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Monte Carlo simulation of diffusion and reaction in water radiolysis – a study of reactant 'jump through' and jump distances

Abstract In Monte Carlo simulations of water radiolysis, the diffusion of reactants can be approximated by "jumping" all species randomly, to represent the passage of a short period of time, and then checking their separations. If, at the end of a jump, two reactant species are within a distance equal to the reaction radius for the pair, they are allowed to react in the model. In principle, the possibility exists that two reactants could "jump through" one another and end up with a separation larger than the reaction radius with no reaction being scored. Ignoring this possibility would thus reduce the rate of reaction below that intended by such a model. By making the jump times and jump distances shorter, any error introduced by 'jump through' is made smaller. This paper reports numerical results of a systematic study of 'jump through' in Monte Carlo simulations of water radiolysis. With a nominal jump time of 3 ps, it is found that more than 40% of the reactions of the hydrated electron with itself and of the H atom with itself occur when reactions during 'jump through' are allowed. For all other reactions, for which the effect is smaller, the contributions of 'jump through' lie in the range l%–16% of the total. Corrections to computed rate constants for two reactions are evaluated for jump times between 0.1 and 30 ps. It is concluded that jump-through corrections are desirable in such models for jump times that exceed about 1 ps or even less. In a separate study, we find that giving all species of a given type the same size jump in a random direction yields results that are indistinguishable from those when the jump sizes are selected from a Gaussian distribution. In this comparison, the constant jump size is taken to be the root-mean-square jump size from the Gaussian distribution.

Introduction

Studies of charged-particle track structure yield important insights into the physical and chemical processes that occur in the radiolysis of water and aqueous chemical solutions. A number of investigators have modeled in various ways the initial formation of radicals along a track and their subsequent chemical behavior in both pure water and water containing solutes [1–8]. The chemical development can be simulated by a jump scheme, using Monte Carlo techniques, in which individual reactant species are allowed to diffuse by taking random steps and to react when they come into close proximity with another species. One can determine a statistical average from computations with a large number of tracks in order to compute time-dependent yields for radicals and molecular products for comparison with experiment. While agreement with measurement does not serve to validate such models, which are necessarily replete with detailed assumptions in place of actual data, such agreement is a requirement for any theory. The Monte Carlo track-structure models, which provide an event-by-event temporal accounting of the radiolysis of water, are extremely useful, to the extent that they can simulate actual events as they occur statistically in nature.

The present paper reports on an analysis of two aspects common to jump schemes in some Monte Carlo models for water radiolysis. The first aspect deals with the possibility that two reactants could 'jump through' one another dur-

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ing a diffusive step without interacting. The second compares the results of calculations that use a fixed step size for reactants or a step size selected from a continuous (e.g., Gaussian) distribution.

To represent the diffusion of species in the track of a charged particle during a small interval of time τ, all species are simultaneously given single, small, random jumps. After jumping, the separations of all potentially reacting pairs are checked. Two species then react if their separation falls within a distance equal to a reaction radius, which is specified for the pair in the model. By repeating the jump and reaction scheme over and over, the passage of time in steps of τ and the radiolysis of water are simulated. Diffusion is thus carried out as a random walk. In applying this procedure, the jump time τ is normally taken to be short, in order to avoid having two reactants 'jump through' one another without reacting, their separation after the jump being greater than their reaction radius. As a practical matter, shorter time intervals reduce the probability of missing jump-through reactions but increase the computer time required to simulate the passage of a given interval of time. In this study we investigate 'jump through' and assess its effect in the individual radiolysis reactions used by a number of authors in such Monte Carlo models. We also compare results when we let individual species of a given type all take jumps of (1) the same size or (2) different sizes, selected from a Gaussian distribution. While these comparisons have not been made exhaustively, we found no perceptible differences in our calculated results when the fixed size is equal to the root-mean-square value for the Gaussian distribution.

Reaction radii

For unlike reactant species, the reaction radius R is defined in terms of the diffusion-controlled rate constant k_d by the relationship [9–11]

$$k_d = 4\pi DR \qquad (1)$$

where D is the sum of the diffusion constants for the reacting species pair. If the species are identical, a factor of 2 instead of 4 appears in Eq. (1). In the model computations, an activation rate constant k_a for a colliding pair is given by [11]

$$k_a = \pi R^2 \frac{\bar{\lambda}}{\tau} \qquad (2)$$

where $\bar{\lambda}$ is the mean jump distance. For Gaussian jumps, the mean-square jump distance for time τ is

$$\overline{\lambda^2} = 6D\tau = \frac{3\pi \overline{\lambda^2}}{8} \qquad (3)$$

The observed rate constant k_{obs} then given by [12, 13]

$$k_{obs} = \frac{k_a k_d}{k_a + k_d} \qquad (4)$$

Combining Eqs. (1) – (4), one obtains

$$k_{obs} = 4\pi DR\left(\frac{3R\bar{\lambda}}{3R\bar{\lambda} + 2\overline{\lambda^2}}\right) = 4\pi Da \qquad (5)$$

which defines the reduced reaction radius, a. The measured rate constant is used to determine a, and the reaction radius is calculated from the second equality in Eq. (5):

$$R = \frac{1}{2}\left(a + \sqrt{a^2 + \frac{8\overline{\lambda^2}a}{3\bar{\lambda}}}\right) \qquad (6)$$

Jump scheme

The radiolysis model begins with a given distribution of the reactants H, OH, e_{aq}^- (hydrated electron), H_3O^+, and OH^- in water at time $t = 0$. The jump scheme is then started. The size of the jump for a given reactant can be chosen from a Gaussian distribution, having a width that depends on the diffusion constant of the reactive species. 'Jump through' without reaction occurs when the separations of a pair of species before and after a jump are both larger than the reaction radius R, but the pair would have passed within the distance R during the time τ.

At any given time step in the chemical development of a track, some species that react form nonreactive molecular products (e.g., H_2), which are removed from further consideration in the computations. Others that react are replaced by new reactive species, which continue in the subsequent chemistry. For the next time increment τ, all remaining species are jumped randomly as described above. The separations of pairs in the new positions are then checked, and additional reactions are scored. Repetition of this process simulates chemical development, during which time the species in the water generally become fewer in number while they continue to diffuse. Statistically, the time-dependent yields of all reactive species and products are obtained explicitly in a calculation, which is repeated randomly many times to obtain computed averages for comparison with experiment.

Table 1 shows the numerical values of D_0 that were used for individual reactive species in this paper [9]. The root-mean-square jump distances, $\sqrt{\overline{\lambda^2}}$, are shown for a jump

Table 1 Diffusion constants D_0 used in computations for individual species and root-mean-square jump distances $\sqrt{\overline{\lambda^2}}$ for 3-ps steps

Species	D (10^{-5} cm^2 s^{-1})	$\sqrt{\overline{\lambda^2}}$ (nm)
H	8.0	0.38
OH	2.5	0.21
e_{aq}^-	5.0	0.30
H_3O^+	9.5	0.41
OH^-	5.3	0.31
H_2O_2	1.4	0.16

time $\tau = 3$ ps, which was typically used for computations. The largest root-mean-square jump distance for a radical, which occurs with H, is then 0.38 nm, which is about 1.4 times the diameter of a water molecule.

Correction for 'jump through'

Figure 1 represents jumps taken by two reactants in time τ. Species 1, initially located at the point P_{01}, moves to P_1 while species 2 moves from P_{02} to P_2. In these positions, the separations between P_{01} and P_{02} and between P_1 and P_2 are both greater than the reaction radius for the pair. We assume that both species move uniformly in time along the straight lines between their initial and final locations. At any time t during τ, the separation of the two species is given by a function $r(t)$, as indicated in the figure. In previous work, the species reacted only if the separation of the final positions P_1 and P_2 after the jump was less than their reaction radius. By making τ small, resulting in small jumps, it was assumed that $r(t)$ would remain larger than the reaction radius if the separation of P_1 and P_2 were greater. We now correct for this assumption.

The current calculation is straightforward under the conditions just described. We express the square of the separation, $r^2(t)$, explicitly as a function of t and find the time t_{min} at which it has a minimum value. This minimum is then evaluated and compared with the reaction radius. If it is smaller, then the reaction is scored as having occurred. We designate the coordinates of the initial positions of the two species at P_{01} and P_{02} by writing ($t = 0$)

$$(x_{10}, y_{10}, z_{10}) \text{ and } (x_{20}, y_{20}, z_{20}) \qquad (7)$$

For the final positions of the two species at P_1 and P_2, we write ($t = \tau$)

$$(x_{10} + \xi_1, y_{01} + \eta_1, z_{01} + \zeta_1) \text{ and }$$

$$(x_{20} + \xi_2, y_{20} + \eta_2, z_{20} + \zeta_2) \qquad (8)$$

The quantities (ξ, η, ζ) are the displacements in the three coordinate directions after time τ. Assuming uniform rectilinear motion during the time $0 \le t \le \tau$, one has for the positions of the two species as functions of time

Fig. 1 Species 1 moves from point P_{01}, to point P_1 and species 2 moves from P_{02} to P_2 during a single jump time of duration τ. See text

In the computations, if t_{min} lies outside the time interval $0 \le t_{min} \le \tau$, then 'jump through' did not happen, and no reaction takes place. If the minimum occurs within τ, then $r(t_{min})$ is evaluated and compared with the reaction radius R for the species. If $r(t_{min}) \le R$, then a reaction is scored, thus providing the 'jump-through' correction. If $r(t_{min}) > R$, then no reaction takes place.

Numerical results for 'jump through'

Table 2 lists the primary reactions for water radiolysis that we have used, together with the rate constants k, reaction radii R, and sum D of diffusion constants from Table 1 [9, 12]. (Several other reactions having rate constants several orders of magnitude smaller than these were not included here.) Separate calculations were performed as follows for each of the ten sets of reactant pairs shown in Table 2. For unlike species, 100 reactants of each type were placed randomly in a water sphere of radius 10 nm at time $t = 0$. For a reaction involving identical species, such as $H + H$, a total of 200 reactants were present initially. Placements were chosen so that no pair of reactive species was initially separated by a distance less than their reaction radius. Calculations were then made by using $\tau = 3$ ps for 1500 jumps to a time of 4.5 ns. At each step, the number of reactions that occurred because of the jump-through correction was tabulated in addition to those that took place independently

$$\left(x_{10} + \frac{\xi_1 t}{\tau}, \ y_{10} + \frac{\eta_1 t}{\tau}, \ z_{10} + \frac{\zeta_1 t}{\tau}\right) \text{ and } \left(x_{20} + \frac{\xi_2 t}{\tau}, \ y_{20} + \frac{\eta_2 t}{\tau}, \ z_{20} + \frac{\zeta_2 t}{\tau}\right) \qquad (9)$$

The square of the separation as a function of time is then

$$r^2(t) = \left[x_{20} - x_{10} + (\xi_2 - \xi_1)\frac{t}{\tau}\right]^2 + \left[y_{20} - y_{10} + (\eta_2 - \eta_1)\frac{t}{\tau}\right]^2 + \left[z_{20} - z_{10} + (\zeta_2 - \zeta_1)\frac{t}{\tau}\right]^2 \qquad (10)$$

Setting the first derivative with respect to t equal to zero and solving for t gives the time at which the separation of the species has its minimum value. The result is

$$t_{min} = \left[\frac{(x_{10} - x_{20})(\xi_2 - \xi_1) + (y_{10} - y_{20})(\eta_2 - \eta_1) + (z_{10} - z_{20})(\zeta_2 - \zeta_1)}{(\xi_2 - \xi_1)^2 + (\eta_2 - \eta_1)^2 + (\zeta_2 - \zeta_1)^2}\right]\tau \qquad (11)$$
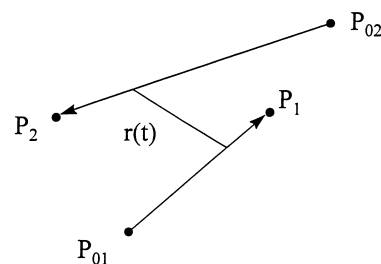
Table 2 Percent 'jump through' calculated for the ten principal water reactions with 100 initial pairs of species taking 3-ps jumps in sphere of radius 10 nm

Reaction	k (10^{10} M^{-1} s^{-1})	R (nm)	D (10^{-5} cm^2 s^{-1})	Jump through (%)
$H + OH \rightarrow H_2O$	2.0	0.43	10.5	9.1
$e_{aq}^- + OH \rightarrow OH^-$	3.0	0.72	7.5	2.1
$e_{aq}^- + H + H_2O \rightarrow H_2 + OH^-$	2.5	0.45	13.0	10.4
$e_{aq}^- + H_3O^+ \rightarrow H + H_2O$	2.2	0.39	14.5	15.8
$H + H \rightarrow H_2$	1.0	0.23	16.0	41.1
$OH + OH \rightarrow H_2O_2$	0.55	0.26	5.0	11.8
$2e_{aq}^- + 2H_2O \rightarrow H_2 + 2OH^-$	0.50	0.18	10.0	40.6
$H_3O^+ + OH^- \rightarrow 2H_2O$	14.3	1.58	14.8	0.79
$e_{aq}^- + H_2O_2 \rightarrow OH + OH^-$	1.2	0.40	6.4	6.2
$OH + OH^- \rightarrow H_2O + O^-$	1.2	0.36	7.8	10.1

of 'jump through'. A total of 50 000 such runs was made and the results averaged for each reaction. The fraction of reactions that are due to 'jump through' for a given reaction appears to be the same at all times, and so one arrives at a value that is characteristic of that reaction. The last column in Table 2 shows the percentages of the total number of reactions that occur because of 'jump through'.

The largest fractions of reactions due to 'jump through' (about 40%) occur for $H + H \rightarrow H_2$ and $2e_{aq}^- + 2H_2O \rightarrow H_2 + 2OH^-$. For the other reactions, the fractions range from 15.8% down to 0.79%. The importance of 'jump through' must depend on the size of the jumps compared with the reaction radius. This expectation is borne out by Fig. 2. The mean-square value for the relative displacement for two species is given by Eq. (3), in which $D = D_1 + D_2$ is the sum of the diffusion coefficients. In Fig. 2, the percentage of reactions due to 'jump through' from Table 2 is shown as the points plotted against the ratio of the square root of the sum of the diffusion constants and the reaction radius. A straight line is drawn over a portion of the figure for comparison. The dependence is seen to be approximately linear. (The reaction radius also depends on the diffusion constants.)

As already pointed out, the size of the jump-through correction for a given reacting pair will depend upon the jump time τ. To study the effect of the magnitude of τ, additional calculations were carried out with different values for two of the reactions in Table 2:

$$2e_{aq}^- + 2H_2O \rightarrow H_2 + 2OH^- \qquad (12)$$

and

$$e_{aq}^- + OH \rightarrow OH^- \qquad (13)$$

The correction in Table 2 is large for reaction (12) and small for (13). The results for the jump-through corrections as functions of the jump time τ are shown in Fig. 3. For reaction (12), the jump-through correction was found to be 68% when $\tau = 30$ ps. It decreases steadily with decreasing τ down to 4.5% for $\tau = 0.1$ ps. For reaction (13), the jump-through correction is only 12% for $\tau = 30$ ps and decreases to 0.1% for $\tau = 0.3$ ps. All of the computations for Fig. 3 were carried out to a time of 4.5 ns. Calculations for a single run with the smallest time, 0.1 ps, thus required 45 000 jump steps. The single point plotted in Fig. 3 at 0.1 ps is
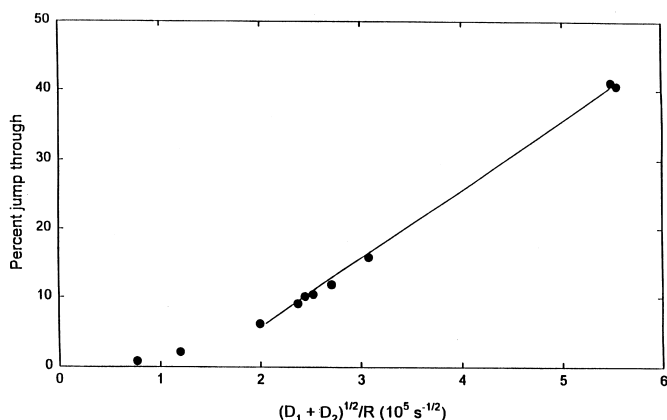

Fig. 2 Percent 'jump through' as a function of the ratio of the root-mean-square relative jump distance (proportional to the square root of the sum of the diffusion constants) and the reaction radius
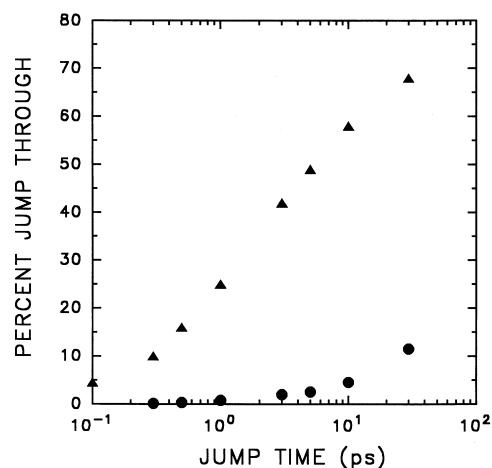

Fig. 3 Percent of reactions due to 'jump through' as a function of jump time for: ▲ reaction (12) in text and ● reaction (13)

the average of 3000 runs. From these results, we conclude that corrections for 'jump through' are needed for a number, if not most, of the reactions in Table 2 at jump times of about 0.5 ps or even less.

With other parameters fixed in the computations, we found that the jump-through correction appears to depend little, if at all, on the density of the reactants in the computations that were made. However, we did not investigate the general question of density dependence, which remains to be explored fully. During the 4500-ps time span of our calculated simulations, the density of reactants decreased by a factor of two for reaction (12) and six for reaction (13). While the density thus changed steadily, the fraction of reactions that occurred during 'jump through' stayed the same in time to within the statistical fluctuations in the computations.

Fixed vs Gaussian jumps

Monte Carlo water radiolysis calculations can consume a considerable amount of computer time, as the last discussion exemplified. Therefore, it is generally worthwhile to make them more efficient whenever possible. In a jump scheme, it takes less computer time to give every species of a given type a jump of one fixed size rather than to select a jump distance independently for each one from a Gaussian distribution.

To compare fixed and Gaussian jumps, the reaction $OH + e_{aq}^- \rightarrow OH^-$ was studied with 100 pairs of reactants initially distributed in a sphere of radius 10 nm. Calculations were performed to 4.5 ns with $\tau = 3$ ps. The second-order rate constant for the reaction was calculated by using the two jump schemes. First, jump distances were chosen from Gaussian distributions for both OH and e_{aq}^-. The root-mean-square jump distances are determined by the diffusion coefficients from Table 1. Second, fixed jump distances, equal to the root-mean-square values from the Gaussian distributions, were used for the two species. In this case, $\bar{\lambda}^2 = \lambda^2$, and the reaction radius R is 0.71 nm. The directions for all jumps were selected at random in three dimensions. The results for the two jump schemes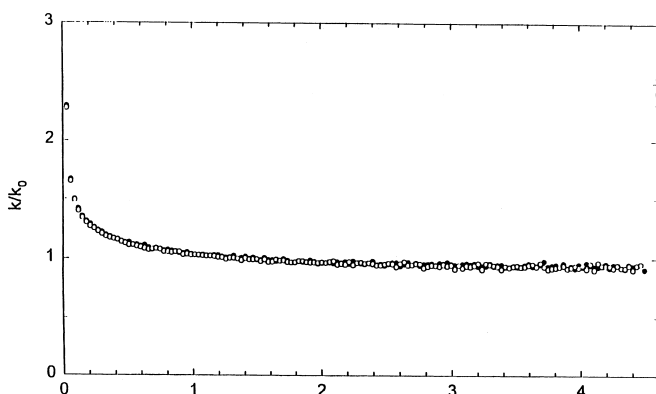, shown in Fig. 4, are virtually indistinguishable. The ordinate gives the ratio of (1) the value of the rate constant computed by the model and (2) its input value, $k_{obs} = 3.0 \times 10$ M^{-1} s^{-1}, as a function of time. Very good agreement is thus found with the input value, which is used to determine the reaction radius. Of particular interest in the present investigation is the virtual identity of the two curves. Our conclusion from this and other similar studies is that using either fixed or Gaussian jumps makes little or no difference in the Monte Carlo calculations of average quantities, such as chemical yields, in water radiolysis.

Discussion

We have shown that 'jump through' has a significant effect in Monte Carlo simulations of water radiolysis on a time scale of the order of $\tau = 1$ ps or even less. Correction for the effect is warranted. In the analysis carried out here, the simplest assumption of uniform rectilinear motion was made to represent the time-dependent positions of two reactant species during the time τ of a single jump in a Monte Carlo simulation (Fig. 1). No account was taken of the presence of other reactants in addition to the pair or of other possible trajectories. Use of other assumptions could affect the details of the computed jump-through results. In practice, when 'jump through' is compensated, some trade-off can be made by taking larger steps and thus reducing computer time.

Our purpose here has been to establish the existence and potential importance of 'jump through' in Monte Carlo simulations of water radiolysis. We are presently revising the computer code, RADLYS, which we employed previously, to include its effect in future track-structure studies. In principle, some calculated time-dependent yields can be expected to be altered in track simulation work. The specific conditions, radiation types, and extent of the presumed changes will be explored in a separate study.

Further work is needed to ascertain the degree to which the fraction of reactions due to 'jump through' is independent of the density and initial spatial distribution of reactant pairs. To the extent that a third body plays no role, the density would not appear to be critical. Within the regimes investigated in this paper, no effect of changing density on 'jump through' was found.

We have also seen in the studies reported here that jumps of fixed size for a given type of species give results that are indistinguishable from those obtained by the lengthier process of choosing random jump sizes from a Gaussian distribution. The fixed size is equal to the root-mean-square value of the Gaussian jump.

Fig. 4 Ratio of the calculated and input rate constants for the reaction $e_{aq}^- + OH \rightarrow OH^-$, computed by using Gaussian (●) and fixed (○) jump sizes and a 3-ps jump time. At early times, most of the Gaussian points are obscured behind the fixed-jump points

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References

1. Turner JE, Magee JL, Wright HA, Chatterjee A, Hamm RN, Ritchie RH (1983) Physical and chemical development of electron tracks in liquid water. Radiat Res 96:437–449
2. Zaider M, Brenner DJ (1984) On the stochastic treatment of fast chemical reactions. Radiat Res 100:245–256
3. Chatterjee A, Magee JL (1985) Theoretical investigation of the production of strand breaks in DNA by water radicals. Radiat Prot Dosim 13:137–140
4. Terrisol M, Beaudre A (1990) Simulation of space and time evolution of radiolytic species induced by electrons in water. Radiat Prot Dosim 31:171–175
5. LaVerne JA, Pimblott SM (1991) Scavenger and time dependences of radicals and molecular products in the electron radiolysis of water: examination of experiments and models. J Phys Chem 95:3196–3206
6. Turner JE, Bolch WE, Yoshida H, Jacobson KB, Wright HA, Hamm RN, Ritchie RH, Klots CE (1991) Radiation damage to a biomolecule: new physical model successively traces molecular events. Appl Radiat Isot 42:995–1001
7. Wilson WE, Paretzke HG (1994) A stochastic model of ion track structure. Radiat Prot Dosim 52:249–253
8. Bolch WE, Turner JE, Yoshida H, Jacobson KB, Wright HA, Hamm RN (1990) Monte Carlo calculations of free ammonia production in deoxygenated solutions of glycylglycine irradiated by X rays and ^{60}Co γ rays. Radiat Res 121:248–256
9. Wright HA, Magee JL, Hamm RN, Chatterjee A, Turner JE, Klots CE (1985) Calculations of physical and chemical reactions produced in irradiated water containing DNA. Radiat Prot Dosim 13:133–136
10. Noyes RM (1963) Effects of diffusion rates on chemical kinetics. Prog React Kinet 1:129–160
11. Klots CE, Hamm RN, Wright HA, Turner JE (1990) Non-homogeneous kinetics in irradiated matter: an appraisal of computational strategies. Radiat Prot Dosim 31:29–36
12. Boyd AW, Carver MB, Dixon RS (1980) Computed and experimental product concentrations in the radiolysis of water. Radiat Phys Chem 15:177–185
13. Mozumder A (1978) Partially diffusion-controlled reactions of isolated pairs in condensed media. J Chem Phys 69:1384–1391