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One-Dimensional Lattice Dynamics of the Diffusion-Limited Reaction $A+A \to A+S$: Transient Behavior

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We use a Boolean cellular automaton model to describe the diffusion-limited dynamics of the irreversible reaction $A+A \to A+S$ on a 1D lattice. We derive a set of equations for the dynamics of the empty interval probabilities from which explicit expressions for the particle concentration and the two-point correlation can be obtained. It is shown that the long-time dynamics is in agreement with the off-lattice solution. The early-time behavior, however, predicts a slower decay of the concentration.

KEY WORDS: Nonequilibrium reaction–diffusion systems; cellular automata; differential-difference equations.

I. INTRODUCTION

In a recent paper,[1] ben-Avraham *et al.* treated the 1D dynamics of the diffusion-limited reaction $A+A \to A+S$. The analysis led to an infinite hierarchy of differential equations (HDE) for the time evolution of the set of quantities $\{E_k(t)\}$, where $E_k(t)$ denotes the probability of finding an interval of k contiguous empty lattice sites (c.f. Eqs. (2.2) and (2.5) in ref. 1). Ben-Avraham *et al.* were primarily interested in the continuum limit for the probability densities $E_k(t)/(\Delta x)^k$ as the lattice spacing Δx is allowed to vanish. Here we rederive the HDE taking as a starting point a detailed cellular automaton description using Boolean occupation numbers.[2, 3]

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Instead of going to the continuum limit, we solve the HDE for a discrete lattice and obtain explicit expressions for the concentration $c(t) = (1 - E_1(t))/\Delta x$ and the two-point nearest neighbor correlation. We consider both the case of an initially fully occupied lattice and the case in which the initial probabilities $E_k(0)$ are given by the random "geometrical" distribution $(1-\rho)^k$, where $\rho < 1$ is the initial probability of a single site being occupied. Some exact solutions to related problems and a special case can be found in ref. 4.

In Section II, we derive the HDE starting from the cellular automaton dynamical rule. The next section is a brief reminder of the off-lattice solution for the HDE obtained in ref. 1. In Section IV, we solve the solution of the HDE for a discrete lattice and discuss the transient dynamics of the concentration. As expected, the long-time behavior is the same as that found in ref. 1. However, the early-time behavior turns out to be significantly different.

II. DERIVATION OF THE HDE

Consider a 1D lattice with N sites. Each lattice site i is characterized by a Boolean occupation number $n_i = 1$ or 0 depending on whether it is occupied by a single particle (A) or empty (S). At each time step Δt, we choose randomly a site i in the lattice via the Boolean stochastic parameter $\xi_N^{(i)}$. This parameter is equal to 1 for the chosen site and 0 for all other sites. Simultaneously, a second Boolean variable is used to select the left ($\xi_L = 1$) or the right neighbour site ($\xi_L = 0$) with equal probability 1/2. If the site i is occupied, the particle will hop to the chosen neighbor site with a rate k_D given by the mean value of the stochastic Boolean parameter ξ_D. In this case, if the neighbour site is empty, the particle will occupy it vacating the site i. We express this by including the loss terms

$$-\xi_N^{(i)}(t)\,\xi_L(t)\,\xi_D(t)\,n_i(t)(1 - n_{i-1}(t)) \tag{1}$$

$$-\xi_N^{(i)}(t)(1 - \xi_L(t))\,\xi_D(t)\,n_i(t)(1 - n_{i+1}(t)) \tag{2}$$

in the dynamical rule for $n_i(t)$. If the neighbor site is filled, the particle will "react" with it and instantaneously disappear. Again, the occupation number at site i will be decreased from 1 to 0. Thus, we have the reactive loss terms:

$$-\xi_N^{(i)}(t)\,\xi_L(t)\,\xi_D(t)\,n_i(t)\,n_{i-1}(t) \tag{3}$$

$$-\xi_N^{(i)}(t)(1 - \xi_L(t))\,\xi_D(t)\,n_i(t)\,n_{i+1}(t) \tag{4}$$

Finally, as an empty site i can only be occupied by hopping from a particle at a neighbor site, one has the two gain terms:

$$+\xi_N^{(i+1)}(t)\,\xi_L(t)\,\xi_D(t)\,n_{i+1}(t)(1-n_i(t)) \tag{5}$$

$$+\xi_N^{(i-1)}(t)(1-\xi_L(t))\,\xi_D(t)\,n_{i-1}(t)(1-n_i(t)) \tag{6}$$

Clearly, the dynamics described above corresponds to the particular implementation of the reaction $A+A\to A+S$ given in ref. 1. Adding up all the contributions (1)–(6), we obtain the following dynamical rule:

$$\begin{aligned} n_i(t+\Delta t) = n_i(t) &- \xi_N^{(i)}(t)\,\xi_D(t)\,n_i(t) \\ &+ \xi_N^{(i+1)}(t)\,\xi_L(t)\,\xi_D(t)\,n_{i+1}(t)(1-n_i(t)) \\ &+ \xi_N^{(i-1)}(t)(1-\xi_L(t))\,\xi_D(t)\,n_{i-1}(t)(1-n_i(t)), \qquad i=1,\dots,N \end{aligned} \tag{7}$$

In the first and last equation (7), we set $n_0(t)=n_{N+1}(t)=n_1(t)$. We can rewrite (7) by using the complementary occupation numbers $s_i(t)=1-n_i(t)$:

$$\begin{aligned} s_i(t+\Delta t) = s_i(t) &+ \xi_N^{(i)}(t)\,\xi_D(t) \\ &- [\xi_N^{(i-1)}(t)(1-\xi_L(t)) + \xi_N^{(i)}(t) + \xi_N^{(i+1)}(t)\xi_L(t)]\,\xi_D(t)\,s_i(t) \\ &+ \xi_N^{(i-1)}(t)(1-\xi_L(t))\,\xi_D(t)\,s_{i-1}(t)\,s_i(t) \\ &+ \xi_N^{(i+1)}(t)\,\xi_L(t)\,\xi_D(t)\,s_i(t)\,s_{i+1}(t), \qquad i=1,\dots,N \end{aligned} \tag{8}$$

This is a more convenient form, since, as it turns out, the evolution law for a string of k consecutive empty sites $\prod_{j=i}^{i+k-1} s_j$ involves only products of contiguous occupation numbers

$$\begin{aligned} \prod_{j=i}^{i+k-1} s_j(t+\Delta t) = \prod_{j=i}^{i+k-1} s_j(t) &+ \xi_N^{(i)}(t)\,\xi_L(t)\,\xi_D(t) \prod_{j=i+1}^{i+k-1} s_j(t) \\ &+ \xi_N^{(i+k-1)}(t)(1-\xi_L(t))\,\xi_D(t) \prod_{j=i}^{i+k-2} s_j(t) \\ &- [\xi_N^{(i-1)}(t)(1-\xi_L(t)) + \xi_N^{(i)}(t)\,\xi_L(t) \\ &+ \xi_N^{(i+k-1)}(t)(1-\xi_L(t)) + \xi_N^{(i+k)}(t)\,\xi_L(t)] \\ &\times \xi_D(t) \prod_{j=i}^{i+k-1} s_j(t) + \xi_N^{(i-1)}(t)(1-\xi_L(t))\,\xi_D(t) \prod_{j=i-1}^{i+k-1} s_j(t) \\ &+ \xi_N^{(i+k)}(t)\,\xi_L(t)\,\xi_D(t) \prod_{j=i}^{i+k} s_j(t), \qquad k\geqslant 2 \end{aligned} \tag{9}$$

Let us take the time step Δt equal to $1/N$, implying that each site has been visited once on average after one time unit. If we now average (9) over an ensemble of realizations for a given initial configuration, we obtain in the thermodynamic limit $N \to \infty$:

$$\frac{dE_k^i}{dt} = \frac{k_D}{2}\left(E_{k-1}^{i+1} + E_{k-1}^i - 4E_k^i + E_{k+1}^{i-1} + E_{k+1}^i\right) \tag{10}$$

where $E_k^i(t) = \overline{\prod_{j=i}^{i+k-1} s_j(t)}$. For a single site $(k=1)$ the corresponding equation

$$\frac{dE_1^i}{dt} = k_D\left(1 - 2E_1^i + \frac{1}{2}E_2^{i-1} + \frac{1}{2}E_2^i\right) \tag{11}$$

is obtained by averaging the dynamical rule (8). If we perform the average over realizations *and* translationally invariant initial conditions, we get the following hierarchy of differential-difference equations for the evolution of the averaged products $E_k(t) = \langle \prod_{j=i}^{i+k-1} s_j(t) \rangle$:

$$\frac{dE_k}{dt} = k_D(E_{k+1} - 2E_k + E_{k-1}), \qquad k = 1, 2, \ldots \tag{12}$$

with the boundary condition $E_0(t) = 1$. As described in ref. 1, the r.h.s. of (12) represents the net flux due to particle diffusion into and out of an empty site interval, whereas the effect of reaction enters through the boundary condition.

III. OFF-LATTICE SOLUTION

Following ref. 1, we set the hopping rate $k_D/2$ to either of both sides equal to $D/(\Delta x)^2$, where Δx is the lattice spacing. On long length and time scales this yields normal diffusion with a diffusion coefficient D. With this definition, Eqs. (12) are identical to those derived in ref. 1. If we now let $\Delta x \to 0$, Eqs. (12) become

$$\frac{\partial E(x, t)}{\partial t} = 2D \frac{\partial^2 E(x, t)}{\partial x^2} \tag{13}$$

with the boundary conditions $E(0, t) = 1$ and $E(\infty, t) = 0$. In this limit, the concentration (number of particles per unit length) is expressed as

$$c(t) = -\left.\frac{\partial E(x, t)}{\partial x}\right|_{x=0} \tag{14}$$

Thus, one can determine the time dependence of the concentration by solving (13) with the boundary conditions given above (see ref. 1 for details). For the special case of an initially random particle distribution with a concentration c_0, one has

$$\frac{c(t)}{c_0} = 1 - \left(\frac{8c_0^2 Dt}{\pi}\right)^{1/2} + o(c_0^2 Dt) \qquad \text{as} \quad t \to 0 \tag{15}$$

and

$$c(t) \to \frac{1}{(2\pi Dt)^{1/2}} \qquad \text{as} \quad t \to \infty \tag{16}$$

IV. SOLUTION FOR A DISCRETE LATTICE

We now proceed to solve the HDE (12) for the case in which one has an initially full lattice, i.e., $E_k(0) = 0$ for all $k \geqslant 1$. To begin with, we absorb the rate constant k_D into the time scale by introducing the dimensionless time variable $\tau = k_D t$. The hierarchy then reads:

$$\frac{dE_k}{d\tau} = E_{k+1} - 2E_k + E_{k-1}, \qquad k = 1, 2,... \tag{17}$$

Next we apply the Laplace transform to both sides of (17) and obtain the homogeneous difference equation

$$\bar{E}_{k+1} - (2+s)\,\bar{E}_k + \bar{E}_{k-1} = 0, \qquad k \geqslant 1 \tag{18}$$

where $\bar{E}_k(s) = L_{\tau \to s}\{E_k(\tau)\} = \int_0^\infty \exp(-s\tau)\, E_k(\tau)\, d\tau$. The boundary condition is given by $\bar{E}_0(s) = 1/s$. This second-order difference equation is solved with the ansatz $E_k(s) = \lambda^k(s)$. This leads to the quadratic equation

$$\lambda^2 - (2+s)\,\lambda + 1 = 0 \tag{19}$$

which has the two solutions

$$\lambda_{\pm} = \frac{s + 2 \pm \sqrt{s^2 + 4s}}{2} \tag{20}$$

The general solution of (18) is obtained as a linear superposition of λ_+^k and λ_-^k:

$$\bar{E}_k(s) = A(s)\, \lambda_-^k(s) + B(s)\, \lambda_+^k(s) \tag{21}$$

For $k \to \infty$, the physically acceptable solution of (18) must satisfy the implicit boundary condition $E_\infty(s) = 0$. To avoid the divergence of the second term in (21), we must therefore set $B(s) = 0$. Using the other boundary condition at $k = 0$, we find $A(s) = 1/s$. Thus, we have:

$$\bar{E}_k(s) = \frac{1}{s}\left(\frac{s+2-\sqrt{s^2+4s}}{2}\right)^k \tag{22}$$

Clearly, the most interesting quantity is $\bar{E}_1(s)$, whose inverse Laplace transform $E_1(\tau)$ is the probability that a randomly chosen site be empty. By virtue of a theorem,[(7)] the inverse transform $L_{s\to\tau}^{-1}\{\bar{E}_k(s)\}$ is given by the integral

$$\int_0^\tau v_k(\tau')\, d\tau', \qquad k = 1, 2,... \tag{23}$$

where

$$v_k(\tau) = L_{s\to\tau}^{-1}\left\{\left(\frac{s+2-\sqrt{s^2+4s}}{2}\right)^k\right\} = k\,\frac{\exp(-2\tau)\, I_k(2\tau)}{2\tau} \tag{24}$$

(see, e.g., [5, p. 379]), where

$$I_n(x) = \sum_{r=0}^{\infty} \frac{(x/2)^{2r+n}}{r!\, \Gamma(r+n+2)} \tag{25}$$

are the modified Bessel functions. In particular, one has

$$E_1(\tau) = \int_0^\tau \frac{\exp(-2\tau')\, I_1(2\tau')}{\tau'}\, d\tau' \tag{26}$$

A. Asymptotics for Early Times

For sufficiently short times ($\tau \ll 1$), we can use (25) and the series expansion of the exponential function $\exp(-2\tau')$ to expand the integrand in (26) in powers of τ'. Neglecting terms of order $o(\tau'^3)$, performing the integration and undoing the time scaling, we obtain:

$$E_1(t) = k_D t - k_D^2 t^2 + \tfrac{5}{6} k_D^3 t^3 + o(t^4) \tag{27}$$

The particle concentration is

$$c(t) = \frac{P_1(t)}{\Delta x} = \frac{1 - E_1(t)}{\Delta x} = c_0[1 - 2c_0^2 Dt + 4c_0^4 D^2 t^2 + o(c_o^6 D^3 t^3)] \quad (28)$$

where $c_0 = 1/\Delta x$. This is in clear disagreement with the decay law (15).

For sufficiently short times, we can neglect the effect of large clusters of vacant sites, since the chain is initially full. This is done by setting $E_k = 0$ for k larger than a certain cutoff size k_c in the truncation hierarchy (17). If we set $k_c = 1$, we obtain the differential equation

$$\frac{dE_1}{d\tau} = 1 - 2E_1(\tau) \quad (29)$$

The solution reads

$$E_1(\tau) = \tfrac{1}{2}(1 - \exp(-2\tau)) = \tau - \tau^2 + \tfrac{2}{3}\tau^3 + o(\tau^4) \quad (30)$$

Setting $\tau = k_D t$, we see that the early times expansion (27) is reproduced correctly up to the quadratic term. The discrepancy between (27) and the off-lattice solution arises due to the finite propagation velocity of a local perturbation in concentration, as opposed to the infinite propagation velocity characteristic of diffusion. Thus, we expect a slower decay of the concentration $c(t)$ on the lattice.

B. Long-Time Asymptotics

For large times ($\tau \gg 1$), we write $E_1(\tau)$ as follows:

$$E_1(\tau) = u - \int_\tau^\infty \frac{\exp(-2\tau')\, I_1(2\tau')}{\tau'}\, d\tau' \quad (31)$$

where u is the definite integral

$$\int_0^\infty \frac{\exp(-2\tau')\, I_1(2\tau')}{\tau'}\, d\tau' \quad (32)$$

which is equal to 1 [6, p. 236]. The integrand in the second term of (31) can be expanded using the asymptotic form

$$I_1(x) = \frac{\exp(x)}{\sqrt{2\pi x}}\left(1 - \frac{3}{8x} + o\left(\frac{1}{x^2}\right)\right) \quad (33)$$

for large x (see e.g., [7, p. 489]). Thus, we get

$$E_1(\tau) = 1 - \frac{1}{2\sqrt{\pi}} \int_\tau^\infty \tau'^{-3/2}\, d\tau' + \frac{3}{32\sqrt{\pi}} \int_\tau^\infty \tau'^{-5/2}\, d\tau' + o(\tau^{-5/2})$$
$$= 1 - \frac{1}{\sqrt{\pi\tau}} + \frac{1}{16\sqrt{\pi\tau^3}} + o(\tau^{-5/2}) \qquad (34)$$

This is in agreement with the long time asymptotics of the continuum limit solution (16).

C. Two-Point Correlation

The explicit expression for the two interval probability

$$E_2(\tau) = 2\int_0^\tau \frac{\exp(-2\tau')\, I_2(2\tau')}{\tau'}\, d\tau' \qquad (35)$$

can be used as a starting point to compute the asymptotics of the two-point nearest neighbor correlation $c^{(2)}(t) = P_2/(\Delta x)^2$, where $P_2 = 1 - 2E_1 + E_2$ is the probability of finding two contiguous particles in the lattice. For early times one gets $c^{(2)}(t) = c_0^2[1 - c_0^2 Dt + o(c_0^4 D^2 t^2)]$, whereas for long times $c^{(2)}(t) \approx 1/c_0\sqrt{32\pi}\,(Dt)^{3/2}$.

D. Solution for an Arbitrary Initial Concentration

In this case, we average over all possible initial configurations of the lattice with a given concentration $c_0 = \rho/\Delta x$ ($\rho < 1$). The initial conditions for the empty interval probabilities now read

$$E_k(0) = (1-\rho)^k, \qquad k = 1, 2, \ldots \qquad (36)$$

The boundary conditions are the same as in the case of an initially full lattice. If we now apply the Laplace transform to (17), we obtain

$$\bar{E}_{k+1} - (2+s)\,\bar{E}_k + \bar{E}_{k-1} = -(1-\rho)^k, \qquad k \geqslant 1 \qquad (37)$$

which differs from (18) by the inhomogeneity on the r.h.s. Like in the theory of ordinary differential equations, the general solution of (37) can be written as the sum of the general solution (21) for (18) and a particular solution which we seek in the form

$$\bar{E}_k^{\text{par}}(s) = (1-\rho)^k\, C(s) \qquad (38)$$

Inserting this ansatz in (37), we find

$$C(s)=\frac{(1-\rho)}{(1-\rho)\,s-\rho^2} \tag{39}$$

The boundary condition for $k \to \infty$ again imposes $B(s)=0$. From the boundary condition for $\bar{E}_0(s)$ we obtain

$$A(s)=\frac{1}{s}-\frac{1-\rho}{(1-\rho)\,s-\rho^2} \tag{40}$$

Putting (39) and (40) into the equation

$$\bar{E}_k(s)=A(s)\,\lambda_-^n(s)+\bar{E}_k^{\text{par}} \tag{41}$$

we find

$$\bar{E}_k(s)=\left(\frac{1}{s}-\frac{1-\rho}{(1-\rho)\,s-\rho^2}\right)\left[\frac{s+2-\sqrt{s^2+4s}}{2}\right]^k + \frac{(1-\rho)^{k+1}}{(1-\rho)\,s-\rho^2}, \qquad k=0,\,1,... \tag{42}$$

We can now use the convolution theorem for the Laplace transform[7] to invert (42). This yields

$$E_k(\tau)=k\int_0^\tau \frac{\exp(-2\tau')\,I_k(2\tau')}{\tau'}\,d\tau' + \left[(1-\rho)^k-k\int_0^\tau \frac{\exp(-[2+(\rho^2/(1-\rho))]\,\tau')\,I_k(2\tau')}{\tau'}\,d\tau'\right] \times \exp\left(\frac{\rho^2\,\tau}{1-\rho}\right) \tag{43}$$

However, we can study the asymptotics directly from (42) by making use of the Tauberian theorems,[8] which allow us to determine the behavior of $E_1(\tau)$ for $\tau \to 0$ and $\tau \to \infty$ by inverting respectively the series expansion of $\bar{E}_1(s)$ around $s=\infty$ and $s=0$. For small s one has

$$\bar{E}_1=\frac{1}{s}-\frac{1}{\sqrt{s}}+\frac{1}{2}+\frac{1-\rho}{\rho}+o(s^{1/2}) \tag{44}$$

from which we get

$$E_1 \approx 1 - \frac{1}{\sqrt{\pi\tau}} \qquad \text{for} \quad \tau \to \infty \tag{45}$$

Again, this is in agreement with (16). The long time asymptotics does not depend on the initial concentration c_0, suggesting that a universal behavior also takes place on a finite lattice. In the opposite limit we have

$$\bar{E}_1 = \frac{1-\rho}{s} + \frac{\rho^2}{s^2} - \frac{\rho^2(1+\rho)}{s^3} + o(s^4) \tag{46}$$

Inverting term by term the r.h.s. of (46), we get

$$E_1 = 1 - \rho + \rho^2\tau - \frac{\rho^2(1+\rho)}{2}\tau^2 + o(\tau^3) \tag{47}$$

leading to

$$c(t) = c_0\left[1 - \frac{2}{\rho}c_0^2 Dt + 2\frac{\rho^2(\rho+1)}{\rho^5}c_0^4 D^2 t^2 + o(c_0^6 D^4 t^4)\right] \tag{48}$$

Thus, the discrepancy with (15) appears to be robust. We can again compare the exact early-time expansion (47) with the solution of the differential equation (29) with the initial condition $E_1(0) = 1 - \rho$, which is given by

$$\tfrac{1}{2} + (\tfrac{1}{2} - \rho)\exp(-2\tau) = 1 - \rho + (2\rho - 1)\,\tau + (1 - 2\rho)\,\tau^2 + o(\tau^3) \tag{49}$$

As expected, the approximation based on the neglect of empty intervals becomes worse as ρ decreases.

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