Gradient Percolation in Three Dimensions and Relation to Diffusion Fronts

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Percolation in a concentration gradient has been carried out for the cubic lattice. In contradistinction with the two-dimensional case, the frontier of the infinite cluster extends over a macroscopic range of concentrations. In that range almost all occupied sites belong to the frontier which has dimension three. This defines an ideally porous material. The ratio of the local concentrations of the frontier and its external perimeter is equal to the ratio of the local overall concentrations of occupied and empty sites.

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The study of microscopic structures generated by diffusion[1] naturally leads to the problem of lattices with a gradient of concentration of occupied sites. This has been revealed to be a fruitful approach to the percolation problem.[1,2] In previous papers, we reported simulations of the so-called "diffusion front" on 2D lattices. This front is a fractal object with dimension 1.75[1,3] and with an erratic time evolution.[4] In the limit of infinite diffusion times, i.e., zero concentration gradient, the front tends to become identical to the "hull" of the infinite percolation cluster.[1,5] Its mean position x_f tends to the position x_c where the concentration of particles is equal to the exact percolation threshold p_c. The width and the length of the front vary as powers of the concentration gradient at x_c, with exponents related to the critical exponent ν of percolation.[1,6] On the basis of the former result, we proposed a most precise determination of p_c on 2D lattices.[2] These results have permitted us to introduce the new concept of "gradient percolation," which we shall now apply to the 3D case, a situation of more general interest for applications. We show that the results are qualitatively different in 2D and in 3D.[7]

In our 2D simulations, particles were distributed at random on the 2D lattice (for example, a square lattice), with monotonically decreasing concentration from 1 at one side to 0 at the other side. In the simplest case, the concentration $p(x)$ is a linear function of the distance x from the lattice row where the concentration is $p=1$.[2] Whatever connections are considered, there exists a set of particles linked together and to the $p=1$ row. This set is obviously bounded on the low-concentration side of the lattice. This boundary has the same definition as the diffusion front previously mentioned.

We use the following definitions: Occupied (empty) sites are called A sites (B sites). This defines A clusters, consisting of connected A sites (on the square lattice we assumed that two A sites are connected if they are first neighbors). In particular there is one "infinite A cluster," which is the set of particles linked to the $p=1$ side. For the B sites on the square lattice we choose connections to first- and second-nearest neighbors. This corresponds to matching pairs (see Ref. 8 and Fig. 1 in Ref. 2). It is well known that percolation thresholds for matching pairs in 2D obey[8] $p_{cA}+p_{cB}=1$.

Because the concentration $p(x)$ varies monotonically from 0 to 1, there exist both one infinite A and one infinite B cluster. Each infinite cluster has an external boundary, called f_A and f_B, respectively. The sites of f_A are first and second neighbors to the sites of f_B and, reciprocally, the sites of f_B are first neighbors to sites of f_A: f_B (f_A) is the so-called external perimeter of the infinite A (infinite B) cluster.[9] It is an essential property of matching pairs in a concentration gradient that the external boundaries of the two infinite clusters are everywhere in contact with each other. In our extension to the 3D case, we wish to keep this duality. For the cubic lattice, with A connections to first nearest neighbors, one can be convinced that complementary B connections are to first, second, and third nearest neighbors. This choice corresponds to the closest possible contact between the two infinite clusters.

Because the connectivity is higher in 3D, both p_{cA} and p_{cB} decrease, and we have $p_{cA}+p_{cB}<1$. Hence, for all values of p such that $p_{cA}\leq p\leq 1-p_{cB}$ there exist simultaneously one infinite A and one infinite B cluster which interpenetrate each other. This situation is very different from the 2D case.[1] In the 2D system the boundary between the infinite A and the infinite B clusters is located only in a small concentration region of width $\sigma_f \sim |\nabla p|^{-0.57}$ around p_c (see Fig. 1). In contrast in the 3D systems, we can guess that the frontier will extend over the entire part of the sample between $p_1=p_{cA}$ and $p_2=1-p_{cB}$.

It is useful to visualize such systems. In Fig. 2 we show three pictures of a simulated sample, with $19\times19\times19$ sites: The concentration of occupied sites (shown as elementary cubes illuminated from above) is decreasing from bottom to top of the sample; it is equal to 1 in the lowest plane, and equal to 0 in the highest plane. In Fig. 2(a) we only show the six lowest planes; the position where the concentration p of occupied sites is equal to $1-p_{cB}$ is indicated. For $p>1-p_{cB}$ the A sites constitute a very dense block with only a few isolated holes. For $p<1-p_{cB}$ "galleries" appear in the block,

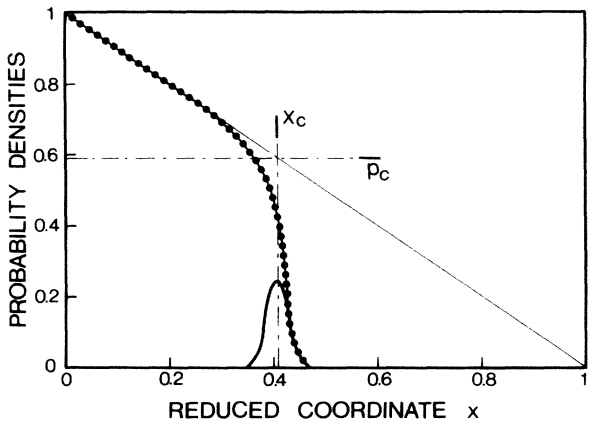

FIG. 1. For a square lattice, variation with the distance x to the $p=1$ line of the probability density p for occupied sites (A sites, thin straight line), probability density $P_{\infty A}$ for the occupied sites connected to the $p=1$ line (A-infinite cluster, dotted line), probability density p_{fA} of the front f_A (thick line). x_c is the position where the probability density of A sites is equal to the percolation threshold p_c in the square lattice.

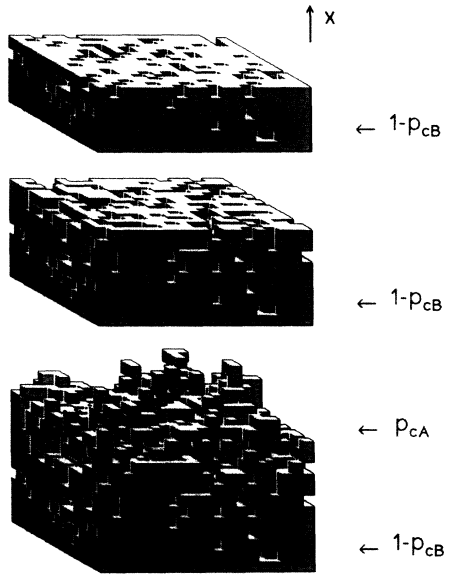

FIG. 2. Picture of a $19\times19\times19$-site system. The probability density of occupied sites shown as elementary cubes is decreasing from 1 at the bottom of the sample to 0 at the top. The only sites connected to the bottom plane are shown. (a) The high-density part of the sample, around $1-p_{cB}$. (b) In the upper plane the concentration of A sites is close to the percolation threshold in the square lattice. (c) The whole block of A sites connected to the bottom plane.

which are connected to the infinite B cluster. In Fig. 2(b) the concentration in the top plane is almost equal to the percolation threshold of the square lattice. One can still observe a continuous path crossing the sample horizontally from one side to the other. In this region the structure of the object becomes more "aerated." In Fig. 2(c) the concentration in the highest plane is 0.2, smaller than p_{cA}: Near p_{cA} the sample should rather be regarded as a system of columns and arches. Small finite A clusters exist, which are not represented for clarity. For concentrations smaller than p_{cA} the system consists essentially of finite A clusters the size of which decreases at the top of the sample.

The results of the simulation in 3D are shown in Fig. 3(a), where we have represented simultaneously the overall A-site concentration $p(x)$ (thin line), the infinite A-cluster concentration $P_{\infty A}(x)$ (dots), and the concentration of A sites belonging to the boundary $p_{fA}(x)$ (thick line). We verify that the boundary extends over a finite concentration region, roughly $p_{cA}\leq p\leq 1-p_{cB}$. Furthermore, one observes that (i) above p_{cA} almost all occupied sites (A sites) belong to the infinite A cluster,[9] and (ii) between $1-p_{cB}$ and p_{cA} the infinite A cluster is almost identical to its boundary, so that in this whole concentration region, practically all A sites belong to the boundary of the infinite A cluster. This constitutes a second basic difference with the 2D case: The density of points belonging to the frontier is very close to the overall density of occupied sites. A similar result is obtained for B sites, as shown in Fig. 3(b).

There is a simple explanation for the fact that between p_{cA} and $1-p_{cB}$, almost all sites belong either to f_A or to f_B. This may be deduced from duality considerations. Between p_{cA} and $1-p_{cB}$, far from both percolation thresholds, most sites that do not belong to any of the frontier are of two kinds: They belong to the bulk of one of the infinite clusters, or they are isolated, i.e., surrounded by sites of the other kind. This reduces to sites embedded in the infinite A cluster, hence surrounded by 26 occupied sites (probability p^{26}); and sites embedded in the infinite B cluster, i.e., surrounded by 6 empty sites [probability $(1-p)^6$]. The total probability for these sites, $p^{26}+(1-p)^6$, is very small between p_{cA} and $1-p_{cB}$. It reaches a minimum at a concentration $p_{\rm inf}$ such that $6(1-p_{\rm inf})^5-26p_{\rm inf}^{25}=0$. One finds $p_{\rm inf}\cong0.727$ and $p_{\rm inf}^{26}+(1-p_{\rm inf})^6\cong6.65\times10^{-4}$

Coming back to the usual percolation problem, one has

$$p=P_\infty(p)+\textstyle\sum_s c_s(p), \tag{1}$$

where p is the probability density of occupied sites, $P_\infty(p)$ is the probability for a site to belong to the infinite cluster, and $c_s(p)$ are the probabilities for a site to belong to a cluster of size s. This should also hold in the case of a concentration gradient and one can write the same relation for the A sites:

$$p(x)=P_{\infty A}(p(x))+\textstyle\sum_s c_{sA}(p(x)). \tag{2a}$$

Now, considering the percolation of B sites (i.e., with

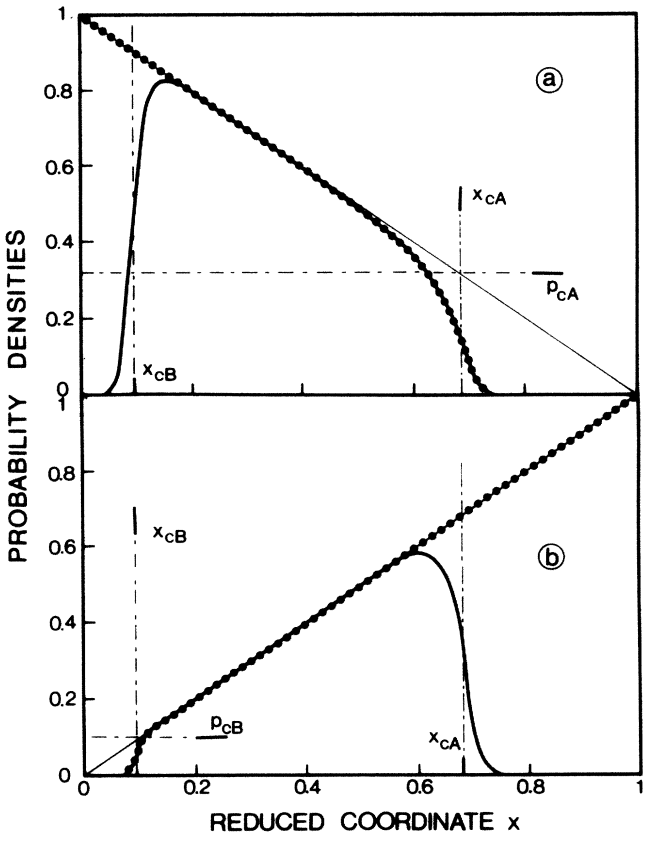

FIG. 3. (A) Same as Fig. 1 but for the cubic lattice. x_{cA} is the position where the probability density of A sites is equal to the percolation threshold p_{cA} in the cubic lattice (first neighbors). x_{cB} is the position where the probability density of B sites is equal to the percolation threshold p_{cB} in the cubic lattice (first, second, and third neighbors). (b) Same as (a), but for empty sites (B sites, thin straight line), empty sites connected to the $p=0$ plane (infinite B cluster, dotted line), front f_B (thick line).

connections to first, second, and third neighbors), one also has

$$1-p(x)=P_{\infty B}(1-p(x))+\sum_s c_{sB}(1-p(x)). \quad (2b)$$

The universal behavior of $P_\infty(p)$ near p_c is a well-known result for usual percolation[9] ($\nabla p=0$) where one has

$$P_{\infty A}(p)\sim(p-p_{cA})^\beta, \quad (3a)$$

$$P_{\infty B}(1-p)\sim[(1-p)-p_{cB}]^\beta, \quad (3b)$$

and where the critical exponent β is about 0.4 in 3D.

One observes in Fig. 3 that $P_{\infty A}(p(x))\approx p_{fA}(p(x))$ and $p_{\infty B}(1-p(x))\approx p_{fB}(1-p(x))$ for $p_{cA}\leq p(x)\leq 1-p_{cB}$. Equations (3a) and (3b) should then hold for $p_{fA}(x)$ and $p_{fB}(x)$, in the critical region, if the gradient is small enough, so that f_A is near p_{cA} and f_B near

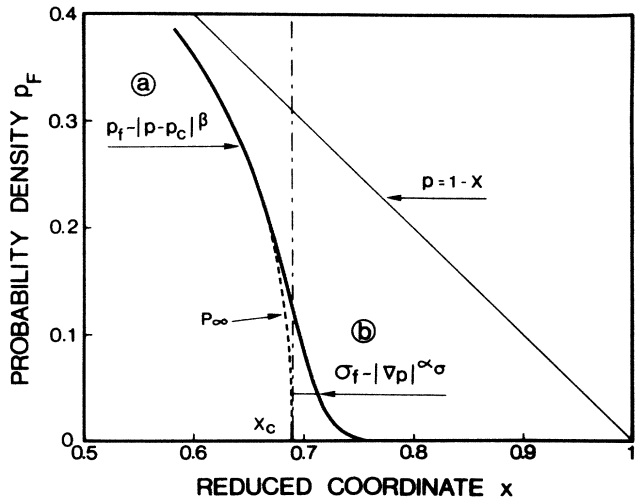

FIG. 4. Probability density $p_{fA}(x)$ of the front f_A near x_{cA}. The probability density p of A sites is shown for comparison (thin straight line). Dashed line: The probability density $p_\infty(x)$ of the infinite cluster deduced from the usual percolation problem.

p_{cB}:

$$p_{fA}\sim(p-p_{cA})^\beta, \quad (4a)$$

$$p_{fB}\sim[(1-p)-p_{cB}]^\beta. \quad (4b)$$

Of course there is a finite gradient effect. The critical behavior (4a) is schematically illustrated in Fig. 4, where we have represented the variation of $p_{fA}(x)$ (thick line), and its expected limit for $\nabla p\to 0$ (dashed line), which varies with x as $(x-x_{pc})^\beta$ (region a of Fig. 4). For finite gradients, one also observes a broadening

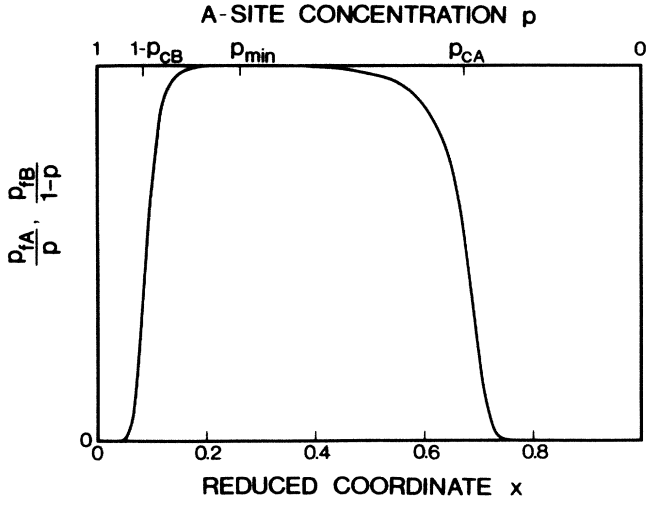

FIG. 5. Normalized probability densities of the fronts f_A and f_B: $p_{fA}(x)/p(x)$ and $p_{fB}(x)/[1-p(x)]$ are found identical and appear as a single curve.

of p_f near p_c with a width $\sigma_f \sim |\nabla p|^{-a_\sigma}$ (region b of Fig. 4), where $a_\sigma = \nu/(1+\nu)$.[1]

A more striking result is that the reduced distributions for the A- and B-infinite cluster boundaries are *identical* within statistical errors: In other words $p_{fA}(x)/p(x)$ and $p_{fB}(x)/[1-p(x)]$ reduce to a single curve, shown in Fig. 5, with a $(p-p_c)^\beta$ behavior both near p_{cA} and near p_{cB}. This leads to

$$p_{fA}(x)/p_{fB}(x) = p(x)/[1-p(x)] \quad \forall x, \tag{5}$$

which is very similar to the corresponding result in 2D observed[10] near p_c:

$$p_h(x)/p_{sh}(x) = p(x)/[1-p(x)], \tag{6}$$

where $p_h(x)$ is the probability density of the "hull" of the infinite cluster, and $p_{sh}(x)$ the probability of surrounding empty sites (the external perimeter). However, in the 3D case, relation (5) is observed in the whole concentration range where f_A and f_B coexist.

Following the 2D results, one may wonder whether it is possible to find a precise determination of p_c. As a result of the existence of two percolation thresholds, the concentration at the mean position x_f is neither close to p_{cA} nor close to $1-p_{cB}$, and the method that we have proposed for the 2D case[2,6] is not applicable here. However, a determination of p_c can be proposed[7] on the basis of the following arguments. When the gradient $\nabla p \to 0$, one can assume that the variation of the probability density p_{fA} as a function of x tends to that deduced from $P_\infty(p)$ in the usual percolation problem (see Fig. 4). This suggests the following determination of p_c: The derivative dp_f/dx presents two extrema which must asymptotically tends towards p_{cA} and $1-p_{cB}$. With $\nabla p = \frac{1}{256}$ and averaging on 100 samples of $64\times64\times256$, we obtain a first promising estimation: $p_{cB} \cong 0.091$ and $p_{cA} \simeq 0.31$. The present accepted values are respectively $p_{cB} = 0.097$[8] and $p_{cA} = 0.3117$.[9]

The study of percolation in a concentration gradient in 3D systems has brought new results, qualitatively different from those obtained in 2D. The boundary between the infinite clusters consisting of occupied and empty sites extends over a wide and finite concentration range. Over that range, almost all occupied sites belong to the frontier of the infinite A cluster and almost all empty sites belong to the frontier of the infinite B cluster. The ratio of probability densities of the frontiers of the infinite A and B clusters remains, for *any* concentration $p(x)$, equal to the ratio $p(x)/[1-p(x)]$ of concentrations of A and B sites. Such conclusions should also be valid in the case of diffusion fronts in 3D.[1] Hence, except in the vicinity of percolation thresholds,[9] the frontier is a dense object of dimension three: From this point of view it behaves like an ordinary solid. However, any point of that solid can be reached from the outside, i.e., belongs to the surface. In that sense, this system is an ideally porous material.

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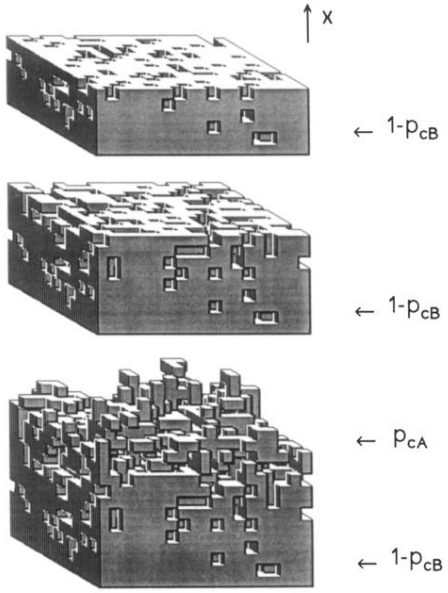

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