Exact Solutions for a Diffusion-Reaction Process in One Dimension

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This paper presents a new method for the solution of diffusion-reaction problems in one dimension. The method is used to derive some new exact results for the polymerization (cl-cl aggregation) and annihilation processes on $\mathbb{R}$ and $\mathbb{Z}$. Through well-known dualities, these results have implications for the $T=0$ limit of the kinetic Ising model and for two interacting-particle processes, the invasion and voter models. Prospectively, the method may be useful in providing one-dimensional verification for speculations in the theory of diffusion reaction.

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This paper considers a diffusion-reaction polymerization process called "Ppoly." Ppoly is a one-dimensional irreversible diffusion-limited cluster-cluster (cl-cl) aggregation process. cl-cl processes in more dimensions provide a theoretical paradigm for many aggregation phenomena, including galaxy formation from cosmic dust, aerosol coalescence, rainfall from clouds, and even chemical polymerization.

Scaling theory,[1] fractals,[2] and the Smoluchowski coagulation equation[3] provide models of aggregation, but make approximations of uncertain accuracy. Models accounting for dimensionality make incidental predictions about one-dimensional aggregation. These predictions can be compared with the exact results in this paper.

This paper also discusses "Pnihil." Pnihil is a one-dimensional model for diffusion-limited binary annihilation such as the thermal soliton-antisoliton interactions occurring after the photoexcitation of *trans*-polyacetylene.[4] Like Ppoly, Pnihil also allows theoretical comparisons of annihilation approximations. I now define Ppoly and Pnihil.

Ppoly takes place on a "medium," which in this paper is either $\mathbb{R}$, the real line, or $\mathbb{Z}$, the lattice of integers. At time $t=0$, there is some probabilistic distribution points on the medium. Polymer chemistry provides a convenient terminology: We call the initial points "monomers." For simplicity, assume that c_0, the monomer concentration (i.e., number per unit length, averaged over the medium), is fixed and finite. On $\mathbb{R}$, c_0 can be normalized to 1; by contrast, on $\mathbb{Z}$, the unit of length is fixed and prevents the normalization.

After $t=0$, all monomers diffuse identically and independently and aggregate irreversibly when they meet. The resulting point aggregates ("polymers") are indistinguishable from monomers in their diffusive behavior and also continue to aggregate when they meet.

A polymer containing k monomers is a "k-mer." Because it is useful to think of a k-mer as containing k monomers, and to think of each of these monomers as retaining a unique history, we distinguish between the 1-mers present at $t=0$ ("monomers"), and those present at later times ("1-mers").

The k-mer concentration is the number of k-mers per unit length, averaged over the medium in question. $c_k(t)$, the *expected* concentration of k-mers at time t, will be the focus of our interest; the expectation (which is usually implicit in the following) is taken over all initial monomer positions and over all realizations of the diffusive processes.

The total concentration of polymers,

$$c_+(t)=\sum_{k=1}^{\infty} c_k(t), \tag{1}$$

is also the concentration of 1-mers in the coalescence process,[5] Pcoal. In Pcoal, the 1-mers diffuse and coalesce when they meet, so that 1-mer + 1-mer → 1-mer. Pcoal on Z is the dual process of the voter model.[6]

In the annihilation process,[7-9] Pnihil, the 1-mers diffuse and annihilate one another when they meet, so that 1-mer + 1-mer → 0-mer. If one considers the 0-mers to be diffusing "ghosts" obeying the reaction rules 0-mer + 1-mer → 1-mer and 0-mer + 0-mer → 0-mer, Pnihil becomes Ppoly (mod 2). Hence, the concentration of 1-mers in Pnihil is

$$c_-(t)=\sum_{k=1}^{\infty} c_{2k-1}(t). \tag{2}$$

Ppoly (mod 1) is Pcoal; Ppoly (mod 2) is Pnihil; and Ppoly (mod n) is the n-ary annihilation process, in which a polymer is annihilated by the nth monomer to join it. Results for Ppoly have implications for all these processes.

I will show that in Ppoly, $kc_k(t)c_0^{-1}$ is the probability that a random monomer chosen at time $t=0$ will be in a k-mer at time t. Since there are k monomers in each k-mer, $kc_k(t)$ is the concentration of monomers contained in k-mers at time t. Because monomers are conserved (note the important distinction between "monomer" and "1-mer" here), c_0 is the total concentration of monomers at any time t. When (as is true in the cases I examine) the averages implicit in the concentrations exist, the quotient of $kc_k(t)$ and c_0 has the stated interpretation.

Each polymer has two directions in which to meet other polymers. Let us call the positive direction "right," and the negative, "left." Within each polymer, define the "left-most" monomer to be the monomer with the left-most (i.e., most negative) initial position. Because exactly one of the k monomers in a k-mer is the left-most monomer, the previous paragraph implies that $c_k(t)c_0^{-1}$ is the probability that a monomer chosen at random at time $t=0$ will be the left-most monomer in a k-mer at time t. This probability can be calculated as follows.

Let $P_{-1}, P_0, \ldots, P_{k-1}, P_k$ be consecutive monomers, ordered in the positive direction at time $t=0$, but otherwise arbitrary. For the time being, let us consider a single initial state so that the initial positions of these monomers are fixed. Let A_0 be the event that the two monomers P_0 and P_{k-1} are in the same polymer at time t. Let A_1 be the same event for P_{-1} and P_{k-1}; A_2 for P_{-1} and P_k; and A_3 for P_0 and P_k. $A_0 \sim (A_1 \cup A_3)$ is the event that P_0 is the left-most monomer in a k-mer containing $P_0, P_1, \ldots, P_{k-1}$.

$A_1 \subset A_0$, because the linear ordering of the monomers in one dimension implies that a polymer containing both P_{-1} and P_{k-1} must also contain P_0. Also, $A_3 \subset A_0$ and $A_1 \cap A_3 = A_2$. A Venn diagram of the A's show that

$$P(A_0 \sim (A_1 \cup A_3)) = \sum_{k=0}^{3} (-1)^k P(A_k). \tag{3}$$

Given the initial positions of the monomers, Eq. (3) gives the probability that P_0 is the left-most monomer in a k-mer at time t. Averaging Eq. (3) over all monomers P_0, and over all initial states [i.e., over the distribution of the initial distances between the monomer pairs (P_0, P_{k-1}), (P_{-1}, P_{k-1}), (P_0, P_k), and (P_{-1}, P_k)] gives $c_k(t)c_0^{-1}$, the probability that a random monomer is the left-most monomer in a k-mer at time t.

If the monomers' initial positions are in a renewal distribution[10] (i.e., the initial distances between consecutive monomers are independently and identically distributed), the distributions of the pairwise initial distances are independent of P_0. This leads to the following simplifications: (a) The initial distances between (P_{-1}, P_{k-1}) and (P_0, P_k) have the same distribution, and (b) averaging Eq. (3) over all monomers P_0 does not make any difference to the common value of Eq. (3). For convenience in what follows, I shall assume an initial renewal distribution.

Let $\beta_k(z)dz$ be the probability that the initial distance between P_0 and P_k lies in the interval $[z, z+dz)$ [the probability density $\beta_k(z)$ is sometimes a generalized function]. For a renewal distribution, $\beta_k(z)$ is independent of the choice of P_0 and determines the concentrations $c_k(t)$.

Let a monomer P begin at a distance z to the right of P_0. Define the annihilation Green's function $a(t;z)$ to be the probability that the two monomers P_0 and P have met by the time t. Integrating over the possible pairwise initial distances gives

$$\begin{aligned} P(A_0) &= \int a(t;z)\beta_{k-1}(z)dz, \\ P(A_1) = P(A_3) &= \int a(t;z)\beta_k(z)dz, \\ P(A_2) &= \int a(t;z)\beta_{k+1}(z)dz, \end{aligned} \tag{4}$$

where the integrations are over the entire medium. Since $P(A_0)=1$ when $k=1$, we define $a(t;0) := 1$ and $\beta_0(z) := \delta(z)$ [$\delta(z)$ is the Dirac delta[11]; $:=$ denotes a definition].

The interpretation of Eq. (3) gives

$$\begin{aligned} c_k(t) &= c_0 \int a(t;z)[\beta_{k-1}(z) - 2\beta_k(z) + \beta_{k+1}(z)]dz \\ &=: c_0 \int a(t;z) b_k(z) dz. \end{aligned} \tag{5}$$

Equations (1) and (2) define analogous functions $b_+(z)$ and $b_-(z)$ for $c_+(t)$ and $c_-(t)$:

$$b_+(z) := \delta(z) - \beta_1(z), \tag{6}$$

$$b_-(z) := \delta(z) + 2\sum_{k=1}^{\infty} (-1)^k \beta_k(z). \tag{7}$$

The substitution of Eq. (6) back into the analog of Eq. (5) explains the simplicity of Eq. (6): The total polymer concentration is equal to the concentration of those monomers which have not met their right-hand neighbor. The sum in Eq. (7) also has a simple interpretation: It is the difference between the probability densities for P_0's having an even and an odd neighbor at z.

Given $\beta_k(z)$, the annihilation Green's function $a(t;z)$ for different media and diffusion processes determines the polymer concentrations. Consider, for example, polymers diffusing without drift on $\mathbb{R}$ with a diffusion constant D. Let z be the initial displacement between monomers P_0 and P. This displacement diffuses with diffusion constant $2D$. Hence, at any given time t, the probability that P_0 and P have met equals the probability that a point starting at z, diffusing constant $2D$, has passed through 0. This equals

$$a(t;z) = \operatorname{erfc}(z/(8Dt)^{1/2}), \tag{8}$$

where

$$\operatorname{erfc}(z) = \frac{2}{\sqrt{\pi}} \int_z^{\infty} e^{-z^2} dz = 1 - \operatorname{erf}(z)$$

is the complementary error function.[12]

When the polymers diffuse without drift on $\mathbb{Z}$ with a diffusion constant D (i.e., they execute a symmetric continuous-time, nearest-neighbor random walk[13]), the displacements between them again diffuse with diffusion constant $2D$. On $\mathbb{Z}$, the probability that the displacement has passed through 0 before time t is

$$a(t;z)=\exp(-4Dt)\left(I_z(4Dt)+2\sum_{k=z+1}^{\infty}I_k(4Dt)\right), \tag{9}$$

where $I_k(z)$ is a modified Bessel function.[14]

The following results are an arbitrary selection of explicit solutions specialized from Eqs. (1)-(9).

For a Poisson distribution of monomers with concentration λ on $\mathbb{R}$,

$$\beta_k(z)=\exp(-\lambda z)[(\lambda z)^{k-1}/(k-1)!]\lambda,$$

$$c_+(t)=\lambda\exp(2\lambda^2Dt)\operatorname{erfc}((2\lambda^2Dt)^{1/2}),\quad c_-(t)=\lambda\exp(8\lambda^2Dt)\operatorname{erfc}((8\lambda^2Dt)^{1/2}).$$

The result for $c_-(t)$ is known.[7,9]

For a deterministic initial distribution on $\mathbb{R}$, with monomer sites spaced λ^{-1} apart and each site occupied,

$$\beta_k(z)=\delta(z-k\lambda^{-1}).$$

On $\mathbb{R}$, the monomer concentration is λ, and so

$$c_k(t)=\lambda\left[\operatorname{erfc}\left(\frac{k-1}{(8\lambda^2Dt)^{1/2}}\right)-2\operatorname{erfc}\left(\frac{k}{(8\lambda^2Dt)^{1/2}}\right)+\operatorname{erfc}\left(\frac{k+1}{(8\lambda^2Dt)^{1/2}}\right)\right],$$

$$c_+(t)=\lambda\operatorname{erf}\left(\frac{1}{(8\lambda^2Dt)^{1/2}}\right),\quad c_-(t)=\lambda\left[1+2\sum_{k=1}^{\infty}(-1)^k\operatorname{erfc}\left(\frac{k}{(8\lambda^2Dt)^{1/2}}\right)\right].$$

The result for $c_-(t)$ is known.[9] For the same initial distribution on $\mathbb{Z}$, with concentration $\lambda=1$,

$$c_k(t)=\exp(-4Dt)[I_{k-1}(4Dt)-I_{k+1}(4Dt)],$$

$$c_+(t)=\exp(-4Dt)[I_0(4Dt)+I_1(4Dt)],$$

$$c_-(t)=\exp(-4Dt)I_0(4Dt).$$

The result for $c_-(t)$ is known.[8,9] These results and the next easily generalize to lattice spacings $\lambda>1$ on $\mathbb{Z}$.

For an initial distribution on either $\mathbb{R}$ or $\mathbb{Z}$, with monomer sites spaced λ^{-1} apart and each site occupied independently with probability $\frac{1}{2}$,

$$\beta_k(z)=\sum_{j=k}^{\infty}2^{-j}\binom{j-1}{k-1}\delta(z-j\lambda^{-1}).$$

On $\mathbb{R}$, the monomer concentration is $\frac{1}{2}\lambda$, so that

$$c_-(t)=\tfrac{1}{2}\lambda\operatorname{erf}((8\lambda^2Dt)^{-1/2}).$$

For the same distribution on $\mathbb{Z}$, with $\lambda=1$ and monomer concentration $\frac{1}{2}$,

$$c_-(t)=\tfrac{1}{2}\exp(-4Dt)[I_0(4Dt)+I_1(4Dt)].$$

The last two results for $c_-(t)$ are new. The interpretation of $b_-(z)$ following Eq. (7) explains their simplicity, since all sites have an independent probability $\frac{1}{2}$ of occupancy. Hence, at any site, excluding those next to P_0, the probability of P_0's having an even neighbor ($P_2,P_4,\ldots$) there equals the probability of P_0's having an odd neighbor ($P_1,P_3,\ldots$) there.

Through linear ordering, Eq. (3) reduces diffusion reaction in one dimension to the investigation of pairwise collisions. Though objects in more dimensions may demonstrate linear ordering (e.g., concentric circles in two dimensions), this method in effect appears confined to one-dimensional processes. The practical solution in Eq. (4) also requires that a monomer's movement be indifferent to any of its encounters. Although subject to linear ordering and monomeric "indifference," the method of this paper can solve many problems.

For example, the assumption of identical monomers is inessential to solution: If the initial mass distribution of the monomers is known, then the evolution of the polymer mass distribution is easily derived from stated results for $c_k(t)$. In addition, a periodic medium, i.e., a circle, $\mathbb{R}$ (mod L), or a periodic lattice, $\mathbb{Z}$ (mod L), presents no essential new difficulties.[9,15] Similarly, following Eq. (3), the restriction to initial renewal distributions was unnecessary for solution, but did remove an averaging of Eq. (3) over monomers P_0. Equation (4) shows that this average is equivalent to the replacement of $\beta_k(z)$ for a single monomer P_0 with the average of $\beta_k(z)$ over all monomers P_0. With the removal of the unnecessary restriction to initial renewal distributions, my annihilation results become as general as Balding's.[9]

Versions of Ppoly based on more exotic random motions are also solvable. For example, consider a discrete-time nearest-neighbor random walk on $\mathbb{Z}$. $a(t;z)$, the probability that two monomers initially separated by a distance z have met by time t, is then complicated by a sum but provides no new conceptual difficulties. Moreover, solutions when the monomers diffuse with drift $d\neq0$ are easily derived from the stated results without drift ($d=0$): The motion of the polymers only enters the solutions through $a(t;z)$, and $a(t;z)$ only depends on the relative motion of monomer pairs. On $\mathbb{R}$, the relative motion when $d \neq 0$ is still a driftless diffusion with diffusion constant $2D$: The solutions are the same whether drift is present or not (this does not agree with the conclusions of Kang and Redner[16]). On $\mathbb{Z}$, the relative motion when $d \neq 0$ is still a driftless diffusion, but has a diffusion constant $2D+d$, which should replace $2D$ in Eq. (9) *et seq.*

Equation (3) can also be generalized to examine correlations and higher moments of the distributions.[9] For example, as in Eq. (3), let $P_{-1}, P_0, \ldots, P_{k-1}, P_k$ be consecutive monomers and $A_0, \ldots, A_3$, the corresponding events. Let $B_0, \ldots, B_3$ be the corresponding events for another group of consecutive momomers Q_{-1}, $Q_0, \ldots, Q_{l-1}, Q_l$. One can show that

$$P([A_0 \sim (A_1 \cup A_3)][B_0 \sim (B_1 \cup B_3)]) = \sum_{i,j=0}^{3} (-1)^{i+j} P(A_i \cap B_j),$$

reducing the correlations between k-mer and l-mer concentrations to events involving four monomers.

Kang and Redner[5] have obtained asymptotic results for Ppoly and Pnihil based on scaling arguments and Monte Carlo simulations. For an initial renewal distribution on $\mathbb{R}$, let the mean and mean square distances between consecutive monomers be $\mu_1 = c_0^{-1}$ and μ_2. As $t \rightarrow \infty$, the asymptotics of the complementary error function[12] in Eq. (8), Parseval's theorem for Fourier transforms,[11] and the convolutional form of renewal distributions[10] imply that

$$c_k(t) \sim (2/\sqrt{\pi})(8Dt)^{-3/2}[\mu_2 + 2(k-1)\mu_1^2],$$

$$c_+(t) \sim (2/\sqrt{\pi})(8Dt)^{-1/2}\mu_1.$$

These results agree with Kang and Redner's conclusions[5] about Ppoly. Some asymptotic analyses [e.g., $c_-(t)$ as $t \rightarrow \infty$, or $c_k(t)$ as $k \rightarrow \infty$] for general initial distributions are delicate, but probably possible, and spatial fluctuations can be followed analytically in one dimension.[15,16] Results along these lines may indicate generalities for more dimensions.

This paper has presented a new method for the solution of diffusion-reaction problems in one dimension. The method allowed the derivation of some new exact results for Ppoly and Pnihil. Through well-known dualities, these results have implications for the $T=0$ limit of the kinetic Ising model[17] and for two interacting-particle processes, the invasion and voter models.[6,18] Prospectively, the method may be useful in the provision of one-dimensional verification for speculations in the theory of diffusion reaction.

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