Complete Exact Solution of Diffusion-Limited Coalescence, $A + A \rightarrow A$

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Some models of diffusion-limited reaction processes in one dimension lend themselves to exact analysis. The known approaches yield exact expressions for a limited number of quantities of interest, such as the particle concentration, or the distribution of distances between nearest particles. However, a full characterization of a particle system is provided only by the infinite hierarchy of multiple-point density correlation functions. We derive an exact description of the full hierarchy of correlation functions for the diffusion-limited irreversible coalescence process $A + A \rightarrow A$. [S0031-9007(98)07742-4]

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Nonequilibrium kinetics of diffusion-limited reactions has been the subject of much recent interest [1–6]. In contrast to equilibrium systems—which are best analyzed with standard thermodynamics—or reaction-limited processes—whose kinetics is well described by classical rate equations [7,8]—there is no general approach to nonequilibrium, diffusion-limited reactions. Some diffusion-limited processes in one dimension can be approached analytically, and exact results for multiple-point density correlation functions have been obtained with the free Majorana fermions formalism [9,10]. In this Letter, we derive an exact analytic recursion relation for the full hierarchy of multiple-point density correlation functions for the irreversible diffusion-limited coalescence process $A + A \rightarrow A$, following the method of empty intervals [11–13].

Our model [11–13] is defined on the line $-\infty < x < \infty$. Particles A are represented by points which perform unbiased diffusion with a diffusion constant D. When two particles meet, they merge into one particle which continues diffusing with the same diffusion constant D as the reacting particles. Since the reaction step is infinitely fast, the system models the *diffusion-limited* coalescence process $A + A \rightarrow A$.

An exact treatment of the problem is possible through the method of empty intervals, known also as the method of interparticle distribution functions (IPDF). The key parameter is $E(x, y; t)$—the probability that the interval $[x, y]$ is empty (contains no particles) at time t. Particles just at the edge of an empty interval may diffuse into or out of the interval, affecting the probability E. With this observation in mind, one can write down a rate equation for the empty interval probability [11,12]. For the model at hand, the rate equation is

$$\frac{\partial E(x, y; t)}{\partial t} = D\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)E(x, y; t). \qquad (1)$$

The coalescence reaction imposes the boundary condition

$$\lim_{y\uparrow x \text{ or } x\downarrow y} E(x, y; t) = 1, \qquad (2)$$

and in addition, as long as there are any particles left in the system,

$$\lim_{\substack{x\to-\infty \\ y\to+\infty}} E(x, y; t) = 0. \qquad (3)$$

From $E(x, y; t)$ one can derive useful parameters, such as the concentration of particles,

$$\rho(x; t) = -\frac{\partial}{\partial y} E(x, y; t)|_{y=x}, \qquad (4)$$

or the probability that given a particle at x the next nearest particle is at y (the IPDF),

$$p(x, y; t) = \rho(x, y; t)^{-1} \frac{\partial^2}{\partial x \partial y} E(x, y; t). \qquad (5)$$

While such a level of description affords us invaluable physical insights into many interesting applications [13], it does not characterize the system completely. For that we need the multiple-point density correlation functions $\rho_n(x_1, x_2, \dots, x_n; t)$, i.e., the joint probability density to find n particles at $x_1, x_2, \dots, x_n$ at time t. For $n = 1$, $\rho_1(x, t)$ is identical with the particle concentration of Eq. (4). However, a complete characterization of the system requires knowledge of the *full* hierarchy of correlation functions $\{\rho_n\}_{n=1}^{\infty}$.

The multiple-point correlation functions may be obtained from a generalization of the method of empty intervals [12]. Let $E_n(x_1, y_1, x_2, y_2, \dots, x_n, y_n; t)$ be the joint probability that the intervals $[x_i, y_i]$ ($i = 1, 2, \dots, n$ are empty at time t. The intervals are nonoverlapping, and ordered: $x_1 < y_1 < \dots < x_n < y_n$. Then, the n-point correlation function is given by

$$\rho_n(x_1, \dots, x_n; t) = (-1)^n \frac{\partial^n}{\partial y_1 \cdots \partial y_n} E_n(x_1, y_1, \dots, x_n, y_n; t)|_{y_1=x_1,\dots,y_n=x_n}. \qquad (6)$$

Doering [12] has shown that for irreversible coalescence the E_n satisfy the partial differential equation,

$$\frac{\partial}{\partial t} E_n(x_1, y_1, \dots, x_n, y_n; t) = D\left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \cdots + \frac{\partial^2}{\partial x_n^2} + \frac{\partial^2}{\partial y_n^2}\right) E_n \,, \tag{7}$$

with the boundary conditions

$$\lim_{x_i \uparrow y_i \text{ or } y_i \downarrow x_i} E_n(x_1, y_1, \dots, x_n, y_n; t) = E_{n-1}(x_1, y_1, \dots, \cancel{x}_i, \cancel{y}_i, \dots, x_n, y_n; t) \,, \tag{8}$$

and

$$\lim_{y_i \uparrow x_{i+1} \text{ or } x_{i+1} \downarrow y_i} E_n(x_1, y_1, \dots, x_n, y_n; t) = E_{n-1}(x_1, y_1, \dots, \cancel{y}_i, \cancel{x}_{i+1}, \dots, x_n, y_n; t) \,. \tag{9}$$

For convenience, we use the notation that crossed out arguments (e.g., $\cancel{x}_i$) have been removed. The E_n are tied together in an hierarchical fashion through the boundary conditions (8) and (9): one must know E_{n-1} in order to compute E_n.

We now provide a full solution of the E_n. At the level of $n = 2$, the solution is [14]

$$\begin{aligned} E_2(x_1, y_1, x_2, y_2; t) = {} & E(x_1, y_1; t) E(x_2, y_2; t) \\ & - E(x_1, x_2; t) E(y_1, y_2; t) \\ & + E(x_1, y_2; t) E(y_1, x_2; t) \,. \end{aligned} \tag{10}$$

Clearly, each term on the right-hand side (r.h.s.) of Eq. (10) satisfies Eq. (7), as well as the boundary conditions (8) and (9)—since $E(x, x; t) = 1$ [Eq. (2)]. Similarly, E_n can also be expressed in terms of products of E's for single intervals:

$$E_n(x_1, y_1, \dots, x_n, y_n; t) = \sum_{p=1}^{(2n-1)!!} \sigma_p E(z_{1,p}, z_{2,p}; t) E(z_{3,p}, z_{4,p}; t) \cdots E(z_{2n-1,p}, z_{2n,p}; t) \,. \tag{11}$$

Here $z_{1,p}, z_{2,p}, \dots, z_{2n,p}$ symbolize an *ordered* permutation, p, of the variables $x_1, y_1, \dots, x_n, y_n$, such that

$$z_{1,p} < z_{2,p}, z_{3,p} < z_{4,p}, \dots, z_{2n-1,p} < z_{2n,p} \,,$$

and

$$z_{1,p} < z_{3,p} < z_{5,p} \cdots < z_{2n-1,p} \,. \tag{12}$$

There are exactly $(2n - 1)!! = 1 \times 3 \times \cdots \times (2n - 1)$ such permutations. σ_p is $+1$ for even permutations (permutations that require an even number of exchanges between pairs of variables), or -1 for odd permutations.

Equation (11) can be proved by induction. For $n = 1$ it reduces to $E_1(x, y; t) = E(x, y; t)$, and for $n = 2$ it reduces to Eq. (10), as required. We need show only that if (11) is true for $n - 1$ ($n \geq 3$), then it is also valid for n. It is easy to see that because each of the E's satisfies Eq. (1), the proposed E_n satisfies Eq. (7). Now test the boundary conditions: Suppose that $x_i = y_i$. The permutations in the r.h.s. of (11) are divided into two groups: (a) those which leave (x_i, y_i) as an argument of one of the E's in the product, and (b) those which separate x_i and y_i into different E's in the product. The permutations in group (a) add up to $E_{n-1}(x_1, y_1, \dots, \cancel{x}_i, \cancel{y}_i, \dots, x_n, y_n; t)$, as required by the boundary condition (8). This is because $E(x_i, y_i;) = 1$ [from Eq. (2)], and because of the induction assumption regarding the validity of (11) for $n - 1$. Notice that the parity of the permutations in group (a) is the same as if x_i and y_i were removed. On the other hand, the permutations in group (b) add up to zero, for the following reason: Suppose that in some permutation x_i and y_i are paired with other variables z_1 and z_2; (x_i, z_1) and (y_i, z_2). Then, there exists a similar permutation of the variables $x_1, y_1, \dots, x_n, y_n$ where individual pairs remain in the same order, but now the pairings of x_i and y_i are exchanged: (x_i, z_2) and (y_i, z_1). When $x_i = y_i$, the product of the E's in these two permutations is identical. But the parity of the two permutations is opposite, and so they add up to zero. The same is true if the pairings of x_i and y_i are (z_1, x_i) and (z_2, y_i), or (z_1, x_i) and (y_i, z_2). [Notice that the pairings (x_i, z_1) and (z_2, y_i) cannot occur, because of the required ordering, Eq. (12).] In summary, the boundary condition (8) is satisfied. The proof of (9) follows a similar line of reasoning.

The ordered permutations of the end points of n intervals ($2n$ variables) may be constructed *recursively* in the following way. The order constraint of Eq. (12) requires that $z_{1,p} = x_1$, for all permutations p. Set then $z_1 = x_1$, and z_2 equal to one of the other $y_1, \dots, x_n, y_n$ variables. Then, arrange the remaining $2n - 2$ variables in all their ordered permutations. Finally, repeat this procedure, selecting sequentially $z_2 = y_1, x_2, y_2, \dots, x_n, y_n$. Thus, the number of permutations for the end points of n intervals, $N(n)$, satisfies the recursion relation $N(n) = (2n - 1)N(n - 1)$, and therefore $N(n) = (2n - 1)!!$—since $N(1) = 1$. The recursive construction allows us also to express E_n more compactly, in terms of E_{n-1},

$$\begin{aligned} E_n(x_1, y_1, \dots, x_n, y_n; t) = {} & +\sum_{j=1}^{n} E(x_1, y_j; t) E_{n-1}(\cancel{x}_i, y_1, \dots, x_j, \cancel{y}_j, \dots, x_n, y_n; t) \\ & - \sum_{j=2}^{n} E(x_1, x_j; t) E_{n-1}(\cancel{x}_1, y_1, \dots, \cancel{x}_j, y_j, \dots, x_n, y_n; t) \,. \end{aligned} \tag{13}$$

Until now we have ignored the issue of *initial conditions*. For the solution (11) to work, it is required that the same relation be satisfied at time $t = 0$ as well. This seems at first sight a formidable restriction, but fortunately some of the most important situations are unaffected by it. If the particles are initially randomly distributed, independently from each other, at a homogeneous concentration ρ_0, then $E(x, y; 0) = e^{-\rho_0(y-x)}$ and

$$E_n(x_1, y_1, \ldots, x_n, y_n; 0) = e^{-\rho_0[(y_1-x_1)+\cdots+(y_n-x_n)]}. \quad (14)$$

One can easily check that Eq. (11) is satisfied. In this case, Eq. (6) yields the obvious relation: $\rho(x_1, x_2, \ldots, x_n; 0) = \rho_0^n$. This uncorrelated random initial distribution gets quickly correlated with time.

Another interesting situation is the state of the system in the long-time asymptotic limit. It can be shown that the system arrives at a *universal* asymptotic state, independent of the initial distribution of particles. (This excludes some exotic situations, such as fractal initial distributions.) The long-time asymptotic solution of Eq. (1), with the boundary conditions (2) and (3), is

$$E(x, y; t) = \operatorname{erfc}\left(\frac{y - x}{\sqrt{8Dt}}\right). \quad (15)$$

Using Eq. (4), the corresponding long-time asymptotic concentration is

$$\rho_{\text{asymp}}(x; t) = \frac{1}{\sqrt{2\pi Dt}}. \quad (16)$$

Using Eqs. (13) and (6) one can produce the n-point correlations. For example, for $n = 2$ we get

$$\frac{\rho_2(x_1, x_2; t)}{\rho_{\text{asymp}}^2} = 1 - e^{-2\xi^2} + \sqrt{\pi}\,\xi e^{-\xi^2} \operatorname{erfc}(\xi), \quad (17)$$

where we used the notation $\xi = (x_2 - x_1)/\sqrt{8Dt}$, and for $n = 3$

$$\begin{aligned}\frac{\rho_3(x_1, x_2, x_3; t)}{\rho_{\text{asymp}}^3} = {} & 1 - e^{-2\xi_{21}^2} - e^{-2\xi_{32}^2} - e^{-2\xi_{31}^2} + 2e^{-\xi_{21}^2-\xi_{32}^2-\xi_{31}^2} + \sqrt{\pi}\,\xi_{21}(e^{-\xi_{21}^2} - e^{-\xi_{32}^2-\xi_{31}^2}) \operatorname{erfc}(\xi_{21}) \\ & + \sqrt{\pi}\,\xi_{32}(e^{-\xi_{32}^2} - e^{-\xi_{21}^2-\xi_{31}^2}) \operatorname{erfc}(\xi_{32}) + \sqrt{\pi}\,\xi_{31}(e^{-\xi_{31}^2} - e^{-\xi_{21}^2-\xi_{32}^2}) \operatorname{erfc}(\xi_{31}), \end{aligned} \quad (18)$$

where now $\xi_{ij} = (x_i - x_j)/\sqrt{8Dt}$ (notice that $\xi_{31} = \xi_{32} + \xi_{21}$ is *not* an independent variable).

In Fig. 1, we show the two-point correlation function in the long-time asymptotic limit [Eq. (17)]. We see that the two points become uncorrelated as the distance between them increases, but that there is an effective strong repulsive interaction (due to the coalescence reaction) between nearby particles. Interestingly, the two-point correlation is a monotonous function of the distance. A simple convolution of the distances between nearest particles predicts an oscillating tail [15].

The three-point correlation function, Eq. (18), is a bit harder to illustrate. Instead of a full description, in Fig. 2 we compare $\rho_3(x_1, x_2, x_3)$ to $\rho_2(x_1, x_2)\rho_2(x_2, x_3)/\rho(x_2)$ (in the spirit of the truncation ansatz that might be used in a Kirkwood approximation, say) along the line $x_3 - x_2 = x_2 - x_1$. Again, we see that as the distance between the three particles increases they become rapidly uncorrelated, but that the approximation ansatz fails for short distances, due to reactions.

In summary, we have obtained the complete hierarchy of n-point density correlation functions for the diffusion-limited irreversible coalescence process, $A + A \to A$, in one dimension. The recursive form of Eq. (13) allows one to obtain successive correlations in a mechanical fashion. We emphasize, however, that the solution is valid only when the initial conditions satisfy the same hierarchy, Eq. (13). While this includes the important

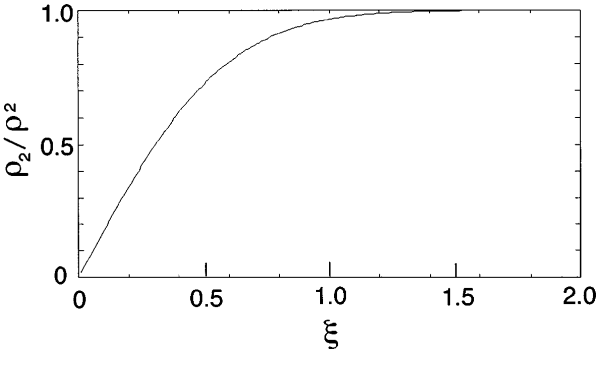

FIG. 1. Two-point correlation function for the coalescence process in the long-time asymptotic limit. Shown is $\rho_2(\xi)/\rho_{\text{asymp}}^2$ vs ξ.

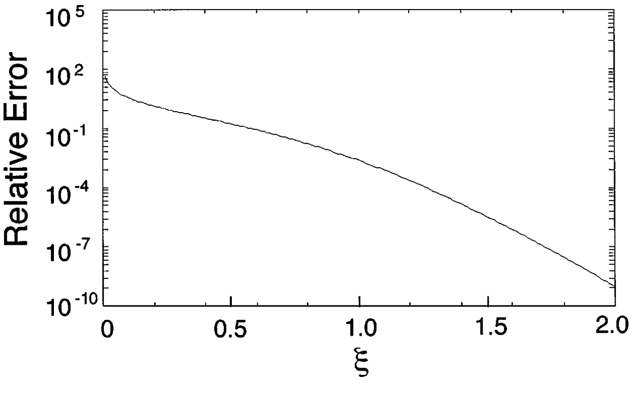

FIG. 2. Three-point correlation function for the coalescence process in the long-time asymptotic limit. Plotted is the relative error made by the Kirkwood approximation, $(\rho_{\text{Kirkwood}} - \rho_3)/\rho_3$, for the line $\xi_{21} = \xi_{32} \equiv \xi$. The Kirkwood approximation in this case is $\rho_{\text{Kirkwood}} = \rho_2(\xi)^2/\rho_{\text{asymp}}$.

cases of initially uncorrelated particles and the long-time asymptotic behavior (which is independent of initial conditions), it remains an open question to determine the full class of systems which satisfy this requirement.

The more general problems of reversible coalescence—when the back reaction $A \to A + A$ is allowed—and coalescence with different kinds of particle input can also be handled, in principle, by the empty interval approach. That is, in both cases (even both at the same time) there is a closed hierarchy of linear partial differential equations, coupled through their boundary conditions, similar to Eqs. (7), (8), and (9) [12]. But the linear operators involved break the simple x-y symmetry of Eq. (7), and a complete solution remains an open challenge. The empty intervals formalism can also be extended to other diffusion-limited processes through a simple variable change [9,10,16–18]. It will also be interesting to study how the present method can be extended to those cases.

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