

# EUROPHYSICS LETTERS

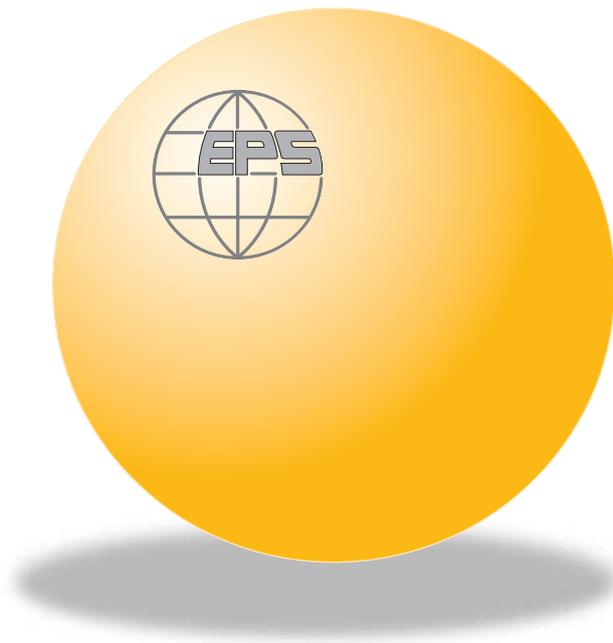
OFFPRINT

Vol. 62 • Number 1 • pp. 69–75

**Exactly solvable model of  $A + A \rightarrow 0$  reactions  
on a heterogeneous catalytic chain**

\* \* \*

G. OSHANIN, O. BÉNICHOU and A. BLUMEN



Published under the scientific responsibility of the  
**EUROPEAN PHYSICAL SOCIETY**  
Incorporating  
JOURNAL DE PHYSIQUE LETTRES • LETTERE AL NUOVO CIMENTO



## Exactly solvable model of $A + A \rightarrow 0$ reactions on a heterogeneous catalytic chain

G. OSHANIN<sup>1</sup>, O. BÉNICHOU<sup>2</sup> and A. BLUMEN<sup>3</sup>

<sup>1</sup> *Laboratoire de Physique Théorique des Liquides, Université Paris VI  
4 Place Jussieu, 75252 Paris Cedex 05, France*

<sup>2</sup> *Laboratoire de Physique de la Matière Condensée, Collège de France  
11 Place M. Berthelot, 75252 Paris Cedex 05, France*

<sup>3</sup> *Theoretische Polymerphysik, Universität Freiburg  
Hermann-Herder-Str. 3, D-79104 Freiburg, Germany*

(received 4 November 2002; accepted in final form 21 January 2003)

PACS. 68.43.De – Statistical mechanics of adsorbates.

PACS. 82.65.+r – Surface and interface chemistry; heterogeneous catalysis at surfaces.

**Abstract.** – We present an exact solution describing equilibrium properties of the catalytically activated  $A + A \rightarrow 0$  reaction taking place on a one-dimensional lattice, where some of the sites possess special “catalytic” properties. The  $A$ -particles undergo continuous exchanges with the vapor phase; two neighboring adsorbed  $A$ 's react when at least one of them resides on a catalytic site (CS). We consider three situations for the CS distribution: regular, *annealed* random and *quenched* random. For all three CS distribution types, we derive *exact* results for the disorder-averaged pressure and present exact asymptotic expressions for the particles' mean density.

*Introduction.* – Catalytically activated reactions (CARs), *i.e.* reactions involving particles which may recombine only in the presence of some third substance —a catalyst— are widespread in nature [1]. The properties of such reactions have attracted considerable interest recently, following an early analysis of a particular reaction scheme, namely the CO-oxidation in the presence of metal surfaces with catalytic properties [2]. It has been realized that this reaction exhibits an essentially different behavior when compared to the predictions of the classical, formal kinetic scheme [1] and that under certain conditions such collective phenomena as phase transitions or the formation of bifurcation patterns may occur [2–4].

A common assumption of these studies [2–4] is that the catalyst is modelled as an ideal surface with homogeneous catalytic properties. On the other hand, in realistic systems, the catalyst is often not a well-defined object, but rather consists of mobile or localized catalytic sites (CSs) or islands, whose spatial distribution is complex [1]. Metallic catalysts, for instance, are often disordered compact aggregates, the building blocks of which are imperfect crystallites with broken facets, kinks and steps. In porous materials with convoluted surfaces, such as, *e.g.*, silica, alumina or carbons, the effective catalyst occupies only a portion of the total surface; in solution, the catalyst can consist of active groups attached to polymer chains.

Such complex morphologies render the theoretical analysis difficult and, as yet, only empirical approaches have been proposed (see, *e.g.*, ref. [1]). Consequently, analytical solutions even of idealized or simplified models are highly desirable, since such studies may provide an understanding of the effects of heterogeneities on the properties of CARs.

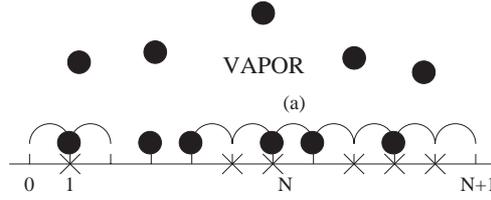


Fig. 1 – 1D lattice of  $N$  adsorption sites in contact with the vapor phase. The filled circles denote  $A$ -particles. The crosses denote the adsorption sites with catalytic properties (CS). (a) denotes a “forbidden” particle configuration.

In this letter we study the equilibrium properties of a heterogeneous, catalytically activated  $A + A \rightarrow 0$  reaction in a simple, one-dimensional (1D) model. The catalyst is modelled here as an array of special catalytic sites (CSs). In regard to the CS distribution, we focus on three situations: regular, *annealed* random and *quenched* random. For all three cases we derive *exact* results, taking into account equilibrium fluctuations, for the disorder-averaged pressure and present exact asymptotic expressions for the particles’ mean density. We show that despite the apparent simplicity of the model, one obtains highly non-trivial behaviors.

*Model.* – Consider a 1D regular lattice containing  $N$  adsorption sites (fig. 1), which is brought in contact with a reservoir (vapor phase) of non-interacting  $A$ -particles with hard cores, maintained at a constant chemical potential  $\mu$ ; the activity is hence  $z = \exp[\beta\mu]$ .

The  $A$ -particles from the vapor phase can adsorb onto vacant adsorption sites and desorb back to the reservoir. The occupation of the “ $i$ ”-th adsorption site is described by the variable  $n_i$  such that  $n_i = 1$ , if the “ $i$ ”-th site is occupied, and  $n_i = 0$ , otherwise. We assume that some of the adsorption sites possess “catalytic” properties (denoted by crosses in fig. 1) in the sense that they induce an immediate reaction  $A + A \rightarrow 0$  between neighboring  $A$ -particles; that is, if at least one of two neighboring adsorbed  $A$ -particles resides on a catalytic site, these two particles instantaneously react and leave the chain. In case when both neighboring sites are occupied, the  $A$ -particle landing on the CS reacts with either of its neighbors with equal probability. The positions of the catalytic sites are specified by the variable  $\zeta_i$ , such that  $\zeta_i = 1$  if the “ $i$ ”-th site is catalytic, and  $\zeta_i = 0$ , otherwise. For convenience, we add two boundary sites, *i.e.*  $i = 0$  and  $i = N + 1$ , and stipulate that these sites are always non-catalytic, *i.e.*  $\zeta_0 = \zeta_{N+1} = 0$ , and always unoccupied,  $n_0 = n_{N+1} = 0$ .

We focus here on the equilibrium properties of the model under study. For a given CS distribution, the partition function  $Z_N(\zeta)$  of the adsorbate, being in equilibrium with the reservoir and constrained locally by the condition that no two  $A$ -particles can occupy simultaneously two neighboring sites if at least one of them is a CS, can be written as

$$Z_N(\zeta) = \sum_{\{n_i\}} \prod_{i=1}^N z^{n_i} (1 - \zeta_i n_i n_{i-1}) (1 - \zeta_i n_i n_{i+1}). \quad (1)$$

In this way, any two neighboring sites  $i$  and  $i - 1$  are coupled by the factor  $(1 - n_i n_{i-1})$  when at least one of these sites is catalytic. These coupling factors are depicted in fig. 1 as arcs connecting neighboring sites; note that the configurations  $\{n_i\}$  in which the variables  $n_i$  and  $n_{i-1}$  of two connected sites assume both the value 1 are excluded. Note also that the partition function in eq. (1) involves effectively three-site interactions. We introduce now the notion of a “ $K$ -cluster”, as being a set of  $K$  sites connected to each other by arcs. Note that the boundary between adjacent clusters is given by a pair of two neighboring, non-catalytic

sites, *i.e.* when two consecutive variables  $\zeta_i = \zeta_{i+1} \equiv 0$  (see fig. 1). In this case the chain decomposes into disjunct clusters and  $Z_N(\zeta)$  factorizes into independent terms.

We finally remark that for  $\zeta \equiv 1$ ,  $Z_N(\zeta)$  in eq. (1) can be thought of as a 1D version of models describing adsorption of hard-molecules, such as, *e.g.*, the so-called “hard-squares” [5] or the “hard-hexagons” models [6].

*Periodic CS distribution.* – Consider first a situation with a periodic (with period  $L$ ) CS distribution, such that  $\zeta_i = \delta(i, nL + 1)$  with  $n = 0, 1, \dots, \max(n)$ , where  $\delta(k, m)$  is the Kronecker-delta symbol,  $\delta(k, m) = 1$ , if  $k = m$  and  $\delta(k, m) = 0$ , otherwise,  $\max(n) = [(N - 1)/L]$  and  $[x]$  denotes the integer part of the number  $x$ . In this case, the CS density is  $p = 1/L$ .

We have now to distinguish between two situations: namely, when  $L \geq 3$  and when  $L = 1$  or  $L = 2$ . In the former case, evidently, the factors  $(1 - \zeta_i n_i n_{i\pm 1})$  in eq. (1) are non-overlapping;  $Z_N(\zeta)$  decomposes into elementary three clusters centered around each catalytic site and (possibly) into uncoupled, “free” sites, unaffected by any of the factors  $(1 - \zeta_i n_i n_{i\pm 1})$ . On the other hand, for  $L = 1$  or  $L = 2$  we deal with a single cluster spanning the entire chain. In fact, the role of  $L = 1$  and  $L = 2$  is, chemically speaking, identical.

In the case  $L \geq 3$ , the partition function in eq. (1) decomposes into the product

$$Z_N(\zeta) = Z_3^{\mathcal{N}_3} Z_2^{\mathcal{N}_2} Z_1^{\mathcal{N}_1}, \quad (2)$$

where  $Z_K$  ( $K = 1, 2, 3$ ) are the partition functions for 1, 2 and 3 clusters, respectively:

$$\begin{aligned} Z_1 &= \sum_{\{n_1=0,1\}} z^{n_1} = (1 + z), & Z_2 &= \sum_{\{n_1, n_2=0,1\}} z^{n_1+n_2} (1 - n_1 n_2) = (1 + 2z), \\ Z_3 &= \sum_{\{n_1, n_2, n_3=0,1\}} z^{n_1+n_2+n_3} (1 - n_1 n_2)(1 - n_2 n_3) = (1 + 3z + z^2), \end{aligned} \quad (3)$$

while  $\mathcal{N}_K$  stand for the numbers of such clusters in the  $N$ -chain. Noticing next that  $\mathcal{N}_3 = \max(n) - \delta(\max(n), (N - 1)/L)$ ,  $\mathcal{N}_2 = 1 + \delta(\max(n), (N - 1)/L)$  and using the conservation law  $3\mathcal{N}_3 + 2\mathcal{N}_2 + \mathcal{N}_1 \equiv N$ , we find that here the pressure per site is given by

$$\beta P^{(\text{reg})}(L) = \lim_{N \rightarrow \infty} (\ln Z_N(\zeta)/N) = p \ln(1 + 3z + z^2) + (1 - 3p) \ln(1 + z) \quad (L \geq 3). \quad (4)$$

Now, in the periodic case with  $L = 1$  or  $L = 2$ , one finds that the partition function of an  $N$ -site chain obeys the three-term recursion,  $Z_N = Z_{N-1} + z Z_{N-2}$ , whose first three terms are given by eqs. (3). Consequently, the  $Z_N$  are polynomial functions of the activity  $z$ , so that

$$Z_N = \sum_{l=0}^{[(N+1)/2]} \binom{N-l+1}{l} z^l = z^{(N+1)/2} F_{N+2}(1/\sqrt{z}), \quad (5)$$

where  $F_N(x)$  are the Fibonacci polynomials [7] and  $\binom{N}{l}$  denote the binomial coefficients. In this case, the pressure  $P^{(\text{reg})}$  per site for  $L = 1$  or  $L = 2$  turns out to be

$$\beta P^{(\text{reg})} = \ln \left( \frac{\sqrt{1+4z} + 1}{2} \right) \quad (L = 1 \quad \text{or} \quad L = 2). \quad (6)$$

By differentiating the results in eqs. (4) and (6) with respect to the chemical potential  $\mu$ , we

find that in the asymptotic limit  $z \rightarrow \infty$  the mean density  $n^{(\text{reg})}$  of adsorbed particles is

$$n^{(\text{reg})}(p) = \begin{cases} (1-p) - \frac{1}{z} + \mathcal{O}\left(\frac{1}{z^2}\right), & L \geq 3, \\ \frac{1}{2} - \frac{1}{4\sqrt{z}} + \mathcal{O}\left(\frac{1}{z^{3/2}}\right), & L = 1 \quad \text{and} \quad L = 2. \end{cases} \quad (7)$$

This signifies that for  $L = 1$  or  $L = 2$  and  $z \rightarrow \infty$  the system undergoes an ordering transition.

*Random CS distribution. Annealed disorder.* – In this case the disorder-average pressure  $P^{(\text{ann})}(p)$  per site obeys  $\beta P^{(\text{ann})}(p) = \lim_{N \rightarrow \infty} (\ln \langle Z_N(\zeta) \rangle / N)$  and our aim is to evaluate  $\langle Z_N(\zeta) \rangle$ . Averaging  $Z_N(\zeta)$  in eq. (1), we obtain

$$\langle Z_N(\zeta) \rangle = \sum_{\{n_i\}} (z^{\sum_{i=1}^N n_i}) \left( (1-p)^{\sum_{i=1}^N \Psi_i} \right), \quad (8)$$

where  $\Psi_i$  is the three-site indicator function of the form  $\Psi_i = (n_i n_{i+1} + n_i n_{i-1} - n_{i-1} n_i n_{i+1})$ . Note now that  $\Psi_i$  always equals zero for unoccupied sites ( $n_i = 0$ ) and assumes the value  $\Psi_i = 1$  only for the occupied sites ( $n_i = 1$ ) which have at least one (or two) occupied neighboring sites. Consequently, one has that  $\sum_{i=1}^N \Psi_i = \mathcal{N}_+[\{n_i\}] - \mathcal{N}_{is}[\{n_i\}]$ , where  $\mathcal{N}_+[\{n_i\}]$  is the number of lattice sites on which (in a given realization  $\{n_i\}$ ) the occupation variable  $n_i$  assumes the value 1, while  $\mathcal{N}_{is}[\{n_i\}]$  is the realization-dependent number of isolated occupied sites (elementary cells of the form  $(0, 1, 0)$ ). Hence,  $\langle Z_N(\zeta) \rangle$  in eq. (8) can be rewritten as

$$\langle Z_N(\zeta) \rangle = \sum_{N_+=0}^N (z(1-p))^{N_+} \sum_{m=0}^{N-N_++1} (1-p)^{-m} M_m(N_+ | N), \quad (9)$$

where  $M_m(N_+ | N)$  stands for the number of realizations  $\{n_i\}$  that have a fixed  $N_+$  and contain *exactly*  $m$  elementary cells  $(0, 1, 0)$ . Using combinatorial arguments, we get [8]

$$M_m(N_+ | N) = \frac{1}{2\pi i} \frac{(N_+ + 1)!}{m!(N_+ + 1 - m)!} \oint_{\mathcal{C}} \frac{d\tau}{\tau} \tau^{(N_+ - m)} \left( \frac{1 - \tau + \tau^2}{1 - \tau} \right)^{N - N_+ + 1 - m}, \quad (10)$$

where  $\mathcal{C}$  stands for any closed contour which encircles the origin counterclockwise. Substituting  $M_m(N_+ | N)$ , eq. (10), into eq. (9), and performing the summations, we are able to determine  $\langle Z_N(\zeta) \rangle$ , and hence, also  $P^{(\text{ann})}(p)$ ; in the thermodynamic limit  $P^{(\text{ann})}(p)$  obeys

$$\beta P^{(\text{ann})}(p) = \ln \left( 3z(1-p) / \left[ 1 - 6\sqrt{Q} \sin \left( \frac{1}{3} \arcsin (R/\sqrt{Q^3}) \right) \right] \right), \quad (11)$$

where

$$R = \frac{1}{27} + \frac{1}{6} \left( \frac{(1-p)}{p} (1 + z(1-p)) - \frac{3z(1-p)^2}{p} \right), \quad Q = \frac{1}{9} + \frac{(1-p)}{3p} (1 + z(1-p)). \quad (12)$$

Next, differentiating eq. (11) with respect to  $\mu$ , one finds the particles' mean density  $n^{(\text{ann})}(p)$ . The resulting expression is rather cumbersome and we present it elsewhere [8]; here we merely display the asymptotic behavior of  $n^{(\text{ann})}(p)$  in the large- $z$  limit.

We note that in this limit the forms of  $n^{(\text{ann})}(p)$  for  $p < 1$  and for  $p \equiv 1$  are quite different, which implies that  $p \equiv 1$  is a special point. For  $p < 1$  and  $z \gg (1-p)^{-2}$ , we obtain

$$n^{(\text{ann})}(p) = 1 - \frac{1}{(1-p)z} + \frac{(1-3p)}{(1-p)^3 z^2} + \mathcal{O}\left(\frac{1}{z^3}\right), \quad (13)$$

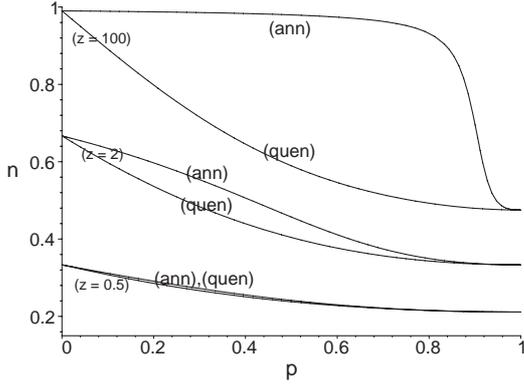


Fig. 2

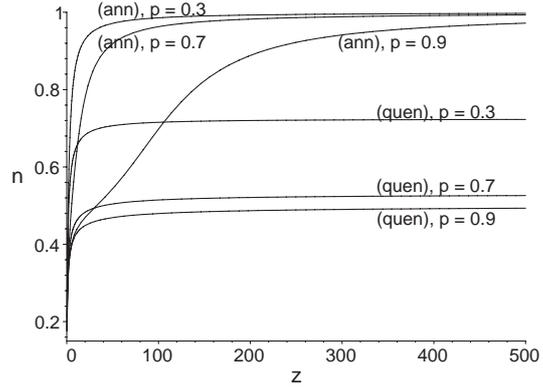


Fig. 3

Fig. 2 – Particles' mean density  $n$  vs. the CSs mean density  $p$  for different values of  $z = \exp[\beta\mu]$ . Curves with the signs (ann) and (quen) depict the behavior of  $n$  in case of annealed and quenched random CS distributions, respectively.

Fig. 3 – Particles' mean density  $n$  in the annealed and quenched disorder cases vs. the activity  $z$  for several different values of  $p$ .

while for  $p \equiv 1$  and  $z \rightarrow \infty$  the particles' mean density obeys the expression valid for  $L = 1$  or  $L = 2$ , given in the second line of eq. (7). Note that for  $p$  arbitrarily close but not equal to unity,  $n^{(\text{ann})} \equiv 1$  as  $z \rightarrow \infty$ , while for  $p \equiv 1$  one has  $n^{(\text{ann})} \equiv 1/2$  as  $z \rightarrow \infty$ .

This behavior can be understood as follows: In the annealed disorder case, instead of averaging  $\ln Z_N(\zeta)$ , we can average  $Z_N(\zeta)$  itself. Then, the disorder-averaged pressure is defined by the “effective” partition function in eq. (8). Here, a strict constraint that no particle pairs can occupy neighboring sites if at least one of them sits on the CS, is replaced by a more tolerant condition, which allows for such pairs to be present but a penalty  $\epsilon = 2 \ln(1 - p)$  is to be paid. For any  $p < 1$ , the penalty  $|\epsilon| < \infty$  is finite and one thus expects that for  $p < 1$  and  $\beta\mu \gg |\epsilon|$  the leading behavior is that of the trivial Langmuir adsorption model; hence,  $n^{(\text{ann})} \sim z/(1 + z) \rightarrow 1$  as  $z \rightarrow \infty$ . On the other hand, for  $p \equiv 1$ ,  $\epsilon$  becomes infinitely large and cannot be compensated by increasing  $\beta\mu$ .

*Random CS distribution. Quenched disorder.* – We finally turn to the most challenging situation, namely that of quenched random CS placement. Here we only briefly outline the derivation, which is rather lengthy and will be presented in detail elsewhere [8].

Consider an  $N$ -chain which contains a fixed number  $N - N_{\text{nc}}$  of catalytic sites, and hence  $N_{\text{nc}}$  non-catalytic sites, the latter being placed at the positions  $\{X_n\}$ ,  $n = 1, 2, \dots, N_{\text{nc}}$ . Next, we introduce a set of  $N_{\text{nc}} + 1$  intervals  $\{l_n\}$  connecting consecutive non-catalytic sites, such that  $l_n = X_n - X_{n-1}$  (with  $X_0 = 0$ ) and  $l_{N_{\text{nc}}+1} = N + 1 - X_{N_{\text{nc}}}$ . That is, the first interval reaches from the boundary site  $i = 0$  to the first non-catalytic site, closest to it, the second interval goes from this site to the next non-catalytic site and so on, while the interval  $l_{N_{\text{nc}}+1}$  goes from the last non-catalytic site of the chain to the site  $i = N + 1$ .

Now, the logarithm of the partition function in eq. (1), averaged over all realizations of the quenched random variable  $\{\zeta_i\}$ , can be formally written as

$$\langle \ln Z_N(\zeta) \rangle = \sum_{N_{\text{nc}}=0}^N p^{N-N_{\text{nc}}} (1-p)^{N_{\text{nc}}} \sum_{\{l_n\}} \ln Z_N(\{l_n\}), \quad (14)$$

where the inner sum with the sign  $\{l_n\}$  extends over all possible solutions of the equation

$$l_1 + l_2 + l_3 + \cdots + l_{N_{\text{nc}}+1} = N + 1, \quad l_i \geq 1, \quad (15)$$

while  $Z_N(\{l_n\})$  stands for the partition function corresponding to a given set  $\{l_n\}$  of intervals. For each set of intervals  $Z_N(\{l_n\})$  decomposes into smaller clusters,

$$Z_N(\{l_n\}) = Z_1^{\mathcal{N}_1(\{l_n\}|N)} Z_2^{\mathcal{N}_2(\{l_n\}|N)} Z_3^{\mathcal{N}_3(\{l_n\}|N)} \cdots Z_N^{\mathcal{N}_N(\{l_n\}|N)}, \quad (16)$$

where  $Z_K$ , ( $K = 1, 2, \dots, N$ ), is the  $K$ -cluster partition function, which obeys eq. (5) (with  $N$  replaced by  $K$ ), while  $\mathcal{N}_K(\{l_n\} | N)$  denotes the (realization-dependent) number of  $K$ -clusters in the  $N$ -chain with  $N_{\text{nc}}$  non-catalytic sites. Taking the logarithm of both sides of eq. (16), we obtain

$$\ln Z_N(\{l_n\}) = \sum_{K=1}^N \mathcal{N}_K(\{l_n\} | N) \ln Z_K, \quad (17)$$

and consequently,  $\langle \ln Z_N(\zeta) \rangle$  has the form

$$\langle \ln Z_N(\zeta) \rangle = \sum_{K=1}^N w_{K,N}(p) \ln Z_K, \quad (18)$$

where  $w_{K,N}(p)$  is the statistical weight of the  $K$ -clusters in an  $N$ -chain:

$$w_{K,N}(p) = \sum_{N_{\text{nc}}=0}^N p^{N-N_{\text{nc}}} (1-p)^{N_{\text{nc}}} \sum_{\{l_n\}} \mathcal{N}_K(\{l_n\} | N). \quad (19)$$

The weights  $w_{K,N}(p)$  can be also evaluated combinatorially [8]; after some straightforward but rather tedious calculations, we find that for  $K \neq 1$  and  $K \neq N$ :

$$w_{K,N}(p) = p^{(K-1)/2} (1-p)^{(K+3)/2} \{2F_K(\phi) + (1-p)(N-K-1)F_{K-2}(\phi)\}, \quad (20)$$

where  $\phi = \sqrt{p/(1-p)}$  and  $F_K(\phi)$  are the Fibonacci polynomials [7], while for  $K = N$  one has

$$w_{N,N}(p) = p^{N/2} (1-p)^{N/2} \{2F_{N-1}(\phi) + \phi F_{N-2}(\phi) + \phi F_N(\phi)\}. \quad (21)$$

Eventually, we arrive at the following exact expression, which determines the disorder-averaged pressure  $P^{(\text{quen})}(p)$  per site in the *quenched* disorder case (for arbitrary  $p$  and  $z$ ):

$$\begin{aligned} \beta P^{(\text{quen})}(p) &= \lim_{N \rightarrow \infty} \frac{1}{N} \langle \ln Z_N(\zeta) \rangle = \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{K=1}^N w_{K,N}(p) \ln Z_K = (1-p)^3 \ln(1+z) + \\ &+ p(5-7p+3p^2) \ln \left( \frac{\sqrt{1+4z}+1}{2} \right) - \frac{p(1-p)^2}{2} \ln(1+4z) - \\ &- \frac{p(1-p)^4}{\sqrt{p(4-3p)}} \times \sum_{m=0}^{\infty} \left[ \left( \frac{2p(1-p)}{\sqrt{p(4-3p)}-p} \right)^m - \left( \frac{-2p(1-p)}{\sqrt{p(4-3p)}+p} \right)^m \right] \times \\ &\times \ln \left( 1 - \left( \frac{1-\sqrt{1+4z}}{1+\sqrt{1+4z}} \right)^{m+5} \right). \end{aligned} \quad (22)$$

Differentiating eq. (22) and turning to the large- $z$  limit, we find that

$$\lim_{z \rightarrow \infty} n^{(\text{quen})}(p) = 1 - \frac{p}{1 + p^2}. \quad (23)$$

This is different from the behavior observed in the annealed-disorder case:  $\lim_{z \rightarrow \infty} n^{(\text{ann})}(p) \equiv 1$  for any  $p < 1$ ; it also differs from our result for the periodic CS distribution:  $\lim_{z \rightarrow \infty} n^{(\text{reg})}(L) = 1 - p$  for  $p \leq 1/2$  and  $\lim_{z \rightarrow \infty} n^{(\text{reg})}(L = 1 \text{ or } L = 2) \equiv 1/2$  for  $p = 1/2$  and  $p = 1$ . Note that here, distinct from the annealed-disorder case,  $n^{(\text{quen})}(p)$  does not show any discontinuity in the limit  $z \rightarrow \infty$  and  $p \rightarrow 1$ . The behavior of the particles' mean density in the quenched-disorder case is also given in figs. 2 and 3.

*Conclusions.* – We have presented here an exact lattice solution describing the equilibrium properties of the heterogeneous catalytically activated  $A + A \rightarrow 0$  reaction in the case when the  $A$ -particles undergo continuous exchanges with a reservoir and react immediately if at least one  $A$  of a neighboring  $AA$ -pair sits on a catalytic site. We have considered three possible situations for the CSs placement on the 1D lattice: regular, *annealed* random and *quenched* random. In all three cases we have calculated the disorder-averaged pressure of the adsorbate exactly and have presented asymptotic results for the particles' mean density. Remarkably, at equal mean densities of the CSs, the asymptotic values of the mean densities differ in all three cases. We close by noting that the model studied here furnishes another example (see, *e.g.*, refs. [9, 10]) of a 1D Ising-type system with random multi-site interactions which admits an exact solution.

\* \* \*

The support of the Deutsche Forschungsgemeinschaft and of the Fonds der Chemischen Industrie is gratefully acknowledged.

## REFERENCES

- [1] BOND G. C., *Heterogeneous Catalysis: Principles and Applications* (Clarendon Press, Oxford) 1987; AVNIR D., GUTFRAIND R. and FARIN D., in *Fractals in Science*, edited by BUNDE A. and HAVLIN S. (Springer, Berlin) 1994.
- [2] ZIFF R. M., GULARI E. and BARSHAD Y., *Phys. Rev. Lett.*, **50** (1986) 2553; FICHTHORN K., GULARI E. and ZIFF R., *Phys. Rev. Lett.*, **63** (1989) 1527.
- [3] See, *e.g.*, CONSIDINE D., REDNER S. and TAKAYASU H., *Phys. Rev. Lett.*, **63** (1989) 2857; MAI J., VON NIESSEN W. and BLUMEN A., *J. Chem. Phys.*, **93** (1990) 3685; KRAPIVSKY P. L., *Phys. Rev. A*, **45** (1992) 1067; EVANS J. W. and RAY T. R., *Phys. Rev. E*, **47** (1993) 1018; MOBILIA M. and BARES P.-A., *Phys. Rev. E*, **63** (2001) 036121; ARGYRAKIS P., BURLATSKY S. F., CLÉMENT E. and OSHANIN G., *Phys. Rev. E*, **63** (2001) 021110 and references therein.
- [4] For a recent review see: MARRO J. and DICKMAN R., *Nonequilibrium Phase Transitions in Lattice Models* (Cambridge University Press, Cambridge) 1999.
- [5] DOMB C., *Nuovo Cimento*, **9** (1958) 9.
- [6] BAXTER R. J., *Exactly Solved Models in Statistical Mechanics* (Academic, New York) 1982.
- [7] See, *e.g.*, <http://mathworld.wolfram.com/FibonacciPolynomial.html>.
- [8] OSHANIN G., BÉNICHOU O. and BLUMEN A., in preparation.
- [9] DERRIDA B., VANNIMENUS J. and POMEAU Y., *J. Phys. C*, **11** (1978) 4749; DERRIDA B. and HILHORST H., *J. Phys. C*, **14** (1981) L539; *J. Phys. A*, **16** (1983) 2641.
- [10] CRISANTI A., PALADIN G. and VULPIANI A., *Products of Random Matrices in Statistical Physics* (Springer-Verlag, Berlin, Heidelberg) 1993.