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The $A + B \rightarrow 0$ reaction on a disordered lattice

J. Mai^a, V.N. Kuzovkov^{b,c}, W. von Niessen^b^a *Institut für Theoretische Polymerphysik, Universität Freiburg, Rheinstrasse 12, D-79104 Freiburg, Germany*^b *Institut für Physikalische und Theoretische Chemie, Technische Universität Braunschweig, D-38106 Braunschweig, Germany*^c *Institute of Theoretical Physics, University of Latvia, Rainis Boulevard 19, Riga, Latvia*¹

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Abstract

In this paper a stochastic model for the $A + B \rightarrow 0$ reaction with creation of particles on a disordered surface is studied for $d = 2$ and $d = 3$ spatial dimensions. Densities and correlations of the particles are examined in detail. We find that the stationary state which exists for $d = 3$ in case of an ordered lattice vanishes in the case of a disordered lattice. A stationary state for $d = 2$ never exists.

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1. Introduction

The $A + B \rightarrow 0$ reaction with creation of particles is well known in the field of stochastic processes [1–9]. The reaction itself is physically meaningful for the description of Frenkel defect recombination [10]. It is well known that chemical reactions depend critically on the spatial dimension d . For the $A + B \rightarrow 0$ reaction with creation of particles a critical dimension $d_0 = 2$ exists. For $d > d_0$ the system reaches a stationary state with the particle densities $C_A(\infty) = C_B(\infty) = C(\infty)$ for the case of equal creation rates $p_A = p_B = p$. In continuous models the particle densities for $d \leq d_0$ increase with time if one neglects hard-core interaction. The hard-core interaction (representing e.g. the exclusion principle on the lattice: one particle per site) bounds the concentration from above. This means that at longer times the concentration inevitably stagnates.

It is important to note that this stagnation of concentration does not mean a steady state of the system: the segregation of particles proceeds with time, although their concentration does not change. In this paper we focus our interest on a discrete lattice representation with hard core interaction.

The behavior of the $A + B \rightarrow 0$ reaction as discussed above is well understood today. In this paper we want to study another important factor which influences the behavior of the reaction: the role of a disordered lattice. On such a lattice not all sites are accessible to the particles. We denote by S the fraction of accessible sites. In the case of an ordered lattice S is equal to unity. In this paper we want to study the behavior of the $A + B \rightarrow 0$ reaction as a function of S for $d = 2$ and $d = 3$. We know that for $d = 3$ and $S = 1$ a stationary state exists. How is this state influenced by a disordered lattice with $S < 1$? It is possible that this state vanishes for $S < 1$. Of special interest is the percolation threshold of the lattice $S = S_c$ ($S_c = 0.31 \dots$

¹ Permanent address.

for $d = 3$ and $S_c = 0.59 \dots$ for $d = 2$). The disordered lattice is prepared from a lattice in which all sites are inaccessible. Then accessible sites are distributed randomly on the lattice with density S . For $S > S_c$ an infinite cluster of accessible sites develops while for $S < S_c$ only finite clusters will exist. This difference is very important for the reaction: Finite clusters can be completely occupied by one particle type. Due to the fact that these finite clusters of accessible sites are separated by inaccessible ones, the reaction on such a cluster comes to a stop. (It should be noted that without the hard-core interaction the reaction in a finite cluster would never end and the number of particles would increase unbounded from above.) This is not possible for an infinite cluster which appears for $S > S_c$. Therefore we may expect a dramatic change of the behavior of the reaction for the different regimes of S which may lead to an instability of the stationary state existing for $S = 1$.

Also the case $d = 2$ is interesting. Here one may expect quantitative (but not as for $d = 3$ qualitative) changes of the behavior. Even for $S = 1$ no stationary state exists. Therefore we do not expect a dramatic change of the reaction behavior by lowering S .

As we have pointed out above, the aspect of a disordered lattice is very interesting from a theoretical point of view. Moreover this model is motivated by real chemical reactions taking place on surfaces. The reaction can be promoted or inhibited by specific sites of the lattice (surface). We have shown the influence of such disordered lattices on the NH_3 formation [11] and on the $\text{A} + \frac{1}{2}\text{B}_2 \rightarrow 0$ reaction (a model of the CO oxidation on a Pt/Sn catalyst) [12]. Both reactions depend strongly on the degree of disorder of the lattice. We would like to study this dependency in detail but the NH_3 formation and the $\text{A} + \frac{1}{2}\text{B}_2 \rightarrow 0$ are too complex to allow the pursuit of such an ansatz. Therefore we will focus our interest on the much simpler $\text{A} + \text{B} \rightarrow 0$ reaction.

The paper is structured as follows: In Section 2 we introduce the model and give the necessary definitions. The results are presented in Section 3 and discussed in Section 4.

2. The model

We will use the formalism introduced for a general reaction system in Refs. [13,14]. The reaction system is described by master equations using the Markovian behavior of the reaction. The obtained temporal evolution equations for the particle densities are solved numerically on a lattice. The state of cell l of the lattice is characterized by the variable $\sigma_l \in \{\text{N}, 0, \text{A}, \text{B}\}$, where N means a cell on which creation of a particle is not possible, 0 stands for an empty cell and A, B for a cell occupied by an A or a B particle, respectively. The passive cells (state N) are randomly distributed in the lattice. The density of active cells are denoted by S and the other densities by C_N, C_0, C_A and C_B . The following sum rule holds for the densities,

$$C_0 + C_A + C_B = S, \quad C_N = 1 - S. \quad (1)$$

Let us now define the dynamics of the system by two monomolecular steps



(which represents the creation of A and B with the rate $p_A = p_B = p$) and a bimolecular reaction step



In this paper we want to study the case of an infinitely fast reaction ($k = \infty$). This leads to specific problems in the stochastic description of the reaction. These problems are discussed and solved in Ref. [14]. In what follows we define the time in such a way that $p = 1$ holds. This leads to a reaction system which depends only on d and S (density of active cells).

From the definition of the model it is clear that $C_A(t) = C_B(t) = C(t)$. The upper limit of $C(t)$ is given by $C = S/2$ for $C_0 = 0$ (see Eq. (1)). Therefore it is convenient to introduce an effective occupation $\Theta = 2C/S$ which has a maximum value of unity.

In order to study the particle configuration we will use the correlation functions $F_{\lambda\mu}(r)$ with $\lambda, \mu \in \{\text{N}, 0, \text{A}, \text{B}\}$. The product $c_\lambda^{(\mu)}(r) = C_\lambda F_{\lambda\mu}(r)$ describes the mean density of cells of state λ which have a distance r from a center cell which is in state μ . In the case of randomly distributed particles the correlation function $F_{\lambda\mu}(r) \equiv 1$ and the mean density $c_\lambda^{(\mu)}(r) = C_\lambda$. For $\lambda = \mu = \text{A}$ (or B) the variable

$$\delta c(r) = C_A(F_{AA}(r) - 1) \tag{4}$$

describes the difference density of *correlated* A particles (beyond the mean density) which are located at distance r from a center which is occupied by an A particle. For the $A + B \rightarrow 0$ reaction $\delta c(r) \geq 0$ which allows us to use it as a weight function and define

$$N(t) = 1 + \sum_r \delta c(r) \tag{5}$$

as the effective number of A particles in an A-cluster. The addition of unity in the last equation takes into account the fact that the center ($r = 0$) is occupied by an A particle. $N(t)$ is different from unity if segregation occurs.

With the help of Eq. (4) it is possible to introduce the correlation length $\xi(t)$,

$$\xi = \frac{1}{N(t)} \sum_r |r| \delta c(r). \tag{6}$$

The correlation length is used in our numerical scheme to determine the size of the used lattice k_{\max} . We use $k_{\max} \approx \xi(t)$. The computing time increases as $t\xi(t)$. For a system in which $\xi(t)$ diverges it is impossible to calculate the evolution equations for large t .

3. Results

The reaction steps occur only on active cells. That means that the passive cells lead to geometric distortions for the reaction. If a cluster of active cells is completely covered by one particle species, say A, the reaction comes to a stop because the B particles are separated from this A-cluster by passive cells. This is completely different to the case of an ordered lattice.

In Fig. 1 the effective occupation θ is shown as a function of time t for different values of active cells S and for $d = 3$ (a) and for $d = 2$ (b). Let us first focus on the case $d = 3$. We know that for an ordered lattice (curve 1) a stationary exists [5,6]. Here θ reaches a minimum value and C_0 is large. It is clear that large values of θ are only possible in the case of segregation of the particles. For $S = 1$ the system is not well segregated but forms a mixture of A and B particles which react easily with each other and the reaction rate R_{AB} is large. Also for large S (curves 2–4) the system approaches a stationary state within a small

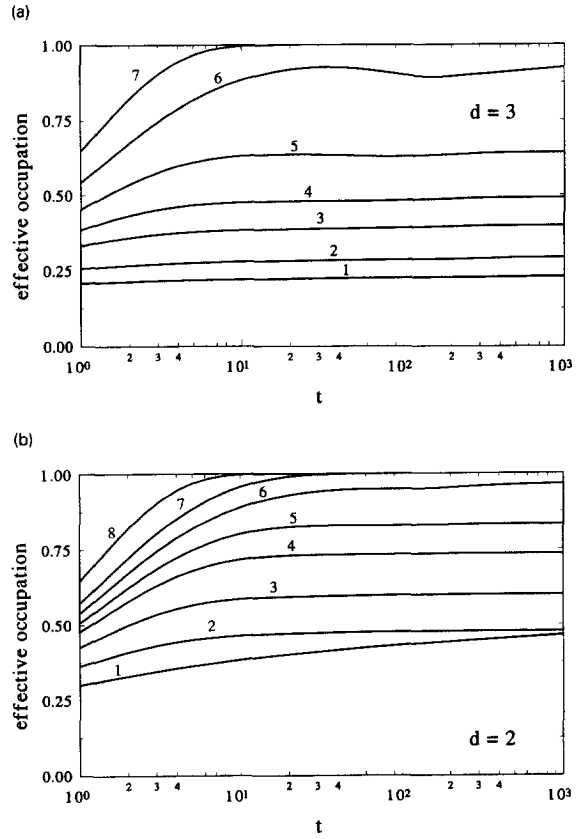


Fig. 1. The effective occupation θ as a function of time t for $d = 3$ (a) and for $d = 2$ (b). (a) The values of S are 1.0 (curve 1), 0.8 (2), 0.6 (3), 0.5 (4), 0.4 (5), 0.3 (6), 0.2 (7). For $d = 2$ (b) the values of S are 1.0 (curve 1), 0.8 (2), 0.65 (3), 0.55 (4), 0.5 (5), 0.45 (6), 0.4 (7), 0.30 (8).

time period. The effective occupation increases with decreasing S due to the segregation of the particles on the lattice. For $S \approx S_c$ (curves 5 and 6) we do not observe a stationary state. Here the disorder of the lattice destabilizes the stationary state. For $S < 0.2$ (curve 7) the system is completely occupied by particles and the reaction comes to a stop.

Let us now discuss the case $d = 2$ (Fig. 1b). We know that here the system does not reach a stationary state on an ordered lattice [5,6]. In a continuum model the particle density grows logarithmic with time [10]. On a lattice we observe the same process (Fig. 1b, curve 1). For no value of S a stationary state is reached. The behavior of the system is qualitatively similar to the case $d = 3$ for $S < 1$. One sees quantitative dif-

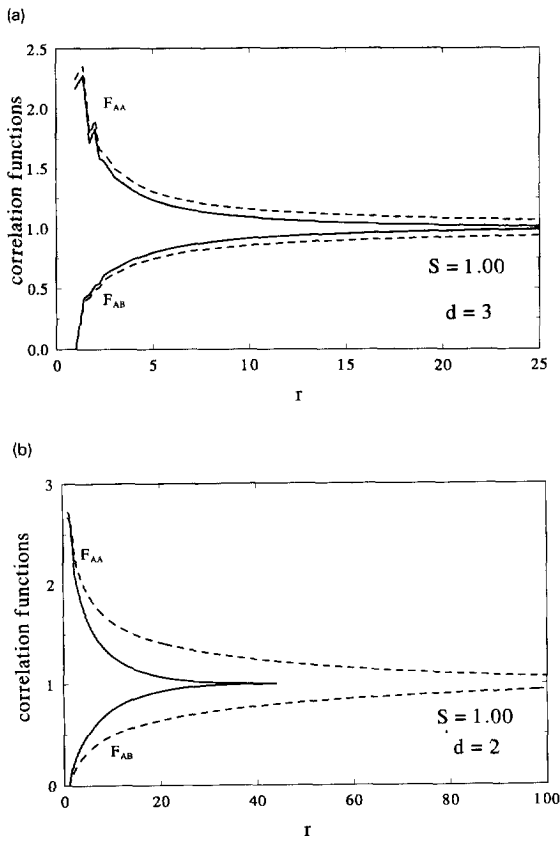


Fig. 2. The correlation functions for $S = 1$ and for $d = 3$ (a) and $d = 2$ (b). The solid curves represent the result for $t = 10^2$ and the dashed curves for $t = 10^3$.

ferences which result from the fact that for $d = 2$ the system is unstable against segregation even for an ordered lattice ($S = 1$).

In Fig. 2 the correlation functions are shown for two different times for $S = 1$ and for $d = 3$ (a) and $d = 2$ (b). In both cases of the spatial dimension d the correlation functions are approaching slowly the limit value of unity (uncorrelated particle distribution). The main qualitative difference between $d = 2$ and $d = 3$ is that for $d = 3$ the correlations are stationary for $t \rightarrow \infty$ for all r . In the case $d = 2$ such a state is not reached but the correlations are evolving with time even for small r . This behavior is expected due to the fact that for $d = 2$ a stationary state does not exist.

In Fig. 3 the correlation length $\xi(t)$ is shown as a function of time. For $S = 1$, $\xi(t)$ diverges with time, $\xi(t) \rightarrow \infty$. That means that the $A + B \rightarrow 0$ reaction

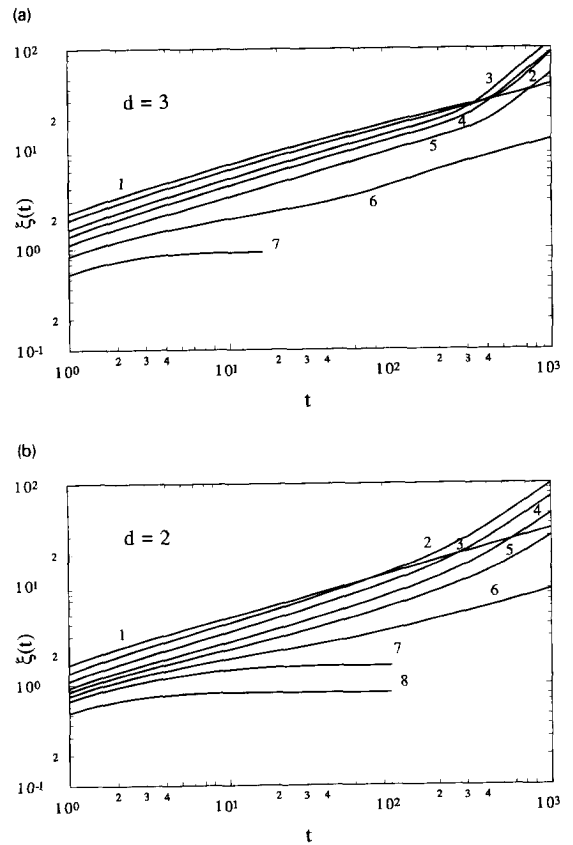


Fig. 3. The correlation length $\xi(t)$ as a function of time for $d = 3$ (a) and $d = 2$ (b). The values of S are the same as in Fig. 1.

reaches the limit of stability of the segregation even for an ordered lattice. In the language of phase transitions [15] the point $t = \infty$ is a critical point for this reaction where the correlation length diverges ($\xi \rightarrow \infty$). One can expect that

$$\delta c(r) = \text{const} \times \frac{\exp[-(r/\xi)^\alpha]}{r^\gamma} \quad (7)$$

goes to zero for $|r| \rightarrow \infty$. (It should be noted that the presented results do not depend on the exact form of $\delta c(r)$. It is only important that this form is a product of two functions from which one grows slowly and the one which depend on ξ grows fast.) With this equality we are able to calculate $N(t)$. We see that $N(t)$ diverges for large t . That means that if the representation Eq. (7) is possible, γ must be smaller than 3. At the critical point $\xi = \infty$, the tail of $\delta c(r)$ is a power in r ($\delta c(r) = \text{const} \times r^{-\gamma}$). From this result we can

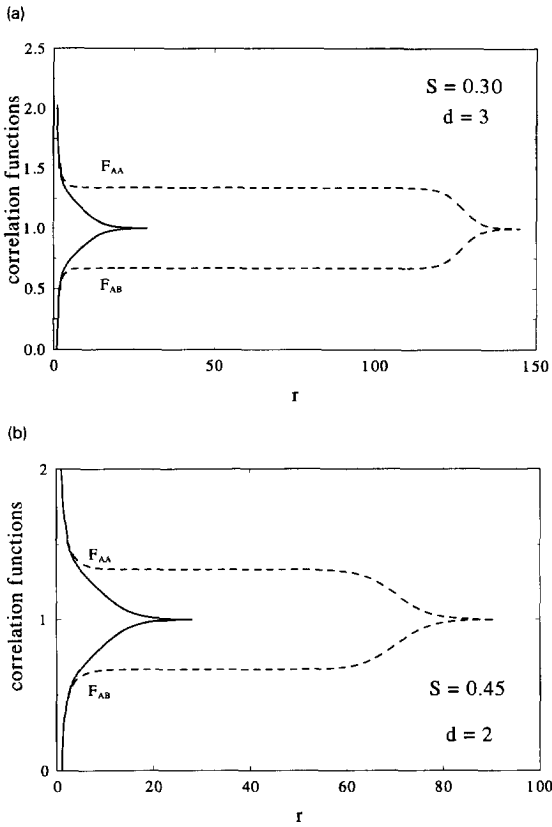


Fig. 4. The correlation functions for $d = 3$ and $S = 0.3$ (a), and for $d = 2$ and $S = 0.45$ (b). The solid curves represent the result for $t = 10^3$ and the dashed curves for $t = 10^4$.

conclude that even for $d = 3$ and $S = 1$ the reaction has reached the limit of stability.

For $S < 1$ we expect that this instability increases. This is exactly what we observe. The effective occupation increases with decreasing S (see Fig. 1) because reactive A and B particles are now separated by lattice sites which cannot be occupied by particles. In Fig. 3 (curves 2–5) the slope of the correlation length changes in the region of $t \propto 10^3$. In fact two correlation lengths $\xi_1(t)$ and $\xi_2(t)$ are developing. $\xi_1(t)$ describes the propagation of spatial correlations by the process of the tail growing. For $S < 1$ a crossover to a new mechanism occurs which describes a wave of segregation running through the lattice ($\xi_2(t)$).

The different behavior of the correlation lengths can be seen in Fig. 4. For $t < 10^3$ (solid curve) we observe only the growth process of the tail of the cor-

relation function. For $t > 10^3$ another spatial structure develops. We obtain for $r < \xi_2(t)$ (in this figure $\xi_2(t) \approx 100$) that the particles are strongly correlated and $\xi_2(t)$ describes the complete segregation of A and B particles.

Comparing $\xi(t)$ for $d = 2$ and $d = 3$ we observe only qualitative differences. This means that (with the exception of the logarithmic growth) the case $d = 2$ and $d = 3$ are similar.

The percolation threshold $S_c = 0.31 \dots$ for $d = 3$ (or $S_c = 0.59 \dots$ for $d = 2$) is another interesting point for the reaction system. At this point the temporal evolution is very slow and therefore we were not able to study the system at this point in detail. But it is clear what will happen: For $S < S_c$ the active cells are distributed over finite clusters on the lattice. These finite clusters can be completely occupied by one particle type and the reaction comes to a stop. For $S > S_c$ an infinite cluster of active cells appears which cannot be completely occupied by one particle type. For $S = 0.2$ (Fig. 1a, curve 7) the time for a complete occupation (and segregation) of the lattice is very small ($t \propto 10^1$). Near the percolation threshold S_c the segregation is connected with the appearance of oscillations of Θ and R_{AB} (Fig. 1a, curve 6). For $S \rightarrow S_c$ the mean size of the cluster of active cells increases rapidly. Therefore the time t which is necessary to reach the state of complete segregation increases dramatically (for $S = 0.28$, $t \propto 10^5$).

For $S > S_c$ the time for a complete segregation approaches infinity. We have studied this process near S_c for t up to 10^4 time steps. For $S = 0.28$ one observes a complete segregation and $R_{AB} \rightarrow 0$. This process is connected with oscillations as discussed above. For larger values of S these oscillations are very small and R_{AB} reaches a quasi stationary state. The effective number of A particles in an A cluster, $N(t)$, as a function of $\xi(t)$ is nearly independent of values of S which are near S_c and we obtain a universal function. (For values of S which are far away from S_c this result does not hold.) The results for $d = 2$ are very similar to the case $d = 3$ for $S < 1$. Therefore we will not discuss this case here.

For large values $\xi \gg 10^1$ the simple dependency $N(t) \propto \xi(t)^d$ holds where the d accounts for the dimension of the lattice. This dependency is easy to understand: From Fig. 4 follows that the correlation function $F_{AA}(r)$ for the case of strong segregation, is

very similar to a step function: $F_{AA}(r) - 1 \approx \text{const}$ for $r < \xi(t)$ and $F_{AA}(r) - 1 \approx 0$ for $r > \xi(t)$. From this follows the dependency of $N(t)$ and $\xi(t)$ discussed above.

4. Discussion

In this paper we studied the $A + B \rightarrow 0$ reaction on an ordered and on a disordered lattice of spatial dimensions two and three. For $d = 3$ the particles on an ordered lattice form a reactive mixture. Therefore the occupation of the lattice is small and the reaction rate large. Large clusters of particles do not exist. But even for $S = 1$ the system is already at the limit of stability where the correlation length ξ diverges for $t \rightarrow \infty$. This instability increases for decreasing S and the system approaches a completely segregated and correlated state. For $S < S_c$ the active cells of the lattice are distributed over the lattice in form of finite clusters which can be occupied by one particle type (complete segregation). This leads to a stop of the reaction. The time required for this process is very small. For $S \rightarrow S_c$ the time for this process grows dramatically. Near S_c we observe the appearance of oscillations in the particle densities and in the reaction rate. We obtain the simple relation $N(t) \propto \xi(t)^d$ for large ξ near S_c . Due to the large time of this process we were not able to study the system behavior at this point in detail.

For $d = 2$ the system is unstable against complete segregation even on an ordered lattice. The particle densities grow logarithmic with time ($S = 1$). Qualitatively the behavior for this case is similar to the case $d = 3$. The temporal evolution of the correlation functions, correlation lengths etc. is quantitative different. Near S_c the relation between $N(t)$ and $\xi(t)$ ($N(t) \propto$

$\xi(t)^d$) is valid for a much larger interval of values of S compared to the case $d = 3$.

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