Research Article

Stochastic Signatures of Phase Space Decomposition

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We explore the consequences of metrically decomposing a *finite* phase space, modeled as a d -dimensional lattice, into disjoint subspaces (lattices). Ergodic flows of a test particle undergoing an unbiased random walk are characterized by implementing the theory of finite Markov processes. Insights drawn from number theory are used to design the sublattices, the roles of lattice symmetry and system dimensionality are separately considered, and new lattice invariance relations are derived to corroborate the numerical accuracy of the calculated results. We find that the reaction efficiency in a finite system is strongly dependent not only on whether the system is compartmentalized, but also on whether the overall reaction space of the microreactor is further partitioned into separable reactors. We find that the reaction efficiency in a finite system is strongly dependent not only on whether the system is compartmentalized, but also on whether the overall reaction space of the microreactor is further partitioned into separable reactors. The sensitivity of kinetic processes in nanoassemblies to the dimensionality of compartmentalized reaction spaces is quantified.

1. Introduction

To provide a physical motivation for the present study, understanding the factors influencing self-assembly in nanophase materials is a major experimental and theoretical challenge [1, 2]. Modeling even the early stages of self-assembly already introduces fundamental questions, for example, whether the process is reducible to a sequence of elementary steps occurring under equilibrium conditions [3, 4]. The role of different system geometries in influencing the efficiency of reactions in a finite, compartmentalized system [5] is an ongoing problem, one aspect of which is explored quantitatively here.

Before discussing the technical aspects of our work, we illustrate the main idea with a simple example. Consider a $d = 2$ dimensional lattice of $N = 100$ sites. One possible representation of such a lattice would be a 10×10 system (see Figure 1). But, another representation that comprises $N = 100$ sites would be the disjoint pair of lattices, a 6×6 lattice with $N = 36$ sites, and an 8×8 lattice with $N = 64$ sites, linked at a common corner site. To monitor ergodic flows on the assigned phase space(s), we place a sink (trap)

at one of the corner vertices of the 10×10 lattice and at the common vertex of the two sublattices. The transit time of a test particle undergoing unbiased, random displacements until, eventually, it is (irreversibly) localized at the trap can be determined by formulating and then solving numerically the stochastic master equation [6] for the problem. By extracting the first moment of the underlying probability distribution function, specified by the set of site-specific mean walklengths $\langle n(i) \rangle$, the overall mean number $\langle n \rangle$ of steps before localization, a signature of the mean transit time, can be obtained.

One fully expects to get different values of $\langle n \rangle$ for these two lattice representations, but the question is “how different?” Also, the problem was illustrated above using (three) $n \times n$ lattices. How do the results change if one or more of the disjoint spaces are $n \times m$ lattices, that is, not approximately “square?” Is the difference in reaction efficiency magnified or suppressed? And, further, do these differences persist if one considers phase spaces of higher ($d = 3$) dimension? It is to the above questions that the present contribution is directed.

FIGURE 1: A $d = 2$ dimensional lattice of $N = 100$ sites. One possible representation of such a lattice would be a 10×10 system. But, another representation that comprises $N = 100$ sites would be the disjoint pair of lattices, a 6×6 lattice with $N = 36$ sites and an 8×8 lattice with $N = 64$ sites, linked at a common corner site (articulation point).

Fundamental results in number theory can be used to motivate the choices of lattices for which the metric decomposability of phase space can be studied. For dimension $d = 2$, one can take advantage of Fermat's last theorem, namely, that one *can* find three positive integers a , b , and c that satisfy the equation $a^n + b^n = c^n$ for $n = 2$ for a given choice of c^n . In $d = 2$, the decomposition is not unique; for any given c , there may be (and usually is) more than one choice of $\{a, b\}$ that satisfies the theorem.

In three dimensions, however, the possibility of finding multiple lattices with such a degeneracy is *much* more limited, in fact, just the set of Hardy-Ramanujan numbers. The first is $2 = 1^3 + 1^3$; the second “taxi cab” number is

$$1729 = 1^3 + 12^3 = 9^3 + 10^3 = 7 \times 13 \times 19. \quad (1)$$

These lattices are, practically speaking, as far as one can go. The next smallest Hardy-Ramanujan number is

$$\begin{aligned} 87539319 &= 167^3 + 436^3 = 228^3 + 423^3 \\ &= 255^3 + 414^3 = 223 \times 469 \times 837, \end{aligned} \quad (2)$$

the last factorization one of several possible. Given the computational demands in implementing the theory of finite Markov processes, these lattices are just too large; hence, our results for dimension $d = 3$ presented in Section 3 are (much) more limited than for $d = 2$.

The following section specifies the lattice statistical parameters needed to develop the Markovian theory. Section 3 presents the results of a series of calculations for $d = 2$ and $d = 3$ dimensional lattices. In Section 4, site-specific walk-length data are used to deduce two *new* invariance relations, valid for *finite* lattices, which must be satisfied exactly to confirm that the computational results are numerically exact. In the final section, we comment on the relevance of our results to self-assembly in nanosystems.

TABLE 1: $d = 2$ dimensional Lattices.

d	Sites	Lattice	$\langle n \rangle$	Lattice	$\langle n \rangle$	$\langle n \rangle_T$
2	50	1×1	0.0	7×7	212.354	212.354
		5×5	88.690	5×5	88.690	177.380
		5×10				240.537
65	65	1×1	0.0	8×8	297.846	297.846
		4×4	48.762	7×7	212.354	261.116
		5×13				363.840
85	85	2×2	6.667	9×9	400.071	406.738
		6×6	142.902	7×7	212.354	355.256
		5×17				563.571
100	100	6×6	142.902	8×8	297.846	440.748
		10×10				519.637

2. Formulation

We consider *finite* planar lattices, each site of which is of valence (connectivity) $\nu = 4$, and *finite* $d = 3$ dimensional lattices, each site of which is of valence $\nu = 6$. At any interior site of the lattice, the test particle can move with equal a priori probability in any one of ν directions. If the particle initiates its motion at an edge site on a $d = 2$ lattice, it can move in one of three directions on the lattice, but if it attempts to step “out of” the lattice, it is reset at the starting position. If the particle happens to be at a corner site, it can move to two adjacent lattice sites, remaining on the lattice, or is “reset” (stalls) at the corner site twice, rather than leaving the lattice. A similar protocol is implemented on $d = 3$ lattices, where a particle on an interior site can move in ν directions, on a face site in $\nu - 1$ directions with one reset, on an edge site in $\nu - 2$ directions with two resets, and on a corner site in $\nu - 3$ directions with three resets.

In all calculations here, the sink is placed at one corner site. Previous studies [5] have documented that moving the trap away from a centrosymmetric location will increase the walklength. However, the parent lattice or the lattices that result when one deconstructs a given initial lattice may not have a unique centrosymmetric site; for definiteness, we anchor the trap at a corner site. All calculations were carried out for nearest-neighbor displacements only and in the absence of any governing potentials; both restrictions can be lifted in further work.

All results reported here, Tables 1–3, are numerically exact (see Section 4). Once the problem is formulated, no further approximations are made in carrying out the computational program.

3. Results

Displayed in Table 1 are representative results for the $d = 2$ dimensional case. In every instance, one expects and finds that the results for $\langle n \rangle$ are systematically larger for the “parent” lattice than for the corresponding two disjoint lattices. The more “symmetric” and “similar” are the pair of disjoint lattices, the more efficient is the underlying ergodic process. Computing the percent difference between results

TABLE 2: $N = 1759$.

d	Lattice	$\langle n \rangle$	Lattice	$\langle n \rangle$	Lattice	$\langle n \rangle$	$\langle n \rangle_C$
2	5×5	88.690	11×11	657.085	71×71	51060.819	17268.865 ^a
	19×91						20438.245
3	$1 \times 1 \times 1$	0.0	$12 \times 12 \times 12$	6691.079			6691.079
	$9 \times 9 \times 9$	2716.171	$10 \times 10 \times 10$	3784.118			6500.289
	$7 \times 13 \times 19$						6939.812

^a $1729 = (5^2 + 11^2 + 71^2)/3$.

Here, $\langle n \rangle_C = (\langle n \rangle_{5 \times 5} + \langle n \rangle_{11 \times 11} + \langle n \rangle_{71 \times 71})/3$.

TABLE 3: Invariance relations.

$d = 2$	Lattice	N	$\Sigma(1)$	$\Sigma(2)$
	2×2	4	12	40
	4×4	16	60	232
	5×5	25	96	376
	6×6	36	140	552
	7×7	49	192	760
	5×10	50	196	776
	8×8	64	252	1000
	5×13	65	256	1016
	9×9	81	320	1272
	5×17	85	336	1336
	10×10	100	396	1576
	11×11	121	480	1912
	19×91	1729	6912	27640
	71×71	5041	20160	80632
$d = 3$	Lattice	N	$\Sigma(1)$	$\Sigma(2)$
	$3 \times 3 \times 3$	27	156	918
	$9 \times 9 \times 9$	729	4368	26190
	$10 \times 10 \times 10$	1000	5994	35946
	$12 \times 12 \times 12$	1728	10362	62154
	$7 \times 13 \times 19$	1729	10368	62190

for the composite lattice versus two disjoint (but linked) lattices, one finds that the difference is always greater than 10%, and frequently much greater (in the range from 10%–30%, depending on lattice symmetry).

In Table 2, we find that the difference in results for $d = 3$ dimensions is much less severe. For $N = 1729$, the percentage is less than 4%. Hence, dimensionality appears to play the critical role in cases studied here. Note that there is a companion, $d = 2$ dimensional result in Table 2 which was obtained by taking advantage of the decomposition of $N = 1729$ into the average of the greatest member in each pair of Brown numbers (5, 4), (11, 5), and (71, 7). Once again, the difference between the (here) three disjoint lattices and the parent 19×91 lattices is $\sim 15\%$.

We present in the following section results for two *new* lattice invariance relations that can be used to check the accuracy of the site-specific $\langle n(i) \rangle$ values that underlie the data given in Tables 1 and 2.

4. Invariance Relations

Over 40 years ago, Montroll and Weiss [7] reported for lattices subject to *periodic* boundary conditions an exact, analytic result for the average number of steps taken by a random walker from a site which is a first nearest-neighbor to a (deep) trap. Further, they discussed how one would proceed to derive similar analytic expressions starting from sites second, third, $\dots$ n th nearest neighbor(s) to the trap, emphasizing that the derived expressions will depend on the structure of the lattice.

In previous work, we pursued the Montroll-Weiss program and obtained additional invariance relations for hexagonal, square planar, and cubic lattices subject to *periodic* boundary conditions, each having a single, centro-symmetric, deep trap [8–10]. Since satisfaction of lattice invariance relations is an “acid test” on the accuracy of numerical calculations of the site-specific $\langle n(i) \rangle$ (and overall

mean $\langle n \rangle$), we used the methods described in [8–10] to develop invariance relations for *finite* lattices.

The corresponding first Montroll-Weiss invariance relation for finite lattices

$$\begin{aligned} \sum(1) &\equiv \text{Sum of the } \langle n(i) \rangle \text{ values} \\ &\quad \text{for all sites first nearest-neighbor to the trap} \\ &= v(N - 1) \end{aligned} \quad (3)$$

holds for a trap positioned either at an interior site or a surface site. The second invariance relation obtained for finite lattices is

$$\begin{aligned} \sum(2) &\equiv \text{Sum of the } \langle n(i) \rangle \text{ values} \\ &\quad \text{for all sites second nearest neighbor to the trap} \\ &= v[v(N - 1)] + 2v \end{aligned} \quad (4)$$

for $d = 2$ lattices with a trap at a corner site and

$$\begin{aligned} \sum(2) &\equiv \text{Sum of the } \langle n(i) \rangle \text{ values} \\ &\quad \text{for all sites second nearest neighbor to the trap} \\ &= v[v(N - 1)] + 3v \end{aligned} \quad (5)$$

for $d = 3$ lattices with a trap at a corner site.

It is important to stress that the right-hand side of each of the above expressions is an *integer*. Hence, calculating the $\langle n(i) \rangle$ in integer format, constructing $\sum(1)$, and $\sum(2)$, and comparing the results obtained with the (integer) results predicted by the right-hand side of the exact formulae above confirms (or not) the numerical accuracy of our calculations. Table 3 gives the results for $\sum(1)$, and $\sum(2)$ for all the lattices considered in this study and provides the desired confirmation.

5. Conclusions

In this contribution we have studied ergodic flows of a random walker undergoing unbiased displacements in a positional phase space represented by a host lattice, and characterized quantitatively the consequences of different metric decompositions of a given, *finite* parent lattice. As a model for studying the early stages of self-assembly of nanoparticles, the results here complement those reported in [3, 4] where the phase (reaction) space was defined by a host, periodic lattice. Specifically, by breaking the translational symmetry of the reaction space, we find that the reaction efficiency in a *finite* system is strongly dependent *not only* on whether the system is compartmentalized, *but also* on whether the overall reaction space of the microreactor is further decoupled into separable reactors.

Finally, the influence of system dimensionality on the efficiency of kinetic processes carried out in compartmentalized microreactors is quantified. We find that more

significant differences are encountered when a $d = 2$ reaction space is deconstructed than a $d = 3$ reaction space. Phrased in the language of experimental studies on nanoparticle kinetics, our results suggest that reactions carried out on articulated *surfaces* of a compartmentalized nanoparticle are likely to influence the efficiency of reaction to a greater extent than if the same reaction occurs in the partitioned *interior* of a $d = 3$ nanoassembly.

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