Annihilation of Immobile Reactants on the Bethe Lattice

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ABSTRACT

Two-particle annihilation reaction, $A + A \rightarrow$ inert, for immobile reactants on the Bethe lattice is solved exactly for the initially random distribution. The process reaches an absorbing state in which no nearest-neighbor reactants are left. The approach of the concentration to the limiting value is exponential. The solution reproduces the known one-dimensional result which is further extended to the reaction $A+B \rightarrow$ inert.

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Recent studies of reaction-diffusion systems have emphasized fluctuation effects and breakdown of the standard chemical rate equations in low dimensions. For the simplest reactions of two-particle coagulation, $A + A \to A$, and annihilation, $A + A \to$ inert, on the one-dimensional lattice, several exact results have been reported [1-13]. In the diffusion-limited, instantaneous-reaction case, these processes show non-mean-field power-law decay of the A-particle density.

Another solvable limit, in one dimension [14], is the case of no diffusion at all. Generally such models of *immobile reactants* have received less attention in the recent literature [14-16]. The reason is that unless longer-range reactions are allowed for [15-16], the time dependence involves exponential relaxation to an absorbing state rather than power-law behavior typical of the fast-diffusion reactions. Thus there are no universal fluctuation effects involved.

On the other hand, immobile-reactant systems provide an example of freezing in an absorbing state with an explicitly nonuniversal, initial-condition-dependent behavior persistent at all times and, again, not consistent with the mean-field rate equations. It is therefore of interest to derive exact results whenever possible. Thus far, they were available only in one dimension [14]. In this work we report an exact solution for $A + A \to$ inert on the Bethe lattice. We also derive exact results for the reaction $A + B \to$ inert, limited to one dimension.

Examination of the one-dimensional solution of $A + A \to$ inert, [14], suggests close similarity to the models of random sequential adsorption [17-19]. Specifically, the annihilation reaction resulting in removal of two nearest-neighbor fixed reactants is equivalent to "deposition" of a "dimer" of two empty (reacted) sites. The two processes are dual to each other in that nearest-neighbor pairs of sites available for deposition correspond to unreacted pairs of reactants. Mathematically, the only difference is in the initial conditions. In deposition, the lattice is usually assumed empty at time $t = 0$ which would correspond to the full occupancy for reaction.

This connection to random sequential adsorption models suggests that exact solutions can be sought for models of multiparticle annihilation reactions corresponding to n-mer deposition [19], and for models formulated on high-connectivity lattices such as the Bethe lattice, etc.; see [18,20-21]. In this work we consider the Bethe-lattice case; the methods of [20-21] are adapted for reactions. Besides notational differences, this essentially amounts to a more careful treatment of random initial conditions. The latter is achieved by a method different from the techniques used in deposition model studies [20-23]. Since the Bethe lattice of coordination number 2 is identical to the one-dimensional lattice, we obtain the $d = 1$ solution as well. However, further simplification in $d = 1$ allows us to also solve exactly the reaction $A + B \to$ inert.

The Bethe lattice of coordination number $z \geq 2$ can be viewed as an interior part of the infinite Cayley tree: each site is connected by bonds to z nearest neighbor sites, and there are no closed loops formed by bonds. In fact the details of the lattice connectivity are not important for our considerations. However, we disregard any end-effects. Since the number of "boundary" sites in a finite-number-of-generations Cayley tree grows proportional to the total number of sites provided $z > 2$ (i.e., there is branching in each generation), the boundary effects can be profound when long-range spatial correlations are present such as at phase transitions, both static [24] and dynamical [25]. The model considered here does not have any "dangerous" spatial correlations; size effects can be safely ignored.

Consider a k-site connected cluster on the Bethe lattice. One interesting feature of a loopless lattice, shared with the $d = 1$ lattice for which $z = 2$, is that in such a cluster the k sites are connected by exactly $k - 1$ internal bonds. This statement is well known and easily established by induction: each new site can only be connected to one existing cluster site, by one bond, because loops are not possible. Another useful conclusion is that the number of bonds shared by the cluster sites and the nearest neighbor sites immediately outside the cluster under consideration, is $zk - 2(k-1)$. Here zk is the total number of neighbors seen by all the k cluster sites, while the term $2(k-1)$ subtracts the number of neighbors internal to the cluster (twice the number of bonds).

In the model of immobile reactants we assume that the lattice sites are initially occupied at random with probability ρ, and empty with probability $1-\rho$. The initial reactant density per site is $c(0) = \rho$, and we would like to calculate the time-dependence of the density $c(t)$ at later times $t > 0$, given that each nearest-neighbor reactant pair annihilates with the rate R per unit time. In fact, it is convenient to absorb the rate in the dimensionless time variable

$$\tau = Rt \quad . \tag{1}$$

Similar to the random sequential adsorption studies [17,22] and some recent results for particle-exchange dynamical models [26-27], we consider the probability $P_k(\tau)$ that a connected k-site cluster is fully occupied by reactants at time t. Configuration of the sites which are nearest-neighbor but exterior to the cluster can be arbitrary. Thus, initially,

$$P_k(0) = \rho^k \quad . \tag{2}$$

At times $\tau > 0$, the quantities $P_k(\tau)$ remain the same for all cluster topologies on a loopless lattice, provided the initial conditions are topology independent. This is because the topology dependence is not generated dynamically by the evolution equations for the $P_k(\tau)$. Indeed, their time variation is only determined by the number of possible reaction events within the cluster, which is equal the number of bonds, $k-1$, and the number of possible reaction events in which the reacting pair has one site within the cluster and another outside the cluster. The latter again is not dependent on the cluster topology for loopless clusters. We argued earlier that the number of such pairs is $zk-2k+2$. Thus, the time-dependence can be obtained from the relations

$$\frac{dP_k}{d\tau} = -(k-1)P_k - (zk-2k+2)P_{k+1} \quad . \tag{3}$$

Here the first term is self-explanatory. In the second term, the probability P_{k+1} is used because a larger cluster must be actually occupied in order for a reaction event involving a site outside the original k-site cluster to proceed.

Relations (3) apply for all $k \geq 1$. The most interesting quantity is $P_1(\tau) = c(\tau)$. It is expected to decrease in time but remain finite as $\tau \to \infty$. All other probabilities $P_{k>1}$ are expected to vanish for large times.

The solution of the recursion relations (3) can be obtained by various methods. Perhaps the simplest is to note that the Ansatz

$$P_k(\tau) = c(\tau)\,[\sigma(\tau)]^{k-1} \quad , \tag{4}$$

where $\sigma(0) = \rho$, eliminates the k-dependence. Indeed, substitution in (3) shows that the solution of the form (4) is possible provided

$$\frac{d\sigma}{d\tau} = -\sigma - (z-2)\sigma^2 \quad , \tag{5}$$

$$\frac{dc}{d\tau} = -z\sigma c \ . \tag{6}$$

The solution is

$$\sigma = \frac{\rho e^{-\tau}}{1 + (z-2)\rho\,(1 - e^{-\tau})} \ , \tag{7}$$

$$c = \rho\left[1 + (z-2)\rho\left(1 - e^{-\tau}\right)\right]^{-z/(z-2)} \ . \tag{8}$$

For $z = 2$ the $d = 1$ solution is obtained either as a limit of (8) or directly,

$$c_{z=2} = \rho e^{-2\rho\left(1-e^{-\tau}\right)} \ . \tag{9}$$

An interesting feature of expressions (8)-(9) is the explicit nonlinear dependence of the surviving reactant density for all times on the initial density ρ. The approach to the limiting density as $\tau \to \infty$ is exponential, $\sim e^{-\tau}$.

We now turn to the strictly one-dimensional case. Additional restrictions on the cluster topology now allow solution of the two-species reaction $A + B \to$ inert. Let us assume that initially the $d = 1$ lattice sites are occupied by reactant species A with probability α, and by species B with probability β, where $\alpha + \beta \leq 1$. The sites are empty with probability $1 - \alpha - \beta$. Nearest-neighbor AB and BA pairs react with rate R; see (1).

As before, we consider the probability that a k-site-long cluster is "fully reactive." Let $A_k(\tau)$ denote the fraction of k-site clusters which are fully filled, with reactants in the configuration $ABAB\ldots$, i.e., the leftmost site is A and the sequence is fully alternating. Similarly, let $B_k(\tau)$ denote the fraction of k-site clusters of the type

$BABA\ldots$, with the leftmost site B and otherwise fully alternating order. The state of the neighbor sites outside the k-cluster is not important in the definition of these probabilities which are conditioned only on the internal cluster configuration.

Let us introduce the quantities

$$\omega = \frac{\alpha+\beta}{2} \quad , \tag{10}$$

$$\rho = \sqrt{\alpha\beta} \quad , \tag{11}$$

where the notation ρ in (11) will become clear later on. Then initially we have

$$A_{k\text{-even}}(0) = B_{k\text{-even}}(0) = \rho^k \quad , \tag{12}$$

$$A_{k\text{-odd}}(0)/\alpha = B_{k\text{-odd}}(0)/\beta = \rho^{k-1} \quad . \tag{13}$$

Let us denote the concentrations, per site, of reactant species A and B by $a(\tau) \equiv A_1(\tau)$ and $b(\tau) \equiv B_1(\tau)$, respectively. We have

$$a(0) = \alpha \quad , \tag{14}$$

$$b(0) = \beta \quad , \tag{15}$$

$$a(\tau) - b(\tau) = \alpha - \beta \quad . \tag{16}$$

The latter relation is obvious. Thus we only have to calculate the sum $a+b$. It proves useful to introduce the quantities

$$P_k(\tau) = \left[A_k(\tau) + B_k(\tau)\right]/2 \quad , \tag{17}$$

so that the sum $a+b$ is given by $2P_1$.

Now the probabilities A_k and B_k satisfy the relations

$$\frac{dA_k}{d\tau} = -(k-1)A_k - A_{k+1} - B_{k+1} \quad , \tag{18}$$

$$\frac{dB_k}{d\tau} = -(k-1)B_k - B_{k+1} - A_{k+1} \quad . \tag{19}$$

Here the first term corresponds to internal pairs reacting, the second term corresponds to the rightmost site reacting with an occupied external site, while the third term in both relations corresponds to the leftmost site reacting "externally."

For P_k we get, by summing (18) and (19),

$$\frac{dP_k}{d\tau} = -(k-1)P_k - 2P_{k+1} \quad , \tag{20}$$

which is in fact identical to the $d=1$ random sequential adsorption recursion [17,19,22], as well as to the $z=2$ variant of (3). However, the initial conditions are more complicated,

$$P_{k\text{-even}}(0) = \rho^k \quad , \tag{21}$$

$$P_{k\text{-odd}}(0) = \omega\rho^{k-1} \quad . \tag{22}$$

The solution is obtained by methods similar to solving the Bethe-lattice recursions. We try forms similar to (4),

$$P_{k\text{-even}} = C_{\text{even}}(\tau)\,[\Sigma(\tau)]^{k-1} \quad , \tag{23}$$

$$P_{k\text{-odd}} = C_{\text{odd}}(\tau)\,[\Sigma(\tau)]^{k-1} \quad . \tag{24}$$

These, when substituted in (20), yield coupled first-order differential equations which can be solved explicitly to give

$$2P_k = \rho^{k-1}e^{-(k-1)\tau}\left[(\rho+\omega)e^{-2\rho\left(1-e^{-\tau}\right)} + (-1)^k(\rho-\omega)e^{2\rho\left(1-e^{-\tau}\right)}\right] \quad . \tag{25}$$

The reactant concentrations then follow as

$$a(\tau) = \frac{1}{2}\left[\alpha-\beta+(\rho+\omega)e^{-2\rho\left(1-e^{-\tau}\right)} - (\rho-\omega)e^{2\rho\left(1-e^{-\tau}\right)}\right] \quad , \tag{26}$$

$$b(\tau) = \frac{1}{2}\left[\beta-\alpha+(\rho+\omega)e^{-2\rho\left(1-e^{-\tau}\right)} - (\rho-\omega)e^{2\rho\left(1-e^{-\tau}\right)}\right] \quad , \tag{27}$$

where the parameters are related via (10)-(11).

As in the fast-diffusion case, which was not solved exactly even in $d=1$ but only analyzed asymptotically [7,28], the functional form of the concentration is different depending on if the initial concentrations are equal or not, although the difference here is less spectacular. For $\alpha = \beta$ $(= \omega = \rho)$, the time-dependence of <u>*each*</u> of the species concentrations is identical to the $d = 1$ result (9). The time-dependence via the double-exponential expressions entering the general results (26) and (27) is also similar to (9) with the effective concentration given by the geometrical mean ρ; see (11). However, for $\alpha \neq \beta$ the full time-dependence is more complicated than for the single-species reaction, involving both the double-exponential term and its inverse.

In summary we presented exact solutions for two-particle annihilation reaction on the Bethe lattice. For the coordination number $z > 2$, results were reported for the single-species case. In $d = 1$, where $z = 2$, we reproduced the known exact single-species result and extended the solution to two-species reaction.

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