Fluctuation dominated recombination kinetics with traps

Jayendran C. Rasaiah and Jianjun Zhu
Department of Chemistry, University of Maine, Orono, Maine 04469

Joseph B. Hubbard
Center for Chemical Engineering, Thermophysics Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

Robert J. Rubin
Laboratory of Chemical Physics, National Institutes of Health (NIDDK), Bethesda, Maryland 20892

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Theoretical and computer simulation studies of annihilation reactions with traps on two and in three dimensional lattice systems are reported for the following reactions: (1) Bimolecular trapping/annihilation: \( A + A \rightarrow \bullet; A + T \rightarrow A_T; A + A_T \rightarrow T \); (2) unimolecular trapping/annihilation: \( A + A \rightarrow \bullet; A \rightarrow A_T; A + A_T \rightarrow \bullet \). The mean field analysis and combinatorial calculations of the rate constants given previously for a square lattice are generalized to lattices in two and three dimensions. It is found that the kinetics of trapped \( A \)'s can be described by mean field theory for bimolecular but not for unimolecular trapping reactions. The kinetics of free \( A \)'s obeys mean field theory at short times, but at longer times and at low trap densities the free \( A \) population decays as a stretched exponential when large density fluctuations dominate the reaction. This stretched exponential behavior of the Donsker–Varadhan form \( A(t) \sim \exp\left[-t^{d/(d+2)}\right] \), where \( d \) is the dimensionality, already found for the reactant decay in \( A \rightarrow A \) annihilation reactions with traps on a square lattice [Rasaiah et al., J. Phys. Chem. 94, 652 (1990)] was tested for universality by studying triangular and hexagonal lattices in two dimensions (2D) and a cubic lattice in three dimensions (3D). The same behavior is also observed when the free particle annihilation is turned off. The effect of a finite staying probability \( p_s \) on the kinetics of these reactions is also investigated.

I. INTRODUCTION

Quite recently attention has been focused on the role that density fluctuations play in governing the kinetics of diffusion controlled reactions at long times when deviations from the classical (i.e., mean field) kinetic equations, which assume a uniform density distribution, are observed.\(^1\)\(^-\)\(^5\) For the recombination (or annihilation) reaction

\[ A + A \rightarrow \bullet \]  
(1.1)

in \( d \) dimensions, it is known that at large times\(^3\)

\[ A(t) \sim t^{-(d+1)/(d+2)}(d \leq 2), \quad A(t) \sim t^{-1} \ln t(d = 2), \quad A(t) \sim t^{-1}(d > 2), \]
(1.2)

which implies that mean field behavior for all practical purposes obtains when \( d > 2 \). In contrast to this the annihilation reaction

\[ A + B \rightarrow \bullet \]  
(1.3)

between two distinct species is sensitive to the initial concentrations of \( A \) and \( B \). For instance, when the initial concentrations \( A(0) \) and \( B(0) \) are the same, one finds that at long times\(^1\)\(^-\)\(^5\)

\[ A(t) \sim t^{-(d+1)(d > 4)}, \quad A(t) \sim t^{-(d+2)/4}(d \leq 4), \]
(1.4)

while if \( A(0) < B(0) \), Bramson and Lebowitz have shown\(^5\)

\[ A(t) \sim \exp\left(-t/3\right), \quad A(t) \sim \exp\left(-t/\ln t(d = 2)\right), \]
\[ A(t) \sim \exp\left(-t^{1/2}\right)d = 1), \]
(1.5)

In the first instance mean field theory (MFT) obtains for \( d > 4 \), while in the second, mean field behavior is observed, when the dimensionality is greater than or equal to 3.

Another example of fluctuation dominated kinetics is the catalytic annihilation (\( \bullet \)) of particles by a random distribution of static traps:\(^6\)\(^-\)\(^9\)

\[ A + T \rightarrow T + \bullet. \]  
(1.6)

Several workers, notably Donsker and Varadhan,\(^7\) have shown that the decay of particles at large times is governed by a stretched exponential\(^10\) of the form

\[ A(t) \sim \exp\left[-t^{d/(d+2)}\right]. \]  
(1.7)

Grassberger and Procaccia\(^8\) found that their Monte Carlo simulations on a two dimensional square lattice with a high trap density of 0.125 is consistent with this asymptotic form. However, several other attempts to verify this prediction by computer simulation in two and three dimensions have failed because of the statistical sampling problems that arise in the algorithms that have been employed; for example, the exact enumeration of random configurations method (ERC method) is efficient only at very high trap densities.\(^14\)

Recently\(^11\) we have investigated a combination of free particle annihilation and trapping (permanent immobilization) reactions on a square lattice by computer simulation which shows the onset of stretched exponential DV behavior at relatively short times. In this paper, we confirm the universality of this stretched exponential behavior by studying annihilation/trapping reactions on triangular and hexagon-
al lattices in 2D \((D=d)\) and in a cubic lattice in 3D. We also find the same behavior at low trap densities, albeit at different times, when the free particle annihilation is turned off. This is equivalent to a direct simulation of the Donsker–Varadhan model.

II. MODELS OF RECOMBINATION KINETICS WITH TRAPPING: MEAN FIELD THEORY AND COMPUTER SIMULATIONS

Two distinct but related reaction schemes were considered. In one of these (the bimolecular trapping/annihilation reaction) we start with a static random distribution of nonoverlapping traps (immobilization sites) and free particles and allow each free particle to move randomly in each time step in one of \(n \) directions to a nearest neighbor site with probability \((1-p_s)/n\), where \(p_s\) is the staying probability (the probability of remaining fixed during a time step) and \(n\) is the coordination number of the lattice. Annihilation \((\ast)\) occurs in pairs between free and trapped \(A\)'s as well as between free \(A\)'s when they meet at the same site. Irreversible trapping occurs when a free particle encounters a fixed trapping site. The elementary steps governing the kinetics are

\[
A + A \rightarrow \ast, \quad A + T \rightarrow A_T, \quad A + A_T \rightarrow T. \tag{2.1}
\]

Here \(k\) is the rate constant for free particle annihilation while the rate constants \(k_T\) for trapping (immobilizing) a free \(A\) or for the annihilation of a trapped \(A\) are the same because a free particle falling into a trap does not know whether it is empty or not. The recombination of hydrogen atoms on a surface in the presence of impurities which act as traps is an example of this reaction scheme. The mean field equations for the rate process are

\[
\frac{dA(t)}{dt} = -A(t)[kA(t) + k_T T(0)] \tag{2.2}
\]

\[
\frac{dT(t)}{dt} = -\frac{dA_T(t)}{dt} = -k_T A(t) [T(t) - A_T(t)], \tag{2.3}
\]

where we have used the fact that

\[
T(0) = T(t) + A_T(t). \tag{2.4}
\]

Solving these equations it is found\(^{11}\) that the free particle density decays as

\[
A(t) = A(0)e^{-x[t + K(1 - e^{-xt})]}^{-1} \tag{2.5}
\]

while the growth \(A_T(t)\) of trapped particles is governed by

\[
A_T(t) = \left[\frac{T(0)}{2}\right]^{1 - \left[1 + K(1 - e^{-xt})\right]^{-2b}}. \tag{2.6}
\]

Here \(A(0)\) and \(T(0)\) are the initial densities of free particles and traps, respectively, and \(x = k_T T(0), \quad K = a/b, \quad a = A(0)/T(0)\) and \(b = k_T/k\). MFT predicts that the free particle density \(A(t)\) decays exponentially at long times. Also, as \(t \to \infty\),

\[
A_T(\infty) = \left[\frac{T(0)}{2}\right]^{1 - \left[1 + K\right]^{-2b}} \tag{2.7}
\]

which implies that \(T(0)/2\) is an upper bound for \(A_T(t)\).

The rate constants \(k\) and \(k_T\) for a lattice of coordination number \(n\) in any dimension are calculated by an extension of our previous perfect mixing combinatorial argument\(^{11}\) for a square lattice with the details presented in the Appendix. We find that, to second order in the density (i.e., neglecting ternary and higher order collisions),

\[
k = (n - 1)/n + 2p_s/n - (n + 1)p_s^2/n \tag{2.8}
\]

\[
k_T = 1 - p_s. \tag{2.9}
\]

Apparently only the rate constant \(k\), and not \(k_T\), is a function of the coordination number \(n\). The rate constants are independent of the trap density \(T(0)\) but depend on the staying probability \(p_s\). As expected intuitively, both rate constants are zero when the staying probability \(p_s\) is unity.

The computer simulations were carried out on lattices of size \((100 \times 100)\) in 2D and a lattice of size \((50 \times 50 \times 50)\) in 3D; periodic boundary conditions being invoked in all cases. Every free particle was allowed to move in every time step in one of \(n \) directions with probability \((1 - p_s)/n\). The simulations reported here are mostly for \(p_s = 0\) but also include a few studies with \(p_s \neq 0\); the initial density of free particles \(A(0)\) ranged between 0.1 and 0.5, while the trap densities \(T(0)\) ranged from 0.001 to 0.5. Averages of the free and trapped particle densities as a function of time were calculated over several hundred initial configurations of free particles and traps distributed randomly.

The results of the computer simulations of bimolecular trapping reactions are compared with mean field theory in Figs. 1 and 2 and in Tables I and II respectively. The density of the trapped particles \(A_T(t)\) is seen to obey mean field theory [Eq. (2.6)] at all times, and the theoretical prediction that no more than half the traps can be filled at an infinitely large time, observed in previous simulations on a square lattice,\(^{11}\) is also verified for triangular \((n = 3)\) and hexagonal \((n = 6)\) lattices in 2D and for a cubic lattice \((n = 6)\) in 3D (see Figs. 1 and 2 and tables I and II). This implies that the detection and enumeration of filled traps at

![FIG. 1. Simulation results (● and ○) for trapped particle densities at infinite time compared with mean field theory (---) for bimolecular and unimolecular annihilation/trapping reactions on a hexagonal lattice.](http://jcp.aip.org/jcp/copyright.jsp)
infinite time could be used to determine the initial number of empty traps. This may be useful in experiments in which the detection of empty traps is difficult or impossible. In contrast to the growth of trapped particles $A_T(t)$ with time, the long time decay of free $A$’s does not obey mean field theory [Eq. (2.5)], especially when the trap density is small (see Fig. 2). This discrepancy occurs relatively soon and the free particle density at large times appears to conform to the stretched exponential behavior predicted by Donsker and Varadhan for the catalytic annihilation of free $A$’s. We show our results in Fig. 4 for triangular and hexagonal lattices in 2D and in Fig. 5 for a cubic lattice in 3D. In Fig. 6 we see that the onset of this stretched exponential behavior at low trap densities is modified when the free particle annihilation is turned off with two or more free particles prevented from occupying the same site; nevertheless it does occur. In contrast to the Monte Carlo simulations of Grassberger and Proccaccia on a 2D square lattice with a trap density of 0.125, our MD simulations seem to indicate that the stretched exponential behavior breaks down at high trap densities.

The DV stretched exponential was also observed in a related reaction scheme called unimolecular trapping/annihilation (see Fig. 3), in which there are no traps at the beginning, but each particle can be immobilized permanently at each time step with a probability $k^r$ which corresponds to the trap density $T(0)$ in the previous scheme. This unimolecular immobilization may be envisioned as being due to a conformational change in the diffusing particle. The elementary steps are now

$$A + A \rightarrow *, \quad A \rightarrow A_T, \quad A + A_T \rightarrow *.$$  

The kinetic (mean field) equations for the reaction rates are

$$\frac{dA(t)}{dt} = -A(t) \left[ kA(t) + k' + k_A(t) \right]$$  

$$\frac{dA_T(t)}{dt} = A(t) \left[ k' - k_T A_T(t) \right].$$  

### Table I

<table>
<thead>
<tr>
<th>$A(0)/T(0)$</th>
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<th>$A_T(\infty)/T(0)$ (sim)</th>
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</table>

| $d = 2$; Hexagonal lattice ($n = 6$) |
| 0.2 | 0.5 | 0.155 | 0.155 |
| 0.4 | 0.5 | 0.249 | 0.250 |
| 0.5 | 0.5 | 0.283 | 0.290 |
| 0.6 | 0.5 | 0.311 | 0.317 |
| 1.0 | 0.5 | 0.383 | 0.393 |
| 1.25 | 0.4 | 0.410 | 0.416 |
| 2.5 | 0.2 | 0.466 | 0.463 |
| 5.0 | 0.1 | 0.490 | 0.487 |
| 10.0 | 0.01 | 0.497 | 0.495 |
| 100.0 | 0.001 | 0.500 | 0.499 |
which have the solutions\textsuperscript{11}

\[ A_T(t) = \left( k'/k_T \right) \left( 1 - \exp[-k_T I(t)] \right), \]

\[ A(t) = -2k'/k + k' \exp[-k_T I(t)]/(k - k_T) \]

\[ + C \exp[-k I(t)], \]

where \( C = A(0) + 2k'/k - k'/\left(k - k_T\right) \) and \( I(t) = \int_0^t A(t')dt' \). Note the similarity of Eq. (2.13) to Eq. (2.6). The solutions, which depend on \( I(t) \), are not in closed form, compelling us to solve the differential equations numerically in order to follow the time dependence of the free and trapped particles. Since the integral \( I(\infty) \) is positive it follows that \( k'/k_T \) is an upper bound for \( A_T(\infty) \). At infinite time \( (t = \infty) \), the number of free particles is zero, i.e., \( A(\infty) = 0 \), which leads, when \( k \neq k_T \) (i.e., \( b \neq 1 \)), to the following transcendental equation:

\[ -2 + \left( 1/(1 - b) \right) Y + \left( A(0) k'/k_T - 2 - 1/(1 - b) \right) Y^{1/b} = 0, \]

where \( Y = \exp[-k_T I(\infty)] \) is the root of Eq. (2.15). It is seen that \( Y \) is a function of \( A(0) k'/k_T \) and \( b \). When \( t \to \infty \), Eq. (2.13) implies that

\[ A_T(\infty)/k' = (1/k_T)(1 - Y). \]

Comparison of Eqs. (2.16) and (2.7) shows that the trapping probability \( k' \) in our unimolecular scheme corresponds to the trap density \( T(0) \) in bimolecular trapping/annihilation reactions.

The rate constants \( k \) and \( k_T \) for unimolecular trapping/annihilation can also be expressed by Eqs. (2.8) and (2.9) if we identify \( k' \) with the staying probability \( p_s \),\textsuperscript{11} when we get a quadratic equation for \( k_T \):

\[ (1 + n)k_T - 2nk_T + nk = 0, \]

which provides an explicit expression for the coupling between the rate constants and leads to \( b = k_T/k = n/[n(n - 1) + k'(n + 1)] \). Figure 1 shows that the agreement between the mean field calculations [Eq. (2.16)] and simulations of \( A_T(\infty)/k' \) for unimolecular trapping on a hexagonal lattice is limited, unlike bimolecular trapping on the same lattice. More detailed comparisons for triangular and hexagonal lattices in 2D and a cubic lattice in 3D are provided in Tables II and III. Also Fig. 3 shows the departure of both \( A_T(t) \) and \( A_T(t) \) from MFT in a unimolecular trapping reaction on a triangular lattice when \( k' = 0.01 \). It appears that this always occurs, in unimolecular trapping reactions on any lattice, except when \( k' \) is large (see Fig. 1). However, DV behavior of the free particle decay is observed in all cases. The stretched exponential decay of free particles in bimolecular and unimolecular trapping/annihilation reactions on a cubic lattice \( (d = 3) \) for the same value of \( k' \) and \( T(0) \) are compared in Fig. 6.

As observed earlier, the rate constants \( k \) and \( k_T \) given in Eqs. (2.8) and (2.9) (see the Appendix for the derivation) depend on the staying probability \( p_s \). If we differentiate Eq. (2.8) with respect to \( p_s \) and set the result equal to zero, we get the optimal value of \( p_s \) for which \( k' \) is a maximum.

\[ \text{FIG. 4. Stretched exponential DV behavior of the decay of free particles in bimolecular annihilation/trapping reactions on triangular and hexagonal lattices in 2D. Note DV behavior obtains for low but not high trap densities.} \]
\[ p_i^* = \frac{1}{(n+1)} \]  

\[ k^* = \frac{(n-1)}{n + 1} \left( \frac{n}{(n+1)} \right) \]

The effect of the staying probability \( p_i \) on the kinetics of trapping/annihilation reactions by computer simulation has also been studied by us; the results for bimolecular trapping/annihilation reactions on a 2D triangular lattice are shown in Fig. 7. When \( A(t) \) decays at its maximum rate, \( A(0)/A(t) \) will be largest. It is seen that the simulation results agree qualitatively with the prediction of Eq. (2.18). Similar behavior was also found for unimolecular reactions.

III. DISCUSSION

Our analysis indicates that the perfect mixing mean field description of trapped \( A \)'s in bimolecular trapping reactions on triangular and hexagonal lattices in 2D and on a cubic lattice in 3D agrees very well with the simulation results. However, agreement of trapped \( A \)'s with mean field theory is found only for large trapping probabilities \( k' \) in unimolecular trapping reactions. The explanation of this difference between unimolecular and bimolecular reactions is that, unlike unimolecular reactions, the traps in bimolecular trapping reactions are static and are uniformly distributed. This leads to an absence of fluctuations in the density distribution of trapped \( A \)'s which ensures that their evolution obeys mean field theory.

We have identified \( k' \) with \( p_i \) in our mean field analysis of unimolecular trapping reactions. The difference between the two is that the rate constant \( k' \) causes a particle to be trapped permanently with probability \( k' \), whereas the trapping probability \( p_i \) immobilizes the particle only for one time step. However, our derivation of the kinetic rate constants includes no memory effects which distinguish between \( k' \) and \( p_i \), which may contribute to the discrepancy between our mean field calculations of the trapped particle density and the simulations. Another explanation for the failure of the mean field theory in unimolecular trapping reactions is that there may be correlations between trapped \( A \)'s which are neglected in the derivation of the rate constants.

For both bimolecular and unimolecular trapping/annihilation reactions the free \( A \) population deviates rapidly from mean field theory when the trap density \( T(0) \) or the trapping probability \( k' \) is small. This is in accord with our earlier observations of annihilation reactions with trapping on a square lattice\(^{11}\) in two dimensions and can be understood by noting that a high trap density (or large \( k' \)) will reduce the fluctuations in free \( A \)'s. When the trap density \( T(0) \) is low or \( k' \) is small, the discrepancy between mean field theory and the simulation results for \( A(t) \) grows with increasing time (see Figs. 2 and 3), and mean field theory eventually fails completely. Thus, fluctuations of free \( A \)'s become dominant at long times when the density of traps or the value of \( k' \) is small.

Our most important observation is the universality of the stretched exponential found earlier for a square lattice\(^{11}\) and in the present paper in both bimolecular and unimolecular trapping reactions on a variety of lattices in 2D and 3D. The question is why do both bimolecular and unimolecular trapping reactions have the same asymptotic behavior as that of simple trapping reactions? We know that the...
TABLE III. The ratio $A_r(\infty)/k'$ as a function of $A(0)/k'$ for unimolecular trapping reactions when the staying probability $p_i = 0$; comparison of computer simulation with predictions of MFT and combinatorial analysis of rate constants.

<table>
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$d = 2$; Hexagonal lattice ($n = 6$)

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*Calc from Eq. (2.16) in which $Y$ is obtained as the solution to Eq. (2.15) assuming $k_r = 1 - k'$, $k = n - 1/n + 2k'/n - (n + 1)/n k'^2$, and $b = k_r/k = n/(n - 1 + (n + 1)k')$.

Donsker–Varadhan mechanism for the observation of a stretched exponential requires large areas totally devoid of traps. This can be realized at low trap densities in bimolecular trapping reactions and small values of the trapping probability $k'$ for unimolecular trapping reactions. In the long time limit, when the density of the free $A$'s is very low, the annihilation of free particles becomes relatively unimportant. There is then no difference between the bimolecular and unimolecular reactions, between trapping annihilation reactions and simple trapping reactions and, in the long time limit, the only process observed will be the diffusion of free $A$'s among the sparsely distributed traps. The decay of free $A$'s in all of these cases should show similar asymptotic behavior which depends on the dimensionality. In this way the universality of the stretched exponential can be understood.

The relatively rapid cross over from mean field behavior to stretched exponential decay of the Donsker–Varadhan form observed by us is in sharp contrast to the very slow approach to DV behavior predicted or observed by other workers. For example, the survival probability at which DV behavior sets in is calculated by Fixman$^{12}$ as $10^{-67}$ or less for $d = 3$, whereas Klafter et al.$^{13}$ obtain $10^{-21}$ for $d = 2$ and Havlin et al.$^{14}$ estimate $10^{-13}$ or less for $d = 2$ and $d = 3$. In our $A-A$ annihilation/trapping simulations, crossover from mean field behavior to DV behavior is observed at a survival fraction of about $10^{-1}$ (or larger) for $d = 2$ at low trap densities, and our results (Fig. 3) for $d = 3$ are quite similar to the two dimensional case (in $d = 3$ the DV exponent is 3/5) except that the crossover occurs when the survival fraction is much smaller $\sim 10^{-2}$. This will not be difficult to understand if we notice the fact that annihilation among free particles will enhance the decay process. It should be emphasized that our kinetic scheme of trapping with free particle annihilation differs from that assumed in the DV model, and, furthermore, our simulation method, unlike some, allows for spontaneous density fluctuations as the reaction proceeds since every particle has a finite probability of moving in every time step. With free particle annihilation turned off in the bimolecular scheme, the DV model is recovered and the stretched exponential is observed at a low trap density (see Fig. 6) with a longer induction time.

We conclude with a few comments concerning the difficulties associated with a simulation of this type. It is well known that DV asymptotic relaxation is due to the existence of large trap-free voids which occur with an exponentially small probability, and that it is the balance between the long lifetime in such a void vs the small probability of finding this void which produces the DV stretched exponential. It has also been shown that the relative mean square fluctuation in the density of free particles strongly diverges at large times, and we suspect that this condition holds for the higher moments as well. This would imply that the probability $P(N_A,t)$ of $N_A$ particles surviving at time $t$ is very broad and pathological at long times. In other words, configurations with several particles in a trap-free void are just as relevant statistically as a single particle in such a void, and this implies that a very large number of particle–trap configurations are necessary to produce the cross over from mean field behavior to the DV asymptotic form. In our opinion, adequate sampling in this simulation is much more important than finite system size effects so long as the system is large enough so that only a few periodic images can be explored by a random walker before it is trapped. Although our "pure simulation technique" could lead to simple exponential decay at sufficiently long times due to periodic boundary conditions$^{14}$ we have taken care to choose a sufficiently large
lattice size, along with free particle and trap densities so that the periodic image artifact is not observed. While a scrupulous study of system size effects is desirable, we feel that these novel observations of both perfect mixing mean field kinetics and DV stretched exponential behavior are statistically valid, with significant implications for diffusion limited chemical recombination kinetics in heterogeneous (trapping) media.

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APPENDIX. COMBINATORIAL CALCULATION OF THE RATE CONSTANTS WITH A STAYING PROBABILITY $p_s$

The details of the calculation for square lattice has been given in Ref. 11. Here we generalize our results to any lattice type with no limit to the dimensionality. We use $A(t)$, $A_T(t)$, and $T(t)$ to represent the normalized densities or the probabilities of the free $A$, trapped $A$, and traps at time $t$, and $n$ to represent the coordination number of a site. We will focus our attention on a central site and calculate the change in probability for a site to be occupied in two successive time steps. We consider different arrangements of free particles adjacent to the central site at time $t + 1$ and calculate all contributions to the probabilities of occupation at time $t + 1$. At time $t$, we assume $A(t)$ is the probability for a central site to be occupied by a free particle $A$. Because each particle has been assigned a staying probability $p_s$, the net probability of a move will be $(1 - p_s)$. When two or more particles occupy the same site simultaneously, annihilation occurs in pairs.

The probabilities $I_t$, for the central site to be occupied by a free particle at time $t + 1$ are calculated for the following initial configurations at time $t$:

1. A free particle is at the central site and all neighboring sites are empty:

$$I_0 = p_s A(t)[1 - A(t)]^n.$$  \hspace{1cm} (A1)

Here the region enclosed in parenthesis represents a central site and the dot represents a free particle.

2. The central site is either empty or occupied by a free $A$ and a neighboring site is occupied by a free $A$:

$$I_1 = (1 - p_s) A(t)[1 - A(t)]^n - T(0) \times (1 - p_s) A(t)[1 - A(t)]^{n - 1},$$  \hspace{1cm} (A2)

$$I_1' = [p_s (n - 1 + p_s) + (1 - p_s)^2] A(t)^2 [1 - A(t)]^{n - 2}.$$  \hspace{1cm} (A3)

(3) The central site is either empty or occupied by a free $A$ and each of two neighboring sites are occupied by a free $A$:

$$I_2 = [(n - 1)/n] (1 - p_s) (n - 1 + p_s)$$

$$\times A(t)^2 [1 - A(t)]^{n - 1} - T(0) \{[n - 1]/n \}

$$\times (1 - p_s) (n - 1 + p_s) A(t)^2 [1 - A(t)]^{n - 2}.$$  \hspace{1cm} (A4)

$$I_2' = [(n - 1)/2n] (1 - p_s)^2$$

$$\times A(t)^2 [1 - A(t)]^{n - 2}.$$  \hspace{1cm} (A5)

We need not consider the other configurations with three or more particles in the neighborhood of a central site since they give rise to terms beyond $A(t)^3$ and $T(0)A(t)$ in the calculation of $A(t + 1)$. Thus we have

$$A(t + 1) = I_0 + I_1 + I_1' + I_2 + I_2' + \cdots.$$  \hspace{1cm} (A6)

Substituting (A1)–(A5) into Eq. (A6) and keeping only the terms to orders $A(t)^2$ and $T(0)A(t)$, we find

$$A(t + 1) = A(t) + \{ - n [p_s(n - 1 + p_s) + (1 - p_s)^2]

$$+ [(n - 1)/n] (1 - p_s) (n - 1 + p_s) A(t)^2$$

$$- T(0)A(t)(1 - p_s).$$  \hspace{1cm} (A7)

Comparing Eq. (A7) with Eq. (2.2) we have

$$k = n [p_s(n - 1 + p_s) + (1 - p_s)^2]$$

$$- [(n - 1)/n] (1 - p_s) (n - 1 + p_s)$$

$$+ 2p_s/n - (n + 1)p_s^2/n,$$  \hspace{1cm} (A8)

$$k_T = 1 - p_s.$$  \hspace{1cm} (A9)


