

Unimolecular reaction kinetics

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We use generating functions to analyze the kinetics of the reaction $A + B \rightarrow (1 + \epsilon)A + B$ where $-1 \leq \epsilon < 0$ and $\epsilon > 0$ correspond, respectively, to B particles that are traps or "sources." For an arbitrary configuration and strengths of static B 's and mobile A 's, an exact formal expression for the kinetics of the reaction is derived. This solution yields either exponential growth, power-law growth or decay, or no growth asymptotically, depending on the configuration and strength of the B 's.

Consider a system of mobile A particles which interact only with stationary B particles according to the reaction $A + B \rightarrow (1 + \epsilon)A + B$. For $-1 \leq \epsilon < 0$, the B particles may be regarded as traps for the A 's, with the limit $\epsilon = -1$ corresponding to perfect traps. Such a trapping reaction has been the focus of considerable attention in the literature, both for its intrinsic theoretical interest¹⁻⁸ as well as for its many applications.⁹⁻¹³ For a single trap,¹⁻³ the survival probability for an A particle decays with time as $t^{-1/2}$ for spatial dimension $d=1$, and as $1/\ln t$ for $d=2$. For $d > 2$, the survival probability approaches a finite limit which depends on $1 - R$, where R is the probability that a random walk eventually returns to its starting point. The intriguing case of a random distribution of traps has been extensively studied,⁴⁻⁸ and it is now established that the survival probability decays as

$$\exp\{[\ln(1 - c)]^{-2/d + 2/d^{d+2}}\},$$

where c is the trap concentration.

While there is considerable information about the asymptotic behavior in the trapping reaction, very little appears to be known about the complementary situation of a unimolecular growth reaction, i.e., the case $\epsilon > 0$, where the B particles may be regarded as catalytic "sources" for A particles. This unimolecular growth reaction is too idealized to describe more complicated and realistic problems such as population dynamics¹⁴⁻¹⁶ or chemical reactions with source terms.^{17,18} However, we believe that the insights gained from studying the simplified purely growth reaction will provide a starting point for understanding the realistic effects of competing growth and trapping or decay displayed by physical systems.

The chemical reaction models are often studied by rate equations or by reaction-diffusion equations which represent approximations in the spirit of a mean-field theory as the spatial distribution of the reactants is assumed to be uniform. In this Rapid Communication, we employ generating function methods^{19,20} to derive the asymptotic properties of general diffusion-controlled unimolecular growth processes and a simple mixed unimolecular growth and trapping process. While generating function techniques are well known, they have not been applied to growth reactions, and we obtain new exact solutions for a number of interesting situations. Our exact generating function solutions indicate that rate-equation solutions are not always an accurate description of the kinetics, suggesting that similar modifications of the kinetic laws will occur in more realistic model reactions.

Several prototypical examples are treated such as a single source, a regular or a random distribution of sources, and a system containing one source and one trap, to illustrate the possible kinetic behaviors. Our calculational approach is equally valid for the trapping reaction, and we can reproduce many of the known results for this reaction in a very simple manner.

We begin our analysis by treating the case of a single B source particle at \bar{s} , and a single random walker (A particle) at the origin at $t=0$. We model the Brownian diffusion of A by a discrete-time isotropic random walk; at unit time intervals, the A particle moves with equal probability to one of its nearest-neighbor sites. When the original A first reaches the source at \bar{s} , ϵ new A 's are produced. The particles in this first generation can then reproduce upon subsequent returns to \bar{s} . At the n th step, the number of new particles produced by the source is denoted by $a_n(\bar{s})$.

The exact growth rate for the A 's can be calculated by the following approach. Let $P_n(\bar{r})$ denote the probability that a particle is at \bar{r} on the n th step if it starts at the origin in the pure random-walk model. Similarly, let $Q_n(\bar{r})$ be the expectation value for the total number of particles at \bar{r} on the n th step if a particle starts at the origin and one source is at \bar{s} in the reacting system. Then by the definition of the reaction, $Q_n(\bar{r})$ equals the probability for the random walker to propagate to \bar{r} without touching the source plus the sum over all earlier times, of the number of A particles created at the source, multiplied by the appropriate random-walk probability of propagating from \bar{s} to \bar{r} . That is,

$$Q_n(\bar{r}) = P_n(\bar{r}) + a_1(\bar{s})P_{n-1}(\bar{r} - \bar{s}) + a_2(\bar{s})P_{n-2}(\bar{r} - \bar{s}) + \cdots + a_n(\bar{s})P_0(\bar{r} - \bar{s}). \quad (1a)$$

By construction, $a_n(\bar{s})$ is simply equal to $[\epsilon/(1 + \epsilon)] \times Q_n(\bar{s})$. Substituting this in Eq. (1a) and using the fact that $P_0(0) = 1$ gives

$$a_n(\bar{s}) = [P_n(\bar{s}) + a_1(\bar{s})P_{n-1}(0) + a_2(\bar{s})P_{n-2}(0) + \cdots + a_{n-1}(\bar{s})P_1(0)]. \quad (1b)$$

Now defining the generating functions

$$Q(z, \bar{r}) = \sum_{n=0}^{\infty} Q_n(\bar{r}) z^n,$$

and similarly for $P(z, \bar{r})$ and $a(z, \bar{s})$, we find

$$Q(z, \bar{r}) = P(z, \bar{r}) + \frac{[P(z, \bar{r} - \bar{s})P(z, \bar{s})]}{1 + \epsilon - \epsilon P(z, 0)}. \quad (2a)$$

By summing over all \bar{r} , we obtain the generating function for the total number of particles on the lattice at the n th step,

$$Q(z) = \sum_{\bar{r}} Q(z, \bar{r}) \equiv \sum_{n=0}^{\infty} Q_n z^n;$$

Q_n is the total number of A 's at the n th step. Using^{19,20}

$$P(z) = \sum_{\bar{r}} P(z, \bar{r}) = (1-z)^{-1}$$

(corresponding to particle conservation in the pure random-walk model), we find

$$Q(z) = \frac{1}{1-z} \frac{1 + \epsilon + \epsilon [P(z, \bar{s}) - P(z, 0)]}{1 + \epsilon - \epsilon P(z, 0)} \quad (2b)$$

For the trapping reaction, $-1 \leq \epsilon < 0$, Q_n may be interpreted as the probability for a random walker to survive to n steps if the trap absorbs an incident particle with probability $-\epsilon$.

The asymptotic properties for the single source reaction may now be derived by examining the singular behavior of $Q(z)$. In one dimension,^{19,20}

$$P(z, \bar{r}) = \frac{[1 - (1-z^2)^{1/2}]/z \cdot |\bar{r}|}{(1-z^2)^{1/2}}$$

and substituting this in Eq. (2b) yields a simple pole in $Q(z)$ at $z_c = \sqrt{1+2\epsilon}/(1+\epsilon) < 1$. Therefore, the total particle number at the n th step, Q_n , grows asymptotically as

$$[(1+\epsilon)/\sqrt{1+2\epsilon}]^n \quad (3)$$

Moreover, from Eq. (2a), the A 's have an exponential distribution about the source; $Q_n(\bar{r}) \sim Q_n(\bar{s})(1+2\epsilon)^{|\bar{r}-\bar{s}|/2}$. Thus, the mean-square displacement from the source, averaged over the ensemble of all A particles, approaches a finite limit proportional to $[\ln(1+2\epsilon)]^{-2}$ as $n \rightarrow \infty$.

In two dimensions, a similar picture is obtained. From the asymptotic behaviors^{10,11} $P(z, 0) \cong (1/\pi) \ln(1-z) + \dots$, when $z \rightarrow 1$, and $P(z, 0) \cong 1 + P_2(0)z^2 + \dots$, for $z \ll 1$, we find that $Q(z)$ has a simple pole at $z_c \cong 1 - e^{-\pi/\epsilon}$ for ϵ small, and at $z_c = 2/\sqrt{\epsilon}$ for ϵ large. This leads to

$$Q_n \sim (1 + e^{-\pi/\epsilon})^n, \quad \epsilon \ll 1 \quad (4a)$$

$$\sim (\sqrt{\epsilon}/2)^n, \quad \epsilon \gg 1. \quad (4b)$$

An additional interesting situation is the single source reaction on a fractal set with fracton dimension²¹ $d_f \leq 2$. The singular behavior of $P(z, 0)$ (Ref. 22) leads to the asymptotic kinetics

$$Q_n \sim n^{d_f/2-1} \quad (\text{one trap}) \\ \sim [1 - [\epsilon/(1+\epsilon)]^{2/(2-d_f)}]^{-n} \quad (\text{one source}). \quad (5)$$

The exponential growth for d (or d_f) ≤ 2 is predicated on a random walk being recurrent, that is, the probability of eventual return to the starting point, R , equals unity.^{19,20} This means that every new particle born at the source returns to produce further generations. However, for $d > 2$, a random walk is transient, corresponding to $R < 1$. Now the competition between the eventual return probability and the source strength ϵ leads to three possibilities. Substituting in

$Q(z)$ the asymptotic form valid for $d > 2$,

$$P(z, 0) = (1-R)^{-1} + \alpha(1-z)^{d/2-1} + \dots$$

(with α a lattice-dependent constant), we find after some straightforward analysis

$$Q_n \sim \frac{1-R}{1-R(1+\epsilon)}, \quad 0 < \epsilon < \epsilon_c \\ \sim n^{d/2-1}, \quad \epsilon = \epsilon_c = (1-R)/R \\ \sim (\sqrt{\epsilon/2d})^n, \quad \epsilon \gg \epsilon_c. \quad (6)$$

These results illustrate the competing effects of the random-walk transience and the source strength in governing the kinetics.

The above results can be generalized to a uniformly biased random walker. The asymptotic behavior can be easily appreciated by employing the Gaussian approximation for $P_n(\bar{r})$ valid for a small drift velocity ∇ . Thus using

$$P_n(\bar{r}) \sim n^{-d/2} \exp[-(\bar{r} - \nabla n)^2/n],$$

we obtain the approximate generating function $P(z, 0) \sim (z - z_0)^{d/2-1}$ for $d \neq 2$, and $P(z, 0) \sim \ln(z - z_0)$ for $d = 2$, with $z_0 \sim e^{v^2}$. Substituting this in $Q(z)$, we find in $d = 1$ three possible growth laws

$$Q_n \sim \left[e^{v^2} - \frac{\epsilon^2}{(1+\epsilon)^2} \right]^{-n}, \quad v < v_c \\ \sim n, \quad v = v_c \cong \left[\ln \left(\frac{1+2\epsilon}{1+\epsilon} \right) \right]^{2/1/2} \\ \sim [(1+\epsilon) - \epsilon/(e^{v^2} - 1)^{1/2}]^{-1}, \quad v > v_c. \quad (7)$$

again illustrating the competing effects of transience (due to the drift) and the source strength. Figure 1 summarizes the results of our analysis for $d = 1, 2$, and $d > 2$. As the dimension increases, the random walk becomes more strongly transient and the portion of the diagram in which exponential growth occurs decreases. In $d = 2$, the exponential growth region extends to $\epsilon = 0$ within an area whose width vanishes exponentially in ϵ .

For an arbitrary configuration of B particles (sources or traps), we may derive an exact expression for $Q(z)$ by a generalization of the methods used for the single source problem. For a system containing N B particles each with strength $\epsilon_i \geq -1$ and located at \bar{s}_i , the recursion relation for $Q_n(\bar{r})$ is [in analogy with Eq. (1a)]

$$Q_n(\bar{r}) = P_n(\bar{r}) + \sum_{m, \bar{s}_i} a_m(\bar{s}_i) P_{n-m}(\bar{r} - \bar{s}_i), \quad (8)$$

where $a_m(\bar{s}_i)$ denotes the number of new particles produced by a source at \bar{s}_i on the m th step. Now using $a_m(\bar{s}_i) = (\epsilon_i/1 + \epsilon_i) Q_m(\bar{s}_i)$, we first rewrite Eq. (8) in terms of the $a_m(\bar{s}_i)$, $i = 1, 2, \dots, N$, and solve the resulting system of linear equations by generating functions. After a number of steps we find

$$Q(z) = \frac{1}{1-z} \left[1 + \frac{1}{\det \mathcal{A}} \sum_k \det \mathcal{A}'(k) \right], \quad (9)$$

where \mathcal{A}_{ij} is the $N \times N$ matrix

$$(1 + \epsilon_i) - \epsilon_i P(z, 0), \quad i = j, \\ -\epsilon_i P(z, \bar{s}_i - \bar{s}_j), \quad i \neq j,$$

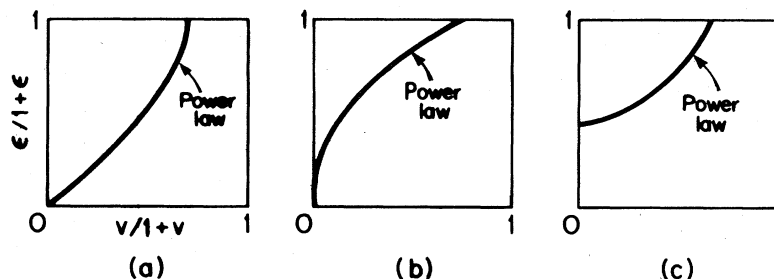


FIG. 1. Phase diagram of the single source growth reaction for (a) $d=1$, (b) $d=2$ and (c) $d > 2$. Exponential growth occurs in the upper-left portion of the squares while a finite limit for the number of particles occurs in the lower-right. On the boundary dividing exponential growth from no asymptotic growth, power-law growth occurs. In $d=2$, the region of exponential growth is exponentially small as $\epsilon \rightarrow 0$. For $d > 2$, the phase boundary is described by $\epsilon_c = [1 - R(v)]/R(v)$, where $R(v)$ is the eventual return probability for a biased random walk.

and $\mathcal{R}'(k)$ is a matrix obtained from \mathcal{R} by replacing the k th column with a vector whose i th component is $\epsilon_i P(z, \bar{s}_i)$. The expression (9) is essentially the same as that of Rubin and Weiss²³ who used it to treat the statistical properties of the number of visits to a subset of points on a lattice.

The expression (9) for $Q(z)$ is exact, and from it we can deduce that for a fixed arbitrary configuration containing finitely many sources, the growth law is purely exponential. For a random distribution of sources, it does not appear possible to perform the average over source configurations exactly. Nevertheless, our numerical calculations indicate that the growth law remains purely exponential, in contrast to the slower than exponential decay associated with a random distribution of traps.⁴⁻⁸ The exponential growth coincides with the mean-field or rate-equation prediction for the growth rate, $Q_n \sim e^{\bar{\epsilon}cn}$, where $\bar{\epsilon}$ is the average strength of the sources, and c their concentration.

For a regular distribution of equal strength sources on a lattice with periodic boundary conditions, we use the fact that the matrix \mathcal{R} has a treelike structure and the determinant in Eq. (9) can be computed straightforwardly.²⁴ Now the relevant pole in $Q(z)$ which governs the long-time behavior of Q_n is determined by

$$1 + \epsilon - \epsilon \sum_{\bar{s}_i} P(z, \bar{s}_i) = 0 \tag{10}$$

when sources are located at the regular array of sites $\{\bar{s}_i\}$. From this expression, we can discuss the asymptotics of two cases by taking the limit where the size of the system goes to infinity. One is a regular but spatially inhomogeneous source distribution, such as a single line or plane of sources. In this situation, the relevant quantity to classify the reaction is the co-dimension $d_{co} = d - d'$, where d' is the dimension of the source set. For $d_{co} \leq 2$, a random walk is recurrent with respect to the source set, and the sum in Eq. (10) diverges as $z \rightarrow 1$. Therefore, a pole in $Q(z)$ occurs at a value $z_c < 1$, leading to exponential growth, independent of ϵ . For $d_{co} > 2$, the random walk is transient with respect to the source set and the possibilities outlined in Eq. (6) can occur.

For a regular and spatially homogeneous source distribution, a random walk is always recurrent with respect to the source set, implying exponential growth. Although the time dependence of the growth law is simple, the dependence on

the source density c and on ϵ is more complicated. We may approximately treat these dependences by employing the continuum Gaussian approximation for $P_n(\bar{r})$ in Eq. (9). This yields the growth law

$$Q_n \sim \left(\frac{1 + \epsilon}{1 + \epsilon(1 - c)} \right)^n \tag{11}$$

for any dimension. This growth rate is expected to be accurate in the limits of $c \geq \frac{1}{2}$ and $\epsilon \ll 1$, as can be verified by comparing with the exact growth law for a completely occupied lattice [$Q_n = (1 + \epsilon)^n$], and a lattice with alternating sites occupied [$Q_n = (1 + \epsilon)^{n/2}$].

Finally, from Eq. (9), we have treated the simplest case of a "mixed" reaction, a dipolar system containing one source and one trap. In one dimension, the effects of source and the trap compete to give either exponential growth or power-law decay as indicated in Fig. 2.

In conclusion, we have discussed the unique kinetics of random walkers which interact with static sources or static traps by a unimolecular reaction. Generating function methods have been used to derive an exact formal expres-

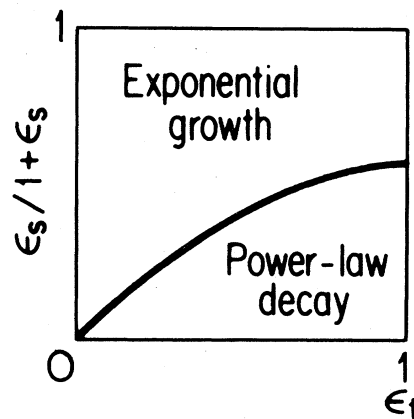


FIG. 2. Phase diagram of a system consisting of one source of strength ϵ_s and one trap of strength ϵ_t , separated by a distance l in one dimension. The boundary separating exponential growth from power-law decay is given by $\epsilon_s = \{\epsilon_t/[1 + 2(l-1)\epsilon_t]\}$.

sion of the number of A 's as a function of time. A variety of kinetic behaviors are found, which depend on the configuration and the reactivities of the B 's. Several generalizations of the model are amenable to the exact generating function approach including a distribution of source strengths, and competing growth and trapping. These

models should serve as useful systems to make contact with realistic kinetic phenomena.

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