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Non-classical kinetics and reactant segregation in d-dimensional tubular spaces

Raoul Kopelman [a,1], Anna L. Lin [a,2], Panos Argyrakis [b,3]

[a] *Department of Chemistry, University of Michigan, Ann Arbor, MI 48109-1055, USA*
[b] *Department of Physics, University of Thessaloniki, 54006 Thessaloniki, Greece*

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Abstract

For the diffusion-controlled A + B → products reaction in d-dimensional tubular spaces, with length L and width W, where $L \gg W$, we show that the Ovchinnikov–Zeldovich reactant segregation has no upper critical dimension and that the reciprocal density ρ^{-1} scales asymptotically with $W^{(d-1)/2}t^{1/4}$. This is consistent with Li's scaling ansatz for $d = 2$, 3 and with Monte Carlo simulations. For the crossover time t_c this gives a scaling relation $t_c \sim W^{\alpha}$ provided that W is wide enough to allow segregation at $t < t_c$. Similar scaling arguments are used to derive the scaling relations between ρ^{-1} and W and between t_c and W for the A + A → 0 and A + C → C reactions in d-dimensional tubular lattices. We also extend these scaling relations to square slab spaces of volume $L^2 \times W^{d-2}$ and to tubular or square-slab spaces with fractal cross sections.

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1. Introduction

The topic of the dimensional crossover in baguette-like lattices has been recently investigated [1–4] for three diffusion controlled processes: the number of distinct sites S_t visited by a single random walker in time t, and the diffusion-limited A + A → 0 and A + B → 0 reaction processes. These processes, as well as the A + C → C reaction, have been studied before by a variety of methods [5–19] in one, two, and three dimensions, but under isotropic space conditions where length equals width equals height (i.e. $L = W = H$). We have recently [1,2] employed Monte Carlo simulation methods to model the behavior of the first three processes on tubular lattices where $L \gg W$ and determined the scaling of the dimensional crossover time with lattice width W. The Einstein diffusion relation, $t \sim W^2$, which successfully describes the onset of finite size effects for these processes in isotropic lattices, where W is the linear length in any dimension, does not necessarily describe the scaling of the dimensional crossovers [1,2] from higher-dimensional behavior to the one-dimensional behavior found in tubular spaces. However, algebraic scaling equations of the form

$$t_c \sim W^{\alpha}, \tag{1}$$

where t_c is the time at which the density ρ crosses over from a higher-dimensional behavior to the one-

[1] E-mail: kopelman@umich.edu.
[2] E-mail: alin@chem.lsa.umich.edu.
[3] E-mail: argyrakis@physics.auth.gr.

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dimensional behavior, were found to hold. An analytical solution to the random walk problem, i.e. S_t, on tubular lattices was recently given by Li [3], which he extended, by an argument put forth in Ref. [9], to predict a scaling for the $A + A \rightarrow 0$ process. Our emphasis here is on the *asymptotic* scaling expressions for these three binary elementary reactions in tubular and related spaces of interest; in particular, for the $A + B \rightarrow 0$ reaction and its concomitant segregation. From these expressions we derive general expressions for the scaling relation between W and t_c for the dimensional crossover of the $A + B \rightarrow$ products, $A + A \rightarrow$ products, and $A + C \rightarrow C +$ products processes occurring in tubular ($L \times W^{(d-1)}$) or in slab ($L^2 \times W$) spaces.

2. Scaling of dimensional crossover for S_t in tubes

For completeness, Li's derivation of the $t_c \sim W^{\alpha}$ scaling relation for S_t is briefly described. Li found the t_c dependence on W for the single random walker by setting equal the equations describing the short-time and long-time behavior of S_t, the number of distinct sites visited, in a tube. He argued that the *short-time* behavior of S_t is described by the well known asymptotic solutions in free space [20]

$$S_t \sim \frac{t}{\ln(t)}, \quad \text{2-D}, \tag{2}$$

$$S_t \sim t, \quad \text{3-D}, \tag{3}$$

while the *long-time* behavior is described by the relation

$$S_t \sim W^{d-1} t^{1/2}, \tag{4}$$

where W is the linear size of the tubular lattice along the transverse directions and d is the embedding dimension. The point of intersection of these two solutions is defined as t_c. Thus, solving the equation $t_c \sim \sqrt{t_c}\, W^2$ for 3-D baguettes yields the scaling relationship between t_c and W,

$$t_c \sim W^4 \tag{5}$$

and thus $\alpha = 4$, in excellent agreement with the exponent that we reported earlier for this scaling relation [1,2]. Similarly, for 2-D, Li found

$$\frac{\sqrt{t_c}}{\ln\sqrt{t_c}} \sim W, \tag{6}$$

which has no simple global scaling behavior. For large W (thus large t_c), this asymptotic solution is justified and approximates the scaling relationship $t_c \sim W^2$, or even better, $t_c \sim W^{2.3}$, for 2-D tubes of reasonably large W. The value of the scaling exponent of S_t measured in our simulations [1,2] for 2-D tubes was $\alpha = 2.6 \pm 0.4$ which is consistent with this expectation, though for smaller W's the early-time Henyey–Seshardri formula [21] should be used rather than (2).

3. $A + A \rightarrow A$ and $A + C \rightarrow C$ in n-dimensional tubular spaces, based on S_t scaling

When discussing the non-classical behavior of elementary reaction–diffusion processes, it is conventional to express the progress of the reaction in terms of the instantaneous reactant density ρ, or its inverse ρ^{-1}. For the $A + A \rightarrow$ products reaction–diffusion system, the crossover time can be defined as the point at which the reactant density changes its temporal scaling behavior from that predicted for 2-D or 3-D to that predicted for 1-D. The scaling exponents which give the dependence of t_c on W for S_t in tubular lattices can also be assumed to describe the scaling of the $A + A \rightarrow$ products reaction–diffusion process on such lattices, based on the ansatz given in Ref. [9], which employs the concept of a *depletion zone* S_t formed around surviving A particles as a consequence of the distinct volume S_t swept out by such particles [10]. Thus, for $A + A \rightarrow 0$ or $A + A \rightarrow A$,

$$\rho^{-1} - \rho_0^{-1} \sim S_t \sim W^{d-1} t^{1/2}, \tag{7}$$

giving the same theoretical α exponents as those found for S_t. Our simulations of $A + A \rightarrow 0$ indeed gave $\alpha = 4.2 \pm 1$ for 3-D tubes and $\alpha = 2.8 \pm 0.8$ for 2-D tubes. This same argument concerning the temporal effect on the rate law of a *depletion zone formed around surviving particles* is even more clearly applied to the reaction $A + C \rightarrow C$, where both the A and C particles are mobile, and does result in the same values for α and β as are found for the $A + A \rightarrow$ products reaction.

An alternative way to obtain the above results is to describe the reaction probability for both the

A + A → A and A + C → C reactions in terms of the reaction probability P per particle,

$$P = \rho^{-1}\frac{\partial \rho}{\partial t} \sim \frac{\partial S}{\partial t}, \tag{8}$$

where $\partial S/\partial t$ is the *rate* of exploration of particle A or C, i.e. the rate of growth of the Wiener sausage describing its exploration volume. We note that in $d = 3$ we get the classical *rate constant* $k = \partial S/\partial t$ at long time, i.e. $P = \text{const}$. Thus, while *classically there is no crossover*, it is obvious that the crossovers of these two reactions follow the scaling of S_t with W. As (3) applies for $d \geq 3$, we get from it and from (4)

$$t_c \sim W^{2(d-1)}, \quad d \geq 3 \tag{9}$$

and thus $\alpha = 2(d-1)$ for S_t, as well as for A + A → A and A + C → C. Below we generalize this expression for fractals and for slabs. We also give an equivalent argument, based on the scaling of Toussaint and Wilczek [6], and of Kang and Redner [7,8], for the result of (7) in the asymptotic limit ($t \sim \infty$) applied to the most interesting case, i.e. the reaction A + B → 0, which leads to reactant segregation in d-dimensional tubes, slabs and fractals.

4. A + B → 0 in n-dimensional tubular spaces

To develop a scaling relation between the long-time density ρ and W, as well as between t_c and W, for the A + B → 0 process on baguette-like lattices, we applied the scaling argument initiated by Ovchinnikov and Zeldovich [5] and then later successfully applied by Toussaint and Wilczek [6], as well as Kang and Redner [7,8], to describe the asymptotic time dependence of $1/\rho$, where $\rho = \rho_A = \rho_B$, in free space.

We first reproduce the Toussaint–Wilczek [6] argument for A + B → 0 *without segregation*. Conceptually the argument is for the A + A → 0 reaction or, more intuitively, for the A + A → A reaction, since the argument is based on the surviving particle sweeping out a local volume $v \sim l^d$ in time $t \sim l^2$. The reciprocal density in the case of compact random walk is

$$\rho^{-1} \sim v \sim t^{d/2}, \quad d \leq 2, \quad t \sim \infty, \tag{10}$$

with $d = 2$ being the critical dimension, requiring a logarithmic correction for the above equation. We note that for fractals this expression simply has the spectral dimension d_s replacing d [7,8]. For the baguette we again write $v = W^{d-1}l$ and $t \sim l^2$, which gives

$$\rho^{-1} \sim W^{d-1}t^{1/2}, \quad t \to \infty \tag{11}$$

for all dimensions d, because asymptotically the random walk is always compact. This result is consistent with Eq. (7).

We now turn to the Toussaint–Wilczek argument for the A + B → 0 reaction *with segregation*, i.e. an initial random distribution of the A and B particles with $N_A = N_B = N$ and fluctuations $\sqrt{N_A} = \sqrt{N_B} = \sqrt{N}$ in the *local* volume v,

$$N_A(t=0) = N_B(t=0) = \rho_0 v \pm \sqrt{\rho_0 v}, \tag{12}$$

where $N_{A(B)}$ is the *local* number of A (B) particles and where ρ_0 is the *global* density at $t = 0$. The usual scaling argument again proceeds from $v = l^d$, where l is the linear length of the local volume, and by again relating the time needed to sweep out this volume to the surviving particles' diffusion time: $t \sim l^2$. This now results in the well known Ovchinnikov–Zeldovich scaling relation for ρ^{-1} as $t \to \infty$,

$$\rho^{-1} \sim t^{d/4}, \quad 1 \leq d \leq 4, \quad t \sim \infty. \tag{13}$$

We generalize this approach to the baguette problem by writing

$$v = lW^{d-1} \tag{14}$$

and thus re-writing (12) as

$$N_A(0) = N_B(0) = \rho_0 lW^{d-1} \pm \sqrt{\rho_0 lW^{d-1}}. \tag{15}$$

In the asymptotic limit of this equation where the *second term* of (15), which is a measure of the local fluctuations in the reactant density around the mean, dominates, we find the expression for the quantity of interest

$$\rho = \rho_A(t) = \rho_B(t) \sim \frac{\sqrt{N}}{v} = \frac{\sqrt{\rho_0 lW^{d-1}}}{lW^{d-1}}$$
$$= \sqrt{\rho_0}\, l^{-1/2} W^{-(d-1)/2}. \tag{16}$$

Since we are interested in the relationship between the reactant density and *time* [5–8], we substitute

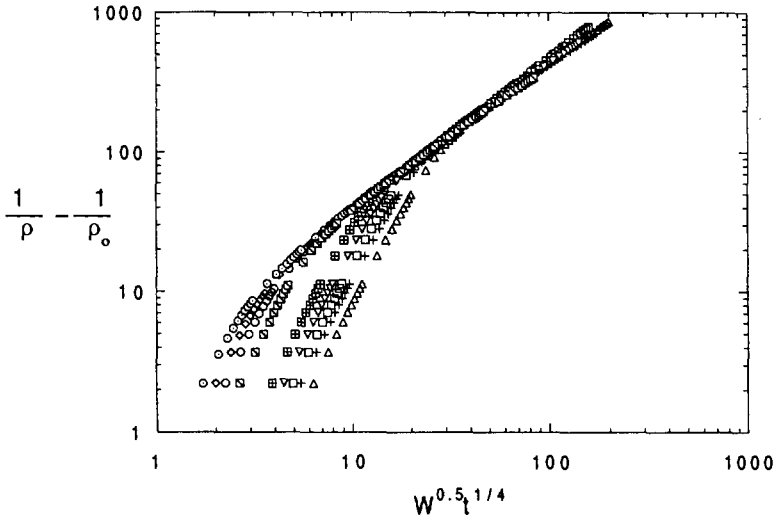

Fig. 1. Plot of $\langle \rho(t) \rangle^{-1} - \rho_0^{-1}$ versus $W^{0.5} t^{1/4}$ for the A + B reaction in 2-dimensional tubes. The different symbols correspond to the widths: $W = 3$, 4, 5, 7, 10, 15, 20, 25, 30, and 40. The length $L = 10^5$ in all cases. A total of 10 realizations were used in each case. The initial density, ρ_0, is 0.4 particle/site in each species (in A and B).

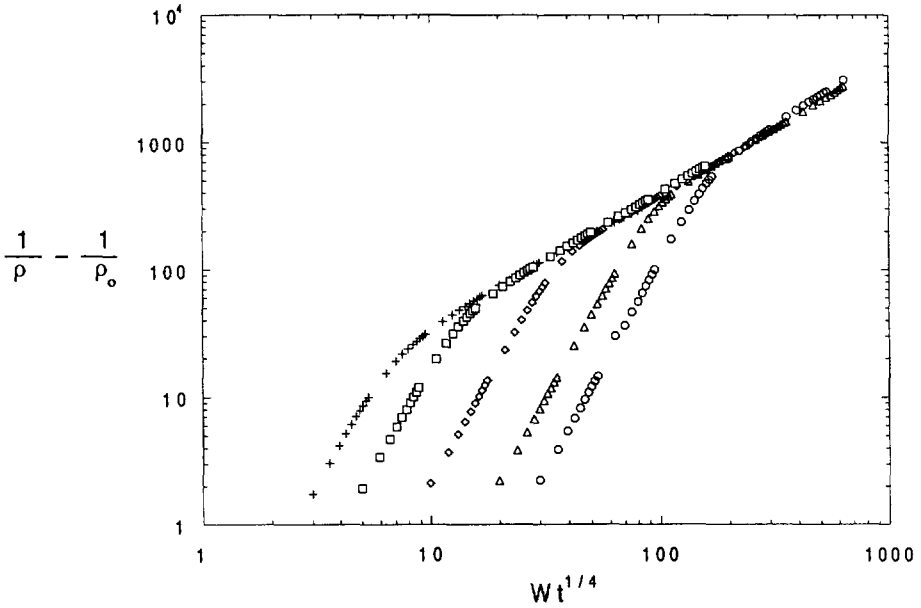

Fig. 2. Plot similar to Fig. 1 except that the x-axis is $Wt^{1/4}$, i.e. the value of the exponent β is 1.0. The reaction is in 3-dimensional tubes of width × height = 3 × 3, 4 × 4, 5 × 5, 10 × 10, 20 × 20, 30 × 30 and 50 × 50. The tube lengths vary from $L = 10^3$ to 1.2×10^5. The initial density ρ_0 is 0.4 particle/site in each species (type A and type B).

into (16) the Einstein diffusion relation $l \sim Dt^{1/2}$, where D is the diffusion constant, to obtain

$$\rho \sim t^{-1/4} W^{-\beta}, \tag{17}$$

where

$$\beta = \frac{d-1}{2}. \tag{18}$$

From this derivation, when $d = 2$, $\beta = 1/2$ and when $d = 3$, $\beta = 1$, in agreement with the values of β obtained numerically (see below). We note that (18) has no upper critical dimension, i.e. is valid for arbitrarily high dimension d. Thus, segregation persists in arbitrarily high-dimensional *tubes*, in contrast to *cubes* with $d > 4$.

Figs. 1 and 2 give plots of $\rho_A^{-1} - \rho_{A_0}^{-1}$ versus $W^{\beta} t^{1/4}$, which depict the progress of the A + B → 0 reaction process in 2-D and 3-D baguettes, respectively. In the plots shown, $\beta = 1/2$ for Fig. 1, the 2-D case, and $\beta = 1$ for Fig. 2, the 3-D case. The different curves in each figure are the data obtained from simulations which employed different tube widths. The data collapse of these curves illustrates the effectiveness of the scaling relation (17). As the scaling exponents β are derived for the limit of large W, it is not surprising that the data collapse for the small W's of our simulations is rough, similar to the result of Li [3].

As described before for the A + A → A and A + C → C reactions, the crossover time scaling exponent α (see (1)) can be derived from β by equating, at t_c, the power of (17) with the power of the early-time behavior. For $d = 2,3$ and 4:

$$t_c^{d/4} = t_c^{1/4} W^{\beta} = t_c^{1/4} t^{\beta/\alpha} = t_c^{1/4} t_c^{(d-1)/2\alpha}, \quad D \le 4 \tag{19}$$

and therefore $\alpha = 2$. We note that for $d > 4$, the classical regime is always valid at early times, thus

$$\rho^{-1} \sim t \sim t^{1/4} t^{(d-1)/2\alpha}, \tag{20}$$

and therefore $\alpha = 2(d-1)/3$ so that $\alpha > 2$ for $d > 4$.

5. A + A → A and A + C → C in *n*-dimensional tubular spaces, based on A + B scaling

We apply a similar scaling analysis to the A + A → A problem, noting that for $d \le 2$ the random walk executed by each particle is reentrant and thus the probability that its walk passes through any given point approaches one [6]. Any surviving particle has swept out a region of linear size l and occupies a volume l^d in isotropic space. Generalized to the tubular geometry, the volume per particle is

$$\rho(t)^{-1} \sim W^{d-1} l, \quad d \le 2. \tag{21}$$

Using the Einstein relation $l \sim \sqrt{t}$ gives the time dependence of ρ,

$$\rho^{-1} \sim W^{\beta} \sqrt{t}, \tag{22}$$

where

$$\rho = d - 1, \tag{23}$$

which is the same exponent as is found in (4) for S_t, as expected. Equating the early-time 3-D behavior, $\rho^{-1} \sim t$, to the asymptotic (1-D) behavior (22), $t \sim W^{\beta}\sqrt{t}$, yields the scaling relationship between t_c and W

$$t_c \sim W^{2(d-1)}. \tag{24}$$

This gives $t_c \sim W^4$ for $d = 3$ and $t_c \sim W^2$ for $d = 2$, i.e. $\alpha = 4$ and $\alpha = 2$, respectively, the same values of α and β as determined by Li [3] via a somewhat different scaling argument, as pointed out before. Obviously for the A + C → C reaction (with both A and C mobile) a completely analogous argument can be given for the particle C sweeping out the volume $v = W^{(d-1)} l$. Finally, we note that the results of this section are fully consistent with Section 3, and in particular Eq. (7).

6. A + B → 0 in 3-dimensional slabs

A very similar scaling argument can be applied to an A + B → 0 reaction occurring in a square slab of finite width, W, where the length L in two of the dimensions is much larger than W. In this case the local particle density can be expressed by re-writing (12) as

$$N_A = N_B(0) = \rho_0 l^2 W^{d-2} \pm \sqrt{\rho_0 l^2 W^{d-2}}. \tag{25}$$

Again, we are interested in the relationship between the reactant density and time. We here express (25) in terms of the density, as $t \to \infty$, by dividing the $\sqrt{N}$ terms by v, which for the finite width slab is $v =$

$l^2 W^{d-2}$. Substituting $l^2 \sim Dt$ gives the desired relation between ρ and t

$$\rho_A \sim t^{-1/2} W^{-\beta}, \tag{26}$$

where

$$\rho = \frac{d-2}{2}. \tag{27}$$

Therefore, in a 3-D square slab lattice with a finite width W, $\beta = 1/2$. Again there is no upper critical dimension limit to this scaling relation. From this relation one easily derives α (see Table 1).

7. Scaling relations in tubular and slab spaces with fractal cross sections

The form of the scaling exponents α and β derived in the previous three sections can be generalized to tubular and slab spaces with fractal cross sections by substituting the spectral dimension d_s for the Euclidean dimension d in the equations for α and substituting the fractal dimension d_f for the Euclidean dimension d in the equations for β, e.g. see Table 1. These substitutions reflect that β accounts for the *static* spatial constraint of the space, while α is a measure of the *dynamic* dimension imposed on the particles within the tubular or slab space.

8. Summary

A scaling argument, first proposed by Ovchinnikov and Zeldovich and later adopted by Toussaint and Wilczek and by Kang and Redner, describing the reaction kinetics of the diffusion-limited $A + B \to 0$ (and also implicitly the $A + A \to A$) reaction in free space, was used to describe the scaling behavior of the above reactions, as well as the $A + C \to C$ reaction and S_t, in tubular and square slab spaces. We showed that the Ovchinnikov–Zeldovich reactant segregation has no upper critical dimension in tubular spaces and that the reciprocal density ρ^{-1} scales asymptotically with $W^{(d-1)/2} t^{1/4}$, in agreement with the scaling ansatz proposed by Li, and with Monte Carlo simulations. We also generalized this analysis to square slab geometries. From this scaling analysis we are able to find the values of the exponent α of the relation $t_c \sim W^{\alpha}$ between the dimensional crossover time t_c and the tube (or slab) width W. The analysis was generalized to tubular and slab spaces with fractal cross sections by making the

Table 1
Scaling exponents α and β for different reaction processes occurring in various anisotropic spaces

Substrate type	Reaction class	α	β
tube	$A + B \to 0$	$2,\ d \le 4$	$(d-1)/2$
		$2(d-1)/3,\ d > 4$	$(d-1)/2$
tube	$A + A \to 0$	$2,\ d \le 2$	$d-1$
		$2(d-1),\ d > 2$	$d-1$
tube	$A + C \to C$	$2,\ d \le 2$	$d-1$
		$2(d-1),\ d > 2$	$d-1$
slab	$A + B \to 0$	$2,\ d \le 4$	$(d-2)/2$
		$d-2,\ d > 4$	$(d-2)/2$
slab	$A + A \to 0$	a	$d-2$
slab	$A + C \to C$	a	$d-2$
fractal tube	$A + B \to 0$	$2(d_f-1)/(d_s-1)$	$(d_f-1)/2$
fractal tube	$A + A \to 0$	$2(d_j-1)/(d_s-1),\ d \le 2$	d_f-1
fractal tube	$A + C \to C$	$2(d_f-1)/(d_s-1),\ d \le 2$	d_f-1
fractal slab	$A + B \to 0$	$2(d_f-2)/(d_s-2),\ d \le 4$	$(d_f-2)/2$
		$d_f-2,\ d > 4$	$(d_f-2)/2$
fractal slab	$A + A \to 0$	a	d_f-2
fractal slab	$A + C \to C$	a	d_f-2

[a] α is undefined because there is no crossover.

appropriate substitutions of d_f and d_s for d in the equations for α and β. Monte Carlo simulations on wider tubes as well as fractal tubes and slabs are in progress.

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