Annihilations of stationary particles on a lattice

V. M. Kenkre and H. M. Van Horn
Department of Physics and Astronomy, University of Rochester, Rochester, New York 14627
(Received 30 December 1980)

The time evolution of a system of particles which initially occupy points on a lattice and subsequently undergo pairwise annihilation, is investigated with the help of the Master equation. An exact analysis is given for a one-dimensional lattice of finite as well as infinite extent. Hierarchy equations are derived with the help of a generating function technique, and are solved to give expressions for the number of particles, pairs, and n-tuples for arbitrary time. Computer calculations for the number of singletons left behind are given for lattices of various sizes and shown to be in complete agreement with the analytical results. The motivation of this study comes primarily from pycnonuclear reactions in the interiors of dense stars and secondarily from recombination of free radicals on surfaces and annihilation of Frenkel excitons in molecular crystals.

I. INTRODUCTION

Systems of mutually annihilating particles occur in various fields of physics. The annihilation process may stem from nuclear reactions, chemical combination, or other interactions. The present paper was motivated by a problem concerning the so-called "pycnonuclear" reactions[1-3] in the interior of dense stars, but it should be of interest also in the area of chemical reactions on surfaces, e.g., the recombination of condensed-gas radicals,[4] and in the context of exciton annihilation in molecular crystals.[5,6]

At the high densities in the cores of stars near the end points of stellar evolution, the nuclei of atoms become frozen into a regular crystalline lattice structure. If the stellar matter is compressed to densities that are sufficiently great, as in the core of a presupernova star, for example, nuclear reactions can be caused even as a result of the zero-point motions of the ions about their equilibrium lattice sites. These are termed pycnonuclear reactions.[1-3] Their rates have been previously calculated in the limit where the fractional concentration of the reacting species is approximately unity. No calculations have been reported, however, in the opposite limit of small concentration. This situation differs significantly from the case in which the reacting ions are trace elements in a gas. In the latter case, the reaction rate at low concentration is simply proportional to the product of the concentrations of the reacting particles, because it is equally probable that a reactive ion may be found anywhere within the gas. However, in a lattice, where each ion is restricted to the vicinity of its equilibrium lattice site, it is easy to see that reactive ions may become isolated by the previous history of the reaction process and may therefore remain isolated indefinitely. This has two important consequences. First, when all reactions that can take place have occurred, a finite concentration of singletons may be left behind. Second, the volume-averaged reaction rate must rapidly approach zero as the concentration of the reacting species approaches this asymptotic concentration of singletons.

Reactive free radicals of gases such as oxygen and hydrogen, produced through dissociation as a result of passing the gases through a discharge, provide another example[4,7] of the above physical process. When the free radicals are condensed on surfaces at low temperatures, they combine with their neighbors. Here again, when all possible reactions have occurred, a finite concentration of singletons may be left behind. The time dependence and the asymptotic value of the number of radicals are of interest in this context.

Yet another example of a physical phenomenon involving the above process is exciton annihilation in molecular crystals.[5,6] Optical absorption in molecular crystals generally results in the formation of Frenkel excitons which may annihilate one another. While it is true that in contrast to the above two cases motion within the crystal is of considerable importance in the exciton context, a study of the process under investigation in this paper will provide a starting point for the analysis of exciton annihilation at high exciton densities.

The process of pairwise-annihilation interactions among particles on a lattice is thus of interest in a variety of contexts in astrophysics and in chemical physics. In this paper we restrict ourselves to the following idealization: We consider a rigid lattice, each of whose sites may either be occupied or unoccupied by a particle. Only particles which are nearest neighbors may undergo reactions. They do so with a constant reaction probability per unit time, and when a pair of particles has reacted, they annihilate

each other, leaving the lattice sites they had previously occupied empty. The sites are all occupied initially and we address the problem of calculating the time dependence of the volume-averaged reaction rate, and the asymptotic concentration of singletons left at infinite time.

The plan of this paper is as follows. We formulate the problem in Sec. II with the help of a Master equation for the probabilities of realization of the possible configurations in the lattice. We give an exact analytic solution for the one-dimensional system in Secs. III and IV and display explicitly the time dependence and the asymptotic limit. The analytic results are compared to those of computer simulations in Sec. V. Concluding remarks, including a brief discussion of the source of the difference between our results and those of an earlier analysis[5] of a related problem, are presented in Sec. VI.

II. FORMULATION OF THE PROBLEM

We address the problem with the help of a Master equation for the probabilities of realization of the various configurations. We define variables σ_m, each of which can take the value zero or one. These correspond, respectively, to the site m being empty or occupied by a particle, and m can be a vector of appropriate dimensions. A system configuration is given by a set of σ's and is represented by $|\xi\rangle$, $|\xi'\rangle$, etc. Thus, for instance, in a one-dimensional lattice of N sites

$$|\xi\rangle = |\sigma_1^\xi, \sigma_2^\xi, \ldots, \sigma_m^\xi \ldots, \sigma_N^\xi\rangle. \tag{2.1}$$

The system state is specified by giving the values of the probabilities $P_\xi(t)$ that the configuration $|\xi\rangle$ is realized at time t. The time evolution of the system is given by the Master equation

$$\frac{dP_\xi(t)}{dt} = \sum_{\xi'} [R_{\xi\xi'} P_{\xi'}(t) - R_{\xi'\xi} P_\xi(t)], \tag{2.2}$$

where $R_{\xi\xi'}$ is the transition rate from state $|\xi'\rangle$ to state $|\xi\rangle$.

The number of particles at site j (j is generally a vector) is $\bar{\sigma}_j$:

$$\bar{\sigma}_j = \sum_\xi \sigma_j^\xi P_\xi(t). \tag{2.3}$$

The quantity of primary interest to us is the ratio of the number of particles at time t to that number at $t=0$, or equivalently to N, the number of lattice sites. This ratio is given by

$$f_1(t) = \frac{1}{N} \sum_j \bar{\sigma}_j. \tag{2.4}$$

As we show below, a set of evolution equations for the quantity $f_1(t)$ can be extracted from (2.2). We shall see that a hierarchy of coupled equations similar to the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy[8] is obtained and that exact solutions can be found for the one-dimensional system.

For the sake of clarity as well as analytic tractability, let us restrict our analysis to a one-dimensional lattice with nearest-neighbor annihilation interactions. The indices i, j, m, etc., are now scalars. The Master equation (2.2) takes the form

$$\frac{dP_\xi(t)}{dt} = R \sum_i [\sigma_i^{\xi_i'} \sigma_{i+1}^{\xi_i'} P_{\xi_i'}(t) - \sigma_i^\xi \sigma_{i+1}^\xi P_\xi(t)], \tag{2.5}$$

where R, a constant, is the rate for nearest-neighbor annihilation. The summation in (2.5) is over the sites of the lattice in contrast to that in (2.2) which is over the configurations $|\xi'\rangle$. The superscript ξ_i' in the first term on the right side of (2.5) denotes the state $|\xi_i'\rangle$ wherein all σ's have the same values as in the state $|\xi\rangle$, with the exception of σ_i^ξ and σ_{i+1}^ξ. These equal $(\sigma_i^\xi + 1)$ and $(\sigma_{i+1}^\xi + 1)$, respectively. In other words, in (2.5),

$$\sigma_j^\xi = \sigma_j^{\xi_i'}(1 - \delta_{i,j})(1 - \delta_{i+1,j}) + (\sigma_j^{\xi_i'} - 1)(\delta_{i,j} + \delta_{i+1,j}). \tag{2.6}$$

Note that we consider the lattice to be either a finite ring (i.e., obeying periodic boundary conditions) or infinite. It is therefore unnecessary to include separate terms involving σ_{i-1} in (2.5).

A useful device in analyzing Master equations is the transformation to a generating function[9] equation. We define the generating function $U(z,t)$:

$$U(z_1, z_2, \ldots z_m, \ldots z_N, t) = \sum_{\sigma_1^\xi} \sum_{\sigma_2^\xi} \cdots \sum_{\sigma_m^\xi} \cdots \sum_{\sigma_N^\xi} [(z_1)^{\sigma_1^\xi} (z_2)^{\sigma_2^\xi} \cdots (z_m)^{\sigma_m^\xi} \cdots (z_N)^{\sigma_N^\xi} P_\xi(t)], \tag{2.7}$$

where each summation contains the terms corresponding to $\sigma=0$ and $\sigma=1$. All states $|\xi\rangle$ are thus "sampled" by $U(z,t)$. An immediate consequence of (2.7) is

$$\bar{\sigma}_j = \left(\frac{\partial U(z,t)}{\partial z_j}\right)_{z=1}, \tag{2.8}$$

$$\overline{\sigma_j \sigma_{j+1}} = \left(\frac{\partial^2 U(z,t)}{\partial z_j \partial z_{j+1}}\right)_{z=1}, \tag{2.9}$$

where $z=1$ represents $z_m = 1$ for all m's.

All the information about the system evolution contained in the Master equation (2.5) is also included in the generating function equation

$$\frac{\partial U(z,\tau)}{\partial \tau} = \sum_i \frac{\partial^2 U(z,\tau)}{\partial z_i \, \partial z_{i+1}} (1 - z_i z_{i+1}) \tag{2.10}$$

which may be obtained from (2.5) and (2.7). Note that we have put $Rt = \tau$ in (2.10).

III. HIERARCHY OF COUPLED EQUATIONS

The initial conditions satisfied by the generating function can be written from those satisfied by $P_\xi(t)$. Since all lattice sites are initially occupied by particles, $P_\xi(0)$ is zero for all ξ's except that for which all σ's equal 1. For this ξ, we have $P_\xi(0) = 1$. Substitution in (2.7) gives

$$U(z_1, z_2, \ldots z_m, \ldots z_N, 0) = z_1 z_2 \ldots z_m \ldots z_N . \tag{3.1}$$

There are also the following additional conditions:

$$\frac{\partial^2 U(z,\tau)}{\partial z_m^2} = 0 = \frac{\partial^2 U(z,\tau)}{\partial z_m \, \partial z_{m+N}} , \tag{3.2}$$

which hold for all times and arise from the fact that two differentiations with respect to the same z_m would produce a product of σ_m and $(\sigma_m - 1)$, at least one of which is always zero, since $\sigma_m = 0$ or 1. From (2.8) we now derive a hierarchy of coupled equations for the quantities $\partial U/\partial z_m$, $\partial^2 U/\partial z_m \, \partial z_{m+1}$, etc. We shall first consider $N = \infty$ (i.e., an infinite chain) and later on allow N also to be finite. Using

$$\sum_i a_i \frac{\partial}{\partial z_n} (1 - z_i z_{i+1}) = -(z_{n-1} a_{n-1} + z_{n+1} a_n) , \tag{3.3}$$

where a_i is arbitrary, straightforward differentiations of (2.8) give, for instance,

$$\frac{\partial}{\partial \tau} \frac{\partial U}{\partial z_m} = -\left(z_{m-1} \frac{\partial^2 U}{\partial z_{m-1} \, \partial z_m} + z_{m+1} \frac{\partial^2 U}{\partial z_m \, \partial z_{m+1}} \right) + \sum_{i=1}^{\infty} \frac{\partial^3 U}{\partial z_m \, \partial z_i \, \partial z_{i+1}} (1 - z_i z_{i+1}) , \tag{3.4}$$

$$\frac{\partial}{\partial \tau} \frac{\partial^2 U}{\partial z_m \, \partial z_{m+1}} + \frac{\partial^2 U}{\partial z_m \, \partial z_{m+1}} = -\left(z_{m-1} \frac{\partial^3 U}{\partial z_{m-1} \, \partial z_m \, \partial z_{m+1}} + z_{m+2} \frac{\partial^3 U}{\partial z_m \, \partial z_{m+1} \, \partial z_{m+2}} \right) + \sum_{i=1}^{\infty} \frac{\partial^4 U}{\partial z_m \, \partial z_{m+1} \, \partial z_i \, \partial z_{i+1}} (1 - z_i z_{i+1}) . \tag{3.5}$$

We observe that (3.4) and (3.5) are, respectively, the $\eta = 1$ and 2 cases of the general equation

$$\left(\frac{\partial}{\partial \tau} + (\eta - 1) \right) \frac{\partial^\eta U}{\partial z_m \, \partial z_{m+1} \cdots \partial z_{m+\eta-1}} = -\left(z_{m-1} \frac{\partial^{\eta+1} U}{\partial z_{m-1} \, \partial z_m \cdots \partial z_{m+\eta-1}} + z_{m+\eta} \frac{\partial^{\eta+1} U}{\partial z_m \, \partial z_{m+1} \cdots \partial z_{m+\eta}} \right) + \sum_{i=1}^{\infty} \frac{\partial^{\eta+2} U}{\partial z_m \, \partial z_{m+1} \cdots \partial z_{m+\eta-1} \, \partial z_i \, \partial z_{i+1}} (1 - z_i z_{i+1}) . \tag{3.6}$$

Differentiation of (3.6) with respect to $z_{m+\eta}$ and use of (2.8), (2.9), and (3.3) gives an equation which is identical to (3.6) except for the replacement of η by $\eta+1$. We have thus established the validity of (3.6) by an induction proof. For we have shown that assuming it is valid for η we can prove its validity for $\eta+1$. And from (3.4) and (3.5) we have demonstrated its explicit validity for $\eta = 1$ and 2.

The average number of particles at site j at a time t is given by (2.3). From the symmetry inherent in the initial condition of our problem it is clear that $\bar{\sigma}_j$ is independent of j. Equation (2.4) shows that it equals the fraction $f_1(t)$ of the initial number of particles left at time t. Denoting by $f_\eta(t)$, the quantity $\overline{\sigma_j \sigma_{j+1} \cdots \sigma_{j+\eta-1}}$, we find that the replacement $z = 1$ in (3.4)–(3.6) gives

$$\frac{df_\eta(\tau)}{d\tau} + (\eta - 1) f_\eta(\tau) = -2 f_{\eta+1}(\tau) \tag{3.7}$$

with particular cases

$$\frac{df_1(\tau)}{d\tau} = -2 f_2(\tau) , \tag{3.8}$$

$$\frac{df_2(\tau)}{d\tau} + f_2(\tau) = -2 f_3(\tau) . \tag{3.9}$$

Equations (3.7)–(3.9) constitute a coupled hierarchy of equations. Such hierarchies are typical[8] of many-body systems. In more general cases such hierarchies can be solved only approximately through truncations and such procedures. However, for the present system, we shall give an exact solution in the next section.

IV. EXACT SOLUTION

We Laplace transform (3.8) and develop an infinite series for the transform of $f_1(\tau)$ by repeated substitution of (3.7). We define the transform

$$\tilde{g}(\epsilon) = \int_0^\infty d\tau \, e^{-\epsilon\tau} g(\tau) \tag{4.1}$$

for any function $g(\tau)$. The observation that the initial conditions of our problem give $f_\eta(0)=1$ for all η, leads then to

$$\tilde{f}_1(\epsilon)=\frac{1}{\epsilon}+\frac{(-2)}{\epsilon(\epsilon+1)}+\frac{(-2)^2}{\epsilon(\epsilon+1)(\epsilon+2)}+\cdots$$
$$=\sum_{M=0}^{\infty}\frac{(-2)^M}{\epsilon(\epsilon+1)\cdots(\epsilon+M)}. \tag{4.2}$$

The use of partial fractions allows the Laplace inversion of (4.2) into

$$f_1(\tau)=\sum_{M=0}^{\infty}\sum_{r=0}^{M}\frac{(-2)^M(-1)^r}{r!(M-r)!}e^{-r\tau}. \tag{4.3}$$

Collecting coefficients of $e^{-l\tau}$ for $l=0,1,2,\ldots$, etc., we obtain from (4.3),

$$f_1(\tau)=e^{-2}\left(1+2e^{-\tau}+\frac{(2e^{-\tau})^2}{2!}+\cdots\right)$$
$$=e^{-2(1-e^{-\tau})}. \tag{4.4}$$

Equation (4.4) is one of the primary results of this paper. It shows that the fraction of occupied sites reduces from the values 1 at $t=0$ to $e^{-2}=0.1353$ as $t\to\infty$. This latter limit may also be obtained directly from (3.11) with the help of an Abelian theorem:

$$\lim_{\tau\to\infty}f_1(\tau)=\lim_{\epsilon\to 0}\epsilon\tilde{f}_1(\epsilon)=\sum_{M=0}^{\infty}\frac{(-2)^M}{M!}=e^{-2}. \tag{4.5}$$

It is possible to obtain the exact solution for all members f_η of the hierarchy. Repeated Laplace transforms of (3.7) give

$$\tilde{f}_\eta(\epsilon)=\frac{1}{\epsilon+\eta-1}+\frac{(-2)}{(\epsilon+\eta-1)(\epsilon+\eta)}$$
$$+\frac{(-2)^2}{(\epsilon+\eta-1)(\epsilon+\eta)(\epsilon+\eta+1)}+\cdots$$
$$=\tilde{f}_1(\epsilon+\eta-1). \tag{4.6}$$

The Laplace inverse of (4.6) shows that $f_\eta(\tau)$ is connected simply to $f_1(\tau)$:

$$f_\eta(\tau)=e^{-(\eta-1)\tau}f_1(\tau). \tag{4.7}$$

In particular, $f_2(\tau)$, the fraction of adjacent pairs, is given by

$$f_2(\tau)=e^{-\tau}e^{-2(1-e^{-\tau})}. \tag{4.8}$$

It is also of interest to eliminate τ and express the f_η's in terms of f_1. For this purpose we write (4.4) as

$$e^{-\tau}=1+\tfrac{1}{2}[\ln f_1(\tau)]. \tag{4.9}$$

Equation (4.7) then gives

$$f_\eta(\tau)=\{1+\tfrac{1}{2}[\ln f_1(\tau)]\}^{\eta-1}f_1(\tau). \tag{4.10}$$

Its particular case for $\eta=2$ shows the relation between the fraction of particles and of pairs valid for all times

$$f_2(\tau)=f_1(\tau)+\tfrac{1}{2}[f_1(\tau)\ln f_1(\tau)]. \tag{4.11}$$

For the sake of completeness we now comment on the modification that occurs in Eqs. (3.4)–(4.11) when the lattice is not infinite but is a ring of N sites. Equations (3.4)–(3.6) have now only a summation from $i=1$ to $i=N$ but are otherwise still applicable. The result $z_{m+N-1}=z_{m-1}$, which is a consequence of periodic boundary conditions, gives

$$\left(\frac{\partial}{\partial\tau}+(N-2)\right)\frac{\partial^{N-1}U}{\partial z_m\partial z_{m+1}\cdots\partial z_{m+N-2}}$$
$$=-2z_{m+N-1}\frac{\partial^N U}{\partial z_m\partial z_{m+1}\cdots\partial z_{m+N-1}}$$
$$+\sum_{i=1}^{N}\frac{\partial^{N+1}U}{\partial z_m\partial z_{m+1}\cdots\partial z_{m+N-2}\partial z_i\partial z_{i+1}}(1-z_iz_{i+1}). \tag{4.12}$$

Since the second equality in (3.2) makes $\partial^2U/\partial z_m^2=0$ for any m, and $z_m=z_{m+N}$, the last term in (4.12) is identically zero. The next differentiation with respect to z_{m+N-1} produces

$$\left(\frac{\partial}{\partial\tau}+N\right)\frac{\partial^N U}{\partial z_m\partial z_{m+1}\cdots\partial z_{m+N-1}}=0. \tag{4.13}$$

Equation (4.13) gives

$$\frac{df_N(\tau)}{d\tau}+Nf_N(\tau)=0 \tag{4.14}$$

which differs from (3.7) in two ways: there is no coupling to any higher member of the hierarchy, and the decay rate of f_N is proportional to Nf_N rather than to $(N-1)f_N$. The general hierarchy equation for the finite ring is therefore (3.7) for $\eta<N$ and (4.14) for $\eta=N$. Thus

$$\frac{df_\eta(\tau)}{d\tau}+(\eta-1)f_\eta(\tau)=-2f_{\eta+1}(\tau)$$
$$+\delta_{\eta,N}[2f_{N+1}(\tau)-f_N(\tau)], \tag{4.15}$$

where η assumes values smaller than or equal to N. The $N=\infty$ result (4.2) is now replaced, for the finite lattice, by

$$\tilde{f}_1(\epsilon)=\sum_{M=0}^{N-2}\left(\frac{(-2)^M}{\epsilon(\epsilon+1)\cdots(\epsilon+M)}\right)$$
$$+\left(\frac{(-2)^{N-1}}{\epsilon(\epsilon+1)\cdots(\epsilon+N-1)}\right)\left(\frac{\epsilon+N-1}{\epsilon+N}\right). \tag{4.16}$$

The correction factor in (4.16) removes $(\epsilon+N-1)$ and introduces $(\epsilon+N)$.

It is straightforward to invert (4.16) and obtain $f_1(\tau)$ as a finite summation of exponentials. We shall not give the details. However, we shall exhibit the asymptotic limit of $f_1(\tau)$ for use in

the comparison to the numerical simulations to be carried out in the next section:

$$\lim_{\tau\to\infty} f_1(\tau) = \lim_{\epsilon\to 0} \epsilon\tilde{f}_1(\epsilon)$$

$$= \sum_{M=0}^{N-1} \frac{(-2)^M}{M!} - \frac{1}{N}\frac{(-2)^{N-1}}{(N-1)!}. \qquad (4.17)$$

The difference between (4.15) for the finite ring and (3.7) for the infinite ring, which we discussed above, makes its presence felt through the "end-correction term" in (4.17).

V. NUMERICAL SIMULATION

Generalization of the analytic results presented in Secs. III and IV to systems of more than one dimension appears to be a difficult task. In order to provide a basis for carrying out numerical simulations of the pair-annihilation process in higher dimensions, we have therefore begun a number of such simulations in the one-dimensional system. We display the infinite time limit of the fraction of singletons left behind obtained in this manner. It will be seen that complete agreement with our analytic results occurs.

We begin with a ring of N sites, each of which is initially occupied by a particle as in Fig. 1. To take the first step in the resulting Markov sequence, we select one pair of lattice sites at random and allow the particles to react, annihilating each other. We are then left with a lattice in which two of the sites are empty, leaving $N_1 = N-2$ singletons and N_2 different pairs which are available for subsequent reactions. For a ring, $N_2 = N_1 = N$ initially, and $N_2 = N-3$ after the first Markov step. To make subsequent steps in the Markov sequence, we again pick a particular pair of lattice sites at random. Now, however, we must first make sure that *both* sites are occupied by particles; if either lattice site is empty, no reaction can take place for that pair. In this case, another pair of sites on the lattice is selected at random, and the site occupancy tests are repeated. The first pair of randomly selected sites to be identified in this way, both of which are occupied, terminates the search. Both particles are annihilated, completing this step of the Markov sequence. This process is continued until there are no pairs of particles left on adjacent lattice sites, at which stage we have reached the end of the Markov pair-annihilation sequence.

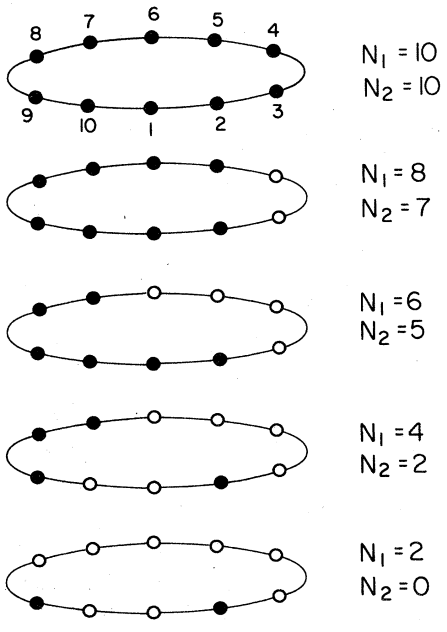

FIG. 1. Example of a Markov pair-annihilation sequence on a one-dimensional ring.

TABLE I. Ensemble average number of singletons left at the end of Markov pair-annihilation sequences on one-dimensional rings.

N	$\langle f_1(\infty)\rangle$ [a]	$\langle f_1(\infty)\rangle$ [b]	L
2	0	0 [c]	
3	$\frac{1}{3}$	0.3333 [c]	
4	0	0 [c]	
5	$\frac{1}{5}$	0.2000 [c]	
6	$\frac{1}{9}$	0.1111	100 000
7	0.142 85···	0.1429	
8	0.133 3···	0.1331	100 000
9	0.135 8···	0.1358	100 000
10	0.135 2···	0.1353	100 000
30	0.135 3···	0.1354	75 000
100	0.135 3···	0.1352	6 000
1000	0.135 3···	0.136	70

[a] Analytic result from Eq. (4.17).
[b] Numerical result from the average of L Markov sequences.
[c] Exact result, holds for all Markov sequences.

Because the fraction of singletons left at the end of a Markov pair-annihilation sequence, which we denote by $f_1(\infty)$, depends upon the (random) sequence of annihilations, different Markov sequences lead to different values. A particular example of such a sequence on a ring of $N=10$ sites is shown in Fig. 1; this sequence left two isolated particles at the end. To obtain the ensemble avarage number of singletons, we have carried out large numbers of repetitions of each Markov pair-annihilation sequence and have

averaged the results to obtain the results given in Table I below. The column headings in this table have the following meanings: The number of lattice sites (which equals initial number of particles) is given in the column labeled N. The ensemble average fraction of singletons left at the end of the annihilations is denoted by $\langle f_1(\infty)\rangle$ and the number of configurations in the ensemble is L.

VI. CONCLUDING REMARKS

The agreement between the numerical results and the analytic predictions is excellent. Note particularly that for small N, the fraction of singletons left behind, $f_1(\infty)$, shows considerable variation with N. It vanishes for $N=2$, equals $\frac{1}{3}$ for $N=3$, vanishes again for $N=4$, equals $\frac{1}{2}$ for $N=5$, and so on. This nonmonotonic behavior, whose source can be understood by considering the annihilation process step by step, is faithfully reproduced by our analytic results (4.17). The last term in (4.17), which provides the end correction as explained in Sec. IV, oscillates in sign as N changes and makes considerable contribution to the behavior of $f_1(\infty)$ for small N. As this term is proportional to $1/N$, its contribution is negligible for large ring sizes. Therefore $f_1(\infty)$ converges to $\exp(-2)=0.1353$ in the limit $N\to\infty$. The accurate description of all the variations that is provided by (4.17) is a convincing indicator of the validity of the analytic formulation presented in this paper.

However, our results differ significantly from those given in an apparently related context by Jackson and Montroll.[7] They treated the problem of free-radical statistics by using time-independent considerations. Their analytical result shows that the singleton fraction for their problem equals 0.1770 as $N\to\infty$. As their analysis is also exact, it is important to understand the reason for the difference. Unfortunately, a direct comparison for small N cannot be made because the analysis in Ref. 7 is for open chains, whereas our analysis is for rings. It is only for large N that the two systems become identical.

The method of Ref. 7 consists of an enumeration of all possible configurations of the system at $t=\infty$. The singleton numbers in each configuration are added together and the sum is divided by the number of all possible configurations (at $t=\infty$) to give the expected fraction of singletons. As in Ref. 7 we shall denote this fraction by f. To understand why f does not equal our $f_1(\infty)$ let us examine a ring of six sites and apply the technique of Ref. 7 to calculate f. If we list all possible configurations, we find as many with singletons left at opposite corners of the "hexagon" as with no singletons left. The fraction f is therefore $\frac{1}{6}$. On the other hand, if we begin with all corners of the hexagon occupied at $t=0$ and follow the actual evolution in time, we arrive at a different end situation. After any one pair is annihilated, there are *two* ways the next annihilation can take place in such a manner that no singletons are left, but only *one* way it can lead to two surviving singletons. The weight of the state with two singletons is therefore $\frac{1}{3}$ in the time-dependent argument, in contrast to $\frac{1}{2}$ in the time-independent argument. We thus find $f_1(\infty)=\frac{1}{9}$ as in Table I.

The difference in our results and those of Ref. 7 arises from different weights attached to the various possible configurations. In Ref. 7 an assumption of equal weights is used. In our analysis we make no additional assumption about the weights. They are decided by the system dynamics and are generally smaller than those in Ref. 7. Our $f_1(\infty)$ therefore tends to be smaller than their f. For large N the result 0.1770 for the eventual fraction of singletons is exact for the formulation given in Ref. 7. The result $\exp(-2)=0.1353$ is exact for the formulation given in this paper. Our formulation is the appropriate one wherever a fully populated lattice evolves through annihilation processes as we have described.

We comment in passing that our result (4.4) for the time evolution of the fraction $f_1(t)$ has an interesting structure. It is exponential at short times with the exponent $-2Rt$ and its general form is called the Gumbel distribution. It is encountered in contexts as varied as diffusion in a harmonic well[10] and vibrational relaxation of a molecule.[11] It is poorly approximated by the solution of a bilinear equation such as

$$\frac{df_1(t)}{dt} = -(\text{const}) f_1^2(t) \tag{6.1}$$

which is sometimes said to provide a natural description of annihilation processes.

We conclude by recalling our primary results for the infinite system: For the infinite system, the hierarchy equation (3.7), its solutions

$$f_1(t) = e^{-2(1-e^{-Rt})}, \tag{6.2}$$

$$f_\eta(t) = e^{-(\eta-1)Rt} e^{-2(1-e^{-Rt})}, \tag{6.3}$$

and the asymptotic limit (4.5); for the finite system the hierarchy equation (4.15), its solution (4.16) for the Laplace transform of $f_1(\tau)$, and the asymptotic limit (4.17). We have also developed approximation procedures and have determined bounds for two- and three-dimensional systems. These will be reported in a future publication.

ACKNOWLEDGMENTS

We wish to thank Dr. E. Schatzman for his questions about the astrophysical problems which led us to undertake this work. This research has been supported in part by the National Science Foundation under Grants Nos. AST 79-09391 and DMR 79-19539.

[1]A. G. W. Cameron, Ap. J. 130, 916 (1959).
[2]R. A. Wolf, Phys. Rev. 137, B1634 (1965).
[3]E. E. Salpeter and H. M. Van Horn, Ap. J. 155, 193 (1969).
[4]H. P. Broida, Ann. N. Y. Acad. Sci. 67, 530 (1957).
[5]N. E. Geacintov and C. E. Swenberg, in *Organic Molecular Photophysics*, edited by J. B. Birks (Wiley, New York, 1973), Vol. I.
[6]V. M. Kenkre, Phys. Rev. B 22, 2089 (1980).
[7]J. L. Jackson and E. W. Montroll, J. Chem. Phys. 28, 1101 (1958).
[8]See, e.g., M. Dresden, Rev. Mod. Phys. 33, 265 (1961); R. L. Liboff, *Introduction to the Theory of Kinetic Equations* (Wiley, New York, 1969).
[9]See, e.g., M. Kac, in 3rd Berkeley Symposium on Mathematical Statistics, University of California 171, (1956); E. W. Montroll, in *Energetics of Metallurgical Phenomena* (Gordon and Breach, New York, 1967), Vol. 3.
[10]G. G. Emch, Acta Phys. Austr. Suppl. XV, 79 (1976).
[11]V. M. Kenkre and V. Seshadri, Phys. Rev. A 15, 197 (1977).