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The $A + B \to 0$ Diffusion-Limited Reaction with Correlated Initial Condition

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We show some inaccuracies in recent arguments claiming that in the long-time limit the initially correlated $A + B \to 0$ diffusion-limited reaction can be faster than the $A + A \to 0$ one. With the errors corrected, these arguments seem to confirm the former theory of Toussant and Wilczek according to which the global rate of both reactions should ultimately be the same. This hypothesis is also supported by our numerical simulations of a two-dimensional lattice system.

KEY WORDS: Diffusion-limited reaction; numerical simulations.

1. INTRODUCTION

The anomalous behavior of diffusion-limited annihilation reactions is of much current interest, and several rigorous results have already been obtained for these problems. In particular, it is known[1,2] that the global density of particles $\rho(t)$ in the $A + A \to 0$ process is, as time t goes to infinity, proportional to ρ^A, where

$$\rho^A(t) = \begin{cases} t^{-1/2}, & d < 2 \\ \ln(t)/t, & d = 2 \\ t^{-1}, & d > 2 \end{cases} \tag{1}$$

and d is the (Euclidean) space dimension. Another rigorous result[3] is that the density of particles in the $A + B \to 0$ process with an uncorrelated initial condition decays as ρ^U, where

$$\rho^U(t) = \begin{cases} t^{-d/4}, & d < 4 \\ t^{-1}, & d \geqslant 4 \end{cases} \tag{2}$$

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and where we assumed the global initial concentrations of both species to be exactly the same.

However, there are also diffusion-limited reactions for which no rigorous results are known. Here we shall consider one of them—the $A + B \to 0$ problem with initially correlated concentrations of A's and B's. Following refs. 4 and 5, we shall assume that a correlated initial condition is prepared by depositing *pairs* A–B at random locations in the system, the distance between the members of each pair being a constant c. Notice that with this definition c can be interpreted as the radius of correlations, and as it approaches infinity, the correlated initial condition turns into the uncorrelated one.

There are two heuristic theories describing the initially correlated $A + B \to 0$ reaction in the long-time limit, each giving different predictions. According to Toussant and Wilczek,[6] such a reaction should proceed exactly like the $A + A \to 0$ one, so we should expect $\rho(t)$, the density of particles, to be proportional to $\rho^A(t)$. On the other hand, Lindenberg *et al.*[4] came to the conclusion that it should decay as ρ^L, where

$$\rho^L(t) = \begin{cases} t^{-(d+2)/4}, & d < 2 \\ t^{-1}, & d \geqslant 2 \end{cases} \tag{3}$$

This result is somewhat puzzling, as the comparison of Eqs. (1) and (3) implies that for $d \leqslant 2$ the $A + B \to 0$ process should be faster than the $A + A \to 0$ one, which is at odds with our intuitive picture of the diffusion-limited reactions. In the $A + B \to 0$ system only collisions between unlike particles can result in decrease in $\rho(t)$, whereas in the latter process any collision can have such effect. Thus the $A + A \to 0$ reaction should be at least as fast as the $A + B \to 0$ one.

The main purpose of this paper is to compare the two theories and determine which of them gives a better description of the initially correlated $A + B \to 0$ reaction. For better comparison they are briefly outlined in Section 2. In the next section we argue that they refer to two essentially different models and therefore their predictions can be completely inconsistent with each other. In Section 4 we present results of our numerical simulations of a two-dimensional initially correlated $A + B \to 0$ reaction. Our data seem to confirm that the density of this system behaves in accordance with Eq. (1). Finally, Section 5 is devoted to conclusions.

2. SURVEY OF PREVIOUS THEORIES

2.1. Scaling Theory of Toussant and Wilczek

One of the problems examined by Toussant and Wilczek[6] was how to determine the behavior of a system $A + B \to 0$ of particles A and anti-

particles B with a correlated initial condition. They noticed that for $d \leqslant 2$ the random walk executed by each particle is reentrant, i.e., the probability of a random walker visiting any given point approaches one. The volume so covered in a time t, V_t, is proportional to $t^{1/2}$ and $t/\ln t$ for $d=1$ and $d=2$, respectively,[1] and any antiparticle B in this region should probably have been annihilated. It is then argued that the initially correlated system cannot separate into single-species patches of linear size much bigger than c. Therefore the number N_t of like particles remaining in V_t should, for sufficiently large time t, be $O(1)$, which leads to (1) since $\rho \sim N_t/V_t$. This is so because if N_t could grow in the long-time limit, then V_t would constitute an inflating patch of like particles whose linear size $l_A \sim V_t^{1/d}$ could be made arbitrarily large. Notice that the above reasoning leads to the conclusion that Eq. (1) constitutes the lower boundary for the density of any system with the $A + B \to 0$ reaction in the long-time limit, which implies that in this limit the $A + B \to 0$ reaction cannot be faster than the $A + A \to 0$ one. As for the case $d > 2$, the result $\rho(t) \sim t^{-1}$ was obtained by a simple dimensional argument.

2.2. Continuous Approach of Lindenberg, West, and Kopelman

Lindenberg *et al.*[4] assumed that the evolution of the initially correlated $A + B \to 0$ problem can be described with the equation

$$\dot{\rho}_A(\mathbf{r}, t) = D\nabla^2 \rho_A(\mathbf{r}, t) - k\rho_A(\mathbf{r}, t)\,\rho_B(\mathbf{r}, t) \tag{4}$$

and similarly for ρ_B, where ρ_A and ρ_B are the local concentrations of A's and B's, D is the diffusion constant, and k is a constant controlling the local reaction rate. Let $\gamma(\mathbf{r}, t) \equiv \frac{1}{2}[\rho_A(\mathbf{r}, t) - \rho_B(\mathbf{r}, t)]$ and $\rho(\mathbf{r}, t) \equiv \frac{1}{2}[\rho_A(\mathbf{r}, t) + \rho_B(\mathbf{r}, t)]$. Then short analytic reasoning yields

$$\langle \gamma^2(\mathbf{r}, t) \rangle = \frac{\rho_0}{2(8\pi D t)^{d/2}} (1 - \exp^{-c^2/8Dt}) \tag{5}$$

where ρ_0 is the initial global concentration of either species, and $\langle \cdots \rangle$ denotes the average over the ensemble of correlated initial conditions parametrized by the distance between the members of each pair c. The initial conditions imply that $\langle \rho(\mathbf{r}, t) \rangle$ is independent of $\mathbf{r}$ for all time, and therefore it is equal to the global density $\rho(t)$. By taking the averages of Eq. (4) one arrives at

$$\langle \dot{\rho}(\mathbf{r}, t) \rangle = -k[\langle \rho^2(\mathbf{r}, t) \rangle - \langle \gamma^2(\mathbf{r}, t) \rangle] \tag{6}$$

Now Lindenberg *et al.* assume that as t goes to infinity, $\langle \rho^2(\mathbf{r}, t) \rangle \sim \langle \rho(\mathbf{r}, t) \rangle^2$, $\rho(t) \sim t^{-\alpha}$, and $\langle \gamma^2(\mathbf{r}, t) \rangle \sim t^{-2\mu}$ for some α and μ. With all

these assumptions Eqs. (5) and (6) imply $\alpha = \min(\mu, 1)$. Since for finite c, or a correlated initial condition, Eq. (5) gives $\mu = (d+2)/4$, one arrives at the conclusion that in this case $\rho(t) \sim \rho^{L}(t)$. In the limit $c \to \infty$, or for an uncorrelated initial condition, one has $\mu = d/2$ and consequently $\rho(t) \sim \rho^{U}(t)$. The case $c = 0$ was overlooked in ref. 4. Clearly in this case $\rho_A = \rho_B$ and Eq. (4) turns into an equation for the $A + A \to 0$ reaction

$$\dot{\rho}_A(\mathbf{r}, t) = D\nabla^2 \rho_A(\mathbf{r}, t) - k\rho_A^2(\mathbf{r}, t) \tag{7}$$

Moreover, as in this case $\langle \gamma^2(\mathbf{r}, t) \rangle = 0$, Eq. (6) turns into $\dot{\rho}(t) \sim -k\rho^2(t)$, i.e., $\rho(t) \sim t^{-1}$ regardless of the space dimension d. Henceforth we shall refer to the above reasoning as the LWK model.

2.3. Heuristic Reasoning of Lindenberg, Shen, and Kopelman

In another paper Lindenberg *et al.*[5] presented another argument to support their conclusion that the initially correlated $A + B \to 0$ process can be faster than the $A + A \to 0$ one. Let χ^{-1} denote the probability that a particle has a nearest neighbor with which it can react. In the $A + A \to 0$ reaction any particle can react with any other, so $\chi^{-1} = 1$. However, in the $A + B \to 0$ case χ^{-1} may deviate from unity due to the presence of aggregates of like particles, which, by definition, cannot react with each other. For example, in the case of an uncorrelated initial condition $\chi^{-1} \sim t^{-1/2}$. Assume that generally for some γ

$$\chi^{-1} \sim t^{-\gamma/2} \tag{8}$$

Then a simple scaling argument leads to $\rho(t) \sim t^{-\alpha}$, where

$$\alpha = \min\left(\frac{d}{2}\left(1 - \frac{\gamma}{2}\right), 1\right) \tag{9}$$

This formula recovers properly the behavior of $A + A \to 0$ ($\gamma = 0$) and initially uncorrelated $A + B \to 0$ ($\gamma = 1$) systems. Lindenberg *et al.* noticed that it would also be consistent with their main result for initially correlated $A + B \to 0$ systems, $\rho(t) \sim \rho^{L}(t)$ if, for $d < 2$,

$$\gamma = (d-2)/d$$

To account for the *negative* value of γ for $d = 1$, they considered the following, in a way extreme situation in one dimension: pairs A–B are distributed at random a distance c lattice constants apart, with B always to the right of A. Initially the largest possible size of aggregates is c. As the reaction proceeds, the particles at the ends of the aggregates react, the number of

particles per aggregate decreases, and consequently χ^{-1} increases. Thus, according to ref. 5, for one-dimensional systems γ must be negative. As the global reaction rate is proportional to $\chi^{-1} \sim t^{-\gamma/2}$, $A + B \to 0$ reactions must be faster than $A + A \to 0$ ones.

3. ANALYSIS

Several questions may arise after comparing the arguments outlined above. Can the $A + B \to 0$ reaction be really faster than the $A + A \to 0$ one? Why do these approaches yield different results? And which of them is correct?

First of all notice that in contrast to the scaling theory of Toussant and Wilczek, the LWK model fails to predict the correct form of decay of the density in $A + A \to 0$ systems. It is not difficult to find a mathematical reason for this. As pointed out by Doering and ben-Avraham,[7] Eq. (7), even with random initial conditions, necessarily leads to the mean-field result $\rho_A(t) \sim t^{-1}$ for any space dimension. The physical reason for this is that the anomalous behavior of $A + A \to 0$ systems in low dimensions arises from an anomalous form of correlation functions, which, in turn, results from averaging over all possible random walks of the particles. As we noticed above, these walks are highly (negatively) correlated for $d \leqslant 2$. On the other hand, the averages in the LWK model are taken only over the initial conditions, the evolution of the system assumed to be fully governed by a deterministic equation (7) in which no correlations are taken into account.

One might hope that this drawback could be removed if one assumed that $\rho_A(\mathbf{r}, t)$ in Eq. (7) represents not the concentration, but rather the probability of finding a particle at $(\mathbf{r}, t)$. This, however, would not help much, as to tackle the problem so posed one would have to replace in this equation the simple mean-field reaction term $-k\rho_A^2$ with an appropriate two-particle correlation function. This function, in turn, would depend on a three-particle correlation function and so on *ad infinitum*.[6]

As we can see, the two approaches considered here, though they refer to the same physical problem, are based on essentially different assumptions and therefore can lead to different conclusions. Because of this the procedure employed in ref. 3—comparing Toussant and Wilczek's results for the $A + A \to 0$ problem with the predictions of the LWK model for the $A + B \to 0$ reaction—could, and actually did, lead to puzzling conclusions. The proper procedure is to compare results obtained within the same model. In this case Toussant and Wilczek's scaling theory predicts both types of reaction to be equally fast for any space dimension. The LWK model predicts such behavior for $d \geqslant 2$ and the $A + A \to 0$ reaction to be

faster than the $A + B \to 0$ one for $d < 2$. Thus none of these theories, if properly applied, leads to the conclusion that the $A + B \to 0$ reaction can be faster than the $A + A \to 0$ one.

Notice, however, that the LWK model gives the correct result $\rho(t) \sim \rho^U(t)$ in the case of uncorrelated $A + B \to 0$ systems. This property reflects the fact that such processes are essentially "fluctuation-dominated" —the impact of initial fluctuations in concentrations of the two species turns out to be so great that correlations in the motion of the particles, whether or not accounted for, become irrelevant.

However, there is still the third, heuristic argument of Lindenberg *et al.*,[5] which, despite accounting for the correlations, leads to the conclusion that initially correlated $A + B \to 0$ reactions are unavoidably faster than $A + A \to 0$ ones. We shall show not only some inaccuracies in this reasoning, but that a simple correction of it confirms the prediction of Toussant and Wilczek. First of all notice that if γ in Eq. (8) were negative, χ^{-1} would go to infinity. This is impossible since χ^{-1} is interpreted as probability. Therefore the reasoning of ref. 5 can be applied only to finite intervals rather than to the $t \to \infty$ limit. The main thread of the next argument, which refers to the one-dimensional system of pairs A–B distributed so that B is always to the right of A, is that the size of initially big aggregates of like particles decreases with time, and so the probability χ^{-1} ($\sim t^{-\gamma/2}$) that a particle can react with its nearest neighbor increases, leading to a negative value of γ. This argument, however, does not take into account the fact that the increase of this probability starts from a relatively small value (caused by the existence of the aggregates) and then slowly grows to its limiting value. The reaction rate is proportional to χ^{-1}. Since in the $A + A \to 0$ case $\chi^{-1} = 1$ by definition, we again conclude that in the long-time limit $A + B \to 0$ reactions cannot be faster than $A + A \to 0$ ones.

We shall finish this section with another example of an initially correlated one-dimensional $A + B \to 0$ systems which can be easily shown to behave in accordance with Toussant and Wilczek theory rather than the LWK model. Consider an infinite chain of particles ...-A-B-A-B-... such that the distance between each pair of neighboring particles is a constant c. Initially each particle can react with any of its nearest neighbors (and so $\chi^{-1} = 1$) and evidently this property remains satisfied as the reaction proceeds, too. Thus this initially correlated $A + B \to 0$ system behaves exactly like the $A + A \to 0$ one, i.e., $\rho(t) \sim t^{-1/2}$, whereas the LWK model predicts $\rho(t) \sim t^{-3/4}$.

4. NUMERICAL SIMULATIONS

The algorithm we employed is a faithful implementation of a cellular automata technique developed by Chopard and Droz,[8] the initial condi-

tions being the only difference. Briefly speaking, we used a square lattice $L \times L$ with periodic boundary conditions in all directions. We assumed that there were two kinds of particles (A and B). At each time step each particle hopped at random to one of the four nearest-neighbor sites, but no pair of particles was allowed to move simultaneously along the same bond in the same direction ("exclusion rule"). Thus there could be up to four particles at a given site at a time, each moving in different direction. When two unlike particles head-on collided, they necessarily reacted and disappeared from the system. Usually we used the lattice with $L = 2500$ and carried out as any as $t_{\max} = 10^6$ iterations. This was possible because the speed of our program was inversely proportional to the rapidly decreasing density of particles rather than to the (constant) volume of the lattice.

We started our numerical analysis with a few simulations of the uncorrelated $A + B \to 0$ problem with $L = 2500$ and $t_{\max} = 10^6$. Several numerical simulations have been carried out for these systems by other authors.[6,9] Usually they used Monte Carlo models in which only one particle was allowed to move at a time. They also assumed the reaction to occur simply on contact of two unlike particles. Comparison of their results with ours reveals no qualitative differences. Thus we conclude that neither the cellular automata character of our algorithm nor the fact that we allowed only head-on collisions to result in reaction affects the qualitative behavior of the system.

The main part of our simulations was devoted to the initially correlated $A + B \to 0$ problem. Again we chose $L = 2500$ and $t_{\max} = 10^6$, but this time we averaged the data over $N = 100$ samples. Initially we distributed the particles so that there was a single pair A–B at each lattice site. The directions of their velocities were chosen at random, but in such a way

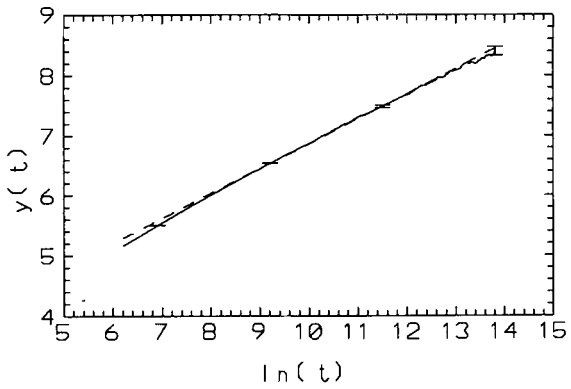

Fig. 1. Plot of $y(t) \equiv t \cdot \rho(t)$ vs. $\ln(t)$ for $L = 2500$ averaged over 100 samples. The dashed line is only a guide to the eye. The error bars are computed as standard deviations of the mean value at $t = 10^3$, 10^4, 10^5, and 10^6.

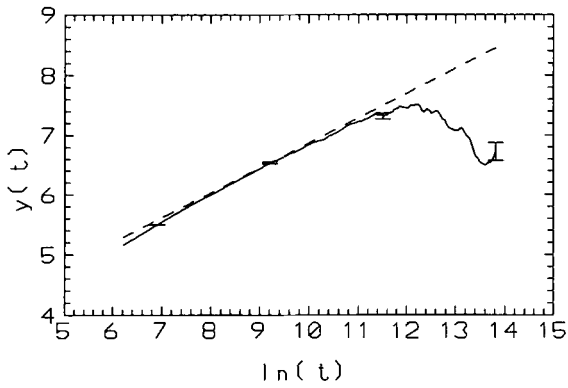

Fig. 2. The same as in Fig. 1, but for $L = 1000$. The dashed line is the same as in Fig. 1 for easier comparison.

that the exclusion rule was satisfied. In this way we obtained extremely correlated initial conditions with no fluctuations in density. Any anomalous behavior of this system must be caused only by correlations in the trajectories of the random walkers.

To determine whether the density in our model goes as t^{-1} or $\ln(t)/t$ we plotted $y(t) \equiv t \cdot \rho(t)$ vs. $\ln(t)$ (Fig. 1). Though the plot can be quite well estimated with a straight line, the slope of $y(t)$ shows a slight, but clear tendency to diminish. Similar tendency was also observed in previous simulations of the initially random $A + B \to 0$ problem.[6,9] Due to size effects the density found in their simulations tended, for large t, to decay faster than the theoretical value derived for infinite systems. Notice also that in our simulations after 10^6 iterations a random walker covers on average the distance of 1000 lattice constants. As this quantity is very close to half of the linear size of the lattice, by this time the influence of size effects should have already shown. We tried to estimate their magnitude by comparing the results obtained for $L = 2500$ and $L = 1000$ (Fig. 2). We can see that as the size of the system gets larger, the range in which the plot of $t \cdot \rho(t)$ vs. $\ln(t)$ is (nearly) linear becomes wider. This property strongly suggests that in the limit $t \to \infty$ the density of the initially correlated $A + B \to 0$ reaction decays as $\ln(t)/t$, i.e., exactly as in the $A + A \to 0$ problem.

5. CONCLUSIONS

We showed several inaccuracies in the arguments of Lindenberg *et al.*[4] First of all they overlooked the mean-field character of their main

equation (4). The negative correlations in the motion of particles are equivalent to their effective "repelling," which is the cause of a decrease in the reaction rate. In other words, mean-field theories should tend to overestimate the reaction rate of annihilation systems. This explains why comparison of their results with the exact ones for the $A + A \to 0$ problem led Lindenberg *et al.* to a puzzling conclusion that the $A + B \to 0$ reaction can be faster than the $A + A \to 0$ one. By reinterpreting their results we showed, however, that as long as one compares only the results obtained within the same model, one always gets that the $A + A \to 0$ reaction is at least as fast as the $A + B \to 0$ one.

Next we considered the heuristic reasoning of Lindenberg *et al.*[5] We showed that their principal assumption, $\gamma < 0$, leads to several contradictions, and hence cannot be accepted. As evidently γ cannot be positive either, it must equal 0, which is the value valid "by definition" for the $A + A \to 0$ problems. In this way the two types of reaction turn out to be equally fast, and the prediction of Toussant and Wilczek has been supported again.

This prediction has also been corroborated by our numerical simulations. The system size and the number of iterations we carried out were large enough not only to find the exponent α in $\rho(t) \sim t^{-\alpha}$, but the logarithmic term as well [compare Eq. (1) for $d = 2$]. In this way the cellular automata technique which we employed proved to be a very convenient and effective means of simulations of diffusion-limited annihilation reactions.

One advantage of the LWK model is that it allows us to analyze how the rate of different diffusion-limited reactions depends, in low dimensions, on two factors: randomness of the initial condition and the correlations in the motion of random walkers. In the case of the $A + A \to 0$ reaction ($c = 0$) the initial condition turns out to be irrelevant, and anomalous kinetics of the system is entirely due to the correlations in the motion of particles. The opposite situation takes place in the random $A + B \to 0$ problem ($c \to \infty$), in which the slowing down of the reaction rate is caused exclusively by randomness (fluctuations) of the initial condition. An interesting situation arises in the third, intermediate problem of the initially correlated $A + B \to 0$ reaction ($0 < c < \infty$). In this case the randomness of the initial condition reduces the decay of the density from the mean-field form $\rho \sim t^{-1}$ down to the form predicted by the LWK model, $\rho \sim \rho^{L} \sim t^{-(d+2)/4}$. However, the negative correlations in the motion of particles slow this decay even more, down to $\rho^{A} \sim t^{-d/2}$, which makes the randomness of the initial condition irrelevant to this problem, and constitutes the main reason why the LWK model fails to give the correct description of initially correlated $A + B \to 0$ reactions for large time.

NOTE ADDED

In a series of recent papers Lindenberg *et al.*[10] found that before the behavior of the system reaches the long-time limit (and this is the only case considered in the present paper), the initially correlated $A + B \to 0$ diffusion-limited reaction goes through several stages characterized by various scaling properties. In particular, they found that the $A + B \to 0$ process can be faster than the $A + A \to 0$ one before the final stage of the evolution has been attained.

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