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Reversible Diffusion-Influenced Reactions: Comparison of Theory and Simulation for a Simple Model

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Computer simulations of a simple model of a reversible diffusion-influenced reaction are used to test various approximate theoretical treatments. The model is a random walk in continuous time of N particles on a one-dimensional lattice. The particles can be trapped reversibly at the origin. They move independently, except that only one particle at a time can occupy the origin. The theory is formulated in general terms using master equations for the probability distribution of occupancy numbers of different lattice sites. The general theoretical problem is not solved, although some exact consequences are presented. Several approximation schemes are described and tested by comparison with the simulations.

KEY WORDS: Chemical kinetics; reversible reactions; diffusion; bimolecular; master equation; simulation.

1. INTRODUCTION

This paper is about a model for bimolecular diffusion-influenced reactions, its simulation on a computer, and its use in testing various theoretical proposals for treating such reactions.

What is arguably the simplest model of a bimolecular diffusion-influenced reaction can be formulated as follows. Consider a one-dimensional lattice with $L+1$ sites labeled $i = 0, 1, 2,..., L$. A single particle on the

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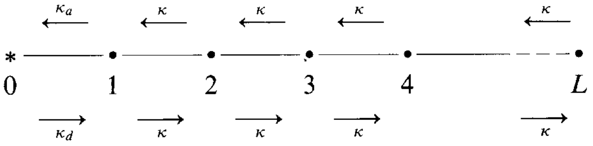
lattice is assumed to undergo a random walk in continuous time with transition rates described by the scheme



The association reaction has rate κ_a; the dissociation reaction has rate κ_d; and the hopping rate between all other sites is κ. Now suppose that N particles are placed on this lattice, with the restriction that the origin can hold only one particle at a time. All other sites can have multiple occupancy. To emphasize the special nature of the site $i = 0$, we labeled it by $*$. It is a reversible trap. Particles that are away from the origin are invisible to each other and move independently. However, the constraint of single occupancy at the origin gives rise to a coupling of the particle motions.

Consider a large number of replicas of the lattice, i.e., an ensemble, with initial particle locations taken from some specified probability distribution. (This is in fact how the simulations to be described later were done.) For any arbitrary initial distribution, this ensemble will come to equilibrium at long times. In the thermodynamic limit $N \to \infty$, $L \to \infty$, with $C = N/L$ fixed, the fractional occupancy of the trap at equilibrium is $K_{\text{eq}} C/(1 + K_{\text{eq}} C)$, where the equilibrium constant K_{eq} is κ_a/κ_d. This paper deals with the evolution of certain initial states and their approach to equilibrium. In particular, we are interested in the survival probability (defined as one minus the fractional occupancy) of the trap as a function of time.

The problem is simple when the reaction is irreversible, i.e., the dissociation rate κ_d is zero. Since in this case all the particles move independently, the N-particle survival probability is just the product of the one-particle survival probabilities. In fact, the Smoluchowski description of irreversible reactions is exact for this model.(1,2) We shall obtain an analytic expression for the survival probability of this model in the thermodynamic limit, in the special case where the association rate κ_a is the same as the hopping rate κ.

When the reaction is reversible, the complexity of the problem increases dramatically. The only *exact* results we have been able to obtain are certain relations among trap survival probabilities corresponding to different initial conditions.

However, the exact kinetic behavior of this model can be readily simulated on a computer. Simulations can be used to evaluate various approximate theoretical approaches to the description of more general reversible diffusion-influenced reactions. We focus on three approaches that are exact for this model in the irreversible case $\kappa_d = 0$, and which give the correct equilibrium limit in the reversible case. The first(3) is based on a modification of the rate equations that are used to describe irreversible reactions in the framework of the Smoluchowski theory. The second(4) involves generalizations of certain convolution relations that describe exactly reversible trapping in a system containing a single particle. The third(3,5) can be obtained by using a superposition approximation to truncate a hierarchy of reduced particle-trap distribution functions. These approaches were originally formulated to treat reactions in a three-dimensional continuum. They describe the association reaction at contact by means of the radiation or partially absorbing boundary condition. They can all be implemented(3) once one knows the time-dependent rate coefficient for the irreversible reaction. This allows us to apply these approaches to our discrete one-dimensional lattice model without modification.

The outline of the paper is as follows. In Section 2, we present a pedagogical treatment of irreversible reactions and obtain an exact analytical expression for the survival probability in the special case $\kappa_a = \kappa$. As was just observed, this is needed in order to implement approaches to the reversible case. In Section 3, we briefly describe the three approximate treatments mentioned above. In Section 4, we present a rigorous formulation of the dynamical behavior of our model, based on the master equation for the probability distribution of occupation numbers of all sites at time t. Since the difficulty of our problem comes from the constraint of single occupancy of the trap, an occupation number approach appears natural. By making suitable approximations, we show how the various approaches described in Section 3 can be obtained in a unified way. We conclude Section 4 by deriving exact relations between survival probabilities for certain different initial conditions. In Section 5 we describe the simulations, and compare them with the predictions of the various approximate treatments. Finally, we make some concluding comments in Section 6.

2. IRREVERSIBLE TRAPPING

When there is no dissociation, or $\kappa_d = 0$, the kinetics of this model can be worked out easily since one is dealing with independent particles. The single-occupancy constraint does not have any effect on the survival probability in this case. Once the trap in any replica is occupied, it stays occupied and does not produce any interaction between the other particles. The Smoluchowski treament of irreversible reactions turns out to be exact for this model.(1,2) We present it here in an elementary way that highlights the close analogy that exists between the continuum and lattice descriptions.

The survival probability of a single particle initially at lattice site i is $S(t\,|\,i)$. (Throughout the paper, we consistently use a capital Roman S for a single-particle survival probability. Many-particle survival probabilities will be denoted by a capital script $\mathscr{S}$.) By the choice of initial condition, it is clear that $S(0\,|\,i)=1$. For our model, this quantity satisfies a discrete analog of the diffusion equation. For $i=2, 3,\ldots$ we have

$$\frac{dS(t\,|\,i)}{dt}=\kappa(S(t\,|\,i+1)-2S(t\,|\,i)+S(t\,|\,i-1)) \tag{2.1}$$

and for $i=1$ we have

$$\frac{dS(t\,|\,1)}{dt}=-(\kappa_a+\kappa)\,S(t\,|\,1)+\kappa S(t\,|\,2) \tag{2.2}$$

One can use Eq. (2.1) for $i=1$ also, by formally requiring that

$$\kappa(S(t\,|\,1)-S(t\,|\,0))=\kappa_a S(t\,|\,1) \tag{2.3}$$

This condition is the discrete analog of the radiation (partially reflecting) boundary condition in continuum theories. This becomes clearer if we introduce the backward difference operator ∇ defined by $\nabla f(i)=f(i)-f(i-1)$ and we rewrite Eq. (2.3) as

$$\kappa\,\nabla S(t\,|\,1)=\kappa_a S(t\,|\,1) \tag{2.4}$$

Compare this with the boundary condition that describes the reaction of two spherically symmetric molecules at contact ($r=R$):

$$4\pi DR^2\left[\frac{dS(t\,|\,r)}{dr}\right]_{r=R}=\kappa_a S(t\,|\,R) \tag{2.5}$$

The similarity between Eqs. (2.4) and (2.5) allows us to treat lattice and continuum problems in a formally identical way.

Consider a system of N particles initially in lattice sites i_n, $n=1, 2,\ldots, N$. Let $\mathscr{S}_N(t\,|\,\{i_n\})$ be the corresponding survival probability. (As noted before, we denote many-particle survival probabilities by a script $\mathscr{S}$.) Since the particles are independent, we have

$$\mathscr{S}_N(t\,|\,\{i_n\})=\prod_{n=1}^{N} S(t\,|\,i_n) \tag{2.6}$$

Suppose that initially the particles are distributed randomly on the lattice, and the trap is empty. In the absence of reaction, or $\kappa_a = 0$, this is the equilibrium distribution for our model. Since the probability that one particle is on a given lattice site is $1/L$, the resulting many-particle survival probability is

$$\begin{aligned}\mathscr{S}_N(t \mid \mathrm{eq}) &= \left[\frac{1}{L} \sum_{i=1}^{L} S(t \mid i)\right]^N \\ &= \left[1 - \frac{1}{L}\left(\sum_{i=1}^{L} [1 - S(t \mid i)]\right)\right]^N \end{aligned} \tag{2.7}$$

In the thermodynamic limit ($N \to \infty$, $L \to \infty$, $N/L = C$), this gives

$$\mathscr{S}(t \mid \mathrm{eq}) = \exp\left(-C \sum_{i=1}^{\infty} [1 - S(t \mid i)]\right) \tag{2.8}$$

By summing Eq. (2.1) over $i = 2, 3, \ldots$, and adding Eq. (2.2), we obtain

$$\frac{d}{dt} \sum_{i=1}^{\infty} S(t \mid i) = -\kappa_a S(t \mid 1) \tag{2.9}$$

This allows us to rewrite Eq. (2.8) as

$$\mathscr{S}(t \mid \mathrm{eq}) = \exp\left[-C \int_0^t k(t')\, dt'\right] \tag{2.10}$$

where we have defined the time-dependent rate coefficient $k(t)$ as

$$k(t) = \kappa_a S(t \mid 1) \tag{2.11}$$

Note that by using Eq. (2.4), this can be rewritten as

$$k(t) = \kappa \nabla S(t \mid 1) \tag{2.12}$$

Finally, by differentiating Eq. (2.10) with respect to time, we find

$$\frac{d\mathscr{S}(t \mid \mathrm{eq})}{dt} = -k(t)\, C \mathscr{S}(t \mid \mathrm{eq}) \tag{2.13}$$

which is in fact the starting point of the Smoluchowski approach. For this model, the one particle survival probability corresponds to the trap–particle pair distribution function of Smoluchowski theory. Equation (2.12) expresses $k(t)$ as the reactive flux at contact (which in our problem is lattice site 1).

Now we find $k(t)$ for our model by following closely the steps used in the continuum case. The Laplace transform [we use the notation $\hat{f}(z)=\int_0^\infty dt\, e^{-zt}f(t)$] of Eq. (2.1) is

$$-1+z\hat{S}(z\mid i)=\kappa[\hat{S}(z\mid i+1)-2\hat{S}(z\mid i)+\hat{S}(z\mid i-1)] \tag{2.14}$$

Make the substitution

$$\hat{S}(z\mid i)=\frac{1}{z}+C(z)[\hat{f}(z)]^i \tag{2.15}$$

where $\hat{f}(z)$ is determined by requiring that Eq. (2.14) is satisfied for all i, and $C(z)$ is determined by satisfying the boundary condition (2.3). The first requirement leads to a quadratic equation for $\hat{f}(z)$; the solution

$$\hat{f}(z)=\frac{2\kappa+z-[z(z+4\kappa)]^{1/2}}{2\kappa} \tag{2.16}$$

is the root which gives $\hat{f}(z)=0$ when $\kappa=0$. On using the boundary condition, we find $C(z)$,

$$C(z)=\frac{\kappa_a}{z[\kappa(\hat{f}-1)-\kappa_a\hat{f}]} \tag{2.17}$$

Finally, the transform of the time-dependent rate constant is

$$\hat{k}(z)=\frac{\kappa_a}{z}\frac{\kappa(1-\hat{f})}{\kappa+(\kappa_a-\kappa)\hat{f}} \tag{2.18}$$

In the special case where the association rate κ_a is the same as the hopping rate κ, this reduces to

$$\hat{k}(z)=\frac{1}{2}\left[\left(\frac{z+4\kappa}{z}\right)^{1/2}-1\right] \tag{2.19}$$

which can be inverted to give $k(t)$,

$$k(t)=\kappa e^{-2\kappa t}[I_0(2\kappa t)+I_1(2\kappa t)] \tag{2.20}$$

where I_n is a modified Bessel function of the first kind. This can be integrated so that

$$\int_0^t dt'\, k(t')=2\kappa te^{-2\kappa t}[I_0(2\kappa t)+I_1(2\kappa t)] + \tfrac{1}{2}e^{-2\kappa t}I_0(2\kappa t)-\tfrac{1}{2} \tag{2.21}$$

This means that we can find $\mathscr{S}(t\mid \mathrm{eq})$ analytically in the special case $\kappa_a=\kappa$.

The many-particle survival probability clearly depends on the initial distribution of particles. For future reference, we consider the situation where initially the trap is empty, the particles are distributed randomly with concentration C, and site 1 contains an extra "geminate" particle. This initial condition describes an essentially irreversible reaction in which dissociation of a particle in a trap is induced photochemically.$^{(6)}$ We denote the resulting survival probability by $\mathscr{S}(t \mid 1)$, where the "1" serves as a reminder that there is an extra particle at site 1. Since all the particles are independent, it is clear that$^{(4,6)}$

$$\mathscr{S}(t \mid 1) = S(t \mid 1)\, \mathscr{S}(t \mid \mathrm{eq}) = \frac{k(t)}{\kappa_a} \mathscr{S}(t \mid \mathrm{eq}) \tag{2.22}$$

where $S(t \mid 1)$ is the survival probability of a single particle initially at site 1, and where Eq. (2.11) was used to relate it to $k(t)$. By using Eq. (2.10), this can be rewritten as

$$\mathscr{S}(t \mid 1) = -\frac{1}{\kappa_a C} \frac{d}{dt} \mathscr{S}(t \mid \mathrm{eq}) \tag{2.23}$$

3. APPROXIMATE APPROACHES TO REVERSIBLE TRAPPING

Recently Szabo$^{(3)}$ discussed and compared three approximate ways of handling the complications that arise when the reaction is reversible. Here we describe how these approaches may be applied to our model. They all have the property that they are exact for our model in the irreversible limit. In addition they all predict the correct equilibrium limit in the reversible case. In the following section we will show that they can be obtained in a unified way by making appropriate approximations to a rigorous formulation of the problem.

3.1. Rate Equations

The simplest approach is based on modifying the Smoluchowski rate equation (2.13) that is used to treat an irreversible reaction. Suppose that initially the trap is empty and the particles are at equilibrium on the rest of the lattice. We denote the survival probability of the trap by $\mathscr{S}_{\mathrm{rev}}(t \mid \mathrm{eq})$; the subscript rev indicates that we are dealing with the reversible case, and $\mid \mathrm{eq})$ labels the initial condition. The probability that the trap is occupied at time t is $1 - \mathscr{S}_{\mathrm{rev}}(t \mid \mathrm{eq})$. Perhaps the simplest modification of the Smoluchowski approach that one can try is to add a dissociation term $\kappa_d[1 - \mathscr{S}_{\mathrm{rev}}(t \mid \mathrm{eq})]$ to the right-hand side of Eq. (2.13). This clearly reduces to the correct behavior when $\kappa_d = 0$, but unfortunately it predicts the wrong equilibrium limit when $\kappa_d \neq 0$. A modification that does lead to the correct equilibrium limit is

$$\frac{d}{dt}\mathscr{S}_{\text{rev}}(t\,|\,\text{eq}) = -\frac{k(t)}{\kappa_a}\left(\kappa_a C \mathscr{S}_{\text{rev}}(t\,|\,\text{eq}) - \kappa_d[1 - \mathscr{S}_{\text{rev}}(t\,|\,\text{eq})]\right) \tag{3.1}$$

where $k(t)$ is the irreversible time-dependent rate coefficient that was introduced in the previous section. The solution of this equation, with the initial condition $\mathscr{S}_{\text{rev}}(0\,|\,\text{eq}) = 1$, is

$$\mathscr{S}_{\text{rev}}(t\,|\,\text{eq}) = \frac{1}{1 + K_{\text{eq}}C}\left(1 + K_{\text{eq}} C \exp\left[-(C + K_{\text{eq}}^{-1}) \int_0^t k(t')\,dt'\right]\right) \tag{3.2}$$

where $K_{\text{eq}} = \kappa_a/\kappa_d$. This approach is clearly very easy to use. As we shall see later, while it turns out to be exact at short times and gives the correct equilibrium limit, it does not work very well at intermediate times. However, in three dimensions, where diffusion plays a much less significant role, this may be a much more useful approximation.

3.2. An Approach Based on Convolution Relations

A more sophisticated treatment of pseudo-first-order reactions has been given by Agmon and Szabo.(4) The basic ideas behind their approach can be best understood by first considering the initial condition where the trap is occupied and the other particles are randomly distributed outside the trap. We denote the resulting trap survival probability by $\mathscr{S}_{\text{rev}}(t\,|\,*)$, where $|*)$ indicates that the trap is initially filled. When the bound particle dissociates from the trap for the first time, there is an extra particle at site 1. The irreversible survival probability of this configuration [see Eq. (2.22)] is $\mathscr{S}(t\,|\,1)$. We will call this extra particle the geminate particle. All other particles will be referred to as bulk particles. The trap can now be reoccupied by either the geminate particle or one of the bulk particles. In the first case, a subsequent dissociation again produces the configuration where the geminate particle is at site 1 and the bulk particles are in equilibrium. However, in the second case, the resulting distribution of particles is not necessarily the equilibrium one. If the trap remains occupied for a sufficiently long time, this distribution will eventually relax to equilibrium before the next dissociation event.

The crucial approximation made in this approach is that every dissociation event is assumed to produce a configuration with a geminate particle at site 1 and bulk particles in equilibrium. The evolution or response of this configuration is described by $\mathscr{S}(t \mid 1)$. The rate at which this configuration is produced is $\kappa_d[1-\mathscr{S}_{\text{rev}}(t \mid *)]$. Therefore, one can express $\mathscr{S}_{\text{rev}}(t \mid *)$ as the convolution of the rate with the response,

$$\mathscr{S}_{\text{rev}}(t \mid *) = \kappa_d \int_0^t dt' [1 - \mathscr{S}_{\text{rev}}(t-t' \mid *)]\, \mathscr{S}(t' \mid 1) \tag{3.3}$$

which implicitly determines the time evolution of the trap survival probability. In the one-particle case, $C \to 0$, $\mathscr{S}(t \mid 1) = S(t \mid 1)$ and Eq. (3.3) is exact. In other words, this formalism provides an exact description of the reversible binding of a single particle.(4)

One of the attractive features of this approach is that it can handle different initial conditions with equal ease. For example, let $\mathscr{S}_{\text{rev}}(t \mid \text{eq})$ be the survival probability when initially the trap is empty and the bulk particles are in equilibrium. The generalization of Eq. (3.3) is(4)

$$\mathscr{S}_{\text{rev}}(t \mid \text{eq}) = \mathscr{S}(t \mid \text{eq}) + \kappa_d \int_0^t dt' [1 - \mathscr{S}_{\text{rev}}(t-t' \mid \text{eq})]\, \mathscr{S}(t' \mid 1) \tag{3.4}$$

where the first term is just the irreversible survival probability of the trap. Finally, suppose that the trap is empty, the bulk particles are in equilibrium, and there is a geminate particle at site 1. The resulting survival probability, denoted by $\mathscr{S}_{\text{rev}}(t \mid 1)$, satisfies

$$\mathscr{S}_{\text{rev}}(t \mid 1) = \mathscr{S}(t \mid 1) + \kappa_d \int_0^t dt' [1 - \mathscr{S}_{\text{rev}}(t-t' \mid 1)]\, \mathscr{S}(t' \mid 1) \tag{3.5}$$

By Laplace-transforming these equations, and using Eq. (2.23), it is possible to express the transforms of each of the reversible survival probabilities in terms of the transform of the irreversible survival probability $\mathscr{S}(t \mid \text{eq})$. In applications, it may be more convenient to solve the convolution equations directly in the time domain by discretizing the integrals.

By eliminating the transform of $\mathscr{S}(t \mid \text{eq})$ between the transforms of $\mathscr{S}_{\text{rev}}(t \mid \text{eq})$, $\mathscr{S}_{\text{rev}}(t \mid *)$, and $\mathscr{S}_{\text{rev}}(t \mid 1)$, one can obtain relations between these quantities. In particular one can show that(4)

$$\mathscr{S}_{\text{rev}}(t \mid \text{eq}) + K_{\text{eq}} C \mathscr{S}_{\text{rev}}(t \mid *) = 1 \tag{3.6}$$

and

$$\frac{d}{dt} \mathscr{S}_{\text{rev}}(t \mid \text{eq}) = -\kappa_a C \mathscr{S}_{\text{rev}}(t \mid 1) + \kappa_d [1 - \mathscr{S}_{\text{rev}}(t \mid \text{eq})] \tag{3.7}$$

The utility of these relations is that once the survival probability is calculated for one initial condition, say |eq) where the trap is empty and the bulk particles are in equilibrium, they can be used to find survival probabilities for the other initial conditions.

Although these relations were obtained within the framework of an approximate theory, they are in fact *exact*. This will be shown later.

3.3. Superposition Approximation

Lee and Karplus$^{(5)}$ treated reversible diffusion-influenced reactions by generalizing the theory developed by Monchick *et al.*$^{(7)}$ and Waite$^{(8)}$ for irreversible reactions. They derived an infinite hierarchy of equations for the reduced n-particle distribution functions. They truncated or decoupled the hierarchy at the lowest level by a superposition approximation. In this way they obtained a coupled set of equations for the trap survival probability $\mathscr{S}_{\text{rev}}(t\,|\,\text{eq})$ and the trap–particle distribution function $p(i, t)$. For the model considered in this paper, the lattice version of these equations is

$$\frac{d}{dt}\mathscr{S}_{\text{rev}}(t\,|\,\text{eq}) = -k_f(t)\,C\mathscr{S}_{\text{rev}}(t\,|\,\text{eq}) + \kappa_d[1-\mathscr{S}_{\text{rev}}(t\,|\,\text{eq})] \tag{3.8}$$

where $k_f(t)$ is related to the trap–particle distribution function by

$$k_f(t) = \kappa_a p(1, t) \tag{3.9}$$

This distribution function satisfies

$$\frac{\partial}{\partial t}p(i, t) = \kappa[p(i+1, t) - 2p(i, t) + p(i-1, t)] \tag{3.10}$$

with the initial condition $p(i, 0) = 1$ and the boundary condition

$$\kappa[p(1, t) - p(0, t)] \equiv \kappa\,\nabla p(1, t) = \kappa_a p(1, t) - \kappa_d\frac{1-\mathscr{S}_{\text{rev}}(t\,|\,\text{eq})}{C\mathscr{S}_{\text{rev}}(t\,|\,\text{eq})} \tag{3.11}$$

When the dissociation rate κ_d vanishes, this theory reduces to the one developed for irreversible reactions in Section 2. To see this, recall that for this model $p(i, t) = S(t\,|\,i)$, and compare Eqs. (3.8)–(3.11) with Eqs. (2.13), (2.11), (2.1), and (2.4), respectively.

It has been shown$^{(3)}$ that Eqs. (3.9)–(3.11) can be solved formally to give

$$k_f(t) = k(t) - \frac{1}{K_{\text{eq}}}\int_0^t dt'\,\phi(t-t')\,\frac{dk(t')}{dt'} \tag{3.12a}$$

where we have defined $\phi(t)$ by

$$\phi(t)=\frac{1-\mathscr{S}_{\text{rev}}(t\,|\,\text{eq})}{C\mathscr{S}_{\text{rev}}(t\,|\,\text{eq})} \tag{3.12b}$$

and where $k(t)$ is the time-dependent rate coefficient for an irreversible reaction [e.g., Eq. (2.20) when $\kappa_a=\kappa$]. The proof given in ref. 3 was for the continuum case; however, the details of the derivation are immediately applicable to the lattice problem. Equations (3.8) and (3.12) now form a closed set that can be solved numerically once $k(t)$ is specified. In practice, it is convenient to use Eq. (3.8) to obtain rate equations directly for $\phi(t)$. One can show that

$$\frac{d\phi(t)}{dt}=[k_f(t)-\kappa_a\phi(t)][1+C\phi(t)] \tag{3.13}$$

which must be solved in conjunction with Eq. (3.12a) with $\phi(0)=0$. Once $\phi(t)$ is found, $\mathscr{S}_{\text{rev}}(t\,|\,\text{eq})$ can be obtained from Eq. (3.12b).

These equations are highly nonlinear, but can be linearized near equilibrium. If one writes

$$\mathscr{S}_{\text{rev}}(t\,|\,\text{eq})=\frac{1}{1+K_{\text{eq}}C}+\Delta(t) \tag{3.14}$$

then to lowest order in Δ,(3)

$$\frac{\hat{\Delta}(z)}{\Delta(0)}=\frac{1}{z+(C+K_{\text{eq}}^{-1})\,z\hat{k}(z)} \tag{3.15}$$

This is of course valid only if the initial state is very close to equilibrium. It describes how some small deviation $\Delta(0)$ produced by perturbing the equilibrium system at $t=0$ decays to zero. On using Eq. (2.19) for $\hat{k}(z)$ in Eq. (3.15), we find

$$\Delta(t)\to\Delta(0)\frac{K_{\text{eq}}}{1+K_{\text{eq}}C}\frac{1}{(\pi\kappa t)^{1/2}} \qquad \text{as} \quad t\to\infty \tag{3.16}$$

Thus, equilibrium is approached as $t^{-1/2}$ in one dimension. This asymptotic behavior has been predicted by Zeldovich and Ovchinnikov(9) and by Kang and Redner,(10) based on an analysis of density fluctuations.

Finally, we note that the superposition approach does not appear to be applicable to the initial condition $|*)$ where the trap is occupied, since in this case $\phi(0)=\infty$. However, one can use the identity in Eq. (3.6) to obtain $\mathscr{S}_{\text{rev}}(t\,|\,*)$ from $\mathscr{S}_{\text{rev}}(t\,|\,\text{eq})$. Having done this, one is now in a position to gain some insight into the range of validity of this approach. Recall that in the limit $C \to 0$, $\mathcal{S}_{\mathrm{rev}}(t \mid *)$ describes the reversible binding of a single particle (i.e., it is the probability that the trap is unoccupied, given that it was occupied initially). The convolution approach is exact in this limit.$^{(4)}$ By calculating $\mathcal{S}_{\mathrm{rev}}(t \mid *)$ from $\mathcal{S}_{\mathrm{rev}}(t \mid \mathrm{eq})$, determined from Eqs. (3.8) and (3.12), and taking the limit $C \to 0$, one can show that the approach based on the superposition approximation is also exact in this limit.

4. OCCUPATION NUMBER FORMULATION

In this section we present an exact description of the dynamical behavior of our model. It is based on the master equation for the probability $P(n_0, n_1, n_2,...; t)$ that site i is occupied by n_i particles ($i = 0, 1, 2,...$) at time t. For brevity, the set of occupation numbers $\{n_1, n_2,...\}$ will often be denoted by $\mathbf{n}$, and the probability by $P(n_0, \mathbf{n}; t)$. Because site $i = 0$ is the trap, n_0 can only be 0 or 1. Otherwise the particles are independent; thus all other occupation numbers can have any nonnegative integer value subject to a constraint on the total number of particles. If the thermodynamic limit is taken, this constraint no longer applies, and the $\mathbf{n}$ are unbounded. $P(n_0, \mathbf{n}; t)$ vanishes if n_0 is not 0 or 1, or if any other n_i is negative.

The master equations can be found by inspection of the kinetic scheme given in the Introduction. For each nearest neighbor pair of sites, one can move a particle to the left or to the right. Each move leads to a gain term and a loss term. The master equations are

$$\begin{aligned}\frac{d}{dt} P(0, \mathbf{n}; t) \\ &= -\kappa_a n_1 P(0, n_1,...; t) + \kappa_d P(1, n_1 - 1,...; t) \\ &\quad + \kappa(n_1 + 1)\, P(0, n_1 + 1, n_2 - 1,...; t) - \kappa n_1 P(0, n_1, n_2,...; t) \\ &\quad + \kappa(n_2 + 1)\, P(0, n_1 - 1, n_2 + 1,...; t) - \kappa n_2 P(0, n_1, n_2,...; t) + \cdots\end{aligned} \tag{4.1a}$$

$$\begin{aligned}\frac{d}{dt} P(1, \mathbf{n}; t) \\ &= \kappa_a(n_1 + 1)\, P(0, n_1 + 1, n_2,...; t) - \kappa_d P(1, n_1, n_2,...; t) \\ &\quad + \kappa(n_1 + 1)\, P(1, n_1 + 1, n_2 - 1,...; t) - \kappa n_1 P(1, n_1, n_2,...; t) \\ &\quad + \kappa(n_2 + 1)\, P(1, n_1 - 1, n_2 + 1,...; t) - \kappa n_2 P(1, n_1, n_2,...; t) + \cdots\end{aligned} \tag{4.1b}$$

Because of the complexity of these equations, it is helpful to use a shorthand notation. We introduce the operators

$$
\begin{aligned}
E_j f(\cdots n_j \cdots) &= f(\cdots n_j + 1 \cdots)\\
E_j^{-1} f(\cdots n_j \cdots) &= f(\cdots n_j - 1 \cdots)
\end{aligned}
$$

$$
\begin{aligned}
&\mathscr{D} = \kappa \sum_{j=1} [(E_j E_{j+1}^{-1} - 1) n_j + (E_j^{-1} E_{j+1} - 1) n_{j+1}]\\
&L_{00} = -\kappa_a n_1 + \mathscr{D} \qquad L_{01} = \kappa_d E_1^{-1}\\
&L_{10} = \kappa_a E_1 n_1 \qquad L_{11} = -\kappa_d + \mathscr{D}
\end{aligned}
\tag{4.2}
$$

Now the master equations may be written in the compact form

$$\frac{d}{dt} P(0, \mathbf{n}; t) = L_{00} P(0, \mathbf{n}; t) + L_{01} P(1, \mathbf{n}; t) \tag{4.3a}$$

$$\frac{d}{dt} P(1, \mathbf{n}; t) = L_{10} P(0, \mathbf{n}; t) + L_{11} P(1, \mathbf{n}; t) \tag{4.3b}$$

The operator E_j adds a particle to site j, and E_j^{-1} removes one. The operator $\mathscr{D}$ describes diffusion between pairs of sites $(j, j+1)$ for $j \geqslant 1$. It does not involve the pair (0, 1). It operates only on functions of $\mathbf{n}$. It has an invariant or equilibrium distribution which is a product of Poisson distributions for each n_j, determined by some concentration C,

$$P_{\text{eq}}(\mathbf{n}) = \prod_{j=1} \frac{C^{n_j}}{n_j!} e^{-C} \tag{4.4}$$

One can easily verify these identities:

$$\mathscr{D} P_{\text{eq}}(\mathbf{n}) = 0; \qquad \sum_{\mathbf{n}} P_{\text{eq}}(\mathbf{n}) = 1; \qquad \sum_{\mathbf{n}} n_i P_{\text{eq}}(\mathbf{n}) = C \tag{4.5}$$

The equilibrium distribution for the entire system $\{0, \mathbf{n}\}$ is

$$P_{\text{eq}}(0, \mathbf{n}) = \frac{1}{1 + K_{\text{eq}} C} P_{\text{eq}}(\mathbf{n}), \qquad P_{\text{eq}}(1, \mathbf{n}) = \frac{K_{\text{eq}} C}{1 + K_{\text{eq}} C} P_{\text{eq}}(\mathbf{n}) \tag{4.6}$$

where $K_{\text{eq}} = \kappa_a / \kappa_d$. This can be verified by substitution, using the above identities and also

$$E_1^{-1} P_{\text{eq}}(\mathbf{n}) = \frac{n_1}{C} P_{\text{eq}}(\mathbf{n}), \qquad E_1 n_1 P_{\text{eq}}(\mathbf{n}) = C P_{\text{eq}}(\mathbf{n}) \tag{4.7}$$

The survival probability of the trap is given by

$$\mathscr{S}_{\text{rev}}(t)=\sum_{\mathbf{n}} P(0,\mathbf{n};t)=1-\sum_{\mathbf{n}} P(1,\mathbf{n};t) \tag{4.8}$$

where $P(n_0,\mathbf{n};t)$ is the solution of Eq. (4.3) subject to the appropriate initial conditions. For example, if the trap is initially unoccupied and the particles are randomly distributed over the rest of the lattice, the initial conditions are

$$|\text{eq}):\quad \begin{pmatrix} P(0,\mathbf{n};0) \\ P(1,\mathbf{n};0)\end{pmatrix}=\begin{pmatrix} P_{\text{eq}}(\mathbf{n}) \\ 0\end{pmatrix} \tag{4.9}$$

The corresponding survival probability is $\mathscr{S}_{\text{rev}}(t\,|\,\text{eq})$. On the other hand, if the trap is initially occupied and the other particles are randomly distributed, the initial conditions are

$$|*):\quad \begin{pmatrix} P(0,\mathbf{n};0) \\ P(1,\mathbf{n};0)\end{pmatrix}=\begin{pmatrix} 0 \\ P_{\text{eq}}(\mathbf{n})\end{pmatrix} \tag{4.10}$$

The corresponding survival probability is $\mathscr{S}_{\text{rev}}(t\,|\,*)$. Finally, if the trap is empty, the particles are distributed randomly, and there is an extra geminate particle at site 1, the initial conditions are

$$|1):\quad \begin{pmatrix} P(0,\mathbf{n};0) \\ P(1,\mathbf{n};0)\end{pmatrix}=\begin{pmatrix} (n_1/C)\,P_{\text{eq}}(\mathbf{n}) \\ 0\end{pmatrix} \tag{4.11}$$

The mean occupation number of site 1 is $C+1$. The corresponding survival probability is $\mathscr{S}_{\text{rev}}(t\,|\,1)$.

4.1. Irreversible Binding

As a first illustration of the use of the occupation number master equation, consider the irreversible case $\kappa_d=0$. Suppose the trap is initially empty, and the other particles are randomly distributed. The survival probability is

$$\mathscr{S}(t\,|\,\text{eq})=\sum_{\mathbf{n}} P(0,\mathbf{n};t) \tag{4.12}$$

where $P(0,\mathbf{n};t)$ satisfies Eq. (4.3a) with $\kappa_d=0$,

$$\frac{d}{dt}P(0,\mathbf{n};t)=(-\kappa_a n_1+\mathscr{D})\,P(0,\mathbf{n};t)=L_{00}P(0,\mathbf{n};t) \tag{4.13}$$

The initial condition is

$$P(0,\mathbf{n};0)=P_{\text{eq}}(\mathbf{n}) \tag{4.14}$$

Note that $P(1, \mathbf{n}; t)$ does not appear here; its evolution is driven by $P(0, \mathbf{n}; t)$, according to Eq. (4.3b). Let us guess that the solution has a local equilibrium form. That is, the distribution of occupation numbers at each site is still Poisson, but with a mean value that varies over the lattice. The concentration C, for reasons that will immediately become apparent, is replaced by $CS(t \mid i)$. Then the trial solution is

$$P(0, \mathbf{n}; t) = \prod_{i=1} \frac{[CS(t \mid i)]^{n_i}}{n_i!} e^{-C} \tag{4.15}$$

To satisfy the initial condition, we require that $S(0 \mid i) = 1$. One finds by direct substitution that this trial solution indeed satisfies Eq. (4.13) if $S(t \mid i)$ obeys Eqs. (2.1) and (2.2). On using this solution in Eq. (4.12), we obtain the survival probability,

$$\mathscr{S}(t \mid \mathrm{eq}) = \sum_{\mathbf{n}} \prod_{i} \frac{[CS(t \mid i)]^{n_i}}{n_i!} e^{-C} = \exp\left(-C \sum_{i} [1 - S(t \mid i)]\right) \tag{4.16}$$

which is identical with Eq. (2.8). Note that the result may also be written as

$$\mathscr{S}(t \mid \mathrm{eq}) = \sum_{\mathbf{n}} \exp(L_{00} t)\, P_{\mathrm{eq}}(\mathbf{n}) \tag{4.17}$$

As another example, consider the initial condition where the trap is empty, the particles are randomly distributed, and there is an extra geminate particle at site 1. The initial condition is

$$P(0, \mathbf{n}; 0) = (n_1/C)\, P_{\mathrm{eq}}(\mathbf{n}) \tag{4.18}$$

The resulting survival probability is

$$\mathscr{S}(t \mid 1) = \sum_{\mathbf{n}} \exp(L_{00} t)(n_1/C)\, P_{\mathrm{eq}}(\mathbf{n}) \tag{4.19}$$

But we have $L_{00} P_{\mathrm{eq}}(\mathbf{n}) = -\kappa_a n_1 P_{\mathrm{eq}}(\mathbf{n})$, so that this can be rewritten as

$$\begin{aligned} \mathscr{S}(t \mid 1) &= \sum_{\mathbf{n}} \exp(L_{00} t) \frac{-L_{00} P_{\mathrm{eq}}(\mathbf{n})}{\kappa_a C} \\ &= -\frac{1}{\kappa_a C} \frac{d}{dt} \sum_{\mathbf{n}} \exp(L_{00} t)\, P_{\mathrm{eq}}(\mathbf{n}) \\ &= -\frac{1}{\kappa_a C} \frac{d}{dt} \mathscr{S}(t \mid \mathrm{eq}) \end{aligned} \tag{4.20}$$

which is precisely Eq. (2.23).

For future reference, we calculate the average occupation numbers, and their correlations, defined by

$$\langle n_i\rangle_0=\sum_{\mathbf{n}} n_i P(0,\mathbf{n};t), \qquad \langle n_i n_j\rangle_0=\sum_{\mathbf{n}} n_i n_j P(0,\mathbf{n};t) \tag{4.21}$$

On using Eq. (4.15), we find

$$\langle n_i\rangle_0=CS(t\,|\,i)\,\mathscr{S}(t\,|\,\mathrm{eq}) \tag{4.22}$$

$$\langle n_i n_j\rangle_0=[C^2S(t\,|\,i)\,S(t\,|\,j)+\delta_{ij}CS(t\,|\,i)]\,\mathscr{S}(t\,|\,\mathrm{eq}) \tag{4.23}$$

Note the appearance of the survival probability; this is present because the distribution $P(0,\mathbf{n};t)$ has a normalization $\mathscr{S}(t\,|\,\mathrm{eq})$ that decays in time.

4.2. Convolution Approximation

Having developed all this machinery, it is now easy to see how to obtain the convolution formalism discussed in Section 3.2. Let us focus on $\mathscr{S}_{\mathrm{rev}}(t\,|\,\mathrm{eq})$. The formal solution of Eq. (4.3a) with the initial condition $P(0,\mathbf{n};0)=P_{\mathrm{eq}}(\mathbf{n})$ can be written as

$$\begin{aligned}P(0,\mathbf{n};t)&=\exp(L_{00}t)\,P_{\mathrm{eq}}(\mathbf{n})+\int_0^t dt'\,\exp(L_{00}t')\,L_{01}P(1,\mathbf{n};t-t')\\&=\exp(L_{00}t)\,P_{\mathrm{eq}}(\mathbf{n})+\kappa_d\int_0^t dt'\,\exp(L_{00}t')\\&\quad\times E_1^{-1}P(1,\mathbf{n};t-t')\end{aligned} \tag{4.24}$$

On summing over $\mathbf{n}$ and using Eq. (4.17), we have

$$\begin{aligned}\mathscr{S}_{\mathrm{rev}}(t\,|\,\mathrm{eq})&=\mathscr{S}(t\,|\,\mathrm{eq})+\kappa_d\sum_{\mathbf{n}}\int_0^t dt'\,\exp(L_{00}t')\\&\quad\times E_1^{-1}P(1,\mathbf{n};t-t')\end{aligned} \tag{4.25}$$

We now assume that when the trap is occupied, the distribution of the other particles is completely random. This is the essence of the approximation invoked by Agmon and Szabo.$^{(4)}$ In the present context, this means

$$P(1,\mathbf{n};t)\cong[1-\mathscr{S}_{\mathrm{rev}}(t\,|\,\mathrm{eq})]\,P_{\mathrm{eq}}(\mathbf{n}) \tag{4.26}$$

After substituting in Eq. (4.26) and using the identity (4.7), we obtain

$$\begin{aligned}\mathscr{S}_{\mathrm{rev}}(t\,|\,\mathrm{eq})&\cong\mathscr{S}(t\,|\,\mathrm{eq})\\&\quad+\kappa_d\sum_{\mathbf{n}}\int_0^t dt'[1-\mathscr{S}_{\mathrm{rev}}(t-t'\,|\,\mathrm{eq})]\\&\quad\times\exp(L_{00}t')(n_1/C)\,P_{\mathrm{eq}}(\mathbf{n})\end{aligned} \tag{4.27}$$

Finally, the use of Eq. (4.19) gives

$$\mathscr{S}_{\text{rev}}(t\,|\,\text{eq}) \cong \mathscr{S}(t\,|\,\text{eq}) + \kappa_d \int_0^t dt'[1 - \mathscr{S}_{\text{rev}}(t-t'\,|\,\text{eq})]\,\mathscr{S}(t'\,|\,1) \tag{4.28}$$

which is Eq. (3.4).

4.3. Superposition Approximation

The superposition approximation discussed in Section 3.3 can be obtained by making the right approximations in the occupation number formalism. First we get an equation for $\mathscr{S}_{\text{rev}}(t)$ by summing the master equation (4.3a) over $\mathbf{n}$,

$$\begin{aligned}\frac{d}{dt}\mathscr{S}_{\text{rev}}(t) &= -\kappa_a \sum_{\mathbf{n}} n_1 P(0, \mathbf{n}; t) + \sum_{\mathbf{n}} \mathscr{D}P(0, \mathbf{n}; t)\\ &\quad + \kappa_d \sum_{\mathbf{n}} P(1, n_1 - 1,...,; t)\\ &= -\kappa_a \sum_{\mathbf{n}} n_1 P(0, \mathbf{n}; t) + \kappa_d \sum_{\mathbf{n}} P(1, \mathbf{n}; t)\end{aligned} \tag{4.29}$$

{The sum over all $\mathbf{n}$ of $\mathscr{D}[\cdot] = 0$, and $P(1, -1,...) = 0$.} We define an average

$$\langle(\cdots)\rangle_0 = \sum_{\mathbf{n}} (\cdots)\, P(0, \mathbf{n}; t) \tag{4.30}$$

and use Eq. (4.8) to write

$$\frac{d}{dt}\mathscr{S}_{\text{rev}}(t) = -\kappa_a \langle n_1 \rangle_0 + \kappa_d[1 - \mathscr{S}_{\text{rev}}(t)] \tag{4.31}$$

Now we need to find an equation for $\langle n_1 \rangle_0$; so we multiply the master equation (4.3a) by n_1 and sum over $\mathbf{n}$. This leads to

$$\begin{aligned}\frac{d}{dt}\langle n_1 \rangle_0 &= -\kappa_a \langle n_1^2 \rangle_0 + \kappa(\langle n_2 \rangle_0 - \langle n_1 \rangle_0) + \kappa_d \langle n_1 \rangle_1\\ &\quad + \kappa_d[1 - \mathscr{S}_{\text{rev}}(t)]\end{aligned} \tag{4.32}$$

where we have introduced another average, defined by

$$\langle(\cdots)\rangle_1 = \sum_{\mathbf{n}} (\cdots)\, P(1, \mathbf{n}; t) \tag{4.33}$$

In the same way, we find equations for the other average occupation numbers (for $i = 2, 3, \ldots$),

$$\frac{d}{dt}\langle n_i\rangle_0 = -\kappa_a\langle n_i n_1\rangle_0 + \kappa(\langle n_{i+1}\rangle_0 - 2\langle n_i\rangle_0 + \langle n_{i-1}\rangle_0) + \kappa_d\langle n_i\rangle_1 \tag{4.34}$$

While these equations are exact, they are not particularly helpful in their present form. Now we attempt to close them by invoking a superposition approximation, suggested by Eqs. (4.22) and (4.23). (This is exact in the irreversible case.) The approximation is

$$\langle n_i\rangle_0 = Cp(i, t)\,\mathcal{S}_{\text{rev}}(t\,|\,\text{eq}) \tag{4.35a}$$

$$\langle n_i\rangle_1 = Cp(i, t)[1 - \mathcal{S}_{\text{rev}}(t\,|\,\text{eq})] \tag{4.35b}$$

$$\langle n_i n_j\rangle_0 = [C^2 p(i, t)\,p(j, t) + \delta_{ij} Cp(i, t)]\,\mathcal{S}_{\text{rev}}(t\,|\,\text{eq}) \tag{4.35c}$$

Then the equations for $\mathcal{S}_{\text{rev}}$ and $\langle n_i\rangle_0$ are transformed to

$$\frac{d}{dt}\mathcal{S}_{\text{rev}}(t\,|\,\text{eq}) = -\kappa_a Cp(1, t)\,\mathcal{S}_{\text{rev}}(t\,|\,\text{eq}) + \kappa_d[1 - \mathcal{S}_{\text{rev}}(t\,|\,\text{eq})] \tag{4.36}$$

$$\begin{aligned}\frac{d}{dt}p(1, t) = {} & \frac{\kappa_d[1 - \mathcal{S}_{\text{rev}}(t\,|\,\text{eq})]}{C\mathcal{S}_{\text{rev}}(t\,|\,\text{eq})} - \kappa_a p(1, t) \\ & + \kappa[p(2, t) - p(1, t)]\end{aligned} \tag{4.37}$$

$$\frac{d}{dt}p(i, t) = \kappa[p(i+1, t) - 2p(i, t) + p(i-1, t)] \tag{4.38}$$

The final equation holds for $i = 2, 3, \ldots$, but can be made valid for $i = 1$ also by imposing the boundary condition

$$\kappa\,\nabla p(1, t) = \kappa_a p(1, t) - \kappa_d \frac{1 - \mathcal{S}_{\text{rev}}(t\,|\,\text{eq})}{C\mathcal{S}_{\text{rev}}(t\,|\,\text{eq})} \tag{4.39}$$

The resulting equations are identical with those presented in Section 3.3. The approximations in Eq. (4.35) are equivalent to those made in that section.

4.4. The Chemical Approximation

In the chemical approximation one focuses on the average occupation numbers

$$\langle n_i\rangle = \sum_{n_0}\sum_{\mathbf{n}} n_i P(n_0, \mathbf{n}; t) = \langle n_i\rangle_0 + \langle n_i\rangle_1 \tag{4.40}$$

These correspond to concentrations that one would actually measure in an experiment: hence the name "chemical." The master equation leads to

$$\frac{d}{dt}\langle n_0\rangle = -\kappa_d\langle n_0\rangle + \kappa_a\langle (1-n_0)\, n_1\rangle \tag{4.41a}$$

$$\frac{d}{dt}\langle n_1\rangle = \kappa_d\langle n_0\rangle - \kappa_a\langle (1-n_0)\, n_1\rangle + \kappa(\langle n_2\rangle - \langle n_1\rangle) \tag{4.41b}$$

$$\frac{d}{dt}\langle n_i\rangle = \kappa(\langle n_{i+1}\rangle - 2\langle n_i\rangle + \langle n_{i-1}\rangle), \qquad i \geqslant 2 \tag{4.41c}$$

The first of these is actually identical to Eq. (4.31). To see this, note that

$$\langle n_0\rangle = \sum_{n_0}\sum_{\mathbf{n}} n_0 P(n_0, \mathbf{n}; t) = \sum_{\mathbf{n}} P(1, \mathbf{n}; t) = 1 - \mathscr{S}_{\text{rev}}(t) \tag{4.42a}$$

$$\langle (1-n_0)\, n_1\rangle = \langle n_1\rangle_0 \tag{4.42b}$$

As with all procedures involving hierarchies of equations, these are exact, but not helpful unless some closure approximation is made. A reasonable guess is to break the average,

$$\langle (1-n_0)\, n_1\rangle \cong \langle 1-n_0\rangle\langle n_1\rangle = \langle n_1\rangle\, \mathscr{S}_{\text{rev}}(t) \tag{4.43}$$

as one does in the stochastic theory of chemical reactions. Let us make this approximation and define $\langle n_i\rangle = Cp(i, t)$ for $i = 1, 2, \ldots$. Then the above equations are equivalent to

$$\frac{d}{dt}\mathscr{S}_{\text{rev}}(t) = -\kappa_a Cp(1, t)\, \mathscr{S}_{\text{rev}}(t) + \kappa_d[1 - \mathscr{S}_{\text{rev}}(t)] \tag{4.44a}$$

$$\frac{d}{dt}p(i, t) = \kappa[p(i+1, t) - 2p(i, t) + p(i-1, t)], \quad i = 1, 2, 3, \ldots \tag{4.44b}$$

$$\kappa\, \nabla p(1, t) = \kappa_a p(1, t)\, \mathscr{S}_{\text{rev}}(t) - \kappa_d \frac{1 - \mathscr{S}_{\text{rev}}(t)}{C} \tag{4.44c}$$

Similar results were obtained by Agmon *et al.*,$^{(11)}$ using different considerations.

It is interesting to compare these equations with those obtained by means of the superposition approximation, Eqs. (4.36), (4.38), and (4.39). They differ only in the form of the boundary conditions [compare Eqs. (4.39) and (4.44c)]. As a result of this difference, the chemical approximation does *not* reduce to the Smoluchowski theory of irreversible reactions when $\kappa_d = 0$ and hence is not exact for our model in this limit.

By linearizing Eqs. (4.44a)–(4.44c) near equilibrium, one can show that a small deviation from equilibrium decays as $t^{-1/2}$ at long times. This is the same behavior that was obtained within the framework of the superposition approximation; see Eq. (3.16). However, the coefficient differs from that in Eq. (3.16) by an extra factor of $1 + K_{\text{eq}} C$ in the denominator.

4.5. Derivation of some Identities

In Section 3.2 we discussed some identities relating survival probabilities for different initial conditions. Here the occupation number formalism is used to show that those identities are in fact exact for our model. The proofs make use of formal solutions of the master equations (4.3a), (4.3b) by means of Green's functions,

$$\begin{pmatrix} P(0, \mathbf{n}; t) \\ P(1, \mathbf{n}; t) \end{pmatrix} = \begin{pmatrix} G_{00}(t) & G_{01}(t) \\ G_{10}(t) & G_{11}(t) \end{pmatrix} \begin{pmatrix} P(0, \mathbf{n}; 0) \\ P(1, \mathbf{n}; 0) \end{pmatrix} \tag{4.45}$$

The Green's functions are operators, but that is not a problem here.

If the initial distribution is equilibrium, the distribution at time t is also equilibrium. This means that for all times,

$$P_{\text{eq}}(0, \mathbf{n}) = G_{00}(t)\, P_{\text{eq}}(0, \mathbf{n}) + G_{01}(t)\, P_{\text{eq}}(1, \mathbf{n}) \tag{4.46}$$

where the individual equilibrium distributions are defined in Eqs. (4.6a), (4.66). Another useful formula is

$$\frac{d}{dt} G_{00}(t) = G_{00}(t)\, L_{00} + G_{01}(t)\, L_{10} \tag{4.47}$$

The proofs involve these last two equations.

For the initial condition (4.9), where the trap is empty and the particles are randomly distributed, Eq. (4.45) leads to

$$\mathscr{S}_{\text{rev}}(t \mid \text{eq}) = \sum_{\mathbf{n}} G_{00}(t)\, P_{\text{eq}}(\mathbf{n}) \tag{4.48}$$

Similarly, for the initial condition (4.10), where the trap is occupied and the other particles are randomly distributed, we find

$$\mathscr{S}_{\text{rev}}(t \mid *) = \sum_{n} G_{01}(t)\, P_{\text{eq}}(\mathbf{n}) \tag{4.49}$$

Now consider the left-hand side of Eq. (3.6), and use the last two equations,

$$\begin{aligned}
&\mathscr{S}_{\text{rev}}(t \mid \text{eq}) + K_{\text{eq}} C \mathscr{S}_{\text{rev}}(t \mid *) \\
&\quad = \sum_{\mathbf{n}} G_{00}(t)\, P_{\text{eq}}(\mathbf{n}) + \sum_{\mathbf{n}} K_{\text{eq}} C G_{01}(t)\, P_{\text{eq}}(\mathbf{n}) \\
&\quad = (1 + K_{\text{eq}} C) \left[\sum_{\mathbf{n}} G_{00}(t)\, P_{\text{eq}}(0, \mathbf{n}) + \sum_{\mathbf{n}} G_{01}(t)\, P_{\text{eq}}(1, \mathbf{n}) \right] \\
&\quad = (1 + K_{\text{eq}} C) \sum_{\mathbf{n}} P_{\text{eq}}(0, \mathbf{n}) = (1 + K_{\text{eq}} C) \frac{1}{1 + K_{\text{eq}} C} = 1
\end{aligned} \tag{4.50}$$

Thus we have proved Eq. (3.6).

The other identity, Eq. (3.7), involves also $\mathscr{S}_{\text{rev}}(t \mid 1)$, which evolves from the initial condition given in Eq. (4.11),

$$\begin{aligned}
\mathscr{S}_{\text{rev}}(t \mid 1) &= \sum_{\mathbf{n}} G_{00}(t)(n_1/C)\, P_{\text{eq}}(\mathbf{n}) \\
&= -\frac{1}{\kappa_a C} \sum_{\mathbf{n}} G_{00}(t)\, L_{00} P_{\text{eq}}(\mathbf{n})
\end{aligned} \tag{4.51}$$

where we have used the definition of L_{00} to arrive at the last term. Now take the operator identity in Eq. (4.47), multiply on the right by $P_{\text{eq}}(\mathbf{n})$, and sum over $\mathbf{n}$, to get

$$\frac{d}{dt} \mathscr{S}_{\text{rev}}(t \mid \text{eq}) = \sum_{\mathbf{n}} G_{00}(t)\, L_{00} P_{\text{eq}}(\mathbf{n}) + \sum_{\mathbf{n}} G_{01}(t)\, L_{10} P_{\text{eq}}(\mathbf{n}) \tag{4.52}$$

By using Eq. (4.51) to rewrite the first term, and the definition of L_{10} in the second term, this becomes

$$\frac{d}{dt} \mathscr{S}_{\text{rev}}(t \mid \text{eq}) = -\kappa_a C \mathscr{S}_{\text{rev}}(t \mid 1) + \kappa_a \sum_{\mathbf{n}} G_{01}(t)\, E_1 n_1 P_{\text{eq}}(\mathbf{n}) \tag{4.53}$$

The second part of Eq. (4.7) provides a simplification of the last term,

$$\begin{aligned}
\frac{d}{dt} \mathscr{S}_{\text{rev}}(t \mid \text{eq}) &= -\kappa_a C \mathscr{S}_{\text{rev}}(t \mid 1) + \kappa_a C \sum_{\mathbf{n}} G_{01}(t)\, P_{\text{eq}}(\mathbf{n}) \\
&= -\kappa_a C \mathscr{S}_{\text{rev}}(t \mid 1) + \kappa_a C \mathscr{S}_{\text{rev}}(t \mid *)
\end{aligned} \tag{4.54}$$

The earlier identity, Eq. (3.6), allows us to eliminate $\mathscr{S}_{\text{rev}}(t \mid *)$; this leads directly to Eq. (3.7), and completes the proof.

5. COMPARISON OF THEORY WITH SIMULATIONS

In this section we compare the various approximate theoretical predictions with the results of numerical simulations. We simulated $\mathscr{S}_{\text{rev}}(t \mid \text{eq})$ using an algorithm described by Richards.$^{(12)}$

The theoretical treatments previously discussed were all for our model in the thermodynamic limit. The simulations were performed on a finite lattice with $L+1$ sites containing N particles. We tried to choose N (typically 100) and L (typically 200) large enough that the simulation accurately represents the thermodynamic limit over the time range of interest. If one defines C as N/L, the equilibrium probability that a particle is bound in the finite system turns out to be the same as it is in an infinite system in the thermodynamic limit, $K_{\text{eq}} C/(1+K_{\text{eq}} C)$.

The rules for the simulation were as follows. A single experiment begins with randomly distributing N particles on L sites. At each time step, a labeled particle is selected at random, and one of its neighboring sites is selected at random. If this particle is not at the trap, and the designated neighbor is not the trap, and a random number r between 0 and 1 is less than κ, then the particle is moved to the designated neighbor. Otherwise the particle stays put, and a new particle is selected at random. (Typically we used $\kappa = 0.1$, in the hope that the simulations accurately describe a continuous-time random walk.) If the designated neighbor is $L+1$, the particle is immediately moved back to site L. If the particle is at 1, and the designated neighbor is an empty trap, and r is less than κ_a, the particle moves into the trap. If the selected particle is in the trap, and the designated neighbor is 1, and r is less than κ_d, then the particle moves to site 1. Otherwise it stays put and a new particle is selected at random. This cycle is repeated for N_{rep} (typically 10^5) initial conditions or experiments, and the fractional occupancy of the trap is obtained at each time step n. The dimensionless time $\tau = \kappa t$ that appears in the analytic theories is related to the number of steps n by $\tau = \kappa n/2N = 0.05n/N$. Thus, if $N = 100$ and $\kappa = 0.1$, 20,000 time steps are required to reach $\tau = 10$. (Simulations of this model have also been performed by Agmon *et al.*$^{(11)}$)

In Figs. 1–3, we compare the simulation results with the predictions of three analytic schemes, respectively the rate equation, convolution, and superposition approaches. These all involve $\kappa_a = \kappa$ and $K_{\text{eq}} = 0.5$, 1, 2, 5, and ∞ (i.e., irreversible binding). The simulations shown here were all with $N = 100$, $L = 200$, $\kappa = 0.1$, and $N_{\text{rep}} = 10^5$. In these figures, the fraction bound $\mathscr{B} = 1 - \mathscr{S}_{\text{rev}}$ is plotted against the dimensionless time $\tau = \kappa t$. The rate equation results were obtained using Eqs. (3.2) and (2.21). The convolution results were obtained by solving Eq. (3.4) numerically (after discretizing the time integral). The superposition results were obtained by solving Eqs. (3.13) and (3.12a) numerically [using the forward difference approximation for the time derivative in Eq. (3.13) and using the trapezoidal rule to discretize the time integral in Eq. (3.12a)]. Once $\phi(t)$ was calculated, $\mathscr{B}(t)$ was found using $\mathscr{B}(t) = C\phi(t)/[1 + C\phi(t)]$.

In the case of irreversible binding, $K_{\text{eq}} = \infty$, all three approaches are known to be exact for this model. The excellent agreement between theory and simulations for the top curves in each of the three figures shows that over this time range, the simulations accurately reflect the behavior of the model in the thermodynamic limit. In other words, the choices made for N and L are sufficiently large, and the time step is sufficiently small.

It can be seen from Fig. 1 that the rate equation approach is exact at short times. While it predicts the correct equilibrium limit, it does rather poorly at intermediate times. This is not unexpected, since one-dimensional problems are particularly demanding for an approach based on rate equations. This is because in one dimension, the long-time limit of the irreversible rate coefficient is zero. In three dimensions, it tends to a finite (steady-state) value. Thus diffusion plays a much more significant role in one-dimensional problems. Consequently, our simple model provides a rather stringent test of any approach to reversible diffusion-influenced reactions. The rate equation approach appears to be a more useful approximation in three dimensions.(3, 13)

Figure 2 shows that the convolution approximation works much better. Nevertheless, there is still a small, but significant difference between this theory and simulations at long times. The equilibrium limit is approached too quickly.

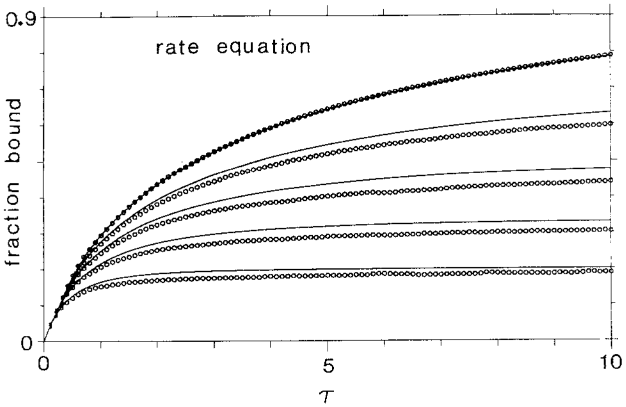


Fig. 1. Comparison of simulations (circles) with the rate equation approach for $\kappa_a = \kappa$ and $C = 0.5$. The fraction bound $\mathscr{B}(\tau)$ is given as a function of $\tau = \kappa t$ for (top to bottom) $K_{\text{eq}} = \infty$, 5, 2, 1, 0.5.

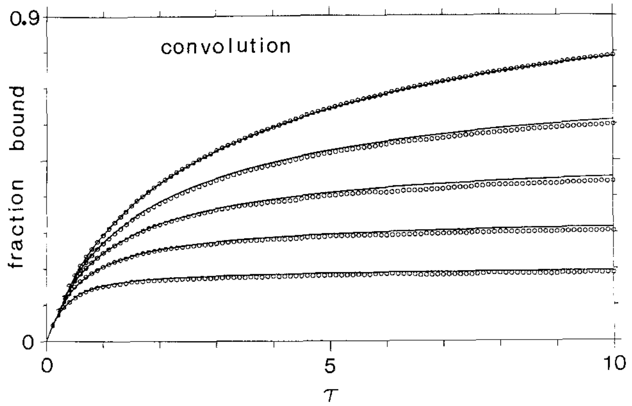


Fig. 2. Comparison of simulations (circles) with the convolution approach for $\kappa_a = \kappa$ and $C = 0.5$. The fraction bound $\mathscr{B}(\tau)$ is given as a function of $\tau = \kappa t$ for (top to bottom) $K_{eq} = \infty$, 5, 2, 1, 0.5.

Finally, it can be seen from Fig. 3 that the superposition approximation results, while comparable to the convolution results when $K_{eq} > 1$, are clearly more accurate for $K_{eq} = 0.5$. While neither approach is exact, both give semiquantitative results over the entire parameter range examined. Thus, they provide a useful description of reversible diffusion-influenced reactions.

We have also examined the predictions of the chemical approximation by solving Eqs. (4.44a)–(4.44c) numerically for a finite lattice. For $K_{eq} = 1$,

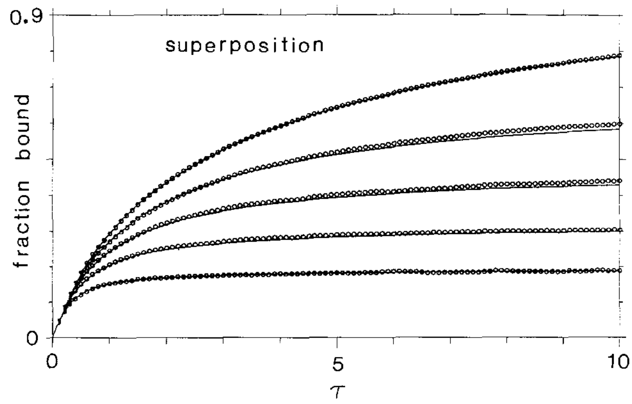


Fig. 3. Comparison of simulations (circles) with the superposition approach for $\kappa_a = \kappa$ and $C = 0.5$. The fraction bound $\mathscr{B}(\tau)$ is given as a function of $\tau = \kappa t$ for (top to bottom) $K_{eq} = \infty$, 5, 2, 1, 0.5.

this approximation was found to work better than any of the three approaches discussed above (the results are not shown here) for $\mathcal{S}_{\text{rev}}(t\,|\,\text{eq})$. For larger K_{eq}, the chemical approximation deteriorates significantly; this is to be expected, since we know that it is not exact for an irreversible reaction. This is in agreement with the work of Agmon *et al.*(11) Moreover, even for $K_{\text{eq}} = 1$, when we used the chemical approximation to calculate $\mathcal{S}_{\text{rev}}(t\,|\,*)$ (i.e., the trap is initially occupied), we found that the identity in Eq. (3.6) was violated at intermediate times.

Finally, we examined how the equilibrium limit is approached. Both the superposition and chemical approximation treatments (as well as analysis of density fluctuations(9,10)) predict that the deviation from equilibrium decays to zero as $t^{-1/2}$ in one dimension. In an attempt to find the exact decay, we performed a simulation for $K_{\text{eq}} = 0.5$ with the lattice jump rate $\kappa = 1$ and $N_{\text{rep}} = 10^6$. (When $\kappa = 1$, a particle moves at each time step, unless it tries to move into an occupied trap.) A linear least squares fit to a log–log plot gave a slope of -0.54. This is in agreement with the simulations of Agmon *et al.*,(11) who found a slope somewhat larger than -0.5. Since a slope near -0.54 is somewhat unexpected, we tried to see whether it is an artifact of the finite size of the lattice. Therefore we carried out a simulation with $N = 200$, $L = 400$, and $N_{\text{rep}} = 10^6$ (see Fig. 4). The resulting slope is -0.51. This suggests that in the thermodynamic limit, equilibrium is approached as $t^{-1/2}$ in one dimension. Simulations of a second-order, one-dimensional reaction by Kang and Redner(10) led to the same conclusion.

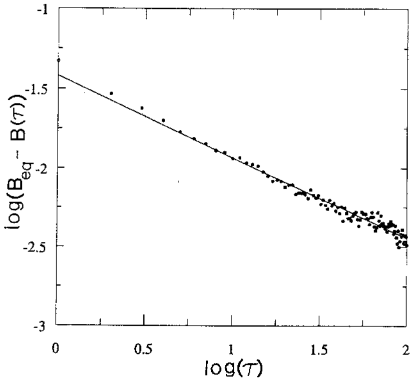


Fig. 4. Simulation results ($N = 200$, $L = 400$) showing how equilibrium is approached for $K_{\text{eq}} = 0.5$, $C = 0.5$. The logarithm of the deviation of the fraction bound from its equilibrium value is plotted as a function of $\ln \tau$. The points at $\tau = 1, 2, 3, \ldots, 100$ were obtained by averaging 10^6 initial conditions. The solid line is a linear least squares fit of the data ($\tau \geqslant 3$) with slope -0.51.

6. CONCLUDING REMARKS

We have studied three formulations of increasing complexity that all approximately describe the kinetics of reversible diffusion-influenced reactions. Although these approaches were considered in the context of a very simple one-dimensional lattice model, they are applicable without modification to more realistic three-dimensional continuum models. While one-dimensional problems are of limited interest from an experimental point of view, they do provide a demanding test for theories of diffusion-influenced reactions. An approximate approach that has a solid theoretical foundation is expected to work much better in three dimensions.

By comparing the predictions of these approaches with simulations, we found that the rate equation formalism was the least accurate. The convolution and superposition approaches worked much better, although they were still not completely satisfactory at moderately long times. In three dimensions, for reactions that are only partially diffusion-controlled, the difference between the rate equation and convolution formalisms is smaller(3) than one would expect from the present work. The superposition approach predicts that a small fluctuation about equilibrium will decay to zero as $t^{-1/2}$ in one dimension. This appears to be exact.

Although we were able to derive certain exact relations between survival probabilities corresponding to different initial conditions, we were not able to find a closed set of equations to describe exactly the kinetics of our model. Even if such an exact solution is found in one dimension, it is likely that three-dimensional problems will remain intractable. Thus, the approximate approaches we have considered in this paper should still be of interest.

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