Hierarchies of nonclassical reaction kinetics due to anisotropic confinements

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In contrast to classical chemical reaction kinetics, for diffusion limited chemical reactions the anisotropy of the geometry has far reaching effects. We use tubular two and three-dimensional spaces to illustrate and discuss the dimensional crossover in $A+B \to 0$ reactions due to dimensional compactification. We find that the crossover time $t_c = W^\alpha$ scales as $\alpha = \beta/(a-b)$, where a, b, and β are given by the earlier and the late time inverse density scaling of $\rho^{-1} \sim t^a$ and $\rho^{-1} \sim t^b W^\beta$, respectively. We also obtain a critical width W_c below (above) which the chemical reaction progresses without (with) traversing a two or three-dimensional Ovchinnikov–Zeldovich (OZ) reaction regime. As a result we find that there exist different hierarchies of dimensionally forced crossovers, depending on the initial conditions and geometric restrictions. Kinetic phase diagrams are employed, and exponents are given for various Euclidean and fractal compactified geometries, for the $A+B$ and $A+A$ elementary reactions. Monte Carlo simulations illustrate some of the kinetic hierarchies. © *1999 American Institute of Physics.* [S0021-9606(99)00504-8]

I. INTRODUCTION

It is well known that in diffusion-limited reactions the reaction rate is slower than in the case when the reactants are well mixed. This is valid for any spatial dimensionality, with the only assumption being that the geometry of the reaction container is isotropic. This anomaly is well understood for the prototype reactions $A+C \to C$, $A+A \to 0$, and $A+B \to 0$, and the asymptotic behavior is known for the latter case as the Ovchinnikov–Zeldovich (OZ) regime.[1,2] The slowdown in reaction rate originates from various kinds of density fluctuations, such as the reactant segregation in the bimolecular reaction of $A+B \to 0$,[3,4] and the depletion zone of the reactant in the reactions $A+C \to C$, $A+A \to A$ or $A+A \to 0$.

Recently anisotropic geometries, such as of tubular shapes, were introduced in order to investigate the behavior of experimental systems with reactions in micropipettes, capillaries, etc.[5–9] The introduction of the anisotropy poses a challenge; to understand how the reaction mechanism changes in the early time period, including the crossover between the classical and the nonclassical reactions with and without the anisotropy forced dimensional crossover, as well as the anisotropy forced crossover from one nonclassical reaction regime to another. In the classical chemical reaction, the change in the density of the reactants depends only on the global concentration, which is also the local concentration, and the reaction process does not depend on the dimensionality of the container. However, for the $A+B \to 0$ diffusion-limited reaction, there appears a reactant segregation which is due to the local concentration fluctuation stemming from the initial randomness of the reactant distribution. Due to this density fluctuation, in the bimolecular reaction $A+B \to 0$,

with equal initial densities, $\rho_A(0) = \rho_B(0)$, the density scales asymptotically as $\rho(t) \sim t^{-d/4}$, for isotropic spaces with $d \leqslant 4$, instead of the classical result $\rho_A(t) \sim t^{-1}$. Thus the governing differential equation of this reaction is

$$\frac{d\rho_A(t)}{dt} \sim -\rho_A(t)^x \qquad (1)$$

with the reaction power (order) given by $x = (4/d) + 1$, where the inverse density exponent of $\rho^{-1} \sim t^f$ is given by

$$f = \frac{1}{x-1}. \qquad (2)$$

As the reaction progresses, the segregated reactant zones keep growing until the front of the segregated reactant reaches the boundary of the container, at which time the boundary effect makes the density decrease exponentially. On the other hand, for the *anisotropic spaces*, for example *tubular*, when the front of the segregated reactant reaches the shorter boundary of the geometry, it already "feels" the boundary and the reaction rate changes dramatically when this occurs. We may call this phenomenon "dimensional compactification"[10] and we expect the time when this happens to depend on the width W of the tubular space, specifically as $t_c \sim W^\alpha$. Before this crossover, the reaction progresses "without knowing" the width of the tube but, after the crossover, the reaction follows a one-dimensional chemical reaction behavior, asymptotically, such as[7]

$$\rho^{-1} \sim t^{1/4} W^\beta. \qquad (3)$$

We define $f=a$ for $t \ll t_c$ and $f=b$ for $t \gg t_c$. While the exponents a and b have been investigated before, the W-dependence of t_c has not been studied in detail, and one

would like to know how does the early time behavior of the reaction and, in particular, the crossover time t_c (before or after the onset of the d-dimensional Ovchinnikov–Zeldovich effect) depend on W.

In this paper, in Sec. II we consider the relations between the scaling exponents α, β, and f, using the scaling ansatz in various reaction regimes and anisotropic geometries. In Sec. III we consider the early time behaviors with emphasis on the dimensional crossovers, between classical and nonclassical reactions as well as between nonclassical reactions, and also on crossovers not due to dimensional compactification. In Sec. IV we discuss the method of the calculations (simulation algorithms), while in Sec. V we present the results, with emphasis on the method developed to measure f accurately when using Monte Carlo simulation. Finally in Sec. VI we give the conclusions.

II. SCALING ANSATZ APPROACH

The scenario of the reaction in the anisotropic geometry that we use here is that at early times, before the fluctuations (which are amplified by the local chemical reaction) reach the size of the width W, the reactant density follows the power law:

$$\rho^{-1}\sim t^a. \tag{4}$$

Then there is a crossover at time t_c, which obeys a power law with W,

$$t_c=W^\alpha. \tag{5}$$

Finally, when the fluctuation is larger than the finite size W, the time power law [Eq. (4)] changes to another exponent b,

$$\rho^{-1}\sim t^b, \tag{6}$$

accompanied by a W scaling law as well (double scaling law),

$$\rho^{-1}\sim t^b W^\beta. \tag{7}$$

We call a and b the earlier and the late time exponents, respectively, and observe the inverse density scaling before and after the dimensional crossover. The exponent a can be either 1, when the dimensional crossover happens while the classical reaction is still going on, or, for instance, for $A+B\to0$, $a=d/4$ in d-dimensional tubes ($d\leq4$) if the Ovchinnikov–Zeldovich (OZ) nonclassical anomaly already has appeared before the crossover happens. If the crossover happens during the interim behavior between the classical and the OZ regimes, a has a certain effective value between 1 and $d/4$, corresponding to how much the OZ reaction has developed.

A similar approach is applied to the late time exponent b. It could be 1 if the classical reaction is still going on even in the reduced geometry, but usually it will be $b=1/4$ in tubular spaces (for any d) when the OZ reaction already has started. Also b can be any number between 1 and 1/4 if the reaction is in between these regimes, or if we have a reaction different from $A+B\to0$. Furthermore, for slabs or slices b would be 1/2, etc. (Table I).

Now we can assume a scaling ansatz such that it satisfies the above scenario,

TABLE I. Scaling exponents of chemical reactions in anisotropic spaces.

Reaction class	Geometry	a	b	$\alpha=\dfrac{\beta}{a-b}$	α'	β
$A+A\to0$	$d=d_1+1$	1	$\frac{1}{2}$	$2d_1$		d_1
	$d=d_1+2$	1	1	∞		d_1
	$d=d_f+1$	1	$\frac{1}{2}$	$2d_f$		d_f
	$d=d_f+2$	1	1	∞		d_f
	$d=1+d_f$	1	$\frac{d_s}{2}$	$\frac{2}{2-d_s}$		1
	$d=2+d_f$	1	$\frac{s_s}{2}$	$\frac{4}{2-d_s}$		2
$A+B\to0$[a]	$d=d_1+1\leq4$	$\frac{d_1+1}{4}$	$\frac{1}{4}$	2	$\frac{2d_1}{3}$	$\frac{d_1}{2}$
	$d=d_1+1>4$	1	$\frac{1}{4}$	$\frac{2d_1}{3}$	$\frac{2d_1}{3}$	$\frac{d_1}{2}$
	$d=d_1+2\leq4$	$\frac{d_1+2}{4}$	$\frac{1}{2}$	2	d_1	$\frac{d_1}{2}$
	$d=d_1+2>4$	1	$\frac{1}{2}$	d_1	d_1	$\frac{d_1}{2}$
	$d=d_f+1$	$\frac{d_s+1}{4}$	$\frac{1}{4}$	$\frac{2d_f}{d_s}=d_w$	$\frac{2d_f}{3}$	$\frac{d_f}{2}$
	$d=d_f+2$	$\frac{d_s+2}{4}$	$\frac{1}{2}$	$\frac{2d_f}{d_s}=d_w$	d_f	$\frac{d_f}{2}$
	$d=1+d_f$	$\frac{1+d_s}{4}$	$\frac{d_s}{4}$	2	$\frac{2}{4-d_s}$	$\frac{1}{2}$
	$d=2+d_f$	$\frac{2+d_s}{4}$	$\frac{d_s}{4}$	2	$\frac{4}{4-d_s}$	1

[a]For the $A+B\to0$ the column for a assumes that the crossover to segregation (Refs. 3, 4) occurs before the crossover due to dimensional compactification.

$$\rho^{-1}\sim t^a f(t/W^\alpha), \tag{8}$$

where $f(x)$ satisfies

$$f(x)=1 \quad \text{for} \quad x\ll1, \tag{9a}$$

$$f(x)=x^{b-a} \quad \text{for} \quad x\gg1. \tag{9b}$$

At this point, we can easily find out the relation between α and β

$$\alpha=\frac{\beta}{a-b} \tag{10}$$

and it becomes even simpler when we notice that $\beta=d_1$, for $A+A\to0$ and $\beta=d_1/2$ for $A+B\to0$, as

$$\alpha=\frac{d_1}{a-b} \quad \text{for} \quad A+A\to0, \tag{11a}$$

$$\alpha=\frac{d_1}{2(a-b)} \quad \text{for} \quad A+B\to0, \tag{11b}$$

where d_1 denotes the original dimensionality minus the dimensionality of the reduced geometry, for example $d_1=d-1$ for tubular and $d_1=d-2$ for slablike spaces.

For the $A+B\rightarrow 0$ reaction, we have two kinds of most important dimensional crossovers; one is called the α-transition with $a=d/4$ (for $d\leqslant 4$) and $b=1/4$, and the other is the α'-transition with $a=1$ and $b=1/4$. The scaling exponents corresponding to the α and α' transitions are shown in Table I. The scaling law for the exponent β [Eq. (7)] was derived before[8] and is also given in Table I. The scaling law derivation for the exponent α [Eq. (5)] was sketched out before[8] and relies on equating, at t_c, Eq. (7) with Eq. (4). However, there are two different cases.

Single crossover case (I): Here Eq. (4) describes the classical kinetics regime, where (we ignore the logarithmic correction for $d=2$) $a=1$ and t_c is a dimensionally forced crossover which leads directly to the one-dimensional OZ segregation regime; hence $b=1/4$. Now substituting $t=t_c$ in both Eqs. (4) and (7), and using $\beta=(d-1)/2$, gives $t_c \sim W^{2(d-1)/3}$, and thus $\alpha'=2(d-1)/3$ for any d. Note that in this case I we use ''alpha prime'' for α. Also note that in Table I we use $d_1=d-1$, the number of compactified dimensions.

Two crossovers case (II): Here the first crossover time (τ_c) is not due to the dimensional constraint but simply describes the classical to OZ crossover of Lindenberg *et al.*[11,12] for noncompactified dimensions (e.g., d-dimensional cubes where $d=2$, 3, and possibly 4). This crossover time (τ_c) is independent of the width W. Thus the dimensionally forced crossover (the second crossover) at t_c is from a time power law of $a=d/4$ to $b=1/4$. Equating again Eqs. (4) and (7), and using again $\beta=(d-1)/2$ gives $\alpha=2$. This result is limited to $2\leqslant d\leqslant 4$ and is analogous to the Einstein diffusion formula.

In principle there is also the two crossovers case III, where the dimensionality forced crossover leads to a nonclassical nonsegregated reaction regime, the so-called $A+A$ regime of the $A+B\rightarrow 0$ reaction in one dimension.[11,12] This case gives the same result as the $A+A$ reaction derived previously[8,9] and is also given in Table I. However, we doubt that this case is relevant, except possibly for very low initial densities. Here t_c is followed, eventually, by τ_c for one-dimensional systems.

Finally, we note that Table I extends the scaling results to $A+A$ reactions (which also covers the $A+C\rightarrow C$), to fractal tubes (e.g., ''toblerones'') as well as to slabs and fractal slices (e.g., ''toblerone slices'').

III. KINETIC PHASE DIAGRAM

We observe that we have various kinds of crossovers present in the systems of tubular geometry. By monitoring the density of the reactants, we noticed that the inverse density scaling changes into a different value as the reaction meets a new crossover. For a certain geometrical condition, i.e., with a fixed W, the reaction develops in a certain path, for example in two-dimensional tubes it may go from $f=1$ to $f=1/2$ and then to $f=1/4$, or from $f=1$ directly to $f=1/4$. Therefore, the understanding of the reaction mechanism behind the density change follows the full understanding of the possible paths of f-changes in time and in various geometric conditions. We consider f to be the order parameter for the chemical reaction and we draw the phase diagram

in a time–space coordinate system. In three-dimensional tubular spaces, four coordinates, t, L_x, L_y, and L_z, are allowed but normally we take $L_x=L_y=W$ and L_z is considered to be infinite so, without considering the finite size effect of the L_z-direction, we need only 2 coordinates, t and W.

However, compared to other order parameters in physics such as the density of particles in a gas–liquid phase transition or the magnetic moment in para-ferromagnetism, this density scaling exponent f is not so well defined, for it has a distinct number only asymptotically, in a large size system and only at the long time limit. Also, the transition between the phases (regimes), for example from $f=1$ to $f=1/2$, is not like those of the first order but more like the titration curves in chemistry or crossovers in percolation; the analytic behavior is approximate even at the large size limit, the so-called thermodynamic limit. However, in dealing with the kinetic behaviors of the chemical reactions in anisotropic geometries, those kinetic regimes which come from the dimensionality and the reaction process do appear in a hierarchy, and the order of appearance may be switched, depending on the geometric conditions, which can be well described by using the concept of phases and crossovers between them.

In regular (large) lattices of $V=L^d$ with $2\leqslant d\leqslant 4$, there exist only, as far as we know, two clear phases of $f=1$ and $d/4$, where the former corresponds to the classical reaction regime and the latter to the OZ regime, though we may measure many intermediate values of f which do not exist as clear phases. The classical regime is well defined in the limit of $t\rightarrow 0$ and the OZ regime at $t\rightarrow\infty$ (for infinite containers) and the crossover, t_{OZ}, depends on the initial reactant densities and on the dimensionality. The reason why ρ_O affects t_{OZ} is as follows: t_{OZ} is a time when the initial randomness of the reactant distribution changes considerably towards reactant segregation, i.e., at $t=0$ each reactant has neighbors of the same and the opposite species with equal probability but after t_c it sees its own species with much higher probability. In a randomly distributed reactant, $V\rho^2\delta t$ reactants disappear in δt, so we guess that a considerable change in the distribution is made after $t_r\sim\rho^{-2}$. Therefore now we think of t_r as a typical time when the initial randomness of reactants disappears.

Also the dimensionality is very important in the formation of the density fluctuations or the segregation, i.e., OZ reaction. We consider an ensemble of small volumes of v in which the A and B particles exist randomly with the initial density $\rho_A(0)=\rho_B(0)=\rho$. Then, due to the statistical fluctuations, each volume has $\rho v\pm\sqrt{\rho v}$ particles. As the particles move randomly, maximally $v(t)=\xi^d=t^{d/2}$ is correlated, i.e., those density fluctuations in smaller areas than $v(t)$ disappear, forming unimolecular domains. Therefore we can think of such a time necessary for washing out the density fluctuations in a certain volume (where the difference between A and B particles is constant) by equating

$$\tau_{OZ}\sim V^{2/d}\sim\rho_0^{-2/d}. \tag{12}$$

This agrees with previously derived results for τ_{OZ}.[12] Therefore, for a very sparse density condition, higher dimensional density fluctuations disappear faster than the low dimensional ones. In other words, the three-dimensional OZ al-

ways appears earlier than the one-dimensional OZ reaction regime. Although the characteristic time for the appearance of the one-dimensional OZ scales with the same power ρ^{-2} as the characteristic time for the disappearance of randomness, t_r, the higher dimensional OZ reaction appears faster than the one-dimensional OZ, and thus the higher dimensional OZ is faster than t_r in the tubular geometry.

For $2 \leq d \leq 4$ tubes there exist only the $f=1$ classical regime at $t=0$ and the OZ reaction regime of $f=1/4$ at $t=\infty$ (or $f=d/4$ if $W \approx L$). In a tube, as the reaction progresses, the $f=1$ classical regime changes to the $f=d/4$ OZ regime, if the growth of the density fluctuation domain is not blocked by the tubular width W. Then the crossover time is fixed by the initial density condition which will scale as $\tau_{OZ} \sim \rho_0^{-2/d}$ without dependence on W. Later the dimensional crossover happens at $t_c = W^\alpha$, with $\alpha=2$, in tubular spaces, when $a=d/4$ and $b=1/4$ [see Eq. (10)].

However, if the width is small enough for the reaction to feel the tubular wall before the three-dimensional fluctuation domains form themselves, $f=1$ of the d dimensional classical regime directly crosses over to $f=1/4$, the one-dimensional OZ regime (where the reaction skips the $f=d/4$, d dimensional OZ regime). We call this crossover the α'-transition and the crossover time is $t_c = W^{\alpha'}$, with $\alpha' = 2(d-1)/3$, if $a=1$ and $b=1/4$. We note that this α' depends on the dimensionality d while α does not. For $d > 5$, this is the case for all W.

We expect the upper limit of the time when the d dimensional *classical* reaction feels the W boundary to be $W \approx \sqrt{t}$, so the critical width below which the α'-transition exists is obtained from

$$\tau_{OZ} \sim \rho_0^{-2/d} \sim W^2 \qquad (13)$$

giving $W_c \sim \rho_0^{-1/d}$. Therefore the tubular space whose width is less than W_c will have a dimensional crossover with time-scaling with the α' and the reaction skips the d dimensional OZ reaction regime.

The complete phase diagram (for a given ρ_0) of the inverse density scaling f, in $t-W$ space, is given in Fig. 1. We need to keep in mind when considering this conceptual phase diagram that due to the continuous changes in the f value even in large systems, there may or may not exist a clear α'-transition, especially for high ρ_0.

IV. METHOD OF CALCULATIONS

Monte Carlo simulations were employed as follows: first we prepare the tubular lattice of volume $V = LW^{d-1}$ in the computer memory. Then all reactants are placed on the lattice in this manner: One A particle is placed in a random position using customary random number generators. One B particle is also placed in the same manner. Any number of particles can occupy a given site at one moment. Thus the incoming particle ignores the presence of the former particle or particles (they are "bosons"). We repeat the same procedure over and over again until the total number of $N = V\rho(0) = LW^{d-1}\rho(0)$ pairs have been placed on the lattice. In doing so, all A and B particles totally ignore all the other particle locations, regardless whether they are of the same
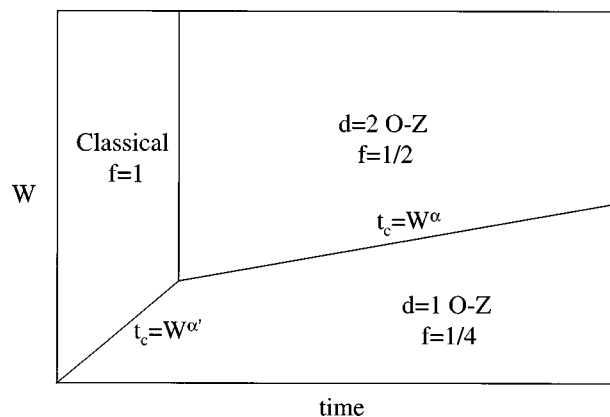

FIG. 1. Schematic phase diagram (for a given ρ_0) of the behavior of f, as a function of time and lattice width W, for the $A+B$ reaction in two-dimensional tubular lattices. One can distinguish at early times the classical kinetics result of the slope $f=1$, and at long times the higher ($2d$) and one-dimensional OZ results of 1/2 and 1/4, respectively. Different values of the exponent characterize the scaling laws in the different regions, while there exists one "triple" point ($W = W_c$) where these trends come together. For a 3-dim tube replace $f=1/2$ by $f=3/4$ (and $d=2$ by $d=3$).

species or not. Eventually a total of $2N$ particles are created. The number of A particles is exactly equal to the number of B particles. The reaction starts by letting the particles diffuse on the lattice. We randomly pick particles, one at a time, regardless of their type, which then move to one of their neighboring sites. Each move (and all subsequent moves) consume a certain time, which increases the reaction clock by an amount equal to $\Delta t = 1/N(t)$, where $N(t)$ is the number of particles present at this particular time. If the new site is empty or if it is occupied by particle(s) of the same type, then the particle move is completed, and we go on to the next particle. But if the new site contains a particle of the opposite species, then both of them are taken out from the lattice (annihilated), and the total number of particles is decreased by 2. The reaction proceeds with the rest of the particles. Notice that reactions occur only due to diffusion, while any opposite particles that are initially (at time $t=0$) placed on the same lattice site do not react, but are free to diffuse when the clock is turned on. Since the shape of the reaction volume is tubular, and we want to investigate the effect of the finite size of the short dimensions, we use reflective boundary conditions in the short dimensions, but cyclic conditions in the long dimension. When the particle attempts to move out of the boundary in the short dimension the move is not allowed, but consumes a regular time unit (as in the so-called myopic ant model). We monitor the particle density $N(t)/N(0) = \rho(t)$ as a function of time.

V. RESULTS

Conventionally the exponent f has been measured from the slope of a log–log graph of $[1/\rho(t)] - [1/\rho(0)]$ vs t, which produces a variety of different regimes, as a function of time. The use of the quantity $[1/\rho(t)] - [1/\rho(0)]$ relates to the value of $x=2$ in the rate equation [Eq. (1)]. We generalize now this equation, in the spirit of the discussion of the previous sections, and develop a direct way to measure f, as follows: From Eq. (1) we get a general solution,
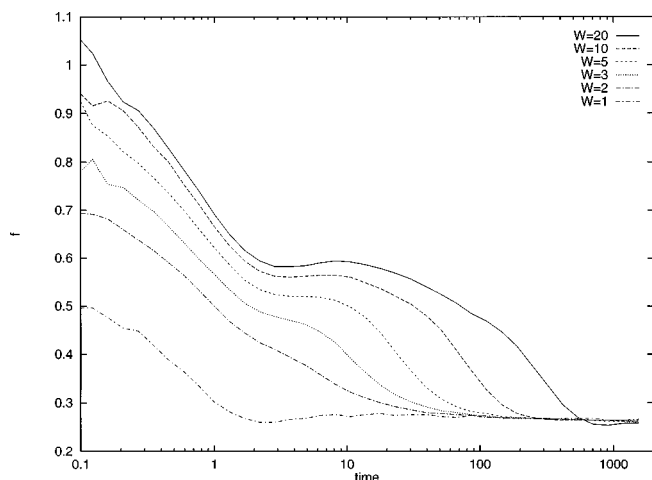
FIG. 2. The exponent f as a function of time for the $A+B$ reaction in 2-dim tubular lattices. Top to bottom: $W=20$, 10, 5, 3, 2, and 1. $L=10\,000$ and averages of 10 000 runs. Notice that the case $W=1$ corresponds to a simple 1-dim lattice.

FIG. 3. Similar plot of the scaling exponent f, as in Fig. 2, but now for the case of 3-dim tubular lattices. Top to bottom: $W=10$, 5, 3, 2, and 1. $L=5000$ and averages of 2000 runs.

$$\frac{1}{\rho(t)^{x-1}}-\frac{1}{\rho(t_1)^{x-1}}\sim t-t_1 \tag{14}$$

that includes the exponent x as a parameter. Obviously, it is very difficult to solve this equation in the entire time domain using a single x value, so we do this piecewise, and we plot only three consecutive data points at a time, thus covering a very limited time domain. However, in this small domain only one value of x will produce a straight line segment, while all other x values will give either concave or convex curves. By varying x we can find the value that produces a straight line, and save it. Next, the same is done for the next set of three points, and we thus find x in the entire time domain. Specifically, we use data points at time t_1, t, and $t+\tau$ to fit the data, in the form

$$\log\frac{\dfrac{1}{\rho(t+\tau)^f}-\dfrac{1}{\rho(t_1)^f}}{\dfrac{1}{\rho(t)^f}-\dfrac{1}{\rho(t_1)^f}}=\log\frac{t+\tau-t_1}{t-t_1}. \tag{15}$$

The reason why we chose the log-scale on both sides is because the linear relation is seen only in a log–log scale. Now we use the computer program for f to get the best fitting values which satisfy the above equation. Those f values which satisfy $0.995<\text{LHS/RHS}<1.005$ were collected so as to compare the uncertainties in this measurement. A typical measurement is seen in Fig. 2, which shows clear transitions from $f=1$ to $f=1/2$ and then to $f=1/4$ in the two-dimensional tubular chemical reaction.

In Figs. 2 and 3 we show a plot of f vs time, for several different W values. Included is the case of $W=1$, which is simply the one-dimensional lattice. We observe that at early times, $t\ll 1$, we have a very large amount of noise for all cases. An approximate average value can still be estimated; for $W=1$, we clearly see that the average value is about 0.5, while for all larger W values, we see that it is of the order of 1. This result is consistent with previous works and the literature, because for the $W=1$ case we have at early times
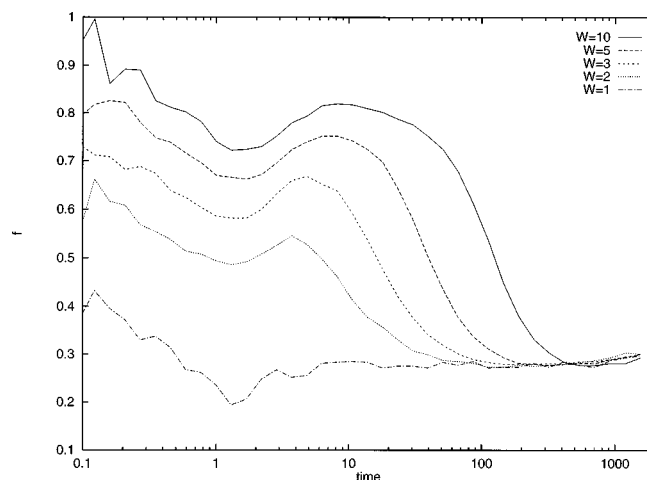
the $A+A$ behavior, which has an exponent $f=1/2$, while for $W>1$ we have the $A+A$ behavior in two and three-dimensional lattices, since the effect of the tubular structure (one-dimensional character) is not felt yet at such early times. The 2-dim $A+A$ case has a logarithmic correction factor to the classical behavior, which typically is of the order of 10%, but this is within the level of noise in the present figure. Further we notice, that for the $W=1$ case f falls quickly to a constant value of 1/4, which is the OZ expected result. In this case we have only one crossover, that from the early time behavior to the OZ result. As W is increased we observe that the curves start having a second plateau, whose extent increases with increasing W. The plateau is approximately at the value $f=0.5$, for Fig. 2 and $f=0.75$ for Fig. 3, which shows that in these systems, in this intermediate time domain, the reaction proceeds in the high dimensional OZ regime until the effect of the restricted W is felt. At that point the f values are further decreased to reach the asymptotic value of 1/4, which is simply the expected long-time behavior of the OZ one-dimensional system. This is the second crossover, which is dimensionally forced. Thus, this figure contains a pictorial representation of both crossovers present, and the trend by which they collapse to one. It is seen that at higher W's the first crossover happens about the same time for all W's. This is expected for the τ_c transition, which is W independent (see Fig. 1). However, the second transition is W dependent and t_c rises monotonically with W, which is expected from the scaling $t_c\sim W^\alpha$ (compare Fig. 1). On the other hand, the lowest W curves ($W=2,3$) approach the case (I) of a single crossover (compare Fig. 1). It thus appears that W_c is about 2 or 3 for this high density case.

The apparent ''overshoot'' during the τ_c crossover in Fig. 3 ($d=3$) also appears for $d=2$, but for lower initial densities (ρ_0). Its origin is not clear to us, but the fluctuations (noise) in the simulations prevent clear-cut conclusions.

Regarding the exponents α, we note that the scaling result for α is valid only for $W\gg W_c$ and for α' for $W\ll W_c$. Our present simulations do not cover either one of these

limits, but fall close to W_c, and slightly above. For $d=2$ we expect $\alpha=2$ and $\alpha'=2/3$. We obtain an effective value of about 1.4 from the simulations, which is indeed intermediate to the expected limits. Previous work gave about 1.0 for $d=2$ (and 1.4 for $d=3$, where we expect $\alpha'=4/3$ and $\alpha=2$). We note that the exponent β is independent of W_c and thus easier to obtain and satisfactory simulation values have been obtained in previous work.[5–9]

VI. CONCLUSIONS

Geometries with compactified dimensions show a rich kinetic behavior for elementary bimolecular reactions. As an example, the $A+B\rightarrow0$ reaction in a tube shows several cases of crossovers, with different kinetic regimes and distinct crossover exponents relating the crossover time t_c to the tube-width W. Critical tube widths W_c, which scale with initial density, separate these crossover cases. Case I (below W_c) has a single W-dependent, dimensionally forced kinetical crossover, from classical to one-dimensional Ovchinnikov–Zeldovich (OZ) behavior. Case II (above W_c) has a first, W-independent crossover from classical to d-dimensional ($d=2,3$) OZ behavior, followed by a W-dependent crossover from d-dimensional to one-dimensional OZ kinetic behavior. Case III (low density) has a dimensionally forced W-dependent crossover to a depletion zone controlled $A+A$ like regime, followed by a W-independent crossover to one-dimensional OZ behavior.

These different kinetic regimes can be described by kinetic phase diagrams. The tubular geometry $A+B$ reaction cases are generalized to other bimolecular reactions and to other compactified geometries, Euclidean and fractal. The scaling arguments are consistent with Monte Carlo simulations and are amenable to experimental verification in capillaries and other confined domains.

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