Binary reaction 1+1→0 in one dimension

A. A. Lushnikov

L. Ya. Karpov Physicochemical Research Institute
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An exact solution is presented of the problem of the kinetics of a binary reaction in which a passive product is formed. The time dependence of the particle density is calculated under the assumption that particles can diffuse from their sites of a one-dimensional lattice and annihilate when they encounter one another in one site.

1. INTRODUCTION

Much attention is paid lately to diffusion-controllable reactions (an extensive bibliography can be found in Ref. 1). The main purpose of the research in this field is to determine the anomalous asymptotic time dependence of the reagent concentrations. The point is that, say, for the annihilation reaction the usual time dependence of the concentration $c \sim t^{-1}$ predicted by formal kinetics is replaced by another that depends on the dimensionality of space. This poses the following problem. We must find sufficiently simple initial premises that enable us to write correct equations for the anomalous asymptotic ones and replace the formal-kinetics equation $\dot{c} = -kc^2$. Of course, this formulation of the problem pertains not only to a $1+1\to 0$ reaction but also to all other diffusion-controllable reactions.

1. Treatment based on similarity considerations. This approach is highly recommended in Ref. 1. Although this yields qualitatively the anomalous asymptotics, it is impossible to indicate simple methods of constructing means for a quantitative treatment of diffusion-controllable reaction (other than direct numerical modeling).

2. Derivation of systems of kinetic equations by starting from the expressions for multiparticle distribution functions and using some closure problem to obtain the equations.[2] In my opinion, this is a very cumbersome way, and the reliability of the corresponding closure procedures is not obvious. Nonetheless, this approach reproduces correctly some of the anomalous asymptotics.

3. Derivation and solution of evolution equations for the generating functions. This means the following idea, which is easiest to realize for lattice models of reactions: The state of the lattice is characterized by the degree of occupation of its sites. Each state is ascribed a time-dependent probability, for which one introduces a generating function Ψ such that each state corresponds to a product of variables whose powers are determined by the occupation of the corresponding sites. Next, in accord with the notions concerning the character of the process, an evolution operator $\mathscr{L}$ is constructed and the dependence of $\mathscr{L}$ on the time t is obtained from the evolution equation:

$$\partial_t \Psi = \mathscr{L}\Psi. \tag{1}$$

The choice of single-site variables and the form of the operator are determined by the specifics of the problem. It will be shown in the next section how this is actually done. This is usually a simple matter, and it is much more difficult to solve Eq. (1). The difficulties here are of the same kind as in the quantum many-body problem. This very circumstance, however, alleviates things—use can be made of the well developed variants of perturbation theory or of algebraic methods for the construction of the exact solution. All this gives grounds for assuming that this briefly outlined approach will turn out to be promising for the development of a complete theory of diffusion-controllable reactions.

We have demonstrated the effectiveness of this approach, using as an example an exact solution of the problem of a diffusion-controllable annihilation reaction in one dimension. In this case it is convenient to construct Ψ by using spin variables. The evolution operator is then quadratic in the spin matrices, and it can be diagonalized in the one-dimensional case. The obtained exact expression for Ψ is used to calculate the time dependence of the average density. Solutions are obtained both for a freely reacting system and for a system with a source of particle pairs. The latter result is used to consider the reversible reaction $1+1\leftrightarrow 0$. To this end it suffices to regard the source intensity as proportional to the density of the particles that took part in the reaction.

2. EVOLUTION OPERATOR

To describe the kinetics of the reaction $1+1\to 0$ on a one-dimensional lattice we use the following simple model. Assume that the reacting particles can occupy the sites of a one-dimensional lattice closed into a ring. Each particle is capable of jumping over to one of the neighboring sites, and if it lands on an occupied site, both particles are instantaneously annihilated, and the site becomes free. The probability of particle displacement per unit time is specified and assumed equal to D.

Clearly, in such a model each site can be either free or occupied by one particle. Therefore each state Q of the system can be characterized by a set of zeros and ones: $Q = \{0, 0, 1, 0 \ldots\}$. The ones and zeros indicate whether the site is occupied or free. To each state Q is ascribed a probability $W(Q,t)$, normalized to unity and having a time dependence given by

$$d_t W(Q,t) = \sum_{Q^+} A(Q^+, Q) W(Q^+, t) - W(Q,t) \sum_{Q^-} A(Q, Q^-). \tag{2}$$

Here Q^+ are states preceding A, i.e., those to which a transition to Q is possible by a single jump of a particle to an occupied or free place. For example, if $Q = \{0, 0, 1 \ldots\}$, Q^+ can

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stand for either $Q^+\{0,1,0\ldots\}$ (the transition into Q is via a jump of a particle from the second site to the third), or $Q^+=\{1,1,1\ldots\}$ (transition to Q via a reaction in the first and second sites).

It is convenient to introduce in place of $W(Q,t)$ the generating function Ψ:

$$\Psi=\sum_Q W(Q,t)\prod_m s_m(Q)\,|0\rangle, \tag{3}$$

where $s_m(Q)=\sigma_m^+$ if the site numbered m is occupied in the state Q, and $s_m(Q)=1$ in the opposite case. As always, σ^+ and σ^- denote respectively a raising and a lowering Pauli matrix, and $|0\rangle$ is a vacuum state defined by the equations $\sigma_m^-|0\rangle=0$ for all m.

We shall show that for a freely reacting system (without a source) the function Ψ satisfies equation (1) with the evolution operator

$$\mathscr{L}=\mathscr{L}_D=D\sum_m(\sigma_m^-\sigma_{m+1}^+ +\sigma_m^-\sigma_{m-1}^+ -2\sigma_m^+\sigma_m^- +2\sigma_m^-\sigma_{m+1}^-). \tag{4}$$

We substitute Ψ in the form (3) in Eq. (1) with the evolution operator in form (4) and track the result of the action of each term of $\mathscr{L}_D$. The operator $\sigma_m^-\sigma_{m+1}^+ +\sigma_m^-\sigma_{m-1}^+$ moves a particle from a site numbered m to a site numbered $m+1$ or $m-1$, if the former (m) is occupied and the latter are free. Action of the operator on any other state yields zero. The corresponding expansion coefficient in the function

$$D\sum_m(\sigma_m^-\sigma_{m+1}^+ +\sigma_m^-\sigma_{m-1}^+)\,\Psi \tag{5}$$

will contain arrival terms from all the states Q^+ that differ from Q by the position of one particle.

To determine correctly the terms of departure from Q to Q^- by particle jumps from occupied to free sites, we must substrate from (5)

$$D\sum_m(\sigma_m^-\sigma_m^+\sigma_{m+1}^+\sigma_{m+1}^- +\sigma_m^-\sigma_m^+\sigma_{m-1}^+\sigma_{m-1}^-)\,\Psi. \tag{6}$$

The contribution of this term is proportional to the number of free places adjacent to occupied ones, and the corresponding expansion coefficient (6) gives the second term of (2).

Corresponding to particle jumps to occupied sites and to vanishing of the pair is the term

$$2D\sum_m(\sigma_m^-\sigma_{m+1}^- -\sigma_m^+\sigma_m^-\sigma_{m+1}^+\sigma_{m+1}^-)\,\Psi. \tag{7}$$

The operator $\sigma_m^-\sigma_{m+1}^-$ changes the number of particles by two and is responsible for arrival from states Q^+ that differ from Q by two particles. The second term lists the number of particle pairs capable of entering in a reaction, and accounts for the terms of Eq. (2) that are made to depart by the reaction.

Gathering the results of (5)–(7) we arrive at Eq. (4), while the terms of order σ^4 are cancelled.

There are several ways of introducing an external source of particles. We discuss one of them. Assume that the particles are added in pairs to neighboring sites. If both sites are free, the particles survive and can participate in the ensuing process. If one site is free and the other occupied, only the particle that lands on the free site survives. The second annihilates with the particle that occupied the site, and the site becomes free. If both sites are occupied, the action of the source makes them free. Such a model can correspond physically to reaction-product decay under the influence, say, of light.

The evolution operator corresponding to the process described above is of the form

$$\mathscr{L}_J=J\sum_m(\sigma_m^+\sigma_{m+1}^+ +\sigma_m^+\sigma_{m+1}^- +\sigma_m^-\sigma_{m+1}^+ +\sigma_m^-\sigma_{m+1}^- -1), \tag{8}$$

where J is the intensity of the source (the number of pairs added to the lattice per unit time).

The total evolution operator is the result of adding Eqs. (4) and (8):

$$\begin{aligned}\mathscr{L}&=\mathscr{L}_J+\mathscr{L}_D\\ &=(J+D)\sum_m(\sigma_m^+\sigma_{m+1}^+ +\sigma_m^+\sigma_{m+1}^- +\sigma_m^-\sigma_{m+1}^+ +\sigma_m^-\sigma_{m+1}^-)\\ &+D\sum_m(\sigma_{m+1}^-\sigma_m^- -\sigma_{m+1}^+\sigma_m^+ -2\sigma_m^+\sigma_m^-) -JN,\end{aligned} \tag{9}$$

where N is the total number of sites in the lattice. The last term in (9) leads to the appearance of a factor $\exp(-JNt)$ in Ψ. Both will be left out of the intermediate calculations.

3. SOLUTION OF EVOLUTION EQUATION

In the one-dimensional case, the evolution operator (9) can be diagonalized, and on this is the solution of the evolution equation based. The strategy of the solution is to replace the spin operator by fermion operators, after which $\mathscr{L}$ becomes quadratic in the fermion operators. A Fourier transform is taken next. The solution of Eq. (1) then becomes trivial.

We introduce thus the fermion operators a_m and a_m^+ by the equations[3]

$$\sigma_m^-=(-1)^A a_m,\quad \sigma_m^+=(-1)^A a_m^+, \tag{10}$$
$$A=\sum_{j<m} n_j,\quad n_j\equiv\sigma_j^+\sigma_j^-=a_j^+a_j.$$

Substitution of (10) in (9) yields

$$\begin{aligned}\mathscr{L}=(J+D)&\sum_m(a_m^+a_{m+1}^+ +a_m^+a_{m+1} +a_{m+1}^+a_m +a_{m+1}a_m)\\ &+D\sum_m(a_{m+1}a_m -a_m^+a_{m+1}^+ -2a_m^+a_m).\end{aligned} \tag{11}$$

The next step is taking the Fourier transforms of the fermion operators, using the equations

$$a_m=\frac{e^{-i\pi/4}}{N^{1/2}}\sum_q a_q e^{iqm},\qquad a_q=\frac{e^{i\pi/4}}{N^{1/2}}\sum_m a_m e^{-iqm}, \tag{12}$$

where[3]

$$q=\pm(2k-1)\pi/N,\ k=1,2,\dots\ M \tag{13}$$

and $N=2M$ is an even number.

Substitution of (12) in (11) makes $\mathscr{L}$ diagonal in q:

$$\mathscr{L}=\sum_{q>0}\mathscr{L}_q,$$

$$\mathscr{L}_q=2(J+D)[\cos q(n_q+n_{-q})+\sin q(a_qa_{-q}-a_q^+a_{-q}^+) +2D[\sin q(a_qa_{-q}+a_q^+a_{-q}^+)-(n_q+n_{-q})], \tag{14}$$

where $n_q\equiv a_q^+a_q$.

We can now find the solution of Eq. (1) in the form

$$\Psi=\prod_{q>0}\Psi_q, \tag{15}$$

where each of the factors satisfies the equation

$$\partial_t\Psi_q=\mathscr{L}_q\Psi_q. \tag{16}$$

We seek the function Ψ_q in the form

$$\Psi_q=(\alpha_qa_q^+a_{-q}^++\beta_q)|0\rangle. \tag{17}$$

Substituting (17) in (16) with $\mathscr{L}_q$ in the form (14), we arrive at a system of equations for α_q and β_q:

$$\dot\alpha_q=4\alpha_q[(J+D)\cos q-D]-2J\beta_q\sin q,$$

$$\dot\beta_q=-2\alpha_q(J+2D)\sin q. \tag{18}$$

Let us find the fundamental solutions of this system. For the initial conditions $\alpha_q(0)=1$ and $\beta_q(0)=0$ we have

$$\alpha_q(t)=\frac{1}{4(J+2D\sin^2(q/2))}(p_2e^{p_2t}-p_1e^{p_1t}),$$
$$\beta_q(t)=-\frac{(J+2D)\sin q}{2(J+2D\sin^2(q/2))}(e^{p_2t}-e^{p_1t}), \tag{19}$$

and if $\alpha_q(0)=0$ and $\beta_q(0)=1$,

$$\alpha_q(t)=\frac{J\sin q}{2(J+2D\sin^2(q/2))}(e^{p_1t}-e^{p_2t}), \tag{20}$$

$$\beta_q(t)=\frac{1}{4(J+2D\sin^2(q/2))}(p_2e^{p_1t}-p_1e^{p_2t}), \tag{21}$$

where p_1 and p_2 are the roots of the characteristic equation of the system (18):

$$p_1=-2(J+2D)(1-\cos q),\ p_2=2J(1+\cos q).$$

4. CALCULATION OF THE MEAN VALUES

We consider next a system with an even number of particles. We calculate the generating function

$$F(z,t)=\sum_Q z^{n(Q)}W(Q,t), \tag{22}$$

where $n(Q)$ is the total number of particles in the state Q.

Using Eq. (3), we readily verify that

$$F(z,t)=\langle0|\exp\Big(z\sum_m\sigma_m^-\Big)\prod_{q>0}(\alpha_qa_q^+a_{-q}^++\beta_q)|0\rangle. \tag{23}$$

A series expansion of the exponential in (23) gives rise to products

$$\langle0|\sigma_{i_1}^-\sigma_{i_2}^-\dots\sigma_{i_s}^-. \tag{24}$$

We arrange the σ^- operators in each such product in such a way that the one on the extreme left has the greatest number, and then transform to fermion operators in accordance with Eq. (10). It can be seen then that all the powers of (-1) vanish following action on $\langle0|$. We next arrange the pairs in the products $a_q^+a_{-q}^+$. In accordance with (12), we have

$$a_q^+a_{-q}^+=\frac{2}{N}\sum_{m_1>m_2}a_{m_1}^+a_{m_2}^+\sin q(m_1-m_2). \tag{25}$$

If the product (24) contains a pair of operators $a_{m_1}a_{m_2}$, on averaging in (23) this pair leads to a factor

$$-\frac{2}{N}\sum_{m_1>m_2}\sin q(m_1-m_2)=-\operatorname{ctg}(q/2). \tag{26}$$

This result was obtained with account taken of the rule (13) for the quantization of q.

It is now easy to guess that $F(z,t)$ is obtained from Ψ by replacing the operator pair $a_q^+a_{-q}^+$ by $-z_2\cot(q/2)$, i.e.,

$$F(z,t)=\prod_{q>0}(-z^2\alpha_q\operatorname{ctg}(q/2)+\beta_q). \tag{27}$$

We calculate $F(z,t)$ below for two sets of initial conditions: 1) all the sites are initially occupied, and 2) the lattice is empty.

In the first case,

$$\Psi(t=0)\equiv\Psi_0=(-1)^M\prod_{q>0}a_q^+a_{-q}^+|0\rangle. \tag{28}$$

This can be easily verified by projecting Ψ on $\langle0|\sigma_1^-\sigma_2^-\dots\sigma_N^-$. In accordance with (26) we have

$$(-1)^M\langle0|\sigma_1^-\sigma_2^-\dots\sigma_N^-\prod_{q>0}a_q^+a_{-q}^+|0\rangle=\prod_{q>0}\operatorname{ctg}(q/2)=1. \tag{29}$$

The last equation is again the consequence of the conditions (13) for the quantization of q. Rather laborious calculations, using the solution (19), lead to

$$F_1(z,t)=\prod_{q>0}[z^2-(z^2-1)\gamma_q^{-1}(1-e^{-\gamma_qt})(J+2D)\sin^2(q/2)]. \tag{30}$$

Here $\gamma_q\equiv J+2D\sin^2(q/2)$. In the derivation of (3) we took into account the factor $\exp(-JNt)$ in Ψ, and the equality,

$$\sum_{q>0}\cos q=0. \tag{31}$$

In the second case $\Psi_0=|0\rangle$, $\alpha_q(0)=0$, and $\beta_q(0)=1$. The corresponding generating function, obtained by using (20), is

$$F_2(z,t)=\prod_{q>0}[(z^2-1)J\gamma_q^{-1}\cos^2(q/2)(1-\exp(-4\gamma_qt))+1]. \tag{32}$$

In the stationary limit $t\to\infty$ the two functions are identical and are equal to

$$F_\infty(z)=\prod_{q>0}\left[\frac{J\cos^2(q/2)\,(z^2-1)}{J+2D\sin^2(q/2)}+1\right]. \tag{33}$$

The average number of particles is expressed in terms of $F(z,t)$ as follows:

$$\bar{n}=\sum_Q n(Q)\,W(Q,t)=\partial_z F(z,t)\,|_{z=1}.$$

Introducing the density $c=\bar{n}/N$ and taking the limit as $N\to\infty$ we get from (30), (32), and (33)

$$c_1(t)=\frac{1}{\pi}\int_0^\pi\left[1-\frac{(J+2D)\sin^2(q/2)}{J+2D\sin^2(q/2)}(1-\exp(-4\gamma_q t))\right]dq, \tag{34}$$

$$c_2(t)=\frac{J}{\pi}\int_0^\pi\frac{\cos^2(q/2)\,(1-e^{-4\gamma_q t})}{J+2D\sin^2(q/2)}\,dq, \tag{35}$$

$$c_\infty=\frac{J}{\pi}\int_0^\pi\frac{\cos^2(q/2)}{J+2D\sin^2(q/2)}\,dq. \tag{36}$$

To obtain these equations we replaced the sum by an integral

$$\sum_q\to\frac{N}{2\pi}\int_0^\pi dq.$$

5. ANALYSIS OF RESULTS

By simple manipulations we transform the integrals in Eqs. (34)–(36) into

$$c_1=c_2+\exp[-4(J+D)t]I_0(4Dt), \tag{37}$$

$$c_2=c_\infty+(J/2D)\exp[-4(J-D)t]I_0(4Dt)-2J(J+2D) \tag{38}$$

$$\times\int_t^\infty\exp[-4(J+D)\tau]I_0(4D\tau)\,d\tau,\qquad c_\infty=J^{1/2}/[J^{1/2}+(J+2D)^{1/2}], \tag{39}$$

where $I_0(x)$ is a modified Bessel function.

It can be seen from (37) that at $J=0$

$$c_1(t)=\exp(-4Dt)I_0(4Dt)\approx(8\pi Dt)^{-1/2}\ (t\to\infty). \tag{40}$$

In the opposite limiting case $D=0$ we easily get from (35) and (37)

$$c_{1,2}(t)=(1\pm e^{-4Jt})/2. \tag{41}$$

At $D\sim J$ and $Dt\gg 1$ the densities c_1 and c_2 approach in different manners the equilibrium value c_∞:

$$c_1(t)=c_\infty+\frac{\exp(-4Jt)}{8Jt(8\pi Dt)^{1/2}}\left(1+\frac{J}{2D}\right),$$

$$c_2(t)=c_\infty-\frac{\exp(-4Jt)}{(8\pi Dt)^{1/2}}.$$

This result takes into account the asymptotic equality

$$4J\int_t^\infty\exp(-4(J+D)\tau)I_0(4D\tau)\,d\tau$$

$$\approx(8\pi Dt)^{-1/2}\exp(-4Jt)\left[1-\frac{1}{8Jt}+\frac{1}{32Dt}\right].$$

We now use the results to consider the reversible reaction $1+1\rightleftarrows 0$. We assume that a neutral product breaks up into two molecules of the active component, and these molecules land on neighboring lattice sites. This model is equivalent to the one considered above with a source proportional to the density of the neutral product or, equivalently, of the difference between the initial and the instantaneous densities of the active component:

$$J(t)=\eta[c(0)-c(t)]. \tag{42}$$

We assume below that $c(0)=1$. We obtain the equilibrium density $c(\infty)\equiv c_e$. To this end we replace J in (39) by expression (42). Then, introducing $\varkappa\equiv\eta/D$, we obtain the following equation for c_e:

$$c_e=\frac{[\varkappa(1-c_e)]^{1/2}}{[\varkappa(1-c_e)]^{1/2}+[2+\varkappa(1-c_e)]^{1/2}}.$$

Its solution is

$$c_e=\frac{2\varkappa}{(\varkappa^2+8\varkappa)^{1/2}+3\varkappa}. \tag{43}$$

6. CONCLUSION

The method proposed in this paper permits a relatively simple investigation of the kinetics of the simplest binary reaction $1+1\to 0$. In the one-dimensional case this problem was reduced to diagonalization of the evolution operator which turned out ultimately to be quadratic in the fermion creation and annihilation operators. The solution procedure is very similar to that used in Ref. 3 to calculate the partition function of a two-dimensional Ising lattice. An analogy is obtained here with the problem of the dynamics of a one-dimensional Bose gas with infinite repulsion. More detailed data on the use of the model of non-interpenetrable spheres to analyze the kinetics of binary reactions can be found in Ref. 4. The asymptotic result for the case $J=0$ is the same, but the solution method proposed here has obvious advantages. A different formulation of the problem of binary-reaction kinetics on a lattice can be found in Ref. 5.

The algebraic method used in this paper can be used to obtain an exact solution only in the one-dimensional case. However, the structure (9) of the evolution operator itself is independent of the dimensionality of the sphere. The kinetics of the reaction $1+1\to 0$ can therefore be investigated by the approximate methods developed for the description of the dynamics of spin lattices. This is not the best way, since it is by far less convenient to deal with spin operators than with Bose or Fermi operators. It is therefore advisable, at the cost of somewhat complicating the model, to change to another treatment. This can be done by permitting an arbitrary number of particles to stay in one site, and allow only these particles to react. In this model the generating function $\Psi(x_1, x_2,\ldots; t)$ for the probability of realizing a specified occupation on a lattice obeys Eq. (1) with evolution operators of the type

$$\mathscr{L}=D\sum_m(x_{m+1}+x_{m-1}-2x_m)\frac{\partial}{\partial x_m}+\frac{\lambda}{2}\sum_m(1-x_m^2)\frac{\partial^2}{\partial x_m^2}, \tag{44}$$

where λ is the reaction rate constant, and the degree of the variable x_m determines the occupation of the site numbered m. An approach of this type was used in Ref. 6 to consider coagulation, and in Ref. 7 to obtain a solution of Eq. (1) in the form of a functional integral. The model used in that reference corresponds to the limit $\lambda \to \infty$.

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