

## Dimensional crossovers and anomalous scaling of single and reacting random walkers in baguettelike lattices: Monte Carlo simulations of the number of distinct sites visited and of bimolecular $A + A$ and $A + B$ reactions

Anna L. Lin\* and Raoul Kopelman†

*Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109-1055*

Panos Argyrakis‡

*Department of Physics, University of Thessaloniki, 54006 Thessaloniki, Greece*

(Received 13 September 1996)

We performed Monte Carlo simulations on baguettelike lattices of random-walk-based bimolecular  $A + A$  and  $A + B$  reactions, and of the number of distinct sites visited. The emphasis is on the crossover times, from high (two- or three-) dimensional behavior to one-dimensional behavior, and their scaling laws with respect to tube width. We find that these dimensional crossovers deviate significantly from a mean square displacement law and are specific to both tube dimensionality (2 or 3) and reaction type (e.g.,  $A + A$  or  $A + B$ ), instead of an expected power of 2, the exponents range between 1 and 4. Thus, the global information propagation is either faster or slower than single particle diffusion. The fractional densities of the  $A + B$  reactions at the dimensional crossover are compared to the fractional densities at the segregation crossover in nonconfined media. The time evolutions of the  $A + A$  reactions approximately mimic those of the average number of distinct sites visited. All asymptotic time behaviors exhibit one-dimensional character. [S1063-651X(96)50412-5]

PACS number(s): 05.40.+j

Nonclassical reaction kinetics in quasi-one-dimensional systems with one-dimensional rate-law characteristics have been clearly demonstrated experimentally for several systems [1–3], including bimolecular reactions in solution filled pores [4,5] and binary exciton annihilation in crystalline media embedded inside pores [6–8], as well as for exciton annihilation on isolated guest chains [9] in polymer blends. The dynamics of the diffusion controlled photochemical and photophysical processes in most of these systems, including the well characterized nucleopore membranes [2], revealed cylindrical pore structures. These cylindrical systems exhibited crossover times dependent on width or, alternatively, crossover widths for given experimental time scales.

The nonclassical, anomalous behavior of the  $A + A$  elementary reaction [1–12] has been shown [3,8–12] to be caused by the anomalously large and continuously growing kinetic depletion zones, i.e., fluctuating mesoscopic domains, where the reactants have been depleted. Even more dramatic nonclassical effects have been demonstrated for elementary  $A + B$  reactions [3,13–15] where kinetic self-segregation between  $A$  and  $B$ , the Ovchinnikov-Zeldovich effect [13], has been demonstrated for an initially random system, as well as for steady state conditions [16,17]. This purely kinetic self-segregation of reactants in an elementary reaction has not yet been observed experimentally. The Ovchinnikov-Zeldovich rate law deviates from classical kinetics only slightly in three dimensions, more in two, and most prominently in one dimension. Searching for experimental realizations of this effect, one-dimensional cases should yield the clearest results.

While strictly one-dimensional reaction systems are hard to come by experimentally, it is much easier to find or to construct systems that are effectively one-dimensional, such as capillaries, pores, or tubules. Such systems are, or can be made to be, immune to convection currents that otherwise might frustrate [18] the Ovchinnikov-Zeldovich effect. Towards this goal, we performed here simulations of such tubular systems, using “baguettelike” lattices, with the aim of quantifying the conditions necessary for the experimental observation of the Ovchinnikov-Zeldovich effect. Since in the short time regime (too short to reach the Ovchinnikov-Zeldovich effect) the  $A + B$  reaction mimics the behavior of the  $A + A$  reaction [19], we have also simulated the  $A + A$  case. Also, as the  $A + A$  reaction generally follows the scaling of the number of distinct sites visited, we also simulated this case. For completeness, we have simulated two-dimensional “flat” tube reactions to compare with the three-dimensional square tube results.

The dimensional sensitivity of nonclassical kinetics implies crossover times that depend on tube diameter. Previous work [14,19–21] has effectively used scaling arguments based on the mean square displacement law (Einstein diffusion) to describe the time dependence of diffusion controlled reaction kinetics. The latter law has also been found [15,19] to describe correctly the crossover times for the onset of finite size effects in regular lattices (1D, 2D, and 3D). To determine if this law is also relevant to the crossover times resulting from the finite width of the tube, Monte Carlo simulations were performed here for elementary  $A + A$  and  $A + B$  irreversible reactions, and for the average number of distinct sites visited, in two- and three-dimensional baguettelike lattices. The boundary conditions for these lattices were reflective in the shorter dimension(s) and cyclic in the long dimension. The simulation methods have been detailed before [15,22].

\*Electronic address: alin@chem.lsa.umich.edu

†Electronic address: kopelman@umich.edu

‡Electronic address: argyrakis@physics.auth.gr

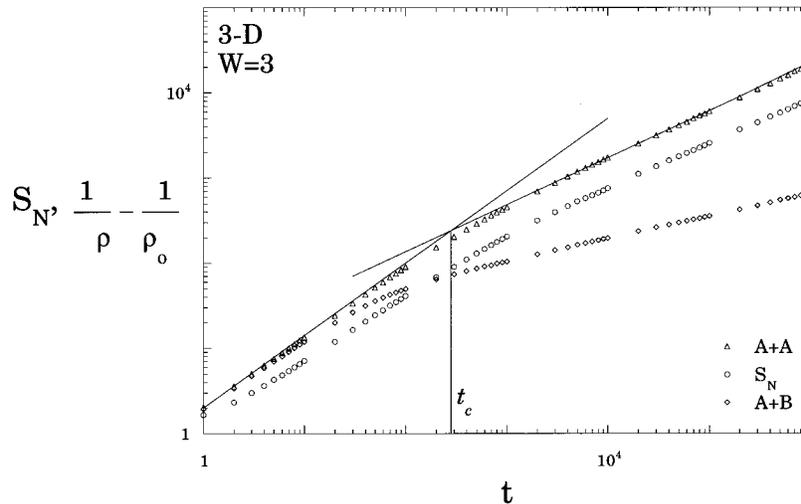


FIG. 1. Representative data plots for three processes:  $S_N$ , the average number of distinct sites visited (200 runs averaged), and the reaction progress of both  $A+A\rightarrow 0$  (25 runs averaged) and  $A+B\rightarrow 0$  (7 runs averaged), as measured by  $\langle \rho(t) \rangle^{-1} - \rho_0^{-1}$  vs time, all occurring on a spatially anisotropic, ‘‘baguettelike’’ lattice of size  $3 \times 3 \times 10^5$ . The initial density,  $\rho_0$ , is 0.8 *particle/site* for the  $A+A$  simulations and 0.4 in each species for the  $A+B$  simulations. The crossover time  $t_c$  from 3D behavior at early times to 1D behavior at asymptotic times is found from the intersection of the two solid lines, which are drawn as best straight line fits to the data at early and asymptotic times.

Seen in Fig. 1 are data representing each of the three processes which we discuss here: the number of distinct sites visited,  $S_N$ ; the elementary reaction process  $A+A\rightarrow 0$ ; and the elementary reaction process  $A+B\rightarrow 0$ . The latter two are both measured in terms of the reaction progress,  $\langle \rho(t) \rangle^{-1} - \rho_0^{-1}$ , where  $\rho_0$  is the initial  $A$  particle density. In Fig. 1, the solid line fits to the  $A+A$  data represent how we determined the crossover time,  $t_c$ , between the early time and asymptotic time behavior of the  $A+A$  and the  $A+B$  reactions. To determine  $t_c$  for the single random walker, we utilized analytical expressions to fit the data before and after the dimensional crossover.

The analytical expressions for the behavior of  $S_N$  in the asymptotic limit of  $N \rightarrow \infty$ , where  $N$  is the number of steps, have been given by Montroll and Weiss [23]. In 1D,  $S_N$  follows a  $t^{1/2}$  power law.

For 1D,

$$S_N \sim \left( \frac{8N}{\pi} \right)^{1/2}, \quad N \rightarrow \infty. \quad (1)$$

Correction terms to the asymptotic solutions, which add accuracy to the early time behavior [23,24], have also been determined. In 2D and 3D these analytical expressions are as follows.

For 2D (Ref. [24]),

$$S_N = \frac{AN}{\ln(BN)} \sum_{j=0}^{\infty} \frac{-\delta_{\beta}^j}{\ln BN} \Big|_{\beta=2} \left[ 1 + O\left(\frac{1}{N}\right) \right]. \quad (2)$$

For 3D (Ref. [23]),

$$S_N = 0.65946267N + 0.573921N^{1/2} + 0.449530 + 0.40732N^{-1/2} + \dots, \quad (3)$$

where  $A$  and  $B$  in Eq. (2) are constants. The crossover time  $t_c$ , defined as the point in time at which the system changes its effective behavior from that in 2D or 3D to that in 1D, is calculated separately for every curve. We implement Eqs. (1), (2), and (3) to compare the behavior of  $S_N$  on isotropic lattices to that observed on our anisotropic, baguettelike lattices. We also use these expressions to determine the crossover time  $t_c$  of  $S_N$  from 3D or 2D behavior into 1D behavior, by fitting Eqs. (2) and (3) to the early time region of the  $S_N$  vs  $N$  curves in 2D and 3D, respectively, while fitting Eq. (1) to the asymptotic region of those curves. The time axis value corresponding to the intersection of these two curve fits is defined as  $t_c$ . The other method, which we employ to determine the crossover time  $t_c$  for the  $A+A\rightarrow 0$  and  $A+B\rightarrow 0$  processes, involves drawing ‘‘best’’ linear fits to both the early time and the asymptotic time portions of the curve. Again, the corresponding time axis value where these two straight lines intersect is defined as  $t_c$  (see Fig. 1). Utilizing both methods to determine  $t_c$  for the  $S_N$  or the  $A+A$  data results in different absolute values of  $t_c$  for a given process. However, if each method is applied in a self-consistent manner, the resulting scaling relations agree within the associated errors given in Table I. The single random walker simulations were done on baguettelike lattices with ample lengths, such that site revisitations, due to finite size effects, did not occur in the length direction.

In Fig. 2, the crossover times  $t_c$  for  $S_N$  and for the reaction progress of the  $A+A\rightarrow 0$  and  $A+B\rightarrow 0$  reactions are

TABLE I. Dimensional scaling exponents for the relation between  $t_c$  and  $W$  ( $\pm$  designates estimated accuracies).

	$S_N$	$A+A$	$A+B$
2D	$2.6 \pm 0.4$	$2.8 \pm 0.8$	$1.0 \pm 0.2$
3D	$4.0 \pm 0.4$	$4.2 \pm 1$	$1.4 \pm 0.3$

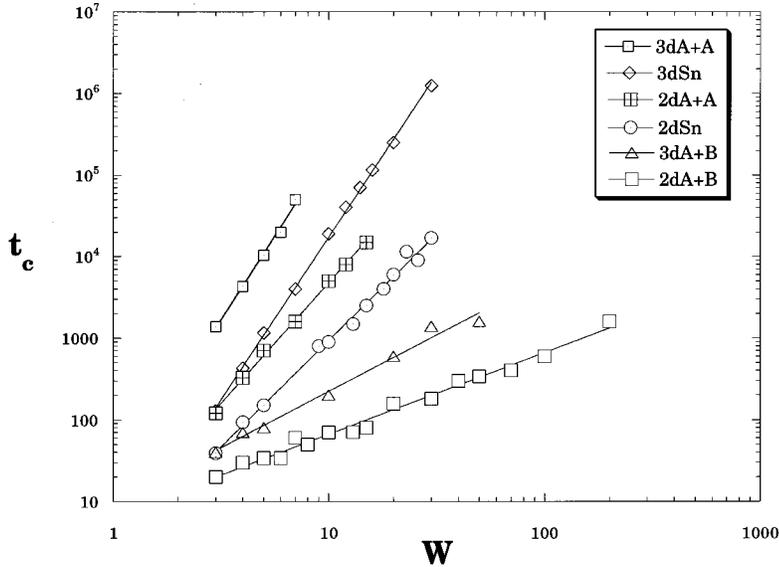


FIG. 2. The plot of  $t_c$  vs  $W$  for  $S_N$  and for the progress of the two reactions,  $A+A \rightarrow 0$  and  $A+B \rightarrow 0$ , on spatially anisotropic, “Baguette-like” lattices, showing the scaling relation between the width  $W$  and the time  $t_c$  at which the process exhibits a crossover from its behavior in 2D or 3D lattices to that in a 1D lattice.

plotted as a function of tube width  $W$ , revealing the existence of scaling relations between these two parameters. The complex pattern of these scaling relations is possibly the most interesting behavior exhibited in these two- and three-dimensional tubelike lattices. We write this scaling relation in the form

$$t_c \sim W^x, \quad (4)$$

where  $x$  is the crossover time scaling exponent. Table I lists these exponents. We see a dependence on both the dimensionality of the problem and the specific nature of the reaction. (Note that  $S_N$  represents directly some trapping reactions [25,26].)

Based on an analogy to the finite size effect crossovers found for isotropic lattices [19], one might have expected a universal crossover power of 2 in Eq. (4), i.e.,  $x=2$  or  $t_c \sim W^2$ , in analogy to the Einstein mean-square displacement diffusion law. Indeed, current arguments concerning both depletion zone growth in time (for trapping and  $A+A$  reactions) and aggregate size growth in time (for  $A+B$  reactions) are usually based on this mean-square scaling law [14,19–21,27]. Furthermore, we note that in classical chemical reaction kinetics there is *no* dependence of any elementary reaction progress on dimensionality. The reaction progress, measured by  $\langle \rho(t) \rangle^{-1} - \rho_0^{-1}$  is simply *linear in time at all times* and thus no crossover time can be defined (in a scaling sense).

In contrast to the above expectations, we see from Table I that even the simplest case,  $S_N$ , does not scale as the mean-square displacement law ( $x=2$ ) but rather exhibits anomalous scalings on these 2D and 3D spatially anisotropic lattices. Within the associated errors, the crossover times of the  $A+A \rightarrow 0$  reaction process follow (at least roughly) those of  $S_N$ . The  $A+A$  data are found only over a relatively narrow range of widths because the  $A+A$  reaction process occurs quickly in these Baguette-like lattices and finite size effects set in (the particle density becomes too dilute) before the dimensional crossover can be reached for lattices with  $W > 20$  in 2D and with  $W \geq 10$  in 3D, approximately. We

emphasize that the powers of  $S_N$  and of the 3D  $A+A$  reaction are significantly *larger* than two. On the other hand, the crossover powers for the  $A+B \rightarrow 0$  processes are significantly *smaller* than two in both 2D and 3D baguettelike lattices. We also note that while the precision of scaling exponents is very high, the accuracy of the values listed (Table I) is less certain. Still, all but one of the values of these scaling exponents are well away from two.

In Fig. 3, we plot vs  $W$  the ratio  $\rho_c/\rho_0$  which is the density of  $A$  particles remaining on the lattice at  $t_c$ , normalized by  $\rho_0$ , for the  $A+B$  process occurring in 2D and 3D, respectively. We note that, in general,  $\rho(t)/\rho_0$  is the “survival probability,” at time  $t$ , of the original particles. For comparison, we plot another “survival probability,”  $\rho'_c/\rho_0$ , namely, the normalized densities at  $t=t'_c$  where  $t'_c$  is the crossover time to the segregated (Ovchinnikov-Zeldovich) time regime in *isotropic*, linear, square, and cubic lattices, found in earlier work [15,19], where this ratio was called  $f_d$  ( $d=1,2,3$ ).

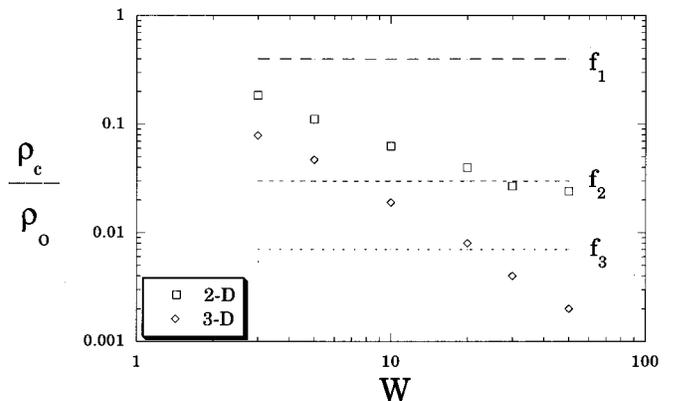


FIG. 3. The density of particles remaining on the baguettelike lattice at the dimensional crossover time normalized by the initial particle density  $\rho_c/\rho_0$  as a function of lattice width  $W$ . For comparison, the horizontal lines represent the normalized density of particles,  $f_d$ , remaining on a regular, isotropic lattice at the crossover to the Ovchinnikov-Zeldovich regime. The values of  $f_d$ , where  $d$  is the dimension 1, 2, or 3, are taken from [15,19].

These values are, of course, unrelated to the “baguette” width,  $W$ , in our baguettelike lattices, and are represented in Fig. 3 by horizontal,  $W$  independent lines, for  $d=1, 2$ , and 3. From this plot one can observe that, for  $W \leq 10$ , the density ratios  $\rho_c/\rho_0$  at the times of the dimensional crossovers ( $t_c$ ) in the 2D and 3D baguettelike lattices occur well above the density ratios needed for crossover into the Ovchinnikov-Zeldovich regime, given by  $f_d = \rho'_c/\rho_0$ , where  $d$  is the dimension of the isotropic lattice [19], i.e.,  $t_c < t'_c$  for “thin baguettes.” This implies that aggregates of like particles begin to form within the first few time steps on our narrow Baguette-like lattices. This can be seen visually in our simulation movies of the  $A$  and  $B$  particles “diffusing” and “reacting” on 2D “tube” lattices. This aggregation also seems to result in a slowing down of the reaction process and the deviation from the  $A+A$  type behavior (see Fig. 1) in these Baguettes, in contrast to the behavior observed for the

$A+B$  reaction, at early times, on isotropic lattices [15,19]. Furthermore, the scaling of  $t_c$  with  $W$  appears to be universal on the length scales we studied — for both the small  $W$  lattices, where  $\rho_c/\rho_0 > f_d$ , and the large  $W$  lattices, where  $\rho_c/\rho_0 < f_d$ .

In summary, we find that the crossover times  $t_c$  do scale with lattice width, but with unexpected powers. Their values range from one to four, compared to the expected value of two. Thus, the global information propagation is either faster or slower than single particle diffusion. At times well beyond the crossover time, the number of distinct sites visited,  $S_N$ , as well as both the  $A+A$  and the  $A+B$  reactions, display the characteristic, asymptotic, nonclassical behavior of a one-dimensional system.

This project was supported by NSF Grant No. DMR9410709 and by NATO Grant No. CRG920029 (P.A.).

- 
- [1] *Molecular Dynamics in Restricted Geometries*, edited by J. Klafter and J. M. Drake (Wiley, New York, 1989).
- [2] *Nonequilibrium Statistical Mechanics in One Dimension*, edited by V. Privman (Cambridge University Press, Cambridge, in press), Chaps. 20 and 21.
- [3] R. Kopelman, *Science* **41**, 1620 (1988).
- [4] J. Prasad and R. Kopelman, *Chem. Phys. Lett.* **157**, 535 (1989).
- [5] J. Prasad and R. Kopelman, *J. Phys. Chem.* **91**, 265 (1987).
- [6] R. Kopelman, S. J. Parus, and J. Prasad, in *Excited State Relaxation and Transport Phenomena in Solids*, edited by J. L. Skinner and M. D. Fayer [special issue of *Chem. Phys.* **128**, 209 (1988)].
- [7] R. Kopelman, S. Parus, and J. Prasad, *Phys. Rev. Lett.* **56**, 1742 (1986).
- [8] R. Kopelman, S. J. Parus, and J. Prasad, *Chem. Phys.* **128**, 209 (1988).
- [9] R. Kopelman, Z.-Y. Shi, and C. S. Li, *J. Lumin.* **48&49**, 143 (1991).
- [10] S. J. Parus and R. Kopelman, *Phys. Rev. B* **39**, 889 (1989).
- [11] C. R. Doering and D. Ben-Avraham, *Phys. Rev. A* **38**, 3035 (1988).
- [12] C. R. Doering and D. Ben-Avraham, *Phys. Rev. Lett.* **62**, 2563 (1989).
- [13] A. A. Ovchinnikov and Y. G. Zeldovich, *Chem. Phys. B* **28**, 215 (1978).
- [14] D. Toussaint and F. Wilczek, *J. Chem. Phys.* **78**, 2642 (1983).
- [15] A. Lin, R. Kopelman, and P. Argyrakis, *Phys. Rev. E* **53**, 1502 (1996).
- [16] L. W. Anacker and R. Kopelman, *Phys. Rev. Lett.* **58**, 289 (1987).
- [17] K. Lindenberg, B. J. West, and R. Kopelman, *Phys. Rev. Lett.* **60**, 1777 (1988).
- [18] P. Argyrakis and R. Kopelman, *J. Phys. Chem.* **91**, 2699 (1987).
- [19] P. Argyrakis, R. Kopelman, and K. Lindenberg, *Chem. Phys.* **177**, 693 (1993).
- [20] K. Kang and S. Redner, *Phys. Rev. Lett.* **52**, 955 (1984).
- [21] K. Kang and S. Redner, *Phys. Rev. A* **32**, 435 (1985).
- [22] P. Argyrakis, *Comput. Phys.* **6**, 525 (1992).
- [23] E. W. Montroll and G. H. Weiss, *J. Math. Phys. (N.Y.)* **6**, 167 (1965).
- [24] F. S. Henyey and V. Seshadri, *J. Chem. Phys.* **76**, 5530 (1982).
- [25] R. Kopelman and P. Argyrakis, *J. Chem. Phys.* **72**, 3050 (1980).
- [26] P. G. de Gennes, *C. R. Acad. Sci. Ser. B* **296**, 881 (1983).
- [27] F. Leyvraz and S. Redner, *Phys. Rev. A* **46**, 3132 (1992).