

Nonclassical $A + B \rightarrow 0$ batch reactions: Effect of mobility on rate, order, aggregation and segregation

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Monte Carlo simulations are performed for the elementary batch reaction $A + B \rightarrow 0$ on a one-dimensional lattice. The initial densities of the A and B species are always identical but the relative mobility is varied. We investigate the rates, rate laws, and particle distribution functions. The rate power law is conserved, i.e., the density always decays in time algebraically with exponent $\frac{1}{4}$. The rate coefficient is proportional to the relative mobility, as expected. The interparticle distribution functions ("gaps" and nearest-neighbor distances) show that the aggregation does depend on the relative mobility but the segregation does not. However, this subtle difference has no effect on the asymptotic reaction order, which is close to 5.

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I. INTRODUCTION

Nonclassical reaction kinetics has been of much interest over the last decade, evidenced by the recent special volume of *The Journal of Statistical Physics* [1]. The most striking nonclassical anomaly is no doubt the spontaneous reactant segregation for the $A + B \rightarrow 0$ reaction (0 symbolizes an inert product that can be totally ignored, such as an irreversibly desorbed product of a surface reaction). This spontaneous segregation and its concomitant anomalous rate law were first suggested by Ovchinnikov and Zeldovich [2] for a diffusion-limited batch reaction. It was shown later to hold even for steady-state reactions [3–5] on low-dimensional media. In most of the early literature it was assumed that the species A and B have strictly the same concentration (density) and the same diffusion constant (mobility). This was followed by treatments for unequal concentrations [6,7]. There were also treatments of unequal mobilities [7–10]. While, at steady state, the mobility affects both the degree of segregation and the rate law [8], it was recently indicated [7] that this is not the case for the power law in batch reactions [7]. How the immobility affects segregation and aggregation is still an open question. This question is addressed below for batch reactions.

Experimentally (real experiments, not computer simulations) there have not yet been any published confirmations of the striking nonclassical anomalies predicted for the $A + B$ reactions. The experiments that did spawn nonclassical kinetics [10–12] are of the type $A + A \rightarrow$ products (annihilation, homofusion, coagulation) and $A + B \rightarrow B$ (trapping, quenching). These reactions only result in subtle, mesoscopic spatial self-ordering [13], in contrast to the striking macroscopic effects predicted for the $A + B \rightarrow 0$ reactions. The first step in this direction was recently achieved by Koo and Kopelman [14,15] in reactions that *start* under segregation (separation of the A 's from the B 's, but no aggregation of A 's or B 's). Here the surprise is the *preservation* of the segregation and, concomitantly, its nonclassical effects on the rate laws [16,17]. Furthermore, neither the

concentration nor the mobility of the A 's and B 's are equal. Such unequal mobilities have some unexpectedly dire consequences [15], affecting both the segregation and the rate laws. In all $A + B \rightarrow 0$ experimental reaction studies, it is easy to assure effectively equal concentrations of species A and B . However, equal mobilities are hard to come by. To encourage and support such experiments has been the rationale for the present work. We note here that experimentally it may be easier to observe segregation (at least qualitatively) than the anomalous powers of the asymptotic rate laws. The present investigation not only confirms and extends earlier conclusions [7] regarding the rate laws, but also presents the particle distribution functions (various nearest-neighbor distributions) which give an excellent measure [19–22] of the spatial self-ordering, i.e., segregation of unlike particles (A and B) and aggregation of like particles (AA and BB).

In the present study, we examine in detail the effects of unequal mobilities of the two reacting species. We treat the limiting case of $d=1$, since if there are going to be any differences, they will be most pronounced in this case. In the extreme case of mobility differences, one of the species will be totally immobile. This problem resembles the well-known trapping problem, where the static traps "capture" all particles landing on them; however, the important difference here is that the static trap is also removed from the system when the capture occurs. Thus the $A + B \rightarrow 0$ and $A + B \rightarrow B$ problems are quite different [15,17,18], e.g., they belong to different universality classes with different critical dimensions and exponents.

II. METHOD OF MONTE CARLO SIMULATIONS

The $A + B$ reaction with the species possessing different mobilities is simulated directly in the usual way [20,23], paying attention to the different rates of motion. Particles diffuse via random walk, independently of each other. One of the two species is set to perform one nearest-neighbor transition per time step, while the other performs one transition after a certain number of steps,

this number being directly a measure of the particle mobility. In the extreme case, the second species does not move at all, this case being referred to in this paper as the mobile-immobile species reaction. The rest is similar to the usual simulation techniques: Particles are distributed initially at random on a lattice of size $L=10\,000$ or $100\,000$ sites, with initial particle density $\rho_0=\rho_A=\rho_B$. The A particles react with B upon encounter, i.e., if they occupy the same site on the lattice at any moment. Upon reaction, the two reacting particles are removed from the system. Particles A do not react with other A 's, and similarly for the B 's. Cyclic boundary conditions are used at the edges of the lattice. We use the excluded volume model, in which only one particle can occupy a lattice site. We monitor the decay of the particle density as a function of time and the reaction rate as a function of density. We also calculate the nearest-neighbor distance distribution function for the A and B particles, and compare them to the results of the normal case of two mobile species. Finally, we calculate the distribution of the gaps between particles, and also compare this to the mobile-particle case.

III. RESULTS AND DISCUSSION

For the normal $A+B\rightarrow 0$ reaction on one-dimensional lattices, the asymptotic ($t\rightarrow\infty$) density decay behaves as [1,2]

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

where ρ is the density of the A or B species, and the densities are always equal. This well-known result is shown in Fig. 1 (top curve), where we plot $1/\rho-1/\rho_0$ as a func-

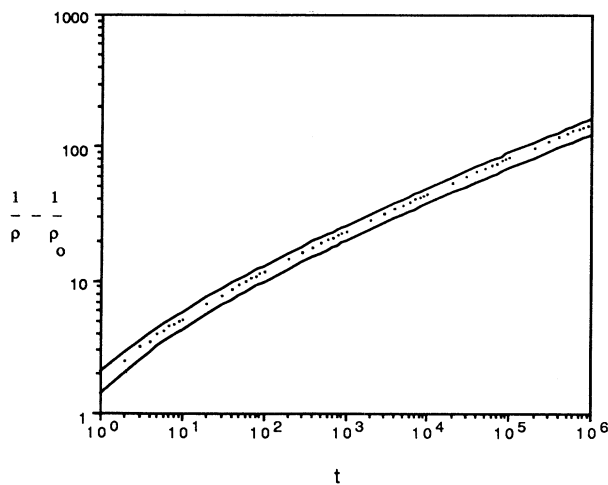


FIG. 1. The plot of $1/\rho-1/\rho_0$ vs time in log-log form, for the one-dimensional $A+B$ reaction showing the difference between the cases when some species have different mobility. Calculations were performed on lattices of size $100\,000$ sites, and the data shown are averages of 25 realizations. The initial concentration $\rho_0=0.4$. Top curve: both species mobile; bottom curve: one mobile, one immobile; middle curve (dotted line): one species mobile, and the second species with half the mobility of the first.

tion of time. Here ρ_0 is the initial density at $t=0$, and it is $\rho_0=0.4$ for A and B . The slope f of about $\frac{1}{4}$ is immediately recovered from this log-log plot. The detailed analysis of this data was recently reported [23]. In the same figure, we also show the data for the case where one of the species is immobile (lower curve), giving the same slope f of about $\frac{1}{4}$. We observe that, in absolute values, in the mobile-immobile case the particles react at half the rate of the normal mobile-mobile case. However, the rate law has the same exponent. All this is in agreement with very recent previous work [7].

In addition, the dotted line represents the in-between case, in which one of the reacting species has half the mobility of the first. This is attained by simply letting this species perform one jump only after two time steps (instead of one jump per step). As expected the slope is the same, again, and the only difference is in the absolute number of reacting encounters. Also, the rate is intermediate between the two extremes cases.

Figure 2 shows the reaction rate as a function of the particle density. The rate is simply calculated from the $d\rho/dt$ differential at the different densities, which correspond to different times in the course of the reaction. We show the two extreme cases, that with both mobile species and that with one mobile, one immobile species. As in the previous figure, the slope of the lines are the same, while the absolute values are different. For the one-dimensional reaction rate, one expects

$$\frac{d\rho}{dt}=k\rho^x.$$

Here a least-squares fit for the slope of the rate curve gives $x=4.9\pm 0.1$, which is close to the expected value for the asymptotic limit $x=1+1/f$, f being the time exponent given in Fig. 1, i.e., $f\cong\frac{1}{4}$, giving $x\cong 5$. Reactions with species having partial mobilities are expected to fall in between, as shown in Fig. 1, but with the same slope. This high value for x (the reaction order) is not surprising

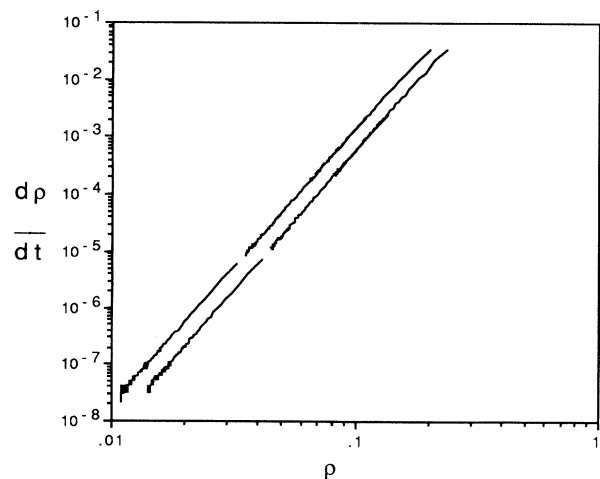


FIG. 2. The plot of the reaction rate vs the reactant density for the same reaction and the same data as in Fig. 1, i.e., top curve: mobile-mobile; bottom curve: mobile-immobile.

[11] for the one-dimensional reaction, as it manifests the spatial correlations that are being built in the course of the reaction (as opposed to $x=2$ for the case of randomly distributed reactants). The same least-squares fit also produces the intercept, which in this case yields the k values, the rate constants. The results are $\log_{10}k=2.1\pm 0.1$ (mobile-mobile case) and $\log_{10}k=1.8\pm 0.1$ (mobile-immobile case). Thus we get a ratio of $k(\text{mobile-mobile})/k(\text{mobile-immobile})=2.0$. This is in excellent agreement with the factor of 2 ratio expected from the particle mobilities for the two cases [18]. Also, for the case where one species moves with only half the mobility, the ratio $k(\text{mobile-mobile})/k(\text{mobile}-\frac{1}{2}\text{mobile})$ is close to $\sqrt{2}$, as expected in such situations [18].

In Fig. 3, we show the results of the nearest-neighbor distance distributions (NNDD), [19–22] for the mobile-immobile case, and also, for comparison purposes, the data for the mobile-mobile case. Actually, in this plot (and the subsequent Fig. 4) the distribution of the quantity $(r-1)/(\langle r \rangle - 1)$ is plotted. Here $\langle r \rangle$ is the average nearest-neighbor distance of all particle pairs, and it is used as a normalizing factor. The -1 term is used so that the first x -axis value is at zero. Note that for a given A particle, the AA NND ignores possible intervening B particles, while the AB NND ignores possible intervening A particles. We notice the crossover from a decaying-type curve at $t=0$ (Poisson type) to a skewed Gaussian type [11,13] at $t=1000$ steps, as expected [20]. Furthermore, the AB (mobile-mobile) distribution is the same as the Ab (mobile-immobile) one. However, the AA distributions appear to be different, and there is a

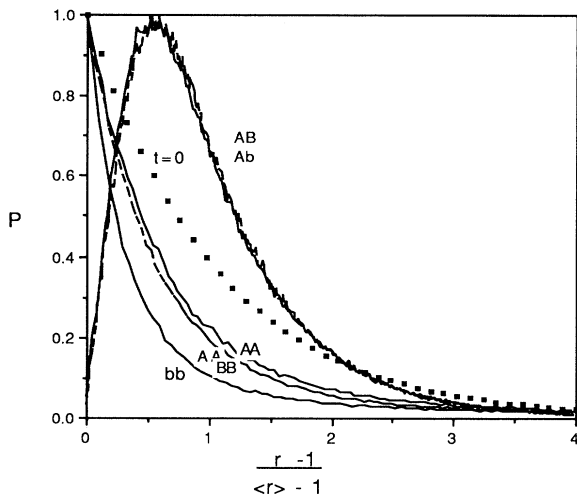


FIG. 3. Nearest-neighbor distance distributions for the one-dimensional $A+B$ reaction. All curves are averages of 2000 runs performed on lattices of size $L=10\,000$ sites, for $t=1000$ steps. Initial concentration $\rho_0=0.05$. Dashed lines: mobile-mobile; solid-lines: mobile-immobile. Notice that the AA - BB is calculated from the contribution of both the A - A and B - B pairs (but not AB pairs). Dots indicate distribution before any reaction has started at time $t=0$. A capital letter signifies a mobile species, a lowercase letter an immobile species. Each curve is normalized separately.

clear-cut difference between the BB and the bb distributions (note that the bb distribution is *not* random).

Figure 4 shows the distribution of the gaps for the same reaction mechanism as the previous figures. For the one-dimensional model that we have here, the “gap” is simply defined as the distance between two closest particles. Therefore, the total number of “gaps” (with cyclic boundary conditions) is equal to the number of particles. This total number of gaps is made up of all the AA , BB , and AB gaps. There are similarities and differences compared to the NNDD. First, the AB (mobile-mobile) and Ab (mobile-immobile) distributions are again the same. Second, the bb (immobile-immobile) distribution again differs from that of the AA (mobile-mobile). The AA distribution for the mobile-immobile reaction is again quite similar to the AA distribution for the mobile-mobile reaction (which is obviously the same, by symmetry, as the mobile-mobile BB distribution). All of the latter are quite close to the Poissonian distribution for the gaps, in contrast to the NNDD. We note here that while, for the $A+A\rightarrow 0$ reaction, the NNDD and gap distributions give essentially the same result and information, this is not true, in general, for $A+B\rightarrow 0$ reactions. Here the macroscopic aggregation and segregation makes the AA (or BB or bb) gap distributions chemically “irrelevant.” While the NNDD AA (or BB or bb) always pertain to particles within the *same* aggregate (after segregation), this is no longer true for the gap distribution, which includes contributions from A - A “gaps” that span a large B (or b) aggregate. This peculiarity is a result of the gap definition used in our simulations. Thus the contributions from the very large gaps prevent the “like-like” distributions from being “squeezed” (due to aggregation) and pushes them to become just about ran-

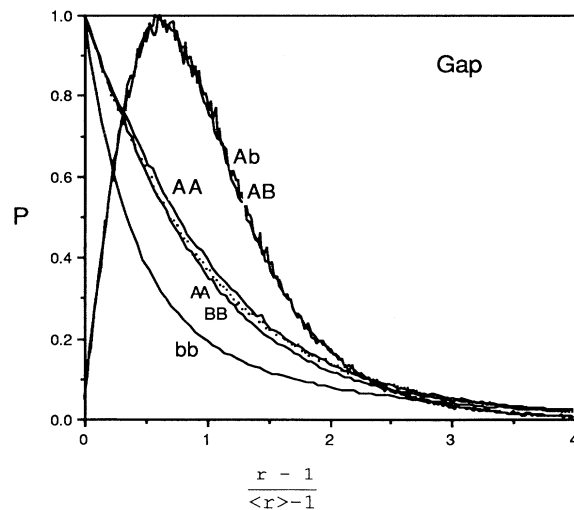


FIG. 4. The normalized gap distribution for the one-dimensional $A+B$ reaction. Curves are averages of 5000 runs on lattices of size $L=10\,000$ sites, for $t=1000$ steps, and initial concentration $\rho_0=0.05$. Same designations as in the previous figure. The dotted line shows the distribution before the start of the reaction at $t=0$.

dom (Poissonian) distributions, with little relevance to the reaction kinetics and self-ordering.

IV. SUMMARY

We investigated the effects of varying mobilities on the elementary reaction $A + B \rightarrow 0$ in one-dimensional lattices. We derived directly the reaction order and the density decay as a function of time for a small but comprehensive range of the particle mobilities. Our results show that the scaling law for the density decay obeys the well-known Ovchinnikov-Zeldovich hypothesis for the $A + B$ reactions, irrespective of the particle mobilities. Also, the rate coefficients are simply related

to the particle mobilities. The nearest-neighbor and gap distributions for these reactions confirm these findings, as the distributions for the A - B distances (which determine the rate [11, 19–21]) are practically identical in all cases, showing that the segregation proceeds in a similar way, regardless of the mobilities.

Note added in proof. A very relevant paper has just appeared: S. Redner and F. Leyvaraz, Phys. Rev. A **46**, 3132 (1992).

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- [1] Conference on Models of Nonclassical Reaction Rates [J. Stat. Phys. **65** (1991)].
- [2] A. A. Ovchinnikov and Y. B. Zeldovich, Chem. Phys. **28**, 215 (1978).
- [3] L. W. Anacker and R. Kopelman, Phys. Rev. Lett. **58**, 289 (1987).
- [4] K. Lindenberg, B. J. West, and R. Kopelman, Phys. Rev. Lett. **60**, 1777 (1988); B. J. West, R. Kopelman, and K. Lindenberg, J. Stat. Phys. **54**, 1429 (1989); K. Lindenberg, B. J. West, and R. Kopelman, in *Noise and Chaos in Nonlinear Dynamical Systems*, edited by F. Moss, L. Lugiab, and W. Schleich (Cambridge University Press, Cambridge, 1990).
- [5] E. Clement, L. M. Sander, and R. Kopelman, Phys. Rev. A **39**, 6455 (1989); **39**, 6466 (1989); **39**, 6472 (1989).
- [6] M. Bramson and J. Lebowitz, J. Stat. Phys. **65**, 941 (1991).
- [7] I. M. Sokolov, H. Schnorer, and A. Blumen, Phys. Rev. A **44**, 2388 (1991).
- [8] L. A. Anacker and R. Kopelman, in *Dynamics in Small Materials*, edited by J. M. Drake, J. Klafter, and R. Kopelman (Materials Research Society, Pittsburgh, 1990), p. 97.
- [9] L. W. Anacker and R. Kopelman, Video Film, von Neumann Supercomputing Center, Princeton (1990).
- [10] P. W. Klymko and R. Kopelman, J. Phys. Chem. **87**, 4565 (1983).
- [11] R. Kopelman, in *The Fractal Approach to Heterogeneous Chemistry*, edited by D. Avnir (Wiley, New York, 1989).
- [12] V. M. Agranovich and M. D. Galanin, *Electronic Excitation Energy Transfer in Condensed Matter*, (North-Holland, Amsterdam, 1982).
- [13] R. Kopelman, S. J. Parus, and J. Prasad, Chem. Phys. **128**, 209 (1988).
- [14] Y. E. Koo and R. Kopelman, J. Stat. Phys. **65**, 893 (1991).
- [15] R. Kopelman and Y. E. Koo, Isr. J. Chem. **31**, 147 (1991).
- [16] L. Galfi and Z. Racz, Phys. Rev. A **38**, 3151 (1988).
- [17] H. Taitelbaum, S. Havlin, J. E. Kiefer, B. Trus, and G. H. Weiss, J. Stat. Phys. **65**, 873 (1991).
- [18] H. Taitelbaum, Y.-E. L. Koo, S. Havlin, R. Kopelman, and G. H. Weiss, Phys. Rev. A **46**, 2151 (1993).
- [19] L. A. Harmon, L. Li, L. W. Anacker, and R. Kopelman, Chem. Phys. Lett. **163**, 463 (1989).
- [20] P. Argyrakis and R. Kopelman, Phys. Rev. A **41**, 2121 (1990).
- [21] S. Redner and F. Leyvraz, J. Stat. Phys. **65**, 1043 (1991).
- [22] G. Zumofen, J. Klafter, and A. Blumen, Phys. Rev. A **44**, 8394 (1991).
- [23] P. Argyrakis and R. Kopelman, Phys. Rev. A **45**, 5814 (1992).