Monte Carlo simulation study of recombination dynamics in solution

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A Monte Carlo (MC) simulation study of radical recombination dynamics in solution is presented. Random walks on a three-dimensional lattice are used to simulate the diffusion of radical pairs initially prepared by photolysis. The survival probability as a function of time is calculated by the dynamical interpretation of the MC methods. For the dynamics of radical pairs, the interplay of the geminate and the bulk recombinations is important at high concentrations. In most previous simulations only the dynamics of isolated geminate pairs were considered. In our simulations such interplay is clearly demonstrated by studying the intermediate to long time dynamics of many radical pairs. We compare our results with the predictions of the diffusion and the kinetic theories to examine the validity of their approximations. For low concentrations, results of the simulations show good agreement with theoretical predictions and provide a microscopic basis for understanding the recombination process. But notable deviations are found for high concentrations, which can be attributed to the approximations in theoretical studies. © *1996 American Institute of Physics.* [S0021-9606(96)03041-3]

I. INTRODUCTION

Photolytic radical recombination reactions have been studied extensively.[1] As a result of photodissociation, an initial distribution of fragment pairs is produced, typically with a small separation. The subsequent fate of these pairs reflects general aspects of the reactive pair dynamics in liquids such as diffusion or cage effect. The overall radical recombination reaction in liquids can be divided into two regimes, namely, the geminate and the bulk recombination phases. Geminate recombination refers to the process where the original pair of fragments from the same parent molecule recombine with each other. In this case, most recombination occurs within a few nanoseconds. Bulk recombination involves radicals which have diffused away from their geminate counterparts to the bulk solution. The time after which bulk recombination dominates geminate recombination depends on the initial concentration of radical pairs or the ratio of the initial separation of radical pairs (intra-pair separation) to the average distance from the neighboring ones (inter-pair separation). When the concentration of the photodissociated radical pairs is small, the bulk recombination phase is well separated in time scale from the geminate recombination phase and typically occurs for over microseconds. For a high initial concentration of radical pairs, the interplay between the geminate and the bulk recombination cannot be ignored.

The standard approach to the theoretical description of radical recombination phenomena makes use of a diffusion equation for pair probability distribution functions.[1,2] The diffusion equation is then solved subject to suitable boundary conditions at contact to account for the reaction and the initial conditions appropriate to the experimental situations. For the very short distance and time scale involved in geminate recombination, the diffusion equation may not be assumed to apply with confidence and its range of validity must be tested. One needs to go beyond the phenomenological Fick's law in describing microscopic details of the dynamical properties of liquids. Shin and Kapral[3] proposed a theory of reactive pair dynamics in liquids based on the kinetic theory of chemical reactions in dense fluids. Given initial pair distributions, the probability that the pair of particles will remain unreacted (Survival probability) can be calculated. The results of kinetic theory were shown to be a generalization of the simple diffusion equation approach to the problem.

The kinetic theory has not been extended to include the bulk radical recombination. Since the bulk recombination phase is usually well separated from the geminate recombination phase, the diffusion equation approach can be applied with more confidence. Waite[4] proposed a general formulation for treating diffusion-influenced bimolecular reactions that was based on a hierarchical system of many-body Smoluchowski equations for the reactant molecule distribution functions. He derived the rate equation which takes account of the interplay between geminate and bulk recombination. Recently, Jung and Lee[5] presented a pedagogical derivation of the rate equation for the recombination reactions based on the Lee and Karplus[6] reformulation of the nonequilibrium distribution function approach to general diffusion-influenced bimolecular reactions.

Computer simulations have been used to study the chemical reactions in solution for a long time and will certainly be extended to more complex systems with the development of more powerful computer technologies.[7] One usually uses molecular dynamics (MD) simulations to obtain dynamical information involved in reaction dynamics in liquids.[8] For the processes occurring in liquids, one may also use stochastic trajectory simulations or Brownian dynamics methods in which the dynamical solvent effects are accounted for by a random force and frictional terms.[9] The MD simulations intrinsically face the finite sample size and the

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finite time limitations for integration of the equations of motions when using a large number of particles. Monte Carlo (MC) simulations can be more efficient in studying complex systems with many particles for a long period of time. Even though the MC technique is in principle concerned with the static properties of the system, there have been many attempts to utilize the MC method in studying dynamical phenomena. Such applications include the adsorption–desorption phenomena and various chemical reaction systems on a surface or in liquids.[10–15]

Random walk provides a well-established model for studying various physical processes such as reaction rates, biological problems, and transports in solid state systems, both in bulk and on surfaces.[16–18] Simple random walks can be modified in such a way to describe many different physical situations.[19] There has been a lot of interest in diffusion-controlled reaction kinetics based on random walk models such as uni- or bimolecular recombinations with trapping or annihilation.[20–26] The main concern of such studies is to understand scaling behavior at long times by using analytical theories and computer simulations. The dimensionality of the system, the initial distribution of particles, and the exact mechanism of reaction kinetics are found to influence the long time behavior of such systems in a fundamental way.

The main purpose of the present study is to investigate the interplay between the geminate and bulk recombination processes using the MC method based on random walks. Direct quantitative description of the interplay has not been available from any of existing analytic theories but this can be done in the MC simulation by following the fate of radicals individually. In this way, we can obtain a better picture of the process and test the validity of analytic theories developed previously. The diffusive motion of the radicals is described by random walks on a lattice and the dynamical properties, such as survival probability, are obtained by appropriate interpretations of the MC simulation. Results of the simulations are compared with theoretical predictions. Since our interest is focused on the interplay between geminate recombination occurring at early times and bulk recombination, which becomes dominant at long times, we have carried out the simulation up to times when there is no longer any geminate recombination occurring. This may not be a long enough time to investigate the scaling behaviors; separate works are being carried out in this direction.

II. THEORETICAL BACKGROUND

In this section we briefly review the main results of the analytical theories for geminate and bulk recombination dynamics, with which the simulations will be compared. As introduced in the previous section, our focus is on the kinetic theory by Shin and Kapral[3] and the theory for bulk recombination based on a hierarchical many-body Smoluchowski equation by Jung and Lee.[5]

The survival probability obtained from the kinetic theory can be written as

$$p(\tau)=1-\tilde{L}^{-1}\left\{\frac{(k_f^0/\kappa)\exp[-(\kappa-1)\sqrt{\tilde{z}}]}{\tilde{z}[k_f^0+k_D(\tilde{z})]}\right\}, \tag{1}$$

where $\tau=t/\tau_0$, $\tilde{z}=\tau_0 z$, $\tau_0=\sigma^2/D$, $\kappa=\sigma_d/\sigma$, $\alpha^2=\sigma^2 z/D$, $k_D=4\pi\sigma D$, and $k_D(z)=2\alpha k_D/[1-\exp(-2\alpha)]$. Here σ is the relative distance at which the recombination reaction occurs, σ_d is the initial separation of the geminate pair, D is the sum of individual self-diffusion coefficients of each fragments, and k_f^0 is the equilibrium rate constant. $\tilde{L}^{-1}$ denotes the inverse Laplace transform in complex $\tilde{z}$ plane. The small frequency limit (or long time limit) of the survival probability can be obtained by taking the small frequency form for $k_D(\tilde{z})$, namely, $k_D(\tilde{z})\cong k_D\cdot(1+\sqrt{\tilde{z}})$. With this approximation the inverse Laplace transform can be solved analytically to yield

$$p(\tau)=1-\frac{\lambda}{\kappa(1+\lambda)}\left\{\operatorname{erfc}\left(\frac{\kappa-1}{2\sqrt{\tau}}\right)-\exp[(1+\lambda)(\kappa-1)]\times\exp[(1+\lambda)^2\tau]\operatorname{erfc}\left[(1+\lambda)\sqrt{\tau}+\frac{\kappa-1}{2\sqrt{\tau}}\right]\right\}, \tag{2}$$

where $\lambda=k_f^0/k_D$. This result is the same as the diffusion approach with the Collins–Kimball boundary condition.[1]

It is interesting to note that as τ goes to infinity, $p(\tau)$ converges to the following value:

$$\lim_{\tau\to\infty}p(\tau)=1-\frac{\lambda}{\kappa(1+\lambda)}. \tag{3}$$

The result indicates that an isolated pair of radicals may not recombine even for a long time, because they infinitely fall apart in liquids. When the equilibrium rate constant, k_f^0, goes to infinity, namely, in the Smoluchowski boundary condition,[1] the result of the kinetic theory reduces to that of the diffusion theory:

$$p(\tau)=1-\frac{1}{\kappa}\operatorname{erfc}\left(\frac{\kappa-1}{2\sqrt{\tau}}\right). \tag{4}$$

It is noted that this result can be obtained directly from Eq. (1) by using the Smoluchowski boundary condition, and the kinetic and diffusion approaches give the same result in this limit.

Shin and Kapral[3] compared the kinetic theory with diffusion equation approaches and shows that the major deviations for most circumstances occur for reduced times less than $t/\tau_0=2$, which is in the range of 40–100 ps for iodine recombination in CCl_4. For short times, the diffusion equation leads to a faster rate of reaction compared with the kinetic theory results. In this time range, the diffusion equation suffers from lack of information concerning microscopic phenomena, which has also been noted experimentally by Langhoff *et al.*[27]

Jung and Lee obtained the rate equation for the general recombination reaction, $A+B \rightarrow AB$, given by[5]

$$-\frac{d[A]_t}{dt} = k_g^0(t)\exp\left\{-\int_0 d\tau k_b(\tau)([A]_\tau+[B]_\tau)\right\}[A]_0 + k_b(t)[A]_t[B]_t. \tag{5}$$

$[A]_t$ is the concentration of A at time t, and the first and the second terms on the right-hand side represent geminate and bulk recombination rates, respectively. $k_g^0(t)$ is the decreasing rate of the survival probability of an isolated A-B pair. $k_b(t)$ is the rate coefficient for the diffusion-influenced bimolecular recombination of A and B molecules that are randomly distributed at $t=0$ with no geminate correlation. They obtained the following expressions for the rate coefficients:

$$k_g^0(t) = \lambda(\sqrt{D}/\sigma_d)[1/\sqrt{\pi t} - X\Omega(X\sqrt{t} + Y/\sqrt{t})] \times \exp(-Y^2 t), \tag{6}$$

$$k_b(t) = [k_f^0/(1+\lambda)][1+\lambda\Omega(X\sqrt{t})], \tag{7}$$

where $X=(1+\lambda)(\sqrt{D}/\sigma)$, $Y=(\sigma_d-\sigma)/2\sqrt{D}$, $\Omega(x)=\exp(x^2)\times\mathrm{erfc}(x)$, and the other terms are the same as in Eqs. (1) and (2). When $[A]=[B]$, or the species A and B are the same, the Eq. (5) reduces to Waite's rate equation.[4]

To avoid the complexities which result from many-particle correlations, Jung and Lee[5] used the superposition approximation and neglected the correlation between like-particles in obtaining the Eq. (5). Three-particle probability density functions were reduced to the superposition of three two-particle probability density functions, and the like-particle correlation was neglected by letting the corresponding distribution function equal to unity. For instance, a three body probability density function would be approximated like the following:

$$\begin{aligned}\sum_{i=1}^{N_A^0}\sum_{\substack{l=1\\ l\neq i}}^{N_A^0} & P_{A_iB_iA_l}(r_A, r_B, r'_A, t) \\ & \cong [A]^2 P_g(|r_B-r_A|,t)\rho_{AB}^b(|r_B-r'_A|,t)\rho_{AA}^b(|r_A-r'_A|,t) \\ & \cong [A]^2 P_g(|r_B-r_A|,t)\rho_{AB}^b(|r_B-r'_A|,t),\end{aligned} \tag{8}$$

where $P_{A_iB_iA_l}(\mathrm{r_A},\mathrm{r_B},\mathrm{r'_A},\mathrm{t})$ is the three-particle probability density function $P_g(|r_B-r_A|,t)$ is the geminate-pair correlation function, and $\rho_{AB}^b(|r_B-r'_A|,t)$ is the bulk-pair correlation function, while $\rho_{AA}^b(|r_A-r'_A|,t)$ represents the correlation between like-particles. More complete definitions of the terms can be found in the original work by Jung and Lee.[5]

In general, rate equation (5) can only be solved numerically. However, when one species are in large excess of the other, this equation reduces to the pseudo-first-order problem and can be integrated exactly. In this limit, Eq. (4) results in the expression for the survival probability which coincides with that obtained by Agmon and Szabo.[28] Also when the effect of bulk recombination is ignored, the survival probability of geminate recombination obtained from the rate equation reproduces that of the kinetic theory by Shin and Kapral[3] in the long time limit [Eq. (2)]. As time goes to infinity, $k_g^0(t)$ goes to zero and $k_b(t)$ becomes a constant, which suggests that the process is dominated by bulk recombination and the rate equation reduces to a simple second-order problem. When the survival probability is plotted as a function of time in logarithmic scales for both variables one obtains a linear curve with the slope of -1 in the very long time limit. This results from the neglect of like-particle correlations, which have been known to lower the reaction rate in the long time.[21]

III. MONTE CARLO SIMULATIONS

The main assumptions of our MC simulations are similar to those of the diffusion equation approach. In the diffusional picture of the recombination process, radical pairs are formed suddenly by the initial separation, σ_d, due to an external agency (e.g., photolysis); then they diffuse apart or recombine together in solvent, which is regarded as a structureless continuum. The solvent molecules are considered not to interact with the radicals directly, but to influence the diffusion motions of the radicals indirectly. When the separation between the radicals equals the encounter or the reaction distance, σ, recombination reaction may occur. Repeated collisions with the surrounding solvent molecules result in a very short velocity relaxation time for the radicals. This leads to the description of the diffusion motions as random walks consisting of a series of small steps. The average displacement of random walks or Brownian motions is given by the Einstein–Smoluchowski relation $\langle \mathbf{r}^2\rangle = 6Dt$. This relation is used to define the displacement for one MC step as

$$\Lambda = \sqrt{6Dt}. \tag{9}$$

This definition of the average displacement, along with a lattice model, provides a connection between the Monte Carlo steps and the real times for the dynamics of the system.

The diffusion of radicals is modeled as simple jumps to neighboring lattice points in a cubic lattice. Based on the relation given by Eq. (9), one needs to find the optimum size of the time step by defining the appropriate distance between lattice points. One of the time scales involved is the velocity relaxation time, $\tau_R = mD/k_BT$, where m is the mass of the particle, k_B is the Boltzmann constant, and T is the temperature. The diffusion process is physically meaningful after this time. The time step of the simulation needs to be sufficiently small so that the force on the radicals can be assumed to be constant during one MC step. The step size should be reduced until the simulation results converge. The periodic boundary condition and the minimum image convention are used for the simulations to minimize the edge effects. The boundary should be large enough to examine the behavior of the system in the long time when the edge effects become important. For geminate recombination, in which only the relative distance between one pair of radicals is important, virtually infinite lattice without the periodic boundary condition can be used.

Initially, a pair of particles are created at the same time on an unoccupied site in a lattice (forced geminate landing).

One particle will move immediately to a neighbor site with random direction. If all the neighbor sites are occupied, the creation process is repeated from the start. The initial creation of the radical pairs is assumed to be done by a photolysis with an instantaneous delta-function radiation. The simulation can be easily extended to the more general case involving a light pulse with finite duration by generating radical pairs continuously during that time. One can also consider the case where there exists a distribution for the initial separation of radical pairs. After all the particles (only one pair of radicals for the geminate case) are placed on the lattice, they start moving in random directions. If one radical moves within the reaction distance σ of the other, which is defined as a collision, a reaction may occur with the presumed reaction probability. If a reaction occurs, both particles are removed from the system. The microscopic reaction probability (W), which is the ratio of the number of reactive collisions to the number of total collisions in a system, is related to the equilibrium rate constant, k_f^0, used in the analytic theories. Unit reaction probability represents the case of infinite rate constant where every collision results in a reaction. In this paper, the excluded volume between nonreactive like-particles is not considered in order to mimic the diffusion theory. Therefore, the overlap between like-particles is allowed in the simulations. The excluded volume effect may be important in some conditions.[29]

The computational cost for the simulation with large number of particles for a very long time ($\sim 10^8$ steps), which is needed in the bulk recombination case, is very high. We have used several methods to reduce the computing time significantly. First all programs of the simulations were coded in the C language for parallel processing. MC simulations can be done by averaging the results of each independent ensemble which can be easily parallelized into each CPU. Therefore, MC simulations are very well suited for the parallel processing. One can obtain the gain in computation speed as many times as the number of CPUs. Our calculations were done on an IBM SP2 model MPP (massively parallel processing) computer with 40 nodes, and a speed gain of 30–40 times could be obtained. Second, using the lattice model can allow one to use only integer operations for the main MC steps of the program. Most computer architectures are more optimized for the integer calculation than the floating point calculation. One can increase the computational speed significantly (up to ~ 10 times) by avoiding the floating point calculations. The fact that all particles move the same distance in the lattice model leads to additional methods of improving the speed. We define the safe distance as the distance a particle can travel without colliding with nearest-neighbor particles. Within this distance, one can move the particle safely without checking reactive collisions which is the most time consuming part of the MC simulation. The safe distance should be updated with the particle moves by that distance. We may introduce the multiple jump method which utilizes such safe distances. If the minimum safe distance of all the particles is larger than the single step size, all particles can move safely within the minimum distance, or the step size can be increased up to the minimum safe distance. From Eq. (9) the speed gain is proportional to the square of the step size increase. The time savings by this method can be larger at low concentrations. However, convergence should be checked because the increase of step size may result in inexact results.

IV. RESULTS

We have performed Monte Carlo simulations for the geminate and the bulk recombination reactions which model the recombination of radical pairs in various solvents. The typical values for some of the parameters used are as follows: the diffusion constant, $D = 2.0\times 10^{-5}$ cm^2/s; the reaction distance $\sigma = 8.0\times 10^{-8}$ cm; the temperature, $T = 300$ K. When using the above values for the parameters, we obtained the velocity relaxation time of $\tau_R = 0.102$ ps. In order to determine an optimum (converged) time step for the simulations, we first consider the geminate recombination reaction with unit reaction probability. Such simulations must give the same results as the simple diffusion approach [Eq. (4)]. It is found that converged results are obtained for time steps <5 fs, which corresponds to the lattice displacements less than $\Lambda = 5\times 10^{-10}$ cm. The converged time step is

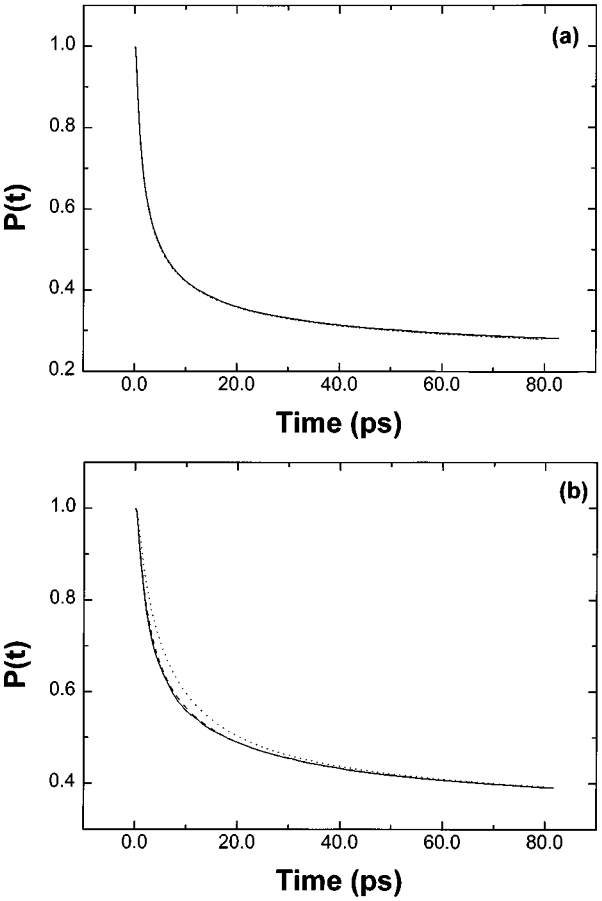

FIG. 1. The comparison of the survival probability, $p(t)$, obtained from the simple diffusion theory (dashed line), the kinetic theory (dotted line), and the MC simulation (solid line). The parameters used are (a) $\kappa = 1.25$ and unit reaction probability and (b) $\kappa = 1.25$ and $\lambda = 2.0$.

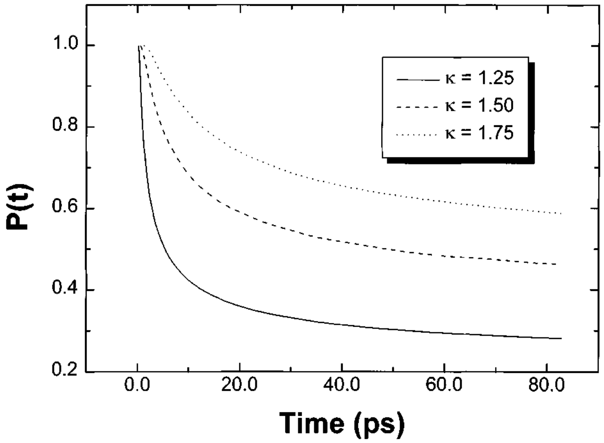

FIG. 2. $p(t)$ calculated from the MC simulations as a function of time for several values of κ with unit reaction probability.

smaller than the velocity relaxation time, which suggests that one step of real diffusion process corresponds to few jumps in the lattice used for MC simulations.

In Fig. 1(a) we plot the survival probability for the geminate recombination reaction with $\kappa=1.25$ and unit reaction probability ($W=1;\lambda\rightarrow\infty$). In this diffusion-controlled limit, the results of the MC simulations are in good agreement with those of the diffusion theory and the kinetic theory. For a finite λ, we determine the corresponding reaction probability by adjusting W until the asymptotic behavior of the survival probability from the simulation is equal to that of the diffusion theory. When the reaction probability is less than unity, the simulation results show deviations from the kinetic theory while they follow more closely with the results of the diffusion theory [Fig. 1(b)]. This is because the MC methods are based on the diffusion-type mechanism. The important difference between the kinetic theory and the diffusion approach is that in the former, the recollision events are incorporated in a systematic fashion. We have also studied the dependence of the survival probability on the initial separation (κ). As shown in Fig. 2, the general trends found are in excellent agreement with the results of Shin and Kapral.[3]

For the bulk recombination case, the simulations are extended to fairly long times (10^7–10^8 steps). We have used a rather large box size to minimize the finite size effect which can be further minimized by the periodic boundary condition. The finite size effect can be important for the bulk

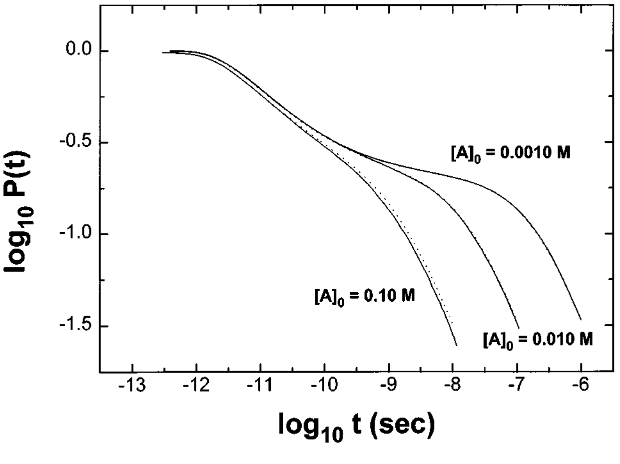

FIG. 3. Time dependence of the survival probability in a log–log plot for the diffusion approach (Ref. 5) (dotted line) and the MC simulation (solid line) with $\kappa=1.25$, with $\sigma=8.0$ Å, and unit reaction probability. The three initial concentrations of A are considered as indicated in the figure.

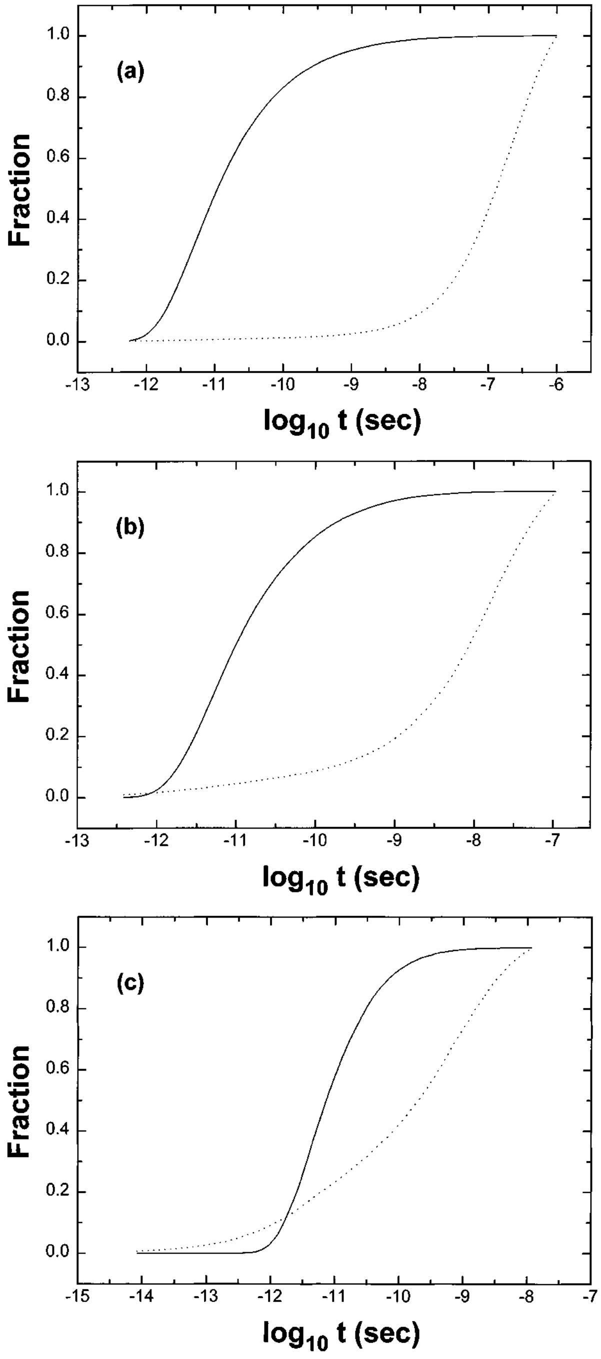

FIG. 4. Time dependence of the fraction of geminate (solid line) and bulk (dotted line) recombinations normalized by the asymptotic (long time) values for each case. The initial concentrations are (a) $[A]_0=0.0010$ M; (b) $[A]_0=0.010$ M; (c) $[A]_0=0.10$ M. The other parameters used are the same as in Fig. 3.

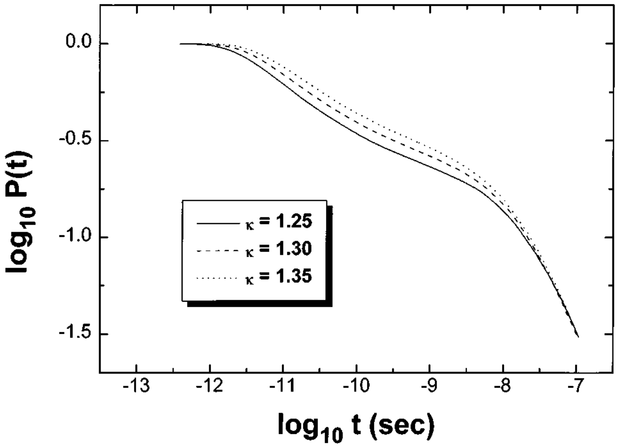

FIG. 5. $\log_{10}[p(t)]$ calculated from the MC simulations as a function of $\log_{10}[t]$ for several values of κ with $[A]_0=0.010$ M and $\sigma=8.0$ Å.

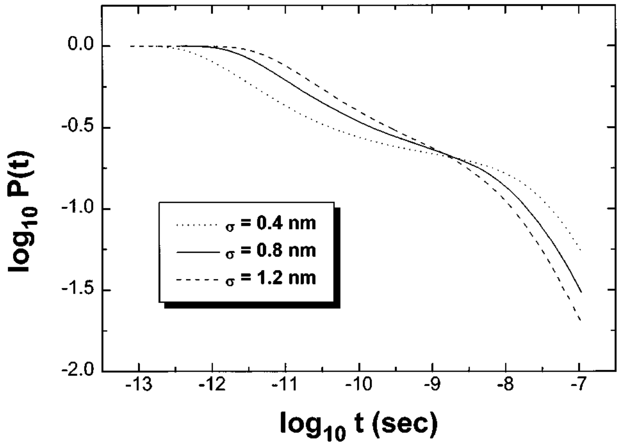

FIG. 7. $\log_{10}[p(t)]$ calculated from the MC simulations as a function of $\log_{10}[t]$ for several values of σ with $[A]_0=0.010$ M and $\kappa=1.25$.

recombination processes at long times, which involves large distance movements. The convergence should be checked carefully by increasing the system size. Using a larger system size with a larger number of particles to maintain the same concentration makes the simulations very expensive computationally. We have done such large simulations very efficiently by using both parallel computation and several algorithmic improvements as discussed in Sec. III.

Figure 3 shows the survival probabilities as a function of time for the MC simulations and the diffusion theory at three different initial concentrations of radicals. The results clearly indicate that there exist two regimes of the recombination process: the initial decrease of the survival probability due to the geminate recombination, and the second decrease after the plateau region due to the bulk recombination.[18] As indicated before, the theory by Jung and Lee[5] neglected the like-particle correlations, while our simulations have all those effects included. The difference between the two cases can be nonnegligible at high densities. As shown in Fig. 3, the results of the simulations show deviations from those of the theory at high concentrations, while they show good agreements for low concentrations. It is not clear whether the agreement between the theory and the simulations at low densities may result from a fortuitous cancellation of errors. Issues concerning the details of microscopic mechanism of recombination dynamics such as competition or like-particle correlation effects will be fully discussed elsewhere.[30]

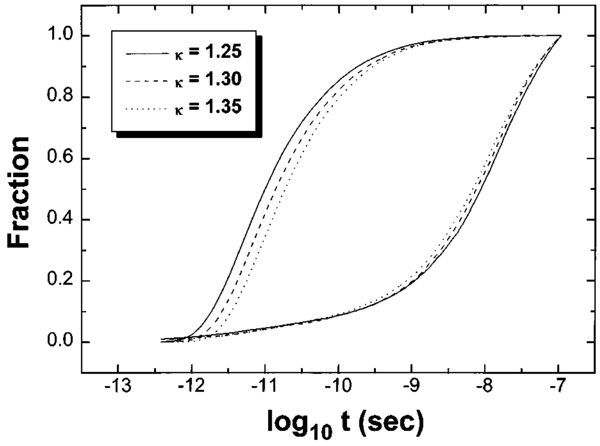

FIG. 6. Time dependence of the fraction of geminate and bulk recombinations for several values of κ. The parameters used and the line specifications are the same as in Fig. 5.

In the simulations one can monitor the time evolution of the two processes separately, which will illuminate detailed mechanism of the recombination dynamics. In Figs. 4(a)–4(c) we plot the time dependence of the fraction of the geminate and the bulk recombinations normalized by the asymptotic (long time) values for each case. In other words, the plot indicates the degree of completion for each phase of recombination processes. One can clearly see the different time scales in which the two processes are occurring. At low initial concentration, bulk recombination starts to occur a fairly long time after geminate recombination. The absolute number of bulk recombination should be very small in this case, because it happens when geminate recombination is almost complete [Fig. 4(a)]. As the concentration of particles is increased, bulk recombination appears at earlier times and the interplay between the germinate and the bulk recombination becomes more important. The survival probability and the fraction of recombination process clearly indicate that the change in concentration affects the bulk recombination more than the geminate one. For high enough initial concentration of radical pairs, it is possible to have the bulk recombination start to occur before the germinate one at early times [Fig. 4(c)].

We also examined the behavior of the system when we change the other parameters: κ (initial separation) and σ (reaction radius). When the initial separation of the radical pair is changed, geminate recombination is more affected (Figs. 5 and 6). The reduced density of the system, which represents the number of pairs within the reaction radius, depends not only on the concentration of particles but also on the reaction radius. When we vary the reaction radius, both the geminate and the bulk recombinations are affected (Figs. 7 and 8).

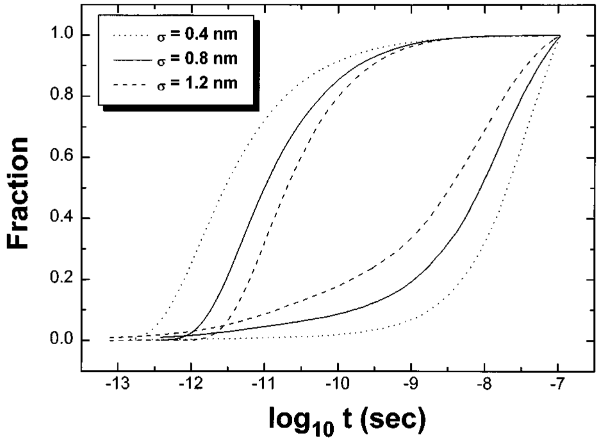

FIG. 8. Time dependence of the fraction of geminate and bulk recombinations for several values of σ. The parameters used and the line specifications are the same as in Fig. 7.

Since $\kappa=\sigma_d/\sigma$ is fixed in this case, large σ corresponds to the large initial separation and the behavior of the geminate recombination changes as explained above. For the large reaction radius, which is equivalent to the decrease in interpair separation, the probability of bulk recombination is increased.

V. CONCLUDING REMARKS

We have presented the results of the Monte Carlo simulations of radical recombination dynamics in solution. The simulation is based on random walks on a lattice after the initial creation of radical pairs by photolysis with the possibility of recombination upon a close approach. Both geminate and the bulk recombination processes are considered. The results of the simulations are shown to reproduce the theoretical predictions fairly well, even at short times when the diffusion equation is valid. For geminate recombination, the MC method mimics the diffusion theory more closely than the kinetic theory, because the molecular details of the solvents are ignored. The interplay of geminate and bulk recombinations is demonstrated by the simulations extended to long times. The results show good agreement with the theory of Jung and Lee[5] at low densities. The onset of bulk recombination is found to be dependent on the initial concentration of radical pairs. For high enough densities, the results of the simulations show deviations from those of the theory, which can be attributed to the like-particle correlations neglected in the theoretical assumptions. Further studies are needed to examine the microscopic details of recombination dynamics in the bulk recombination phase.

Some of the possible extensions of the present MC simulations are to include the effect of finite duration of the excitation pulse in photolysis and examine the role of a scavenger in the recombination process.[31] One may also introduce a distance-dependent rate constant for the recombination reaction to model such processes as electron transfer.[14,32]

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