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Random walks on ordered mixed binary lattices

Panos Argyrakis
Department of Physics, University of Crete, Iraklion, Crete, Greece
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We present results of random-walk simulations in *ordered* mixed binary two-dimensional lattices. We calculate the number of sites visited in an n-step walk and compare this to our previous work on *random* lattices. We also examine the effect of the mean free path of the random walker. We find a considerable difference, as walks in the ordered cases produce a greater efficiency than in the random ones. We rationalize this behavior with the use of the number of reflections on closed sites, which we also find to differ in these two cases. Suggestions for experimental situations are made.

In a recent paper[1] we presented results on properties of random walks in simple and binary lattices by use of simulation techniques. The interest in binary lattices stems from the fact that the sites occupied by the second component are not accessible to the random walker (closed sites) as opposed to the first component (open sites). We had calculated there the number of distinct sites visited, S_n, after a certain number of steps n and expressed our results as ϵ, the efficiency, defined as $\epsilon = S_n/n$. It was shown[1] that ϵ decreases as the concentration C of open sites decreases. This decrease was also strongly dependent on the correlation of each random walk. In that work the composition of all lattices was determined in a random fashion according to the prescribed concentration, i.e., in the binary system the two components were mixed at random before the start of the walk and occupied the same pattern throughout the walk. We wish to report now our results where in the lattices constructed all closed sites are positioned in a periodic way or, in other words, they are symmetrically or orderly arranged. This has an effect of providing some symmetry to the lattice, and the question that arises now is if this imposed order on the two components is going to affect the properties of random walks when compared to the random distribution lattices.[2] Up to date there exists no theoretical formalism to treat any random-walk properties in general complex binary systems, especially for two- and three-dimensional lattices (with the exception of low concentration of the second component[3]), and, of course, no theory accounts for the randomness versus order in lattices. Thus, to gain some insight into the nature of this problem, we again resort to Monte Carlo simulation methods. We first discuss the method of calculations and then we present our results and comparisons between the two different cases.

A binary lattice made of two types of sites (open and closed) is simulated and kept in the computer memory. We vary the ratio of open to closed sites over a wide range (see below). While for random lattices the identity of each site was determined by use of random number generating routines, the case is different here. All closed sites are arranged periodically for several different concentrations. Since for a given concentration there may be more than one way that such lattices could be constructed, the criteria used are the following: For each case (1) the highest-symmetry construction was used; (2) among cases with the same symmetry we used the one with the smallest unit cell. Some examples may clarify this point: For a concentration C of open sites $C = 0.75$, the closed sites are arranged so that each one is exactly two lattice constants away from any nearest-neighbor closed site (so that lines of closed sites are parallel). All other sites are open sites. This has a unit cell of four sites, in which one of the four is a closed site and the other three are all open sites. A structure of $C = 0.75$ with staggered lines of closed sites, and the same symmetry, has a unit cell of 16 sites and is not used. Similarly, structures with $C = 0.8889$, 0.9375, and 0.9600 have closed sites exactly three, four, and five lattice constants away from nearest-neighbor closed sites, respectively, and unit cells of 9, 16, and 25 sites, respectively.

Other lattice concentrations were constructed with the use of the $C = 0.75$ as a basis, and then adding or subtracting closed sites in symmetrical patterns. For $C = 0.7778$ and 0.8125, every third and every second nearest-neighbor closed site was removed, respectively (producing unit cells of 36 and 16 sites, respectively). For $C = 0.7222$ and 0.6875, closed sites were added in the "empty lines" of the $C = 0.75$ pattern every six and every four sites, respectively (producing unit cells of 36 and 16 sites, respectively).

The size of all lattices is slightly above 10^6 sites. This number is chosen so that during the actual run of a random walk the boundaries would not be reached, which might otherwise result in revisitation effects. Of course, this would depend on the magnitude of n, the number of steps taken in each run.

We find that for most runs of n up to 200 000 steps the boundaries are not reached. A general "rule of thumb" for avoiding revisitation effects is found to be that the size of the lattice should be five times the value of n [$5(200\,000) = 10^6$].

All random walks take place in the standard way by use of random number generating routines, as we have described elsewhere.[1] We also utilize a second mechanism and check our results. The mechanism that was previously[1] used implied that, before each step takes place, the probability interval was divided equally among all directions, regardless of how many of these are possible due to the existence of adjacent closed sites. Then, if it happened from the random number generator that one step led to a closed site, and therefore a reflection, this step was simply not performed, it was disregarded, and a new attempt was made until an allowed step took place. A second mechanism is the following: Before each step takes place, all directions leading to closed sites are identified, and then the probability interval is divided only by the number of available directions, thus making it impossible to result in a reflection. The two mechanisms are found here to be equivalent since they give the same (within statistical fluctuations) ϵ values.

For simple random walks we assume that all memory is lost after each jump between two adjacent sites, and here the mean free path l of this walk is $l = 1$. But if memory is to be retained over l sites then the random walker is allowed to make l jumps in a row in the same direction, which is similar but not equal to making a jump length $l = k$, where k is an integer. If a closed site is encountered before the execution of l such jumps, the random walker is reflected back to its previous position and memory is automatically lost. Usually l is an average of a distribution rather than a constant. We used Gaussian distributions, where we define their average and spread.

We compute S_n, the number of sites visited in an n-step walk. We repeat the runs several times for each concentration with different initial random number seeds and average the results. In these simulations we find that, in order to attain a constant standard deviation, we usually need to average about 10–20 runs. Because of the natural scattering in these results, if more runs are included, the standard deviation does not decrease, while the average stays almost constant. We therefore used 20 runs each time.

Random walks in simple one-component lattices have been treated in the past by use of an analytical generating function technique,[3] or numerical series and matrix inversions, and simulations.[4,5] Walks with variable step length have also been treated.[4] We thus have adequate information for such properties, such as the number of sites visited in an n-step walk, the number of steps for trapping, the mean return to the origin, the end-to-end distance, etc. In this paper we concentrate on S_n, the number of sites visited in an n-step walk. It is known that, for a two-dimensional square lattice,[3]

$$S_n = \frac{\pi n}{\ln n} \quad . \tag{1}$$

But the validity of this formula was known to be good only for large values of n. Recently, this formula was modified with use of numerical[4] and analytical[6] formalisms to give

$$S_n = \frac{\pi n}{\ln(c_2 n)} + c_3 \quad , \tag{2}$$

where c_2 is of the order of 5 and is the only important term, the contribution of c_3 to S_n being less than one (1). Equation (2) is valid for any values of n.

Our simulation results verify to excellent agreement the correction terms in Eq. (2), as has been pointed out,[5] up to values of $n = 200\,000$ steps.

We proceed now to report our results for two-component ordered lattices. Figure 1 shows the results for ϵ ($\epsilon = S_n/n$) for an early stage in the walk (2000 steps), and much later (200 000 steps), as a function of concentration C, for the case of simple walks ($l = 1$). Also shown is the behavior of ϵ on random lattices (from Ref. 1). We also report here the statistical spread of ϵ for many individual runs, as it is expressed in the calculated "error bars" given by the standard deviation of the results (see Fig. 1 for details). We see that for small number of steps n the spread is quite large [Fig. 1(a)] while for large n it is much smaller [Fig. 1(b)]. Apparently, the reason for this is that the large n makes it adequate for an internal averaging to take place, while this is not so for small n. The main conclusion, however, is that for high C values, say, $C \geq 0.90$, there is no actual difference between the ordered and random lattices, while in the range of $0.60 < C < 0.90$ the ordered lattice produces a considerably higher ϵ than the disordered one. This result is quite startling and contrary to the intuitive expectation that *on the average* ordered and disordered lattices should produce the same ϵ, since for a given concentration the number of closed sites on the lattice is the same in both cases, regardless of their arrangement, and should thus provide the same hindrance to the random walker. However, this does not happen because it turns out from topological arguments that the number of reflections on closed sites is not the same in both cases (see below).

In Fig. 2 we show results for ϵ for the case of $l = 10$ and plot the same parameters as previously. We observe the same qualitative trends as before, but here they are more pronounced.

The parameter that most probably affects this behavior is the number of reflections R on closed sites. It is certainly true that R depends on the concentration of closed sites. For random lattices the relative ratio of reflections R over the number of attempts

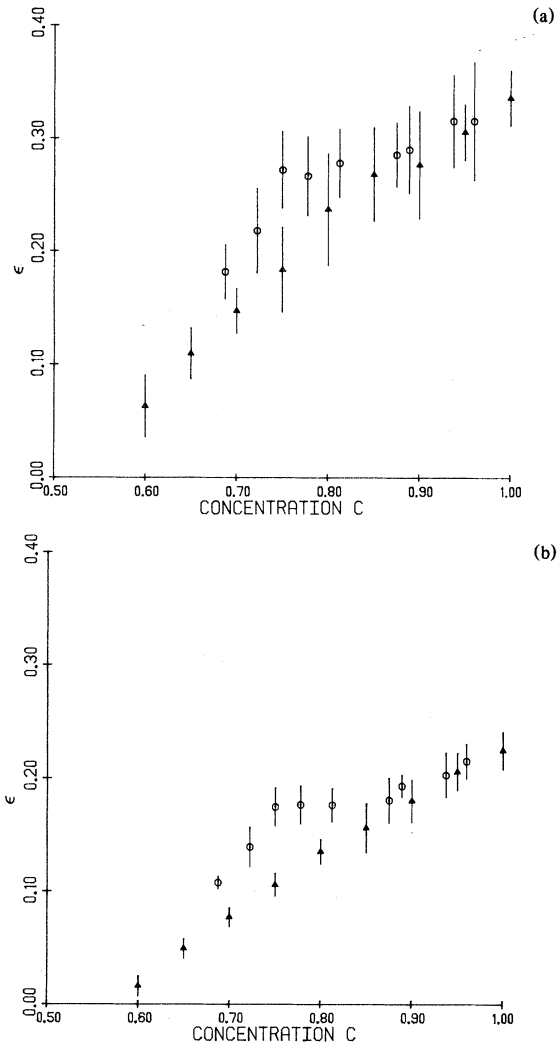

FIG. 1. Plot of the efficiency ϵ vs the concentration C of open sites for ordered (circles) and random (triangles) lattices. The points are averages of 20 runs on lattices of size 1020×1020. The mean free path $l = 1$ and a square lattice topology is employed, allowing jumps on the four nearest neighbors only. The error bars on each point are calculated so that the total length of the bar is 2σ, where σ is the standard deviation of the statistical distribution. Part (a) shows ϵ for $n = 2000$, while part (b) shows ϵ for $n = 200\,000$ steps.

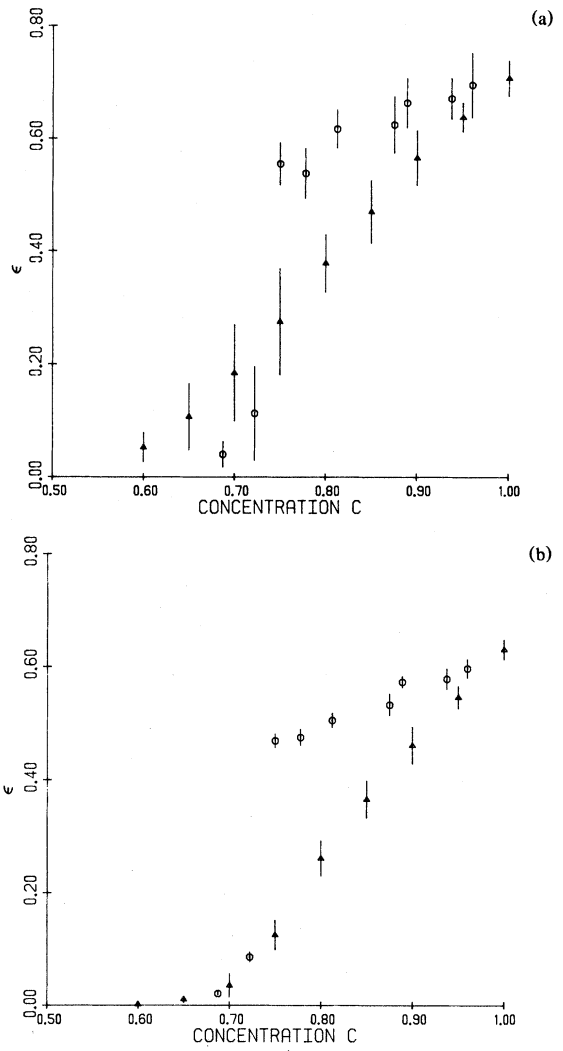

FIG. 2. Plot of the efficiency ϵ vs the concentration C of open sites, similar to the previous plot, but here the mean free path is $l = 10$ (average of a Gaussian distribution with standard deviation $\sigma = 3.0$). Part (a) shows ϵ for $n = 2000$, while part (b) shows ϵ for $n = 200\,000$ steps.

(which is $n + R$) should be equal to the probability P_r of finding a closed site at any instance during the random-walk process, which is equal to $1 - C$. Therefore

$$P_r = \frac{R}{n+R} = 1 - C \quad . \tag{3}$$

Rearranging Eq. (3) we obtain

$$R = \frac{n(1-C)}{C} \quad . \tag{4}$$

Turning now to the ordered lattice we can derive the analogous probability P_0 as follows: Since on the ordered lattice each site has a definite pattern of neighbors, it is easy to estimate, for each concentration C, the probability for scattering. We do this by forming the fraction of jumps that lead to a reflection out of all jumps, and we take into account each individual site on the lattice. As an example, see Table I, where we include four different concentrations: 0.75, 0.8889, 0.9375, and 0.96. The total number of sites in each unit cell in these lattices is 4, 9, 16, and 25, respectively. Thus we have one closed site in each case, and 3, 8, 15, and 24 open sites, respectively. The scattering probability P_0 is given then by the inverse of these numbers, i.e., 0.3333, 0.1250,

TABLE I. Scattering probabilities for random (P_r) and ordered (P_0) lattices.

C	Sites in unit cell	Number of open sites	P_0	P_r
0.7500	4	3	0.3333	0.2500
0.8889	9	8	0.1250	0.1111
0.9375	16	15	0.0667	0.0625
0.9600	25	24	0.0417	0.0400

0.0667, and 0.0417. The respective P_r values as derived from Eq. (3) are 0.25, 0.1111, 0.0625, and 0.04. We can see therefore that, due to the different topology, there is a considerable difference in the number of reflections in the two cases, thus leading to a different ϵ.

In Fig. 3 we plot the scattering fractions P_0 and P_r versus the concentration of open sites. The straight line and curve are simply $P_r = 1 - C$, and P_0 the results from Table I, while the circles and triangles are results of simulations, where we calculated R, P_r, and P_0 directly. It can be seen that the simulation results agree very well with topological arguments for the number of reflections throughout the concentration range.

The question that arises now is to what extent the observed behavior in ϵ depends on the difference in the scattering probabilities. We hypothesize that the larger scattering in ordered lattices forces the random walker to visit more sites, reducing somewhat the revisitation that takes place to a larger extent in random lattices. This, in turn, increases ϵ. This explanation is consistent with the limiting behavior in Figs. 1 and 2 where, close to $C = 1.0$, there is a very small difference in ϵ because (see Table I) there is a very small difference between P_0 and P_r. But around $C = 0.75$ (highest-symmetry, smallest unit cell) we have the greatest difference in ϵ (65%), again because P_0 and P_r differ by about 33%. At $C < 0.70$, these differences are minimized because we get closer to the critical percolation concentration P_c, where ϵ is severely limited and drops close to 0 below P_c.

The problem we studied may be of use for physical or chemical systems of mixed crystals where the second component, due to a generated repulsive potential around each molecule, may be forced to a configuration of minimum potential given by such symmetrical patterns as discussed above. From phonon and vibrational Raman spectra it is believed[7] that this is not the case with isotopic mixed crystals where a totally random pattern is achieved, providing a model system for electronic energy transport studies. A new system has recently been reported[8] where, upon mixing, a highly ordered crystalline complex is formed (naphthalene in perfluorobiphenyl). This complex is in a 1:1 ratio. We hope that this work will generate an interest in divising more new experimental ordered systems.

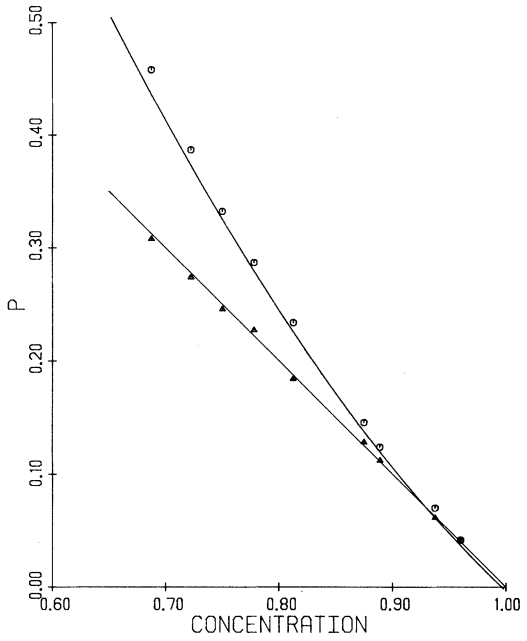

FIG. 3. Plot of the scattering probabilities P_0 (circles) and P_r (triangles) vs the concentration C. The solid lines are calculated (see text), while the circles and triangles are simulation results. Both the calculated P's and the ones derived via simulations are independent of n, and they are constant throughout the random walk. The simulation results here are after 2000 steps. (Incidentally, the P_0 line shape can be fitted to an equation of the form $y = a + bx + cx^2$, and it is found here that $a = 2.42$, $b = -3.90$, and $c = 1.48$.)

Discussions with Professor Raoul Kopelman have been particularly useful.

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