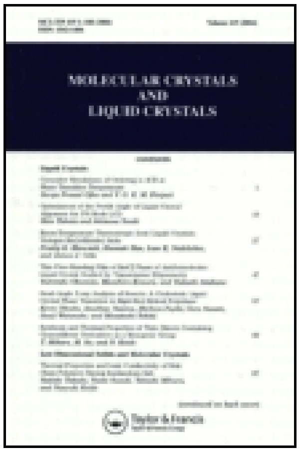

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Trapping Kinetics and Excitation Self-Organization in One-Dimensional Topologies: Monte Carlo Simulations

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TRAPPING KINETICS AND EXCITATION SELF-ORGANIZATION IN ONE-DIMENSIONAL TOPOLOGIES: MONTE CARLO SIMULATIONS

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Abstract Monte Carlo simulations are performed on one-dimensional diffusion-limited reactions $A + T \rightarrow T$, where T is a single trap or scavenger. The results are consistent with analytical theories for the limit (a) where T moves and the A's are fixed as well as for the limit (b) where the A's move and T is fixed. Results are also derived for the hitherto unexplored case (c) where both T and the A's diffuse. Quantitative values are given for the time exponent describing the growth of the depletion zone around T.

INTRODUCTION

There are many processes in which elementary excitation particles are trapped, quenched or annihilated by another kind of excitation or particle. Examples are electron trapping and recombination, exciton trapping, quenching or fusion, soliton-antisoliton recombination, phonon upconversion, free radical scavenging, etc.[1-7] Also, there are several examples of effectively one-dimensional systems such as polydiacetylenes and other quasi-dimensional crystals, polymer chains in dilute blends and crystals grown inside pores and microcapillaries. The study of diffusion-controlled kinetics in such low-dimensional systems has been of much interest lately.[2,5,8-18] Here we present some of the simplest possible models, with results that are neither classical nor intuitive.

The traditional[1] emphasis on trap "fluctuations" (i.e., random distribution of traps) misses the more important point: The kinetic indicators of low-dimensional and disordered morphologies have their origin in the self-organization of particles or excitations in these media. Even if the trap distribution is that of a superlattice, or if there is only a single trap, the major effect is that of particle (excitation) self-organization, resulting in a drastic depletion zone around each trap. We note that such a depletion zone does *not* occur in ordered, 3-dimensional crystals or glasses. It also disappears if the trap has a high reflection probability[18] (i.e., a shallow trap). Indeed, trapping and heterofusion kinetics have not been described correctly by previous theory for both pulsed and steady-state excitation conditions.[2] In one dimension, the more rigorous theories[11] still give the result[1] $R \sim \rho c^2$, where R is the trapping or heterofusion rate, ρ the particle density and c the trap concentration (however, this is valid only for perfectly absorbing or reacting traps). This result generalizes[11] to $R \sim \rho c^{2/d_s}$ for fractals with spectral dimension d_s and to $R \sim \rho c/\ln c$ for d = 2 (for d = 3 the classical result applies: $R \sim \rho c$). In one dimension, the depletion zone around the trap increases in time[4] with $t^{1/4}$, while for the "moving trap" (quencher or target problem)[10] it rises with $t^{1/2}$. However, in d = 3 there is no growth in time (and for d = 2 it is logarithmic). The theoretical results have been confirmed by simulations in d = 1, on percolation clusters (d_s = 4/3 at criticality) and on the Sierpinski gasket (d_s = 1.36).[11,12] Heterofusion experiments on one-dimensional naphthalene crystals[5] are also consistent with the theory, as are older experiments on naphthalene percolation clusters.[6] The analytical theory for trapping[11] is analogous to that for recombination and fusion.[3,7]

The problem of particles that diffuse in one dimension and react with a <u>single fixed trap</u> has recently been solved analytically.[4] Soon thereafter, the opposite case was derived, that of a diffusing trap ("pac man") and fixed particles.[10] There is an interesting difference between these two limiting cases. Here we study the case in which both the trap ("pac man") and the particles are diffusing.

The anomalous kinetics of diffusion-limited reactions has been associated with non-homogeneous particle distributions.[1-8] Recently, some interest has been focused on the nearest neighbor particle distribution,[2,4,8] and it has been directly related to non-classical rate laws.[2,4] For instance, for the A + A reactions the classical rate term, $k\rho^2$, has been replaced[13] by $k\rho K_o(\rho)$, where $K_o(\rho)$ is the nearest neighbor distribution function at distance $r \to 0$, ρ is the density and k a constant. For the homogeneous ("Hertz") distributions, $K_o(\rho) \sim \rho$ in all dimensions, and thus the classical term $k\rho^2$ is recovered.[13] However, it has been shown via simulations[2,13] that for low dimensions ($d < 3$) $K(\rho)$ is non-Hertzian, in general. In particular, for $d = 1$, analytical expressions have been derived by both simulations[2] and analytical theory.[14,15] For instance, for $A + A \rightarrow A$ in one dimension,

$$K(r,\rho) = c\rho^2 r e^{-\gamma r^2} \tag{1}$$

This gives $K_o(\rho) \sim \rho^2$ and thus a $k\rho^3$ term for the rate.[2,13]

For the simple fixed trap case, Weiss et. al.[4] derived $K(\rho)$ in $d = 1$ (and an equivalent expression in $d = 3$). The asymptotic expression is actually similar to Eq. (1):

$$K(r,t,\rho) = (2\rho r/\sqrt{\pi Dt})\ \exp(-\rho r^2/\sqrt{\pi Dt}), \tag{2}$$

where D is the diffusion constant and t the time from the random insertion of the single trap. We note that $\langle r \rangle$ (the average nearest neighbor distance) grows with $t^{1/4}$. On the other hand, for the case of a diffusing trap[10] (scavenger) and fixed particles ("targets") a similar $K(r,t,\rho)$ is obtained. However, here $\langle r \rangle$ grows with $t^{1/2}$ (in $d = 1$). We note that the growth of the particle depletion zone around T (trap or scavenger) is given by the exponent m defined by $\langle r \rangle \sim t^m$.

The intermediate case, which would provide a more realistic model for reacting species allows for both the single trap and the remaining particles to diffuse. The analysis of this case poses a considerably more challenging mathematical problem although some partial results have recently appeared in the literature.[16] Here we approach this problem via Monte Carlo simulations. In particular, we want to test a conjecture[17] that as soon as the trap is allowed to diffuse, even at a pace much below that of the particles, the system will switch to a $t^{1/2}$ behavior. However, we find that the depletion zone growth exponent (m) changes monotonously from 1/4 to 1/2.

SIMULATIONS

We construct a one-dimensional lattice with cyclic boundary conditions (i.e., circular) containing L(usually 1024) sites. The single trap location is chosen at random and the initial particle distribution is uniformly random. We do not allow: 1) multiple particle occupation; 2) crossing of particles; 3) landing of one particle on top of another. The particles move at random. The trap also moves at random (at a higher, lower or equal pace). When a particle collides with the trap it is annihilated. To maintain a constant density ρ (occupation probability, usually 5%), whenever a particle is annihilated, another one is created ("lands") at random on the half of the (circular) lattice opposite the position of the trap. This diffusion-limited reaction is allowed to proceed for 50,000 steps. The nearest neighbor distribution function is derived for various times (averaged over narrow time intervals). To be consistent with the literature[4,10] we replace the notation K(r,t) with f(x,t) and ρ with C.

RESULTS

We first compare the simulation results with the theory[4] for the fixed trap. Figure 1 is a result of 300 runs with C = 0.05 after 40,000 steps. We note that the actual distribution has not yet approached the asymptotic theoretical skewed Gaussian form (eq. 2). This behavior is consistent with previous simulations by Taitelbaum.[4,18]

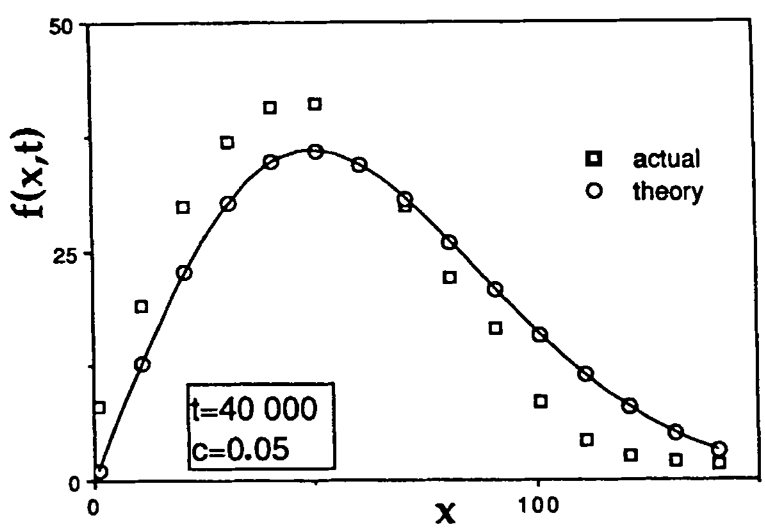

FIGURE 1 Trap-particle nearest neighbor distance (X) distribution function f(X,t) for fixed trap and moving particles at time t = 40 000 and density c = 0.05. Circles: Asymptotic theory (eq. 2) with D = 1/2. Squares: Simulation results on a 1024 site circular lattice (averaged over 300 runs). X is given in lattice units divided by L.

The important test is the dependence of <X> on time. This is seen in Figure 2 for three cases: a) Moving trap and fixed particles. b) Fixed trap and moving particles. c) Moving trap and moving particles (with equal diffusion constant). We see that the slope m (<X> ~ t^m) is close to 1/2 (the theoretical asymptotic result[10]) for case a, i.e., m ≈ 0.46. On the other hand, the slope is close to 1/4 (the theoretical asymptotic result[4]) for case b, i.e., m = 0.23. Finally, we get an intermediate result (m = 0.29) for the intermediate case c, in contrast to the conjecture mentioned above (predicting 0.5). Additional simulations, with various ratios for the particle/trap diffusion constants, give analogous results, with a monotonous change of m from 0.23 through 0.29 to 0.46 (as expected from naive interpolation). Thus the depletion zone growth exponent varies monotonously from 1/4 to 1/2.

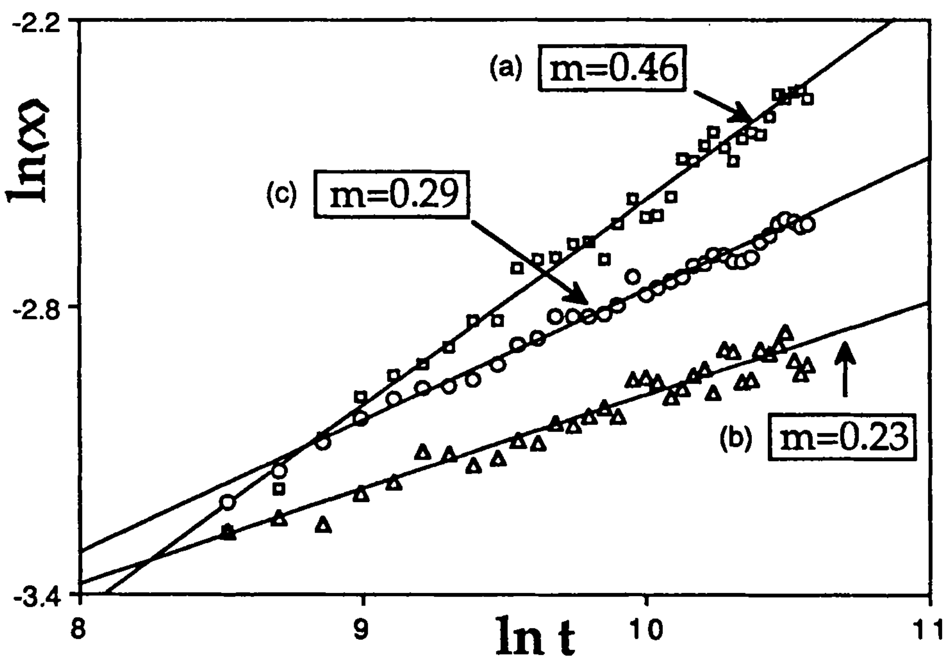

FIGURE 2 Simulated log-log presentation of the average trap-particle nearest neighbor distance vs. time on a one-dimensional circular lattice (c = 0.05, 1024 sites, 300 runs). a. Moving trap, fixed particles. b. Moving particles, fixed trap. c. Moving trap and moving particles (equal D). The least square fitted slopes (m) are given for each case.

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REFERENCES

1. V. M. Agranovich and M. D. Galanin, Electronic Energy Transfer in Condensed Matter (North Holland, Amsterdam, 1982).
2. S. J. Parus and R. Kopelman, Phys. Rev. B, 39, 889 (1989).
3. E. Clement, Ph.D. Thesis, University of Michigan, Ann Arbor, MI (1989).
4. G. H. Weiss, R. Kopelman, and S. Havlin, Phys. Rev. A, 39, 466 (1989).
5. J. Prasad and R. Kopelman, Phys. Rev. Lett., 59, 2103 (1987).
6. P. Argyrakis and R. Kopelman, Chem. Phys., 57, 29 (1981).
7. E. Clement, L. M. Sander, and R. Kopelman, Phys. Rev. A, 39, 6455, 6466, 6472 (1989).
8. R. Kopelman, Science, 241, 1620 (1989).
9. R. Kopelman et al., this issue.
10. D. Ben-Avraham and G. H. Weiss, Phys. Rev. A, 39, 6436 (1989).
11. E. Clement, R. Kopelman, and L. M. Sander, unpublished.
12. L. W. Anacker and R. Kopelman, J. von Neumann National Supercomputer Annual Report for 1988 (1989), p. 11.
13. R. Kopelman, S. J. Paru, and Z-Y. Shi, in Dynamical Processes in Condensed Molecular Systems, edited by J. Klafter, J. Jortner, and A. Blumen (World Scientific, Signapore, 1989), p. 231.
14. C. R. Doering and D. Ben-Avraham, Phys. Rev. A, 38, 3035 (1988).
15. C. R. Doering and D. Ben-Avraham, Phys. Rev. Lett. 62, 2563 (1989).
16. A. Szabo, R. Zwanzig, and N. Agmon, Phys. Rev. Lett. 61, 2496 (1988).
17. G. Weiss, private communication (1988).
18. H. Taitelbaum, R. Kopelman, G. Weiss, and S. Havlin, to be published.