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# The diffusion-controlled annihilation reaction in random adsorptive fields

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**Abstract.** The kinetics of the  $A + A \rightarrow 0$  reaction on a correlated heterogeneous one-dimensional chain is studied. As a novel result it is found that the temporal behaviour of the density of A particles depends on the energetic topography of the surface when A particles are initially located preferentially on the more energetic sites, as happens in the case of thermodynamical equilibrium for the adsorbate.

## 1. Introduction

The kinetics of the annihilation reaction of particles in diffusive motion has increasingly become a topic of research in the last decade due to its wide applicability to many physical phenomena [1–7]. The recombination of particles that collide during diffusion and react, to form an inert species or annihilate, provides an attractive basic model to represent also different physical systems such as the decay of excitations in lattice imperfections, or recombination of interstitials and vacancies in solid-state physics [8], monopole annihilation in theoretical cosmology [2] and surface reactions on supported catalysts in surface science [9].

For the simplest case of one-kind annihilation in the absence of an external field,  $A + A \rightarrow 0$ , where A represents the diffusing species and 0 the inert product of the reaction, exact analytical results for the dependence of the density of the surviving particles on time were first obtained by Torney and McConnell [10, 11] for one dimension and subsequently generalized by Toussaint and Wilczek [2] for  $d$  dimensions and for the  $A+B \rightarrow 0$  reaction.

This kind of reaction has also been investigated for geometrically heterogeneous media, such as percolation fractals in two and three dimensions, and a superuniversal asymptotic behaviour for the density versus time was found [12].

Many efforts have been devoted to investigating the asymptotic regime of the reaction, since in all cases this seems to be independent of the initial configuration of the reacting particles, in the diffusion-controlled as well as in the imperfect annihilation case (two colliding particles reacting with probability  $p < 1$ ) [13–15].

Much less attention has been paid to the transitory period of the kinetics [16, 17]. However for reactions on highly heterogeneous surfaces this period might be long enough

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to be comparable to the overall time taken by the reaction (the time in which the reaction is completed).

Concerning surface reactions on real catalysts, particles adsorb, diffuse, react and desorb from the surface, imbedded in an inhomogeneous external field (as a consequence of the particle-surface interactions). This field, named the adsorptive field, has in general a random character. It has been demonstrated that the morphology of the adsorbed phase as well as the characteristics of the collective surface diffusion at thermodynamic equilibrium are strongly dependent on the properties of the adsorptive field [18–20], and particularly it has been stressed that a self-consistent description of the random adsorptive field is necessary in order to make a theoretical and computational analysis of surface processes on heterogenous media [21].

The aim of this paper is to simulate the instantaneous annihilation reaction  $A + A \rightarrow 0$  of particles diffusing on one-dimensional heterogenous surfaces, in order to investigate the influence of the adsorptive field on the overall reaction kinetics.

A main point of interest is how, from the behaviour of the reaction, information about the adsorptive field can be extracted.

The heterogenous adsorptive field is modelled as a chain of adsorptive 'sites', with an adsorption energy distribution, connected by 'bonds', representing the saddle-point energy between two connected neighbouring adsorptive sites, with a bond energy distribution. From now on we will refer to this as the heterogeneous surface. The site-bond (SB) energy pair distribution is obtained by following a recently proposed self-consistent description of heterogenous surfaces [21]. The kinetics of the diffusion reaction is described through a Monte Carlo simulation procedure. Particles A are assumed to move on the chain by means of thermal activated jumps to neighbouring sites and the annihilation of two particles occurs when one of these arrives at an already occupied site. In all cases the evolution of A particle density versus time is observed and the transitory regime of the reaction is particularly analysed.

In section 2 a short review of the dual site-bond model (SBM) description of the heterogenous adsorptive field is made. The detailed simulation procedure used for generating the set of site and bond energies according to the SBM description is given in section 3. Section 4 is devoted to describing the Monte Carlo simulation of diffusion and annihilation on the heterogenous chain. Results and conclusions are given in section 5.

## 2. A dual description of the adsorptive field

A great deal of effort is being dedicated to the characterization of the adsorptive energy topography of heterogenous surfaces [19, 22–24], such that not only the two well known extreme cases of the random surface and the patchwise surface but also more realistic intermediate topographies can be described.

Most of the studies of adsorption on solids have recognized the adsorptive sites as the main elements of the adsorptive field.

The topography can be taken into account in this case by introducing a variable correlation length on the surface, which characterizes the site energy correlations [19, 24].

However, it has been pointed out that a proper description of the gas-solid interaction on a heterogenous surface must take into account at least the two basic elements of the adsorption field, namely, sites and bonds (saddle-point energies).

A self-consistent description of the heterogenous surface, named the dual site-bond model (SBM), dealing with these two elements, has recently been proposed [21]. We discuss here the conceptual basis and some simple results of this model.

The basis of such a dual description is that sites as well as bonds, observed independently of the adsorptive field, can be statistically characterized by their probability density functions  $F_S(E)$  and  $F_B(E)$  (with distribution functions  $S(E)$  and  $B(E)$ ) respectively. The way of describing the alternation of site and bond energies is to introduce the joint distribution of nearest-neighbour SB energies  $F(E_S, E_B) = F_S(E_S)F_B(E_B)\phi(E_S, E_B)$ , where the correlation function  $\phi$  can be derived from the observation of the elementary principle (the construction principle) that the energy of a given site is higher than, or at least equal to, the energy of any of its delimiting bonds (absolute values of adsorptive energies are used). Two self-consistent laws must be established to derive  $\phi$ : (i)  $B(E) \geq S(E)$  for all  $E$ ; (ii)  $\phi(E_S, E_B) = 0$  for  $E_S < E_B$ . The general expression for  $\phi(E_S, E_B)$  is

$$\phi(E_S, E_B) = \exp\left(-\int_{B(E_B)}^{B(E_S)} \frac{dB}{B-S}\right) [B(E_B) - S(E_B)]^{-1}. \quad (1)$$

This gives the joint energy distribution with the maximum degree of randomness that can be obtained from  $F_S$  and  $F_B$ . Constraints to the set of site and bond energies additional to the construction principle would lead to a stronger correlation. The function  $\phi$ , considered as a function of the degree  $\Omega$  of overlap of  $F_S$  and  $F_B$  (shaded area of  $F_S$  and  $F_B$  in figure 1), has the following properties: (i)  $\phi_{\Omega \rightarrow 0}(E_S, E_B) = 1$  for all  $E_S, E_B$  (energy of sites and bonds distributed totally at random); (ii)  $\phi_{\Omega \rightarrow 1}(E_S, E_B) = \text{constant} \times \delta(E_S - E_B)$  for all  $E_S, E_B$  (large homotactic patches).

Energy profiles arising from this description are schematically shown in figure 1, for two chains of sites and bonds with different degree  $\Omega$  of overlap.

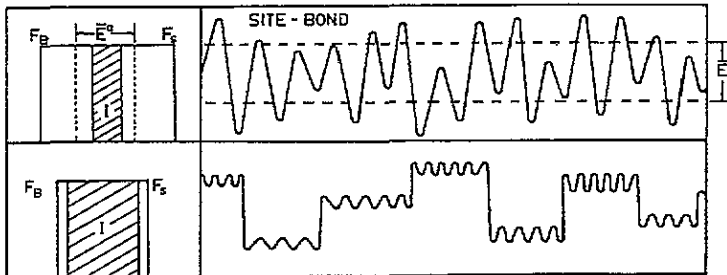


Figure 1. Representation of a heterogeneous adsorptive field along a chain of sites (local minima in the energy profile) and bonds (local maxima) for two different degrees  $\Omega$  of overlap between site- and bond-energy density functions (right-hand side). On the left-hand side density functions  $F_S$  and  $F_B$ , with the overlap area hatched, are shown.  $\bar{E}_a$  denotes the apparent mean activation energy defined by  $\bar{E}_a = \bar{E}_S - \bar{E}_B$ .

From a topological point of view energy correlations can be characterized by means of a correlation length  $r_0$ . This physically meaningful parameter gives a measure of surface regions with similar site (and bond) energies, and can be calculated from

$$\langle E_S(0)E_S(r) \rangle = \langle E_S^2 \rangle C(r) = \langle E_S^2 \rangle e^{-r/r_0} \quad (2)$$

where  $E_S(0)$  and  $E_S(r)$  denote the energies of pair of sites separated by a distance  $r$ ,  $\langle E_S^2 \rangle$  the site energy variance, and  $C(r)$  the typical pair correlation function, and the averages

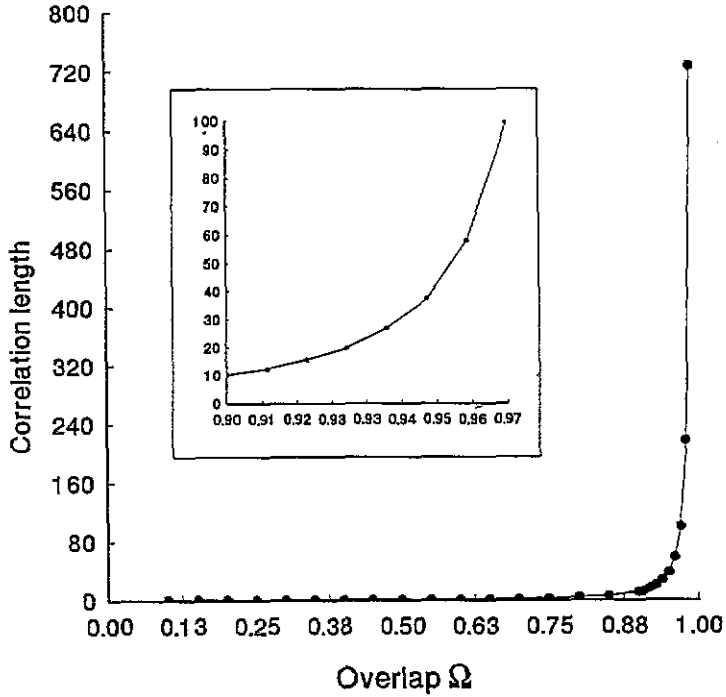


Figure 2. Plot of the correlation length  $r_0$  versus the overlap  $\Omega$  between the density functions  $F_S$  and  $F_B$ , calculated on a simulated chain of  $5 \times 10^6$  sites ( $5 \times 10^6$  bonds), using  $\langle E_S(0) E_S(r) \rangle = \langle E_S^2 \rangle C(r)$ , with  $C(r) = \exp(-r/r_0)$ , where  $E_S(0)$  and  $E_S(r)$  represent the energies of pairs of sites separated by a distance  $r$  and the average  $\langle \dots \rangle$  is taken over all the energy realizations.

$\langle \dots \rangle$  are taken over all energy realizations. The exponential decay of  $C(r)$  is strongly supported by Monte Carlo simulations of SB heterogeneous surfaces [25]. The dependence of  $r_0$  on  $\Omega$  is such that for  $\Omega \rightarrow 0$ ,  $r_0 \rightarrow 0$  (random surface), and for  $\Omega \rightarrow 1$ ,  $r_0 \rightarrow \infty$  (very large homotactic patches) as is shown in figure 2.

### 3. Simulation of the heterogeneous adsorptive field

The simulation of the adsorptive field in the framework of the SBM (i.e. the assignment of adsorption energies to sites and saddle-point energies to bonds from the pair density function  $F(E_S, E_B)$ ) requires a special method consisting of two main stages: (i) an initial setting of site and bond energies through a Markovian sequence of assignment; (ii) a posterior statistical relaxation step consisting of a reassignment of energies to some elements of the chain in order to correct deviations of the simulated pair density function from the proposed theoretical one.

Henceforth, we assume the substrate to be a one-dimensional chain of adsorptive sites connected by bonds. However the simulation procedure described below can easily be used to simulate a two-dimensional substrate [25]. The building of the chain can be summarized as follows.

*First step: Markovian sequence of SB energy assignment.* The chain is considered as an array of  $N$  couples  $(E_S, E_B^R)$ . Each of the couples contains the adsorption energy  $E_S$  of a given site and the energy  $E_B^R$  of the right bond.

The assignation of site and bond energies of the chain is made as follows.

(i) An energy is assigned randomly to the site of the couple 1:

$$E_S = S^{-1}(\text{RND}) \quad S(E_S) = \int_{s_1}^{E_S} F_S(E'_S) dE'_S. \quad (3)$$

(ii) Given the energy of the site, the energy of the right bond of the couple 1 is chosen from the conditional probability distribution function:

$$E_B = \mathcal{F}_{E_S}^{-1}(\text{RND}) \quad \mathcal{F}_{E_S}(E_B) = \int_{b_1}^{E_B \leq E_S} F_B(E'_B) \phi(E_S, E'_B) dE'_B. \quad (4)$$

(iii) The energy for the site of the couple 2 is generated through

$$E_S = \mathcal{F}_{E_B}^{-1}(\text{RND}) \quad \mathcal{F}_{E_B}(E_S) = \int_{s_1}^{E_S \geq E_B} F_S(E'_S) \phi(E'_S, E_B) dE'_S \quad (5)$$

RND being a uniform random number in the range (0,1).

(iv) Steps (ii) and (iii) are repeated until completion of the assignation to the  $N$  couples.

In equations (3)–(5), it has been assumed that  $F_S$  and  $F_B$  are zero out of the ranges  $(s_1, s_2)$  and  $(b_1, b_2)$  respectively.

*Second step: statistical relaxation.* In simulating chains with high overlap ( $\Omega > 0.7$ ), small statistical fluctuations are propagated throughout the first step of the assignation giving rise to strong distortions of the site- and bond-energy frequencies. In this second step small local corrections are made on the chain by replacing some unsuited energies according to a given criterion, and then the correction is propagated by successive application of this criterion.

In one relaxation step each element on the chain (site or bond) is visited and a new value of energy is generated for it according to the method described in the first step. The old value is replaced by the new one only if the updated simulated frequency of the new energy is lower than that of the old one.

The heterogenous lattice-building procedure can be considered as a Monte Carlo procedure of approaching an equilibrium configuration characterized by  $F_{th}(E_S, E_B)$ , starting from an initial configuration  $F_{sim}(E_S, E_B) \neq F_{th}(E_S, E_B)$ , where the subscripts th and sim denote the theoretical and simulated pair density functions. Although the transition probability used in the relaxation step does not satisfy the detailed balance principle (which is a sufficient but not a necessary condition), it is appropriate for obtaining a simulated joint distribution as close to the theoretical one as desired.

#### 4. Simulation of the diffusion-controlled reaction

The physical system represented in the simulation is a one-dimensional heterogeneous surface, assumed to be a chain of adsorptive sites and bonds with an initial coverage  $\rho_0$  of

adsorbed A particles. The particles move through thermally activated jumps between NN sites across the energy barrier separating them.

When a particle arrives at an already occupied site the annihilation reaction occurs and both particles are removed from the system. The result of the procedure is a decrease of the total number of particles  $N(t)$  with time.

One elemental simulation step is performed by selecting at random one of the  $N(t)$  particles present at a given time  $t$ , and by attempting one jump (followed by annihilation if applicable); then the time is incremented by  $1/\text{current number of particles}$ .

Since in the heterogeneous SB chain each bond represents the saddle-point energy between the two connected sites, the activation energy  $E_a^{ij}$  for diffusion from a site  $i$  to a neighbouring one  $j$  is defined by  $E_a^{ij} = E_B^{ij} - E_S^i$ , where  $E_B^{ij}$  is the energy of the bond connecting the two sites and  $E_S^i$  the adsorption energy of site  $i$ .

There are two main features to be considered in order to study the kinetics of the reaction  $A + A \rightarrow 0$  in a heterogenous adsorptive field, namely (i) the initial conditions of the reacting species A, and (ii) the diffusive motion of A particles.

Since, in general, (i) and (ii) will be strongly affected by the characteristics of the adsorptive field, we have performed the simulation under different hypothetical conditions in order to observe separately the influence of the adsorption energy topography, initial conditions and surface diffusion on the overall kinetics.

#### 4.1. Initial conditions for the species A

In the majority of studies of the simplest annihilation reaction  $A + A \rightarrow 0$  (and other related reactions) it has been assumed that at the beginning of the diffusion–reaction process the A particles are located either totally at random or grouped together in a given region on the surface.

Although a random initial configuration could be adequate for a reaction on a homogeneous substrate (neglecting AA interactions), for heterogeneous surfaces geometrical and energetical disorder may force the particles to adopt non-trivial initial configurations.

In the present work we have used correlated initial configurations (CICs) in addition to the already known random initial configurations (RICs). By correlated configuration we mean that in which A particles occupy the most energetic (deeper) adsorptive sites with higher probability before the reaction begins.

For given  $F_S$  and  $F_B$  functions, the site–site (and naturally SB and bond–bond) energy correlation increases with the overlap, as is shown in figure 2, therefore the morphology of the adsorbed phase at  $t = 0$  is not simply dependent on the initial density  $\rho_0$  but also on the energy correlations of the adsorptive field.

It must be noted that the RIC arises naturally from the CIC in the limit of null overlap.

#### 4.2. Random-walk rules for diffusion

As has been mentioned above the migration of A particles is an activated process controlled by the height of the activation barriers on the chain. Thus the jump probability from a site  $i$  to an NN site  $j$  is given, according to the absolute rate theory [26, 27], by

$$P_{ij} = \nu e^{-E_a^{ij}/kT} \quad (6)$$

where  $\nu$  is a typical jump frequency depending on the particularities of the gas–solid system,  $k$  the Boltzmann constant, and  $T$  the temperature of the system. We can choose  $kT = 1$  and  $\nu = 1$  without loss of generality.

On one hand, for a homogeneous adsorptive field (i.e. all activation energies are the same), the jump probability to NN sites has the same value for every jump direction. Hereafter, we name the diffusion process on a homogeneous surface 'homogeneous dynamic'. In particular for a homogeneous chain the jump probabilities to left and to right are equal to 0.5.

On the other hand, in the more general case of a heterogeneous chain, the jump probability is not independent of the jump direction since every site has, in general, barriers of different energy to left and to right. For the sake of clarity, we name the diffusion on this kind of surface 'heterogeneous dynamic'.

The simulation procedure can be summarized as follows.

(i) A surface with a given degree of overlap between site- and bond-energy frequency functions  $F_S$  and  $F_B$  is simulated according to the method outlined in section 2.

(ii) An initial density  $\rho_0$  of A particles is deposited on the adsorptive sites either at random, for the RIC, or by preferentially occupying higher-energetic sites for the CIC.

(iii) A particle is picked at random among the  $N(t)$  particles adsorbed. In the homogeneous dynamic case, after a jump direction is chosen at random, the jump is performed. For the heterogeneous dynamic case, after a jump direction is selected at random, a jump is attempted with probability given by equation (6). In any case, when a particle after a successful jump arrives at an occupied site, the annihilation reaction proceeds and the pair of particles is removed.

(iv) The time is incremented by  $1/N'$ , where  $N'$  is the number of particles surviving after step (iii).

(v) Steps (iii) and (iv) are repeated until the exhaustion of A particles on the surface.

A short comment must be made about the activation-energy density function  $F_a(E_a)$ , which can be obtained from  $F_S(E_S)$  and  $F_B(E_B)$  and the definition of  $E_a = E_B - E_S$ . Thus,

$$F_a(E_a) = \int_{E_S} \int_{E_B} (E_B - E_S) F_S(E_S) F_B(E_B) \delta(E_S + E_B - E_a) dE_B dE_S \quad (7)$$

where

$$\delta(E - E_a) = \begin{cases} 0 & \text{if } E \neq E_a \\ 1 & \text{if } E = E_a. \end{cases} \quad (8)$$

When  $F_S$  and  $F_B$  are uniform functions, the shape of  $F_a$  changes considerably with overlap, ranging from a triangular form for  $\Omega \rightarrow 0$ , to an exponential-like form for  $\Omega \rightarrow 1$ .

To simulate the correlated SB chains, the different overlaps between  $F_S$  and  $F_B$  have been obtained by fixing the domain of the function  $F_S$  and by shifting to the right the function  $F_B$ . Since the interval  $(E_a^{\min}, E_a^{\max})$ , where  $E_a^{\min}$  and  $E_a^{\max}$  denote the minimum and maximum activation energy respectively, was different for each overlap, a rescaling for  $E_a$  to the interval (0,1) was made through

$$E_a^{ij} \rightarrow \frac{E_a^{ij} - E_a^{\min}}{E_a^{\max} - E_a^{\min}} \quad (9)$$

for each overlap.

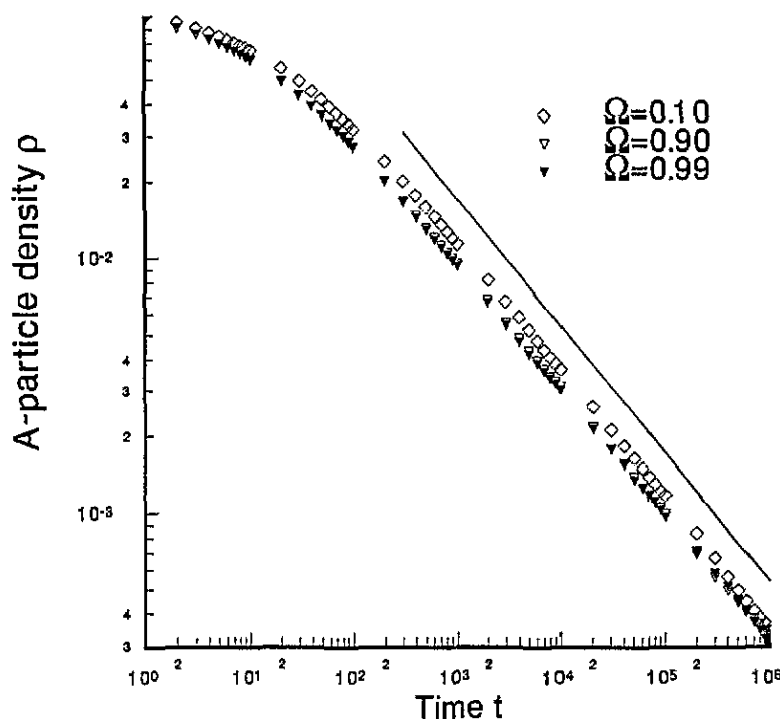


## 5. Results and discussion

### 5.1. Random initial conditions

Firstly, we have performed the reaction on the heterogeneous surface for the RIC and homogeneous dynamic case, for low coverages. It is worth noticing that the use of the RIC on heterogeneous surfaces can be regarded as the consequence of adsorption of the reactants at high temperatures ( $\bar{E}_S/kT \ll 1$ ). In addition, the homogeneous dynamic case on heterogeneous surfaces will occur for diffusion at high temperatures (i.e.  $\bar{E}_a/kT \ll 1$ ).

As is well known [2] the behaviour of  $\log \rho$  versus  $\log t$  for this case is a straight line with slope  $-\frac{1}{2}$ , after a short non-linear portion (until  $t \simeq 10$ ).



**Figure 3.** Dependence of the surviving particle density  $\rho$  on time  $t$ , for the reaction  $A + A \rightarrow 0$  on one-dimensional SB heterogeneous surfaces with different overlaps  $\Omega$ , with RIC and homogeneous dynamic:  $\Omega = 0.10$ ,  $\Omega = 0.90$ ,  $\Omega = 0.99$ . The initial density  $\rho_0$  is set equal to 0.1. The straight full line is the decay corresponding to the well known case of the homogeneous dynamic.

When a heterogeneous dynamic, i.e. diffusion to lower relative temperatures ( $\bar{E}_a/kT \simeq 1$ ), is carried out after the RIC, the behaviour of  $\rho$  does not vary appreciably and it seems to be totally independent of the surface energy correlations, as can be seen in figure 3, where surfaces with very different  $\Omega$  give rise to almost identical kinetics.

### 5.2. Correlated initial conditions

In the case where the adsorption of the reactants occurs at low temperatures (i.e.  $\bar{E}_S/kT \gg 1$ ) and the adsorbed phase is left to reach thermodynamic equilibrium, the adsorbed particles

will preferentially occupy the higher-energetic sites. If the reaction is also carried out at low temperatures ( $\bar{E}_a/kT \gg 1$ ), the process can be modelled by the CIC followed by a heterogeneous dynamic. However, if the temperature is raised after the initial low-temperature adsorption, the reaction proceeds to high temperature ( $\bar{E}_a/kT \ll 1$ ) and the process is well represented by a CIC followed by a homogeneous dynamic.

Results for this last case are shown in figure 4, with a plot of the density versus time for the reaction on surfaces with different degree  $\Omega$  of overlap between site and bond energies. For a low initial coverage, it can be observed that the behaviour of  $\rho(t)$  for  $\Omega = 0.2$  is markedly different from that for  $\Omega = 0.90$ .

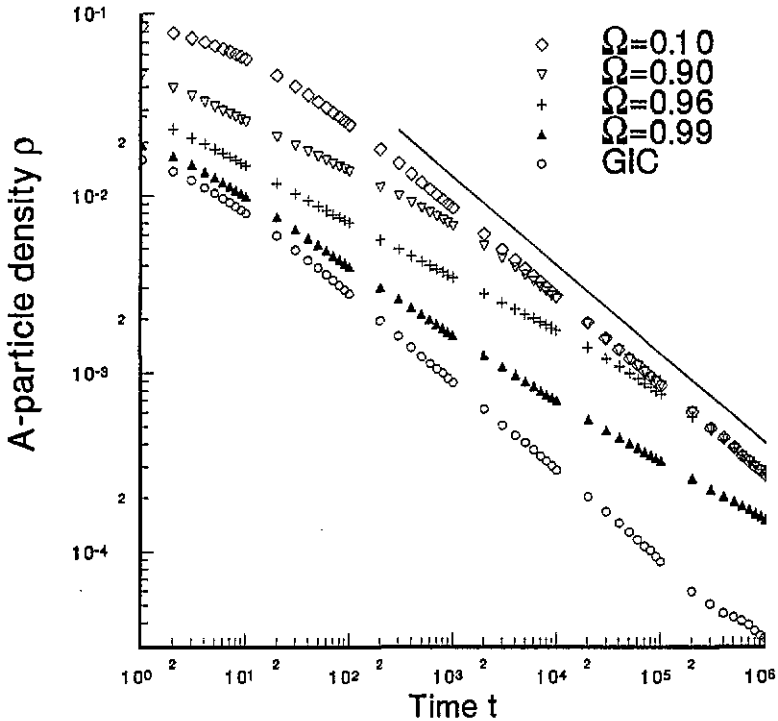


Figure 4. Dependence of  $\rho$  on  $t$ , for  $A + A \rightarrow 0$  on heterogeneous surfaces with CIC and homogeneous dynamic:  $\Omega = 0.10$ ,  $\Omega = 0.90$ ,  $\Omega = 0.96$ ,  $\Omega = 0.99$ . The initial density  $\rho_0$  is set equal to 0.1. The case of initially grouped particles (GIC) is also shown.

One of the most extreme cases is that of  $\rho = 0.1$ , where the asymptotic regime is reached at  $t \simeq 10^2$  for  $\Omega = 0.2$ , and  $t > 10^6$  for  $\Omega = 0.99$ , giving a difference of more than four orders of magnitude between the durations of the transitory regime. For high  $\Omega$  the reaction occurs almost totally in a transitory state (i.e. with  $\rho(t) \neq t^{-1/2}$ ).

Another important feature is that, as  $\Omega$  increases, the behaviour of  $\rho(t)$  does not tend naturally toward matching that corresponding to an initial condition of closely grouped particles (GIC).

If a heterogeneous dynamic with  $\bar{E}_a/kT \simeq 1$ , instead of a homogeneous one, is used after the CIC, the results are similar to those of figure 4. In figure 5 it is shown that the asymptotic decay is attained irrespective of the initial density and overlap.

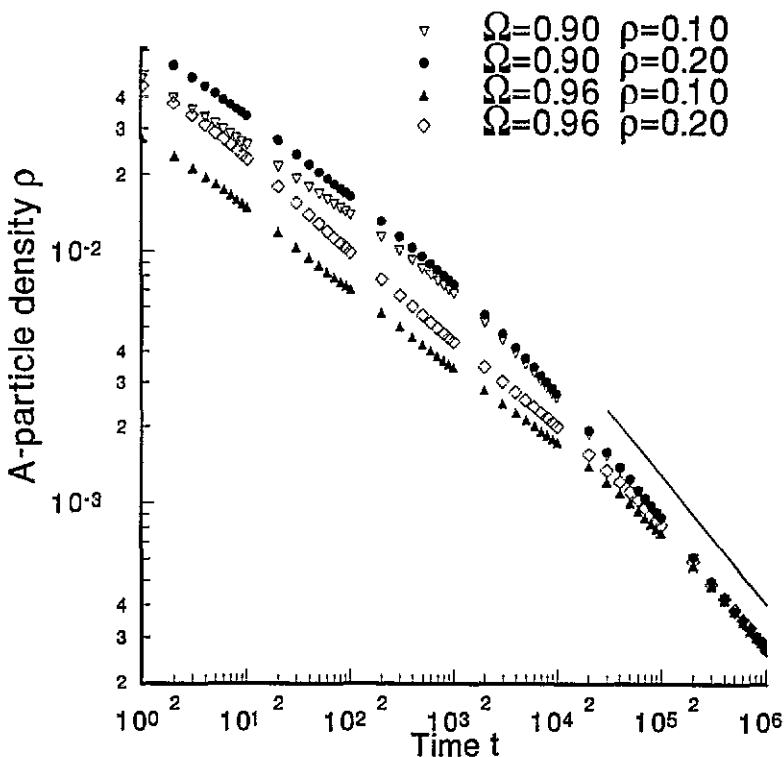


Figure 5. As figure 4 for different initial coverages  $\rho_0$ .

Very large systems have been used in the simulation ( $N \simeq 3 \times 10^6$  sites) in order to minimize finite-size effects appearing in strongly correlated heterogeneous surfaces. Each point of  $\rho$  versus  $t$  was obtained by averaging over 50 realizations.

A conclusion can be drawn out: the kinetics of the annihilation reaction  $A + A \rightarrow 0$  is strongly influenced by energy correlations in the adsorptive field for the CIC.

This apparently anomalous behaviour of  $\rho(t)$  can be understood qualitatively by taking into account the effect of energy correlations on the initial configuration and the role of surface diffusion in controlling the approach to the asymptotic regime.

For a chain of  $N$  sites with a high overlap  $\Omega$ , for instance  $\Omega \simeq 0.95$ , and the CIC, the initial  $N_0$  adsorbed  $A$  particles distribute on the chain by occupying segments of a given length  $r_0$  (the higher  $\Omega$ , the larger  $r_0$ ), alternating with segments of unoccupied sites. Since the interparticle distance within these segments is small the reaction rate is high in the early stage of the reaction (until  $t \simeq 1$ ). At the same time particles diffuse toward the regions of unoccupied sites, giving rise to a slower decrease of  $\rho(t)$ . Finally, for a given crossover time  $t^*$ , the surviving particles of each initially highly occupied segment can mix with others from neighbour regions, reaching the asymptotic regime.

A rough estimation of the dependence of  $t^*$  on  $\rho_0$  and  $\Omega$  can be made through the following reasoning. A chain of  $N$  sites is covered initially by  $N_0$   $A$  particles under the CIC. The overlap  $\Omega$  of SB energies determines the initial correlation length  $r_0$ . Then the length of segments of highly correlated energies is  $2r_0$ , and there are  $N_0/2r_0$  such segments. Since these segments can be considered to be located at random on the chain, the mean separation distance between segments is

$$\frac{N}{N_0/2r_0} = \frac{2r_0}{\rho_0}. \quad (10)$$

**Table 1.** Comparison between the crossover time  $t^*$  obtained from simulation (figure 4 and figure 5) and that calculated through equation (11), for several values of the initial density  $\rho_0$  and the energy correlation length  $r_0$ . For each value of  $\Omega$ ,  $r_0$  is estimated from figure 2.

$\rho_0$	$\Omega$	$r_0(\Omega)$	$t_{th}^*$	$t_{sim}^*$
0.1	0.10	1	100	$2-3 \times 10^2$
	0.90	10	10 000	$1-2 \times 10^4$
	0.96	58	336 400	$3-4 \times 10^5$
	0.99	725	52 562 500	—
0.2	0.90	10	2500	$2-3 \times 10^3$
	0.96	58	84 100	$8-9 \times 10^4$

Provided that in the homogeneous dynamic the particles perform a classical random walk on the chain, then  $R(t) \sim t^{1/2}$ , where  $R(t)$  denotes the displacement at time  $t$ . Since each surviving particle needs to travel a distance  $r_0/\rho_0$  to mix with others from a neighbour segment, then

$$t^* \simeq \left( \frac{r_0}{\rho_0} \right)^2. \quad (11)$$

Although this estimation is obviously valid only for  $r_0 \ll N$  and  $\rho_0 \ll 1$ , it may be useful as a method to obtain information about surface energy topography from crossover time  $t^*$ . An excellent agreement exists between  $t^*$  estimated from equation (11) and that obtained from the simulated kinetics for all  $\rho_0$  and  $\Omega$ , as can be seen from table 1. These results encourage the design of well controlled surface reaction experiments to disclose the virtually inaccessible adsorptive-field topography. The two-dimensional model to describe diffusion-controlled annihilation reactions on heterogeneous surfaces is being developed, and results will be given in a future publication.

### Acknowledgments

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