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Brownian dynamics simulations of diffusion controlled reactions with finite reactivity

J. Srinivasalu Gupta and D. V. Khakhar
Department of Chemical Engineering, Indian Institute of Technology–Bombay, Powai, Bombay 400 076, India

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A new Brownian dynamics simulation technique is presented for the calculation of the effective rate constant for diffusion controlled reactions with a finite intrinsic reactivity. The technique is based on the calculation of the recollision probability of a molecule with a reactive site using a large number of Brownian trajectories, when the probability of reaction upon collision with the reactive site ($\varphi_r$) is less than unity. The technique is a modification of the earlier work of Northrup et al. [J. Chem. Phys. 80, 1517 (1984)], and is applied to the case of a uniformly reactive target sphere and a target sphere with axially symmetric reactive patches. A theoretical analysis is presented to relate $\varphi_r$ to the intrinsic surface reaction rate constant ($k'$). Computational results for the uniformly reactive sphere are in excellent agreement with theory, and those for the sphere with patches are in very good agreement with the results obtained using a different computational technique [Allison et al., J. Phys. Chem. 94, 7133 (1990)]. The proposed method requires the computation of the recollision probability to a high accuracy; however, this does not result in computational times greater than those of Allison et al. [J. Phys. Chem. 94, 7133 (1990)]. The new method has the advantage that the results of the Brownian dynamics simulation are independent of $k'$ and can subsequently be used to calculate the effective rate constant for any given value of $k'$. © 1997 American Institute of Physics. [S0021-9606(97)50230-3]

I. INTRODUCTION

The diffusion of reactive species can be the rate-controlling step when the chemical reaction step is very fast relative to the diffusion. Rapid coagulation in colloidal solutions and aerosols, crystal growth, protein folding, ion recombination reactions, fluorescence quenching of electronically excited species, chain termination reactions in free radical polymerization, and heterogeneous catalytic reactions are just a few examples of processes in which such “diffusion controlled reactions” have been observed. The basic theory for the analysis of such reactions was first established by Smoluchowski for the coagulation of colloidal particles, and the theory has been validated for a wide variety of systems. Enzyme-substrate bimolecular reactions have received more attention recently, and several particular cases have been analyzed, including those with orientational criteria for reaction. The polymerization of rod-like molecules has also been shown to be diffusion controlled, complexities in this case arise from both orientational criteria for reaction and anisotropic translational diffusion. Recently Wu and Nitsche have presented a review of the theoretical analyses of bimolecular diffusion-limited reaction processes with a variety of combinations of species and interactions.

Obtaining analytical solutions for diffusion and reaction in processes involving complex interactions and reaction conditions is difficult. A novel method for evaluating the effective rate constants for diffusion controlled reactions has been developed by Northrup et al., based on the statistics of Brownian motion of a single reactive molecule in the neighborhood of the reactive site. In its simplest version, the effective rate constant of reaction is proportional to the fraction of molecules initiated on a spherical surface that encloses the reactive site, which react (collide with the reactive site) rather than escape (diffuse to large distances from the reactive site). The method obviates the need for solution of the complex diffusion equations to obtain the concentration field, and thus problem formulation from a computational viewpoint is greatly simplified. Other advantages of the method include the ease of parallel computation (parts of the computation can in fact be carried out independently) and the sequential refinement of results (the number of Brownian trajectories can be increased until the standard deviation is low enough). The method has been implemented for many reactions incorporating hydrodynamic interactions, chemically anisotropic species, rotational diffusion, and various intermolecular force models. In all these cases the reaction between the species is instantaneous (every collision results in reaction), corresponding to an infinite surface reaction rate constant.

Northrup et al. have also described a Brownian dynamics algorithm for reactions with a finite intrinsic reactivity, based on a fixed probability of reaction upon collision of the reactive species with the site, and on a computational estimate of the probability of recollision of an unreacted molecule with the reactive site. However, to our knowledge, this procedure has not been applied to any system. Allison et al. have proposed an alternate Brownian dynamics technique for systems with a finite intrinsic reactivity which has been successfully implemented. In this method the probability of reaction for a given trajectory is computed by theoretically estimating the survival probability of the diffusing molecule in each Brownian step. A third approach for the
analysis of diffusion controlled reactions in the context of Brownian dynamics\textsuperscript{21} involves a modification of the boundary condition at the reactive site; the reaction surface is replaced by a reaction zone in which the reactivity decays exponentially with distance. This exponential reactivity model has been found to be particularly suitable for electron transfer reactions.\textsuperscript{21–24}

We focus on the first two methods here. The main objective of the current work is to present a necessary modification of the theory for the method proposed by Northrup et al.\textsuperscript{12} so as to permit a numerical implementation of the method. To illustrate the method we consider the diffusion-limited reaction between spherical molecules with no intermolecular forces or hydrodynamic interactions, in which not all collisions of diffusing molecules with reaction sites lead to reaction. Two specific cases have been dealt with: one in which the total surface of the target molecule is reactive (i.e., a target molecule with reactive patches) (Fig. 1). Computational results for the latter are compared to results obtained following the method of Allison et al.\textsuperscript{20}

\section*{II. THEORY}

We briefly review the theoretical basis of the Brownian dynamics simulation method, first following Northrup et al.\textsuperscript{12} The theory for the modified method is given next, along with the derivation of the probability of reaction upon collision with the reactive site ($\varphi$).

At steady state, the total diffusive flux of molecules to the reactive site (target molecule) is equal to the diffusive flux to any closed surface bounding the target molecule. For simplicity consider a spherical surface of radius $r=b$ surrounding the target molecule. The reaction flux to this surface can be written as

\begin{equation}
\mathcal{J} = \mathcal{J}_0 \beta_\infty, \tag{1}
\end{equation}

where $\mathcal{J}_0$ is the flux of particles starting from $r=\infty$ that visit the surface $r=b$ for the first time, and $\beta_\infty$ is the probability that molecules starting at $r=b$ will react rather than escape to $r=\infty$. $\mathcal{J}_0$ is obtained analytically, and $\beta_\infty$ is obtained by Brownian dynamic simulations as described below.

The first visit flux of the molecules to the surface $r=b$ is $\mathcal{J}_0$, obtained by solving the following diffusion equation

\begin{equation}
\frac{D}{\sqrt{\pi t}} \frac{d^2}{dr^2} \left[ r^2 \frac{dC_0}{dr} \right] = 0, \tag{2}
\end{equation}

along with the boundary conditions

\begin{align}
C_0 &= 0, \quad r = b, \tag{3a} \\
C_0 &= C_\infty, \quad r = \infty, \tag{3b}
\end{align}

where $D$ is the diffusivity. The flux is thus given by

\begin{equation}
\mathcal{J}_0 = 4\pi b^2 D \frac{dC_0}{dr} = 4\pi Db C_\infty. \tag{4}
\end{equation}

The effective rate constant is then obtained as

\begin{equation}
k_{\text{eff}} = \mathcal{J}_0 C_0 = 4\pi Db \beta_\infty. \tag{5}
\end{equation}

The reaction probability $\beta_\infty$ is obtained from Brownian trajectories initiated at $r=b$ and is given by the fraction of trajectories that react rather than diffuse to $r=\infty$. Since not all the collisions with the reaction sink lead to reaction, Northrup et al.\textsuperscript{12} suggested the calculation of $\Delta_\infty$, which is the probability that molecules separating from an unsuccessful collision will recollide rather than escaping to infinite separation. Now, the evaluation of the reaction probability $\beta_\infty$ is obtained as a sum of the probabilities of successive recollisions and reactions as shown by Northrup et al.\textsuperscript{12} The probability that a molecule starting at $r=b$ collides with the reactive sink rather than escaping to $r=\infty$ is denoted as $\xi_\infty$, and the probability of any collision leading to reaction is denoted as $\varphi$. Hence, the probability of reaction after the first collision is $\xi_\infty \varphi$. Those molecules with an unsuccessful first collision will have a probability $\Delta_\infty$ of recolliding rather than escaping to infinite separation. This second collision reaction probability is given by $\xi_\infty (1-\varphi) \Delta_\infty \varphi$. Keeping track of successive collision and reaction attempts gives the total probability of eventual reaction of the molecule starting from surface $b$ as

\begin{equation}
\beta_\infty = \xi_\infty \varphi + \xi_\infty (1-\varphi) \Delta_\infty \varphi + \xi_\infty (1-\varphi)^2 \Delta_\infty \varphi + \cdots, \tag{6}
\end{equation}

so that

\begin{equation}
\beta_\infty = \frac{\xi_\infty \varphi}{1 - (1-\varphi) \Delta_\infty}. \tag{7}
\end{equation}

Thus, the effective rate constant for the case of finite reactions is given by

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{FIG.1.png}
\caption{Schematic showing the target molecule with reactive patches. $\theta_c$ is the patch angle.}
\end{figure}
than going to react rather than escaping to the reactive site. The reaction probability density of the molecules is given by

\[
\frac{\partial P}{\partial t} = D \frac{\partial^2 P}{\partial x^2},
\]

and the initial condition is

\[
P(x,0) = \delta(x),
\]

where \(\delta(x)\) is the delta function. The boundary conditions are

\[
-D \frac{\partial P}{\partial x} = k' P, \quad x = 0,
\]

\[
P = 0, \quad x = L.
\]

Using separation of variables, we obtain the following solution to the above

\[
P(x,t) = \sum_{n=1}^{\infty} C_m f_n(x) e^{-\omega_n^2Dt},
\]

where

\[
f_n(x) = \cos(\omega_n x) + \frac{k'}{D\omega_n} \sin(\omega_n x),
\]

and

\[
C_m = \frac{2\omega_m \sin^2(\omega_m L)}{\omega_m L - \cos(\omega_m L)\sin(\omega_m L)}.
\]

The roots \(\omega_n\) are determined numerically from \(f_n(L) = 0\), and then the probability density can be easily calculated.

To obtain the fraction of molecules that react, we need to consider the flux to each surface \(x = 0\) and \(x = L\). The total number of molecules that arrive at any surface in the domain are

\[
N(x) = -D \int_0^x \frac{\partial P}{\partial x} dt.
\]

On substituting for the probability density we get the number of molecules that react (i.e., flux to \(x = 0\)) as

\[
N(0) = -\sum_{n=1}^{\infty} \frac{2 \cos(\omega_n L)\sin(\omega_n L)}{\omega_n L - \cos(\omega_n L)\sin(\omega_n L)},
\]

and the number of molecules that escape to \(x = L\) as

\[
N(L) = \sum_{n=1}^{\infty} \frac{2 \sin(\omega_n L)}{\omega_n L - \cos(\omega_n L)\sin(\omega_n L)}.
\]

Finally we obtain

\[
\varphi_f = \frac{N(0)}{N(0) + N(L)} = N(0).
\]

Rescaling all distances by the radius of the target sphere \((R)\) and defining the following dimensionless variables and parameters:

\[
k_{\text{eff}} = \frac{4\pi D b \xi_\infty \varphi}{1 - (1 - \varphi)\Delta_\infty}.
\]

Following similar arguments as above, corrections for a finite computational domain were obtained by Northrup et al.12 as

\[
\xi_\infty = \frac{\xi}{1 - (1 - \varphi)\Omega},
\]

and

\[
\Delta_\infty = \Delta + \xi_\infty (1 - \Delta),
\]

where \(\xi\) is the probability that the molecule starting at \(r = b\) collides with the reaction site rather than escaping to \(r = q\), and \(\Delta\) is the probability that a molecule starting at the reactive site collides with it rather than escaping to \(r = b\).

In the above equation \(\Omega\) is the probability that the molecule reaching the surface \(r = q\) will go back to \(r = b\) rather than going to \(r = \infty\), and is given by (Northrup et al.12)

\[
\Omega = b L
\]

for nearly isotropic diffusion in the region \(r > b\). Thus if \(\xi\) and \(\Delta\) are obtained from Brownian dynamics simulations, the effective rate constant for finite reactions can be obtained.

The above procedure suggested by Northrup et al.12 cannot be numerically implemented since the recollision probability \((\Delta)\) as defined above is dependent on the time step \((\Delta t)\) and \(\Delta\rightarrow 1\) as \(\Delta t\rightarrow 0\). Further, there is no direct relationship given between the reaction probability \((\varphi)\) and the surface reaction rate constant \((k')\). In the following we modify the procedure suggested by Northrup et al.12 by redefining the recollision probability and obtaining analytical relations between \(\varphi\) and \(k'\).

We define \(\Delta_{\text{rec}}\) and \(k'\) as the probability that a molecule starting at \(r = f\), an intermediate surface whose radius is less than \(r = b\), collides with the reactive site rather than escaping to \(r = \infty\). Similarly, \(\varphi_f\) is the probability that a molecule starting at the reactive site reacts rather than escaping to \(r = f\). The reaction probability for the case of finite rates of surface reaction is obtained as before in terms of the above probabilities as

\[
\beta_\infty = \frac{\xi_\infty \varphi_f}{1 - (1 - \varphi_f)\Delta_{\text{rec}}},
\]

where \(\xi_\infty\) is the first collision probability. The reaction probability for a finite domain is related to the infinite domain value using the procedure of Northrup et al.12 as

\[
\Delta_{\text{rec}} = \Delta_f + \xi_\infty (1 - \Delta_f),
\]

where \(\Delta_f\) is the probability that a molecule starting from \(r = f\) will collide with the reaction surface rather than escape to \(r = b\). \(\Delta_f\) can be evaluated using Brownian dynamic simulations, and \(\varphi_f\) must be obtained analytically. Here we obtain \(\varphi_f\) for the case when \((f - R)/R \ll 1\) so that the reactive surface can be assumed to be flat.

Consider the diffusion and reaction of a molecule between two parallel flat surfaces separated by a distance \(L = (f - R)\). The surface \(x = 0\) is reactive with a surface reaction rate constant \(k'\), and \(x = L\) is a perfectly absorbing surface. The molecule initially at \(x = 0\) may either react at \(x = 0\) or be absorbed at \(x = L\). \(\varphi_f\) is then the fraction of molecules that react at \(x = 0\). The governing equation for the probability density of the molecules is

\[
\frac{\partial P}{\partial t} = D \frac{\partial^2 P}{\partial x^2},
\]

and the initial condition is

\[
P(x,0) = \delta(x),
\]

where \(\delta(x)\) is the delta function. The boundary conditions are

\[
-D \frac{\partial P}{\partial x} = k' P, \quad x = 0,
\]

\[
P = 0, \quad x = L.
\]
In the above equation, the reaction probability in dimensionless form is

\[ w = k_\text{eff} = k_{\text{eff}}/(4\pi DR), \]

where \( k_{\text{eff}} \) is the reaction probability per unit time, \( k \) is the rate constant, \( R \) is the radius of the reactive site, and \( D \) is the diffusion coefficient of the molecules.

Computation of \( k_{\text{eff}} \) requires integration over the volume of the domain where the reaction can occur. This is done by dividing the domain into small elements and calculating the contribution of each element to the reaction probability. The integration is performed using numerical methods such as Simpson’s rule or Gaussian quadrature.

The collision probability \( \phi \) depends on the angle \( \alpha \) and \( \Theta \) as

\[ \phi_i = \frac{\alpha \Theta}{1 + \alpha \Theta}. \]

III. COMPUTATIONAL PROCEDURE

The core of the simulations is generation of Brownian trajectories of the diffusing molecules. The initiation and truncation conditions are varied depending on the probabilities being calculated. The Brownian displacement of a molecule in a dimensionless time step \( \delta \tau = D \delta t / R^2 \) is

\[ r(\tau + \delta \tau) = r(\tau) + S(\delta \tau), \]

where \( S(\delta \tau) \) is a set of Gaussian random numbers with zero mean and variance \( \langle S_i^2 \rangle = 2 \delta \tau \), where \( i = 1, 2, 3 \) corresponds to the three coordinate axes. Since the Brownian displacements are required to be small only in the neighborhood of boundaries, \( \delta \tau \) is varied with location in the computational domain, resulting in considerable computational time saving. The Box-Muller algorithm is used to generate the Gaussian random numbers.

The collision probability \( \phi \) is calculated by initiating trajectories at \( \bar{r} = \bar{b} \) and truncating them when the molecule collides with the reactive surface at \( \bar{r} = 1 \) or the outer surface \( \bar{r} = \bar{q} \). The collision probability is then simply the fraction of molecules that collide with the reactive surface. A sufficiently large \( b(\delta = 8) \) is used for target molecules with reactive patches, so that the collision probability for molecules initiated at \( \theta = 0 \) is nearly the same as that for molecules initiated at \( \theta = 90 \). The truncation radius is taken to be \( \bar{q} = 12 \). The time step used in the computation is given by

\[ \delta \tau = \frac{\tau_{\text{fac}}(\bar{r} - 1.0)^2(\bar{q} - \bar{r})^2}{\tau_{\text{min}}} \]

with \( \tau_{\text{fac}} = 10^{-4} \) and \( \tau_{\text{min}} = 10^{-4} \). These values are obtained by trial and error as the largest values that give accurate results. The computations consisted of five iterations with 20,000 trajectories each. When the time step \( \delta \tau \) is less than \( \tau_{\text{min}} \), it is set equal to \( \tau_{\text{min}} \).

The recollision probability \( (\Delta \phi_j) \) is the fraction of molecules starting at \( \bar{r} = \bar{f} = 1.01 \) that collide with the reactive surface rather than escaping to \( \bar{r} = \bar{b} \). Hence, trajectories started at \( \bar{r} = \bar{f} \) are terminated when the molecule collides with the target sphere \( (\bar{r} = 1) \) or escapes by passing beyond the initiation boundary \( (\bar{r} = \bar{b} = 8) \). For the case of the target molecule with reactive patches, the recollision probability \( (\Delta \phi_j(\theta)) \) is calculated for a fixed number of \( \theta \)-values in the range \( \theta \in (0, \theta_c) \). Each calculation consisted of five iterations with 30,000 trajectories for each \( \theta \)-value. The time step used in the computations is

\[ \delta \tau = \frac{\tau_{\text{fac}}(\bar{r} - \bar{r}_c)^2(\bar{b} - \bar{r})^2}{\tau_{\text{min}}}, \]

with \( \bar{r}_c = 1.05 \), \( \tau_{\text{fac}} = 10^{-3} \), and \( \tau_{\text{min}} = 10^{-6} \). The effective rate constant is then obtained by numerical integration of Eq. (25) using Simpson’s rule for the computed \( \Delta \phi_j(\theta) \) and \( \xi_{\phi} \) values. For this case as well, \( \delta \tau = \tau_{\text{min}} \) when the value calculated from Eq. (28) is less than \( \tau_{\text{min}} \).

The procedure used for computations based on survival probability is essentially the same as that of Allison et al. Molecules that collide with the reactive site are reflected, and the trajectory is truncated when \( \bar{r} > \bar{q} \). Since the survival probability is unity except very close to the reaction surface, it is calculated only when the diffusing molecule is within a certain critical radius \( \bar{r}_c \), or else it is set equal to unity. (See Ref. 20 for expressions for survival probability.) A single Brownian dynamics simulation is used to calculate the effec-
The effective rate constant for uniform reactivity (α) can be estimated for a uniformly reacting sphere, and is given by

\[ \tilde{k}_{\text{eff}} = \frac{\alpha}{1 + \alpha} \]  

in Fig. 3. The error bars give the standard deviations of the computed values over five iterations. The effective rate constant increases with increase in α, which is as expected. Further, the simulated values match very well with the theoretically evaluated values, validating the new method. We note that Δ_f must be calculated to relatively high accuracy since errors in the calculation of \( \tilde{k}_{\text{eff}} \) are magnified for small \( L \). For example, for a uniformly reactive sphere, the error in calculating the rate constant (\( \delta \tilde{k}_{\text{eff}} \)) for an error \( \epsilon \) in calculating Δ_f is

\[ \frac{\delta \tilde{k}_{\text{eff}}}{\tilde{k}_{\text{eff}}} = \frac{\epsilon}{L(\alpha + 1)}. \]  

Thus a sufficiently large number of trajectories is required to obtain accurate results. The relative error that arises from neglecting the curvature of the surface can be estimated for a uniformly reacting sphere, and is given by

\[ \frac{\delta \tilde{k}_{\text{eff}}}{\tilde{k}_{\text{eff}}} = \frac{\epsilon}{L(\alpha + 1)}. \]  

The above condition requires the use of a small value of \( L \) in the computations.

The computed values of the recollision probability for different initiation angles of the molecule for a particular value of the patch angle of the target molecule are presented in Tables I to IV. For a given value of the surface reactivity (α) the effective rate constant is calculated using the calculated recollision probabilities and \( \xi_\alpha \) (also given in Tables I–IV) from Eq. (25). The values of the effective rate constants obtained for different patch angles are presented in Fig. 4. The effective rate constants obtained using Allison et al.’s method20 for the same patch angles are also presented in the figures. For a particular value of the surface reactivity (α) the effective rate constant \( \tilde{k}_{\text{eff}} \) increases with increase in patch angle. Further, \( \tilde{k}_{\text{eff}} \) increases with increase in α for a given patch angle. Both these trends are as expected. The effective rate constants obtained using the new method, making use of the recollision probabilities, match very well with those obtained using survival probability calculations. For roughly equal values of the standard deviation, the computations...

### Table I. Finite domain (Δ_\( f \)) and infinite domain (Δ_\( f \)) recollision probabilities for different initiation angles (\( \theta \)) for a target molecule with patches. Patch angle: \( \theta = 20^\circ \). The infinite domain first collision probabilities (\( \xi_\alpha \)) is also given.

<table>
<thead>
<tr>
<th>( \theta )</th>
<th>( \Delta_f )</th>
<th>( \Delta_{f\alpha}(\theta) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>0.9724 (0.0009)</td>
<td>0.9733 (0.0025)</td>
</tr>
<tr>
<td>4.0</td>
<td>0.9714 (0.0010)</td>
<td>0.9723 (0.0026)</td>
</tr>
<tr>
<td>6.0</td>
<td>0.9714 (0.0009)</td>
<td>0.9722 (0.0025)</td>
</tr>
<tr>
<td>8.0</td>
<td>0.9704 (0.0007)</td>
<td>0.9713 (0.0022)</td>
</tr>
<tr>
<td>10.0</td>
<td>0.9695 (0.0004)</td>
<td>0.9704 (0.0020)</td>
</tr>
<tr>
<td>12.0</td>
<td>0.9675 (0.0006)</td>
<td>0.9685 (0.0022)</td>
</tr>
<tr>
<td>14.0</td>
<td>0.9633 (0.0008)</td>
<td>0.9644 (0.0024)</td>
</tr>
<tr>
<td>16.0</td>
<td>0.9572 (0.0007)</td>
<td>0.9585 (0.0023)</td>
</tr>
<tr>
<td>18.0</td>
<td>0.9436 (0.0007)</td>
<td>0.9453 (0.0023)</td>
</tr>
<tr>
<td>20.0</td>
<td>0.8573 (0.0018)</td>
<td>0.8616 (0.0034)</td>
</tr>
</tbody>
</table>

### Table II. Finite domain (Δ_\( f \)) and infinite domain (Δ_\( f \)) recollision probabilities for different initiation angles (\( \theta \)) for a target molecule with patches. Patch angle: \( \theta = 40^\circ \). The infinite domain first collision probability (\( \xi_\alpha \)) is also given.

<table>
<thead>
<tr>
<th>( \theta )</th>
<th>( \xi_\alpha = 0.0651 \pm 0.0021 )</th>
<th>( \Delta_f )</th>
<th>( \Delta_{f\alpha}(\theta) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>0.9823 (0.0005)</td>
<td>0.9834 (0.0026)</td>
<td></td>
</tr>
<tr>
<td>8.0</td>
<td>0.9827 (0.0003)</td>
<td>0.9838 (0.0024)</td>
<td></td>
</tr>
<tr>
<td>12.0</td>
<td>0.9825 (0.0008)</td>
<td>0.9836 (0.0029)</td>
<td></td>
</tr>
<tr>
<td>16.0</td>
<td>0.9819 (0.0005)</td>
<td>0.9831 (0.0026)</td>
<td></td>
</tr>
<tr>
<td>20.0</td>
<td>0.9819 (0.0008)</td>
<td>0.9830 (0.0029)</td>
<td></td>
</tr>
<tr>
<td>24.0</td>
<td>0.9800 (0.0004)</td>
<td>0.9813 (0.0025)</td>
<td></td>
</tr>
<tr>
<td>28.0</td>
<td>0.9792 (0.0007)</td>
<td>0.9806 (0.0028)</td>
<td></td>
</tr>
<tr>
<td>32.0</td>
<td>0.9760 (0.0008)</td>
<td>0.9776 (0.0029)</td>
<td></td>
</tr>
<tr>
<td>36.0</td>
<td>0.9680 (0.0014)</td>
<td>0.9701 (0.0035)</td>
<td></td>
</tr>
<tr>
<td>40.0</td>
<td>0.8943 (0.0011)</td>
<td>0.9012 (0.0032)</td>
<td></td>
</tr>
</tbody>
</table>
TABLE III. Finite domain ($\Delta J$) and infinite domain ($\Delta_{\infty J}$) recollision probabilities for different initiation angles ($\theta$) for a target molecule with patches. Patch angle: $\theta_{c}=60^\circ$. The infinite domain first collision probability ($\xi_{\infty}$) is also given.

<table>
<thead>
<tr>
<th>$\theta$</th>
<th>$\Delta J$</th>
<th>$\Delta_{\infty J}(\theta)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.0</td>
<td>0.9861 (0.0004)</td>
<td>0.9874 (0.0028)</td>
</tr>
<tr>
<td>12.0</td>
<td>0.9861 (0.0006)</td>
<td>0.9874 (0.0030)</td>
</tr>
<tr>
<td>18.0</td>
<td>0.9862 (0.0007)</td>
<td>0.9875 (0.0031)</td>
</tr>
<tr>
<td>24.0</td>
<td>0.9861 (0.0007)</td>
<td>0.9874 (0.0031)</td>
</tr>
<tr>
<td>30.0</td>
<td>0.9858 (0.0005)</td>
<td>0.9872 (0.0029)</td>
</tr>
<tr>
<td>36.0</td>
<td>0.9850 (0.0006)</td>
<td>0.9865 (0.0030)</td>
</tr>
<tr>
<td>42.0</td>
<td>0.9840 (0.0004)</td>
<td>0.9855 (0.0028)</td>
</tr>
<tr>
<td>48.0</td>
<td>0.9829 (0.0005)</td>
<td>0.9846 (0.0029)</td>
</tr>
<tr>
<td>54.0</td>
<td>0.9785 (0.0004)</td>
<td>0.9806 (0.0028)</td>
</tr>
<tr>
<td>60.0</td>
<td>0.9177 (0.0011)</td>
<td>0.9256 (0.0035)</td>
</tr>
</tbody>
</table>

TABLE IV. Finite domain ($\Delta J$) and infinite domain ($\Delta_{\infty J}$) recollision probabilities for different initiation angles ($\theta$) for a target molecule with patches. Patch angle: $\theta_{c}=80^\circ$. The infinite domain first collision probability ($\xi_{\infty}$) is also given.

<table>
<thead>
<tr>
<th>$\theta$</th>
<th>$\Delta J$</th>
<th>$\Delta_{\infty J}(\theta)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.0</td>
<td>0.9877 (0.0003)</td>
<td>0.9892 (0.0033)</td>
</tr>
<tr>
<td>16.0</td>
<td>0.9875 (0.0006)</td>
<td>0.9890 (0.0036)</td>
</tr>
<tr>
<td>24.0</td>
<td>0.9876 (0.0006)</td>
<td>0.9891 (0.0036)</td>
</tr>
<tr>
<td>32.0</td>
<td>0.9877 (0.0005)</td>
<td>0.9892 (0.0035)</td>
</tr>
<tr>
<td>40.0</td>
<td>0.9877 (0.0003)</td>
<td>0.9891 (0.0033)</td>
</tr>
<tr>
<td>48.0</td>
<td>0.9872 (0.0006)</td>
<td>0.9888 (0.0036)</td>
</tr>
<tr>
<td>56.0</td>
<td>0.9874 (0.0004)</td>
<td>0.9889 (0.0034)</td>
</tr>
<tr>
<td>64.0</td>
<td>0.9865 (0.0005)</td>
<td>0.9881 (0.0035)</td>
</tr>
<tr>
<td>72.0</td>
<td>0.9853 (0.0005)</td>
<td>0.9871 (0.0035)</td>
</tr>
<tr>
<td>80.0</td>
<td>0.9494 (0.0007)</td>
<td>0.9555 (0.0036)</td>
</tr>
</tbody>
</table>

V. CONCLUSIONS

A new method of evaluating the effective rate constants for diffusion controlled reactions with finite reactivity is presented. The method is a modification of Northrup et al’s [312] procedure. The effective rate constants obtained from simulations for uniformly reactive spheres match very well with the theoretical results. For the target sphere with reactive patches, the effective rate constants obtained using the new method, making use of the recollision probabilities, match well with those obtained using survival probability calculations. The results presented in the paper essentially validate the proposed Brownian dynamic simulation method for the calculation of effective rate constants for finite surface reac-

FIG. 4. Variation of effective rate constant ($\bar{k}_{eff}$) with surface reactivity ($\alpha$) for finite reactions of spherical molecules with different patch angles: (a) $\theta_{c}=20^\circ$, (b) $\theta_{c}=40^\circ$, (c) $\theta_{c}=60^\circ$, and (d) $\theta_{c}=80^\circ$. ×: effective rate constant obtained using recollision probability computations, +: effective rate constant obtained using survival probability computations.
tivity. We briefly compare below this method to the method of Allison et al.20

The primary advantage of the recollision probability method is that the Brownian dynamics simulations (which are computationally intensive) are independent of the surface reactivity \( k' \). Thus, once \( \Delta_{w}(\theta) \) and \( \xi_{w} \) are computed (cf. Tables I–IV), the effective rate constant can easily be obtained from Eq. (25) for any value of \( k' \). The main disadvantage is the magnification of errors due to small values of \( \bar{L} \) [Eq. (31)], which require computation of \( \Delta_{r} \) to a high degree of accuracy. This does not, however, result in any significant increase in computational effort.

The proposed method is particularly useful in cases where the intrinsic rate of reaction is not known \textit{a priori}. For example, in the polymerization of poly(p-phenylene terephthalamide),7,8,27 reaction kinetic data is available only in the diffusion controlled regime. The recollision probability method, in principle, allows the calculation of the effective rate constant for many different values of the intrinsic reactivity from a single Brownian dynamics simulation. Extraction of the intrinsic reactivity from experimental data is thus facilitated.

2 M. V. Smoluchowski, Z. Phys. Chem. 92, 129 (1917).