Journal of Statistical Physics, Vol. 65, Nos. 5/6, 1991

Reversible Trapping on a Cubic Lattice: Comparison of Theory and Simulations

Peter M. Richards[1] **and Attila Szabo**[2]

Simulations of the kinetics of the reversible diffusion-influenced reaction $A + B \rightleftarrows AB$ on a cubic lattice, with initial conditions $[A] = [B]$, $[AB] = 0$, are compared with the predictions of two approximate theoretical formalisms. The first involves a simple rate equation with rate coefficients that are proportional to the time-dependent rate coefficient for an irreversible reaction. The second, which is based on a superposition approximation, contains a rate coefficient that explicitly depends on the bulk concentrations. Both reduce to the Smoluchowski approach in the irreversible limit. The results obtained using the modified rate equation formalism are exact at short times, but tend to approach equilibrium too rapidly. The predictions of the computationally more demanding superposition formalism agree remarkably well with the simulations for all times for the range of parameters examined.

KEY WORDS: Reversible reactions; saturable traps; bimolecular; diffusion; superposition approximation; cubic lattice.

1. INTRODUCTION

Recently Richards$^{(1)}$ studied the time dependence of trapping and detrapping of point particles by saturable point traps on a simple cubic lattice. This system is a prototype of a *reversible* diffusion-influenced reaction $A + B \rightleftarrows AB$, where the A's are the particles and the B's are the traps. Since a B can react with only a single A, the traps can saturate. For the initial condition where the concentration of filled traps is zero and the concentrations of particles and traps are equal, the kinetics of this reaction was simulated and the results compared with the predictions of an effective rate

---

[1] Sandia National Laboratories, Albuquerque, New Mexico 87185.

[2] Laboratory of Chemical Physics, National Institutes of Diabetes and Digestive and Kidney Diseases, National Institutes of Health, Bethesda, Maryland 20892.

0022-4715/91/1200-1085$06.50/0

equation based on an average correlation (AC) approximation. Szabo⁽²⁾ has recently considered a variety of theoretical approaches to the description of reversible reactions in a three-dimensional continuum. Szabo and Zwanzig⁽³⁾ compared the predictions of these formalisms with simulations of a pseudo-first-order reaction on a one-dimensional lattice. A bimolecular reaction is pseudo first order when the concentration of one of the species is in such a large excess that it is essentially independent of time. This paper presents results of an analogous comparison for a second-order reaction on a three-dimensional lattice.

The outline is as follows. In Section 2, we first review the Smoluchowski approach to irreversible diffusion-influenced, second-order reactions in a three-dimensional continuum. We then summarize the analogous formalism when the species undergo a continuous-time random walk on a lattice. In Section 3, we present various approaches to the description of reversible reactions. The emphasis is placed on the mathematical structure of these formalisms. For both the continuum and lattice descriptions, these formalisms can be implemented once the equilibrium constant and the time-dependent rate coefficient for an *irreversible* reaction are specified. In Section 4, simulation and theoretical results are compared. Section 5 contains some concluding remarks.

2. IRREVERSIBLE REACTIONS

To establish notation, we briefly review the standard treatment of the kinetics of the irreversible diffusion-influenced reaction $A + B \to AB$. We assume that A and B are spherical and noninteracting. They diffuse freely until they come in contact at separation R. The reaction at contact is described by the partially reflecting or radiation boundary condition of Collins and Kimball,⁽⁵⁾ which involves an intrinsic bimolecular association rate coefficient κ_a. Given an initial random distribution, the concentrations satisfy

$$\frac{d[\mathrm{A}]}{dt} = \frac{d[\mathrm{B}]}{dt} = -k(t)[\mathrm{A}][\mathrm{B}] \tag{1}$$

where the time-dependent rate coefficient is related to the A–B pair distribution function at contact via $k(t) = \kappa_a p(R, t)$. The pair distribution function satisfies the diffusion equation, involving the relative diffusion coefficient D, with initial condition $p(r, 0) = 1$ and subject to the boundary condition

$$4\pi DR^2 \left(\frac{\partial p(r, t)}{\partial r}\right)_{r=R} = \kappa_a p(R, t) \tag{2}$$

This procedure yields[5]

$$k(t) = \frac{\kappa_a k_S}{\kappa_a + k_S} \left[1 + \frac{\kappa_a}{k_S} e^{\gamma^2 Dt} \operatorname{erfc}(\gamma^2 Dt)^{1/2} \right] \tag{3}$$

where $\gamma = (1 + \kappa_a / k_S)/R$ and

$$k_S = 4\pi DR \tag{4}$$

The initial and final values of $k(t)$ are

$$k(0) = \kappa_a \tag{5}$$

$$k(\infty) = \frac{\kappa_a k_S}{\kappa_a + k_S} \tag{6}$$

Moreover, as $t \to \infty$, Eq. (3) behaves as

$$\lim_{t \to \infty} k(t) = k(\infty) \left(1 + \frac{k(\infty)}{4\pi D(\pi Dt)^{1/2}} + \cdots \right) \tag{7}$$

When $\kappa_a \gg k_S$, and therefore $k(0) \gg k(\infty)$, the reaction is said to be diffusion-controlled. As $\kappa_a / k_S \to 0$, $k(0) = k(\infty) = \kappa_a$ and the reaction-controlled limit is approached.

Finally, we note that[6]

$$k(t) = \kappa_a S(t \mid R) \tag{8}$$

where $S(t \mid R)$ is the probability that an isolated pair A–B, initially at contact, has not yet reacted at time t to form AB (in other words, it is the survival probability of a contact pair). The lattice analogue of this relation will be used here to simulate $k(t)$ (see below).

Let us now consider the corresponding formalism for an irreversible reaction on a lattice. We assume that the A's are noninteracting point particles that undergo a random walk in continuous time on the lattice. The B's are static point traps. Let W_a be the hopping rate of a particle into an empty trap from a nearest neighbor site. The hopping rate into a filled trap is zero. Let W be the particle hopping rate between nearest neighbor sites not occupied by traps. We express concentrations as the number of species/total number of lattice sites.

For an initial random distribution of particles, the concentrations satisfy Eq. (1) with a $k(t)$ given by the lattice analogue of Eq. (8). For a simple cubic lattice (see ref. 3 for a one-dimensional lattice), this can be obtained by setting

$$\kappa_a = 6W_a \tag{9}$$

and identifying $S(t|R)$ with the survival probability of a point particle initially at a site neighboring a single trap. Since this survival probability can be readily simulated, the time dependence of $k(t)$ can be obtained even in the absence of an analytic expression such as Eq. (3).

For a simple cubic lattice, it can be shown$^{(7)}$ that $k(\infty)$ has the same form as the continuum result in Eq. (6), when κ_a is given by Eq. (9) and k_S is given by

$$k_S = \frac{6W}{I-1} \tag{10}$$

where $I = 1.516386...$ is related to the Watson integral.$^{(8)}$ Moreover, the asymptotic behavior of $k(t)$ is given by Eq. (7) when D is identified with W (unit lattice constant is assumed). From these results, it follows that the initial and final values of $k(t)$ are related by $k(0) = (1 + 0.516 W_a/W)\, k(\infty)$. When $W_a = W$, $k(0) = 1.516 k(\infty)$, so that $k(t)$ is not strongly dependent on time and the system is close to being reaction (rather than the diffusion) controlled. A simple interpretation of the limits $W_a = W$ and $W_a \gg W$ is that in the former the trap is a true point defect, whereas in the latter the trap region effectively includes the nearest neighbor sites and thus has a finite extent.

3. REVERSIBLE REACTIONS

In the continuum case, dissociation of AB to form an unbound pair at contact is described by the dissociation rate constant κ_d. In the lattice case, the dissociation of a filled trap occurs when the particle hops to a nearest neighbor site with rate W_d. For a simple cubic lattice, these are related by

$$\kappa_d = 6W_d \tag{11}$$

The equilibrium constant in both cases is given by$^{(1,2)}$

$$K_{\text{eq}} = \frac{[\text{AB}]_{\text{eq}}}{[\text{A}]_{\text{eq}}\,[\text{B}]_{\text{eq}}} = \frac{\kappa_a}{\kappa_d} = \frac{W_a}{W_d} \tag{12}$$

where, as mentioned previously, the concentrations on the lattice are dimensionless.

Any theory of reversible reactions must predict that $[\text{AB}]/[\text{A}][\text{B}] \to K_{\text{eq}}$ as $t \to \infty$. The approaches discussed below all have this property. For the sake of brevity, we shall focus on the mathematical structure, rather than the conceptual basis, of these formalisms. The continuum and lattice cases will be treated in a unified way. Consider the equation

$$\frac{d[\mathrm{A}]}{dt} = -k_a(t)[\mathrm{A}][\mathrm{B}] + k_d(t)[\mathrm{AB}] \tag{13}$$

where $k_a(t)$ and $k_d(t)$ need to be specified. In the modified rate equation approach, these are given by$^{(2)}$

$$k_a(t) = k(t) \tag{14a}$$

$$k_d(t) = k(t)\, K_{\mathrm{eq}}^{-1} \tag{14b}$$

where $k(t)$ is the irreversible time-dependent rate coefficient. Approximating $k(t)$ by its long-time limit, one has

$$k_a(t) \simeq k(\infty) = \frac{\kappa_a k_S}{\kappa_a + k_S} = \frac{6W_a k_S}{6W_a + k_S} \tag{15a}$$

$$k_d(t) \simeq k(\infty)\, K_{\mathrm{eq}}^{-1} = \frac{\kappa_d k_S}{\kappa_a + k_S} = \frac{6W_d k_S}{6W_a + k_S} \tag{15b}$$

where k_S is given by Eqs. (4) and (10) in the continuum and lattice cases, respectively. When the rate coefficients are specified by Eqs. (15a) and (15b), Eq. (13) is identical to the average correlation (AC) approximation of ref. 1; this is a widely used rate equation involving the steady-state diffusion-dependent *on* and *off* rate constants.$^{(9-13)}$ In the modified rate equation approach, where the full time dependence of $k(t)$ is used, Eq. (13) can be analytically solved for the concentrations, since the substitution $k(0)\,\tau_e = \int_0^t k(t')\,dt'$ converts it into an ordinary bimolecular rate equation. The effective time τ_e can be obtained by numerical integration of the simulated survival probability [see Eq. (8)].

In the superposition approximation approach, one has$^{(2)}$

$$k_a(t) = k(t) - K_{\mathrm{eq}}^{-1} \int_0^t \frac{[\mathrm{AB}(t-\tau)]}{[\mathrm{A}(t-\tau)][\mathrm{B}(t-\tau)]} \frac{dk(\tau)}{d\tau}\, d\tau \tag{16a}$$

$$k_d(t) = \kappa_d = 6W_d \tag{16b}$$

Since $k_a(t)$ explicitly depends on the concentrations, Eq. (13) is now nonlinear and has to be solved numerically. This can be done in a straightforward way by treating the integral as a discrete sum and using a finite-difference approximation for the time derivative. Finally, we mention that if the τ dependence of the concentrations in Eq. (16a) is ignored (i.e., $t-\tau$ is replaced by just t), this formalism reduces to the modified rate equation approach.$^{(2)}$

4. COMPARISON OF SIMULATIONS WITH THEORY

The simulations of the time dependence of the concentrations were performed on a $20 \times 20 \times 20$ simple cubic lattice containing 80 traps and about 80 particles[3] using an algorithm described previously.(1) The data shown below represent averages over 10^4 initial configurations in which all traps were empty. The largest Monte Carlo weight used was 0.1 in order to ensure that one is describing a random walk in continuous time. The irreversible time-dependent rate coefficient that is required for the implementation of the various theoretical formalisms was obtained by simulating the survival probability of a system containing a single particle and a single trap, using a true continuous-time algorithm.(7) Thus, the comparison between theory and simulations does not involve any adjustable parameters.

In Fig. 1, the fraction of traps occupied ($[AB(t)]/[B(0)]$) is plotted against $6Wt$ when $W_a = W$ and $K_{eq} = 100$. It can be seen that there is excellent agreement between the various theories and simulations. The results labeled $k(\infty)$, which were obtained using the steady-state rate constants given in Eqs. (15a) and (15b) (the same as the AC approximation of ref. 1), deviate from the simulations at short times, as to be expected. The

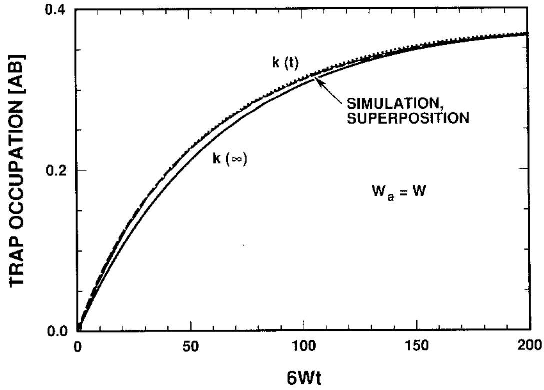

Fig. 1. Fractional occupancy of traps as a function of dimensionless time $6Wt$ for $W_a = W$, $K_{eq} = 100$. Initially all traps were empty. The modified rate equation results are labeled $k(t)$ (dotted line). The results obtained using the steady-state *on* and *off* rate constants (the AC approximation) are labeled by $k(\infty)$ (solid line). The simulation and superposition approximation (dashed line) curves are indistinguishable.

---

[3] In the simulation the $8000 - 80 = 7920$ sites outside of traps were randomly occupied with a probability of 10^{-2}. Thus there was an average of 79.2 particles. This fact was accounted for in the values of the equilibrium concentrations.

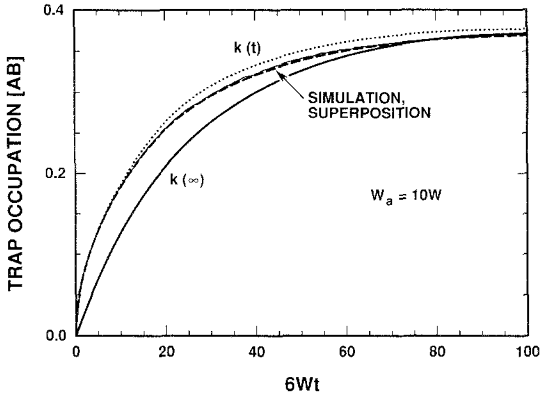

Fig. 2. Same as Fig. 1, but for $W_a = 10W$, $K_{eq} = 100$.

reason for such general good agreement is that when $W = W_a$, $k(t)$ is only weakly time dependent [$k(0) = 1.5k(\infty)$; see above]. Thus, the association reaction is close to being reaction controlled (i.e., diffusion is playing only a modest role). In this limit, all the theories are equivalent.$^{(2)}$ This is in marked contrast to the situation in one dimension,$^{(3)}$ where $k(t)$ is strongly time dependent even when $W = W_a$ ($\kappa = \kappa_a$ in the notation of ref. 3).

In order to provide a more stringent test of the theories, we used the device introduced previously,$^{(1)}$ and increase the hopping rate into the trap over the bulk hopping rate. In Fig. 2, the fraction occupied is shown as a function of $6Wt$ for $W_a = 10W$ and $K_{eq} = 100$. For this parameter set $k(t)$ is strongly dependent [$k(0) = 6.5k(\infty)$]. It can be seen that the

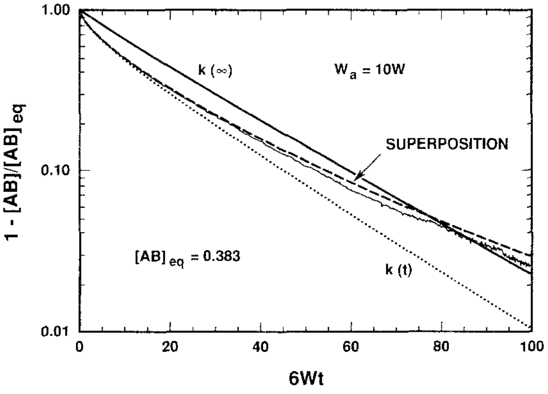

Fig. 3. The deviation from equilibrium of the normalized trap occupation, $1 - [AB(t)]/[AB]_{eq}$), for the same parameters as Fig. 2. The curve with "noise" is the simulation data.

modified rate equation results [labeled $k(t)$] are exact at short times, but the equilibrium limit is approached too rapidly. The results obtained using the steady-state rate constants [$k(\infty)$, AC of ref. 1] are poor at short times, but are superior to the modified rate equation results at long times. The superposition approximation does remarkably well over the entire time range.

A clearer picture of the long-time dependence is given in Fig. 3, where the normalized deviation of the trap occupation from its equilibrium value $((1-[\mathrm{AB}(t)]/[\mathrm{AB}]_{\mathrm{eq}})$ is plotted. It is now apparent that the relatively good agreement of the $k(\infty)$ curve found at the longest time examined would eventually deteriorate.

5. CONCLUDING REMARKS

We have tested two theoretical treatments of second-order reversible reactions against simulations on a cubic lattice. Both these approaches can be implemented once the equilibrium constant and the time-dependent association rate coefficient $k(t)$ for an irreversible reaction are specified. The modified rate equation approach [see Eqs. (13), (14a), and (14b)] is very simple to use. The superposition approximation formalism [see Eqs. (13), (16a), and (16b)] is considerably more computationally demanding. While it is not possible to draw completely general conclusions from a limited comparison, it is clear that the superposition approach is superior, giving remarkably good agreement over the whole time range. The modified rate equation approach is exact at short times. It was found to be accurate for all times only when $k(t)$ is weakly time dependent [$k(0) \lesssim 2k(\infty)$]. However, because of its simplicity, it is a useful approximation if one is willing to settle for only semiquantitive agreement at long times.

The modified rate equation formalism predicts that the concentrations approach their equilibrium values exponentially. The superposition approximation, on the other hand, predicts(2) that equilibrium is approached as $t^{-3/2}$ in three dimensions. This asymptotic behavior was first obtained by Zeldovich and Ovchinnikov(14) (see also Kang and Redner(15)) based on an analysis of fluctuation effects. At first sight it may be surprising that the superposition approximation predicts a power-law decay, since it is basically a pair theory like the Smoluchowski (mean-field) theory of irreversible reactions. However, we note that for a reversible reaction between a *single* A–B pair, the fraction of molecules that are dissociated approaches unity as $t^{-3/2}$ in three dimensions.(16,17) Finally, we emphasize that this power-law behavior is manifested only at very long times when the deviation from equilibrium is very small. For example, for $W = 10W_a$, $K_{\mathrm{eq}} = 100$, the superposition results (extended to times longer than shown in Fig. 3) behave as $t^{-3/2}$ only when $6Wt > 1000$ and $(1 - [AB(t)]/[AB]_{eq}) < 3 \times 10^{-3}$.

ACKNOWLEDGMENT

The work done at Sandia National Laboratories is supported by the U.S. Department of Energy under contract DE-AC04-76DP00789.

REFERENCES

1. P. M. Richards, *J. Chem. Phys.* **92**:1963 (1990).
2. A. Szabo, *J. Chem. Phys.* **95**:2481 (1991).
3. A. Szabo and R. Zwanzig, *J. Stat. Phys.* **65**:1057 (1991).
4. S. A. Rice, Diffusion-limited reactions, in *Complex Chemical Kinetics*, C. H. Bamford, C. F. N. Tipper, and R. G. Compton, eds. (Elsevier, Amsterdam, 1985).
5. F. C. Collins and G. E. Kimball, *J. Colloid Sci.* **4**:425 (1949).
6. O. G. Berg, *Chem. Phys.* **31**:47 (1978); K. Razi Naqvi, K. H. Mork, and S. Waldenström, *J. Phys. Chem.* **84**:1315 (1980); A. Szabo, G. Lamm, and G. H. Weiss, *J. Stat. Phys.* **34**:225 (1984).
7. P. M. Richards, unpublished.
8. M. N. Barber and B. W. Ninham, *Random and Restricted Walls* (Gordon and Breach, New York, 1970).
9. A. McNabb and P. K. Foster, *Trans. Metal. Soc. AJME* **227**:618 (1963).
10. M. Eigen, W. Kurse, G. Maass, and L. DeMaeyer, *Prog. React. Kinet.* **2**:286 (1964).
11. J. M. Schurr, *Biophys. J.* **10**:700 (1970).
12. S. F. Burlatsky, P. P. Levin, I. V. Khudyakov, V. A. Kuzmin, and A. A. Ovchinnikov, *Chem. Phys. Lett.* **66**:565 (1979).
13. D. Shoup and A. Szabo, *Biophys. J.* **40**:33 (1982).
14. Y. B. Zeldovich and A. A. Ovchinnikov, *JETP Lett.* **43**:638 (1977).
15. K. Kang and S. Redner, *Phys. Rev. A* **32**:437 (1985).
16. N. Agmon, E. Pines, and D. Huppert, *J. Chem. Phys.* **88**:5631 (1988).
17. N. Agmon and A. Szabo, *J. Chem. Phys.* **92**:5270 (1990).