One-dimensional reactive systems: The effect of diffusion on rapid bimolecular processes

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One-dimensional reactive systems: The effect of diffusion on rapid bimolecular processes

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Bimolecular reactions in one dimension are studied using the fluctuation–dissipation theory. In particular, we calculate the rate constants for three reactive systems. First, for an infinite straight line, we consider the reaction $A + A \rightarrow A + P$, and the isomerization $2A \rightarrow A_2$. In the first case, we obtain a linear dependence between rate constant and the reactant concentration. In the second, we obtain the same linear dependence only when the characteristic dimerization time τ_d is much greater than the characteristic pumping time τ_p. On the other hand if $\tau_p \gg \tau_d$, we find a rate constant which is independent of the reactant concentration. Our results are in qualitative agreement with recent computer simulations of these reactions. Second, we consider trapping, $A + S \rightarrow S$, by static sinks on a ring. For the cases of interest, we find negligible corrections, due to curvature, to the functional form of the infinite straight line rate constant.

I. INTRODUCTION

One-dimensional reactive systems have been simulated in recent years[1,2] with the help of supercomputers. In the case of diffusion-controlled reaction, Anacker et al.[3,4] reported a linear dependence between the rate constant and the reactant concentration. This result has motivated theorists[5,6] to study one-dimensional systems using different approaches.

Recently, one of us has developed a method for calculating the rate constant for bimolecular reactions using statistical nonequilibrium thermodynamics.[7–9] This method is based on an expression for the rate constant in terms of the nonequilibrium radial distribution function. From a well-known relation[10] the radial distribution function is related to the density–density correlation function. Finally, the mechanistic statistical theory of nonequilibrium thermodynamics, also known as the fluctuation–dissipation theory,[11] at the hydrodynamic level of description is used to calculate the density–density correlation function for the reactants. The fluctuation–dissipation theory, which reduces to previous near-equilibrium formalisms, has been applied to a variety of phenomena such as: the effect of diffusion on chemical reactions in solutions,[12,13] the coupling of density and energy fluctuations by isothermal chemical reactions,[14,15] the effect of diffusion in receptor mediated endocytosis,[16,17] nonlocal fluctuating hydrodynamics,[18–20] and isothermal diffusion in multicomponent fluid.[21]

In this paper, we use the fluctuation–dissipation theory (FD) to study one-dimensional reactions at steady state. In Sec. II, we consider the reaction $A + A \rightarrow A + P$ on an infinite line with a homogeneous external reactant flux. In this case, we obtain a linear relation between the rate constant and the reactant concentration. In Sec. III, we consider the isomerization $2A \rightarrow A_2$ coupled with an external photochemical decomposition $A_2 \rightarrow 2A$. For this system, we have two characteristic times. One, time τ_D, characterizes the dissociation, and the other, time τ_M, is related to the dimerization. Two limits are analyzed, and two different behaviors are obtained for the rate constant. In the case $\tau_D \gg \tau_M$, the rate constant is independent of the reactant concentration. This concentration independent rate has recently been observed by Kopleman.[22] In Sec. IV, we consider trapping by static sinks on a ring, and we study the effect of the ring curvature on the rate constant. Finally, in Sec. V, we discuss and compare our results with computer simulations.

II. CALCULATION OF CHEMICAL RATE CONSTANTS

A. Basic concepts

In this section, we describe our method[7–9] for the calculation of bimolecular rate constants. Let us consider a bimolecular reaction in solution:

$$A + B \overset{k^+}{\rightarrow} \text{products},$$
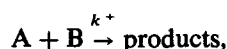
where k^+ is the reaction rate constant. We will consider systems where the viscosity of the solvent impedes the reaction rate significantly compared to the rate based on bimolecular collision theory.

Assuming stationary ensemble, as it develops at asymptotically stable states, one considers the following relation between k^+ and the radial distribution function of A molecules around a central B molecule, $g_{AB}(r)$,

$$k^+ = 4\pi \int_0^\infty k^0(r) g_{AB}(r) r^2 \, dr, \tag{1}$$

where we have assumed that the system is isotropic. The function $k^0(r)$ is called the intrinsic chemical reactivity and can be obtained from consideration of the reaction rate as a

function of position using quantum mechanics. One of the simplest reactivities is the Smoluchowski reactivity[9]

$$k^0(r) = \left(\frac{k^0}{4\pi r^2}\right)\delta(r - R),\qquad(2)$$

where R is called the encounter radius. In this case, Eq. (1). yields

$$k^+ = k^0 g_{AB}(R).\qquad(3)$$

The radial distribution function is related to the density–density correlation function via the relation[10,23]

$$g_{ij}(r) = 1 - \delta(r)\frac{\delta_{ij}}{\bar{n}_i} + \frac{\sigma_{ij}(r)}{\bar{n}_i\bar{n}_j},\qquad(4)$$

where $\bar{n}_i$ is the macroscopic number density of the ith species, and $\sigma_{ij}(r)$ is the density–density correlation function defined by

$$\sigma_{ij}(\mathbf{r} - \mathbf{r}') \equiv \langle[n_i(\mathbf{r},t) - \bar{n}_i][n_j(\mathbf{r}',t) - \bar{n}_j]\rangle.\qquad(5)$$

In general, the intrinsic reactivity is modified by the radical distribution function. In the case of the Smoluchowski reactivity, one obtains a direct relation, i.e., Eq. (3). For dilute solutions at equilibrium, the radial distribution functions is unity and $k^+ = k^0$. Away from equilibrium or in concentrated solutions, g_{AB} is not unity, and k^0 is renormalized.[15]

At this point in the method, one is required to calculate the nonequilibrium radial distribution function. In principle, different approaches can be used for this purpose, one of which is the fluctuation–dissipation theory.[11] This theory allows us to describe the dynamics of density fluctuations using linear stochastic differential equations, and to calculate nonequilibrium and concentration effects on the radial distribution function.

B. One-dimensional reactive systems

In this section we apply the method described in Sec. II A to the reaction

$$2A \xrightarrow{k^+} A + P.\qquad(6)$$

We will be concerned exclusively with the rate constant k^+ in a stationary ensemble corresponding to an asymptotic stable steady state. Also, we will consider a system that on the average is spatially uniform in temperature and in all number densities.

The only molecular processes that we will consider in our calculation of number density fluctuations are the bimolecular reaction and translational diffusion. Since it has been discussed elsewhere,[15,24] we will ignore momentum and energy fluctuations in our calculations. Under these conditions, the macroscopic mass action law satisfied by Eq. (6) is

$$\frac{d\bar{n}_A}{dt} = -k^+\bar{n}_A^2 + R,\qquad(7)$$

where R is a homogeneous external flux needed to achieve a true steady state.

According to the FD theory,[11] the number density fluctuations of A at steady state, $\delta n_A = n_A(\mathbf{r},t) - \bar{n}_A^{ss}$, satisfy a linear stochastic equation

$$\frac{\partial\delta n_A}{\partial t} = [D\nabla^2 - 2k^+\bar{n}_A^{ss}]\delta n_A + f_A,\qquad(8)$$

where D is the diffusion coefficient.

The random effect of diffusion and reaction is represented by f_A. This term is a Gaussian white noise that vanishes on the average and has the covariance

$$\langle f_A(\mathbf{r},t)f_A(\mathbf{r}',t')\rangle$$
$$= [k^+\bar{n}_A^{ss} - 2D\bar{n}_A^{ss}\nabla_r^2]\delta(\mathbf{r} - \mathbf{r}')\delta(t - t').\qquad(9)$$

The density–density correlation function is calculated from the generalized fluctuation–dissipation theorem.[11] In Fourier transformed variables this reduces to an algebraic equation that is easy to solve for

$$\langle\delta\hat{n}_A(\mathbf{k},t)\delta\hat{n}_A(\mathbf{k}',t)\rangle = (2\pi)^3\hat{\sigma}_{AA}(\mathbf{k})\delta(\mathbf{k} - \mathbf{k}').\qquad(10)$$

Namely if one uses the Fourier transform

$$\hat{h}(\mathbf{k}) = \int e^{-i\mathbf{k}\cdot\mathbf{r}}h(\mathbf{r},t)d\mathbf{r}\qquad(11)$$

on Eq. (9), one gets

$$\frac{\partial\delta\hat{n}_A}{\partial t} = \hat{H}^{ss}(k)\delta\hat{n}_A + \hat{f}_A,\qquad(12)$$

where

$$\hat{H}^{ss}(k) = -[Dk^2 + 2k^+\bar{n}_A^{ss}].\qquad(13)$$

The covariance of $\hat{f}_A$ is calculated if one double Fourier transforms Eq. (9):

$$\iint e^{-i\mathbf{k}\cdot\mathbf{r} + \mathbf{k}'\cdot\mathbf{r}'}\langle f_A(\mathbf{r},t)f_A(\mathbf{r}',t')\rangle d\mathbf{r}' d\mathbf{r}$$
$$\equiv \langle\hat{f}_A(\mathbf{k},t)\hat{f}_A(\mathbf{k}',t)\rangle.\qquad(14)$$

Using the right-hand side of Eq. (9) in Eq. (14), one finds the following expression:

$$\langle\hat{f}_A(\mathbf{k},t)\hat{f}_A(\mathbf{k}',t')\rangle$$
$$= (2\pi)^3\hat{\gamma}_{AA}^{ss}(k)\delta(\mathbf{k} - \mathbf{k}')\delta(t - t'),\qquad(15)$$

with

$$\hat{\gamma}_{AA}^{ss}(k) = 2Dk^2 + k^+\bar{n}_A^{ss\,2}.\qquad(16)$$

Finally, for a multicomponent system at a steady state, one finds that the generalized fluctuation–dissipation theorem in k space reduces to[11]

$$\hat{H}^{ss}(k)\hat{\sigma}^{ss}(k) + \hat{\sigma}^{ss}(k)\hat{H}^{ssT}(k) = -\hat{\gamma}_{ss}(k),\qquad(17)$$

where the T stands for the transpose of $\hat{H}^{ss}(k)$.

Combining Eqs. (13) and (16) in Eq. (17), we find that

$$\hat{\sigma}_{AA}(k) = \bar{n}_A^{ss}\left[1 - \frac{3k^+\bar{n}_A^{ss}}{2D}\frac{1}{k^2 + \xi^2}\right],\qquad(18)$$

where the coherence length^{-1} ξ is given by

$$\xi^{-1} = \sqrt{D/2\bar{n}_A^{ss}k^+}.\qquad(19)$$

Up to this point, we have not made use of the dimensionality of the system, and Eqs. (13) and (16) are valid for one, two, and three dimensions. If we consider a one-dimensional system, the reaction $2A \to A + P$ occurs on a infinite straight line. Moreover, Eq. (18) can be inverse Fourier transformed in either one, two, or three dimensions.[7,16,17,19]

In the present case, the inverse Fourier transform of Eq.

(18) in one dimension yields the following expression for the rate constant:

$$k^+ = k^0\left[1 - \frac{3}{2}\frac{k^+}{D}\frac{e^{-R\xi}}{2\xi}\right], \tag{20}$$

where we have used Eqs. (3) and (4) and assumed the Smoluchowski reactivity. If one solves for k^+, one gets a relation between k^+ and the intrinsic reactivity

$$k^+ = (k^0\frac{4D\xi}{3}e^{R\xi})/(k^0 + \frac{4D\xi}{3}e^{R\xi}). \tag{21}$$

Since k^+ appears in the right-hand side of Eq. (21) through ξ in an exponential form, Eq. (21) is a transcendental equation that has to be solved, in most cases, by numerical methods. In other cases, some simplification is possible, and simpler relations are obtained. For example in the case of fast reaction, Eq. (21) gives us, in a natural way, a condition for diffusion-controlled reactions, i.e.,

$$k^0 \gg \frac{4D\xi e^{R\xi}}{3}. \tag{22}$$

When this condition is satisfied, Eq. (21) yields the diffusion-controlled rate constant given by

$$k_{DC}^+ = \left(\frac{4D\xi}{3}\right)e^{R\xi}. \tag{23}$$

Again, Eq. (23) is a transcendental equation but now independent of the intrinsic reactivity, and it is valid as long as Eq. (22) is satisfied.

In the case of one-dimensional simulations, the diffusion-controlled condition, Eq. (22), is always satisfied. A second important simplification applies to this simulation. Namely, one observes that the encounter radius is equal to zero. By setting $R = 0$ in Eq. (23) and squaring both sides of the equation, we find the following expression for the reaction constant:

$$k_{DC}^+ = (\tfrac{32}{9})\, D\bar{n}_A^{ss}. \tag{24}$$

This linear relation between k_{DC}^+ and $\bar{n}_A^{ss}$ implies a reaction rate proportional to the third power of the reactant concentration

$$V^+ \equiv k_{DC}^+ \bar{n}_A^{ss^2} = (\tfrac{32}{9})\, D\bar{n}_A^{ss3}. \tag{25}$$

This cubic behavior of the rate for the reaction $A + A \rightarrow A + P$ in one dimension was first reported by Anacker and Kopelman.[3] Even though the value of the proportionality constant was not reported, we expect that our result 32/9 is of the right order of magnitude. This minor discrepancy could result from the fact that our one-dimensional model does not mimic in every single detail the simulations of Kopelman.[22]

III. One-dimensional Dimerization

In this section, we consider the case of a dimerization reaction

$$2A \xrightarrow{k^+} A_2. \tag{26}$$

For this system, an external reactant flux, which depends on the concentration of A_2, is considered. One could associate

this condition with a photochemical dissociation reaction

$$A_2 \xrightarrow{h\nu} 2A \tag{27}$$

which is driving the system away from equilibrium.

Under the same assumptions as in Sec. II, the average number densities satisfy the following equations:

$$\frac{d\bar{n}_A}{dt} = -2k^+\bar{n}_A^2 + 2K\bar{n}_{A_2}, \tag{28}$$

$$\frac{d\bar{n}_{A_2}}{dt} = -\frac{1}{2}\frac{\partial\bar{n}_A}{\partial t}, \tag{29}$$

where $\bar{n}_A$ and $\bar{n}_{A_2}$ are the macroscopic number densities, k^+ is the observed rate constant, and K is the dissociation rate.

As in Sec. II, the next step in our method consists in constructing the stochastic equations satisfied by the number density fluctuations at steady state[11]:

$$\frac{\partial\delta n_A}{\partial t} = [D_A\nabla^2 - 4k^+\bar{n}_A^{ss}]\delta n_A + 2K\delta n_{A_2} + f_A, \tag{30}$$

$$\frac{\partial\delta n_{A_2}}{\delta t} = 2k^+\bar{n}_A^{ss}\delta n_A + [D_{A_2}\nabla^2 - K]\delta n_{A_2} + f_{A_2}, \tag{31}$$

where the D's are the diffusion coefficients, and the f's are Gaussian white noises that vanish on the average and have the covariance[9]

$$\begin{aligned}
\langle f(r,t)f(r',t)\rangle \\
= \begin{bmatrix} 4k^+\bar{n}_A^{ss2} - 2D_A\bar{n}_A^{ss}\nabla^2 & -2k^+\bar{n}_A^{ss2} \\ -2k^+\bar{n}_A^{ss2} & k^+\bar{n}_A^{ss2} - 2D_{A_2}\bar{n}_{A_2}^{ss}\nabla^2 \end{bmatrix} \\
\times \delta(r-r')\delta(t-t').
\end{aligned} \tag{32}$$

After Fourier transform Eqs. (30)–(32) and some algebra, we obtained in Appendix A the following expression for the density–density correlation function in k space:

$$\hat{\sigma}_{AA}(k) = \bar{n}_A^{ss}\left[1 - \frac{2\bar{n}_A^{ss}k^+}{D_A}\frac{1}{k^2 + \xi^2}\right], \tag{33}$$

where we have considered the limiting case of static dimers, $D_A \gg D_{A_2}$, and defined

$$\xi^2 = \frac{4\bar{n}_A^{ss}}{D_A}\tilde{k}, \tag{34}$$

$$\tilde{k} = k^+ + \frac{K}{4\bar{n}_A^{ss}}. \tag{35}$$

The limit considered in the calculation of Eq. (33) will allow us to compare our results to Kopelman's simulations of annihilation of excitons by static traps.

In one dimension and for the Smoluchowski reactivity, we find the relation between the rate constant and the intrinsic reactivity

$$k^+ = k^0\left[1 - \frac{k^+}{D_A}\frac{e^{-R\xi}}{\xi}\right], \tag{36}$$

where R is the encounter radius.

For computer simulations, the conditions $R = 0$ and $k^0 \gg D\xi e^{R\xi}$ are satisfied. These simplifications yield an

expression for the diffusion-controlled rate constant which is similar to Eq. (23), Namely,

$$k_{DC} = D_A \xi . \quad (37)$$

Using the definitions in Eqs. (34) and (35), we find a transcendental equation for k_{DC}^+,

$$k_{DC}^+ = 4D_A \bar{n}_A^{ss} \left[1 + \frac{K}{4\bar{n}_A^{ss} k_{DC}^+} \right] . \quad (38)$$

Equation (38) has to be solved for k_{DC}^+. It is worthwhile to consider two limiting situations. First, let us $\tau_M \ll \tau_D$, where the taus are defined as follows:

$$\tau_M \equiv 1/k_{DC}^+ \bar{n}_A^{ss} , \quad (39)$$

$$\tau_D \equiv 1/K . \quad (40)$$

In this case, the mean life of the monomer, τ_M, is extremely short compared with the mean life of the dimer, τ_D. This condition simplifies Eq. (38) even further. Finally, we find that the rate constant is proportional to $\bar{n}_A^{ss}$,

$$k_{DC}^< = 4D_A \bar{n}_A^{ss}, \quad (41)$$

where $k_{DC}^<$ is the diffusion-controlled rate constant when $\tau_M \ll \tau_D$. As in Sec. II, the rate of the reaction behaves as a cubic power of the number density

$$V_<^+ = 4D_A \bar{n}_A^{ss3} . \quad (42)$$

Let us now consider a second limiting situation $\tau_M \ll \tau_D$. In this case, dissociation of A_2 is fast compared with the dimerization of A. In this limit, the solution to Eq. (38) is given by

$$k_{DC}^> = \sqrt{D_A K} . \quad (43)$$

Notice that this rate constant is independent of the number density, and it yields the following rate:

$$V_>^+ = \sqrt{D_A K} \, \bar{n}_A^{ss2} . \quad (44)$$

This rate has the usual quadratic dependence on the number density. Thus, depending on the external fluxes, the rate of a reaction could have different behaviors. This quadratic behavior has been observed by Kopelman[22] in his one-dimensional simulation of the annihilation of excitons with homogeneous pair production of excitons. In our model, the pair production of excitons is localized on static traps (namely, the dimers, which are, nonetheless, homogeneously distributed). This minor difference may change slightly the value of the proportionality constant but not the overall behavior of the rate of the reactions. Finally, we predict that the cubic behavior will be recovered if the proper changes in the rate of exciton pair production are made.

IV. TRAPPING BY STATIC SINKS ON A RING

In this section, we study the trapping of particle A by static sinks S, on a ring of radius R_r. Our purpose is to evaluate the rate constant and assess the effect of the curvature on it.

The system is described by the process

$$A + S \xrightarrow{k^+} S. \quad (45)$$

The mass rate laws for this system are

$$\frac{\partial \bar{n}_A}{\partial t} = -k^+ \bar{n}_S \bar{n}_A + D_A \nabla^2 \bar{n}_A + K, \quad (46)$$

$$\frac{\partial \bar{n}_S}{\partial t} = D_S \nabla^2 \bar{n}_S , \quad (47)$$

where the $\bar{n}$'s are the macroscopic number densities, k^+ is the observed trapping rate, the D's are the diffusion coefficients, and K is an external controlled flux of A molecules. Notice that for a homogeneous medium, one finds the following relation at a steady state: $K = k^+ \bar{n}_S^{ss} \bar{n}_A^{ss}$.

According to the FD theory, the fluctuations, $\delta n_i = n_i(t) - \bar{n}_i^{ss}$, around a homogeneous steady state satisfy the following equations:

$$\frac{\partial \delta n_A}{\partial t} = [D_A \nabla^2 - k^+ \bar{n}_S^{ss}] \delta n_A - k^+ \bar{n}_A^{ss} \delta n_S + f_A , \quad (48)$$

$$\frac{\partial \delta n_S}{\partial t} = D_S \nabla^2 \delta n_S + f_S . \quad (49)$$

The f_i's are zero centered random terms with covariance

$$\langle \mathbf{f}(\mathbf{r},t)\mathbf{f}(\mathbf{r}',t') \rangle = \gamma(\mathbf{r},\mathbf{r}')\delta(t - t'), \quad (50)$$

where

$$\gamma(\mathbf{r},\mathbf{r}') = \begin{bmatrix} k^+ \bar{n}_A^{ss} \bar{n}_S^{ss} - 2D_A \bar{n}_A^{ss} \nabla^2 & 0 \\ 0 & -2D_S \bar{n}_S^{ss} \nabla^2 \end{bmatrix}$$
$$\times \delta(\mathbf{r} - \mathbf{r}') . \quad (51)$$

In order to use FD theory, we have to considered polar coordinates and, since the ring's radius is fixed, to write the Laplacian in terms of the distance s along the ring, i.e., $s = R_r \theta$,

$$\nabla^2 = \frac{1}{R_r^2} \frac{\partial^2}{\partial \theta^2} = \frac{\partial^2}{\partial s^2} , \quad (52)$$

where θ is the polar angle. Now, instead of using the Fourier transform, one has to use a Fourier series. Namely,

$$f(s) = \frac{1}{2\pi} \sum_{n=-\infty}^{\infty} f_n e^{-ins/R_r} , \quad (53)$$

with

$$f_n = \frac{1}{R_r} \int_{-\pi R_r}^{\pi R_r} f(s') e^{ins'/R_r} ds' . \quad (54)$$

Using Eq. (54), one could transform Eqs. (48)–(51) into

$$\frac{\partial \delta \hat{n}_n}{\partial t} = \hat{H}_n \delta \hat{n}_n + \hat{f}_n , \quad (55)$$

with

$$\hat{H}_n = \begin{bmatrix} -D_A (n/R_r)^2 - k^+ \bar{n}_S^{ss} & -k^+ \bar{n}_A^{ss} \\ 0 & -D_S (n/R_r)^2 \end{bmatrix} . \quad (56)$$

The covariance of the random term is given by

$$\langle \hat{f}_n \hat{f}_{n'} \rangle \equiv \hat{\gamma}_n 2\pi \delta_{n,n'}, \quad (57)$$

where

$$\hat{\gamma}_n = \begin{bmatrix} 2D_A \bar{n}_A^{ss} (n/R_r)^2 + k^+ \bar{n}_A^{ss} \bar{n}_S^{ss} & 0 \\ 0 & 2D_S \bar{n}_S^{ss} (n/R_r)^2 \end{bmatrix} . \quad (58)$$

In order to calculate the correlation functions, we, again, use the fluctuation–dissipation theorem

$$\hat{H}_n^{ss}\hat{\sigma}_n^{ss} + \hat{\sigma}_n^{ss}\hat{H}_n^{ssT} - \hat{\gamma}_n^{ss},\tag{59}$$

where we have defined

$$\langle \delta\hat{n}_n \delta\hat{n}_{n'}^T \rangle \equiv \hat{\sigma}_{nn'} = \hat{\sigma}_n \delta_{nn'} \frac{2\pi}{R_r},\tag{60}$$

where the T stands for the transpose of a vector or a matrix. Finally, using Eq. (59), we get the transformed density-density correlation function for sinks (S) and molecules (A):

$$(\hat{\sigma}_n)_{AS} = -\frac{k^+ \bar{n}_A^{ss} \bar{n}_S^{ss}}{D_A}$$

$$\times \left[\frac{1}{(1 + D_S/D_A)(n/R_r)^2 + (k^+ \bar{n}_S^{ss})/D_A} \right].\tag{61}$$

Since we are considering static traps, we have to take the limit whe $D_S/D_A \ll 1$. In this limit, we inverse transform Eq. (61) in Appendix B and solve for the radial distribution function

$$g_{AS}(s,s') = 1 - \frac{k^+}{2D_A\xi} \frac{\cosh\left[\xi(R_r\pi - |s - s'|)\right]}{\sinh(\xi\pi R_r)},\tag{62}$$

where we have defined the coherence length ξ^{-1} as

$$\xi^2 = \frac{k^+ \bar{n}_S^{ss}}{D_A}.\tag{63}$$

We use the Smoluchowski reactivity in the calculation of the rate constant. In this case, one obtains for the diffusion-controlled rate constant

$$k_{DC}^+ = 4D_A \bar{n}_S^{ss} e^{2\xi R} \left[\frac{1 - e^{-2\pi R_r\xi}}{1 + e^{-(2\pi R_r - 2R)\xi}} \right]^2,\tag{64}$$

with $R \equiv |s - s'|$ being the encounter arc.

Since we are interested in comparing with computer simulations, we can set R equal to zero. In this case, we get the following equation:

$$k_{DC}^+ = 4D_A \bar{n}_S^{ss}(\tanh(\pi R_r\xi))^2,\tag{65}$$

which is the main result in this section. From this equation, we can easily obtain an expression for the rate constant when the trapping occurs on an infinite straight line, where $R_r \gg 1$ and $\bar{n}_S^{ss}$ is held constant. In this case, one finds a rate constant which depends linearly only on the number concentration of traps. Thus, the rate predicted is

$$V^+ = 4D_A \bar{n}_A^{ss} \bar{n}_S^{ss2},\tag{66}$$

where we have used $k_{DC}^+ = 4D_A \bar{n}_S^{ss}$. Again in this case, we obtain a renormalized rate constant that modifies the rate of trapping from the usual behavior expected for bimolecular process.

In Appendix C we derive an alternative expression for the steady state diffusion controlled rate constant for static sinks on a straight line. This expression depends on the fact that sinks divide the line into finite segments in each of which the diffusion equation is easy to solve. Averaging over the

distribution of segment lengths and equating the rate of loss of A particles by reaction to their input flux gives $k^+ = 2D_A \bar{n}_S^{ss}$. This exhibits the same linear dependence on $\bar{n}_S^{ss}$ as derived above using the FD theory, except that the prefactor $2D_A$ is only half the size. While one can show that the radial distribution functions calculated in both ways satisfy the appropriate flux boundary conditions, i.e., $2D_A(dg_{AS}/dx)_{x=0} = k^+$, the correlation lengths in the two approaches are different. For the fluctuation–dissipation theory one has $\xi^{-1} = (D_A/k^+ \bar{n}_S^{ss})^{1/2} = 1/2\bar{n}_S^{ss}$, whereas for the calculation in Appendix C the characteristic distance between sinks, $\langle l \rangle$, is $1/\bar{n}_S^{ss}$. This difference seems to be due to the fact that in one dimension the A particles are always confined between two sinks. This imposes correlations that, evidently, cannot be accounted for simply by requiring that the radial distribution function vanishes at sinks, as is done in the fluctuation–dissipation theory. For point particles, this problem does not occur in two and three dimensions, although near close packing densities analogous discrepancies probably occur for particles with finite volumes. Since the calculation outlined in Appendix C is modeled after computer simulations, we expect that simulations with impenetrable traps and a uniform flux of mobile particles would yield the result $k_{DC}^+ = 2D_A \bar{n}_S^{ss}$. Although we have no other exact results with which to compare, we suspect that the factor of two difference between the fluctuation–dissipation theory result and the calculation in Appendix C is representative of differences with other types of simulations in one dimension.

In general, one is able to construct, from Eq. (65), a nonlinear relation for $\sqrt{k^+} \equiv w(\bar{n}_S^{ss})$,

$$w = 2\sqrt{D_A \bar{n}_S^{ss}} \tanh\left(\pi R_r \sqrt{\frac{\bar{n}_S^{ss}\omega}{D_A}} \right).\tag{67}$$

As a check, notice that for the infinite straight line case, $w = 2\sqrt{D_A \bar{n}_S^{ss}}$ satisfies Eq. (67). To assess the corrections to this expression due to the finite size of the ring, we use Eq. (67) in an iterative way and starting with $w^{(0)} = 2\sqrt{D_A \bar{n}_S^{ss}}$. The second iteration yields

$$w^{(2)} = 2\sqrt{D_S \bar{n}^{ss}} \tanh\left[N_S \tanh(N_S)\right],\tag{68}$$

where $2\pi R_r \bar{n}_S^{ss} = N_S$ is the total number of traps.

In most cases of interest, N_S is a large number. Thus, for a constant number of traps, the rate constant, as a function of the R_r, behaves as

$$k_{DC}^+ \approx 4\frac{D_A N_S}{2\pi R_r}[1 - 2e^{-2N_S}(1 - 2e^{-N_S})].\tag{69}$$

Notice that the correction inside the parentheses is small. Even for $N_S = 5$, the correction is only of the order of 10^{-4}. Therefore, for simulations, the size of the ring does not modify the functional form of the rate constant its effect on k^+ is through the change in the number concentration.

V. CONCLUSIONS

Using nonequilibrium statistical thermodynamics[11] and the method to calculate bimolecular rate constants developed by one of us,[7,9] we were able to study one dimensional

reactive systems. In the first example, $A + A \rightarrow A + P$, we obtained a rate constant which depends linearly in number concentration. This functional dependence agrees with Anacker's simulations.[2] The second system consist of a dimerization reaction coupled with a photochemical dissociation. The dissociation, which is externally controlled, influences considerably the functional behavior of the rate constant. We found a rate constant proportional to the number concentration, as in the previous case, only when the average mean life of the monomer τ_M is extremly short compared with the average mean life of the dimer τ_D. On the other hand, when $\tau_M \gg \tau_D$, we found a rate constant which is independent of the number concentration. The later case implies a steady state where most of the A molecules are monomers. Rate constant independent of the number concentration has been observed in Kopelman's simulations[22] of exciton annihilation in one dimension.

Trapping by static sinks on a ring was the third system studied. In this case, we implemented Keizer's method and calculate the rate constant. First, we considered the limiting case of an infinite straight line and found a rate constant proportional to the sink number concentration. Second, we assessed the effect of the size of the ring and found minor functional changes. The major effect of the size is through the changes on the number concentration as we change the radius of the ring. However, this effect is limited by the maximum number of particles that the system can accommodate. Indeed, if we fix the number of particles on the ring, one can vary the size of the ring down to a minimum radius, which is associated with a saturated ring. In other words, the number density does not diverge. Consequently, size corrections to the infinite straight line systems are negligible in the cases of interest.

ACKNOWLEDGMENTS

APPENDIX A

From Eqs. (30) to (32), we have in k space

$$\frac{\partial \delta \hat{n}}{\partial t} = \hat{H} \delta \hat{n} + \hat{f}, \tag{A1}$$

with

$$\hat{H} = \begin{bmatrix} -(D_A k^2 + 4k^+ \bar{n}_A^{ss}) & 2K \\ 2k^+ \bar{n}_A^{ss} & -(D_{A_2} k^2 + K) \end{bmatrix} \tag{A2}$$

and

$$\langle \widehat{ff} \rangle = \begin{bmatrix} 2D_A \bar{n}_A^{ss} k^2 + 4k^+ \bar{n}_A^{ss2} & -2k^+ \bar{n}_A^{ss2} \\ -2k^+ \bar{n}_A^{ss2} & 2D_{A_2} \bar{n}_A^{ss} k^2 + k^+ \bar{n}_A^{ss2} \end{bmatrix}. \tag{A3}$$

In this case, Eq. (17) is a relation between the matrices $\hat{\sigma}, \hat{H}$, and $\hat{\gamma}$. Solving for $\hat{\sigma}_{11}$,

$$\hat{\sigma}_{11} = -\frac{\hat{\gamma}_{11}[\det \hat{H} + \hat{H}_{22}^2] + \hat{\gamma}_{22} \hat{H}_{12}^2 - 2\hat{\gamma}_{12} \hat{H}_{12} \hat{H}_{21}}{2[\hat{H}_{11}(\det \hat{H} + \hat{H}_{22}^2) - \hat{H}_{12} \hat{H}_{21} \hat{H}_{22}]}. \tag{A4}$$

Using Eqs. (A2) and (A3), we get

$$\frac{\hat{\sigma}_{11}(k)}{\bar{n}_A^{ss}} = 1 - \frac{2k^+ \bar{n}_A^{ss}}{D_A + D_{A_2}} \left[\frac{1}{k^2 + \xi^2} + \frac{D_{A_2}}{D_A} \frac{1}{\xi_1^2 - \xi_2^2} \left(\frac{\xi_1^2}{k^2 + \xi_1^2} - \frac{\xi_2^2}{k^2 + \xi_2^2} \right) \right], \tag{A5}$$

where

$$\xi_1^2 = \frac{4k^+ \bar{n}_A^{ss}}{D_A} + \frac{K}{D_{A_2}}, \tag{A6}$$

$$\xi_2^2 = \frac{4k^+ \bar{n}_A^{ss} + K}{D_A + D_{A_2}}. \tag{A7}$$

In the limit $D_A \gg D_{A_2}$, one gets Eq. (33)

Appendix B

In order to calculate the radial distribution function, we use Eqs. (53), (60), and (61),

$$\sigma_{AS}(s,s') = \left(\frac{1}{2\pi}\right)^2 \sum_{n=-\infty}^{\infty} \sum_{n'=-\infty}^{\infty} (\hat{\sigma}_{nn'})_{AS}$$

$$\times \exp\left(-in\frac{s}{R_r} + in'\frac{s'}{R_r}\right)$$

$$= \frac{1}{2\pi R_r} \sum_{n=-\infty}^{\infty} (\hat{\sigma}_n)_{AS} e^{-in(s-s')/R_r}$$

$$= -\frac{R_r k^+ \bar{n}_A^{ss} \bar{n}_S^{ss}}{2\pi D_A} \sum_{n=-\infty}^{\infty} \frac{e^{-in(\theta-\theta')}}{n^2 + (R_r\xi)^2}, \tag{B1}$$

where $\theta = s/R_r$ and

$$\xi^2 = \frac{k^+ \bar{n}_A^{ss}}{D_A}. \tag{B2}$$

One could rewrite Eq. (B1) as
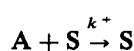
$$\sigma_{AS}(s,s') = -\frac{k^+ \bar{n}_A^{ss} \bar{n}_S^{ss}}{D_A} \frac{R_r}{2\pi}$$

$$\times \left(2 \sum_{n=1}^{\infty} \frac{\cos[n(\theta-\theta')]}{n^2 + (R_r\xi)^2} + \frac{1}{(R_r\xi)^2}\right). \tag{B3}$$

After summing and using the relation between the density-density correlation function and the radial distribution function, one gets

$$\bar{n}_A^{ss} \bar{n}_S^{ss}[-1 + g_{AS}^{ss}(\theta-\theta')]$$

$$= -\frac{k^+ \bar{n}_A^{ss} \bar{n}_S^{ss}}{2D_A \xi} \frac{\cosh[R_r\xi(\pi - |\theta-\theta'|)]}{\sinh[R_r\xi\pi]}. \tag{B4}$$

APPENDIX C

In one dimension the diffusion controlled reaction

$$A + S \xrightarrow{k^+} S$$

of the mobile point particles with randomly distributed, immobile points sinks S, can be treated by considering the diffusion equation

$$\frac{\partial n_A}{\partial t} = D_A \frac{\partial^2 n_A}{\partial x^2} + K \tag{C1}$$

on the domain $-l/2 \leqslant x \leqslant l/2$ with boundary conditions $n_A(\pm l/2, t) = 0$. K represents a uniform flux and a sink is located at each boundary so the l is the separation between adjacent sinks. Since the sinks are fixed, randomly distributed points on $-\infty < x < \infty$ with density $\bar{n}_S$, the separations of adjacent sinks have the exponential distribution $\rho_S(l) = \bar{n}_S^{ss} \exp(-\bar{n}_S^{ss} l)$. The steady state solution of Eq. (C1) is

$$n_A^{ss} = -\left(\frac{K}{2D_A}\right)(x^2 - l^2/4) . \tag{C2}$$

Thus the average number of A particles in a domain of length l is $\bar{N}_A^{ss}(l) = Kl^3/12D$, and the average density of A in all domains is

$$\bar{n}_A = \frac{\int_0^\infty \bar{N}_A^{ss}(l)\rho_S(l)dl}{\int_0^\infty \rho_S(l)l\,dl} = \frac{K}{2D_A \bar{n}_S^{ss2}} . \tag{C3}$$

Equating the flux, K to the steady state reaction rate $k_{DC}^+ \bar{n}_S^{ss} \bar{n}_A^{ss}$, then gives

$$k_{DC}^+ = 2D_A \bar{n}_S^{ss} . \tag{C4}$$

[1] R. Kopelman, J. Stat. Phys. **43**, 185 (1986).
[2] L. W. Anacker, R. P. Parson, and R. Kopelman, J. Phys. Chem. **89**, 579 (1985).
[3] L. W. Anacker and R. Kopelman, J. Chem. Phys. **81**, 6402 (1984).
[4] L. W. Anacker and R. Kopelman, Phys. Rev. Lett. **58**, 289 (1987).
[5] Y. Elkens and H. L. Frisch, Phys. Rev. A **31**, 3812 (1985).
[6] Z. Rácz, Phys. Rev. Lett. **55**, 1707 (1985); N. Agmon, J. Stat. Phys. **43**, 537 (1986).
[7] J. Keizer, Acc. Chem. Res. **18**, 235 (1985).
[8] J. Keizer, Chem. Rev. **87**, 167 (1987).
[9] J. Keizer, J. Phys. Chem. **86**, 5052 (1982).
[10] D. McQuarrie, *Statistical Mechanics* (Harper and Row, New York, 1976).
[11] J. Keizer *Statistical Thermodynamics of Nonequilibrium Process* (Springer, New York, (1987).
[12] J. Keizer, J. Chem. Phys. **79**, 4877 (1983).
[13] J. Keizer, J. Am. Chem. Soc. **105**, 1494 (1984).
[14] J. Keizer, J. Chem. Phys. **80**, 4185 (1984).
[15] J. Keizer and E. Peacock-López, Physica (to be published).
[16] J. Keizer, J. Ramírez, and E. Peacock-López, Biophys. J. **47**, 79 (1985).
[17] E. Peacock-López and J. Ramírez, Biophys. Chem. **25**, 117 (1986).
[18] M. Medina-Noyola and J. Keizer, Physica A **107**, 437 (1981).
[19] J. Keizer and M. Medina-Noyola, Physica A **115**, 301 (1982).
[20] E. Peacock-López and J. Keizer, Phys. Lett. A **108**, 85 (1985).
[21] L. Woodhouse and E. Peacock-López, J. Phys. Chem. (submitted).
[22] R. Kopelman (private communication).
[23] T. L. Hill, *Statistical Mechanics*, (McGraw–Hill, New York, (1956).
[24] J. Keizer, J. Chem. Phys. **87**, 4064, 4074 (1987).