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# Random walks on finite lattices with traps

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We consider dissipative processes involving both chemical reaction and physical diffusion in systems for which the influence of boundaries and system size on the dynamics *cannot* be neglected. We report the results of Monte Carlo simulations on an irreversible reaction in a confined system subject to two sorts of finite boundary conditions. The problem is posed in such a way as to take maximal advantage of two earlier studies: Montroll's work on random walks on $d$-dimensional periodic lattices with traps, and the work of Sanders, Ruijgrok, and ten Bosch on random walks on two-dimensional finite lattices with traps. Our results are used to discuss the concept of reduction of dimensionality as introduced by Adam and Delbrück in their study of biological diffusion processes.

## I. INTRODUCTION

At the recent Solvay Conference[1] on "Order and Fluctuations in Equilibrium and Nonequilibrium Statistical Mechanics," a problem which received much attention was the role of boundaries and the effect of system size $\Omega$ in influencing the dynamics of chemically reacting systems in the far-from-equilibrium regime. This and other problems in the general theory of dissipative processes have been studied extensively in recent years[2-5] using a variety of theoretical approaches; e.g., master equations for discrete stochastic variables, Fokker-Planck equations for continuous stochastic variables, or reaction-diffusion equations. The formal relationships among these three approaches have been investigated in some detail. It has been shown that in the limit of large system size ($\Omega \to \infty$), provided one is well away from phase transitions and critical points, a mapping from one representation to another can be carried through and that results obtained in different formulations of the same physical problem are in correspondence.[6] Some progress has also been made in determining the extent to which this correspondence persists in the description of chemically reacting systems in the neighborhood of first- and second-order transition points. For example, Horsthemke and co-workers[7] have obtained a nonlinear Fokker-Planck equation, derived as an asymptotic representation of a stochastic master equation for large system size, and have shown that results obtained for the Schlögl model[8] using this Fokker-Planck equation are in accord with the exact solution of the master equation for this model, the latter result obtained recently by Nicolis and Turner.[9] Moreover, the Fokker-Planck results are found to constitute an excellent approximation to the exact results even in the neighborhood of first-order transition points. A conceptual question that remains, however, is whether it is possible to pass from a master equation to a Fokker-Planck equation (or reaction-diffusion equation) in the situation where it is not possible on physical grounds to construct the asymptotic limit $\Omega \to \infty$. In particular, it is not known whether a satisfactory correspondence can be realized in the description of far-from-equilibrium chemical dynamic processes involving molecules confined to a reaction volume whose size is *not* orders of magnitude larger than the size of the reacting molecules. Such a question is of more than just theoretical interest: The considerable emphasis today on studying the kinetics of processes in organized molecular assemblies (micelles, bilayers, and monolayers) has stimulated the search for a theoretical framework within which the influence of boundaries on the chemical dynamics can be properly assessed. Moreover, with respect to a problem treated initially by Montroll,[10] the motion of excitons and their trapping in photosynthetic units (modeled as networks or lattices of chlorophyll molecules interspersed with traps), the present study is not without interest. This is because Montroll's analysis was carried out using periodic boundary conditions and it would be instructive to compare his estimates for trapping with those obtained in a study in which it is assumed that the photosynthetic units are isolated and of finite extent.

To address the problem posed in the preceding paragraph we have initiated a study in which the dynamics of elementary and (eventually) coupled chemical reactions are studied via numerical simulation. We consider both reactants and products to be confined to a reaction volume (a lattice) subject to finite boundary conditions, and then study via the Monte Carlo method the influence of spatial extent and dimension on the evolution of the system. The problem is constructed in such a way as

to take maximal advantage of Montroll's results[10] on random walks on periodic lattices with traps. In particular, we consider here the dynamics of a single, irreversible reaction: $A+B\rightarrow C$, where $A$ is the migrating species (a single molecule undergoing random displacements on a given lattice) and $B$ is the fixed trap (a single molecule positioned near the center of the given lattice). The coordinates of the trap for each of the lattices studied here are specified in a later figure. We compute the average number $\langle n\rangle$ of steps required for trapping (walk length) subject to the constraint that upon reaching the boundary the diffusing species $A$ experiences either (i) periodic boundary conditions (the Montroll case) or (ii) finite boundary conditions. The latter conditions were chosen to be of two types and will be described in the following section. Questions of convergence of our Monte Carlo calculations are also dealt with in Sec. II and the results obtained in our simulations are reported. In Sec. III, we correlate these results with those obtained in earlier, analytic studies on the problem of random walks on finite two-dimensional lattices with traps. Finally, on the basis of these comparisons, we offer in Sec. IV some overall conclusions and discuss the relevance of our results to the physical problems mentioned earlier.

## II. NUMERICAL SIMULATIONS

Here we describe the numerical method employed in our study, present relevant data on convergence of our Monte Carlo scheme, and then display the results obtained. Since what distinguishes this work from earlier studies on the problem of random walks on lattices with traps is the emphasis on the role of boundaries, and in particular, the interplay between dimensionality and spatial extent in walks on finite lattices, we describe first the sorts of boundary conditions employed.

The first type of finite boundary condition, which shall be referred to as the *confining* boundary condition, is implemented by imposing the restriction that if the walker attempts to step onto the boundary, he must return to the lattice site from which he started. The second type of finite boundary condition, referred to as the *reflecting* boundary condition (following Chandrasekhar[11]), is implemented by the restriction that if the walker attempts to step onto the boundary he is displaced to one (interior) lattice point further removed from the boundary than the lattice site from which he started. For a simple, graphical realization of these two possibilities for the case $d=2$, see Fig. 1.

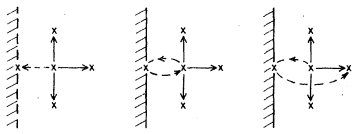
| DIMENSION | LATTICE | <n> PERIODIC BOUNDARIES | <n> CONFINING BOUNDARIES | <n> REFLECTING BOUNDARIES |
|---|---|---|---|---|
| | |  | | |
| 1 | 1 x 8 | 12.0 | 12.6 | 10.3 |
| | 1 x 64 | 694 | 696 | 679 |
| 2 | 8 x 8 | 98.50 | 100.8 | 75.33 |
| | 12 x 12 | 258.0 | 259.9 | 214.9 |
| 3 | 8 x 8 x 8 | 691.4 | 697.1 | 464.4 |

FIG. 1. Monte Carlo determination of the average number $\langle n\rangle$ of steps before trapping on a simple (chain, square, cubic) lattice of $d$ dimensions with $N$ sites and one trap, where periodic or confining or reflecting boundary conditions have been imposed. In the figure we illustrate these three types of boundary conditions for the case of two dimensions; the dashed line denotes the trajectory of the walker as it encounters the boundary, while the solid lines represent alternate paths accessible to the walker.

The number $n$ of steps needed for trapping is averaged over a large number (up to ~10 000 of individual walks), each starting at a particular nontrapping site; in these simulations it is assumed that all nontrapping sites are equally weighted (this restriction will be removed in subsequent work). To gauge the reliability of our calculations, three convergence criteria were imposed: (i) convergence of the average walk length $\langle n\rangle$ from a given nontrapping site; (ii) convergence of the associated standard deviation $\sigma_n$; and (iii) convergence of the symmetry of the resulting lattice with respect to walks from individual lattice sites to the trap. Qualitatively, it was found that the average walk length $\langle n\rangle$ for all sites converged fairly rapidly, while the standard deviation $\sigma_n$ of the average walk length per walk converged somewhat more slowly.

As a quantitative illustration of the convergence properties of these simulations, we note that the average walk length $\langle n\rangle$ on an $8\times 8$ lattice subject to confining boundary conditions converges to within 0.1 steps after 3555 walks have been made from each site; on the other hand, approximately 4300 walks are required for convergence of the standard deviation to within 0.1 steps. A histogram for this case is presented in Fig. 2.

Considering next the convergence properties for walks on lattices with periodic boundary con-

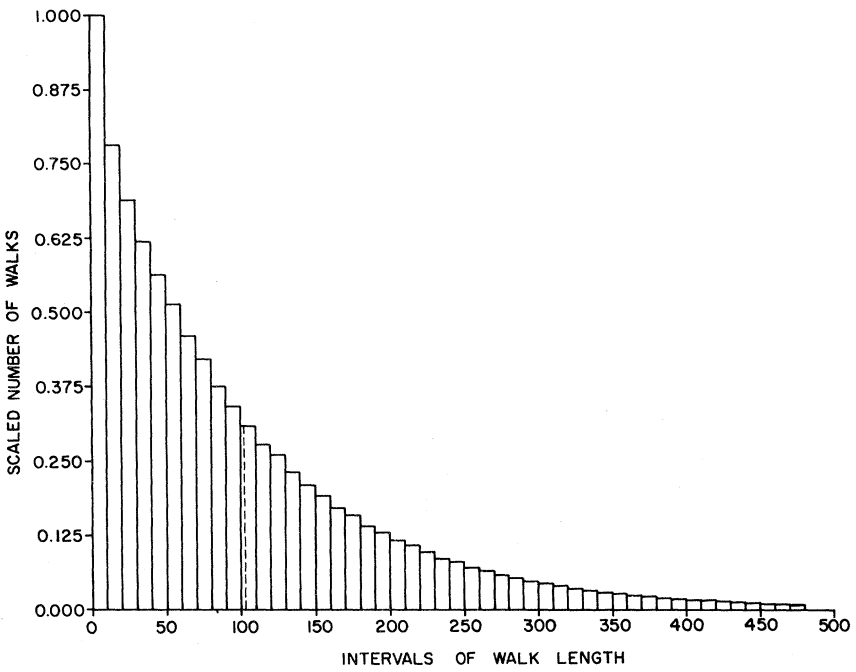



FIG. 2. Histogram for walks on an 8×8 lattice subject to confining boundary conditions.

ditions, one can estimate theoretically the magnitude of the standard deviation by extending Montroll's first moment procedure (for obtaining the average walk length) to the evaluation of the second moments, and from these, to construct estimates of the variance and standard deviation (see Appendix). For dimensions $d \geq 2$, it is found that the standard deviation of the walk length is of the same order of magnitude as the average walk length and this feature is also found in the numerical simulations (see Table I and Fig. 3). Note that since the lattices considered in our Monte Carlo studies are taken to be *even* (e.g., $4\times4\times4$, $8\times8$, etc.), the consequence is that the trap, located at an interior point of the lattice, is thereby asymmetrically positioned with respect to the boundaries. The reasons for this choice of lattice were twofold: first, the even lattice provides the most stringent test of Montroll's original theory and second, with respect to problems involving micellar assemblies, the experimental evidence suggests that the guest molecule is not usually lo-

TABLE I. Determination of the average number $\langle n \rangle$ of steps before trapping on a simple (chain, square, cubic) lattice with $N$ sites and one trap, where *periodic* boundary conditions have been imposed: a comparison of results derived using Montroll's theory with those obtained via Monte Carlo simulation.

| Dimension | Unit cell | Montroll $\langle n \rangle$ | Montroll $O(\cdots)$ [a] | Monte Carlo $\langle n \rangle$ | Monte Carlo $\sigma_n$ [b] |
|---|---|---|---|---|---|
| 1 | $1\times8$ | 12.0 | 0 | 12.0 | 16.9 |
| | $1\times64$ | 693.33 | 0 | 694 | 808 |
| 2 | $8\times8$ | 98.62 | $2\times10^{-4}$ | 98.50 | 99.47 |
| | $12\times12$ | 257.54 | $5\times10^{-5}$ | 258.0 | 260.8 |
| 3 | $8\times8\times8$ | 776.4 [c] | 22.6 | 691.4 | 691.9 |
| | | 691.33 [d] | | | |

[a] Montroll's result in one dimension is exact; in two dimensions the error is $O(N^{-2})$, while in three dimensions it is $O(N^{1/2})$.

[b] The error estimate for the Monte Carlo simulation is reported in terms of the standard deviation $\sigma_n$.

[c] Montroll's original estimate.

[d] Result obtained by refining Montroll's original estimate (see text).

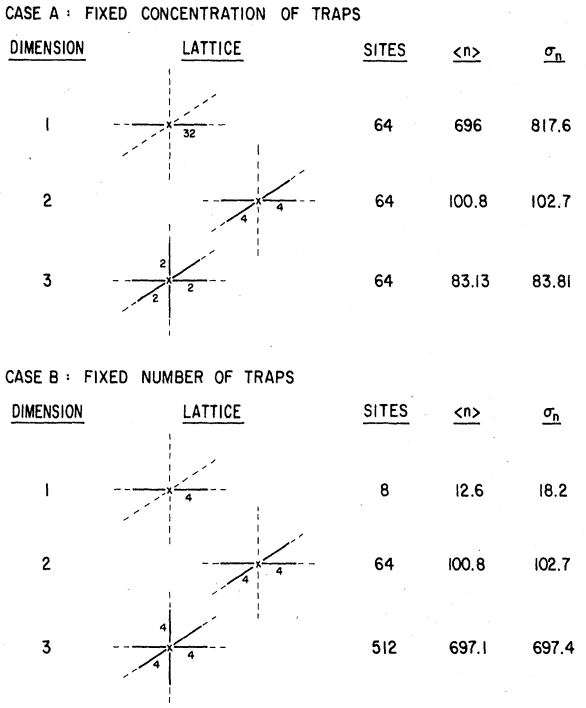



FIG. 3. *Effect of reduction of dimensionality* on the determination of the average number $\langle n \rangle$ of steps before trapping on a simple (chain, square, cubic) lattice of $d$ dimensions with $N$ sites and one trap, where confining boundary conditions have been imposed. For even lattices, the trap is asymmetrically positioned with respect to the boundaries; in each case, the fixed trap is located at the intersection of the coordinate axes (only axes in the positive quadrant of each coordinate system have been labeled). Case $A$ is not drawn to scale.

cated at the exact geometric center of the micelle.[12] Even for such "asymmetric" lattices, however, since one anticipates that the walk length from sites symmetrically positioned with respect to the trap should be approximately equal, we also required for asymmetric lattices that the average walk length to the trap from such symmetrically disposed sites should be the same to within ±1 step (see Table II). If this was not achieved after 10 000 walks/site, the simulation was terminated. In none of the cases reported later was the symmetry worse than ±5 steps.

In Table I we present data on the average number $\langle n \rangle$ of steps needed for trapping on a simple (chain, square, cubic) lattice with $N$ sites and one trap, where *periodic* boundary conditions have been imposed. The Monte Carlo results can be compared directly with results derived using Montroll's theory. We remark that Montroll's estimate for $\langle n \rangle$ for walks on three-dimensional lattices can be improved by summing over the structure function (specific for a periodic lattice with

TABLE II. Average number $\langle n \rangle$ of steps required for trapping from each site (nearest integer only) on an $8 \times 8$ lattice subject to confining boundary conditions. [$\langle n \rangle$ should be symmetric with respect to the principal diagonal (starred).]

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 124* | 122 | 121 | 116 | 112 | 114 | 113 | 114 |
| 123 | 121* | 117 | 109 | 107 | 106 | 108 | 111 |
| 120 | 115 | 108* | 100 | 93 | 98 | 101 | 105 |
| 114 | 110 | 99 | 83* | 65 | 81 | 93 | 97 |
| 112 | 107 | 92 | 65 | 0* | 60 | 83 | 94 |
| 111 | 107 | 94 | 78 | 61 | 74* | 88 | 94 |
| 112 | 109 | 101 | 93 | 83 | 88 | 91* | 97 |
| 113 | 110 | 105 | 96 | 93 | 93 | 96 | 98* |

the appropriate edge length and dimension) reported as Eq. (13) in Ref. 10. Overall, the two sets of results are in excellent accord.

In Fig. 1 we present Monte Carlo data on the average number $\langle n \rangle$ of steps required for trapping on a simple (chain, square, cubic) lattice of $d$ dimensions having $N$ sites (where $N$ is even) with one trap. Three types of boundary conditions were considered, namely, periodic, confining, and reflecting boundary conditions (see earlier text). Systems subject to confining boundary conditions are characterized by an average walk length $\langle n \rangle$ which is slightly longer than the one obtained on the corresponding periodic lattice. This result implies that the effect of imposing confining boundary conditions is to exclude a class of walks which would otherwise be available to a walker on a periodic lattice (specifically, those classes of walks for which the walker passes across the boundary and re-enters the system on the opposite side). In contrast to the behavior found on lattices subjected to periodic or confining boundary conditions, results obtained for the case of reflecting boundary conditions reveal a significantly shorter walk length in all cases, a result in qualitative accord with the known role of reflecting boundaries in the simpler random-walk problem.[11] In effect, the reflecting boundary condition increases the probability that the walker is away from the boundary, and thereby provides a focusing effect which enhances the eventual trapping of the walker. It is likely that this effect is of significant importance in intramicellar kinetic processes,[12] specifically those reactions involving energy transfer between two completely compartmentalized species.

## III. TWO-DIMENSIONAL CASE

The conclusions presented in the preceding section can be sharpened up by considering the problem of determining the average walk length on a lattice with a trap (sink, target) for the particular

case where the dimensionality of the system is restricted to $d=2$. Here, important contributions have been made by Avery, Bay and Szent-Gyorgyi,[13] ten Bosch and Ruijgrok,[14] Pearlstein,[15] Robinson,[16] Knox[17] and, of course, Montroll.[10] Given the emphasis in this paper on lattices of finite extent, we wish to compare the results obtained in our Monte Carlo simulations with the averages reported by Sanders, Ruijgrok, and ten Bosch[18] (SRB) in their study of the random motion of an exciton on a two-dimensional finite square lattice with $(2n+1)^2$ sites. These authors formulate the problem in terms of finite difference equations and, for the finite system case, derive the following recursion relation:

$$D^{(2)}(x,y)=1+\frac{1}{c(x,y)}\sum_{x',y'}^{(x,y)} D^{(2)}(x',y'), \tag{1}$$

with $(x,y)\neq(0,0)$ and $D^{(2)}(0,0)=0$. In deriving this result, SRB assume that the exciton spends a fixed time $\tau$ on each lattice site, and contrast this with the situation, first considered by Knox,[17] where the time spent on a lattice site is inversely proportional to (or otherwise dependent on), the number of neighbors of the site. It is the former case that is closest in spirit to our calculation. As regards the latter case, SRB prove that the recursion relation for this problem

$$D^{(1)}(x,y)=\frac{4}{c(x,y)}\left(1+\frac{1}{4}\sum_{x',y'}^{(x,y)} D^{(1)}(x',y')\right), \tag{2}$$

with $(x,y)\neq(0,0)$ and $D^{(1)}(0,0)=0$ is identical with the one obtained for a system with periodic boundary conditions, a result they verify by making contact with Montroll's earlier work.[10] In expressions (1) and (2), $D(x,y)$ is the average walk length starting from the site $(x,y)$, the coefficient $c(x,y)$ is the number of nearest neighbors of the site $(x,y)$, and the sum extends over all nearest neighbors of the site $(x,y)$. These recursion relations are valid for all planar lattices with $(2n+1)^2$ sites centered at the origin. To mobilize the relation (1) for the case of a square planar lattice of $(2n+1)^2$ sites, the following further properties must be specified:

(a) Three types of sites are identified: central sites, edges and corners.

(b) Central sites have four nearest neighbors $[c(x,y)=4]$; thus, a walker on a central site may walk to any of four adjacent sites with equal probability.

(c) Edge sites have three nearest neighbors $[c(x,y)=3]$; a walker starting from an edge site may walk to any one of three sites with equal probability.

(d) Corner sites have two nearest neighbors $[c(x,y)=2]$; here, a walker starting from a corner site may walk to either of two sites with equal probability.

Given these specifications, the average number of steps required for trapping starting from a site $(x,y)$ is simply related to the average number of steps required for trapping from *each* of those neighboring sites that can be reached by a *single* step from $(x,y)$, with the overall summation weighted by a factor $c(x,y)$ which characterizes the site $(x,y)$ as being a central site, an edge site or a corner site.

The construction introduced by SRB for a finite, planar lattice, and the explicit way in which the role of the boundary is taken into account, differs somewhat from the constructions considered earlier in this paper. In order to compare similarities and differences between our results and those derived using the recursion relation (1) it is necessary to develop expressions analogous to Eq. (1) for lattices subjected to confining boundaries and reflecting boundaries.

We consider first the case of a finite lattice with $(2n+1)^2$ sites subject to confining boundary conditions. Here, we require that a walker situated on a boundary site (edge or corner), on attempting to escape the lattice, returns to the (same) boundary site. Thus, if $(x,y)$ is an edge site, and if $(x-1,y)$ is outside the system, one may write

$$D_c(x,y)=1+\tfrac{1}{4}[D_c(x,y)+D_c(x+1,y)+D_c(x,y+1)+D_c(x,y-1)]. \tag{3a}$$

If $(x,y)$ is a corner site, and if $(x+1,y)$ and $(x,y+1)$ are outside the system, then

$$D_c(x,y)=1+\tfrac{1}{4}[2D_c(x,y)+D_c(x-1,y)+D_c(x,x-1)]. \tag{3b}$$

The interior sites are treated in the same manner as specified by the SRB expression (1).

Considering next the case of a finite lattice with $(2n+1)^2$ sites subject to reflecting boundary conditions, we require that each attempt to leave the finite system from a boundary point results in a displacement of the walker by one lattice site in the direction of the interior. Thus, if $(x,y)$ is an edge site, and $(x-1,y)$ is outside the finite system, then one has

$$D_R(x,y)=1+\tfrac{1}{4}[2D_R(x+1,y)+D_R(x,y+1)+D_R(x,y-1)]. \tag{4a}$$

If $(x,y)$ is a corner site, and if $(x+1,y)$ and $(x,y+1)$ are outside the finite system, then

$$D_R(x,y)=1+\tfrac{1}{2}[D_R(x-1,y)+D_R(x,y-1)]. \tag{4b}$$

Once again, the expression (1) is the recursion relation for the interior sites.

TABLE III. Comparison of the average number $\langle n \rangle$ of steps required for trapping on a planar lattice with $(2n+1)^2$ sites and with the traps symmetrically positioned relative to the boundaries.

| $n$ | Type of boundary condition imposed on the lattice: Periodic [a] | Confining | SRB [b] | Reflecting |
|---|---|---|---|---|
| 1 | 8.92 | 9.00 | 5.50 | 3.50 |
| 2 [c] | 31.64 | 31.67 | 24.50 | 19.06 |
| | (31.61) | (31.72) | | (19.08) |
| 3 | 71.60 | 71.61 | 60.22 | 50.75 |
| 4 | 130.6 | 130.6 | 114.6 | 100.7 |
| 5 | 209.9 | 209.9 | 189.0 | 170.3 |
| 6 | 310.6 | 310.5 | 284.5 | 260.9 |
| 7 | 433.6 | 433.3 | 401.9 | 373.1 |
| 8 | 579.5 | 578.9 | 542.0 | 507.8 |
| 9 | 749.1 | 747.8 | 705.3 | 665.7 |

[a] Results calculated from Montroll's equation (31), Ref. 10.

[b] Results calculated from the SRB recursion relation, Eq. (1).

[c] Numbers in parentheses are the results of Monte Carlo simulation; the standard deviations $\sigma_n$ for periodic, confining, and reflecting boundary conditions are, respectively, 31.55, 31.59, and 18.12.

Calculations based on Eqs. (3) and (4) were performed for the case where the trap at $(x, y) = (0, 0)$ is symmetrically positioned with respect to the planar boundaries. In Table III we list the results obtained using the recursion relation $D^{(2)}(x, y)$, those calculated for lattices subjected to confining and reflecting boundaries, and for completeness, those obtained using the recursion relation $D^{(1)}(x, y)$ and/or Montroll's Eq. (31).[10] Also included in Table III (see footnote c) are the results of a representative Monte Carlo calculation for a $5 \times 5$ lattice subject to periodic, confining and reflecting boundary conditions. As is seen, the average number of steps required for trapping decreases in the order: confining boundary conditions, periodic boundary conditions, the SRB bound lattice $[D^{(2)}(x, y)]$, and reflecting boundary conditions. In other words, a lattice with confining boundaries has the "softest" boundaries whereas a finite lattice with reflecting boundaries presents the "hardest" boundaries. These results may be understood by noting the fate of a random walker attempting to step on a lattice site which lies on one of the edges. For a walker encountering a confining boundary, the probability that the walker will return to an interior point is $\frac{1}{4}$, in the SRB bound lattice it is $\frac{1}{3}$ and for the case of a reflecting boundary it is $\frac{1}{2}$.

We have also generalized the approach taken by SRB to consider the case where the trap at $(x, y) = (0, 0)$ is *not* symmetrically disposed with respect to the boundaries of the finite system, i.e., the case of *even* lattices. The results displayed in Table IV show that the general trends found in the previous case (odd lattices) are sustained. The data reported in Tables II and III may also be compared with the results obtained in our Monte Carlo simulations, Fig. 1, and it is seen that the agreement is good.

TABLE IV. Comparison of the average number $\langle n \rangle$ of steps required for trapping a planar lattice with $(2n)^2$ sites and with the trap asymmetrically positioned relative to the boundaries.

| $n$ | Type of boundary condition imposed on the lattice: Periodic | Confining | SRB | Reflecting |
|---|---|---|---|---|
| 1 | 3.22 | 6.67 | 3.33 | 3.33 |
| 2 | 18.26 | 20.72 | 15.01 | 11.73 |
| 3 | 49.34 | 51.58 | 42.07 | 34.83 |
| 4 [a] | 98.63 | 100.8 | 86.93 | 75.39 |
| 5 | 167.7 | 169.7 | 151.2 | 135.0 |
| 6 [a] | 257.6 | 259.6 | 236.0 | 214.9 |
| 7 | 369.3 | 371.2 | 342.4 | 316.3 |
| 8 | 503.6 | 505.3 | 471.1 | 439.7 |
| 9 | 661.3 | 662.5 | 622.7 | 585.9 |
| 10 | 842.7 | 843.3 | 797.8 | 755.5 |

[a] Results may be compared directly with the Monte Carlo results in Fig. 1.

In conclusion, for the particular case of planar lattices, the average number of steps required for trapping can be calculated either from analytic expressions, or via numerical simulation; both for the case of finite systems subject to various confining boundary conditions and for systems subject to periodic boundary conditions. The results obtained are in good agreement with the Monte Carlo simulations. Accordingly, we may suggest that the numerical results reported in this paper for finite lattices of dimension *three* may be taken as data against which the predictions of theoretical studies on the random-walk problem may be compared.

## IV. DISCUSSION

In this paper we have reported the results of Monte Carlo simulations on an important problem in lattice dynamics: Given a *finite* lattice which contains a trap at a (fixed) internal site, if a random walker has the same probability of starting from any nontrapping point, how many steps $\langle n \rangle$ must be taken on the average before he is trapped. As was pointed out in the introduction to this paper, several lines of research (both theoretical and experimental) raise questions which can be cast into the above language (e.g., the role of dimensionality and spatial extent in

influencing cooperative phenomena far from equilibrium, and the motion of excitons and their trapping in finite photosynthetic units), and hence the Monte Carlo results reported herein may be taken as a first quantitative assessment of the role of boundaries on the dynamics. Since our main objective in this paper has been to provide numerical evidence on the (relative) importance of boundary effects, no attempt will be made here to access the various theoretical approaches to the problem of far-from-equilibrium phenomena. This will be done in a later note where our objective will be to examine the Fokker-Planck equation (including both diffusion and drift contributions) in light of these (and subsequently obtained) data. Our more modest goal here, however, is to reorganize the data presented in this paper in such a way as to illustrate the concept of reduction of dimensionality in reaction-diffusion process, an idea whose importance was emphasized by Adam and Delbrück.[19] These authors proposed that "organisms handle some of the problems of timing and efficiency, in which small numbers of molecules and their diffusion are involved, by reducing the dimensionality in which diffusion takes place from three-dimensional space to two-dimensional surface diffusion." We now discuss this concept in light of results obtained in our Monte Carlo simulations.

In the reaction-diffusion approach taken by Adam and Delbrück one imagines a target (or trap) fixed at the origin of a coordinate system and considers the diffusion of a molecule to the target. To assess the importance of reduction of dimensionality, they solve the corresponding (Fickian) diffusion equation for the three-, two-, and one-dimensional problems, keeping the target (or the number of traps) fixed. In terms of our lattice-dynamic problem, this is the case diagramed in Fig. 3, case *B*, where our Monte Carlo results confirm independently the predictions of the Adam-Delbrück theory. Note that this case (fixed number of traps in spaces of different dimensionality), may be contrasted with the case where one maintains a fixed *concentration* of traps. This latter case is the situation considered initially by Montroll and, as can be seen from Fig. 3, case *A*, very different predictions are obtained on the importance of dimensionality in this case; quite simply, the average number $\langle n\rangle$ *increases* with increasing dimensionality if the concentration of traps is held constant.

The results presented in the preceding paragraph stress the obvious point that dynamical effects in reaction-diffusion problems depend crucially on the specification of both spatial and temporal boundary conditions. Regarded as an initial-value problem, the two different assumptions on the concentration of traps at time $t=0$ are seen to change in a qualitative way the predicted effects due to reduction of dimensionality in the problem. Whereas this interplay between spatial and temporal constraints is very easily displayed in the type of reaction-diffusion problem considered in this paper (where the kinetics is first order, i.e., linear, and analytic results may be obtained), it may be anticipated that when nonlinear kinetic processes are considered, then given the difficulties in solving exactly the Fokker-Planck equation even for the simplest nonlinear models, the type of Monte Carlo study presented in this paper may be the only way of obtaining reliable results on the importance of dimensionality and spatial extent in reaction-diffusion processes.

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## APPENDIX

The generating function developed by Montroll[10] for a $d$-dimensional lattice with $n$ points on an edge is

$$G_D(z)=(N-1)^{-1}\{[(1-z)P(0,z)]^{-1}-1\}, \qquad \text{(A1)}$$

where $N=n^D$ and $P(0,t)$ is the generating function for all walks *from* the origin. The mean number $\langle n\rangle$ is given by

$$\langle n\rangle=\left(\frac{\partial G_D}{\partial z}\right)_{z=1}=\frac{1}{N-1}\frac{\partial}{\partial z}\left(\frac{1}{(1-z)P(0,t)}\right)_{z=1}, \qquad \text{(A2)}$$

while the second moment is

$$\langle n^2\rangle=\left(\frac{\partial^2 G_D}{\partial z^2}\right)_{z=1}=\frac{1}{N-1}\frac{\partial^2}{\partial z^2}\left(\frac{1}{(1-z)P(0,t)}\right)_{z=1}. \qquad \text{(A3)}$$

For a planar lattice ($d=2$) with periodic boundary conditions

$$P(0,t)=\frac{1}{N(1-z)}+\left(C_1\ln N+C_2+\frac{C_3}{N}+\frac{C_4}{N^2}+\cdots\right)+O((1-z)^{1/2}). \qquad \text{(A4)}$$

Simple differentiations then yield the result

$$\langle n^2\rangle=\frac{2N}{N-1}\left(C_1N\ln N+C_2N+C_3+\frac{C_4}{N}+\cdots\right)^2=\frac{2N}{N-1}\langle n\rangle^2.$$

Hence, given the definition of the variance $\nu$,

$$\nu = \langle n^2 \rangle - \langle n \rangle^2 ,$$

we find that

$$\nu = [(N+1)/(N-1)]\langle n \rangle^2 ,$$

and the standard deviation, $\sigma$, is then

$$\sigma = [(N+1)/(N-1)]^{1/2}\langle n \rangle ,$$

which shows that the standard deviation for periodic lattices is somewhat greater than the mean.


[1]Proceedings of the XVII Solvay Conference on Physics in Brussels, 1978 (Wiley-Interscience, New York, to be published).

[2]N. G. Van Kampen, Adv. Chem. Phys. 34, 245 (1976).

[3]G. Nicolis and I. Prigogine, *Self-Organization in Non-equilibrium Systems* (Wiley-Interscience, New York, 1977).

[4]H. Haken, *Synergetics* (Springer, Berlin, 1977).

[5]M. Suzuki, in Ref. 1.

[6]For a representative rigorous result, see T. G. Kurtz, J. Appl. Prob. 8, 344 (1971).

[7](a) W. Horsthemke and L. Brenig, Z. Phys. B 27, 341 (1977); (b) W. Horsthemke and M. Malek-Mansour, and L. Brenig, *ibid.* 28, 135 (1977); (c) see, however, O. Leimar, J. de la Rubia, and C. Blomberg, J. Stat. Phys. (to be published).

[8]F. Schlögl, Z. Phys. 253, 147 (1972).

[9]G. Nicolis and J. Turner, Physica (Utrecht) (to be published).

[10]E. W. Montroll, (a) J. Phys. Soc. Jpn. 26, 6 (1969); (b) J. Math. Phys. 10, 753 (1969).

[11]S. Chandrasekhar, Rev. Mod. Phys. 15, 1 (1943).

[12]See the papers of the Schloss Elmau conference on organized molecular assemblies reported in Ber. Bunsenges. Phys. Chem. 82, 848–1017 (1978).

[13]J. Avery, Z. Bay, and A. Szent-Györgyi, Proc. Natl. Acad. Sci. (U.S.A.) 47, 1742 (1961).

[14]J. J. ten Bosch and Th. W. Ruijgrok, J. Theor. Biol. 4, 225 (1963).

[15]R. M. Pearlstein, thesis, University of Maryland, 1966 (unpublished); Brookhaven Natl. Lab. Symp. 19, 19 (1967).

[16]G. W. Robinson, Brookhaven Natl. Lab. Symp. 19, 16 (1967).

[17]R. S. Knox, J. Theor. Biol. 21, 244 (1968).

[18]J. W. Sanders, Th. W. Ruijgrok, and J. J. ten Bosch, J. Math. Phys. 12, 534 (1971).

[19]G. Adam and M. Delbrück, in *Structural Chemistry and Molecular Biology*, edited by A. Rich and N. Davidson (Freeman, San Francisco, 1968); see also, P. H. Richter and M. Eigen, Biophys. Chem. 2, 255 (1974).