Exact Results for Diffusion-Limited Reactions with Synchronous Dynamics

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ABSTRACT

A new method is introduced allowing to solve exactly the reactions A+A→inert and A+A→A on the 1D lattice with synchronous diffusional dynamics (simultaneous hopping of all particles). Exact connections are found relating densities and certain correlation properties of these two reactions at all times. Asymptotic behavior at large times as well as scaling form describing the regime of low initial density, are derived explicitly.

PACS numbers: 82.20.−w, 05.40.+j

In this work we develop a new method of obtaining exact results for certain one-dimensional reaction-diffusion models. Dynamics of the 1D Ising chain was first solved by Glauber [1]. This famous solution has lead to a host of results explored over the last three decades. However, recently there has been a resurgence of interest in the solvable 1D models with both new emphases and new solution methods, developed by many authors [2-25]. The new emphases have been on those models which have no equilibrium states, such as irreversible reactions [2-17], cluster coarsening at phase separation [17-23], deposition processes [1,24], models of self-organized criticality [25], etc. The solution methods utilized a variety of different approaches both for continuous-time asynchronous, and to a lesser extent for synchronous (discrete time, simultaneous updating, cellular-automaton-type) dynamics [17,26].

While our approach can be applied to a larger class of models [27], the present work is devoted to the diffusion-limited (i.e., instantaneous reaction on each encounter)

coagulation, A+A→A, and annihilation A+A→inert, of particles synchronously hopping on the 1D lattice. The models will be defined in detail later. Besides providing interesting examples of strongly nonclassical fluctuations, 1D reactions also describe certain experimental systems [28] with the reactants being typically excitations in chain-like structures.

Various results for these reactions have been reported in the literature [2-17] and they include several exact solutions, either in the continuum off-lattice limit [8-10,13] or on the lattice. Our results, besides providing previously unavailable (on-lattice) solutions for the synchronous case, resolve two long-standing theoretical issues in this field. Firstly, we elucidate and prove <u>exactly</u> the equivalence of the coagulation and annihilation reactions <u>for all times and densities</u>. This equivalence has been anticipated and explored by several authors [7-8,10,13-15] based on the asymptotic large-time results and on certain similarities between the correlation functions of both reactions. Here we derive an explicit connection, relations (12)-(13) below.

Secondly, earlier exact on-lattice calculations for A+A→inert, based on the mapping [4] to the low-T dynamics of Ising interfaces [4,11-12,17], were for initial conditions corresponding to certain subtle correlations in the particle locations at time $t = 0$; see the discussion in [12]. The initially uncorrelated state was only possible for the (initial) density $\rho = \frac{1}{2}$ (per site). As a result, the asymptotic large-time solution was not universal. Our new results explicitly apply for the random initial distribution of arbitrary density ρ per site. The large-time behavior of both the coagulation and annihilation reactions is found to be universal and not dependent on ρ. The onset of this behavior occurs nonuniformly for small ρ. The latter regime can be described by a scaling form introduced in [29], to be reviewed later on, see relations (19) and (21) below. Our exact results confirm the proposed scaling and also yield explicit form of the appropriate scaling function.

We consider a model of 0 or 1 particles at lattice sites i of the 1D lattice, at times $t = 0, 1, 2, \ldots$. In the time step $t \to t + 1$, all particles hop synchronously, to one of the neighboring sites $i \pm 1$, with equal probability $\frac{1}{2}$. The decision which way to hop is done independently for each particle. However, if two particles end up at the same site they instantaneously "react" according to the annihilation rule (the particle number is reduced from 2 to 0) or coagulation rule (the number is reduced from 2 to 1). It is clear that this dynamics decouples the even-odd and odd-even lattices. Thus, we only consider particles at even lattice sites $i = 0, \pm 2, \pm 4, \ldots$ at even times $t = 0, 2, 4, \ldots$, and at odd lattice sites $i = \pm 1, \pm 3, \ldots$ at odd times. At time $t = 0$ all even lattice sites are randomly occupied (particle number 1) with probability ρ or empty (particle number 0) with probability $1 - \rho$.

The method of exact solution employed here utilizes a system with a certain conservation property which allows simplification of the dynamical behavior. Thus, rather then considering particles directly, we consider integer "charge" variables $q_i(t) = 0, 1, 2, \ldots$ at each lattice site (with the even-odd sublattice convention as before). The charges follow the dynamics introduced in the studies of self-organized criticality [25]: they randomly hop at each time step, similar to the particles. However, if two charges end up at the same site they stick together and move as a single charge (sum of the two original charges) at later time steps. Such dynamics can be represented by the rule

$$q_i(t+1) = a_{i-1}(t) q_{i-1}(t) + \left[1 - a_{i+1}(t)\right] q_{i+1}(t) \ , \tag{1}$$

where the hopping-decision variables $a_j(t)$ are 0 or 1 with probability $\frac{1}{2}$. Specifically, $a_j(t) = 1$ indicates that the charge at j hopped to $j+1$ in the time step $t \to t+1$, whereas the value 0 corresponds to stepping to $j-1$.

The important feature of such dynamical rules [25] is that due to charge conservation the sum of charges in r consecutive sites,

$$s_{r,j} = q_j + q_{j+2} + \ldots + q_{j+2(r-1)} \ , \tag{2}$$

evolves with only two random decisions at the end-points needed,

$$s_{r,j}(t+1) = a_{j-1}(t) q_{j-1}(t) + q_{j+1}(t) + \ldots + q_{j+2r-3}(t) + \left[1 - a_{j+2r-1}(t)\right] q_{j+2r-1}(t) \ , \tag{3}$$

where the random variables a at sites $j-1$ and $j+2r-1$ enter. Relation (3) follows directly from (1) and (2).

Consider now a function $F(s)$ defined on the allowed s values $0, 1, 2, \ldots$. The averages

$$f_r(t) = \langle F\left(s_{r,j}(t)\right) \rangle \ , \tag{4}$$

where the averaging is both over the random hopping decisions $a_i(t)$ and over translationally invariant initial conditions, are translationally invariant, i.e., they do not depend on j. By using relation (3), one can easily verify that

$$f_r(t+1) = \frac{1}{4}\left[f_{r+1}(t) + 2 f_r(t) + f_{r-1}(t)\right] \ , \tag{5}$$

where we define $f_0(t) = F(0)$ to have (5) apply for all $r \geq 1$. Earlier studies used this formulation with the choice $F(s) = e^{i\omega s}$ and a further complication of allowing for added charge "fed in" at each time step, by including inhomogeneous term in (1) with values drawn from a fixed, time-independent distribution. The resulting characteristic functions $f_r(\omega, t)$ can be used to study the self-similar steady state and dynamics [27] of charge systems with various charge variables, — real, positive, integer, etc., — in the framework of self-organized criticality.

Our approach differs in that we employ functions $F(s)$ which are not smooth. Specifically, let us define the empty interval indicator function,

$$F(s) = \begin{cases} 1, & s = 0 \\ 0, & s > 0 \end{cases} \tag{6}$$

We relate the particle and charge systems as follows: a continuous interval of r sites is empty of particles and of charge simultaneously. Thus, we associate charge $q > 0$ at a given site with particle number 1, and charge $q = 0$ with particle number 0. The initial state of 0 or 1 particles at each site is represented by $q_i(0) = 0$ for sites i empty of particles, and by placing an arbitrary initial charge $q_i(0) > 0$ at sites occupied by particles. Then the dynamics of charges at the later times $t > 0$ will also yield the correct dynamics of coagulating particles in the reaction A+A→A, which we will denote by the subscript A for brevity in what follows.

The initial values of the averages are

$$f_r(0) = (1 - \rho)^r \ , \tag{7}$$

and for the particle density per site we get

$$c_{\mathrm{A}}(t) = 1 - f_1(t) \ , \tag{8}$$

while the general difference $1 - f_r(t)$ yields the probability that an interval of r consecutive sites is empty. Empty interval probabilities have been considered in other studies of the coagulation reaction, e.g., [13]. Note that the system of recursion relations (5) for the coagulation reaction must be solved with the initial conditions (7) and "boundary condition"

$$f_0(t) = F(0) = 1 \ . \tag{9}$$

Our emphasis here will be on the density, $c(t)$, which will be calculated exactly. However, let us first introduce the appropriate formulation for the annihilation reaction A+A→inert, which will be denoted by the subscript Ø for brevity. The idea to relate the aggregating "charge" system to

hopping-particle models has been considered in [7,30]. Specifically, Spouge [7] used it to derive various exact continuum-limit expressions for both types of reaction (with asynchronous dynamics). Besides technical differences, the implementation here is more powerful than earlier variants. Firstly, synchronous dynamics and the associated charge-conservation property (3) allow derivation of explicit, discrete-time exact results in a rather straightforward manner. Secondly, extensions and generalizations are more easily identified [27].

For the annihilation reaction, we consider the <u>even-occupancy indicator function</u>,

$$F(s) = \begin{cases} 1, & s = \text{even} \\ 0, & s = \text{odd} \end{cases} \tag{10}$$

Indeed, the mapping to the particle system is now defined by associating even charges with empty sites and odd charges with sites occupied by particles. Initially, each empty site (particle number 0) is assigned an arbitrary <u>even</u> charge value $q(0)$, whereas every occupied site (particle number 1) is assigned an <u>odd</u> charge value. At later times $t > 0$ the dynamics of charges will then describe the annihilation reaction A+A→inert. Specifically, $c_{\emptyset}(t) = 1 - f_1(t)$, while the difference $1 - f_r(t)$ denotes the probability that an r-interval has an even number of particles $(0, 2, 4, \ldots, 2[r/2]_{\text{integer part}})$ in it.

The initial conditions for the annihilation case are more complicated than (7). Indeed, with a little bit of combinatorics one can check that the correct relation is $f_r(0) = \left[1 + (1-2\rho)^r\right]/2$. The boundary condition (9) is unchanged. This suggests consideration of the modified functions

$$g_r(t) = 2f_r(t) - 1 \ . \tag{11}$$

It is obvious that $g_r(t)$ satisfy, for Ø with the initial density $\rho_{\text{Ø}}$, the relations (5), (7) and (9) exactly identical to those satisfied by the original averages $f_r(t)$ for the reaction A provided we put

$$\rho_{\rm A} = 2\rho_{\text{Ø}} \ . \tag{12}$$

Thus we discover that for the particular synchronous dynamics selected for the annihilation and coagulation reactions, the probabilities of finding even occupancy for the former are related to the probabilities of finding empty interval for the latter, with twice the initial density in coagulation as compared to annihilation. The precise relations can be quantified via the identity $[g_r(t)]_{\text{Ø}} = [f_r(t)]_{\rm A}$, with (12). For instance for the densities we find the relation

$$c_{\rm A}(t) = 2c_{\text{Ø}}(t) \ , \tag{13}$$

which for this particular dynamics is <u>exact for all times</u> $t = 1, 2, 3, \ldots$ provided the random initial densities satisfy the relation (16) at $t = 0$; see (12). As mentioned earlier, several authors have explored [7-8,10,13-15] the asymptotic variants of this result for other dynamical rules.

We now consider the coagulation reaction only and derive exact results for the density by solving the recursions (5), with (7) and (9), by the generating function method. Only the outline of the actual solution steps will be presented. The emphasis will be on discussion of results for the density. Thus, we consider the generating functions

$\phi_r(u) = \sum_{t=0}^{\infty} f_r(t)u^t$ which satisfy the relations $\phi_0(u) = 1/(1-u)$, $\phi_r(0) = (1-\rho)^r$, and

$$u\left(\phi_{r+1} + 2\phi_r + \phi_{r-1}\right) = 4\left[\phi_r - (1-\rho)^r\right] \ . \tag{14}$$

The solution of (14) is obtained by first eliminating the exponential-in-r dependence by defining $\phi_r = (1-\rho)^r \psi_r$, which yields an autonomous but inhomogeneous difference equation for

ψ_r. However, the (constant) inhomogeneous term is then removed by the shift, $\psi_r = \theta_r + \Theta$. Finally, the resulting second-order difference equation for θ_r is solved by the exponential form, $\theta_r = \Lambda^r \theta_0$, where only one of the two roots of the characteristic equation gives the physically acceptable (i.e., regular at $u = 0$) Λ value. The resulting expression is

$$\phi_r = \left[1 - (1-u)^{1/2}\right]^{2r} u^{-r}\left[1/(1-u) - \Theta\right] + (1-\rho)^r \Theta \ , \tag{15}$$

$$\Theta^{-1} = 1 - u(2-\rho)^2/[4(1-\rho)] \ . \tag{16}$$

Let us now analyze the generating function for the density,

$$1/(1-u) - \phi_1(u) = \sum_{t=0}^{\infty} c(t)u^t = 2(1-u)^{-1/2}\left[1 + (2-\rho)\rho^{-1}(1-u)^{1/2}\right]^{-1} \ . \tag{17}$$

The final expression was obtained from (15) with (16) and required a rather cumbersome algebraic manipulation.

Its form immediately illustrates that the large-time density,

$$c(t \to \infty) = 2/\sqrt{\pi t} \ , \tag{18}$$

is independent of ρ, as expected by the universality considerations referred to in the opening discussion; the residue of the leading singular term $\propto (1-u)^{-1/2}$ does not depend on ρ.

We also note that the onset of the large-time behavior in (17) is nonuniform in the limit $\rho \to 0$. Indeed, it has been argued in the literature [29] that the universal large-time behavior sets in after the initial state is well "mixed" by the particle diffusion. The (dimensional) time scale for such a mixing is of order $[(\text{dimensional})\ \text{density}]^{-2/\mathrm{D}}/\mathcal{D}$, where D is the dimensionality of space and $\mathcal{D}$ is the diffusion constant of the particle hopping. Here we have D$=1$ and, in our dimensionless units, $\mathcal{D}=\mathrm{O}(1)$. Thus, the onset of the large-time behavior in the limit of small initial densities will be described by a scaling form [29] which in our case is

$$c(t \to \infty, \rho \to 0) = t^{-1/2} R(\rho^2 t) \ . \tag{19}$$

The prefactor was selected to have the correct asymptotic form as $t \to \infty$ for fixed $\rho > 0$, with $R(x=\infty) = 2/\sqrt{\pi}$, while for short times, $t \ll \mathrm{O}\left(\rho^{-2}\right)$, the reaction is ineffective: $R(x \to 0) = \sqrt{x}$.

In order to verify these expectations we need an explicit expression of the power series coefficients of (17). These can be obtained in terms of a hypergeometric function, or as polynomials in ρ, of degree $t+1$, for integer t values, or as a quadrature [27]. We favor the latter expression,

$$c(t) = \frac{\rho(2-\rho)^{2t+1}(2t+1)!!}{(1-\rho)^{t+1}2^{3t+2}t!} \int\limits_0^{\frac{4(1-\rho)}{(2-\rho)^2}} \frac{z^t dz}{(1-z)^{1/2}} \ , \tag{20}$$

because it provides an explicit analytic continuation to all real $t \ge 0$ values (even though the original model was only defined for integer t).

Furthermore, the form (20) was already arranged to allow a relatively simple derivation of the scaling relation (19). We find

$$2R(x) = \sqrt{\frac{x}{\pi}} \int\limits_0^{\infty} \frac{e^{-y/4} dy}{(x+y)^{1/2}} \ , \tag{21}$$

which satisfies all the limiting properties as expected. Note that all the expressions for the coagulation reaction are meaningful for $0 \leq \rho \leq 1$. However, the relation to the annihilation reaction, (12), (13), etc., suggests that the formulas must be well defined for all $0 \leq \rho \leq 2$. Indeed, the appropriate results for the annihilation reaction are obtained by replacing ρ by 2ρ in all the "coagulation" expressions (and of course adding various other factors such as the coefficient $\frac{1}{2}$ in "translating" the density expression). Examination of (20) reveals that the powers of $1-\rho$ in the denominator are cancelled by the appropriate factors from the integral (note $1-\rho$ in the upper bound) so that the resulting expressions are indeed smooth and well defined near $\rho = 1$.

In summary, we obtained new exact results, as well as the low-density scaling relation, for the 1D coagulation and annihilation reactions with synchronous dynamics. These reactions are related to each other for all times. The large-time expressions are universal. We remind the reader that the notion of universality refers not only to the absence of dependence of results such as (18) on the initial density but also to the expectation that universal results apply to a class of models differing only in microscopic details of the dynamics, synchronous or asynchronous. However, for latter comparison the 1D densities must be expressed per unit length, the dimensionless time related to the actual physical time τ, etc. For instance the result (18) for the actual, dimensional density of the coagulation reaction then reduces to $(2\pi\mathcal{D}\tau)^{-1/2}$, etc. Our explicit results for the density of both reactions are universal when thus compared with other calculations available in the literature [2-17].

The author wishes to acknowledge the hospitality and financial assistance of the Institute for Theoretical Physics at the Technion, Israel Institute of Technology, where this work was completed.

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