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## Reaction efficiency effects on binary chemical reactions

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We study the effect of the variation of reaction efficiency in binary reactions. We use the well-known  $A + B \rightarrow 0$  model, which has been extensively studied in the past. We perform simulations on this model where we vary the efficiency of reaction, i.e., when two particles meet they do not instantly react, as has been assumed in previous studies, but they react with a probability  $\gamma$ , where  $\gamma$  is in the range  $0 < \gamma < 1$ . Our results show that at small  $\gamma$  values the system is reaction limited, but as  $\gamma$  increases it crosses over to a diffusion limited behavior. At early times, for small  $\gamma$  values, the particle density falls slower than for larger  $\gamma$  values. This fall-off goes over a crossover point, around the value of  $\gamma = 0.50$  for high initial densities. Under a variety of conditions simulated, we find that the crossover point was dependent on the initial concentration but not on the lattice size. For intermediate and long times simulations, all  $\gamma$  values (in the depleted reciprocal density versus time plot) converge to the same behavior. These theoretical results are useful in models of epidemic reactions and epidemic spreading, where a contagion from one neighbor to the next is not always successful but proceeds with a certain probability, an analogous effect with the reaction probability examined in the current work. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4894791>]

### I. INTRODUCTION

The problem of particle interactions, such as in chemical reactions, has attracted wide interest in all sciences over the years, for obvious reasons. In the last three decades, there has been considerable interest in such binary interactions, which are exemplified as binary chemical reactions in which it takes two agents (particles) to interact (collide) for a reaction to occur.<sup>1-7</sup> Well known systems include the like-like ( $A + A$ ), and the like-unlike ( $A + B$ ) systems, which show rich behavior, such as the generation of the depletion zone, and the segregation of reactants as the reaction proceeds, respectively.<sup>1,3,5,8-13</sup> Several of these properties have been analyzed in detail and are now well understood by use of the position-position correlation function, which follows the evolution of the system with time, bringing up the above mentioned observations.

In all these considerations, the simplest models that were used included the case in which two particles interact irreversibly upon direct encounter. In lattice systems, this means that the two particles interact with complete efficiency when they happen to occupy the same site at the same time. This was the simplest possible model but it was enough to bring out the rich behavior of interacting species. In more recent times, such interactions were extended to take place in networks,<sup>14-16</sup> rather than lattices with some startling results, for example, the disappearance of the depletion zone and the disappearance of segregation when the interactions occur on a scale-free network. This was explained by the presence of the hubs, i.e., nodes of very high connectivity, which, nevertheless, dominated the interaction mechanism by bringing in an “effective bias” of the diffusing particles towards nodes with such high degree. Again, in all these cases, complete efficiency of the interaction was assumed. These models of

interacting particles were furthermore used in the study of spreading phenomena. Populations of such particles originate in some specific point of the system in very limited size compared to the system size and propagate to the remaining system by simple diffusion. A large interest in these models arose when it became evident that it might be possible to study the spreading of diseases using interacting particles, as described above. In these simple models, such as the celebrated SIR model, an agent who is infected propagates from neighbor to neighbor through the system and is able to infect a healthy agent upon encounter on the same node. In simple disease spreading ideas, one should consider that not every single encounter ends up in contagion, i.e., in a successful reaction, but it is reasonable to assume that this may happen with a certain probability  $\gamma$ , where  $0 < \gamma < 1$ . Because of this idea different infection probabilities (in our case here the reaction efficiencies) lead to totally different behavior if examined on different systems. Thus, it has been shown<sup>17</sup> that when the infection probability is varied, the infected system mass undergoes through a sharp transition for random networks but not so for scale-free networks. Thus, when studying the problem of disease spreading one would be interested to study particle interactions by using a reaction efficiency (reaction probability) that is smaller than 1, which has been the traditional case. Some theoretical considerations have been reported on the  $A + B$  system<sup>18</sup> and related types of systems for finite reaction probabilities.<sup>19-23</sup>

In the present work, we use computer simulation for binary reactions, in which we vary the value of  $\gamma$ , and we monitor the rate of the reaction, as a function of time. We find out that we gradually pass from the reaction limited to the diffusion limited regime, and, therefore, it is of interest to examine in detail the crossover from one regime to the other. Our results show that in early times for small reaction

efficiencies the density falls slower than for larger ones. This result is quite reasonable. However, after a certain value of the reaction time the density decrease is independent of the reaction efficiency. All reactions which display diffusion limitations collapse to the same curve for all values of  $\gamma$ . Thus, the system goes over a crossover point in time, which occurs at a different point for each value. We report details of this crossover.

## II. METHOD OF SIMULATION

The  $A + B$  reaction is simulated in the usual way as has been reported in the literature by several groups.<sup>2,6,24–29</sup> A population of reactive particles is initially placed on a two-dimensional (2D) lattice randomly with a predetermined density. In all cases here, the initial population of the two species is exactly the same, typically with  $\rho(0) = 0.8$  such that  $\rho_A(0) = \rho_B(0) = 0.4$ . All particles diffuse on the lattice by independent random walks. Steps are allowed to nearest neighbor sites only. A site can be occupied by one particle only, i.e., we use excluded volume principles. A reaction occurs when an A and a B particle collide, but no reaction occurs if two A particles (or two B particles) collide. When two particles react they are removed from the system. All reactants are generated at time zero, before any reaction has occurred, and thus the particle density decreases as a function of time. If an A (B) particle attempts to land on a site already occupied by another A (B) particle, the particle does not move in that time step. The basis for the time unit is one Monte Carlo step (MCS), which is defined as the time it takes for all present particles at any given time to move (or attempt to move) one step to one of their nearest neighbors. We simulated the reactions on a square lattice (2D) of  $N = L \times L$  sites with periodic boundary conditions, where  $L$  had values up to  $10^4$ . We monitor the decay of the particle density as a function of time.

We introduce the parameter  $\gamma$  that is called the reaction efficiency factor. Every time a particle A lands at the same site with a particle B there is a probability for the reaction to occur which is governed by the value of  $\gamma$ . If a reaction fails to occur then the particles continue to perform the usual random walks.

## III. RESULTS AND DISCUSSION

As has been widely considered in the past the scaling of the density with time goes as<sup>6</sup>

$$\frac{1}{\rho} - \frac{1}{\rho_0} = kt^f, \quad (1)$$

where  $f = 0.5$  for 2D systems, which is the well-known Zeldovich result.<sup>1</sup> In Fig. 1, we plot the quantity  $1/\rho - 1/\rho_0$  vs time on log-log axes for the case where  $\gamma = 1.00$ . As has been discussed in the past, there is a clearly visible early time effect where the slope is not constant at all and also at long times finite size effects are expected to appear. Therefore, the choice of proper region for calculating the slope is between these two limits and contains some uncertainty about the best range where to calculate it. In Fig. 1, this region (Zeldovich regime) appears between  $t = 30\,000$  and  $t = 200\,000$  where

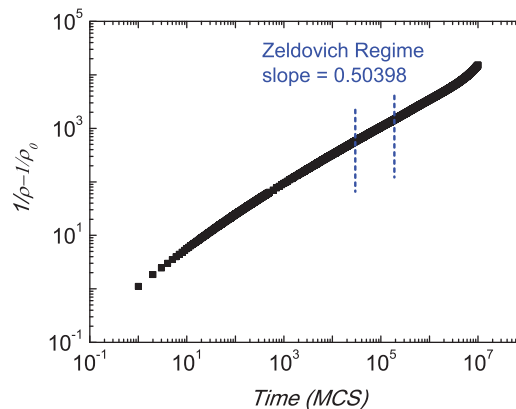


FIG. 1. The  $1/\rho - 1/\rho_0$  vs time plot at log-log for the A+B annihilation diffusion limited reaction for  $\gamma = 1.00$ . We used a square lattice of size  $10^4 \times 10^4 = 10^8$  sites and  $\rho_0 = 0.8$  (0.4 for each type of particles). The results are averaged over 6 runs. The Zeldovich regime appears in the range  $t = 30\,000$  to  $t = 200\,000$ .

the slope of the line is approximately equal to 0.504 with a small deviation from the theoretically expected value (0.500).

In Fig. 2, we plot the quantity  $1/\rho - 1/\rho_0$  vs time on log-log axes for several values of the reaction efficiency  $\gamma$ , ranging from 0.001 to 1. We clearly see that for small values of the reaction efficiency factor ( $\gamma = 0.001$ ) we have a straight line in the entire time domain examined, the slope of which is equal to unity ( $f = 1.00$ ), as a mean field approximation would imply. We can safely state that for small values of  $\gamma$  the overall reaction is reaction limited rather than diffusion limited. The classical rate laws are always valid for reaction limited reactions, but important exceptions exist for the diffusion limited case. For longer times (after  $10^7$  Monte Carlo steps in Figs. 1 and 2), we observe finite size effects, characterized by an exponential increase.<sup>30</sup> As  $\gamma$  increases we see that the slope at early times decreases progressively tending to unity, as the diffusion becomes reaction limited.

In Fig. 2, we see that the simulations converge to having both the same density and the same slope before finite size effects set in, provided that the reaction probabilities are sufficiently high (the higher the reaction probability, the

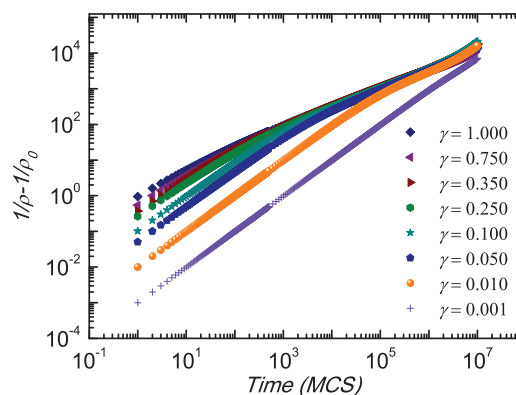


FIG. 2. The  $1/\rho - 1/\rho_0$  vs time plot at log-log for the A + B annihilation diffusion limited reaction for several values of  $\gamma$  (0.001, 0.01, 0.05, 0.1, 0.25, 0.35, 0.75, and 1.0). We used a square lattice of size  $10^4 \times 10^4 = 10^8$  sites and  $\rho_0 = 0.8$  (0.4 for each type of particles). The results are averaged over 5 runs.

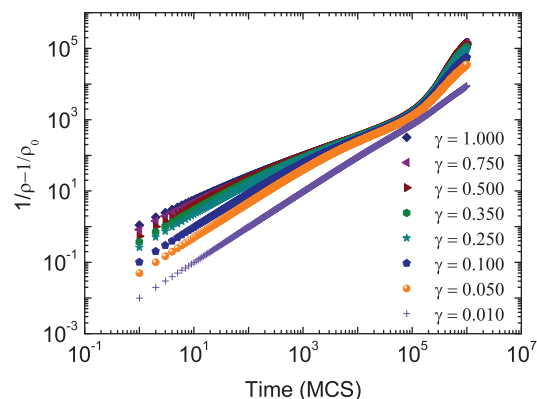


FIG. 3. The  $1/\rho - 1/\rho_0$  vs time plot at log-log for the  $A + B$  annihilation diffusion limited reaction for several values of  $\gamma$  (0.01, 0.05, 0.1, 0.25, 0.35, 0.5, 0.75, and 1.0). We used a square lattice of size  $10^3 \times 10^3 = 10^6$  sites and  $\rho_0 = 0.8$  (0.4 for each type of particles). The results are averaged over 50 runs.

earlier the convergence). With some reaction probabilities this convergence occurs even before the Zeldovich regime. Lower reaction probabilities presumably require more time to converge because more depletion must occur (lower particle density must be achieved) before the reaction becomes diffusion limited.

In Fig. 3, we examine the results of the finite size effects. The reaction is the same as in Fig. 2, but it is performed on a lattice of a smaller size of  $10^3 \times 10^3$ . It has been shown in the past<sup>30</sup> that the time until the beginning of the finite size regime,  $\tau_f$ , is proportional to the size of the lattice, and it goes as  $\tau_f \sim L^2/D$ , where  $D$  is the diffusion constant and  $L$  is the length of the lattice. That same effect was observed here: from Fig. 2 to Fig. 3 the finite size regime onset changes from  $10^7$  to  $10^5$ . Based on derivation of Ref. 30, it has been predicted<sup>31</sup> that the onset time of the finite size regime should also be inversely proportional to the reaction probability, as reducing the reaction probability would be expected to increase the time required for depleting a given region. However, we see here that in both Figs. 2 and 3 the onset time is less sensitive to the reaction probability than are the slopes before and after the finite size regime sets in. Apparently, the depletion time is less affected by reaction probability due to the convergence

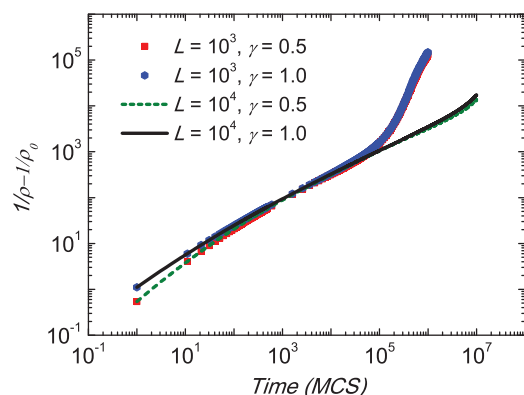


FIG. 4. The  $1/\rho - 1/\rho_0$  vs time plot at log-log for the  $A + B$  annihilation diffusion limited reaction for size  $10^3 \times 10^3$  and  $10^4 \times 10^4$  with high annihilation reaction probabilities (0.5 and 1.0).

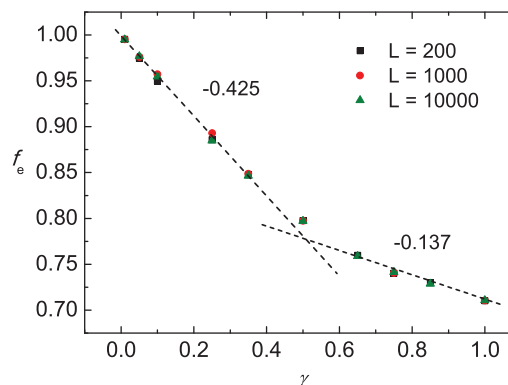


FIG. 5. The early slopes ( $f_e$ ) vs  $\gamma$  plot for the  $A + B$  annihilation diffusion limited reaction for 3 different system sizes ( $L = 200$ ,  $L = 10^3$ , and  $L = 10^4$ ) and  $\rho(0) = 0.8$  (0.4 for each type of particles).

which occurs prior to finite size effects. Note that the only cases which do not converge also do not display finite size effects at all due to very low reaction probabilities (precluding a diffusion limited reaction). In Fig. 3, we see re-divergence of the slopes after the finite size regime.

If we compare the plots for the two lattice sizes in Figs. 2 and 3, we see that in both plots the convergence occurs later for lower reaction probabilities. In Fig. 4, we show that the convergence even shows the exact same profile for different lattice sizes at high reaction probabilities before finite size effects set in, and the simulations for the 2 different lattice sizes subsequently separate because the finite size effects are lattice size dependent. This is counterintuitive: one might expect that a lower reaction efficiency will take longer to deplete the reactants, yet we find that different reaction probabilities result in different depletion profiles at early times but that the kinetic behavior then converges independently of reaction probability (also independently of lattice size for sufficiently high reaction probabilities). As shown in Fig. 3 the convergence for the smaller lattice size is more sensitive to low reaction probability, apparently because finite size effects occur earlier and effectively compete with the convergence. This trend was preserved when an even smaller lattice was used ( $200 \times 200$ , not shown).

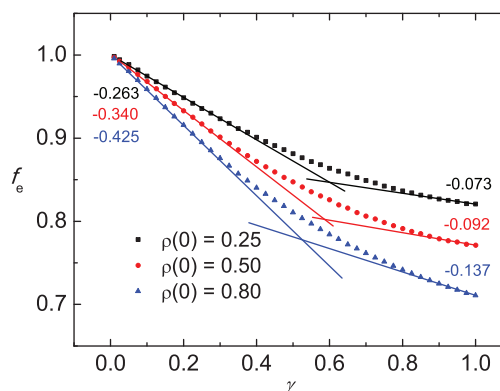


FIG. 6. The early slopes  $f_e$  vs  $\gamma$  plot for the  $A + B$  annihilation diffusion limited reaction for size  $10^3 \times 10^3$  and for 3 different values of  $\rho(0)$  (0.25, 0.5, and 0.8).



TABLE I. Fitting parameters from  $f_e$  vs  $\gamma$  at  $\gamma \rightarrow 0$  and  $\gamma \rightarrow 1$  for various initial coverages.

$\rho(0)$	$f_e = m\gamma + b$ parameters for, $\gamma \rightarrow 0$		$f_e = m\gamma + b$ parameters for, $\gamma \rightarrow 1$	
	m	b	m	b
0.010	-0.200	0.997	-0.081	0.929
0.025	-0.201	0.996	-0.071	0.921
0.100	-0.225	0.997	-0.074	0.917
0.250	-0.263	1.001	-0.073	0.891
0.500	-0.340	1.001	-0.092	0.857
0.800	-0.425	1.000	-0.137	0.856

In Fig. 5, we plot the value of the early slopes,  $f_e$ , as a function of reaction probability  $\gamma$  for different lattice sizes, all with  $\rho(0) = 0.8$  and  $\rho_A(0) = \rho_B(0) = 0.4$ . We observe from the plot of  $f_e$  vs  $\gamma$ , that the system is completely independent of lattice size, but we also see that two different limits are approached, one for  $\gamma \rightarrow 0$  and another one for  $\gamma \rightarrow 1$ . This behavior can be described phenomenologically by linear fits, as shown in Fig. 5 (the slopes of the linear fits are displayed in the figure).

Finally, we monitor the reaction for different initial concentrations  $\rho(0)$ , to see if there is any dependence of the reaction rate on  $\rho(0)$ . The results are shown in Fig. 6. As it can be seen, there is a strong such dependence of  $f_e$  on  $\rho(0)$  in the entire  $\gamma$  range, something that would be expected and in agreement with previous works. To quantify this relationship we performed a linear fit. The resulting parameter values are included in Table I for  $f_e$  vs  $\gamma$ , for both limits of  $\gamma \rightarrow 0$  and  $\gamma \rightarrow 1$ .

#### IV. CONCLUSIONS

We have investigated the effects of the reaction probability  $\gamma$  for the diffusion limited  $A + B \rightarrow 0$  system, with  $\rho_A(0) = \rho_B(0)$ . Several interesting phenomena are observed. For early times the smaller the  $\gamma$  the larger the slope, as the process becomes less diffusion limited (this slope is independent of lattice size). As  $\gamma$  increases the slope decreases progressively, as the process progressively becomes diffusion limited. In more detail:

- The early slopes in a Zeldovich plot are completely independent of the lattice size and depend only on the reaction probability,  $\gamma$ , and initial coverage,  $\rho(0)$ . In Table I, we have included the values from linear fits for  $f_e$  as  $\gamma \rightarrow 0$  and  $\gamma \rightarrow 1$  for various initial coverages. We therefore believe it is general for this specific reaction ( $A + B \rightarrow 0$  on a square lattice) as we have varied both lattice size and reaction probability.
- Non-trivially, when varying the reaction probability within a single lattice size, both the slope and the con-

centration in a Zeldovich plot eventually converge to the same value provided that the reaction probability is sufficiently high to allow diffusion limited reaction. With very low reaction probabilities (e.g., 0.001) the reaction is not diffusion limited which precludes the convergence. For sufficiently high reaction probabilities, the convergence occurs with the exact same profile for different lattice sizes given the same reaction probability.

- The convergence for smaller lattice sizes is more sensitive to lower reaction probability,  $\gamma$ , apparently because finite size effects set in earlier and compete with the convergence.

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