COMMENTS

Comments are short papers which criticize or correct papers of other authors previously published in the **Physical Review.** *Each Comment should state clearly to which paper it refers and must be accompanied by a brief abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

Comment on ''Crossover time of diffusion-limited reactions on a tubular lattice''

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 17 April 1997)

Li derived a scaling argument concerning the dimensional crossover of the bimolecular diffusion-limited $A+B\rightarrow 0$ reaction in two- and three-dimensional tubular lattices, showing significant disagreements with Monte Carlo simulations [Phys. Rev. E **55**, 6646 (1997)]. Here we explain that this apparent discrepancy originates from the finite-size effects related to the short dimensions of the tubes. Depending on tube width, two different cases arise: one where segregation occurs before the crossover (the Li case) and another where it only occurs after the crossover (the simulation case). [S1063-651X(97)07311-X]

PACS number(s): 05.40.+j

In a recent paper [1], Li elaborated on the dynamics of random walks and model chemical reactions in tubular lattices. These are lattices of length L, width W, and volume $W^{d-1}L$, where $d=2,3$ and $L\gg W$. The properties investigated include the number of distinct sites visited in t steps by a single particle performing a random walk S_t and the decay of the density of reacting particles as a function of time in the model reaction systems $A+A$ and $A+B$. The one-dimensional behavior is evident in these lattices at long t. At short t, however, the particles do not yet ''feel'' the constraints of the short W and the two-dimensional (or three-dimensional) behavior is apparent. The dynamical property of interest in such tubular systems is the crossover time from dimension d to dimension one. This crossover time t_c is a strong function of W. Li gave theoretical and scaling arguments for the t_c dependence on W, resulting in good agreement with some of our earlier [2] calculations (for S_t and the $A+A$ reaction), but in disagreement with others (for the $A+B$ reaction). The purpose of this Comment is to clarify the apparent discrepancy.

The function S_t for a random walk and the reactant density $\rho(t)$ have been studied in detail for regular homogeneous spaces [3,4]. For S_t, both the long- and short-time behaviors are well understood. For the reactant density, the asymptotic (long-t) formalisms are known and have been verified by computer simulations [2,5]. However, the short-time behavior is more subtle and does not follow a simple universal scaling law [5].

Li derived the t_c dependence on W by equating the long-time with the short-time behaviors, which is valid strictly at the crossover point. For S_t and the $A+A$ reaction, he finds that the scaling is of the form

$$S_t \sim \frac{1}{\rho} \sim t^{1/2} W^{\beta}, \tag{1}$$

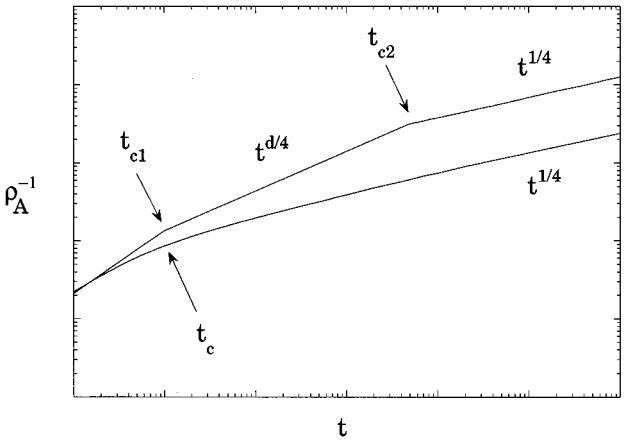

FIG. 1. Schematics of crossover regimes. The top (''wide tube'') scheme has two crossover times. The first is the ''Zeldovich'' (or segregation) crossover t_{c1}, discussed quantitatively by Argyrakis, Kopelman, and Lindenberg [5]. The second is the ''tubular'' crossover t_{c2} of interest here [2]. For smaller and smaller W values t_{c2} moves closer and closer to t_{c1} until they ''merge.'' From there on (for a W_c that can be estimated) there is no t_{c1}, only t_c, which is still a tubular crossover, but with a different character. In this ''narrow tube'' crossover scheme (bottom), the onset of the segregation is forced by the tubular walls, i.e., the imposed one-dimensional geometry.

*Electronic address: alin@u.chem.lsa.umich.edu
†Electronic address: kopelman@umich.edu
‡Electronic address: argyrakis@physics.auth.gr

where $\beta = d - 1$, leading to the crossover t_c:

$$t_c \sim W^4 \tag{2}$$

for $d = 3$, where $\beta = 2$. This is in perfect agreement with our previous results. In analogy to Eq. (1), Li proposes for the $A + B$ system

$$\rho^{-1} = t^{d/4} \quad (\text{short } t), \tag{3}$$

$$\rho^{-1} = W^{\beta} t^{1/4} \quad (\text{long } t) \tag{4}$$

and then similarly sets equal Eqs. (3) and (4). This results in a scaling

$$t_c \sim W^{\alpha}, \quad \alpha = 2, \tag{5}$$

for $d = 2,3$. This result is in disagreement with our earlier reported values of $a = 1.4 \pm 0.3$ (in three dimensions) and $a = 1.0 \pm 0.2$ (in two dimensions). Li's assumption implies that

$$\rho^{-1} \sim t^{d/4}, \tag{6}$$

i.e., Ovchinnikov-Zeldovich asymptotic result, is valid at short times t. However, Eq. (6) is correct only asymptotically, for large isotropic lattices [5]. This is because the $d/4$ law is a manifestation of the segregation effect taking place between the A and B particles [4,5]. We believe that for large enough W this expectation would be justified, as segregation in the higher dimension may appear *before* the crossover to the one-dimensional behavior occurs. In effect, there are then two crossover points, as shown schematically in Fig. 1. The first crossover (the ''Zeldovich'' crossover) is from the early-time behavior to the segregation regime and shows up in all isotropic lattices. The second crossover is the dimensional crossover from the three-dimensional to the one-dimensional character (the ''tubular'' crossover), which is characteristic of our tubular systems only. It is important to ascertain which crossover occurs first. If the Zeldovich crossover occurs first, then the Li scaling should be correct. However, if the tubular crossover occurs first, then there is no second crossover and we must modify the exponents in Eq. (6). For small W (the case of Ref. [2]) we thus believe that the tubular crossover occurs first and there is not enough time for the Zeldovich effect to take place. If we fit carefully the early-time slopes, i.e., $\rho^{-1} \sim t^x$, we find the values $x = 0.70 \pm 0.05$ in two dimensions and $x = 0.85 \pm 0.05$ in three dimensions. Using these values in Eq. (3) instead of $d/4$, we get for the scaling exponents $\alpha = 1.1$ in two dimensions and $\alpha = 1.6$ in three dimensions, in agreement with our previously reported [2] simulation results, $\alpha = 1.0 \pm 0.2$ in two dimensions, and $\alpha = 1.4 \pm 0.3$ in three dimensions.

It was also argued by Li that, for small W, finite-size effects dominate and there may not be an exact scaling relation for t_c vs W. Strictly speaking, this may well be the case. However, the same is true for the S_t and $A + A$ reactions of Eq. (1). Our previous results [2] indicate that empirically a scaling relation holds (see Fig. 11 of Ref. [2]) for the $A + B$ reactions, even for low W, e.g., for this finite-size regime, which is not covered by Li's formalism.

Finally, we note that from an experimental point of view the ''merged,'' single t_c case (see Fig. 1) is the most interesting property. It speeds up the onset of segregation, i.e., anomalous kinetics, and makes it more pronounced in the sense that a power of 1/4 deviates much more from the classical power of unity than the power of 3/4. It is this that makes thin tubular geometries into ideal environments for the experimental observation of the Zeldovich anomalous kinetics.

We would like to thank Ji Li and Leonard Sander for useful discussions. This project was supported by NSF Grant No. DMR9410709 and by NATO Grant No. CRG920029 (P.A.).

[1] J. Li, Phys. Rev. E **55**, 6646 (1997).

[2] A. L. Lin, R. Kopelman, and P. Argyrakis, Phys. Rev. E **53**, 1502 (1996).

[3] G. Weiss, *Aspects and Applications of the Random Walk* (North-Holland, Amsterdam, 1994).

[4] *Fractals and Disordered Systems*, edited by A. Bunde and S. Havlin (Springer-Verlag, Berlin, 1991); *Fractals in Science*, edited by S. Havlin and A. Bunde (Springer-Verlag, Berlin, 1994).

[5] P. Argyrakis, R. Kopelman, and K. Lindenberg, Chem. Phys. **177**, 693 (1993).