of percolation lines is the most general and is traditionally neglected. Only two limiting cases are usually considered. In a lattice of sites (site problem), the magnitude of parameter  $\omega$  is varied and it is assumed that parameter  $\gamma$  is identically equal to unity, which means that all the lattice bonds are liquid-penetrable. In a lattice of bonds (bond problem), the magnitude of parameter  $\gamma$  is varied and it is assumed that parameter  $\omega$  is identically equal to unity, which means that all the lattice sites are liquid-penetrable. Critical values of the  $\gamma$  and  $\omega$  parameters for these two limiting cases (instances when percolation probabilities become other than zero) are denoted as  $\gamma_c$  and  $\omega_c$  and are called the percolation thresholds.

Exact results may be obtained in the percolation problems only in isolated cases. For a straight line comprising bonds and sites (unidimensional space,  $d = 1$ ), the solution is trivial, because it is obvious that the presence of even a single site or bond impenetrable for a liquid is capable of preventing a further percolation of the liquid. Hence,

$$\gamma_c = \omega_c = 1 \quad (5)$$

We are aware only of four exact values of the percolation thresholds for plane regular lattices (two-dimensional space,  $d = 2$ ) presented in Fig. 1 [36, 37]. For a square lattice of bonds (Fig. 1a),  $\gamma_c = 1/2$ . For a triangle lattice of bonds (Fig. 1b),  $\gamma_c = 2 \sin(\pi/18) = 0.3473$  and  $\omega_c = 1/2$ . In this case,  $\gamma_c$  is a real root of the equation

$$\gamma^3 - 3\gamma + 1 = 0 \quad (6)$$

For a cellular lattice of bonds (Fig. 1c),  $\gamma_c = 1 - 2 \sin(\pi/18) = 0.6527$ , which is a real root of the equation

$$\gamma^3 - 3\gamma^2 + 1 = 0 \quad (7)$$

We are unaware of any exact values of percolation thresholds determined mathematically in a three-dimensional space ( $d = 3$ ). Hence, the aim of this work to point out the way to find exact values of percolation thresholds for lattices of bonds and sites in spaces with any number of dimensions and a technique for calculating percolation lines in them. The latter is of importance, because, in real porous electrodes, it is rather difficult to explicitly recognize the limiting cases, i.e. pure lattices of bonds or lattices of sites. In real porous media produced by randomly mixing, pressing, or sintering initial components constituting a porous electrode, such as a catalyst (metal), hydrophobizing agent (polytetrafluoroethylene), hydrophilizing agent, and grains of a solid polymer electrolyte, the distinction between a site and a bond is rather indefinite. Therefore, strictly speaking, in porous electrodes, percolating liquids (their roles may be played by electrons, ions, gas and liquid reagents, etc.) may be delayed most frequently in the percolation lines, i.e. simultaneously in sites and bonds.

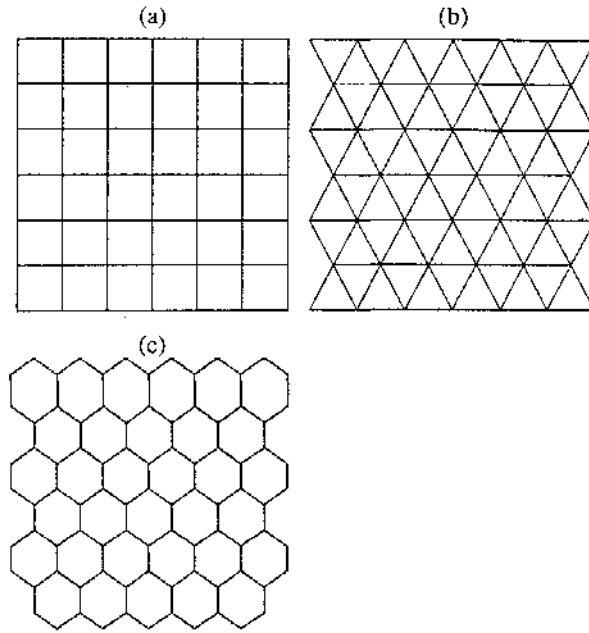


Fig. 1. Regular plane lattices: (a) square, (b) triangular, and (c) cellular.

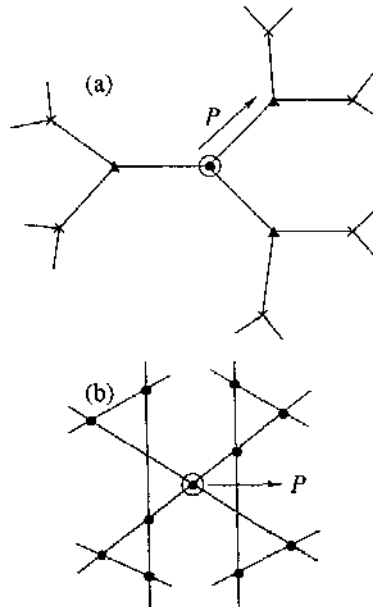


Fig. 2. Pseudolattices: (a) tree with the coordination number  $k = 3$ , and (b) cactus.

### PSEUDOLATTICES

The percolation problem can be solved completely in the case of pseudolattices, i.e. trees (Fig. 2a) and cactuses (Fig. 2b). The principal characteristics of these structures are the recurrence of their elements and the uniformness of the percolation process. These characteristics make it possible to calculate exact values of the percolation probability and the percolation threshold even without resorting to the apparatus of generating functions [38, 39].

In a tree of bonds (we could show that, in the trees,  $\gamma = \omega$ .) with the coordination number  $k$ , the percolation probability  $P$  obeys the obvious equation

$$P = [1 - (1 - P)^{k-1}] \quad (8)$$

A liquid, when traveling along any of  $k$  bonds of a tree, may percolate from an initial site, a source of liquid (marked with a circlet in Fig. 2a), infinitely far with the probability  $P$  in the left-hand part of equation (8), provided the nearest bond is penetrable for a liquid (factor  $\gamma$ ) and at least one of the remaining  $k - 1$  bonds adjacent to the next site is capable of promoting the movement of the liquid to an infinite distance. The term  $(1 - P)^{k-1}$  represents the probability that none of the  $k - 1$  bonds is capable of ensuring an infinite motion of the liquid. After solving equation (8), one can find out how  $P$  depends on  $\gamma$ . There is a trivial solution:  $P$  is identically equal to zero. However, at  $\gamma = \gamma_c$ , a nontrivial solution emerges as well. For example, for a tree with  $k = 3$  (Fig. 2a), the solution is

$$P = 2 - 1/\gamma. \quad (9)$$

In addition to yielding the probability  $P$ , equation (8) makes it possible to determine the percolation threshold as well. Prior to reaching the percolation threshold, the percolation probability is identically equal to zero, i.e.  $P = 0$ . As seen from relationship (9), with the  $\gamma$  parameter tending indefinitely close to the percolation threshold  $\gamma_c$  from the right, the percolation probability tends to zero. With this condition taken into account, it follows from equation (8) (all nonlinear terms in the right-hand part of this equation should be set to zero, because these quantities are of the next order of smallness) that the percolation thresholds for a tree with the coordination number  $k$  is

$$\gamma_c = 1 / (k - 1) \quad (10)$$

This result may be produced in a different manner. When traveling from the initial site which is a source of a liquid, via  $k$  bonds ( $k = 3$  in Fig. 2a), the liquid may percolate into a first layer of sites marked with triangles, then into a second layer of sites marked with crosses, and so on. Due to the tree uniformness, the same process occurs repeatedly in each stage of the transfer from the  $n$ th layer of sites to the  $n + 1$ -th layer of sites. The liquid must have a chance to overcome the same barrier: to travel into the next layer of sites via  $k$  bonds leading from any site situated in the  $n$ th layer of sites. This means that the following condition must be obeyed:

$$P = \sum C_{k-1}^s \gamma^s (1 - \gamma)^{k-1-s} [1 - (1-P)^s]. \quad (11)$$

In the percolation point, the probability  $P$  tends to zero. Hence, retaining only linear, with respect to  $P$ , terms in the right-hand part of equation (11), we again obtain condition (10) for  $\gamma_c$ . The methods used for calculating the percolation threshold for cactuses are as simple as those for trees. For example, for a triangular cactus presented in Fig. 2b, bearing in mind that the percolation probability  $P$  tends to zero at a threshold value of  $\gamma_c$ , in the problem of bonds, we have

$$[\gamma^3 + 3\gamma^2(1 - \gamma)] 2 + 2\gamma(1 - \gamma)^2 = 1. \quad (12)$$

A solution of this equation with respect to  $\gamma$  yields  $\gamma_c = 0.403$ .

Let us draw some preliminary conclusions. Studying the percolation process in pseudolattices revealed two fundamental principles underlying the percolation, which will be valid for lattices as well. These are as follows.

**Principle I.** In a point critical for the percolation process (percolation threshold), and exclusively in this point only, a hypothetical possibility arises for the emergence of an infinite cluster consisting of the lattice elements wetted with a liquid. The probability of the realization of such a possibility is equal to zero. Such a cluster, should it materialize, has the shape of a nonbranching liquid "cord" which extends infinitely far from the site which is the source of the liquid.

**Principle II.** In a point critical for the percolation process, it may be possible to determine the magnitude of the percolation threshold most simply if the percolation of the liquid from the site which is the source of the liquid, proceeds via a chain of repeatedly occurring uniform barriers. Obviously, for the realization of an infinite liquid cluster to be possible, it is enough to impose the condition that the probability of overcoming a barrier should equal unity.

## LATTICES

The true lattices (Fig. 1) differ from pseudolattices (Fig. 2) in that, when solving the percolation problem for the former, one should take into account an infinite number of closed loops. This circumstance makes the calculations exceedingly difficult. However, one can circumvent this difficulty. By the example of regular plane lattices of bonds (Fig. 1), one can try to find out how the liquid spreads from the initial site which is the source of the liquid. Such an attempt reveals the following pattern. As seen from Figs. 3a-3c, the liquid spreads in two qualitatively different regions. At first, the liquid spreading occurs in a relatively small region situated around the site, which is the source of the liquid. This is the region of nonuniformness, which is denoted here as region I. In this region, the number of bonds per site  $\xi_n$ , which allow the liquid percolate from the  $n$ th layer of sites into the  $n + 1$ -th layer of sites, gradually diminishes. In Fig. 3a, for example, for the site which is the source of the liquid,  $\xi = 4$ ; in the first layer of sites,  $\xi = 3$ , and so on. It is obvious that, in the case of a plane square lattice (Fig. 3a), the number of sites  $S_n$  and the number of bonds  $B_n$  leading from the  $n$ th layer of sites to the  $n + 1$ -th layer of sites, as well as their ratio  $\xi_n = B_n / S_n$  depend on  $n$  as follow:

$$S_n = 4n \quad B_n = 8n + 4 \quad \xi_n = 2 + 1/n \quad (13)$$

Having passed through region I of nonuniformness, the liquid starts to spread over the remaining infinite fraction of the space. This is region II (region of uniformness). Region II comprises, as if it were a pseudolattice, infinitely recurring structural elements. Obviously, it is region II that determines the magnitude of the percolation threshold, because the percolation of the liquid in this region is extremely hampered. The hampering is due to a maximum lack of bonds in this region: as follows from relationship (13), parameter  $\xi_n$  in region II tends to as minimum a value as possible.

By the example of a square lattice, we can formulate two more fundamental principles that allow one to determine thresholds and lines of percolation. These are as follows.

**Principle III.** In a point critical for the percolation process, and exclusively in this point only, the fate of the percolation process is determined by an infinite periphery (with respect to the site which is the source of the liquid) where the spread of the liquid is tree-like, i.e. has a recurring uniform character.

**Principle IV.** The percolation of the liquid in region II (region of uniformness) makes it possible to determine the percolation threshold. This region is characterized by partial lack of bonds. The effective coordination number  $k^*$  in this region is less than  $k$ , i.e.  $k^*$  is less than the true coordination number of the lattice.

These two simple considerations make it possible to determine percolation thresholds in some lattices of bonds. As follows from Fig. 3a, for a square lattice of bonds, in the percolation periphery (region II), one can assume, in accordance with relationship (13), that parameter  $\xi_n$  is constant and equal to two. From the  $n$ th layer of sites, one can get into the  $n + 1$ -th layer of sites via two bonds only (Fig. 3d). The situation in this case is identical to that in the case of the liquid percolation in a tree with the coordination number  $k = 3$  (Fig. 2a). Hence, for a square lattice of bonds, the percolation threshold  $\gamma_c = 0.5$ . Thus, we obtained an absolutely accurate result that was obtained by the authors of [36, 37] as far back as in 1964.

Let us now analyze a plane triangular lattice of bonds. The count of sites and bonds in the course of the liquid percolation from the site which is the source of the liquid in such a lattice, which is similar to relationship (13), yields the following result:

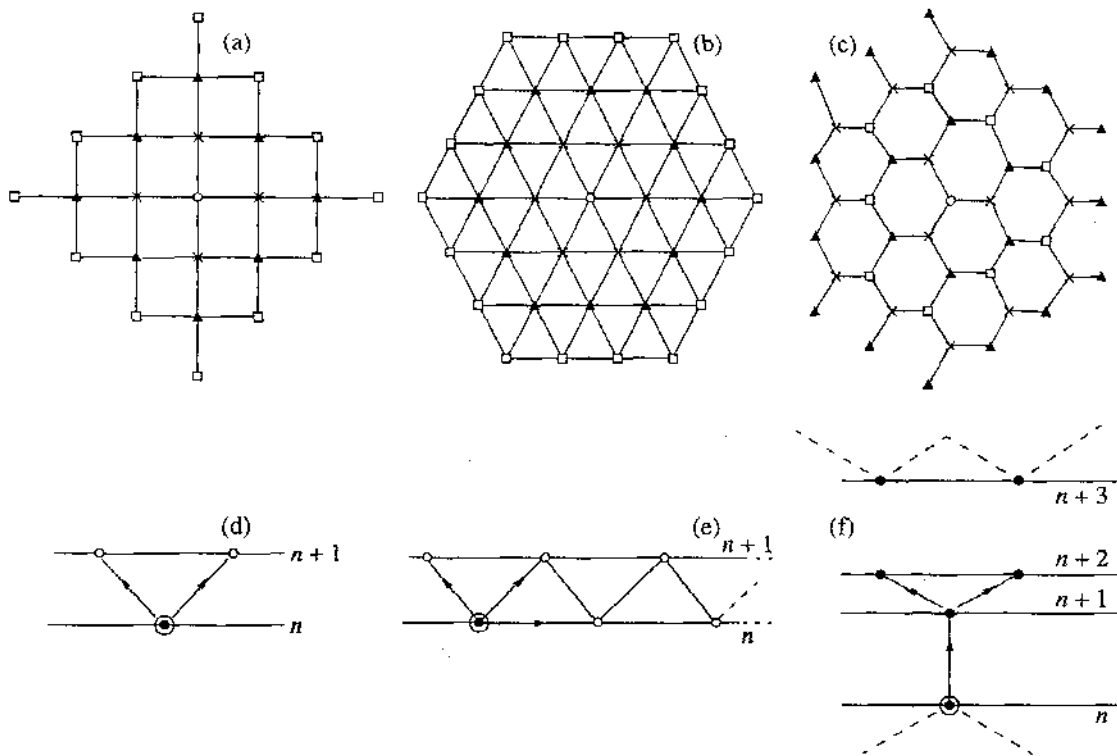
$$S_n = 6n \quad B_n = 18n + 6 \quad \xi_n = 3 + 1/n \quad (14)$$

In the uniformness region II, one can assume that parameter  $\xi_n = 3$ . In this case, the three bonds leading from the  $n$ th layer of sites to the  $n + 1$ -th layer of sites are arranged as shown in Fig. 3e. Summing possible probability of the liquid transfer and setting this sum to unity (fulfilling principles I through IV), we obtain

$$\gamma + (\gamma + \gamma^2 - \gamma^3) \sum \gamma^{s-1} = \gamma(2 - \gamma^2)/(1 - \gamma) = 1 \quad (15)$$

This equation defines the percolation threshold for a plane triangular lattice of bonds. It is easy to verify that this equation coincides to the full with equation (6). Thus, we obtained one more accurate result that was obtained by the authors of [36, 37] thirty five years ago.

Let us now focus our attention on a plane cellular lattice of bonds (Fig. 3c). The situation here is more complicated than that in the square and triangular lattices of bonds: no chain of uniform recurring barriers is present in the uniformness region II. As follows from Fig. 3f, parameter  $\xi_n$  alternately equals unity and two for even and odd  $n$ , respectively. Therefore, the magnitude of the percolation threshold is now determined by the liquid flow through an infinite number of layers of sites, rather than by its passing between two random neighboring layers of sites. In [40-42], we developed a graphics technique for calculating two-terminal networks. We also proposed to use successive approximations in order to determine an accurate value of the percolation threshold with any degree of accuracy for a cellular lattice of bonds.



**Fig. 3.** Character of percolation of a liquid in (a, d) square, (b, e) triangular, and (c, f) cellular plane regular lattices; see text for explanations.

#### PERCOLATION GRAPHS

Up to now, we discussed only the problem concerned with the calculation of percolation thresholds in lattice of bonds. However, the problem of lattices of sites also exists. Such a situation calls for a general method of calculation of percolation thresholds, which would be suitable for both lattices of bonds and lattices of sites. Moreover, up to now, our deliberations did not touch upon the notion of the space dimensionality  $d$ . Let us make allowances for this substantial imperfection. We assume that a space of any number of dimensions may stratify into subspace of the dimensionality  $d - 1$  and bond-site connecting these subspaces, i.e. collecting these subspaces into a space of the dimensionality  $d$ . Let us illustrate this notion by some examples. All regular plane lattices ( $d = 2$ , Fig. 1) may be interpreted as regular collections of lines of similar type ( $d = 1$ ) connected by a collection of bonds of similar type connecting them. Any regular three-dimensional lattice ( $d = 3$ ) may be interpreted as a collection of selected in a certain manner surfaces ( $d = 2$ ) that are connected in a regular manner by bonds. Similar considerations may be expanded to spaces of any arbitrary number of dimensions. Classifying lattice bonds into two types (bonds in subspaces of dimensionality  $d - 1$  and bonds connecting these subspaces) allows us to explain why percolation thresholds in a plane triangular lattice characterized by  $\gamma_c = 0.3473$  (Fig. 1b) and in a three-dimensional cubic lattice of bonds whose  $\gamma_c$ , according to numerical calculations, is close to 0.25, are different, although coordination numbers for these lattices are identical, specifically,  $k = 6$ .

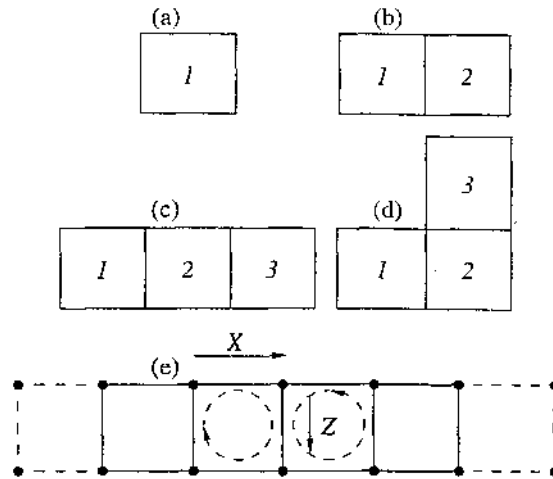
Let us now isolate any infinite straight line of bonds in a plane square lattice of bonds (Fig. 1a). Should a liquid have been capable of percolating only along this straight line, an infinite cluster of bonds wetted with the liquid would have formed

only at  $\gamma = 1$ . However, the percolation threshold in a plane square lattice of bonds occurs far earlier, specifically, at  $\gamma = 0.5$ . Such a decrease in the percolation threshold is caused by the fact that each site in the straight-line chains of bonds attaches two bonds of different nature. The latter are normal to the initial line of bonds and are capable of transferring the liquid onto neighboring lines. Such “hops” of the liquid allow it to effectively circumvent obstacles it meets when moving along a straight line of bonds. This feature of the percolation process is of a fundamental nature and must be taken into account when designing methods for calculating percolation threshold. Therefore, we formulate the last principle which makes it possible to estimate magnitudes of thresholds and lines of percolation, namely, the principle of hops.

**Principle V.** In a random lattice of dimensionality  $d$  with a coordination number  $k$ , one must discriminate between percolation processes proceeding via bonds of two types: bonds in sublattices of dimensionality  $d - 1$  with the coordination number  $k_1$ , and bonds (their number in each site is equal to the difference  $k - k_1$ ) which connect the sublattices.

All the preceding speculations about a general character of a liquid percolation in lattices and trees, coupled with the five principles which must be taken into account when calculating thresholds and lines of percolation, allow us to formulate the following general recipe for actions suitable for lattices of any arbitrary dimensionality  $d$ : it is necessary (1) to consider the percolation of a liquid from the site which is the source of the liquid in an infinite region of uniformness, i.e. region II (principle III); (2) to design separate barriers: it is exactly in infinite succession of such barriers that constitutes region II (principle II); (3) that the effective coordination number  $k^*$  in such a barrier should be less than the coordination number  $k$  of the initial lattice (principle IV); (4) to distinguish in such a barrier the nature of bonds constituting it (principle V); and (5) to represent, upon reaching a threshold or a line of percolation, the cluster consisting of infinite liquid bonds by nonbranching liquid cord (principle I).

The physically meaningful features of percolation processes enumerated above may find their natural expression in special structures. In [34], we called such structures the percolation graphs. For example, for a plane square lattice, a percolation graph is constructed in the following manner. Take an arbitrary cell (a square in Fig. 4a). A second cell is added to the first so that both should have a common edge (Fig. 4b). A third cell should be fixed to the second so that both also had a common edge. In the case of a square lattice, the last operation may be performed using two techniques (Fig. 4c, 4d). For the construction process to become a unique one, the third cell is added to the second one with the understanding that the number of elements, i.e. bonds and sites, that are common for the next and previous cells should be as small as possible. Therefore, the version presented in Fig. 4d must be rejected. Continuing the process of adding cells to the initial one indefinitely in accordance with the above rules, we obtained a structure of an infinite length (Fig. 4e). This is precisely the percolation graph for a plane square lattice. A percolation graph has all the properties necessary for a successful calculation of the thresholds and lines of percolation. As compared with the initial lattice (Fig. 1a), its coordination number  $k^*$  equals three, which corresponds to a transition into a peripheral region of uniformness of percolation. Both the possibility of spreading via lines (in subspace with dimensionality  $d = 1$ ; probability  $X$  in Fig. 4e) and the liquid movement by hopping from one line onto a neighboring line (probability  $Z$  in Fig. 4e) are explicitly realized in a percolation graph. Moreover, a percolation graph must be treated as a sublattice (a hybrid tree designed in a certain manner). Finally, infinite chains of a liquid in a percolation graph must not branch off, when calculating, one must leave in the equations only terms that are linear with respect to the percolation probabilities.



**Fig. 4.** Schematics of the construction of a percolation graph for a plane square lattice; see text for explanations.

Now, we turn to particular calculations. Consider the problem of bonds in a square lattice of bonds. As follows from the percolation graph presented in Fig. 4e, probabilities  $X$  and  $Z$  must be related through the equations

$$X = \gamma(X + Z) \quad Z = \gamma 2X \quad (16)$$

To derive a nontrivial solution, one must set to zero the determinant of this system. This yields the equation which determines the magnitude of the percolation threshold

$$2\gamma^2 + \gamma - 1 = (2\gamma - 1)(\gamma + 1) = 0 \quad (17)$$

It follows that, in a square lattice of bonds,  $\gamma = 1/2$ .

A percolation graph gives us a chance to solve the problem of site as well. In doing so, one must remember that probability  $X$  and  $Z$  became now conditional probabilities. Taking into account this circumstance and the fact that, upon reaching

the percolation threshold, liquid cords cannot yet branch off (the example of loops which may arise are shown in Fig. 4e by dashed lines), we obtain the set of equations

$$X = \omega (X + Z) \quad Z = \omega [\omega^2 2 X + 2 \omega (1 - \omega) X] = 2 \omega^2 X \quad (18)$$

Should the second equation in the set (18) have been written in the form  $Z = \omega 2X$ , we would have obtained for the percolation threshold in a lattice of sites  $\omega = \gamma = 1/2$ . However, as follows from the percolation theory,  $\omega > \gamma$  in any lattice. That is why it became necessary to consider the fate of two more nearest sites, which is reflected by the second multiplier in the middle part of the second equation in set (18). One should add a simple  $X$  as the multiplier, rather than  $X + Z$ , because the liquid motion in a lateral direction (multiplier  $Z$ ) is open to the possibility of the emergence of loops. According to principle I, this must be forbidden. Setting the determinant of the set of equations (18) to zero, we find the characteristic equation

$$2 \omega^3 + \omega - 1 = 0 \quad (19)$$

Its single real root is

$$\omega = [1/4 + (29/3)^{1/2}/12]^{1/3} + [1/4 - (29/3)^{1/2}/12]^{1/3} = 0.58975, \quad (20)$$

which well conforms to the results derived by the authors of [43-45] who used numerical methods. The Monte-Carlo method yielded the value  $0.581 \pm 0.015$ , and the series method produced the value  $0.590 \pm 0.010$ .

Let us make a substantial note. The outcome of constructing a percolation graph may be two-pronged. A percolation graph may have a single shape, as it happened in the case of a plane square lattice; then, one can manage to obtain accurate values of thresholds and lines of percolation. On the other hand, the number of versions of realizations of a percolation graph may be infinite, as took place in the case of a plane cellular lattice; then, one can obtain only approximate values of thresholds and lines of percolation. In Fig. 5, we present three versions of a percolation graph for a plane cellular lattice which have each a regular structure. Note that cells of a plane cellular lattice in a percolation graph may be added at random. We can demonstrate that, in the problem of bonds, the characteristic equations for percolation graph depicted in Figs. 5a and 5b are, respectively,

$$2 \gamma^5 + 2 \gamma^4 + \gamma^2 - 1 = 0 \quad (21)$$

$$2 \gamma^3 + \gamma^2 - 1 = 0 \quad (22)$$

Equations (21) and (22) differ from equation (7) which yields accurate solution of the problem. Nevertheless, the roots of equations (21) and (22) differ but slightly from the value  $\gamma = 0.6527$  which is the root of equation (7).

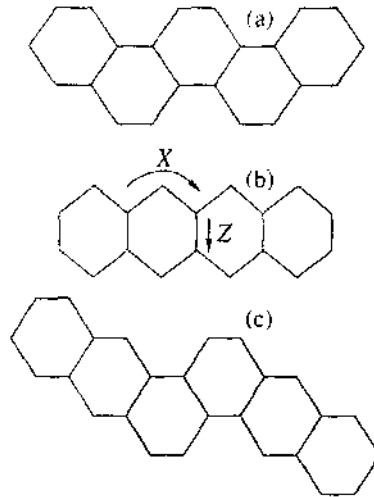


Fig. 5. Examples of regular percolation graphs for a plane cellular lattice; see text for explanations.

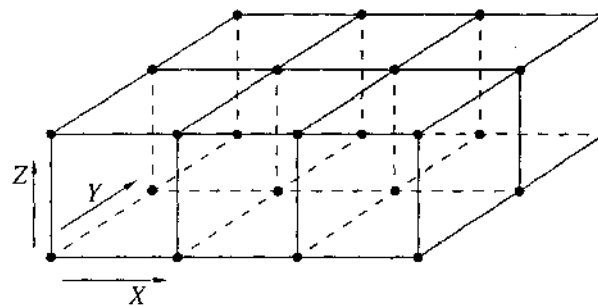


Fig. 6. Percolation graph for a cubic lattice.

#### GENERALIZATIONS

The method of estimating  $\gamma$  and  $\omega$  with the aid of percolation graphs is universal. The method is the same for lattices of any number of dimensions. Consider, for example, a cubic lattice. The elementary cell of a cubic lattice is a cube. According

to principles I-V, in a three-dimensional space, one should construct surfaces, rather than cell chains. The percolation graph for a cubic lattice is a plane constructed of cubes (Fig. 6) in accordance with the rules described above. Every two neighboring cells must have a common face. The number of sites and bonds in nearest neighbors must be minimum. A cubic lattice has only one percolation graph; therefore, it becomes feasible to obtain accurate values of thresholds and lines of percolation. As follows from the symmetry considerations, probability X and Y in Fig. 6 are identical. Then, for the problem of bonds, we obtain the set of equations

$$X = \gamma (3X + Z) \quad Z = \gamma 4X \quad (23)$$

Setting the determinant of this set of equations to zero, then

$$4\gamma^2 + 3\gamma - 1 = 0 \quad (24)$$

This yields the value  $\gamma = 1/4$  for the percolation threshold in a cubic lattice of bonds. This result well conforms to the results of numerical calculations of the same quantity conducted by the authors of [44, 46]. The Monte-Carlo method yielded the value  $0.254 \pm 0.013$ , and the series method produced the value  $0.247 \pm 0.005$ .

Consider now a cubic lattice of sites. Parameters X and Z are in this case conditional probabilities. Bearing in mind that a percolation graph must not contain any loops, we obtain the set of equations

$$X = \omega (3X + Z) \quad Z = \omega \sum C_4^p \omega^{4-p} (1-\omega)^p \quad (4-p) X = 4 \omega^2 X \quad (25)$$

Solving the characteristic equation

$$4\omega^3 + 3\omega - 1 = 0, \quad (26)$$

we obtain

$$\omega = [(1 + 2^{1/2})^{1/3} + (1 - 2^{1/2})^{1/3}]/2 = 0,298 \quad (27)$$

Numerical calculations conducted by the authors of [43, 44] yielded close values of  $\omega$ .

The results obtained for a plane square lattice and a three-dimensional cubic lattice are easy to generalize for any number of dimensions by introducing the notion of rectangular lattices. In the latter, the number of dimensions d and the coordination number k are linked through the relationship  $k = 2d$ . At  $d = 1$ , we have a linear chain; at  $d = 2$ , a square lattice; at  $d = 3$ , a cubic lattice; and so on. For rectangular lattices of any number of dimensions, it is possible to establish a general shape of the percolation lines as well. These are determined by solutions of the following characteristic equation:

$$2(d-1)\gamma^2\omega^3 + (2d-3)\gamma\omega - 1 = 0. \quad (28)$$

Setting  $\omega = 1$  in (28), we can derive the general expression for the percolation threshold in the problem of bonds

$$\gamma = 1/2(d-1) \quad (29)$$

On the other hand, we can select  $\gamma = 1$  in (28); then we will obtain the general expression for the percolation threshold in the problem of sites

$$\omega = \{ [1 + \{1 + 2(2d-3)^3/27(d-1)\}^{1/2}]/4(d-1) \}^{1/3} + \{ [1 - \{1 + 2(2d-3)^3/27(d-1)\}^{1/2}]/4(d-1) \}^{1/3} \quad (30)$$

Having solved quadratic equation (28) with respect to  $\gamma$ , we obtain a percolation line for rectangular lattices in an arbitrary space of measurements:

$$\gamma = \{ [(2d-3)^2 + 8(d-1)\omega]^{1/2} + (3-2d) \} / 4(d-1)\omega^2 \quad (31)$$

Percolation lines calculated with expression (31) for a number of values of the d parameter are presented in Fig. 7. At  $d = 1$ , the percolation line degenerates into a points with the coordinates  $\gamma = \omega = 1$ . At very large values of the d parameter, after expanding the right-hand part of equation (31) into a series by the 1/d parameter and restricting ourselves to the linear term of the expansion, we obtain

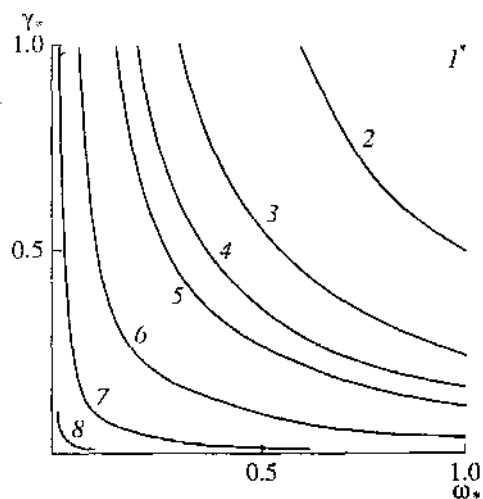
$$\gamma = 1/d\omega \quad (32)$$

Thus, in the case where the space dimensionality d tends to infinity, percolation thresholds for lattices of bonds and lattices of sites in rectangular lattices converge unrestrictedly and become identical:

$$\gamma = \omega = 1/d \quad (33)$$

With parameter d tending to infinity, the percolation line degenerates into the point  $\gamma = \omega = 0$ .





**Fig. 7.** Percolation lines for rectangular lattices in spaces with numbers of dimensions  $d$  as follows: (1) 1, (2) 2, (3) 3, (4) 4, (5) 5, (6) 10, (7) 50, and (8) 500.

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