Exact solution of the one-dimensional immobile trapping problem with and without sources

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We consider the one-dimensional trapping problem $A + S \rightarrow S$ when the traps S as well as the reactants A are immobile. The trapping rate $k(r)$ depends on the distance r between the reactant and the trap, and is characterized by an "effective reaction radius" r_0, which is a measure of the first moment of $k(r)$. We find that the decay of an initial density of A particles is exponential in time at short times and an inverse power law at long times. In the presence of sources, we find that a steady state exists only if the effective reaction radius is larger than half of the average distance between sinks, and we find an inverse-power-law approach to the steady state. If this condition is not met, then there is an unbounded accumulation of A particles in regions that can not be effectively depleted by the reaction. The growth of the density in this case is of power-law form.

I. INTRODUCTION

Diffusion-controlled annihilation reactions of the form $A + A \rightarrow A$ (Ref. 1) or $A + A \rightarrow 0$ or $A + B \rightarrow 0$ (Refs. 2 and 3) and diffusion-controlled trapping of the form $A + S \rightarrow S$ (Refs. 4 and 5) have been of considerable interest because of the "anomalous" kinetic laws that govern the evolution of these reactions in low-dimensional systems. The kinetics are viewed as anomalous because they do not follow the mean-field "classical" textbook form.[6] The reasons for these anomalies are fairly clear and are related to the spatial distributions of reactants. In the case of a single reactant species A, the distribution of nearest-neighbor distances in low dimensions differs from the Hertz form that underlies the classical rate laws. As the reaction proceeds, near neighbors are depleted and diffusion is not effective in replacing them as quickly as they react. Therefore, nearest neighbors tend to be farther apart in lower dimensions in an arrangement that is almost latticelike. The reaction is then slower than predicted by mean-field theories. In the trapping problem the anomalies arise from the distribution of reactants A around the traps S: depleted regions around the latter are not replenished by diffusion as effectively in low dimensions as they are in higher dimensions. In the two-species case, anomalies occur in sufficiently low dimensions due to the spontaneous formation of macroscopic aggregates of like particles that are not effectively mixed by diffusion. As a result, reaction only takes place at aggregate interfaces rather than in the entire volume. As a consequence, the time evolution of the densities is slower than predicted by the usual kinetic laws.

A related problem that has been investigated recently via numerical simulations and approximate analytic approaches involves the $A + B \rightarrow 0$ reaction in one dimension in the *absence* of diffusion.[7] The particles react via an exchange interaction (i.e., exponential in the distance between them). Here, too, the authors find spontaneous segregation of species and the associated "anomalous" kinetic laws. This system provides a particularly stringent test of approximate theories since "...possible deviations of the theory from the computer experiments are not obscured by diffusion effects...."

Another problem related to those posed above is that of trapping, $A + S \rightarrow S$, when both the traps S and the reactants A are immobile. The trapping occurs via a long-range interaction that is most conveniently taken to be of the exchange form. In this paper we explore the kinetic behavior of this system in one dimension in the absence (Sec. II) and in the presence (Sec. III) of reactant sources. Our conclusions are summarized in Sec. IV.

II. EVOLUTION IN THE ABSENCE OF SOURCES

Consider the immobile trapping problem $A + S \rightarrow S$ in an infinite one-dimensional system. The rate coefficient for trapping, $k(r) \equiv w\kappa(r/r_0)$, depends only on the distance r between the reactant and the sink, r_0 is a distance scaling parameter which can be interpreted as an "effective reaction distance," and $\kappa(u)$ is a dimensionless function whose integral over all space is r_0. The total trapping rate of each A particle is wr_0. For instance, if the trapping rate is assumed to be of the exchange form, then it depends exponentially on the distance between A and S:

$$k(r) = we^{-r/r_0} . \tag{1}$$

The reactants A and the traps S are initially deposited at random locations with density ρ_s and n_0, respectively.

We use the many-point density approach of Kuzovkov and Kotomin[2] and define the many-point function $\rho_{1,m}(r'; r_1, r_2, \ldots, r_m; t)$ as the probability density that one A particle is located at r' and that m S sinks are at $r_1, r_2, \ldots, r_m$ at time t. The reactivity of a particular A is independent of the number and locations of the other A's. Therefore, only one A need be considered in the definition and construction of the many-point densities. Furthermore, the $\rho_{1,m}$ depend only on the relative distances between the A particle and the sinks. Without loss of generality, we set $r' \equiv 0$.

Following Kuzovkov and Kotomin, it is convenient to introduce the many-point correlation function $g_m(r_1, r_2, \ldots, r_m; t)$ via the relation

$$\rho_{1,m} = \rho_s^m n(t) g_m(r_1, r_2, \ldots, r_m; t) ,\tag{2}$$

where $n(t)$ is the density of A at time t. Due to the initially random (uncorrelated) distribution of particles and sinks, $g_m(r_1, r_2, \ldots, r_m; 0) = 1$. Using standard manipulations it is possible to construct a hierarchy of integro-differential equations connecting the correlation function

of order m with that of order $m + 1$. The hierarchy begins with the density $n(t)$. Its first member is the evolution equation for $n(t)$:

$$\frac{d}{dt} \ln n(t) = -2\rho_s \int_0^\infty dr_1 k(r_1) g_1(r_1; t) ,\tag{3}$$

where the factor of 2 reflects the location of sinks on either side of A. The subsequent members of the hierarchy give the correlation dynamics [Kuzovkov and Kotomin, Ref. 2, p. 1507, Eqs. (3.7) and (3.8)]

$$\frac{\partial g_m(r_1, r_2, \ldots, r_m; t)}{\partial t} = - \sum_{j=1}^{m} k(r_j) g_m(r_1, r_2, \ldots, r_m; t)$$

$$-\rho_s g_m(r_1, r_2, \ldots, r_m; t) \int_0^\infty dr_{m+1} k(r_{m+1}) \left[\frac{g_{m+1}(r_1, r_2, \ldots, r_m, r_{m+1}; t)}{g_m(r_1, r_2, \ldots, r_m; t)} - g_1(r_{m+1}; t) \right] .$$

$$\tag{4}$$

Infinite hierarchies of nonlinear equations connecting correlation functions of ever higher orders can in general not be solved analytically, and neither would it be possible to do so in the trapping problem if the reactants could diffuse. However, in the present case of immobile reactants the hierarchy can be solved exactly with the multiplicative solution:

$$g_m = \prod_{j=1}^{m} g_1(r_j).\tag{5}$$

In particular, the hierarchy (4) reduces to the single equation

$$\frac{\partial g_1(r)}{\partial t} = -k(r) g_1(r) ,\tag{6}$$

which can be integrated trivially. When the result is inserted into (3) and the latter is integrated, we find for the density $n(t)$ the expression

$$n(t) = n_0 e^{-2\rho_s r_0 F(t)} ,\tag{7}$$

where

$$F(t) = -wt \int_0^\infty du \, u \kappa'(u) e^{-\kappa(u)wt}\tag{8}$$

and the prime denotes a derivative with respect to the argument. If the trapping rate is of the exchange form (1), then it is convenient to first carry out the spatial integration and then the time integration to obtain for $F(t)$ an expression involving the familiar exponential integral

$$F(t) = \int_0^{wt} d\tau \frac{1 - e^{-\tau}}{\tau} = \gamma + \ln wt + \int_{wt}^\infty du \frac{e^{-u}}{u} ,\tag{9}$$

where $\gamma = 0.5772\ldots$ is the Euler-Mascheroni constant. Equation (8) or Eq. (9) can easily be evaluated numerically. We have thus reduced the problem to quadrature.

Although in general $F(t)$ cannot be expressed in terms of simple analytic functions for all time, the long-time and short-time behavior of $n(t)$ can be found explicitly. At short times we can expand $F(t)$ in (8) in a power series of the form

$$F(t) = wt + O(t^2) ,\tag{10}$$

which for early times yields an exponential decay for the density,

$$n(t) = n_0 e^{-2\rho_s r_0 wt} .\tag{11}$$

If we further expand the exponent we find an initial decay that is linear in time, which is to be contrasted with the short-time behavior of the density in the diffusion-limited trapping problem;[5] in that case, the initial decay is proportional to $\sqrt{Dt}$, where D is the diffusion coefficient of the A particles:

$$n_D(t) = n_0 \left[1 - \frac{4\rho_s \sqrt{Dt}}{\sqrt{\pi}} + 4 \ln 2 \rho_s^2 Dt \right] .\tag{12}$$

The long-time behavior depends on the specific form of the trapping rate function. For an exponential trapping rate we use (9) and observe that the exponential integral can be neglected in comparison with the other two terms. Equation (9) in (7) then gives

$$n(t) = \frac{n_0 e^{-2\gamma \rho_s r_0}}{(wt)^{2\rho_s r_0}} .\tag{13}$$

The density thus decays as a power law with the power $2\rho_s r_0$, the number of sinks within the reaction radius. This inverse-power-law behavior should be contrasted with the stretched exponential long-time decay of the density in the diffusion-limited trapping problem:[5]

$$n_D(t) = \frac{32}{(3\pi^3)^{1/2}} n_0 (Bt)^{1/2} e^{-3(Bt)^{1/3}}\tag{14}$$

with $B = \pi^2 \rho_s^2 D / 4$. Note that, whereas (14) cannot be expressed in terms of a rate law with a constant rate coefficient [i.e., $\dot{n}_D(t)$ cannot be expressed in terms of a power of $n_D(t)$ with a constant coefficient], such a rate law is possible for (13). Finally, we also note that Eq. (13) is only valid when r_0 is finite. To consider the case $r_0 \to \infty$ it is necessary to return to the beginning of the

problem and to take this limit at the outset in Eq. (3). The resulting decay law for the density of A particles is exponential in time. The difference arises from the order in which the infinite limits of r_0 and of the size of the system are taken.

III. EVOLUTION IN THE PRESENCE OF SOURCES

In addition to the initial random distribution of A particles, suppose that these particles are subsequently and continually fed into the system at a rate R in units of density per unit time. We have shown elsewhere[5] that the density $n_s(t)$ in the presence of this source can be expressed in terms of the density $n(t)$ calculated in Sec. II as

$$n_s(t) = n_{SS} + n(t) - \frac{R}{n_0} \int_t^\infty d\tau \, n(\tau) , \qquad (15)$$

where n_{SS} is the steady-state density of A, given by

$$n_{SS} = \frac{R}{n_0} \int_0^\infty dt \, n(t) = R \int_0^\infty dt \, e^{-2\rho_s r_0 F(t)} . \qquad (16)$$

The steady-state density cannot be calculated analytically (although it can be evaluated numerically). However, useful bounds on the steady-state density can be established by noting that $F(t)$ in Eq. (16) is bounded. We show these bounds to be given by

$$\ln(1 + wt) \le F(t) \le \gamma + \ln(1 + wt) . \qquad (17)$$

To establish the lower bound we must show [with the form (9) for $F(t)$] that

$$\int_0^{wt} d\tau \, X(\tau) \ge 0 , \qquad (18)$$

where

$$X(\tau) \equiv \frac{1 - e^{-\tau}}{\tau} - \frac{1}{1+\tau} . \qquad (19)$$

In writing (18) and (19) we have expressed the logarithm in the inequality (17) as an integral. Straightforward manipulations allow us to rewrite $X(\tau)$ as

$$X(\tau) = \frac{1}{\tau} e^{-\tau} (e^{Y(\tau)} - 1) , \qquad (20)$$

where $Y(\tau) = \tau - \ln(1+\tau)$ and therefore $X(\tau)$ is positive for all τ if $Y(\tau) \ge 0$, which is indeed the case. Thus (18) and consequently the lower bound in (17) are established. The upper bound is easily established by noting that the positivity of $X(\tau)$ implies that $F(t) - \ln(1 + wt)$ is a monotonically increasing function of t. Since the limit as $t \to \infty$ of $F(t)$ is $\gamma + \ln wt$ [cf. (9)], and in this limit $\ln(1 + wt)$ and $\ln wt$ are the same to $O(t^0)$, the upper inequality is established. The bounds (17) in the steady-state density expression yield (provided $2\rho_s r_0 > 1$)

$$\frac{R}{w(2\rho_s r_0 - 1)} e^{-2\gamma\rho_s r_0} \le n_{SS} \le \frac{R}{w(2\rho_s r_0 - 1)} . \qquad (21)$$

We have thus found that the exponential trapping rate

function leads to a divergence of n_{SS} if $\rho_s r_0 \le \frac{1}{2}$, i.e., a steady state with a finite concentration exists only if $\rho_s r_0 > \frac{1}{2}$. In other words, to inhibit the unbounded accumulation of A particles it is necessary for the reaction radius to be greater than half of the average distance between sinks. Otherwise the accumulation of A can not be counteracted sufficiently rapidly by the reaction, resulting in a divergence of the density. A divergence of this type would occur with any trapping rate function that has finite moments; the unbounded growth would obviously be limited by a finite size of the reactant particles.

Equation (15) describes the density of A at all times. The time evolution near the steady state can be found analytically using (13):

$$n(t) = n_{SS} - \frac{R \, e^{-2\gamma\rho_s r_0}}{w(2\rho_s r_0 - 1)} \frac{1}{(wt)^{2\rho_s r_0 - 1}} , \qquad (22)$$

so that the approach to the steady state is of inverse-power-law form and always occurs from below. This behavior is again to be contrasted with the diffusion-limited case, where the approach to the steady state, although also from below, is of the stretched exponential form[5]

$$n_{s,D}(t) = n_{SS,D} - \frac{32R}{(3\pi^3)^{1/2}} B^{1/6} t^{7/6} e^{-3(Bt)^{1/3}} , \qquad (23)$$

with B defined as before. In the absence of a steady state it can easily be seen that the growth of the unbounded density is of power-law form. Finally, if the sources of A particles are time dependent, then (15) must be replaced by the more general expression[5]

$$n_s(t) = n(t) + \int_0^t d\tau \frac{n(t-\tau)}{n_0} S(\tau) , \qquad (24)$$

where $S(t)$ is the source density per unit time.

IV. CONCLUSIONS

We have calculated the density $n(t)$ of A particles as a function of time for the trapping problem $A + S \to S$ when the traps and the particles are immobile and trapping occurs via a long-range trapping rate function $k(r)$. In the absence of sources other than the initial distribution we find that the short-time decay of $n(t)$ is exponential (typical of a spatially random distribution), while at long times the decay is of inverse-power-law form. This latter slow decay reflects the depletion of reactant near the sinks. In the presence of steady sources of A particles, we find that a steady state is established if the average distance between sinks is at most comparable to the effective reaction radius, and that the approach to the steady state is of inverse-power-law form. If the distance between sinks is too large, then we find unbounded power-law growth of the reactant density.

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