LETTER TO THE EDITOR

Single-species reactions on a random catalytic chain

G Oshanin[1] **and S F Burlatsky**[2]

[1] Laboratoire de Physique Théorique des Liquides, Université Paris 6, 4 Place Jussieu,
75252 Paris, France
[2] United Technologies Research Center, United Technologies Corporation, 411 Silver Lane,
129-21 East Hartford, CT 06108, USA

Abstract
We present an exact solution for a catalytically activated annihilation $A + A \rightarrow 0$ reaction taking place on a one-dimensional chain in which some segments (placed at random, with mean concentration p) possess special, catalytic properties. An annihilation reaction takes place as soon as any two A particles land from the reservoir onto two vacant sites at the extremities of the catalytic segment, or when any A particle lands onto a vacant site on a catalytic segment while the site at the other extremity of this segment is already occupied by another A particle. We find that the disorder-average pressure $P^{(\text{quen})}$ per site of such a chain is given by $P^{(\text{quen})} = P^{(\text{Lan})} + \beta^{-1}F$, where $P^{(\text{Lan})} = \beta^{-1}\ln(1 + z)$ is the Langmuir adsorption pressure, (z being the activity and β^{-1} the temperature), while $\beta^{-1}F$ is the reaction-induced contribution, which can be expressed, under appropriate change of notation, as the Lyapunov exponent for the product of 2×2 random matrices, obtained exactly by Derrida and Hilhorst (1983 *J. Phys. A: Math. Gen.* **16** 2641). Explicit asymptotic formulae for the particle mean density and the compressibility are also presented.

PACS numbers: 82.65.+r, 64.60.Cn, 68.43.De

1. Introduction

Catalytically activated reactions (CARs), i.e. reactions between chemically inactive molecules which recombine only when some third substance—the catalytic substrate—is present, are widespread in nature [1, 2]. Recently, such reactions have attracted considerable attention following an early observation [3] of remarkable non-mean-field behaviour exhibited by a specific reaction—CO-oxidation in the presence of metal surfaces with catalytic properties [1, 2]. An extensive analysis of this CAR has substantiated the emergence of an essentially different behaviour compared to the predictions of the classical, formal-kinetics scheme and have shown that under certain conditions collective phenomena such as phase transitions or the

formation of bifurcation patterns may take place [3]. Prior to these works on catalytic systems, anomalous behaviour was amply demonstrated in other schemes [4], involving reactions on contact between two particles at any point of the reaction volume (i.e. the 'completely' catalytic sysems). It was realized [4] that the departure from the textbook, formal-kinetic predictions is due to many-particle effects associated with fluctuations in the spatial distribution of the reacting species. This suggests that, similar to such 'completely' catalytic reaction schemes, the behaviour of the CARs may be influenced by many-particle effects.

Apart from the many-particle effects, the behaviour of the CARs in practically involved systems might be affected by the very structure of the catalytic substrate, which is often not well-defined geometrically, but must be viewed as an assembly of mobile or localized catalytic sites 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 faces, kinks and steps. Another example is furnished by porous materials with convoluted surfaces, such as, e.g. silica, alumina or carbons. Here the effective catalytic substrate is also only a portion of the total surface area because of the selective participation of different surface sites to the reaction. Finally, for liquid-phase CARs the catalyst can consist of active groups attached to polymer chains in solution.

Such complex morphologies render the theoretical analysis difficult. As yet, only empirical approaches have been used to account for the impact of the geometrical complexity on the behaviour of the CARs, based mostly on heuristic concepts of effective reaction order or on phenomenological generalizations of the formal-kinetic 'law of mass action' (see, e.g. [1] and [2] for more details). In this regard, analytical solutions of even somewhat idealized or simplified models, such as, for instance, those proposed in [3], are already highly desirable since such studies may provide an understanding of the effects of different factors on the properties of the CARs.

In this letter we study a catalytically-activated annihilation $A + A \rightarrow 0$ reaction in a simple, one-dimensional model with random distribution of the catalyst, appropriate to the just-mentioned situation with the catalytically activated reactions on polymer chains. We present here an exact solution for this model with quenched random distribution of the catalyst and show that despite its apparent simplicity it exhibits an interesting non-trivial behaviour. We note finally that kinetics of $A + A \rightarrow 0$ reactions involving diffusive A particles which react upon encounters on randomly placed catalytic sites has been discussed already in [5–8], and a rather surprising behaviour has been found, especially in low-dimensional systems. Additionally, steady-state properties of $A + A \rightarrow 0$ reactions between immobile A particles with long-range reaction probabilities in systems with external particles input have been presented in [9, 10] and revealed non-trivial ordering phenomena with anomalous input intensity dependence of the mean particle density, which agrees with experimental observations [11].

2. The model

Consider a one-dimensional regular lattice of unit spacing comprising N adsorption sites. The lattice is in contact with a reservoir of identical, non-interacting hard-core A particles (see, figure 1)—a vapour phase, which is steadily maintained at a constant pressure.

The A particles from the vapour phase can adsorb onto vacant adsorption sites and desorb back to the reservoir. The occupation of the ith adsorption site is described by the Boolean variable n_i, such that

$$n_i = \begin{cases} 1 & \text{if the } i\text{th site is occupied} \\ 0 & \text{otherwise.} \end{cases} \tag{1}$$
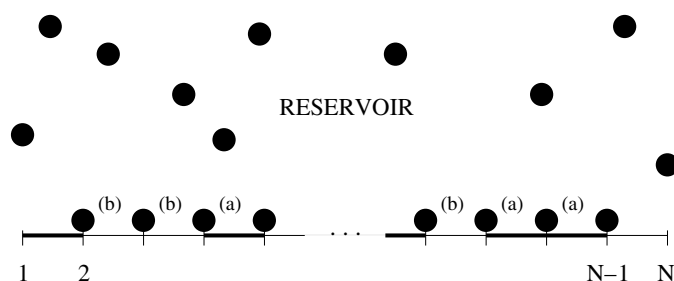
Figure 1. One-dimensional lattice of adsorption sites in contact with a reservoir. Filled circles denote hard-core A particles. Thick black lines denote the segments with catalytic properties. (*a*) Denotes a 'forbidden' particle configuration, which corresponds to immediate reaction. (*b*) Depicts the situation in which two neighbouring A particles may harmlessly coexist.

Suppose next that some of the segments—intervals between neighbouring adsorption sites—possess 'catalytic' properties (thick black lines in figure 1) in the sense that they induce an immediate reaction $A + A \to 0$, as soon as two A particles land onto two vacant sites at the extremities of the catalytic segment, or an A particle lands onto a vacant site at one extremity of the catalytic segment while the site at the other extremity of this segment is already occupied by another A particle. Two reacted A particles instantaneously leave the lattice (desorb back to the reservoir). Any two A particle adsorbed at extremities of a non-catalytic segment harmlessly coexist.

To specify the positions of the catalytic segments, we introduce a Boolean variable ζ_i, so that $\zeta_0 = \zeta_N = 0$ and

$$\zeta_i = \begin{cases} 1 & \text{if the } i\text{th interval is catalytic, } i = 1, 2, \ldots, N-1 \\ 0 & \text{otherwise.} \end{cases} \tag{2}$$

In what follows we suppose that ζ_i are independent, identically distributed quenched random variables with distribution

$$\rho(\zeta) = p\delta(\zeta - 1) + (1 - p)\delta(\zeta). \tag{3}$$

Now, for a given distribution of the catalytic segments, the partition function $Z_N(\zeta)$ of the system under study can be written as follows:

$$Z_N(\zeta) = \sum_{\{n_i\}} z^{\sum_{i=1}^{N} n_i} \prod_{i=1}^{N-1} (1 - \zeta_i n_i n_{i+1}) \tag{4}$$

where the summation $\sum_{\{n_i\}}$ extends over all possible configurations $\{n_i\}$, while

$$z = \exp(\beta\mu) \tag{5}$$

is the activity and μ the chemical potential. Note that $Z_N(\zeta)$ in equation (4) is a functional of the configuration $\zeta = \{\zeta_i\}$.

It is worthwhile to remark that $Z_N(\zeta)$ can also be thought of as a one-dimensional version of models describing adsorption of hard-molecules [12–19], i.e. adsorption limited by the 'kinetic' constraint that any two molecules can neither occupy the same site nor appear on the neighbouring sites. The most celebrated examples of such models are furnished by the so-called hard-squares model [12–16], or by the hard-hexagons model first solved exactly by Baxter [18]. In our case of the CARs on random catalytic substrates the nearest-neighbour exclusion constraint is introduced only locally, at some specified, randomly distributed intervals. Such locally frustrated models of random reaction/adsorption thus represent a

natural and meaningful generalization of the well-studied exclusion models over systems with disorder. Of course, in this context two-dimensional situations are of most interest, but nonetheless it might be instructive to find examples of such models which can be solved exactly in one dimension.

Our main goal here is to calculate the disorder-average pressure per site:

$$P^{(\text{quen})} = \frac{1}{\beta} \lim_{N \to \infty} \frac{1}{N} \langle \ln(Z_N(\zeta)) \rangle_\zeta \tag{6}$$

where the angle brackets with the subscript ζ denote averaging over all possible configurations $\{\zeta_i\}$. Once $P^{(\text{quen})}$ is obtained, all other pertinent thermodynamic properties can be readily evaluated by differentiating $P^{(\text{quen})}$ with respect to the chemical potential μ; in particular, the disorder-average mean particle density $n^{(\text{quen})}$ will be given by

$$n^{(\text{quen})} = \frac{\partial}{\partial \mu} P^{(\text{quen})} \tag{7}$$

while the compressibility k_T obeys

$$k_T^{(\text{quen})} = \frac{1}{(n^{(\text{quen})})^2} \frac{\partial n^{(\text{quen})}}{\partial \mu}. \tag{8}$$

To close this section, we display the results corresponding to two 'regular' cases: namely, when $p = 0$ and $p = 1$, which will serve us in what follows as some benchmarks. In the $p = 0$ all sites are decoupled, and one has the Langmuir results:

$$P^{(\text{Lan})} = \frac{1}{\beta} \ln(1 + z) \qquad n^{(\text{Lan})} = \frac{z}{1 + z} \qquad \text{and} \qquad \beta^{-1} k_T^{(\text{Lan})} = \frac{1}{z} \tag{9}$$

The 'regular' case when $p = 1$ is a bit less trivial, but the solution can still be obtained straightforwardly. In this case, we have

$$P^{(\text{reg})} = \frac{1}{\beta} \ln\left(\frac{\sqrt{1 + 4z} + 1}{2}\right) \qquad n^{(\text{reg})} = 1 - \frac{2z}{1 + 4z - \sqrt{1 + 4z}} \tag{10}$$

and

$$\beta^{-1} k_T^{(\text{reg})} = \frac{2z}{\sqrt{1 + 4z}(1 + 2z - \sqrt{1 + 4z})}. \tag{11}$$

Note that in the $p = 1$ case (the completely catalytic system) the mean particle density tends to $1/2$ as $z \to \infty$ (compared to $n^{(\text{Lan})} \to 1$ behaviour observed for the Langmuir case), which means that the adsorbent undergoes 'ordering' transition and particles distribution on the lattice becomes periodic revealing a spontaneous symmetry breaking between two sublattices. In the limit $z \to \infty$ the compressibility vanishes as $k_T^{(\text{reg})} \propto 1/\sqrt{z}$ compared to the Langmuir behaviour $k_T^{(\text{Lan})} \propto 1/z$.

3. Recursion relations for $Z_N(\zeta)$

Let us first introduce an auxiliary, constrained partition function of the form

$$Z_N'(\zeta) = Z_N(\zeta)|_{n_N=1} = z \sum_{\{n_i\}} z^{\sum_{i=1}^{N-1} n_i} \prod_{i=1}^{N-2} (1 - \zeta_i n_i n_{i+1})(1 - \zeta_{N-1} n_{N-1}) \tag{12}$$

i.e. $Z_N'(\zeta)$ stands for the partition function of a system with fixed set $\zeta = \{\zeta_i\}$ and fixed occupation of the site $i = N$, $n_N = 1$. Evidently, we have that

$$Z_N(\zeta) = Z_{N-1}(\zeta) + Z_N'(\zeta). \tag{13}$$

Next, considering two possible values of the occupation variable n_{N-1}, i.e. $n_{N-1} = 0$ and $n_{N-1} = 1$, we find that $Z'_N(\zeta)$ can be expressed through $Z_{N-2}(\zeta)$ and $Z'_{N-1}(\zeta)$ as

$$Z'_N(\zeta) = z \sum_{\{n_i\}} z^{\sum_{i=1}^{N-2} n_i} \prod_{i=1}^{N-3} (1 - \zeta_i n_i n_{i+1})$$

$$+ z^2 (1 - \zeta_{N-1}) \sum_{\{n_i\}} z^{\sum_{i=1}^{N-2} n_i} \prod_{i=1}^{N-3} (1 - \zeta_i n_i n_{i+1})(1 - \zeta_{N-2} n_{N-2})$$

$$= z Z_{N-2}(\zeta) + z(1 - \zeta_{N-1}) Z'_{N-1}(\zeta) \tag{14}$$

Now, the recursion in equation (13) allows us to eliminate $Z'_N(\zeta)$ in equation (14). From equation (13) we have $Z'_N(\zeta) = Z_N(\zeta) - Z_{N-1}(\zeta)$, and consequently, we find from equation (14) that the unconstrained partition function $Z_N(\zeta)$ in equation (4) obeys the following recursion

$$Z_N(\zeta) = (1 + z(1 - \zeta_{N-1})) Z_{N-1}(\zeta) + z\zeta_{N-1} Z_{N-2}(\zeta), \tag{15}$$

which is to be solved subject to evident initial conditions

$$Z_0(\zeta) \equiv 1 \qquad \text{and} \qquad Z_1(\zeta) \equiv 1 + z. \tag{16}$$

A conventional way (see, e.g. [20–22]) to study linear random three-term recursions is to reduce them to random maps by introducing the Ricatti variable of the form

$$R_N(\zeta) = \frac{Z_N(\zeta)}{Z_{N-1}(\zeta)} \tag{17}$$

In terms of this variable equation (15) becomes

$$R_N(\zeta) = (1 + z(1 - \zeta_{N-1})) + \frac{z\zeta_{N-1}}{R_{N-1}(\zeta)} \qquad \text{with} \qquad R_1(\zeta) \equiv R_1 = 1 + z, \tag{18}$$

which represents a random homographic relation. Once $R_N(\zeta)$ is defined for arbitrary N, the partition function $Z_N(\zeta)$ can be readily determined as the product

$$Z_N(\zeta) = \prod_{i=1}^{N} R_i(\zeta) \tag{19}$$

and hence, the disorder-average logarithm of the partition function will be obtained as

$$\langle \ln Z_N(\zeta) \rangle_\zeta = \sum_{i=1}^{N} \langle \ln R_i(\zeta) \rangle_\zeta. \tag{20}$$

Before we proceed further, we note that recursion schemes of quite a similar form have been discussed already in the literature in different contexts. In particular, two decades ago Derrida and Hilhorst [20] (see also [23] for a more general discussion) have shown that such recursions occur in the analysis of the Lyapunov exponent $F(\epsilon)$ of the product of random 2×2 matrices of the form

$$F(\epsilon) = \lim_{N \to \infty} \frac{1}{N} \left\langle \ln \left(\text{Tr} \left[\prod_{i=1}^{N} \begin{pmatrix} 1 & \epsilon \\ z_i \epsilon & z_i \end{pmatrix} \right] \right) \right\rangle_{\{z_i\}} \tag{21}$$

where z_i are independent positive random numbers with a given probability distribution $\rho(z)$. Equation (21) is related, for instance, to the disorder-average free energy of an Ising chain with nearest-neighbour interactions in a random magnetic field, and appears in the solution of a two-dimensional Ising model with row-wise random vertical interactions [24], the role of ϵ

being played by the wavenumber θ. The recurence scheme in equation (18) emerges also in such an interesting context as the problem of enumeration of primitive words with random errors in the locally free and braid groups [25]. Some other examples of physical systems in which the recursion in equation (18) appears can be found in [22].

Further on, Derrida and Hilhorst [20] have demonstrated that $F(\epsilon)$ can be expressed as

$$F(\epsilon) = \lim_{N \to \infty} \frac{1}{N} \sum_{i=1}^{N} \langle \ln R_i' \rangle_{\{z_i\}} \tag{22}$$

where R_i' are defined through the recursion

$$R_i' = 1 + z_{i-1} + z_{i-1}(\epsilon^2 - 1)/R_{i-1}' \qquad \text{with} \qquad R_1' = 1. \tag{23}$$

Moreover, they have shown that the model admits an exact solution when

$$\rho(z) = (1 - p)\delta(z) + p\delta(z - y) \tag{24}$$

i.e. when similarly to the model under study, z_i are independent, random two-state variables assuming only two values—y with probability p and 0 with probability $1 - p$. Supposing that when i increases, a stationary probability distribution $P(R')$ of the R_i' independent of i exists [26], Derrida and Hilhorst [20] have found the following exact result:

$$F(\epsilon) = p \ln(1 + b) - p(2 - p) \ln \left(1 + b\frac{y - b}{1 - by} \right)$$

$$+ (1 - p)^2 \sum_{N=1}^{\infty} p^N \ln \left(1 + b \left(\frac{y - b}{1 - by} \right)^{N+1} \right) \tag{25}$$

where

$$b = 1 + \frac{(1 - y)^2}{2\epsilon^2 y} \left[1 - \left(1 + 4\frac{\epsilon^2 y}{(1 - y)^2} \right)^{1/2} \right]. \tag{26}$$

4. Disorder-average pressure

We turn now back to our recursion scheme in equation (18) and note that setting

$$R_i(\zeta) = (1 + z)R_i' \tag{27}$$

and choosing

$$y = -\frac{z}{1 + z} = -n^{(\text{Lan})} \qquad \text{and} \qquad \epsilon^2 = \frac{z}{1 + z} = n^{(\text{Lan})} \tag{28}$$

makes the recursion schemes in equations (18) and (23) identical! Consequently, the disorder-average pressure per site in our random catalytically-activated reaction/adsorption model can be expressed as

$$P^{(\text{quen})} \equiv \frac{1}{\beta} \ln(1 + z) + \frac{1}{\beta} F(\epsilon) \tag{29}$$

where $F(\epsilon)$ is the Lyapunov exponent of the product of random 2×2 matrices in equation (21), in which ϵ and z_i are defined by equations (24) and (28).

Note next that the first term on the right-hand side of equation (29) is a trivial Langmuir result for the $p = 0$ case (adsorption without reaction) which would entail $n^{(\text{quen})} = z/(1 + z)$, equation (9). Hence, all non-trivial, disorder-induced behaviour is embodied in the Lyapunov exponent $F(\epsilon)$.

The disorder-averaged pressure per site for the random reaction/adsorption model under study can be thus readily obtained from equations (25) and (26) by defining the parameters y and ϵ as prescribed in equation (28). This yields the following exact result:

$$\beta P^{(\text{quen})} = \ln(\phi_z) - (1-p)\ln(1-\omega^2) + \frac{(1-p)^2}{p} \sum_{N=1}^{\infty} p^N \ln(1-(-1)^N \omega^{N+2}) \tag{30}$$

where

$$\phi_z = \frac{1+\sqrt{1+4z}}{2} \tag{31}$$

and

$$\omega = \frac{\sqrt{1+4z}-1}{\sqrt{1+4z}+1} = z/\phi_z^2 = 1 - \frac{1}{\phi_z}. \tag{32}$$

Note that ϕ_z obeys $\phi_z(\phi_z - 1) = z$; hence, $\phi_{z=1} = (\sqrt{5}+1)/2$ is just the 'golden mean'.

5. Asymptotic behaviour of the disorder-average pressure, mean density and the compressibility

Consider first the asymptotic behaviour of $P^{(\text{quen})}$ in the small-z limit. To do this, it is expedient to use another representation of $P^{(\text{quen})}$. After some straightforward calculations, one can cast $P^{(\text{quen})}$ in equation (30) into the form:

$$\beta P^{(\text{quen})} = \frac{(1-p)}{p} \sum_{n=0}^{\infty} p^n \mathcal{F}_n \tag{33}$$

where $\mathcal{F}_n$ denote natural logarithms of the Stieltjes-type continued fractions of the form

$$\mathcal{F}_n = \ln\left(1 + \cfrac{z}{1 + \cfrac{z}{1 + \cfrac{z}{\cfrac{\cdots}{1 + \cfrac{z}{1+z}}}}}\right). \tag{34}$$

Note now that in the limit $n \to \infty$, one has

$$\lim_{n\to\infty} \mathcal{F}_n = \ln(\phi_z) = \ln\left(\frac{1+\sqrt{1+4z}}{2}\right) \tag{35}$$

i.e. $\mathcal{F}_n$ is the nth approximant of $\ln(\phi_z)$; hence, $P^{(\text{quen})}$ can be thought of as the generating function of such approximants. Now, one finds that for $z < 1$ the sequence of approximants converges quickly to $\ln(\phi_z)$; expanding the nth approximant $\mathcal{F}_n$ into the Taylor series in powers of z, one has that the first n terms of such an expansion coincide with the first n terms of the expansion of $\ln(\phi_z)$, i.e.

$$\ln(\phi_z) = \ln\left(\frac{1+\sqrt{1+4z}}{2}\right) = -\frac{1}{2\sqrt{\pi}} \sum_{n=1}^{\infty} \frac{(-1)^n \Gamma(n+1/2)}{\Gamma(n+1)} \frac{(4z)^n}{n}. \tag{36}$$

Consequently, $\mathcal{F}_n$ and $\mathcal{F}_{n-1}$ differ only by terms of order z^n, which signifies that convergence is good. On the other hand, for $z \geqslant 1$ convergence becomes poor and one has to seek a more suitable representation. As a matter of fact, already for $z = 1$ one has that in the limit $n \to \infty$

the approximant $\mathcal{F}_n$ tends to $\ln(\phi_1)$, i.e. the logarithm of the 'golden mean', which is known as the irrational number worst approximated by rationals.

In the small-z limit, we then find using an expansion in equation (36) that $P^{(\text{quen})}$ follows

$$\beta P^{(\text{quen})} = z - \left(\tfrac{1}{2} + p\right)z^2 + \left(\tfrac{1}{3} + 2p + p^2\right)z^3 - \left(\tfrac{1}{4} + \tfrac{7}{2}p + 4p^2 + p^3\right)z^4 + \mathcal{O}(z^5). \tag{37}$$

Consequently, in the small-z limit the mean density obeys:

$$n^{(\text{quen})} = z - (1 + 2p)z^2 + (1 + 6p + 3p^2)z^3 - (1 + 14p + 16p^2 + 4p^2)z^4 + \mathcal{O}(z^5) \tag{38}$$

while the compressibility $k_T^{(\text{quen})}$ is given by

$$\beta^{-1}k_T^{(\text{quen})} = \frac{1}{z} + p(2 - p)z - 4p(2 - p)z^2 + 3p(8 - p - 2p^2)z^3 + \mathcal{O}(z^4). \tag{39}$$

Note that the coefficients in the small-z expansion coincide with the coefficients in the expansions of $P^{(\text{Lan})}$ and $P^{(\text{reg})}$ when we set in equation (37) $p = 0$ or $p = 1$.

Now, we turn to the analysis of the large-z behaviour which is a bit more complex than the $z \ll 1$ case and requires understanding of the asymptotic behaviour of the sum

$$S = \sum_{N=1}^{\infty} p^N \ln(1 - (-1)^N \omega^{N+2}) \tag{40}$$

entering equation (30). We note first that in this sum the behaviour of the terms with odd and even N is quite different and we have to consider it separately. Let

$$S_{\text{odd}} = \frac{1}{p} \sum_{N=1}^{\infty} p^{2N} \ln(1 + \omega^{2N+1}) \tag{41}$$

denote the contribution of the terms with odd N. Note that when $z \to \infty$ (i.e. $\omega \to 1$) the sum S_{odd} tends to $p\ln(2)/(1 - p^2)$. The corrections to this limiting behaviour can be defined as follows. Expanding $\ln(1 + \omega^{2N+1})$ into the Taylor series in powers of ω and then, using the definition $\omega = 1 - 1/\phi_z$ and the binomial expansion, we construct a series in the inverse powers of ϕ_z:

$$S_{\text{odd}} = \frac{p}{1 - p^2} \ln(2) - \frac{1}{2}\frac{p(3 - p^2)}{(1 - p^2)^2}\frac{1}{\phi_z} + \frac{1}{8}\frac{p(3 + 6p^2 - p^4)}{(1 - p^2)^3}\frac{1}{\phi_z^2}$$
$$+ \frac{1}{24}\frac{p(15 + 10p^2 - p^4)}{(1 - p^2)^3}\frac{1}{\phi_z^3} + \mathcal{O}\left(\frac{1}{\phi_z^4}\right). \tag{42}$$

Note that this expansion is only meaningful when $\phi_z \gg (1 - p)^{-1}$, $(z \gg (1 - p)^{-2})$, which signifies that $p = 1$ is a special point.

Further on, plugging into the latter expansion the definition of ϕ_z, $\phi_z = (1 + \sqrt{1 + 4z})/2$, we obtain the following expansion in the inverse powers of the activity z:

$$S_{\text{odd}} = \frac{p}{1 - p^2} \ln(2) - \frac{p}{2}\frac{(3 - p^2)}{(1 - p^2)^2}\frac{1}{z^{1/2}} + \frac{p}{8}\frac{(9 - 2p^2 + p^4)}{(1 - p^2)^3}\frac{1}{z}$$
$$+ \frac{p}{48}\frac{(3 - 4p^2 + p^4)}{(1 - p^2)^3}\frac{1}{z^{3/2}} + \mathcal{O}\left(\frac{1}{z^2}\right). \tag{43}$$

Consider next the sum

$$S_{\text{even}} = \sum_{N=1}^{\infty} p^{2N} \ln(1 - \omega^{2N+2}) \tag{44}$$

which represents the contribution of terms with even N. Note that in contrast to the behaviour of S_{odd}, the sum in equation (44) diverges when $z \to \infty$ ($\omega \to 1$). Since $1 - \omega^{2N+2} \sim 1 - \omega$ when $\omega \to 1$, we have that in this limit the leading behaviour of S_{even} is described by

$$S_{\mathrm{even}} \sim \frac{p^2}{1 - p^2} \ln(1 - \omega). \tag{45}$$

To obtain several correction terms we make use of one of Gessel's expansions [27]:

$$\ln\left(\frac{2(N + 1)x}{1 - (1 - x)^{2N+2}}\right) = \sum_{k=1}^{\infty} g_k(2N + 2)\frac{(-1)^k x^k}{k} \tag{46}$$

where $g_k(2N + 2)$ are the Dedekind-type sums of the form

$$g_k(2N + 2) = \sum_{\zeta^{2N+2}=1, \zeta \neq 1} \frac{1}{(\zeta - 1)^k} \tag{47}$$

where the summation extends over all ζ being the $(2N + 2)$-th roots of unity (with $\zeta = 1$ excluded). As shown in [27], the weights $g_k(2N + 2)$ are polynomials in N of degree at most k with rational coefficients. Next, setting $x = 1/\phi_z$ in the expansion in equation (46), plugging it into equation (44) and performing summations over N, we find that S_{even} can be written down as

$$S_{\mathrm{even}} = -\frac{p^2}{1 - p^2} \ln(\phi_z) + \frac{p^2}{1 - p^2} \ln(2) + s_p - \sum_{k=1}^{\infty} G_k(p)\frac{(-1)^k}{k \phi_z^k} \tag{48}$$

where s_p is an infinite series of the form[3]

$$s_p = \sum_{N=1}^{\infty} p^{2N} \ln(N + 1) \tag{50}$$

while $G_k(p)$ are the generating functions of the polynomials $g_k(2N + 2)$:

$$G_k(p) = \sum_{N=1}^{\infty} g_k(2N + 2)p^{2N}. \tag{51}$$

Inserting next the definition of ϕ_z, we find the following explicit asymptotic expansion

$$S_{\mathrm{even}} = -\frac{1}{2}\frac{p^2}{1 - p^2} \ln(z) + \frac{p^2}{1 - p^2} \ln(2) + s_p - \frac{p^2(2 - p^2)}{(1 - p^2)^2}\frac{1}{z^{1/2}}$$
$$+ \frac{p^2(21 - 18p^2 + 5p^4)}{24(1 - p^2)^3}\frac{1}{z} + \frac{p^2(2 - p^2)}{24(1 - p^2)^2}\frac{1}{z^{3/2}} + \mathcal{O}\left(\frac{1}{z^2}\right). \tag{52}$$

Finally, combining the expansions in equations (30), (43) and (52), we find the following large-z expansion for the disorder-averaged pressure $P^{(\mathrm{quen})}$:

$$\beta P^{(\mathrm{quen})} = \frac{1}{1 + p} \ln(z) - \frac{(1 - p)^2}{(1 + p)} \ln(2) + \frac{(1 - p)^2}{p} s_p + \frac{1}{6}\frac{6 + 3p - p^3}{(1 + p)^2(1 - p^2)}\frac{1}{z} + \mathcal{O}\left(\frac{1}{z^2}\right) \tag{53}$$

[3] Note that s_p shows a non-analytic behaviour when $p \to 1$. This function can be represented as

$$s_p = -\frac{1}{1 - p^2} \ln(1 - p^2) - \frac{p^2}{1 - p^2} \sum_{n=2}^{\infty} \frac{(-1)^n}{n} \Phi(p^2, n, 1) \tag{49}$$

where $\Phi(p^2, n, 1)$ are the Lerch transcedents, $\Phi(p^2, n, 1) = \sum_{l=0}^{\infty}(1+l)^{-n} p^{2l}$. It is straightforward to find then that $s_p = -\frac{1}{1-p^2} \ln(1 - p^2) - \frac{\gamma}{1-p^2} + \mathcal{O}(\ln(p))$, where γ is the Euler constant.

which yields

$$n^{(\text{quen})} = \frac{1}{1+p} - \frac{1}{6} \frac{6+3p-p^3}{(1+p)^2(1-p^2)} \frac{1}{z} + \mathcal{O}\left(\frac{1}{z^2}\right) \tag{54}$$

and

$$\beta^{-1} k_T^{(\text{quen})} = \frac{1}{6} \frac{6+3p-p^3}{(1+p)(1-p^2)} \frac{1}{z} + \frac{1}{36} \frac{p(6+3p-p^3)^2}{(1+p)^2(1-p^2)^2} \frac{1}{z^2} + \mathcal{O}\left(\frac{1}{z^3}\right). \tag{55}$$

Note that asymptotic expansions in equations (53), (54) and (55) are only meaningful for $z \gg (1-p)^{-2}$ and thus exclude the completely catalytic $p = 1$ case. At this special point $p \equiv 1$ we find from equation (10) that the pressure and mean density exhibit a non-analytic dependence on $1/z$:

$$\beta P^{(\text{reg})} = \frac{1}{2} \ln(z) + \frac{1}{2z^{1/2}} - \frac{1}{48z^{3/2}} + \frac{3}{1280z^{5/2}} + \mathcal{O}\left(\frac{1}{z^{7/2}}\right) \tag{56}$$

and

$$n^{(\text{reg})} = \frac{1}{2} - \frac{1}{4z^{1/2}} + \frac{1}{32z^{3/2}} - \frac{3}{512z^{5/2}} + \mathcal{O}\left(\frac{1}{z^{7/2}}\right) \tag{57}$$

which differs substantially from the asymptotical behaviour in the $p < 1$ case, equations (53) and (54). This happens apparently because the bulk contribution to the disorder-average pressure in equation (53) comes from the intervals devoid of the catalytic segments, in which reactions cannot take place and the mean density $n \sim 1$ in accordance with the Langmuir adsorption/desorption mechanism. Such intervals exist for any p strictly less than unity; their contribution vanishes only when $p \equiv 1$.

6. Conclusions

To conclude, in this letter we have presented an exact solution of a random catalytic reaction/adsorption model, appropriate to the situations with the catalytically-activated reactions on polymer chains containing randomly placed catalytist. More specifically, we have considered here the $A + A \to 0$ reaction on a one-dimensional regular lattice which is brought in contact with a reservoir of A particles. Some portion of the intersite intervals on the regular lattice was supposed to possess special 'catalytic' properties such that they induce an immediate reaction $A + A \to 0$, as soon as two A particles land onto two vacant sites at the extremities of the catalytic segment, or an A particle lands onto a vacant site while the site at the other extremity of the catalytic segment is already occupied by another A particle. For *quenched* random distribution of the catalytic segments, we have determined exactly the disorder-averaged pressure per site and have shown that it can be represented as a sum of a Langmuir-type contribution and a reaction-induced term. The latter can be expressed as the Lyapunov exponent of a product of random 2×2 matrices, obtained by Derrida and Hilhorst [20]. Explicit asymptotic expansions for the mean particle density and the compressibility were also derived.

References

[1] Bond G C 1987 *Heterogeneous Catalysis: Principles and Applications* (Oxford: Clarendon)
    Avnir D, Gutfraind R and Farin D 1994 *Fractals in Science* ed A Bunde and S Havlin (Berlin: Springer)
[2] Clark A 1970 *The Theory of Adsorption and Catalysis* (New York: Academic) Part II
[3] Ziff R M, Gulari E and Barshad Y 1986 *Phys. Rev. Lett.* **50** 2553
    Considine D, Redner S and Takayasu H 1989 *Phys. Rev. Lett.* **63** 2857

Clement E, Leroux-Hugon P and Sander L M 1991 *Phys. Rev. Lett.* **67** 1661

Evans J W 1991 *Langmuir* **7** 2514

Krischer K, Eiswirth M and Ertl G 1992 *J. Chem. Phys.* **96** 9161

Krapivsky P L 1992 *Phys. Rev.* A **45** 1067

Evans J W and Ray T R 1993 *Phys. Rev.* E **47** 1018

Bär M, Gottschalk N, Eiswirth M and Ertl G 1994 *J. Chem. Phys.* **100** 1202

Sholl D S and Skodje R T 1996 *Phys. Rev.* E **53** 335

Suchorski Yu, Beben J, Imbihl R, James E W, Liu D-J and Evans J W 2001 *Phys. Rev.* B **63** 165417

Mobilia M and Bares P-A 2001 *Phys. Rev.* E **63** 036121

Argyrakis P, Burlatsky S F, Clément E and Oshanin G 2001 *Phys. Rev.* E **63** 021110

 [4] Ovchinnikov A A and Zeldovich Ya B 1978 *Chem. Phys.* **28** 215

Burlatsky S F 1978 *Theor. Exp. Chem.* **14** 343

Toussaint D and Wilczek F 1983 *J. Chem. Phys.* **78** 2642

Kang K and Redner S 1984 *Phys. Rev. Lett.* **52** 955

Klafter J, Zumofen G and Blumen A 1984 *J. Phys. Lett. (Paris)* **45** L49

Lindenberg K, West B J and Kopelman R 1988 *Phys. Rev. Lett.* **60** 1777

Bramson M and Lebowitz J L 1988 *Phys. Rev. Lett.* **61** 2397

Bramson M and Lebowitz J L 1991 *J. Stat. Phys.* **62** 297

Burlatsky S F, Ovchinnikov A A and Oshanin G 1989 *Sov. Phys.–JETP* **68** 1153

Burlatsky S F and Oshanin G 1991 *J. Stat. Phys.* **65** 1095

 [5] Burlatsky S F and Moreau M 1995 *Phys. Rev.* E **51** 2363

 [6] Oshanin G and Blumen A 1998 *J. Chem. Phys.* **108** 1140

 [7] Toxvaerd S 1998 *J. Chem. Phys.* **109** 8527

 [8] Naidenov A A and Nechaev S K 2002 *JETP Lett.* **76** 61 (*Preprint* cond-mat/0209271)

 [9] Oshanin G, Burlatsky S F, Clément E, Graff D and Sander L M 1994 *J. Phys. Chem.* **98** 7390

[10] Park J-M and Deem M W 1999 *Eur. Phys. J.* B **10** 35

[11] Benderskii V A *et al* 1976 *Sov. Phys.–JETP* **43** 268

Benderskii V A *et al* 1979 *Phys. Status Solidi* b **95** 47

[12] Domb C 1958 *Nuovo Cimento* **9** 9

[13] Temperley H N V 1959 *Proc. Phys. R. Soc.* **74** 183, 432

Temperley H N V 1961 *Proc. Phys. R. Soc.* **77** 630

Temperley H N V 1962 *Proc. Phys. R. Soc.* **80** 813

[14] Levesque D and Verlet L 1964 *Phys. Lett.* **11** 36

[15] Jancovici B 1965 *Physica* **31** 1017

[16] Gaunt D S and Fisher M E 1965 *J. Chem. Phys.* **43** 2840

[17] Runnels L K, Coombs L L and Salvant J P 1967 *J. Chem. Phys.* **47** 4015

[18] Baxter R J 1980 *J. Phys. A: Math. Gen.* **13** L61

Baxter R J, Enting I G and Tsang S K 1980 *J. Stat. Phys.* **22** 465

Baxter R J 1982 *Exactly Solved Models in Statistical Mechanics* (New York: Academic)

Baxter R J 1999 *Ann. Combinator.* **3** 191

[19] Heringa J R, Blöte H W J and Luijten E 2000 *J. Phys. A: Math. Gen.* **33** 2929

[20] Derrida B and Hilhorst H 1983 *J. Phys. A: Math. Gen.* **16** 2641

[21] Sire C and Krapivsky P 2001 *J. Phys. A: Math. Gen.* **34** 9065

[22] Crisanti A, Paladin G and Vulpiani A 1993 *Products of Random Matrices in Statistical Physics* (Berlin: Springer)

[23] Lima R and Rahibe M 1994 *J. Phys. A: Math. Gen.* **27** 3427

[24] McCoy B and Wu T T 1968 *Phys. Rev.* **176** 631

McCoy B and Wu T T 1969 *Phys. Rev.* **188** 982

[25] Comtet A and Nechaev S 1998 *J. Phys. A: Math. Gen.* **31** 5609

[26] Furstenberg H 1963 *Trans. Am. Math. Soc.* **108** 377

[27] Gessel I M 1997 *Electron. J. Combinator.* **4** R11