Coagulation reaction in a one-dimensional gas

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An extension of previous work on the ballistic annihilation reaction $A+A\rightarrow 0$ to the coagulation reaction $A+A\rightarrow A$ is presented. Three possible velocities c (with probability p), $-c$ (with probability q), and zero are considered. While the long-time behavior is controlled by moving particles when $p=q$, it is controlled by the stationary particles when $p\neq q$. The comparison of the coagulation reaction with the annihilation reaction shows that the long-time results are essentially the same except for a rescaling of the time. In addition, the time dependences of the decay in the ballistic coagulation reaction when $p=q$ and the diffusion-limited coagulation reaction are also identical, but for different physical reasons. The reason for this becomes transparent by rederiving the ballistic coagulation results using a random-walk formalism, which can perhaps be generalized to more complicated ballistic reactions.

I. INTRODUCTION

A great deal of attention has recently been devoted to the anomalous kinetics that frequently occur in diffusion-limited reactions in low-dimensional systems. Two models that have been investigated in detail are the binary annihilation reaction $A+A\rightarrow 0$ (Refs. 1–9) and the coagulation reaction $A+A\rightarrow A$.[10] The former model has also been considered in the case of particles undergoing ballistic rather than diffusive motion.[11] Results formally similar to those for diffusion-limited reactions are obtained for the rate of reaction, even though the physical interpretation of the results is quite different.

In this paper, we extend the study of Ref. 11 to the ballistic analog of the coagulation reaction $A+A\rightarrow A$. In Ref. 11 a dichotomic distribution of velocities c and $-c$ is used to model the ballistic $A+A\rightarrow 0$ reaction; the analysis of the $A+A\rightarrow A$ ballistic reaction requires that we consider a distribution with three possible velocities, c, $-c$, and zero. The particles with velocity c, $-c$, and zero will be denoted by X, Y, and Z, respectively. These particles are initially mutually independent and occur with probability p, q, and $r=1-p-q$, respectively. Observing momentum conservation allows us to divide the $A+A\rightarrow A$ reaction scheme into the following three reactions:

$$Z+X\rightarrow X\ , \tag{1}$$

$$Z+Y\rightarrow Y\ , \tag{2}$$

$$X+Y\rightarrow Z\ . \tag{3}$$

Thus an A moving to the right (left) can react with stationary A to produce an A that continues to move to the right (left). Two A's that move towards each other can react to produce a stationary A. Our purpose is to calculate the survival probability of each "species" and of their sum (i.e., of all A's) as a function of time.

We present two methods of solution. The first is a direct extension of the technique used in Ref. 11 and is presented in Sec. II. The second approach, presented in Sec. III, relates the survival probability to the first-passage-time (FPT) statistics of a nearest-neighbor random walk.

II. DIRECT CALCULATION OF THE SURVIVAL PROBABILITY

The reaction scheme (1)–(3) is most easily considered by first analyzing the modified scheme wherein in place of Eq. (3) we have

$$X+Y\rightarrow 0\ . \tag{4}$$

We henceforth assume with no loss of generality that $p\leq q$.

A. Reaction scheme (1), (2), and (4)

We start by considering the survival probability of the X particles. The situation is very similar to the $A+A\rightarrow 0$ case except that the presence of the stationary Z particles has to be taken into account. Let a_{k+1} be the probability that a given X particle will annihilate with the $(k+1)$th particle to its right, and let b_k be the probability that the *moving* particles located between X and its collision partner are all annihilated, with $b_0\equiv 1$. Since the reaction partner of X must move with velocity $-c$, a_{k+1} is equal to $b_k q$. Note that due to the existence of Z particles, k is not necessarily even. When $k=1$, to contribute to b_1 the particle between X and its annihilation partner had better be a Z particle (otherwise it would annihilate either the given X or its supposed annihilation partner). Therefore, $b_1=r$. When $k=2$ there are two particles between the given annihilation partners. To contribute to b_2 they must either both be Z particles or the first particle is an X and the second a Y. Clearly we cannot have one stationary and one moving (these will not annihilate) nor can the first be a Y and the second an X (or they would each annihilate one of the supposed partners). Continuing this reasoning and noting that the first particle after the given X must be either an X or a Z

gives the recursion relation for b_k for $k \geq 2$,

$$b_k = r b_{k-1} + \sum_{m=0}^{k-2} pq b_m b_{k-m-2} . \tag{5}$$

Introducing the generating function

$$B(s) = \sum_{k=0}^{\infty} b_k s^k \tag{6}$$

and using it in (5) in the standard way yields

$$B(s) = \frac{(1-rs) - [(1-rs)^2 - 4s^2 pq]^{1/2}}{2s^2 pq} . \tag{7}$$

This generating function is used subsequently to calculate the desired quantities.

The survival probability $S_X(t)$ of the chosen X particle is in turn governed by the probability $P(\Delta x \leq 2ct)$ that the initial distance Δx between X and its annihilation partner is smaller than $2ct$ since the latter is the greatest distance that the particles can cover as they move toward each other in the time interval t. Denoting the location of particle k by x_k we can write

$$S_X(t) = 1 - \sum_{k=0}^{\infty} a_{k+1} P(x_{k+1} - x_0 \leq 2ct) . \tag{8}$$

Assuming that the initial distances $x_{k+1} - x_k$ between neighboring particles are identically distributed independent random variables with probability density $\Psi(x_{k+1} - x_k)$, one finds for the Laplace transform of (8)

$$\begin{aligned} \tilde{S}_X(s) &= \frac{1}{s} - \frac{1}{s} \sum_{k=0}^{\infty} q b_k [\tilde{\Psi}(s)]^{k+1} \\ &= \frac{1}{s} - \frac{q\tilde{\Psi}(s)}{s} B(\tilde{\Psi}(s)) , \end{aligned} \tag{9}$$

where we have used the relation between a_{k+1} and b_k and where B is the generating function (7). For a random initial distribution of particles with average spacing equal to σ^{-1}, one has

$$\tilde{\Psi}(s) = \frac{2c\sigma}{s + 2c\sigma} , \tag{10}$$

and one can explicitly perform the inverse Laplace transform of (9) to obtain for the survival probability at time t

$$S_X(t) = 1 - (q/p)^{1/2} \int_0^t e^{-2(1-r)c\sigma\tau} I_1(4c\sigma\sqrt{pq}\,\tau) \frac{1}{\tau} dt , \tag{11}$$

where $I_n (n = 0, 1, 2, \ldots)$ denotes a modified Bessel function. When $r = 0$ we recover the results of Ref. 11. For the case $p = q$, the integration can be done exactly and yields

$$S_X(t) = e^{-2c\sigma(1-r)t} \{ I_0[2c\sigma(1-r)t] + I_1[2c\sigma(1-r)t] \} . \tag{12}$$

The effect of stationary particles on the survival probability of a particle moving with velocity c in the modified reaction scheme is thus merely a rescaling of time by a factor $(1-r)$. For the long-time behavior we obtain for $p = q$

$$S_X(t) = (2\pi c\sigma pt)^{-1/2} , \tag{13}$$

while for $p < q$ the long-time behavior is

$$S_X(t) = \frac{qt^{-3/2} e^{-\beta t}}{\sqrt{8\pi c\sigma} (pq)^{3/4} \beta} , \tag{14}$$

where $\beta \equiv 2(1 - r - 2\sqrt{pq}\,)c\sigma$.

In a similar way or by symmetry, we find the survival probability $S_Y(t)$ for the Y particles to be

$$S_Y(t) = 1 - (p/q)^{1/2} \int_0^t e^{-2(1-r)c\sigma\tau} I_1(4c\sigma\sqrt{pq}\,\tau) \frac{1}{\tau} d\tau . \tag{15}$$

Finding the survival probability $S_Z(t)$ of Z particles is equivalent to finding the probability that each particle avoids an encounter with a Y particle from its right [the factor in the first square brackets in (16)] and with an X particle from its left [the factor in the second square brackets in (16)]:

$$S_Z(t) = \left[1 - (q/p)^{1/2} \int_0^t e^{-(1-r)c\sigma\tau} I_1(2c\sigma\sqrt{pq}\,\tau) \frac{1}{\tau} d\tau \right] \left[1 - (p/q)^{1/2} \int_0^t e^{-(1-r)c\sigma\tau} I_1(2c\sigma\sqrt{pq}\,\tau) \frac{1}{\tau} d\tau \right] . \tag{16}$$

The factor of 2 by which the arguments of the modified Bessel functions and exponents in (16) differ from those in (15) and (11) comes from the fact that the relative velocity of an X-Z or a Y-Z pair is c, instead of $2c$ as in the case of an X-Y pair. For $p = q$, the approach of $S_Z(t)$ to the final null state is proportional to t^{-1}, which is faster than the $t^{-1/2}$ decay of $S_X(t)$ and $S_Y(t)$. When $p \neq q$ the situation is reversed: in this case the decay of $S_Z(t)$ to the final state is proportional to $t^{-3/2} e^{-\beta t/2}$, which is slower than the $t^{-3/2} e^{-\beta t}$ decay of $S_X(t)$ and $S_Y(t)$ [cf. Eq. (14)]. We do not discuss these results further since the reaction scheme considered here is merely one set up for convenience in the analysis of the actual reaction scheme, which now follows.

B. Reaction scheme (1), (2), and (3)

In this scheme, which is the one of actual interest, the survival probabilities for X and Y particles are the same

as in the previous case, (11) and (15), respectively, while the rate of disappearance of Z has to be modified to include the production of Z particles due to (3). The decay of the Z particles that are initially present is given by (16). On the other hand, the rate of Z-particle creation between t and $t+dt$, dZ_p/dt, is determined from the decay rate of X and Y as follows:

$$\frac{dZ_p}{dt}=-\frac{dX}{dt}=-\frac{dY}{dt}=-p\frac{dS_X(t)}{dt} . \tag{17}$$

In addition, for a Z particle created at time τ to contribute to the total survival probability of Z at time t, $S_{t,Z}(t)$ [a notation introduced to distinguish this quantity from the one evaluated in (16)], it has to survive at least until time t, i.e., its lifetime has to be longer than time $t-\tau$. The probability for this newly created Z particle to have a lifetime longer than $t-\tau$ is in turn determined from the "initial" distribution of particles at time τ due to the renewal property of the system. Therefore, as far as Z particles are concerned, the process is identical to that of a trapping problem with a continuous source rate dZ_p/dt.[12] Since Z particles are created continuously in time, the contribution of (3) to $S_{t,Z}(t)$ is through a convolution. Hence[13]

$$S_{t,Z}(t)=rS_Z(t)+\int_0^t S_Z(t-\tau)\frac{dZ_p(\tau)}{d\tau}d\tau , \tag{18}$$

which leads to a long-time decay of the form t^{-1} for $p=q$ and to an exponential decay $e^{-\beta t/2}$ when $p\neq q$. The overall survival probability of all the A particles, $S_t(t)$, is

$$S_t(t)=pS_X(t)+qS_Y(t)+S_{t,Z}(t) . \tag{19}$$

When $p=q$, the decay to the empty state is controlled by the slower decay of $S_X(t)$ and $S_Y(t)$ compared to that of $S_{t,Z}(t)$ and is hence of the form $t^{-1/2}$. When $p\neq q$ the approach to the final state is controlled by the now-slower term $S_{t,Z}(t)$, which decays as $e^{-\beta t/2}$.

Two comparisons between the results just obtained and others obtained earlier are in order. One is the comparison between our ballistic coagulation results and those of the ballistic annihilation reaction $A+A\rightarrow 0$. The only difference between these long-time results is a rescaling of the time by an r-dependent factor, i.e., by the probability that initially a fraction r of the particles is stationary. In fact, it is not unreasonable to investigate the situation in which initially none of the particles are stationary (e.g., that initially no coagulation has taken place) and in that case the long-time results for the annihilation and coagulation reactions are identical when $p=q$. The other comparison that might be made is with a diffusion-limited coagulation reaction of the form $A+A\rightarrow A$, for which it is appropriate to set $p=q$ in our analysis. In both models the decay behaves as $t^{-1/2}$ at long times but, as with the annihilation reaction, the physical reasons are quite different. As in that case, the decay in the ballistic coagulation reaction arises from a central limit effect while that of the diffusion-limited reaction has to do with the space-time scaling connections. That the physical basis of the otherwise similar results is different can be seen from the entirely different nature of the parameters that enter the results.

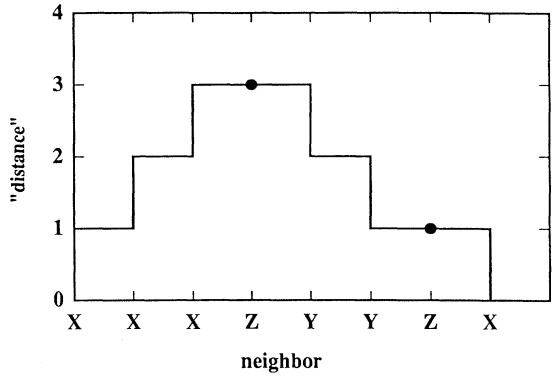

FIG. 1. The neighbors of X are mapped onto the distances of a discrete-time random walk (see text for explanation).

We do not wish to overemphasize the differences between the ballistic and diffusion problems: although they are physically quite different, there is a close formal relation between them that helps to clarify the reasons for the similarity in temporal behaviors. In order to exhibit this formal relation, it is useful to re-solve the ballistic coagulation problem using a stochastic first-passage-time approach. Furthermore, this approach may be more easily generalized to deal with more complicated ballistic reactions. The stochastic approach is the subject of Sec. III.

III. SURVIVAL PROBABILITY CALCULATED FROM FIRST PASSAGE TIMES

We illustrate how the survival probability of X particles can be calculated using the first-passage-time approach. To find the collision partner of an X particle, we make the following mapping to a discrete-time random walk (cf. Fig. 1). We consider a random walk starting at a distance 1 from the x axis at "time" $n=0$. The "time" variable n will correspond to the subsequent neighbors to the right of the given X particle. If such a neighbor is an X particle, we take a step of length 1 away from the x axis (we move "away" from the collision event since this particle will have to be annihilated first). This happens with probability p. If such a neighbor is a Y particle, we take a step of length 1 toward the x axis. The probability for this event is q. For a stationary neighbor, the step length is set equal to zero, and the probability of this event is $r=1-p-q$. Clearly, the collision partner is identified with the first "time" that the random walker reaches the x axis, i.e., the collision partner is the nth neighbor with probability $F_{1\rightarrow 0}(n)$, where $F_{m\rightarrow m'}(n)$ denotes the distribution for first passage from m to m' in n "time" steps.[13] The latter is related to the probability distribution $P_{m\rightarrow m'}(n)$ to go from m to m' in n "time" steps by the following renewal equation:

$$P_{m\rightarrow m'}(n)=\sum_{n'=0}^{n} F_{m\rightarrow m'}(n')P_{m'\rightarrow m'}(n-n') . \tag{20}$$

In terms of the generating functions

$$\tilde{P}_{m\to m'}(s)=\sum_{n=0}^{\infty} s^n P_{m\to m'}(n) \tag{21}$$

and

$$\tilde{F}_{m\to m'}(s)=\sum_{n=0}^{\infty} s^n F_{m\to m'}(n)\ , \tag{22}$$

one finds the relation

$$\tilde{F}_{m\to m'}(s)=\frac{\tilde{P}_{m\to m'}(s)}{\tilde{P}_{m'\to m'}(s)}\ . \tag{23}$$

For the random walk described at the beginning of the section, one has that (see the Appendix)

$$\tilde{P}_{m\to m'}(s)=\gamma^{m-m'}\tilde{P}_{m'\to m'}(s) \quad \text{for } m\geq m' \tag{24a}$$

and

$$\tilde{P}_{m\to m'}(s)=\left[\frac{\gamma q}{p}\right]^{m'-m}\tilde{P}_{m'\to m'}(s) \quad \text{for } m<m'\ , \tag{24b}$$

where $\gamma=\gamma(s)$ is the solution, with $|\gamma|<1$, of the quadratic equation

$$\gamma sq+\frac{sp}{\gamma}=1-sr \tag{25}$$

and $\tilde{P}_{m'\to m'}(s)$, the generating function for the probability of return to the starting point, is

$$\tilde{P}_{m'\to m'}(s)=\frac{1-\gamma}{1-s}\ . \tag{26}$$

The survival time τ of the particle under consideration is equal to the distance it has to cover to meet its collision partner divided by the relative velocity. Hence τ is a random variable of the following form:

$$\tau=\frac{1}{2c}\sum_{i=1}^{n} l_i\ , \tag{27}$$

where l_i is the initial distance between the subsequent right neighbor of the particle under consideration. n is a random variable characterized by the probability distribution $F_{1\to 0}(n)$, and the l_i are independent, identically distributed random variables with density $\Psi(l)$. Consequently, τ is a so-called compound random variable,[14,15] and the Laplace transform of its probability density is the composition of the generating function of the probability distribution for the n variable and the Laplace transform of the probability density of the variable $l/2c$. For the survival probability (i.e., the probability that τ is larger than a given value) one thus obtains

$$1-s\tilde{S}_X(s)=\tilde{F}_{1\to 0}(\tilde{\Psi}(s))=(q\gamma/p)(\tilde{\Psi}(s))\ . \tag{28}$$

Since $\gamma(\tilde{\Psi}(s))=p\tilde{\Psi}(s)B(\tilde{\Psi}(s))$, cf. Eqs. (7) and (25), one recovers the result (9).

IV. DISCUSSION AND CONCLUSIONS

We have extended previous work on the ballistic annihilation reaction $A+A\to 0$ to the coagulation reaction $A+A\to A$. On one hand, we find that the coagulation reaction and the annihilation reaction behave essentially the same way at long times except for a rescaling of the time. On the other hand, the time dependences of the decay in the ballistic coagulation reaction when $p=q$ and the diffusion-limited coagulation reaction are also identical, but for different physical reasons. The difference is reflected in the different parameters that enter the decay laws. Finally, we have derived the ballistic coagulation results using a random-walk formalism that stresses the formal connection with the diffusion-limited case and that can perhaps be generalized to more complicated ballistic reactions.

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APPENDIX

The compact result (24) for the Laplace transform of the probability distribution for return to the starting point can be obtained using the following procedure, which circumvents the use of spatial Fourier transformation. The probability distribution $P_m(n)$ to go from 0 to m in n steps obeys the master equation

$$P_m(n)=pP_{m-1}(n-1)+qP_{m+1}(n-1)+rP_m(n-1)\ . \tag{A1}$$

For the generating function

$$\tilde{P}_m(s)=\sum_{0}^{\infty} s^n P_m(n)\ , \tag{A2}$$

one finds

$$\tilde{P}_m(s)-\delta_{m,0}=s\left[p\tilde{P}_{m-1}(s)+q\tilde{P}_{m+1}(s)+r\tilde{P}_m(s)\right]\ . \tag{A3}$$

This equation can be rewritten in the following recursive form (we omit the explicit s argument for simplicity):

$$\left[sq\tilde{P}_{m+1}-\frac{sp}{\gamma}\tilde{P}_m\right]=\gamma\left[sq\tilde{P}_m-\frac{sp}{\gamma}\tilde{P}_{m-1}\right]-\delta_{m,0}\ , \tag{A4}$$

where γ is a solution of the quadratic equation (25). We consider the solution of this equation with $|\gamma|<1$. By iteration of (A4), one has

$$sq\tilde{P}_m-\frac{sp}{\gamma}\tilde{P}_{m-1}=\begin{cases}-\gamma^{m-1} & \text{for } m>0\\ 0 & \text{for } m\leq 0\ .\end{cases} \tag{A5}$$

Here we have used the fact that for $m\leq 0$ the right-hand

side must vanish because otherwise it diverges for $m \to -\infty$. With a second iteration one obtains the result

$$\tilde{P}_m = \begin{cases} (p/\gamma q)^m \tilde{P}_0 - \dfrac{(p/\gamma q)^m - \gamma^m}{sq(p/\gamma q - \gamma)} & \text{for } m \geq 0 \\ (\gamma q/p)^{|m|} \tilde{P}_0 & \text{for } m < 0 \, . \end{cases} \tag{A6}$$

Using the normalization condition

$$\sum_{m=-\infty}^{\infty} \tilde{P}_m = \frac{1}{1-s} \tag{A7}$$

one finally obtains the result (24) of the main text.

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