Journal of Statistical Physics, Vol. 30, No. 2, 1983

Stochastic Flows, Reaction-Diffusion Processes, and Morphogenesis

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Recently, an *exact* procedure has been introduced [C. A. Walsh and J. J. Kozak, *Phys. Rev. Lett.* **47**:1500 (1981)] for calculating the expected walk length $\langle n \rangle$ for a walker undergoing random displacements on a finite or infinite (periodic) d-dimensional lattice with traps (reactive sites). The method (which is based on a classification of the symmetry of the sites surrounding the central deep trap and a coding of the fate of the random walker as it encounters a site of given symmetry) is applied here to several problems in lattice statistics for each of which *exact* results are presented. First, we assess the importance of lattice geometry in influencing the efficiency of reaction-diffusion processes in simple and multiple trap systems by reporting values of $\langle n \rangle$ for square (cubic) versus hexagonal lattices in $d = 2, 3$. We then show how the method may be applied to variable-step (distance-dependent) walks for a single walker on a given lattice and also demonstrate the calculation of the expected walk length $\langle n \rangle$ for the case of multiple walkers. Finally, we make contact with recent discussions of "mixing" by showing that the degree of chaos associated with flows in certain lattice systems can be calibrated by monitoring the lattice walks induced by the Poincaré map of a certain parabolic function.

KEY WORDS: Reversible/irreversible reactions; effects of dimensionality/spatial extent; chaos.

1. INTRODUCTION

To study reaction-diffusion processes in homogeneous vs. compartmentalized media, we have developed recently a method for calculating exactly the expected walk length $\langle n \rangle$ for random walks on d-dimensional lattices with traps.[1] Although at first sight it appeared that the algorithm introduced was chiefly of interest in obtaining numerical results on lattice

Presented at the Symposium on Random Walks, Gaithersburg, MD, June 1982. The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2369 from the Notre Dame Radiation Laboratory.

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0022-4715/83/0200-0263$03.00/0

problems for which large-scale Monte Carlo calculations would be prohibitively expensive, a more detailed examination of the underlying mathematical structure of the theory[2] revealed that the approach taken might itself serve as a fresh starting point for deriving analytic expressions for $\langle n \rangle$ for a variety of random walk problems. The method proposed in Refs. 1 and 2 is based on a simple use of group theory to classify the site symmetry of the trapping/nontrapping lattice points and a subsquent, self-consistent coding of the fate of a random walker as it encounters a site of given symmetry. The algebraic structure which results upon organizing this information systematically lends itself naturally to analysis via methods of matrix transformation theory. It was demonstrated[2] that the inverse of the underlying transformation matrix leads at once to information on $\langle n \rangle_i$ (the expected walk length from site i), on the fraction of probability space encountered by the random walker in a flight from site i to site j, and on the overall walk length $\langle n \rangle$.

In the present talk, we shall illustrate the potential usefulness of the method as an analytic tool by (re)deriving two closed-form analytic results for walks on a linear chain with a centrosymmetric, deep trap (Section 2). Then, in Section 3, we demonstrate the versatility of the algorithm as a calculational tool by considering several examples: we focus on problems in reaction-diffusion theory for which exact analytic results are presently unavailable. These problems are, of course, accessible to quantitative study via the implementation of Monte Carlo simulation methods, and for each of the problems described in Section 3 we have performed complementary, Monte Carlo calculations to provide "experimental evidence" that the algorithm "works." As noted in our earlier report,[1] from the standpoint of machine time, there is no comparison between the times required to implement the algorithm (involving, as it does, nothing more than Cramer's rule) versus those required to perform the Monte Carlo simulations. For certain of the problems discussed, up to 20,000 walks initiated from *each* site of the underlying d-dimensional lattice are required to obtain good histograms and reliable estimates of $\langle n \rangle$. Since, then, for the same problem a Monte Carlo experiment may require several hours of c.p.u. time, whereas use of the algorithm requires only seconds to implement on the same machine, we believe the procedure introduced opens up the possibility of obtaining exact results on a wide variety of problems previously resistant to systematic study.

2. ILLUSTRATION OF THE METHOD: ANALYTIC RESULTS

Consider a linear chain of N sites consisting of a centrosymmetric deep trap (T) and $(N-1)$ nontrapping (neutral) sites, with the $d = 1$ lattice

subject to periodic boundary conditions. Relative to the central trap, the symmetric disposition of the adjacent, nontrapping sites suggests the following coding: $(N-1)/2, (N-3)/2, \ldots, 4, 3, 2, 1, T, 1, 2, 3, 4, \ldots, (N-3)/2, (N-1)/2$. Suppose for definiteness the walker is situated at one of the two nontrapping sites denoted 1, and let $\langle n \rangle_1$ represent the expected walk length for a walk originating from this site. There is one chance in two that the walker will move in a single step jump to a site labeled 2. Assuming this has been realized, the walker, after having landed on this new site, will have no memory of ever having been on the original site 1. Thus, in this Markovian scenario, the walker will continue his walk just as if he had started from the site 2, except that his walk length must be incremented by the one previously taken step. Taking into account both sites flanking the site labeled 1, together with the attendant probability $p = 1/2$ of a neighboring site being reached in a random displacement from site 1, one has the following relation:

$$\langle n \rangle_1 = \tfrac{1}{2}(\langle n \rangle_T + 1) + \tfrac{1}{2}(\langle n \rangle_2 + 1)$$

Similar equations may be set down for each of the remaining $\langle n \rangle_i$ and the resultant set of equations, comprising $i = 1, 2, \ldots, (N-1)/2$ equations in $(N-1)/2$ unknowns may be organized in terms of the matrix representation[2]:

$$\begin{bmatrix} 1 & -q & 0 & \ldots & 0 & 0 & 0 \\ -q & 1 & -q & \ldots & 0 & 0 & 0 \\ \cdot & \cdot & \cdot & \cdots & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdots & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdots & \cdot & \cdot & \cdot \\ 0 & 0 & 0 & \ldots & -q & 1 & -q \\ 0 & 0 & 0 & \ldots & 0 & -q & (1-q) \end{bmatrix} \begin{bmatrix} \langle n \rangle_1 \\ \langle n \rangle_2 \\ \cdot \\ \cdot \\ \cdot \\ \langle n \rangle_{(N-3)/2} \\ \langle n \rangle_{(N-1)/2} \end{bmatrix} = \begin{bmatrix} 1 \\ 1 \\ \cdot \\ \cdot \\ \cdot \\ 1 \\ 1 \end{bmatrix}$$

where here, $q = \frac{1}{2}$ and $\langle n \rangle_T = 0$. We identify the $[(N-1)/2] \times [(N-1)/2]$ matrix on the left-hand side as the transformation matrix A of the problem and construct the inverse matrix A^{-1} to project out information on the $\langle n \rangle_i$. Thus

$$\begin{bmatrix} 2 & 2 & 2 & 2 & \ldots & 2 \\ 2 & 4 & 4 & 4 & \ldots & 4 \\ 2 & 4 & 6 & 6 & \ldots & 6 \\ 2 & 4 & 6 & 8 & \ldots & 8 \\ \cdot & \cdot & \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdots & \cdot \\ 2 & 4 & 6 & 8 & \ldots & 2[(N-1)/2] \end{bmatrix} \begin{bmatrix} 1 \\ 1 \\ 1 \\ 1 \\ \cdot \\ \cdot \\ 1 \end{bmatrix} = \begin{bmatrix} \langle n \rangle_1 \\ \langle n \rangle_2 \\ \langle n \rangle_3 \\ \langle n \rangle_4 \\ \cdot \\ \cdot \\ \langle n \rangle_{(N-1)/2} \end{bmatrix}$$

It is evident that summing the elements of the first row of the inverse matrix A^{-1} yields $\langle n \rangle_1 = [(N-1)/2] \cdot 2 = N - 1$, a result which is consistent with the Montroll–Weiss result[3–5] that the expected walk length required to return to the origin (for a walk starting from the origin) is N. By inspection, $\langle n \rangle_i = iN - i^2$, and hence the overall expected walk length $\langle n \rangle$ may be computed at once:

$$\langle n \rangle = \frac{2\sum_{i=1}^{(N-1)/2} \langle n \rangle_i}{N-1} = \frac{1}{6} N(N+1)$$

the classic result of Montroll and Weiss.[3–5] If one considers the case of reflecting boundary conditions (implemented by the restriction that if the walker attempts to step on the boundary it is displaced to one (interior) lattice point further removed from the boundary than the lattice site from whence it started), only the elements comprising the last column of the matrix A^{-1} change, viz., the new column elements are (1 2 3 . . . $(N-1)/2$). The information in the consequent inverse matrix can be extracted as above, with the result that $\langle n \rangle_i = iN - i(i+1)$ and

$$\langle n \rangle = \tfrac{1}{12}(N+1)(2N+3)$$

which is just the closed form analytic result found using standard generating function techniques.[6]

We have pointed out[2] that the matrix elements of A^{-1} satisfy a number of invariance relations (similar to the one noted above for periodic lattices, viz., $\langle n \rangle_1 = N - 1$) which, when used in conjunction with scaling relations derived from a sequence of decimationlike transformations (in which neutral sites are replaced by traps), allow calculations on N site, d-dimensional lattices to be replaced by simpler calculations on N' site lattices, where $N' < N$. It is this procedure which is being exploited in our present work in the effort to obtain new analytic results in random walk theory.

3. REACTION-DIFFUSION PROCESSES IN HOMOGENEOUS VS. COMPARTMENTALIZED SYSTEMS

Of the many reaction-diffusion processes that can be modeled by random walks on d-dimensional lattices, two will be considered here. Suppose that A is the diffusing molecule (the random walker) and B is the target molecule (the trap), the latter localized at a point in space. Then, the case $T = 1$ with the remaining $(N-1)$ sites of the lattice nonabsorbing (nonreactive, neutral) corresponds to considering the strictly irreversible reaction: $A + B \rightarrow C$. Or, generalizing this situation, suppose that due to "poisoning" (in the problem of catalyst deactivation) or unfavorable steric

or energetic constraints (in the chlorophyll antenna system), the $(N-1)$ sites surrounding the central trap are also occupied by reactive species B, but that these have a reduced probability $0 < s_i < 1$ of reacting with the diffusing molecule A; in effect, then, we consider the reaction: $A + B \leftrightarrows [AB]^* \rightarrow C$, where $[AB]^*$ may be thought of as an activated complex.

In the reaction schemes described above, any number of factors may affect the efficiency of reaction, the latter monitored by the expected walk length $\langle n \rangle$. Among these factors are (1) the dimensionality and connectivity of the lattice; (2) the spatial extent of the reaction space; (3) for compartmentalized systems (e.g., cells, micelles, vesicles), the nature of the boundary conditions; (4) the importance of background deactivation; and, (5) the possible bias on the motion of the diffusing species due to down-range potential interactions. All of these situations can be dealt with using the algorithm described in the previous section, and in Table I we record some representative results for $d = 2$. (Again, all numbers reported are the algorithm results; corroborative Monte Carlo simulations have been carried out to "check" the numbers and in all cases the agreement is better than 0.3%.)

Consider first the role of lattice connectivity in influencing the efficiency of reaction. The results for hexagonal lattices are always somewhat higher than those for square lattices; a lattice site on a hexagonal array has one fewer exit path than a lattice site on a square lattice, so a diffusing species has fewer channels to exploit in seeking the central trap. As documented in the % Diff $[\equiv (\langle n \rangle_{\text{hex}} - \langle n \rangle_{\text{sq}})/\langle n \rangle_{\text{sq}} \times 100]$ column, there is an interesting interplay between lattice connectivity and the nature of the boundary conditions imposed on the lattice. Differences in $\langle n \rangle$ calculated for square vs. hexagonal arrays are more pronounced for active (reflecting) than for passive (periodic/confining) boundary conditions. The "focusing effect" induced by reflecting boundary conditions is most clearly displayed for the case $s_i = 0$. The most striking feature of the remaining results listed in Table I, i.e., those for nonzero s_i, is the extent to which small departures from chemical neutrality at the $(N-1)$ sites adjacent to the central trap wipe out distinctions due to the geometry of and constraints on the reaction space of the reaction-diffusion process being considered. The process simply becomes chemically controlled (rather than diffusion controlled) once the $(N-1)$ centers are "turned on."

The qualitative conclusions stated above remain unchanged when one examines the results of similar calculations performed for $d = 3$. Rather than present these here, however, we report the results of a different series of calculations in $d = 3$ which have relevance to the problem of morphogensis. The notion of "reduction of dimensionality" as introduced by Adam and Delbrück[7] is the conjecture that living systems handle problems of

Table I. Comparison of Results for Square vs. Hexagonal Lattices in $d = 2$ Subject to Periodic/Confining and Reflecting Boundary Conditions with a Centrosymmetric Deep Trap ($T = 1$) and Background Absorption ($s_i \neq 0$)

N	Square Lattice	$s_i = 0$			$s_i = 0.05$			$s_i = 0.10$		
		$\langle n \rangle_{sq}$	$\langle n \rangle_{hex}$	% Diff	$\langle n \rangle_{sq}$	$\langle n \rangle_{hex}$	% Diff	$\langle n \rangle_{sq}$	$\langle n \rangle_{hex}$	% Diff
25	5×5	31.7[a]	37.5	18.3	12.4	13.0	5.3	7.71	7.92	2.7
		(19.1)[b]	(28.8)	(50.8)	(10.1)	(12.0)	(18.8)	(6.88)	(7.60)	(10.5)
49	7×7	71.6	86.6	21.0	15.6	16.1	3.1	8.79	8.92	1.5
		(50.7)	(72.5)	(43.0)	(14.6)	(15.7)	(7.5)	(8.54)	(8.83)	(3.4)
121	11×11	209.9	257.0	22.4	18.2	18.4	1.2	9.51	9.56	0.53
		(170.4)	(230.8)	(35.4)	(18.0)	(18.3)	(1.7)	(9.48)	(9.55)	(0.7)
169	13×13	310.6	381.8	22.9	18.7	18.8	0.86	9.65	9.69	0.41
		(260.9)	(349.2)	(33.8)	(18.6)	(18.8)	(1.1)	(9.64)	(9.68)	(0.4)

[a] Results *not* in parentheses are for periodic/confining boundary conditions.
[b] Results *in* parentheses are for reflecting boundary conditions.

timing and efficiency of reaction by converting d-dimensional flows, where possible, to $(d-1)$-dimensional flows. This idea was explored within the framework of a continuum diffusion model in Ref. 7, and within the framework of discretized systems in Ref. 8. Use of the algorithm allows one to study the interplay between system size and the advantages gained upon converting from a d dimensional process to one governed by the "tracking" boundary condition (by which one means that the diffusing species moves randomly in a space of d-dimensions until it encounters the boundary for the first time, after which its trajectory is restricted entirely to the lower dimensional boundary of the host lattice). Calculations on lattices of size $5 \times 5 \times 5$ show that a centrosymmetric site for the deep trap is more efficient in trapping the walker than considering any surface site and imposing the tracking condition. However, when one studies the $8 \times 8 \times 8$ lattice,[9] three-dimensional walks to a centrally located site $(5,5,5)$ ($\langle n \rangle = 693.6$) while considerably shorter than three-dimensional walks to a corner site $(1,1,1)$ ($\langle n \rangle = 1844.9$) or to a surface site $(5,5,1)$ ($\langle n \rangle = 2001.0$), nonetheless are longer than a "tracking" walk to a surface site $(5,5,1)$ ($\langle n \rangle = 632.9$). Thus, as regards the efficiency of the underlying reaction-diffusion process, there occurs a crossover in the optimal location of the "active site," and this "phase transition" in reaction space appears to be a remarkably strong function of the size of the system. This conclusion is also borne out and further substantiated when one considers surfaces of fractal dimensions.[8]

The algorithm can also be applied to deal with situations in which the motion of the migrating particle is biased by an interaction potential. Adopting the notation introduced in the preceding section, we consider a 13-site chain subject to periodic boundary conditions with a centrosymmetric deep trap and regard the probability p_{ij} of moving from site i to site j to be governed by a (normalized) potential function of the form $p_{ij} = r_{ij}^{-6} / \sum_j r_{ij}^{-6}$; we determine: $\langle n \rangle_1 = 11.8$, $\langle n \rangle_2 = 21.3$, $\langle n \rangle_3 = 28.8$, $\langle n \rangle_4 = 34.5$, $\langle n \rangle_5 = 38.2$, $\langle n \rangle_6 = 40.1$, and $\langle n \rangle = 29.1$. These numbers are to be contrasted with the ones obtained assuming all the $p_{ij} = 1/2$ viz., $\langle n \rangle_1 = 12.0$, $\langle n \rangle_2 = 22.0$, $\langle n \rangle_3 = 30.0$, $\langle n \rangle_4 = 36.0$, $\langle n \rangle_5 = 40.0$, $\langle n \rangle_6 = 42.0$, and $\langle n \rangle = 30.3$. Comparison shows at once that the governing potential assumes more and more significance in guiding the motion of the walker the farther the site considered is displaced from the central trap.

To study competitive chemical processes, it is instructive to perform the above calculation for *two* reactants, mutually diffusing to a localized reactive site. To date, the algorithm has been applied to this problem only for the case of purely repulsive interactions between walkers. In particular, we imagine one walker to be characterized by a mass and size so much greater than the second diffusing species that the lighter particle is simply

denied access to a site of the lattice on which the migrating heavy particle happens to have landed. As representative of the sorts of results one finds in $d = 2,3$, for a 5×5 lattice the expected walk length for the lighter particle is $\langle n \rangle = 31.3$ whereas for a $5 \times 5 \times 5$ lattice the walk length is $\langle n \rangle = 157.3$. The corresponding results obtained for the case of a *single* random walker are, respectively, $\langle n \rangle = 31.7$ and $\langle n \rangle = 157.3$ indicating that the "blocking" effect of the heavy particle diminishes rapidly in significance with increase in size of the reaction space accessible to the lighter reactant.

4. CONCLUDING REMARKS

Despite the simplicity of the analysis reported in Section 2 (focusing as it does on the one-dimensional problem), it is nonetheless of interest to point out that information embedded in the inverse transformation matrix A^{-1} can cast light on a problem of contemporary importance in the theory of one-dimensional noninvertible maps. For example, with respect to the logistic parabola, $x_{n+1} = bx_n(1 - x_n)$ [with $0 \leqslant x_n \leqslant 1$ and $b = 4a$ with $0 \leqslant a \leqslant 1$], "for values of b where numerically generated sequences appear to be chaotic, it is not, at present, known whether they are truly chaotic, or whether, in fact, they are really periodic, but with exceeding large periods and very long transients required to settle down".[10] To address this question, we adopted the hypothesis that if the logistic parabola were generating truly random sequences, such a map should comprise the "perfect" random number generator. Given this hypothesis, values of $\langle n \rangle_i$ and $\langle n \rangle$ computed for a linear chain subject to periodic/reflecting boundary conditions using the logistic parabola as the "seed" for a Monte Carlo simulation should produce values exactly the same as those generated via the algorithm. Accordingly, we computed $\langle n \rangle_i$ and $\langle n \rangle$ for values of a in the range, $a_c < a < 1$, where a_c is the Feigenbaum number (0.892486417), and discovered[11] that *only* the value $a = 1$ gave results in accord with the exact statistical-mechanical results laid down in Section 2. This result seems to be in agreement with the conclusion of Thomae and Grossmann[12] but stands in contrast to the work of Lorenz,[10] whose numerical studies indicate that at least some of the numerically generated sequences in the range $a_c < a < 1$ are truly chaotic.

Finally, with respect to the calculations reported in Section 3, we are presently attempting to mobilize the algorithm to develop a lattice theory of chemical reactivity. The lines along which such a theory is being developed may be illustrated by considering a particular example, the bromination of toluene. Taking advantage of the (near) hexagonal symmetry of the toluene molecule, we imbedded this structure in a triangular (the dual) lattice of

$N = 126$ sites; altogether seven of the 126 sites will be blocked (six to accommodate the hexagonal structure of the benzene ring and one site for the methyl group). The electron donating character of the methyl group affects the electron density at ortho, meta, and para positions of the ring differently and phenomenological[13] or quantum chemical[14] data may be used to assign the (relative) trap depth (the s_i) for each distinct site. Using the algorithm one can compute the expected walk length $\langle n \rangle_i$ of the bromine ion from each of the 119 surrounding lattice sites to the ortho, meta, and para positions of the chemical lattice. When these data are converted to predicted percentage of product ($\equiv 1/\langle n \rangle_i \div \sum_i 1/\langle n \rangle_i \times 100$), we find: % ortho = 46.6, % meta = 0.3, and % para = 52.8, estimates which may be compared with the experimentally determined values of 32.9, 0.3, and 66.8, respectively.

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