Formation and evolution of fractal structures in a diffusion zone

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Mutual diffusion that proceeds via the vacancion mechanism with formation of a substitutional solid solution is investigated by computer modeling on a square lattice by the Monte Carlo method. The produced stochastic structures studied are the percolation diffusion front and the summary boundary of the clusters. It is shown that they are characterized by a fractal geometry and that their evolution is described by a number of critical exponents. The approach used permits description of the propagation of superconducting, conducting, magnetic phases and other phases undergoing mutual diffusion.

We investigate here the geometry of the structures produced by mutual diffusion in a solid, and study the laws governing the evolution of these structures with time.

Diffusive homogenization gives rise to numerous processes in a solid, such as the onset of mechanical stresses, formation and growth of phases, chemical reactions, change of the electric conductivity, and others. These processes are usually described by using the macroscopic characteristics of the diffusive homogenization picture, viz., the concentration profile and the motion of a plane having a given density. It will be shown below, however, that such an averaged description is utterly insufficient, since it bypasses the most important features of the geometry of the structures produced in the diffusion zone. These features are connected with the stochasticity of the diffusion process, which makes these structures substantially rough. Yet it is just these features which determine, for example, the kinetics of electric contact making in diffusion, the change of the electric properties of semiconductors following the spreading of the dopant (Mott transition, formation of *p-n* junction), and also the course of many other processes in a solid. Their effect is particularly large in objects of small thickness. They play therefore an important role in the formation and degradation of microelectronic elements. The problem plays a vital role also in connection with the recent advances in production of high-temperature superconducting materials. The study of the geometry and of the laws governing the evolution of the superconducting phase obtained by mutual diffusion of sinterable components is of undisputed interest.

We have proposed and implemented an approach, different from the macroscopic one, to the description of mutual diffusion. It provides a more complete description of the diffusion picture in the language of scaling structures. The approach proposed has a bearing on a number of problems concerning the properties of percolation clusters. In contrast to the traditional problems, however, in which the static picture is analyzed, we investigate here a case of physical importance (mutual diffusion), for which it is important to know how the percolation picture evolves with time.

Various structures formed in the course of stochastic processes have been actively investigated in recent years. It was established that these structures have geometric-self-similarity (scaling) properties, and their growth processes are described by a number of critical exponents. The parameter that characterizes the geometric self-similarity of such structures is the fractal dimensionality,[1] So far, however, no attempts have been made to describe mutual diffusion with the aid of the formalism used to describe fractal structures. Sapoval *et al.*[2] used the algorithm developed to simulate percolation clusters to describe the diffusion picture on a two-dimensional lattice in the case when the source of the diffusing atoms is an equal-concentration line. With the aid of the macroscopic relation $c(x) = \mathrm{erfc}(x/l_D)$ (l_D is the diffusion length) the authors of Ref. 2 calculated for each layer with coordinate x the concentration c of the diffusing atoms, and then placed atoms randomly in this layer, the probability of placing an atom in a site being equal to the calculated concentration. This method is quite rapid and therefore permits analysis of the cases of large diffusion lengths. It is not fully consistent, since it combines macroscopic and microscopic approaches. Its adequacy therefore still remains unclear. In particular, according to this method the probability of appearance of an atom in a given site depends only on the average concentration ascribed to the layer in which this site is placed, and does not depend at all on the real surrounding of the site. Even if the potential energy of the atom is independent of the surrounding, such an assumption may turn out to be incorrect for diffusion mechanisms in which a correlated jump of a group of atoms takes place (e.g., for the crowdion mechanism). In addition, this method does not permit simulation of mutual diffusion in the case when the displacement energy differs from zero, nor the growth of the phase and other aspects of a real diffusion process.

We have investigated, by computer simulation, mutual diffusion that proceeds via the vacancion mechanism. Each lattice measuring 100×200 atoms is divided into two 50×200 atom sections. In contrast to Ref. 2, all the lattice sites are occupied. In one half are located atoms A, and in the other atoms B. A vacancy moves randomly over the lattice, and hops over each time, with equal probability, to the location of one of the nearest four neighbors.

We designate the lattice boundaries parallel to the interface as, respectively, boundaries A and B, and we call the two others the lateral boundaries. Boundaries A and B are made reflecting. To decrease edge effects, the two other boundaries are "joined" (cyclic boundary conditions). After every 10^7 hops of the vacancy we analyze the instantaneous locations of the atoms A and B. In the course of the computer experiment, the vacancy executed $3.6 \cdot 10^8$ hops.

We introduce now the concept of a diffusion front. We explain this concept by ascribing to the atoms A and B different electric properties. Let, for example, A be metal atoms and B insulator atoms. Let an electric contact between them be realizable via the nearest four neighbors. Prior to the start of the diffusion the outer boundary of the cluster of atoms A electrically connected with the boundary A coincides with the line separating the atoms A and B. This boundary should be displaced as a unit in the course of the diffusion, and its shape should change by virtue of the stochasticity of the diffusion process. We shall show, in particular, that it becomes essentially rough. We call this boundary the percolation diffusion front. This definition accords with the definition given in Ref. 2 for the diffusion front. In fact, the percolation diffusion front is the interphase boundary. It separates the conducting phase from the nonconducting one. (We shall refer henceforth, for brevity, to conducting and nonconducting phases, although the analysis applies equally well to a number of other problems for which the connectivity of the atoms is important, e.g., in the propagation of magnetic and nonmagnetic phases, etc.). The location and form of the front are determined both by the distribution of the atoms over the lattice sites and by the connectivity radius. In our model, the connectivity radius is equal to unity, since the connection is only via nearest neighbors. It can, however, also be larger. Thus, for the Mott transition the connectivity radius is of the order of the Bohr radius, which amounts to tens of lattice periods in semiconductors.

Clearly, the diffusion-front geometry and the laws governing its displacement should play the primary role in processes such as the diffusion-induced contacts between conductors or the change of the electric properties of semiconductors following the diffusion of the dopant. There are in fact the diffusion-front characteristics studied in the present paper. When the marker moves along the front, certain atoms are passed-through more than once. This means that the diffusion front is a zig-zag line. It is easy also to show that the front is a line without self-crossings.

The form of the front at various instants of time is shown in Fig. 1. The characteristics of the front were investigated by two methods: 1) the front length $L(\lambda)$ was measured with different deviations λ; 2) the points of the front were next numbered in such a way that each was taken into account only once. We then obtained, for different values of d, the average number $N(d)$ of front points inside a circle of diameter d drawn around the front point. Plots of $L(\lambda)$ and $N(d)$ after $2.4\cdot 10^6$ vacancy hops are shown in Fig. 2, from which it is seen that the diffusion front is a fractal curve (i.e., a rough self-similar structure) up to a scale ~ 40. The values of the fractal dimensionality were determined for various instants of time from the relations $L(\lambda)\propto\lambda^{1-D_L}$ and $N(d)\propto d^{D_N}$. Both D_L and D_N have a weak tendency to increase with time against the background of the fluctuations. In the course of the computer experiment, D_L rose from 1.56 ± 0.02 to 1.67 ± 0.02, and D_N from 1.48 ± 0.01 to 1.60 ± 0.01. The inequality $D_L > D_N$ was satistifed at each instant of time, since the dead ends were taken into account in the determination of D_L.

For each analyzed front we determined also the distribution of the front points over layers parallel to the boundaries A and B, the displacement x_F of the average front position, and the mean squared deviation from the central position, σ_F, which characterizes the front width. The distribution of the front points over the layers turned out to be close to Gaussian.

In the course of the diffusion, the front of the atoms A moved in towards the boundary A, and that of atoms B towards the boundary A. We investigated the time evolution of the front characteristics obtained by averaging the characteristics of the fronts A and B. As seen from Fig. 3, the front motion was given initially by $x_F\propto t^{0.51\pm 0.03}$ and later by $x_F\propto t^{1.5\pm 0.1}$. The second regime set in because the diffusion process became such that the limited size of the lattice came into play. The value of the critical exponent in the first regime, corresponding to diffusion in a semi-infinite sample, suggests that the exponent is exactly equal to 0.5. This means that the central line of the front moves like a line of constant concentration c_F.

To continue the analysis, we introduce the diffusion length $l_D = 2(Dt)^{1/2}$. For diffusion by the vacancion mechanism on a square lattice with unity mesh, the diffusion coefficient is $D = fc_v\nu_v/4$, where c_v and ν_v are the concentration and frequency of the vacancy hops, and $f\approx 0.465$ is the corre-

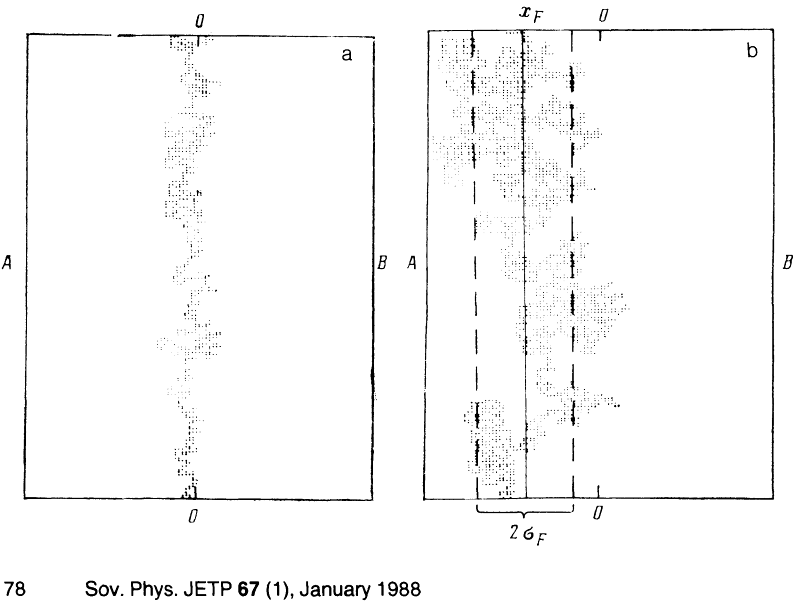

FIG. 1. Form of diffusion front at different instants of time. The number of vacancy hops is 10^7 (a) and $2.4\cdot 10^8$ (b). The points 0 are the end points of the initial boundary between the atoms A and B.

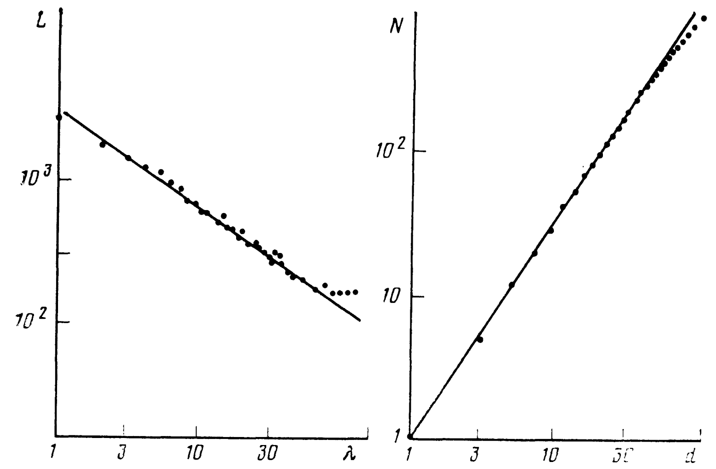

FIG. 2. Scale properties of diffusion front.

lation factor.[3] Hence $l_D = (fn_v/N)^{1/2}$, where n is the number of vacancy hops and N is the number of lattice sites.

Assuming that in the first regime the critical exponent for x_F is exactly 0.5, we get

$$x_F = -(0.18\pm0.02)\,l_D \sim t^{0,5}. \tag{1}$$

The width of the front had a power-law growth:

$$\sigma_F \propto l_D{}^{\alpha_\sigma}, \qquad \alpha_\sigma = 0.58\pm0.05. \tag{2}$$

The number N_F of atoms belonging to the front also increased with time. This growth, however, was against the background of strong fluctuations, so that it was impossible to determine the $N_F(l_D)$ dependence reliably from the computer experiment. It is nevertheless easy to show that this dependence should also follow a power law. Indeed, since the front is a fractal all the way to scales $\sim\sigma_F$, it can be represented as a linear chain consisting of squares $\sim\sigma_F$ on the side, with the front fractal inside each square. The number of such squares is $\sim 1/\sigma_F$ and the number of atoms in each squares is $\sim\sigma_F^{D_N}$. Hence $N_F \sim \sigma_F^{D_N-1} \sim l_D^{\alpha_\sigma(D_N-1)}$.

$$N_F \sim l_D{}^{\alpha_N}, \qquad \alpha_N = \alpha_\sigma(D_N - 1). \tag{3}$$

The values of the fractal dimensionality in our case are somewhat lower than in Ref. 2, where a value $D_N = 1.76 \pm 0.02$ was obtained for a diffusion length $l_D = 12\,800$. This is seemingly due to the fact that our lattice was smaller in size. Indeed, in Ref. 1 the fractal dimensionality for $l_D = 50$ is $D_N = 1.62$. The concentration on the average line of the front, and also the values of the critical exponents for x_F and σ_F, agree with the data of Ref. 2, where it is shown also that $\alpha_\sigma = \nu/(\nu+1) \approx 0.571$ ($\nu = 4/3$ is the critical exponent of percolation theory). The difference between the factors preceding the power is due to the different initial and boundary conditions.

Since, as noted above, the average position of the front at each instant coincides with the line of constant concentration c_F, the question of the value of this concentration arises. From general considerations one can expect it to be close to the critical concentration $c_p \approx 0.593$ of percolation on a square lattice.[4] With the aid of the relation $c_F = 0.5\,\mathrm{erfc}(x_F/l_D)$ we obtain from (1)

$$c_F = 0.60\pm0.01. \tag{4}$$

It can thus be regarded as established that $c_F = c_p$ within the limits of error. This result agrees with that of Ref. 2. Assume that the relation $c_F = c_p$ holds for all types of lattice. This suggests some conclusions regarding the variation of the electric resistance for diffuse homogenization. Since $c_F \approx 0.6$ in our case, and the plane $c = 0.5$ is immobile, the front moves away from the initial position to "its own" lateral boundary. [This circumstance is reflected by the minus sign in Eq. (1).] Therefore in the case of two semi-infinite samples having a square lattice, at unity connectivity radius, no electric contact is produced in the course of diffusion. On the contrary, connectivity is lost in the sample. For a triangular lattice we have $c_p = 0.5$ (Ref. 5). This means that $c_F = 0.5$, i.e., in the case of mutual diffusion of two semi-infinite samples with triangular lattices the line of the front will not move as a unit. A contact should be made, however, as a result of the front's own expansion which is characterized by the function $\sigma_F(t)$.

On a three-dimensional lattice, the diffusion front should move forward and lead ultimately to a contact, since $c_p < 0.5$ for any three-dimensional lattice.[6] In the case when the diffusion of an impurity in a semiconductor leads to a Mott transition, the shape and time behavior of the boundary of a phase having metallic electric conductivity can also be described by the foregoing approach. It is clear here beforehand that the diffuse percolation front will move forward much more rapidly, since the critical percolation concentration for a Mott transition is much less than unity (of order 10^{-4} and lower).

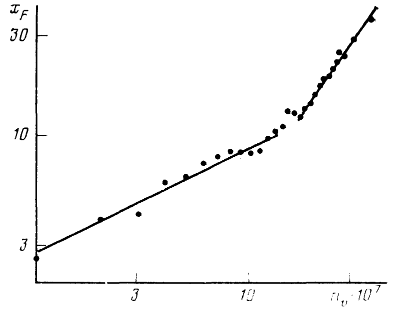

FIG. 3. Displacement of average position upon diffusion.

Analysis of the percolation diffusion front permits thus a new look at the laws governing the variation of the electric properties of a body with diffusion. For large diffusion length, when $x_F \gg \sigma_F$, the contact is produced at an instant when the x_F plane, having a concentration c_p, reaches the opposite boundary. At small dimensions of the diffusion zone, when σ_F is comparable with x_F, it must be taken into account that the front has a width σ_F of its own, so that to make contact it suffices to have the opposite boundary reach the plane $x_F + k\sigma_F$, where k is a certain coefficient of order unity. For a description of the development of the percolation diffusion front it is important that x_F and σ_F have different time dependences. Indeed, in a macroscopic description, the diffusion in an unbounded solid constitutes a self-similar problem, since the diffusion picture is determined completely by the dimensionless variable $x/(Dt)^{1/2}$. When diffusion is described in terms of the diffusion front, it becomes clear that the problem is not self-similar for small diffusion lengths. It becomes self-similar only in the limit of large lengths, when $\sigma_F \ll x_F$, i.e., $l_D \lesssim 10^3$. In such cases the problem is said to be incompletely self-similar.[7] If, however, the front is not displaced during the diffusion ($x_F = 0$, as is the case for a triangular lattice), the contact-making kinetics is determined by the function $\sigma_F(t)$, i.e., in this case the problem is similar but with a different time scale $x(t)$ determined by the critical exponent for $\sigma_F(t)$ and not for $x_F(t)$. Since $x_F(t)$ and $\sigma_F(t)$ fluctuate strongly, one should expect also electric-resistance fluctuations (noise) at the instant of contact making. These fluctuations should be stronger the smaller the sample, and even temporary loss of the already produced contact is possible.

Besides the diffusion front, we investigated also the geometry and the regularities in the development of the summary boundary of all the produced clusters of the atoms A and B. This boundary is defined as the aggregate of bonds of type AB. It is just on this boundary that the mixing energy of the atoms A and B [$\varepsilon = \varepsilon_{AB} - 0.5(\varepsilon_{AA} + \varepsilon_{BB})$, where ε_{AA}, ε_{BB} and ε_{AB} are the binding energies of the corresponding atom pairs] is localized. It is therefore of interest to study the geometry and the time evolution of this boundary.

In our model, the probability of a vacancy hopping in one or another direction does not depend on the surrounding. This corresponds to the limiting case $\varepsilon \ll kT$. Clearly, the front is related to the summary boundary of the clusters just as the continental shore line is related to the shore line that includes also the shores of islands and lakes.[1] The fractal dimensionality of the summary boundary was determined in the same way as for the front, from the $N(d)$ dependence. As expected, it turned out to be higher than the dimensionality of the front. The dimensionality D_b of the summary boundary of the clusters comes close to two. Thus, $D_b = 1.91 \pm 0.01$ after 10^7 vacancy hops and $D_b = 1.97 \pm 0.01$ after $2 \cdot 10^8$ hops. This gives grounds for assuming that in the limit of large diffusion lengths the boundary constitutes a fractal that fills the space. This agrees with results obtained by solving the problem of percolation through a lattice in Refs. 1 and 8, where it was shown that the fractal dimensionality of the boundary of all the clusters is equal to two.

The number of points of the summary boundary increases as a power law: $N_b = (320 \pm 10) l_D^{0.98 \pm 0.02}$. This suggests that the critical exponent for N_b is equal to unity. Then

$$N_b = (1.60 \pm 0.01)\, l l_D \sim t^{0,5}. \tag{5}$$

The total alloy-mixing energy is therefore

$$E = N_b \varepsilon = (1.60 \pm 0.01)\, l l_D \sim t^{0,5}. \tag{6}$$

The relation (5) is evidence that the assumed independence of the population of the lattice site on its surrounding[2] is valid for the vacancion mechanism of diffusion if the inequality $\varepsilon/kT \ll 1$ is valid. Indeed, if this assumption is correct we get, recognizing that $c(x) = 0.5\,\mathrm{erfc}(x/l_D)$, and the number of nearest neighbors is four,

$$N_b = 4l \int_{-\infty}^{\infty} c(x)\,(1 - c(x))\,dx = (8/\pi)^{1/2}\, l l_D \approx 1.60\, l l_D,$$

which corresponds to Eq. (5). We note, however, that for most diffusion pairs the inequality $\varepsilon/kT \ll 1$ is not satisfied, so that the method of Ref. 2 cannot be used for them.

The simulation and the analysis lead to the following conclusions:

1) The geometry and the laws governing the evolution of a percolation diffusion front determine the kinetics of the diffusive growth of the phase for which the presence of connectivity (conductive, superconductive, magnetic, etc.) between definite types of atoms is essential. The diffusion front is the boundary of such phases.

2) The percolation diffusion front is characterized by a fractal geometry, and its evolution is described by a number of critical exponents.

3) In small samples the kinetics of electric contact making is determined not only by the kinetics of the displacement of the front as a whole, but also by the kinetics of the increase of its width.

4) The evolution of the diffusion front is of the fluctuating type, and this should lead in small samples to fluctuations of the corresponding characteristics (e.g., of the electric resistance at the instant of contact making).

5) In the case $\varepsilon \ll kT$ the fractal dimensionality of the summary boundary of the clusters formed in the diffusion zone tends with time to two.

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