Correlation functions for diffusion-limited annihilation, $A+A\to 0$

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The full hierarchy of multiple-point correlation functions for diffusion-limited annihilation, $A+A\to 0$, is obtained analytically and explicitly, following the method of intervals. In the long-time asymptotic limit, the correlation functions of annihilation are identical to those of coalescence, $A+A\to A$, despite differences between the two models in other statistical measures, such as the interparticle distribution function.

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The kinetics of nonequilibrium processes, in particular diffusion-limited reactions, have attracted much recent interest [1–8]. Because of the lack of a comprehensive approach for the study of such systems, models that yield to an exact analysis are of prime importance. In this respect, none have been studied more than diffusion-limited annihilation, $A+A\to 0$ [9–28], and coalescence, $A+A\to A$ [9,13–15,17,21,23,26,28–33]. Known exact results include the time dependence of the particle concentration and the two-point correlation function (for finding two particles at two different points, simultaneously). It has also been shown that the full hierarchy of n-point correlation functions for the two processes is identical [21,23,34,35], but explicit expressions for $n>3$ are unavailable.

Here we attack the problem of correlation functions for annihilation, using the method of parity intervals (or even/odd intervals) [20,26,27,36]. We recover the identity relation of the n-point correlation functions for annihilation and coalescence, and we derive *explicit* expressions, valid in the long time asymptotic limit, for all n.

Consider the annihilation model, 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 annihilate instantly. Since the reaction step is infinitely fast, the system models the *diffusion-limited* annihilation process $A+A\to 0$.

An exact treatment of the problem is possible through the method of parity intervals [20,26,27,36]. The key parameter is $G(x,y;t)$—the probability that the interval $[x,y]$ contains an even number of particles at time t [37]. Particles near the edges of an interval may diffuse into or out of the interval, affecting the probability G. (On the other hand, reactions inside the interval cannot affect its parity.) With this observation in mind, one derives a rate equation for the probability $G(x,y;t)$ [26]:

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

The annihilation reaction imposes the boundary condition

$$\lim_{x\uparrow y \text{ or } y\downarrow x} G(x,y;t)=1, \tag{2a}$$

and G must also obey the conditions required from a probability density function. If the initial distribution of particles is random, then $G(x,y;0)=\frac{1}{2}+\frac{1}{2}\exp[-2c_0(y-x)]$, where c_0 is their initial density. In this case we have the additional boundary condition

$$\lim_{x\to-\infty \text{ or } y\to\infty} G(x,y;t)=\frac{1}{2}. \tag{2b}$$

From $G(x,y;t)$ one can derive the particle concentration

$$\rho(x;t)=-\frac{\partial}{\partial y}G(x,y;t)\big|_{y=x}. \tag{3}$$

Let $\rho_n(x_1,x_2,\ldots,x_n;t)$ be the n-point density correlation function for finding particles at each of the locations $x_1,x_2,\ldots,x_n$ at time t. The particle concentration, $\rho(x,t)\equiv\rho_1(x,t)$, represents merely the first term in the hierarchy $\{\rho_n\},n=1,2,\ldots$.

The correlation functions may be obtained from a generalization of the method of parity intervals in the following way. Let $H_n(x_1,y_1,\overline{x_2,y_2},\ldots,x_n,y_n;t)$ be the joint probability that the interval $[x_1,y_1]$ contains an even number of particles, $[x_2,y_2]$ contains an odd number, etc. (odd intervals are denoted by an overbar), at time t. The intervals are nonoverlapping, and ordered: $x_1<y_1<\cdots<x_n<y_n$. Let $F_n(x_1,y_1,x_2,y_2,\ldots,x_n,y_n;t)$ denote the probability that the total number of particles contained in $\cup_{i=1}^n[x_i,y_i]$ is even. Thus,

$$F_1(x_1,y_1;t)=H_1(x_1,y_1;t)=G(x_1,y_1;t), \tag{4a}$$

$$F_2(x_1,y_1,x_2,y_2;t)=H_2(x_1,y_1,x_2,y_2;t)+H_2(\overline{x_1,y_1},\overline{x_2,y_2};t), \tag{4b}$$

and, in general, F_n is expressible as a sum of 2^{n-1} H_n functions, corresponding to the different combinations of interval parities that contribute to a total number of particles that is even. Then, in view of Eq. (3), the n-point correlation function is given by

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$$\rho_n^{\mathrm{anni}}(x_1,\ldots,x_n;t) = \frac{(-1)^n}{2^{n-1}}\frac{\partial^n}{\partial y_1\cdots\partial y_n} \times F_n(x_1,y_1,\ldots,x_n,y_n;t)\big|_{y_1=x_1,\ldots,y_n=x_n}. \tag{5}$$

The H_n satisfy a $2n$-dimensional diffusion equation, analogous to Eq. (1), and for similar reasons. However, the boundary conditions of this equation are complicated by the following fact. For $y_i \to x_{i+1}$, a particle moving from the ith interval to the $(i+1)$th interval, or vice versa, would flip the parity of the two adjacent intervals. On the other hand, F_n satisfies the same diffusion equation as H_n,

$$\frac{\partial}{\partial t}F_n(x_1,y_1,\ldots,x_n,y_n;t) = D\left(\frac{\partial^2}{\partial x_1^2}+\frac{\partial^2}{\partial y_1^2}+\cdots+\frac{\partial^2}{\partial x_n^2}+\frac{\partial^2}{\partial y_n^2}\right)F_n, \tag{6}$$

but the boundary conditions are simpler: F_n contains also the case where the parity of the intervals i and $(i+1)$ is flipped, so it is not affected by a particle hopping between the two intervals. If interval i is shrunk to zero, Eq. (2a) yields the boundary condition

$$\lim_{x_i\uparrow y_i \text{ or } y_i\downarrow x_i} F_n(x_1,y_1,\ldots,x_n,y_n;t) = F_{n-1}(x_1,y_1,\ldots,\cancel{x}_i,\cancel{y}_i,\ldots,x_n,y_n;t), \tag{7a}$$

where we use the notation that crossed out arguments (e.g., $\cancel{x}_i$) have been removed. If the endpoints of two adjacent intervals are brought together, the intervals merge, resulting in the boundary condition

$$\lim_{y_i\uparrow x_{i+1} \text{ or } x_{i+1}\downarrow y_i} F_n(x_1,y_1,\ldots,x_n,y_n;t) = F_{n-1}(x_1,y_1,\ldots,\cancel{y}_i,\cancel{x}_{i+1},\ldots,x_n,y_n;t). \tag{7b}$$

Finally, for a random initial distribution of particles, we have

$$\lim_{x_1\to-\infty \text{ or } y_n\to\infty} F_n(x_1,y_1,\ldots,x_n,y_n;t) = \frac{1}{2}. \tag{7c}$$

The F_n are tied together in a hierarchical fashion through the boundary conditions (7a) and (7b): one must know F_{n-1} in order to compute F_n. At the root of the hierarchy, $F_1 = G$ is obtained from Eqs. (1) and (2).

The problem posed by Eqs. (1), (2), (6), (7) is similar to that of diffusion-limited coalescence, $A+A\to A$ [32]. In that case one defines $E_n(x_1,y_1,\ldots,x_n,y_n;t)$ as the joint probability of finding the intervals $[x_i,y_i], i=1,2,\ldots,n$, *empty* at time t. $E_1(x,y;t)\equiv E(x,y;t)$ satisfies the same equation as Eq. (1),

$$\frac{\partial}{\partial t}E(x,y;t) = D\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right)E(x,y;t), \tag{8}$$

with the boundary conditions

$$\lim_{x\uparrow y \text{ or } y\downarrow x} E(x,y;t) = 1, \tag{9a}$$

$$\lim_{x\to-\infty \text{ or } y\to\infty} E(x,y;t) = 0. \tag{9b}$$

Note the difference between the boundary conditions (2b) and (9b). Likewise, E_n satisfies the same equation as Eq. (6),

$$\frac{\partial}{\partial t}E_n(x_1,y_1,\ldots,x_n,y_n;t) = D\left(\frac{\partial^2}{\partial x_1^2}+\frac{\partial^2}{\partial y_1^2}+\cdots+\frac{\partial^2}{\partial x_n^2}+\frac{\partial^2}{\partial y_n^2}\right)E_n, \tag{10}$$

with boundary conditions analogous to Eqs. (7a) and (7b),

$$\lim_{x_i\uparrow y_i \text{ or } y_i\downarrow x_i} E_n(x_1,y_1,\ldots,x_n,y_n;t) = E_{n-1}(x_1,y_1,\ldots,\cancel{x}_i,\cancel{y}_i,\ldots,x_n,y_n;t), \tag{11a}$$

$$\lim_{y_i\uparrow x_{i+1} \text{ or } x_{i+1}\downarrow y_i} E_n(x_1,y_1,\ldots,x_n,y_n;t) = E_{n-1}(x_1,y_1,\ldots,\cancel{y}_i,\cancel{x}_{i+1},\ldots,x_n,y_n;t), \tag{11b}$$

but

$$\lim_{x_1\to-\infty \text{ or } y_n\to\infty} E_n(x_1,y_1,\ldots,x_n,y_n;t) = 0, \tag{11c}$$

instead of Eq. (7c). The n-point correlation function for coalescence is

$$\rho_n^{\mathrm{coal}}(x_1,\ldots,x_n;t) = (-1)^n\frac{\partial^n}{\partial y_1\cdots\partial y_n} \times E_n(x_1,y_1,\ldots,x_n,y_n;t)\big|_{y_1=x_1,\ldots,y_n=x_n}. \tag{12}$$

Equations (1), (2), (6), (7), and (8)–(11) imply that the solutions for F_n and E_n are simply related,

$$F_n(x_1,y_1,\ldots,x_n,y_n;t) = \frac{1}{2}+\frac{1}{2}E_n(x_1,y_1,\ldots,x_n,y_n;t), \tag{13}$$

provided that the same relation holds also for the initial conditions. Suppose that the initial distribution of particles is random, with initial concentration c_0^{anni} for annihilation and c_0^{coal} for coalescence. Then $E_n(x_1,\ldots,y_n;0) = \exp[-c_0^{\mathrm{coal}}(y_1-x_1+\cdots+y_n$

$-x_n)]$, while $F_n(x_1,\ldots,y_n;0)=\frac{1}{2}+\frac{1}{2}\exp[-2c_0^{\mathrm{anni}}(y_1-x_1+\cdots+y_nF_n(x_1,\ldots,y_n;0)=\frac{1}{2}12+\frac{1}{2}12\exp[-2c_0^{\mathrm{anni}}(y_1-x_1+\cdots+y_n-x_n)]$. Thus, the relation (13) is satisfied if $c_0^{\mathrm{anni}}=\frac{1}{2}c_0^{\mathrm{coal}}$.
Moreover, Eqs. (5) and (12) imply that in this case

$$\rho_n^{\mathrm{anni}}(x_1,\ldots,x_n;t)=\left(\frac{1}{2}\right)^n\rho_n^{\mathrm{coal}}(x_1,\ldots,x_n;t) \tag{14}$$

for all n. In other words, *the n-point correlation functions for annihilation and coalescence are identical*, as already found by others [21,23,34,35].

We now produce explicit expressions for the n-point correlation functions in the long-time asymptotic limit. Recall first the solution for E_n. For $n=2$ the solution is [38]

$$\begin{aligned}E_2(x_1,y_1,x_2,y_2;t)=&E(x_1,y_1;t)E(x_2,y_2;t)\\&-E(x_1,x_2;t)E(y_1,y_2;t)\\&+E(x_1,y_2;t)E(y_1,x_2;t),\end{aligned} \tag{15}$$

where $E(x,y;t)$ is the solution of Eqs. (8) and (9). Generally, for $n\geqslant 2$ [32],

$$\begin{aligned}E_n(x_1,y_1,\ldots,x_n,y_n;t)=&\sum_{p=1}^{(2n-1)!!}\sigma_pE(z_{1,p},z_{2,p};t)\\&\times E(z_{3,p},z_{4,p};t)\cdots\\&\times E(z_{2n-1,p},z_{2n,p};t),\end{aligned} \tag{16}$$

where $z_{1,p},z_{2,p},\ldots,z_{2n,p}$ is an *ordered* permutation p of the variables $x_1,y_1,\ldots,x_n,y_n$, such that

$$\begin{gathered}z_{1,p}<z_{2,p},\ z_{3,p}<z_{4,p},\ \ldots,z_{2n-1,p}<z_{2n,p},\\ \text{and}\quad z_{1,p}<z_{3,p}<z_{5,p}\cdots<z_{2n-1,p}.\end{gathered} \tag{17}$$

There are exactly $(2n-1)!!=1\times3\times\cdots\times(2n-1)$ 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. Alternatively, the E_n may be obtained through the recursion relation:

$$\begin{aligned}E_n(x_1,y_1,\ldots,x_n,y_n;t)=&+\sum_{j=1}^{n}E(x_1,y_j;t)E_{n-1}\\&\times(\cancel{x}_1,y_1,\ldots,x_j,\cancel{y}_j,\ldots,x_n,y_n;t)\\&-\sum_{j=2}^{n}E(x_1,x_j;t)E_{n-1}\\&\times(\cancel{x}_1,y_1,\ldots,\cancel{x}_j,y_j,\ldots,x_n,y_n;t),\end{aligned} \tag{18}$$

then ρ_n may be computed through the relation (12) or (5) and (13).

Consider the long-time asymptotic limit, where

$$E(x,y;t)=\mathrm{erfc}\left(\frac{y-x}{\sqrt{8Dt}}\right). \tag{19}$$

Then, the long-time asymptotic n-point correlation function is

$$\begin{aligned}\rho_n&(x_1,y_1,\ldots,x_n,y_n;t)\\&\underset{t\to\infty}{\to}(-\rho)^n\sum_{p=1}^{(2n-1)!!}\sigma_pC(z_{1,p},z_{2,p};t)\\&\times C(z_{3,p},z_{4,p};t)\cdots C(z_{2n-1,p},z_{2n,p};t),\end{aligned} \tag{20a}$$

where

$$\rho=\rho_1(x;t)=\begin{cases}1/\sqrt{8\pi Dt} & \text{annihilation}\\ 1/\sqrt{2\pi Dt} & \text{coalescence,}\end{cases} \tag{20b}$$

$$C(z_1,z_2;t)=\begin{cases}-1, & (z_1,z_2)=(x_k,y_k)\\ \mathrm{erfc}(\xi_{lk}), & (z_1,z_2)=(x_k,x_l)\\ -e^{-\xi_{lk}^2}, & (z_1,z_2)=(x_k,y_l)\\ e^{-\xi_{lk}^2}, & (z_1,z_2)=(y_k,x_l)\\ -\sqrt{\pi}\xi_{lk}e^{-\xi_{lk}^2}, & (z_1,z_2)=(y_k,y_l),\end{cases} \tag{20c}$$

and we used the notation $\xi_{lk}=(x_l-x_k)/\sqrt{8Dt}$. For example, for $n=2,3$, we get the long-time asymptotic expressions:

$$\frac{\rho_2(x_1,x_2;t)}{\rho^2}=1-e^{-2\xi_{21}^2}+\sqrt{\pi}\xi_{21}e^{-\xi_{21}^2}\mathrm{erfc}(\xi_{21}), \tag{21a}$$

$$\begin{aligned}\frac{\rho_3(x_1,x_2,x_3;t)}{\rho^3}=&1-e^{-2\xi_{21}^2}-e^{-2\xi_{32}^2}-e^{-2\xi_{31}^2}\\&+2e^{-\xi_{21}^2-\xi_{32}^2-\xi_{31}^2}\\&+\sqrt{\pi}\xi_{21}(e^{-\xi_{21}^2}-e^{-\xi_{32}^2-\xi_{31}^2})\mathrm{erfc}(\xi_{21})\\&+\sqrt{\pi}\xi_{32}(e^{-\xi_{32}^2}-e^{-\xi_{21}^2-\xi_{31}^2})\mathrm{erfc}(\xi_{32})\\&+\sqrt{\pi}\xi_{31}(e^{-\xi_{31}^2}-e^{-\xi_{21}^2-\xi_{32}^2})\mathrm{erfc}(\xi_{31}).\end{aligned} \tag{21b}$$

In summary, we have confirmed the fact that the infinite hierarchies of n-point correlation functions for coalescence and annihilation are identical, using the method of parity intervals. The simplicity of our approach allowed us to obtain explicit expressions for the long-time asymptotic limit, given in Eqs. (20). We note that our results are not restricted to long times. Indeed, for the case of a random distribution of particles, such that the initial concentration for annihilation is half that of coalescence, the identity holds at all times. In this case, explicit expressions for the correlation functions (valid at all times) can be obtained by using the full solution of Eqs. (8) and (9),

$$E(x,y;t)=\mathrm{erfc}\left(\frac{y-x}{\sqrt{8Dt}}\right)-\frac{1}{2}e^{2Dc_0^2t}\times\left\{e^{c_0(y-x)}\left[1-\mathrm{erf}\left(\frac{y-x+4Dc_0t}{\sqrt{8Dt}}\right)\right]-e^{-c_0(y-x)}\left[1+\mathrm{erf}\left(\frac{y-x-4Dc_0t}{\sqrt{8Dt}}\right)\right]\right\},\quad(22)$$

instead of the asymptotic expression of Eq. (19).

Remarkably, the particle distributions in coalescence and annihilation differ, despite the correspondence of the n-point correlation functions. The probability density function $p(x)$ for the distance x between two neighboring particles illustrates this difference. For large $x, p(x)\sim e^{-x^2}$ for coalescence, while $p(x)\sim e^{-x}$ for annihilation. Evidently, the complete hierarchy of n-point correlation functions is not sufficient to determine an infinite-particle system uniquely, and $p(x)$ cannot be computed from a knowledge of the ρ_n. A study of $p(x)$ and $\{\rho_n\}$ in finite systems might illuminate this curious phenomenon.

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