Diffusion-controlled reactions in one dimension: Exact solutions and deterministic approximations

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One-dimensional systems of annihilating and coalescing random walks and Brownian motions with arbitrary initial configurations of particles are studied. Exact results are derived for site-occupancy probabilities (densities), local fluctuations in these probabilities, and distributions of nearest-neighbor distances. Two types of initial configuration are investigated in detail: the homogeneous Poisson process and a one-parameter family of pairwise clustered locations. The systems studied can be regarded as simple models of diffusion-controlled chemical reactions and hence the exact results derived here can be compared with the predictions of traditional, deterministic models that are based on simplifying assumptions about the evolution of the spatial structure of the systems. It is shown that, although the asymptotic behavior of the annihilating systems does depend on the structure of the initial configuration, the deterministic approximations are not able to detect this dependence, and the approximation is poor when the particles are initially highly clustered.

I. INTRODUCTION

Diffusion-controlled reactions in solution, in which the rate of reaction is determined by the rate at which particles encounter each other in the course of their Brownian motions, are the simplest known reactions. Chemical theories of diffusion-controlled reactions are usually formulated in terms of a singlet density, or concentration, which evolves according to a diffusion-reaction equation. Such a formulation,which we label deterministic, disregards the discrete nature of the reacting particles and ignores correlations which may exist in random initial configurations of particles. Even when the particle locations are initially uncorrelated, correlations develop as a consequence of the progress of the reaction. Deterministic models take account approximately of the pairwise correlations which appear, but assume that the effects of higher-order correlations are negligible. Another major drawback of these models is that there is no satisfactory method of estimating errors due to such simplifying assumptions.

Recent results by a number of authors[1-8] show that local spatial fluctuations which are ignored by deterministic models can dominate the large-time reaction kinetics in many important cases and hence more sophisticated models are required. One clear example is the case in which the particles are initially clustered, which occurs in high-energy electron radiolysis.[1-3] Another striking example is that of two types of particles which react according to $A+B\rightarrow\emptyset$ (i.e., the particles annihilate) for which, in dimensions $d\leq 3$, clusters of like particles develop and reaction is largely constrained to the boundaries of these clusters.[4-6] In the special case of the trapping reaction with a single A particle and the B particles fixed, the reaction rate is related to the volume of the Wiener sausage.[7,8] In each of these cases knowledge of the evolution of the spatial structure of the system is crucial to understanding the reaction kinetics and deterministic treatments are inappropriate.

In order to gain insight into the validity of the assumptions inherent in deterministic formulations, attention has recently focused on simple model stochastic systems which incorporate details of spatial structure.[9-19] To simplify the mathematical analysis, these models are usually restricted to one dimension. In this paper we examine some one-dimensional stochastic models of diffusion-controlled reactions which are flexible enough to allow arbitrary initial particle configurations and sophisticated enough to account exactly for the effects of spatial structure on reaction rates, yet remain simple enough to allow the calculation of detailed, explicit results, not only for the asymptotic behavior but for the entire time-dependent evolution of the system. These exact results are compared with the predictions of relevant deterministic models. This work incorporates as special cases many of the models referred to above[9,11,14-18] and provides a unified treatment which includes and extends known results.

The model systems to be considered consist of sizeless particles which move independently according to either (a) symmetric, nearest-neighbor random walk (RW) on the integers $\mathbb{Z}$ with an exponentially distributed waiting time of mean one between jumps; or (b) standard Brownian motion[20] (BM) on the real line $\mathbb{R}$. Chemical reaction is modeled by imposing one of two possible interactions when a pair of particles meet: either both particles vanish (annihilating BM and RW, called ABM and ARW) or one particle vanishes and the other is left undisturbed

(coalescing BM and RW, called CBM and CRW).

The explicit results for ABM and CBM presented here are for standard Brownian motion, in which there is an implicit diffusion coefficient of $\frac{1}{2}$ for each particle. Extension to an arbitrary diffusion coefficient D is obtained simply by replacing t with $2Dt$.

We take two approaches to obtaining results for these systems. The first, more general, approach is based on methods from the mathematical interacting particle systems literature[21,22] and obtains results for the RW systems by exploiting their relationship with the invasion process (IP) introduced by Clifford and Sudbury.[23] Rescaling and taking limits, corresponding results for the BM systems are obtained. The present work extends results reported by Balding, Clifford, and Green.[15] The second, more direct, approach follows from the results of Balding[18] and applies the reflection principle to finite, periodic versions of the annihilating systems, with results for the infinite systems derived by taking appropriate limits.

After describing the mathematical techniques employed, we present general results and applications to some particular initial configurations of interest, including uncorrelated particle locations and a one-parameter family of correlated configurations. For each of our model systems we obtain the probability that a particular site is occupied at any time. For the coalescing systems we describe pairwise occupancy probabilities and the distributions of interparticle distances at large times, while for the annihilating systems we derive the time-dependent mean and variance of the number of particles in a finite interval. In Sec. VI corresponding deterministic models are formulated and appropriate comparisons made. The present paper emphasizes results and applications. Further details and proofs will be published elsewhere.[24]

II. INVASION PROCESS AND DUALITY EQUATIONS

The IP is a system of black and white particles, one at each site of the integer lattice $\mathbb{Z}$. Each particle, after independent, exponentially distributed waiting times of mean one, destroys one of its two neighbors, chosen equiprobably, and replaces the neighbor with a copy of itself. If the particles at two neighboring sites have the same color then no change is observed, all the activity in the system occurring at the borders between regions of black and white particles. A key to describing IP is the observation that these borders perform ARW. Further relationships between ARW, CRW, and IP follow from a joint construction of all three processes on a random graph known in the mathematical literature as the percolation substructure.[21] Briefly, the graph is obtained by associating a time axis with each integer site and constructing directed arcs between neighboring pairs of sites so that the time intervals between the arcs are independently and exponentially distributed with mean 1 and each arc has an independent probability $\frac{1}{2}$ of pointing in each direction.

To construct realizations of CRW and ARW on this graph, a convenient fluid-flow terminology is often used. Let A be a set of sites and imagine that at time 0 unit volume of fluid emanates from each site in A. Each stream of fluid flows in the direction of increasing time until it reaches the tail of an arc, when it follows the arc to the neighboring time axis and then resumes its increasing-time journey. If two flows meet at the head of an arc, they merge into a single stream with the volume of flow added. Notice that a particle exists at site a and time t in CRW with initial configuration A precisely when the fluid flow in the graph reaches the point (a,t), while a particle exists in ARW if the volume of the fluid flow reaching (a,t) is an odd integer.

To construct on the same graph IP with the initial black particles indexed by A, suppose now that each site in A is a source of fluid at some fixed time $s>0$ and flow is in the direction of decreasing time. This flow is suppressed on reaching the tail of an arc but at the head of an arc the stream divides in two, one stream ignoring the arc and the other stream following the arc to its tail and then continuing its decreasing-time flow. For $t\in[0,s)$, there is a black particle at site a and time t in IP precisely when at least one stream reaches $(a,s-t)$ in the graph. For further details of these constructions, see Griffeath.[21]

Let ξ_t^A denote the configuration of particles at time t in CRW with initial configuration A, so that $\xi_0^A=A$; the corresponding set of occupied sites for ARW is denoted by η_t^A and ζ_t^A is the set of sites occupied at time t by black particles in IP when initially the particles located at sites in A are black. For B a finite set of integers, the joint construction of ARW, CRW, and IP described above implies immediately the *duality equations*

$$\mathcal{P}(\xi_t^A\cap B\neq\varnothing)=\mathcal{P}(\zeta_t^B\cap A\neq\varnothing)\ , \tag{1a}$$

$$\mathcal{P}(\eta_t^A\cap B\neq\varnothing)=2^{1-|B|}\sum_{C\subseteq B}\mathcal{P}(|\zeta_t^C\cap A|\text{odd})\ . \tag{1b}$$

More generally, duality equations similar to (1) hold for random initial configurations,[9] when the set of sites initially occupied is chosen according to a probability distribution μ on the set of subsets of $\mathbb{Z}$. The fixed initial configuration A can be considered as the special case that μ assigns probability one to the set A. The utility of the duality equations lies in the fact that probabilities of events for systems with arbitrary (possibly random, possibly infinite) initial configurations can be expressed in terms of probabilities of events for systems with finite initial configurations. Further, it can be shown[24] that the probabilities on the left-hand side of (1) give a complete description of ARW and CRW so that, knowing these probabilities, all questions of interest about the systems can be answered. Analogous duality equations also hold in higher dimensions but it is only in the one-dimensional case that, using the fact that borders in IP perform ARW, the right-hand side of (1) can be explicitly evaluated, which is undertaken in Secs. III and IV.

III. SINGLE SITE OCCUPANCY PROBABILITIES

Consider the case that B consists of a single site b, so that the duality equations express the probabilities that site b is occupied at time t in ARW and CRW in terms of IP with initially only the particle at b black. Incorporat-

ing random initial configurations, Eqs. (1) become in this case

$$\mathcal{P}(b\in\xi_t^\mu)=\sum_{C\subseteq\mathbb{Z}}\mathcal{P}(\zeta_t^{\{b\}}=C)N_\mu(C)\ , \tag{2a}$$

$$\mathcal{P}(b\in\eta_t^\mu)=\sum_{C\subseteq\mathbb{Z}}\mathcal{P}(\zeta_t^{\{b\}}=C)O_\mu(C)\ , \tag{2b}$$

where $N_\mu(C)$ is the probability that in the random initial configuration μ at least one site in C is occupied and $O_\mu(C)$ is the probability that initially an odd number of sites in C are occupied. The two borders of $\zeta_t^{\{b\}}$ form ARW with initially two particles occupying adjacent sites and so $\mathcal{P}(\zeta_t^{\{b\}}=C)$ is readily evaluated using the reflection principle.[15] In many cases of interest the initial configuration μ is spatially stationary, which means that the probability that any set of sites is occupied remains unchanged when all the sites undergo a common displacement. In the stationary case Eqs. (2) are independent of b and, introducing the concise notations S_t^ξ for $\mathcal{P}(b\in\xi_t^\mu)$ and S_t^η for $\mathcal{P}(b\in\eta_t^\mu)$, the duality equations reduce to

$$S_t^\xi=\frac{1}{t}e^{-2t}\sum_{j=1}^{\infty}jI_j(2t)N_\mu(j)\ , \tag{3a}$$

$$S_t^\eta=\frac{1}{t}e^{-2t}\sum_{j=1}^{\infty}jI_j(2t)O_\mu(j)\ , \tag{3b}$$

where I_j is the modified Bessel function, $N_\mu(j)$ abbreviates $N_\mu(\{1,2,\ldots,j\})$ and similarly for $O_\mu(j)$. Some explicit results for ARW with particular initial configurations have been given by Balding, Clifford, and Green,[15] who also show, using the known[25] asymptotic behavior of I_j, that

$$\lim_{t\nearrow\infty}\sqrt{\pi t}\,S_t^\xi=1\ , \tag{4a}$$

$$\lim_{t\nearrow\infty}\sqrt{\pi t}\,S_t^\eta=\gamma\ , \tag{4b}$$

where the parameter γ is defined[24] for all spatially stationary μ by

$$\gamma=\lim_{k\nearrow\infty}\frac{1}{k}\sum_{j=1}^{k}O_\mu(j)\ . \tag{5}$$

Bramson and Griffeath[9] prove (4) when μ is restricted to certain classes, for which γ is always $\frac{1}{2}$.

We see from (4) that details of the initial configuration which are ignored by the deterministic models influence the asymptotic site occupancy probability of ARW, but not that of CRW. Further, ARW "remembers" only the information about the initial spatial structure incorporated by the parameter γ and not, for example, the initial concentration of particles.

Turning now to the continuous state space systems ABM and CBM, the graphical constructions which led to the duality equations (1) are no longer available. However, continuous versions of the duality equations can be obtained by showing that, with a suitable rescaling of the space and time variables, the RW processes converge to the BM systems.[24] A similar development to that outlined above leads to the conclusion that, provided only that the initial configuration of the particles forms a spatially stationary point process, the site-occupancy probability densities for CBM and ABM are given by

$$C_t^\xi=\frac{1}{2t\sqrt{(\pi t)}}\int_0^\infty x\exp(-x^2/4t)\tilde{N}(x)dx\ , \tag{6a}$$

$$C_t^\eta=\frac{1}{2t\sqrt{(\pi t)}}\int_0^\infty x\exp(-x^2/4t)\tilde{O}(x)dx\ , \tag{6b}$$

where $\tilde{N}(x)$ is the probability that in the initial configuration there is at least one particle which lies in the interval $[0,x)$ and $\tilde{O}(x)$ is the probability that there are an odd number of such particles. The asymptotic site-occupancy density is $1/\sqrt{\pi t}$ for CBM and $\tilde{\gamma}/\sqrt{\pi t}$ for ABM, where

$$\tilde{\gamma}=\lim_{x\nearrow\infty}\frac{1}{x}\int_0^x\tilde{O}(y)dy\ . \tag{7}$$

In the case that initially the particles are distributed as a parameter-β Poisson process, so that the probability that a particle occupies a short interval of length dv is $\beta\,dv$ and the particle locations are uncorrelated, we have

$$\tilde{N}(x)=1-e^{-x\beta}\ ,$$

$$\tilde{O}(x)=\tfrac{1}{2}(1-e^{-2x\beta})\ ,$$

and therefore the site-occupancy densities are

$$C_t^\xi=\beta\exp(\beta^2t)\operatorname{erfc}(\beta\sqrt{t}\,)\ , \tag{8a}$$

$$C_t^\eta=C_{4t}^\xi\ , \tag{8b}$$

where $\operatorname{erf}(x)=1-\operatorname{erfc}(x)=2\int_0^x\exp(-u^2)du/\sqrt{\pi}$. Curiously, C_t^ξ and C_t^η have the same functional form, with different time scales. In this case $\tilde{\gamma}=\frac{1}{2}$ and so the asymptotic site-occupancy densities are $1/\sqrt{\pi t}$ and $1/2\sqrt{\pi t}$. Further, taking limits in (8) as $\beta\nearrow\infty$, i.e., as the initial concentration of particles increases, these asymptotic densities are exact at all times.

A simple case of a correlated initial configuration occurs when the separation of the particles alternates between the fixed values $(1-\alpha)\lambda$ and $(1+\alpha)\lambda$, for some $\lambda>0$ and $\alpha\in[0,1)$. Let a particle be located at random uniformly on the interval $[0,2\lambda)$, place another particle a distance $(1-\alpha)\lambda$ to the right of the first, and then continue placing particles along the whole line with alternate spacings. The resulting configuration is spatially stationary with

$$\tilde{N}(x)=\begin{cases}x/\lambda, & x\in[0,(1-\alpha)\lambda)\\ \dfrac{1-\alpha}{2}+\dfrac{x}{2\lambda}, & x\in[(1-\alpha)\lambda,(1+\alpha)\lambda)\\ 1, & x\geq(1+\alpha)\lambda\end{cases}$$

and $\tilde{O}(x)$ is a "blunt sawtooth" function of period 2λ, where

$$\tilde{O}(x)=\begin{cases}x/\lambda, & x\in[0,(1-\alpha)\lambda)\\ 1-\alpha, & x\in[(1-\alpha)\lambda,(1+\alpha)\lambda)\\ 2-x/\lambda, & x\in[(1+\alpha)\lambda,2\lambda)\end{cases}$$

The site-occupancy densities in this case are

$$C_t^{\xi}=\frac{1}{2\lambda}\left[\operatorname{erf}\left[\frac{(1+\alpha)\lambda}{2\sqrt{t}}\right]+\operatorname{erf}\left[\frac{(1-\alpha)\lambda}{2\sqrt{t}}\right]\right], \quad (9a)$$

$$C_t^{\eta}=\frac{1}{\lambda}\sum_{k=1}^{\infty}\operatorname{erfc}\left[\frac{2k-1+(-1)^k}{(4/\lambda)\sqrt{t}}\right] -\operatorname{erfc}\left[\frac{2k-1+(-1)^k(2\alpha-1)}{(4/\lambda)\sqrt{t}}\right]. \quad (9b)$$

Further, $\tilde{\gamma}=\frac{1}{2}(1-\alpha^2)$ and so the asymptotic site-occupancy probabilities are $1/\sqrt{\pi t}$ and $(1-\alpha^2)/2\sqrt{\pi t}$ and, as for the Poisson case, these values become exact at all times in the limit as the initial concentration of particles increases, i.e., as $\lambda\searrow 0$. However, notice that in the alternate separation case C_t^{ξ} is not a time rescaling of C_t^{η}, which held in the Poisson case.

IV. SPATIAL STRUCTURE

We have seen in Sec. III that the duality equations lead readily to expressions for site-occupancy probabilities (or densities) in all our model systems. If we wish to answer more detailed questions concerning spatial structure, such as joint occupancy probabilities for two or more sites, the duality equations can again be employed to convert the original problems for systems with arbitrary initial configurations into problems for ARW or ABM with fixed initial configurations consisting of finite and even numbers of particles. We now describe how these simplified problems can be solved directly using the reflection principle.

Suppose that $A=\{a_1<a_2<\cdots<a_N\}\subset\mathbb{Z}$, with N even. We require $\mathcal{P}(\eta_t^A=B)$, for $B=\{b_1<\cdots<b_M\}$ with M even and $0\le M\le N$. If $M=N$, i.e., the case that no annihilations occur prior to time t, the required probability is[26] the determinant of the $N\times N$ matrix whose ijth element is the probability that a lone random walker starting at a_i occupies site b_j at time t. The case $M=0$ of no particles surviving at time t can be expressed in terms of two particle probabilities by

$$\mathcal{P}(\eta_t^A=\varnothing)=\sum_{w\in W_N}s(w)\prod_{i,j\in w}\mathcal{P}(\eta_t^{\{a_i,a_j\}}=\varnothing), \quad (10)$$

where W_N is the set of all partitions of the integers 1 to N into pairs $\{i,j\}$, abbreviated to ij with $i<j$, and $s(w)=1$ if the permutation obtained by concatenating the pairs in w is even, otherwise $s(w)=-1$; for example, if $N=6$ and $w=\{13,26,45\}$ then $s(w)=-1$ since 132645 is an odd permutation.

Intermediate cases can be expressed in terms of the extremes $M=0$ and $M=N$ discussed above:

$$\mathcal{P}(\eta_t^A=B)=\binom{N/2}{M/2}^{-1}\sum_{\substack{C\subseteq A\\ |C|=M}}s'(C)\mathcal{P}(\eta_t^C=B)\mathcal{P}(\eta_t^{A\setminus C}=\varnothing), \quad (11)$$

where $A\setminus C$ denotes the set of the elements of A which are not also elements of C. In (11), $s'(C)=1$ if the permutation obtained by arranging the indices of the elements of C in increasing order and then appending the indices of $A\setminus C$, also increasingly ordered, is even, otherwise $s'(C)=-1$; for example, if $N=6$, $M=4$, and $C=\{a_1,a_2,a_3,a_6\}$ then $s'(C)=1$ since 123645 is even. A result corresponding to (11) holds for ABM in terms of joint occupancy probability densities. See Balding[24] for further details and proofs.

Using (1), (11), and the fact that the borders of IP perform ARW, the entire spatial evolution of our model systems can be described. In the case of the coalescing systems, it can be shown[24] that asymptotically CRW and CBM are independent of their initial configurations, given only spatial stationarity. In particular, the joint occupancy probability of two sites in CRW with stationary initial configuration μ is described asymptotically by the limit

$$\lim_{t\nearrow\infty}P(\alpha,t)=\frac{1}{\pi}-\frac{1}{\pi}\exp(-2\alpha^2)+\frac{\alpha}{\sqrt{\pi}}\exp(-\alpha^2)\operatorname{erfc}(\alpha), \quad (12)$$

where $(1/t)P(\alpha,t)$ denotes the probability that sites 0 and $[2\alpha\sqrt{t}\,]$ are both occupied, i.e., $P(\alpha,t)=t\,\mathcal{P}(\{0,[2\alpha\sqrt{t}\,]\}\subseteq\xi_t^{\mu})$ and $[x]$ is the largest integer not greater than x. It follows from the convergence of rescaled CRW to CBM that (12) holds also for CBM with stationary initial configuration if we now interpret $P(\alpha,t)$ as the joint occupancy density at locations x and $x+2\alpha\sqrt{t}$.

Another useful description of spatial structure is $(1/t)Q(\alpha,t)$, the probability that sites 0 and $[2\alpha\sqrt{t}\,]$ are both occupied while all the intervening sites are vacant, which at large times is given by

$$\lim_{t\nearrow\infty}Q(\alpha,t)=\frac{\alpha}{\sqrt{\pi}}\exp(-\alpha^2). \quad (13)$$

Further, joint interparticle distances are asymptotically

$$\lim_{t\nearrow\infty}Q(\alpha,\beta,t)=\frac{\beta}{\pi}\{\exp[-(\beta-\alpha)^2-\alpha^2]-\exp(-\beta^2)\}, \quad (14)$$

in which

$$Q(\alpha,\beta,t)=t^{3/2}\mathcal{P}(\{0,1,2,\ldots,[2\beta\sqrt{t}\,]\}\cap\xi_t^{\mu}=\{0,[2\alpha\sqrt{t}\,],[2\beta\sqrt{t}\,]\}),$$

with $0<\alpha<\beta$. Equations (13) and (14) also apply to CBM on interpreting $Q(\alpha,t)$ and $Q(\alpha,\beta,t)$ as corresponding joint site-occupancy densities. Further, it follows from these equations that the interparticle distances are not independent, so that the influence of a particle on the locations of other particles in CRW and CBM extends beyond nearest neighbors at all times. This contrasts with the result of Arratia[27] who shows that, in dimensions $d>1$, CRW with initially each site occupied converges, after appropriate rescaling, to a homogeneous Poisson process.

Unlike the coalescing case, the spatial structure of the annihilating systems does depend at all times on the initial configuration, through the parameters γ and $\tilde{\gamma}$, and it

seems that explicit asymptotic expressions corresponding to (12) through (14) cannot be obtained. However, in the cases $\gamma=\frac{1}{2}$ and $\tilde{\gamma}=\frac{1}{2}$, joint occupancy probabilities for ARW and ABM are $\frac{1}{4}$ those for CRW and CBM given by (12). Further, Bramson and Griffeath have obtained for these cases an approximation to the interparticle distance corresponding to (13). However, in Sec. V we are able to derive expressions for local fluctuations in the annihilating systems which provide useful descriptions of spatial structure.

V. PERIODIC ABM

The methods used to derive Eq. (11) in Sec. IV suggest an alternative method of obtaining results for the annihilating systems which are of interest from the perspective of the diffusion-controlled reactions applications: calculate exact results for finite systems and take appropriate limits. In order to study finite numbers of particles without distinguishing "end" particles, it is convenient to consider ARW and ABM on finite, periodic state spaces. We focus on ABM because it is more amenable to explicit calculations, but entirely similar arguments apply to ARW.

Suppose that initially N particles are located at sites $X=\{x_1<x_2<\cdots<x_N\}$ on a circle of circumference L and they subsequently perform annihilating Brownian motions. This system is called periodic ABM. The large-time behavior depends strongly on whether N is odd or even. Here, we will assume for convenience that N is even, the odd case is treated elsewhere.[24] Let R_t^X represent half the number of surviving particles at time t. The factorial moments of R_t^X are given by[24]

$$M_{[k]}^X(t)=E(R_t^X!/(R_t^X-k)!)$$
$$=k!\sum_{w\in W_N^k} s(w)\prod_{i,j\in w} f_t^L(x_j-x_i)\ , \tag{15}$$

where $f_t^L(y)$ is the survival probability for two-particle ABM with initial separation y on the circle of circumference L, given by

$$f_t^L(y)=\operatorname{erf}\left[\frac{y}{2\sqrt{t}}\right]+\sum_{j=1}^{\infty}(-1)^j\left[\operatorname{erf}\left[\frac{jL+y}{2\sqrt{t}}\right]-\operatorname{erf}\left[\frac{jL-y}{2\sqrt{t}}\right]\right] \tag{16a}$$

and

$$f_t^L(y)=\frac{4}{\pi}\sum_{j=1}^{\infty}\frac{1}{2j+1}\exp\left[-(2j+1)^2\frac{t\pi^2}{4L^2}\right]\times\sin\left[(2j+1)\frac{\pi y}{L}\right]\ . \tag{16b}$$

In (15), W_N^k is the set of all selections of k disjoint pairs $\{i,j\}\subseteq\{1,\ldots,N\}$ and $s(w)=1$ if the permutation obtained by concatenating the pairs in w and appending the remaining integers in increasing order is even, otherwise $s(w)=-1$. An alternative construction of the sign function $s(w)$ is the following: list the integers 1 to N in increasing order; successively choosing each pair ij in w, count the number of integers in the list between i and j and delete i and j from the list; then $s(w)=(-1)^m$, where m is the total count.

In the important case of the first moment, when $M_{[1]}^X(t)$ is half the expected number of surviving particles, each $w\in W_N^1$ consists of a single pair ij, so the product in (15) is redundant and $s(w)$ is simply $-(-1)^{j-i}$. For example, if initially N particles are independently and uniformly distributed on the circle then the site-occupancy density is

$${}^LC_t^\eta=\frac{N}{L}\frac{N-1}{L}\int_0^L\left[1-\frac{2y}{L}\right]^{N-2}f_t^L(y)dy\ . \tag{17}$$

Notice that ${}^LC_t^\eta$ is also the survival probability for two-particle periodic ABM with initial separation x satisfying, for $\alpha\in[0,L/2)$,

$$\mathcal{P}(x>\alpha)=\left[1-\frac{2\alpha}{L}\right]^{N-1}\ .$$

Substituting (16a) into (17) and taking the limit as N and L increase with $\beta=N/L$ constant, we obtain C_t^η in the Poisson case derived already in (8), but we can now additionally observe that C_t^η in this case is precisely the survival probability for ABM with initially two particles whose separation has the exponential distribution with mean $1/2\beta$. An alternative expression for ${}^LC_t^\eta$ in the uniform case, particularly useful for t large, is obtained on substituting (16b) into (17). This expression has the important property of separation of the space and time variables which facilitates the calculation of higher factorial moments. We omit the details which are tedious, and merely report that ${}^LV_t^\eta$, the variance of the number of surviving particles per unit interval can be obtained. Once again taking the limit as N and L increase in constant ratio β, we obtain V_t^η, the variance of the number of surviving particles per unit interval for ABM in the Poisson case, given by

$$V_t^\eta=\left[2+\frac{4x+3x^3}{\sqrt{(\pi/2)}}\right]C_t^\eta-\frac{2x\beta}{\sqrt{\pi}}-\frac{2x^2\beta}{\pi}-(1-2x^2)C_{2t}^\eta-\frac{1}{\beta}(2x^4+5x^2+1)(C_t^\eta)^2\ , \tag{18}$$

in which x stands for $2\beta\sqrt{2t}$ and C_t^η is given at (8). For large times we have

$$\lim_{t\nearrow\infty}\sqrt{\pi t}\,V_t^\eta=1-\frac{1}{\sqrt{2}}\ , \tag{19}$$

and the same limit holds as $\beta\nearrow\infty$.

Turning now to periodic ABM with an initial configuration of fixed, alternate spacings of sizes $(1-\alpha)L/N$ and $(1+\alpha)L/N$, we obtain, in the limit as L and N increase with $L/N=\lambda$, a constant, two expressions for C_t^η in the alternate spacing case, one of which is given already at (9) and the other is

$$C_t^\eta=\frac{1}{\lambda\pi}\int_0^\pi h(x)dx\ , \tag{20}$$

where

$$h(x)=2\sum_{k=1}^{\infty} g((2k-1)\pi+x)+g((2k-1)\pi-x)$$

and

$$g(y)=\exp(-ty^2/\lambda^2)\frac{\cos(\alpha y)-\cos(y)}{y\sin(y)} .$$

Further, we have in this case a concise expression for the variance

$$V_t^{\eta}=\frac{2}{\lambda\pi}\int_0^{\pi} h(x)[1-h(x)]dx , \tag{21}$$

from which we calculate the large-time behavior

$$\lim_{t\nearrow\infty}\sqrt{\pi t}\,V_t^{\eta}=2\tilde{\gamma}(1-\tilde{\gamma}\sqrt{2}) , \tag{22}$$

and we recall that in this case $\tilde{\gamma}=\frac{1}{2}(1-\alpha^2)$.

VI. COMPARISONS WITH DETERMINISTIC MODELS

The deterministic theory of ABM and CBM is based on the model for colloid coagulation proposed by Smoluchowski[28] and subsequently generalized by the same author to diffusion-controlled reactions.[29] The theory describes the evolution of the mean concentration of particles, ignoring local spatial fluctuations,[30] by writing a classical kinetic equation for the concentration c,

$$\frac{dc}{dt}=-k(t)c^2 . \tag{23}$$

The coefficient $k(t)$ is obtained by treating a surviving particle as a fixed sink and assuming that a diffusion equation describes the motions of the other particles relative to this sink. The sink is destroyed by reaction in the case of ABM, but not for CBM. Notice that, in order that the description of the system is independent of the particle chosen to be the sink, this approach can only be applied if the initial configuration is spatially stationary. In this way Smoluchowski takes approximate account of pairwise correlations in the particle locations, but[10,31-33] higher-order correlations are neglected. The approximation inherent in the Smoluchowski formulation can now be tested by comparing the solutions of the deterministic models with the exact results obtained in Secs. III–V.

As for the exact results, an arbitrary diffusion coefficient may be accommodated by replacing t with $2Dt$; of course, expressions for $k(t)$ must also be multiplied by $2D$.

For the one-dimensional case the relative concentration profile $r(x,t)$ satisfies the diffusion equation

$$\frac{\partial r}{\partial t}=\nabla^2 r , \tag{24}$$

subject to the initial condition $r(x,0)=r_0(x)$ and the boundary condition $r(0,t)=0$. The solution is straightforward[34]

$$r(x,t)=\frac{1}{2\sqrt{(\pi t)}}\int_0^{\infty} r_0(y)\left[\exp\left[\frac{-(x-y)^2}{4t}\right]-\exp\left[\frac{-(x+y)^2}{4t}\right]\right]dy . \tag{25}$$

For the annihilation reaction, the rate coefficient $k(t)$, in-

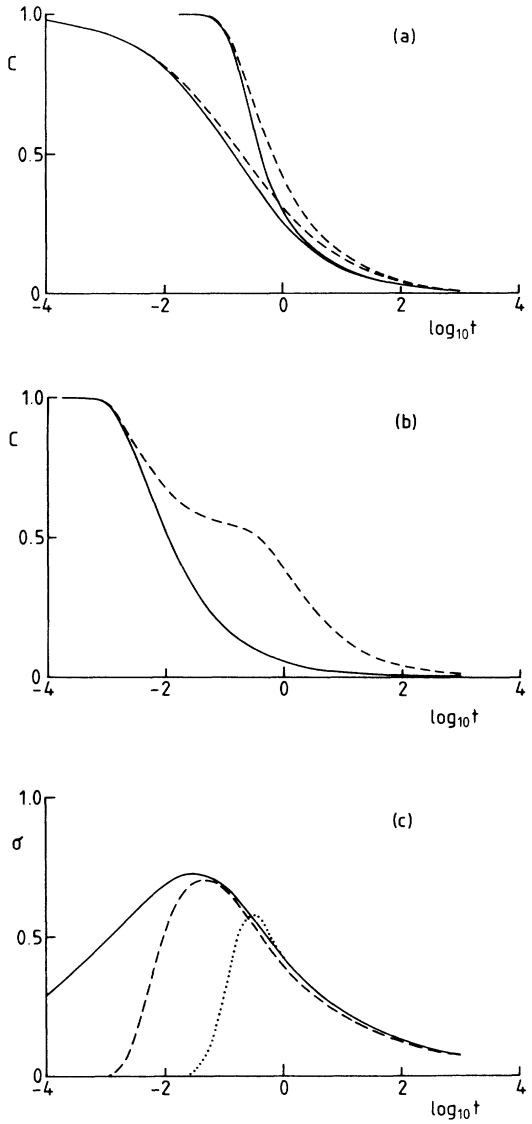

FIG. 1. (a) Exact and deterministic site-occupancy densities for Poisson point process of parameter $\beta=1$ (left-hand curves) and equally spaced points, $\lambda=1$, $\alpha=0$ (right-hand curves). ——, exact solution, Eqs. (8b) and (9b); — — —, deterministic approximation, Eqs. (27) and (29). (b) Exact and deterministic site-occupancy density for pairwise clustered distribution, $\lambda=1$, $\alpha=0.9$. ——, exact solution, Eq. (9b); — — —, deterministic approximation, Eq. (29). (c) Exact site-occupancy standard deviations: ——, Poisson process of parameter $\beta=1$; — — —, pairwise clustered distribution, $\lambda=1$, $\alpha=0.8$; · · · ·, equally spaced points, $\lambda=1$, $\alpha=0$.

troduced in (23), is the total flux into the reactive boundary, given by

$$k(t)=\frac{1}{2t\sqrt{(\pi t)}}\int_0^\infty [r_0(y)+r_0(-y)] \times y \exp\left[\frac{-y^2}{4t}\right]dy \ . \tag{26}$$

In the case that the particle locations initially form a parameter-β Poisson process, we have $r_0(x)=\beta$ for all x. The rate coefficient is $k(t)=2/\sqrt{(\pi t)}$ and hence the deterministic solution for the site occupancy density of ABM in the Poisson case is

$$c(t)=\left[\frac{1}{\beta}+4\sqrt{t/\pi}\right]^{-1}, \tag{27}$$

which may be compared with the exact solutions given at (8). At large times $c(t)$ is approximately $\frac{1}{4}\sqrt{\pi/t}$, a factor of $\pi/2$ larger than the exact value, which was noted by Torney and McConnell.[11]

The same model is applied to the coalescence reaction but with $k(t)$ reduced by a factor of 2 so that the relative error is also $\pi/2$ at large times in this case.

Turning now to the case of initial alternating interparticle distances, for which the exact solution is given at (9), the relative concentration profile $r_0(x)$ has atoms of unit probability mass at each point $i\lambda$ and $(j-\alpha)\lambda$ for every nonzero even integer i and every odd integers j. Therefore the rate coefficient for the annihilation reaction is

$$k(t)=\frac{\lambda}{2t\sqrt{(\pi t)}}\sum_{i=1}^{\infty} f(2i-1+\alpha)+2f(2i)+f(2i-1-\alpha) , \tag{28}$$

where $f(x)=x\exp[-x^2\lambda^2/(4t)]$, and hence the site occupancy density is

$$c(t)=\frac{1}{\lambda}\left[\sum_{k=1}^{\infty}\operatorname{erfc}\left[\frac{2k-1+(-1)^k}{(4/\lambda)\sqrt{t}}\right] +\operatorname{erfc}\left[\frac{2k-1+(-1)^k(2\alpha-1)}{(4/\lambda)\sqrt{t}}\right]\right]^{-1} . \tag{29}$$

Asymptotically, $c(t)$ is $\frac{1}{4}\sqrt{\pi/t}$ for all α and so the deterministic model fails to distinguish the effect of the initial configuration on the long-time kinetics.

Comparisons between exact solutions and the deterministic approximations are shown for several cases in Fig. 1. In all cases the deterministic formula overestimates the site-occupancy density, but a particularly striking discrepancy is found when the clustering is strong, such as the case $\alpha=0.9$, $\lambda=1$, where the deterministic solution shows two phases, one associated with geminate recombination (within the pair) and one associated with recombination outside the pair; the exact solution shows no such behavior, but follows the geminate recombination solution over almost the whole range. In the region dominated by the long-time asymptotics, the deterministic approximation is a factor of $\pi/(4\tilde{\gamma})$ larger than the exact solution, which is arbitrarily large as the pairwise clustering becomes more pronounced.

Comparisons between deterministic and stochastic solutions can also be made for the distribution of interparticle distances in the coalescing systems. This comparison is possible because the deterministic theory calculates the relative concentration profile $r(x,t)$ about a typical particle. Interpreting $r(x,t)$ as the weight function of a nonhomogeneous Poisson point process, the probability $R(\alpha,t)$ that the distance to the nearest neighbor is greater than α is given by

$$R(\alpha,t)=\exp\left[-\int_0^\alpha r(x,t)dx\right] . \tag{30}$$

In the case that the initial configuration is parameter-β Poisson, we have $r(x,t)=\beta\operatorname{erf}(x/2\sqrt{t})$ and hence

$$R(\alpha,t)=\exp\left\{-\beta\left[\alpha\operatorname{erf}\left[\frac{\alpha}{2\sqrt{t}}\right]-\frac{1}{\sqrt{\pi}}(1-e^{-\alpha^2/4t})\right]\right\} ,$$

which is approximately $\exp(-\beta\alpha^2/2\sqrt{(\pi t)})$ for t large. Similarly, for the pairwise clustered initial configuration with alternating distances, the asymptotic interparticle distance has the same distribution with β replaced by $1/\lambda$. Comparison with the exact results given in Sec. IV shows that the interparticle distance is not correctly described by the deterministic theory.

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[1]P. Clifford, N. J. B. Green, and M. J. Pilling, J. R. Stat. Soc. B **49**, 266 (1987).
[2]P. Clifford, N. J. B. Green, M. J. Oldfield, M. J. Pilling, and S. M. Pimblott, J. Chem. Soc. Faraday Trans. 1 **82**, 2673 (1986).
[3]P. Clifford, N. J. B. Green, M. J. Pilling, S. M. Pimblott, and W. G. Burns, Radiat. Phys. Chem. **30**, 125 (1987).
[4]A. A. Ouchinnikov and Ya. B. Zeldovich, Chem. Phys. **28**, 215 (1978).
[5]D. Toussaint and F. Wilczek, J. Chem. Phys. **78**, 2642 (1983).
[6]K. Kang and S. Redner, Phys. Rev. A **32**, 435 (1985).
[7]M. D. Donsker and S. R. S. Varadhan, Commun. Pure Appl. Math. **28**, 525 (1975).
[8]T. Eisele and R. Lang, Prob. Th. Rel. Fields **74**, 125 (1987).
[9]M. Bramson and D. Griffeath, Ann. Prob. **8**, 183 (1980).
[10]N. G. Van Kampen, Int. J. Quantum Chem. **16**, 101 (1982).
[11]D. C. Torney and H. M. McConnell, J. Phys. Chem. **87**, 1941 (1983).

[12]D. C. Torney and H. M. McConnell, Proc. R. Soc. London, Ser. A **387**, 147 (1983).
[13]M. Burschka, J. Stat. Phys. **45**, 715 (1986).
[14]A. A. Lushnikov, Phys. Lett. A **120**, 135 (1987).
[15]D. Balding, P. Clifford, N. J. B. Green, Phys. Lett. A **126**, 481 (1988).
[16]J. L. Spouge, Phys. Rev. Lett. **60**, 871 (1988).
[17]J. L. Spouge, J. Phys. A **21**, 4183 (1988).
[18]D. Balding, J. Appl. Prob. **25**, 733 (1988).
[19]P. Dittrich, Prob. Th. Rel. Fields **79**, 115 (1988).
[20]D. Williams, *Diffusions, Markov Processes and Martingales* (Wiley, New York, 1979).
[21]D. Griffeath, *Additive and Cancellative Interacting Particle Systems,* Vol. 724 of *Springer Lecture Notes in Mathematics* (Springer-Verlag, Berlin, 1979).
[22]T. Liggett, *Interacting Particle Systems* (Springer-Verlag, New York, 1985).
[23]P. Clifford and A. W. Sudbury, Biometrika **60**, 581 (1973).
[24]D. Balding, Ph.D. thesis, Oxford University, Oxford, U.K., 1989.
[25]*Handbook of Mathematical Functions,* edited by M. Abramowitz and I.A. Stegun (Dover, New York, 1965).
[26]S. Karlin and L. McGregor, Pac. J. Math. **9**, 1141 (1959).
[27]R. Arratia, Ann. Prob. **9**, 909 (1981).
[28]M. von Smoluchowski, Phys. Z. **17**, 557 (1916); **17**, 585 (1916).
[29]M. von Smoluchowski, Z. Phys. Chem. **92**, 129 (1917).
[30]J. Keizer, J. Phys. Chem. **85**, 940 (1981).
[31]T. R. Waite, Phys. Rev. **107**, 463 (1957).
[32]R. M. Noyes, Prog. React. Kinet. **1**, 128 (1961).
[33]N. J. B. Green, Chem. Phys. Lett. **110**, 280 (1984).
[34]H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids,* 2nd ed. (Oxford, New York, 1959).