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SIMULATIONS OF ONE-DIMENSIONAL AND FRACTAL LUMINESCENCE KINETICS

Li LI and Raoul KOPELMAN

Department of Chemistry, University of Michigan, Ann Arbor, MI, 48109, USA

Exciton and electron-hole recombination reactions were simulated on one-dimensional and fractal networks. Particle distributions depend on dimensionality and electric fields. Geminate vs. non-geminate and pulsed vs. steady-state generation give very different reaction orders and population distributions.

According to classical considerations both electron-hole and exciton-exciton recombination reactions, in perfect lattices, are second order in overall particle density (ρ):

$$R = K\rho^2 \tag{1}$$

where R is the recombination rate, and K is a time independent and density independent constant.[1] The rate constant K is linearly related to the diffusion constant. It has recently been argued[2] that for the A + A case (exciton recombination), eq.(1) should be replaced by

$$R = K\rho^X \quad \text{(steady state or } t \to \infty) \tag{2}$$

where X = 3 for linear lattices and $2 < X < 3$ for connected fractal lattices (e.g. for percolating clusters X = 2.5). For the A + B case (e.g. electron-hole recombination) evidence for anomalies due to reactant segregation was given for the Sierpinski gasket.[3] The question arises: Do these anomalies apply to real systems which are not exactly one-dimensional or fractal lattices?

We have simulated diffusion-limited reactions on true one-dimensional systems and also on

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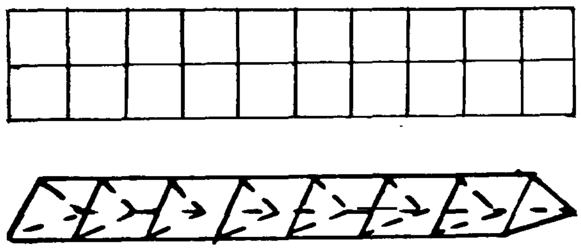

FIGURE 1
Examples of quasi-one-dimensional "wires" (cyclic boundary conditions used only at left and right).

quasi-one-dimensional systems such as the two- and three-dimensional "wires" of Fig. 1. For instance, for the reaction $A + A \to 0$ we find an initial classical behavior, followed quickly by a one-dimensional behavior (for pulsed reactions). For long times we find $X \cong 3.0$, for both geminate and non-geminate generation of A. These are the same results as for a strictly one-dimensional chain.[3] However, at steady-state, X = 3.0 for non-geminate creation but X ranges between 1 and 3 for geminate generation, depending on the steady-state density.

For $A + B \to 0$ reactions, where $\rho_A = \rho_B$, we find even more striking results. For pulsed reactions (after long time) we find $X \cong 3.0$ for geminate generation but $X \cong 5.0$ for non-geminate generation. In the latter case there is a very significant segregation of A and B. For steady-state reactions we find $X \cong 2.0$ for

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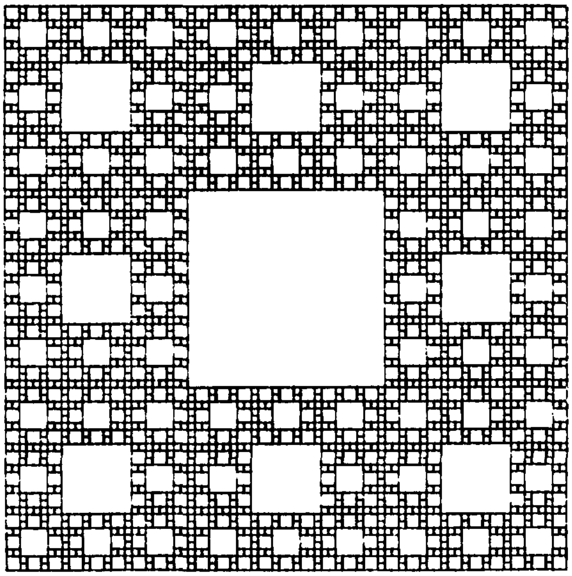

FIGURE 2
Sierpinski Carpet (5-th order). Fractal dimension 1.89 (spectral dimension 1.68).

geminate generation (and no segregation) while X ≅ 4.0 for non-geminate generation (with very significant segregation).

For a typical fractal (Sierpinski carpet[4] - Fig. 2), for A + B → 0, we find X = 2.24 at steady-state for non-geminate generation (with little, but definite, segregation). This differs from pulsed generation, where X = 3.2 (with more segregation). An example of a steady-state simulation is given in Figure 3.

Applying an "electric field" to the A + B → 0 reaction, under steady-source non-geminate generation, we observe increasing densities, and much increased segregation. Similar electric field effects are observed for the one-dimensional systems.

In all our simulations A and B are hard-sphere particles (with only local interactions). The simulations were performed on an IBM 3090-400/VM computer, with MTS (Michigan Terminal System). Quantitative criteria for segregation have been developed[5] and results will be presented.[6] Our A + A results agree well with exciton annihilation in ultra-thin naphthalene wires.[6,7]

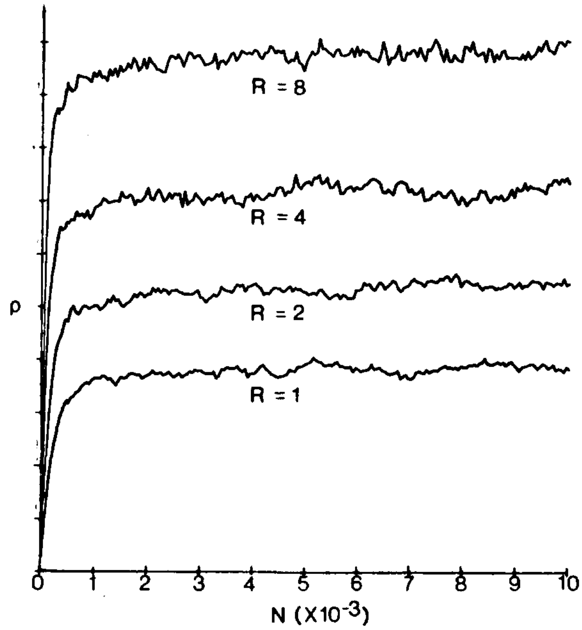

FIGURE 3
Steady-source simulation: A + B reaction on Sierpinski Carpet ($\rho_A = \rho_B = \rho$). R is relative rate of particle addition ($R_A = R_B = R$).

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