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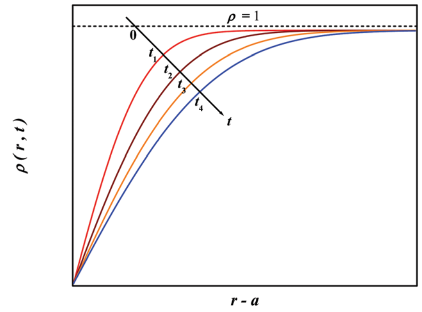

Scavenging and recombination kinetics in radiation chemistry Q1

Eyad H. Al-Samra and Nicholas J. B. Green Q2

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PAPER

Scavenging and recombination kinetics in radiation chemistry†

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This work describes stochastic models developed to study the competition between radical scavenging and recombination for simple model systems typical of radiation chemistry, where the reactive particles are tightly clustered and reactions are assumed fully diffusion limited. Three models are developed: a Monte Carlo random flights model with a periodic boundary condition for scavengers, Monte Carlo simulations in which the scavenging rate is calculated from the Smoluchowski theory for diffusion-limited reactions and a modification of the independent reaction times method where the scavengers close to the spur are explicitly included and the scavengers further away are treated as a continuum. The results indicate that the Smoluchowski theory makes a systematic overestimate of the scavenging rate when such competition is present. A correction for the Smoluchowski rate constant is suggested, an analytical justification is presented and it is tested against the simulations, and shown to be a substantial improvement.

1. Introduction

Radiation chemistry is the study of the chemical processes that take place following the passage of high-energy, ionising radiation. The study of the radiation chemistry of liquids and solutions is important because of the wide range of applications in medicine and industry.[1–3] The theoretical description of the kinetics of such processes poses a number of unusual challenges because the particles produced are highly reactive,[4] their reactions are diffusion controlled (or close to the diffusion limit),[4,5] and the particles are produced with highly non-homogeneous and clustered spatial distributions (radiation tracks).[6,7]

The diffusion-controlled model has been used for reactions in many areas, including radiation chemistry, biochemistry and polymerization.[8–10] A. Einstein proposed the theory of diffusion as Brownian motion early in the last century.[11] This was then developed and applied to chemical reactions by M. Smoluchowski who derived the formula for the time-dependent rate constant for a diffusion-controlled reaction in 1917.[10,12] This work is concerned with the application of this theory to a system in which particles are clustered, similar to the spurs encountered in radiation chemistry, and in particular with the competition kinetics of radical scavenging and recombination in such systems. This is because for some species, the competition between scavenging and recombination is the primary method to gain insight into their track kinetics.[4,13–15] However, the Smoluchowski theory is derived only for the ''theoretical'' case of effectively isolated particles (denoted throughout this work as R for radical) surrounded by a uniform sea of another reactant (denoted S for scavenger), and in radiation chemistry the radicals are produced close together, which introduces competition and correlation effects that are ignored by the Smoluchowski theory, and can be thought of as arising from the overlap of concentration gradients. In this work, a simple correction for this problem is proposed to include the competition and correlation effects appearing in a radiation-generated spur.

The independent reaction time (IRT) method (or the approximation of independent pairs) can be used to justify this correction, as discussed later. For this purpose, it is hypothesized throughout this work that the IRT theory includes a substantial part of the multi-radical correlation effect, by permitting the inclusion of correlations in the initial spatial distribution.[4,6] It is also shown in the current study how the IRT method can be modified, and used to efficiently model the competition between scavenging and recombination in a radiation spur.

This paper is an attempt to isolate only the correlation effects arising from the clustering of reactants. In a radiation track there are additional complications caused by the fact that some of the particles are charged, some of the reactions are not fully diffusion-controlled and possibly controlled by the spin

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dynamics of the radical clusters. None of these effects has been included in this study, although they have been addressed separately in previous studies.[16–19]

There is a brief description of the Smoluchowski theory in the next section. The computer simulation methods used in this work are described in Section 3. In Section 4, the results of the simulations are discussed. In Section 5 a correction to the Smoluchowski theory is proposed, justified and tested against the simulations. Section 6 discusses how the IRT method can be modified and used to simulate the competition between scavenging and recombination. Section 7 is the conclusion and summary section.

2. Smoluchowski theory

In this section, the Smoluchowski theory is outlined for completeness (more detail can be found in the literature).[10,12,20,21] Briefly, consider the reaction R + S in an inert continuum-like solvent, where the concentration of R is very low relative to the concentration of S. Under these conditions, a large distance (and many S molecules) separate two molecules of R and consequently the molecules of R behave independently of one another. Furthermore, C_0, the bulk concentration of S, does not change substantially as a result of the reaction R + S, and can be considered constant throughout the experiment. Denoting the reaction distance as a, a diffusion-controlled reaction happens instantly when the distance between R and S attains a for the first time. In Smoluchowski's formulation, the coordinate system is centred on a single typical R particle, which is treated as an indestructible sink, and the relative diffusion of S is described by a diffusion equation. The reaction reduces the local concentration of S, $C_S(r,t)$, around the central R particle relative to the concentration in the bulk, C_0. Of course, the R particles are not indestructible, they are removed by reaction, and the interpretation of the concentration profile around the centre is that it represents the concentration around surviving particles: R particles initially close to an S react quickly leaving only those where the S are further away. An alternative stochastic derivation, showing how the Smoluchowski theory arises from the independent pairs approximation has been known for a long time (this is discussed in more detail in Section 5).[22–25] Assuming spherical symmetry, the concentration of S will have the general time-dependent profile shown in Fig. 1 where the ratio ρ is defined as follows

$$\rho(r,t) = \frac{C_S(r,t)}{C_0}. \tag{1}$$

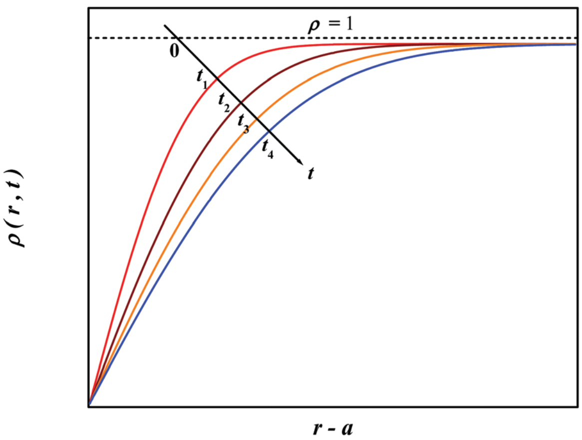

Fig. 1 The concentration profile. This is taken at few times $t_1 < t_2 < t_3 < t_4$ after the introduction of the radical R. At short times (t_1), the disturbance in the concentration due to the reaction is rather localized around the original location of the radical R that has reacted. The reaction is fully diffusion controlled so the concentration (or the ratio ρ) drops to zero for $r = a$.[10]

The diffusion equation for the ratio ρ is

$$\frac{\partial\rho}{\partial t} = D'\left(\frac{\partial^2\rho}{\partial r^2} + \frac{2}{r}\frac{\partial\rho}{\partial r}\right) \tag{2}$$

where D' is the relative diffusion coefficient of R and S. There is an implicit approximation at this stage: the assumption has been made that the diffusion of the S particles relative to R is independent, *i.e.* that S particles diffuse independently in the frame of reference of R. This assumption is only true if R is stationary, and this is equivalent to the independent pairs or superposition approximation, that the RS distances evolve independently. With the following boundary conditions

$$r = a \Rightarrow \rho = 0, \quad r \to \infty \Rightarrow \rho \to 1, \tag{3}$$

the solution of the diffusion equation is

$$\rho(r,t) = 1 - \frac{a}{r}\operatorname{erfc}\left(\frac{r-a}{\sqrt{4D't}}\right) \tag{4}$$

where erfc is the complementary error function. The current of S particles per surviving R particle, denoted $J(a)$, is then given as follows

$$J(a) = 4\pi D' C_0\left[r^2\frac{\partial\rho(r,t)}{\partial r}\right]_{r=a} = 4\pi a D'\left(1 + \frac{a}{\sqrt{\pi D't}}\right)C_0 \tag{5}$$

where C_0 is the bulk concentration of S. The rate of the reaction is then

$$-\frac{\mathrm{d}N}{\mathrm{d}t} = J(a)N = k(t)NC_0 \tag{6}$$

where N is the number of R particles and k is the Smoluchowski rate constant given as follows

$$k(t) = 4\pi a D'\left(1 + \frac{a}{\sqrt{\pi D't}}\right) = k_{D'}\left(1 + \frac{a}{\sqrt{\pi D't}}\right) \tag{7}$$

where $k_{D'}$ is the steady-state (or time-independent) rate constant. The question this work poses is whether the Smoluchowski rate constant, derived on the assumption that the radicals are isolated from one another and where there is no overlap between the concentration gradients of the scavenger molecules, is also applicable to situations in which the radicals are generated close to one another, and there is a competition between scavenging and recombination and a correlation between the R–S distances between different radicals and a given scavenger. Since one application of scavenger experiments is to use this competition to extract information about the recombination kinetics, this is potentially an important question. One of the aims of the current study is to test the Smoluchowski theory and answer the above question using computer simulations, which will be described in the next section.

It is of interest to note the contribution of Fedorenko and Kipriyanov at this point, who have looked at the related problem where a particle that moves by infinite jumps with an exponential waiting time between jumps reacts with a diffusing scavenger.[26,27] This model admits an exact solution of the many body kinetics, but is not easily generalised to the case where both species are diffusing. Another related exact solution is the famous asymptotic solution of Donsker and Varadhan on the reaction of a single diffusing particle in a sea of stationary scavengers.[28] This solution is only applicable in the very long time limit, and it is found by computer simulation that the Smoluchowski theory is perfectly acceptable for the vast majority of the reaction.[29]

3. Details of the simulations

The computer program used here consists of two parts: one runs Monte Carlo random flight (RF) simulations for the purpose of comparison (denoted RF) and second hybrid method runs calculations in which the radical trajectories are modeled by the RF method but scavenging is based on the Smoluchowski theory, described above. It should be noted that an alternative simulation method, with scavenging based on the IRT approximation, is developed and discussed separately in Section 6. The program uses three basic reaction schemes. In scheme one (denoted S1) the two reactions R + R and R + S are allowed, so that the effects of proximity and competition are both present. In scheme two (denoted S2) only the reaction R + S takes place, so that the effects of proximity can be separated from the effects of competition. The third scheme (S3) has two types of radicals and will be discussed later.

3.1. Full RF simulations

The full RF simulations generate the diffusive trajectories of all the reactive particles involved using discrete time-step jumps (or flights) of normally distributed random numbers, this is equivalent to exact sampling of the trajectory implied by the use of a diffusion equation. The RF model (with Bessel bridge interpolation to determine whether encounter has taken place)[30] has been described in detail elsewhere,[4,8,31–33] and only certain aspects of it will be described here. This simulation method is used here as a measure of "reality" because it corresponds to an exact sampling of the many-body diffusion equation which is the basic model of the diffusion kinetics. With a sufficiently small timestep, sufficient independent realisations and the proper bridging processes to describe boundaries, these simulations reproduce exactly soluble diffusion problems to any desired accuracy. It is well-known from the literature that both the RF and IRT approaches generate reliable results under realistic conditions. The methods have been tested against known analytic solutions, and also experimental data. It is therefore not unreasonable to use these methods as a benchmark to test approximations and gain insight, as it is possible to control and isolate parameters in a way that is not possible in experiment.[4,6,8,34–37]

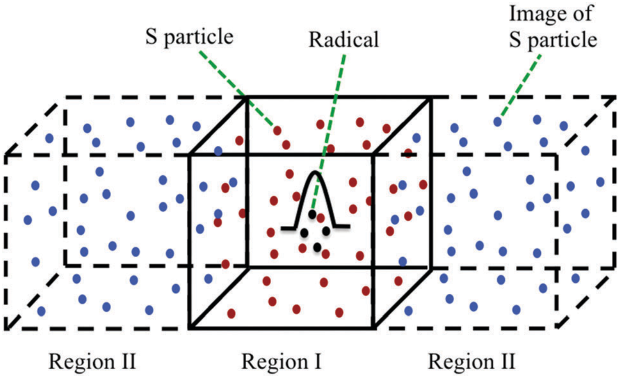

Fig. 2 The simulation box and two of its images. Region I (the central box) contains the radicals (here their coordinates are generated from a Gaussian distribution) and scavenger particles. Region II contains the images of the scavenger particles. It should be noted that the central box has images in all directions and only two of them are shown above.

As symbolically shown in Fig. 2, the radicals are introduced inside a cubic box. Their coordinates are generated randomly from a Gaussian distribution centred at the centre of the box (for some runs a different distribution was used and this will be discussed later). The cubic box divides space into two regions. Region (I) contains a certain number of scavengers uniformly distributed in this region (their coordinates are randomly generated from a uniform distribution). The scavengers in region (I) are repeated using a periodic boundary condition so that each scavenger in region (I) has images periodically repeated outside it; the region containing the images is region (II). The scavengers inside region (I) diffuse freely, and their images move similarly in region (II). If a scavenger in region (I) reaches the edge of the box and moves outside it, it is removed and reintroduced from the opposite side of the box. This ensures that the number of scavengers inside the box does not change as a result of the Brownian motion. The diffusive trajectories of the radicals are generated. At each time step δt, all scavengers and radicals are moved by a normally distributed displacement in each coordinate with a standard deviation $\sqrt{(2D\delta t)}$, where D is the diffusion coefficient. If the distance between a radical and a scavenger (or an image of a scavenger) becomes equal to the corresponding reaction distance, then a scavenging reaction is counted. Thus, the presence of the scavengers' images ensures that the radicals may continue to get scavenged if they diffuse outside the box but limits the number of scavengers that must be explicitly diffused. For the S1 scheme then, as the radicals diffuse, whenever an encounter takes place between two radicals a radical–radical reaction is counted. Because of the way the simulations are constructed, (especially for high number of radicals) each scavenging event eliminates the corresponding scavenger particle and all its images, this reduces the probability of scavenging outside the box.

To reduce this effect, whenever a scavenging event occurs, a new scavenger particle is introduced in a random location in the box with its images outside. This effect is unimportant when considering the S1 scheme as fewer scavenging events occur due to the competition with the radical recombination, but does have an effect for the S2 scheme. Note that the simulations with and without this replacement give upper and lower bounds on the true scavenging kinetics, and there is no material difference between them at the statistical levels used in this work.

3.2. Hybrid simulations

The hybrid simulations are simple. Eqn (7) is used to generate a scavenging time for each radical in the box using the inversion method for generating non-uniform random numbers (the details of this are given in the ESI†).[38] When the S1 scheme is considered, the hybrid simulations use the same initial coordinates and trajectories for the radicals as in the full RF simulations to account for the radical–radical reactions, but scavenging takes place whenever the simulation reaches the scavenging time generated for a radical, and the radical has not yet reacted with another one. Note that because scavenging occurs at different times in the two simulations, the trajectories of radicals in the full simulation must be followed even after they have been scavenged, although, of course they are flagged as having reacted and are not permitted to react a second time. In this case, using the same trajectories and initial coordinates for the radicals in both parts of the simulation program ensures a better comparison between the averaged scavenging kinetics calculated based on eqn (7) and those times obtained from the Monte Carlo simulations in the RF model.

Finally, it should be noted that all particles are considered electrically neutral and similar in all aspects in the simulations (reaction distances and diffusion coefficients *etc.*). The typical number of realizations performed is 10^5 or more (up to 10^6).

4. Results

The starting point is to test the above simulation method and check that it gives the expected results. This is done through introducing one radical into the simulation box (Fig. 2) corresponding to eqn (7) as there is no competition with other radicals, although the approximation of independent relative diffusion, implicit in eqn (7), is lifted in the simulations. The length of the edge of the cubic box was 10 nm (this is consistent throughout all the results presented in this study). The coordinates of the radical were sampled from a Gaussian distribution centred at the center of the box with a standard deviation of 1 nm. The box contained 60 scavenger molecules, *i.e.* $C_0 = 0.06$ scavenger per nm^3 in eqn (5) and (6) (corresponding to about 0.1 mol dm^{-3}). The reaction distance for the scavenging reaction R + S (and also for the recombination reaction R + R in the results presented later) was 0.5 nm. The two simulation methods (full RF and hybrid with Smoluchowski scavenging) are compared in Fig. 3: the results of both simulations are identical within statistical variation.

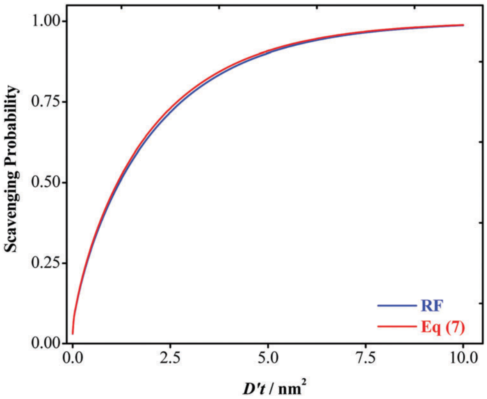

Fig. 3 The simulations for 1 radical. Both simulations (the RF model and the hybrid simulations where eqn (7) is used) are in good agreement (the values at 5 nm^2 are 0.902 (±0.002) for RF and 0.908 (±0.002)) for the hybrid simulations. t is the time and D' is the relative diffusion coefficient.

As more radicals are introduced into the simulation box, the agreement between the two types of simulation breaks down. Simulations have been run for initial numbers of radicals N_0 = 2–12, and an example (N_0 = 6) is shown in Fig. 4 (the scavenging probability) and in Fig. 5 (the recombination probability). Also to indicate the importance of the time-dependent part of the rate constant, results in which only the steady state rate constant $k_{D'}$ (eqn (7)) is used in the hybrid model, are also shown in Fig. 4 and 5. Another example is included in the ESI.† The hybrid method clearly overestimates the scavenging rate and in consequence also the probability of scavenging, but complete neglect of the time dependent part of the rate constant leads to an underestimate of the scavenging. Three possible reasons for this overestimate are (i) a proximity effect resulting in correlations between the radical-scavenger distances, (ii) a reactive depletion effect, in which each scavenger removed by reaction reduces the available scavengers for the remaining radicals and (iii) a competition effect between the two reactions. The third effect can be removed by switching off the radical recombination reaction in the simulation: any remaining

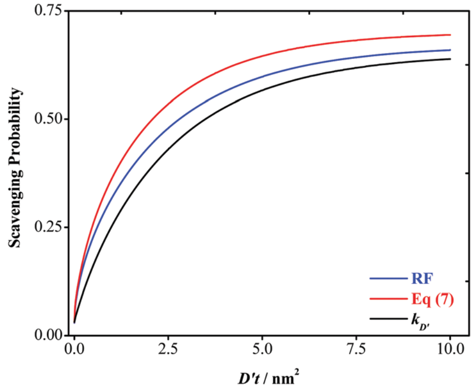

Fig. 4 The scavenging probability in the case of N_0 = 6 (S1 scheme). The values at 5 nm^2 are 0.598 (±0.002) for RF simulations, 0.645 (±0.002) for hybrid simulations where eqn (7) is used and 0.566 (±0.002) for the for hybrid simulations where the steady state rate constant $k_{D'}$ is used.

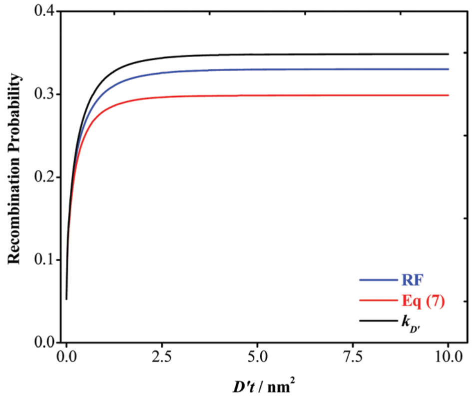

Fig. 5 The recombination probability in the case of N_0 = 6 (S1 scheme). The values at 5 nm^2 are 0.330 (±0.002) for RF simulations, 0.299 (±0.002) for hybrid simulations where eqn (7) is used and 0.348 (±0.002) for the for hybrid simulations where the steady state rate constant $k_{D'}$ is used.

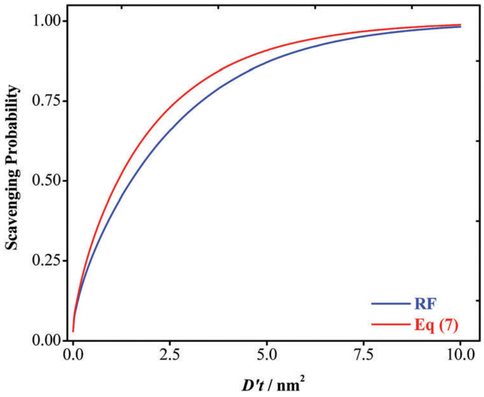

Fig. 6 The scavenging probability in the case of N_0 = 6 (S2 scheme). The values at 5 nm^2 are 0.871 (±0.002) for RF simulations and 0.908 (±0.002) for hybrid simulations where eqn (7) is used.

difference with the hybrid method must be a result of the correlations. The S2 scheme was introduced exactly for this reason, and the simulated scavenging probability in this case is shown in Fig. 6. The hybrid simulations are able to predict well the approach of the scavenging probability to unity at long times, but it is clear that the time dependence is not in agreement with the RF simulations, and that again the scavenging rate constant is overestimated by eqn (7). The apparent improved agreement at long times is simply because in a scavenging only scheme the ultimate scavenging probability is always one. It is interesting to see if a correction for this problem can be found and this will be discussed in the next section.

5. Correction

5.1. Multi-radical correlation effect

In the Smoluchowski theory each radical is surrounded by its own concentration gradient of scavengers (this because the radicals are assumed to be very far from one another) and the scavenging rate is then calculated from the rate of diffusion down this concentration gradient. In a spur the problem is that the concentration gradients overlap and so the scavenger concentration around a radical is reduced, not only by the scavenging reaction of that radical but also by the reduction of the scavenger concentration caused by the presence of the other radicals. This also may result in the breakdown of the assumption of spherical symmetry. The problems associated with the picture of concentration gradients are known,[10,39] and attempts have been made to address this in radiation chemistry before.[8,40] The obvious question is whether a simple correction can be introduced to take into account this multi-radical correlation effect.

Assuming, as an approximation, that spherical symmetry continues to hold in the case when there are more than one radical, then the multi-radical correlation effect described above can be explained in other words as follows: choosing, as an example, the concentration profile taken at time t_2 in Fig. 1, then at each point the value of the ratio ρ will be smaller than the value shown in Fig. 1 (this is because the presence of other radicals will reduce the scavenger concentration in the vicinity of the central particle, as described above). Hence, the concentration profile at t_2 should be modified as shown schematically in Fig. 7. The suggestion is that this can be done by introducing a simple correction into eqn (4). Previous work on two radicals[8] implies that the transient part of the rate constant can be reduced by a factor dependent on the number of particles in the spur, this can be achieved by scaling the argument of the complementary error function in eqn (4), suggesting a generic correction of the form

$$\rho(r,t) = 1 - \frac{a}{r}\operatorname{erfc}\left(\frac{r-a}{f(N_0)\sqrt{4D't}}\right) \tag{8}$$

where N_0 is the number of radicals at zero time. The function f is the correction and it depends on N_0 because the greater the number of overlapping concentration gradients, the more each will be reduced by the others. The observed discrepancy in the

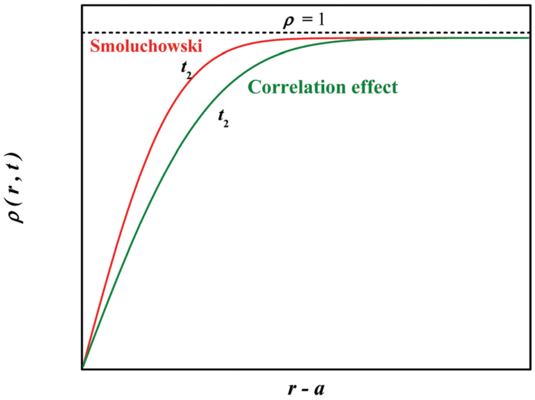

Fig. 7 A schematic concentration profile illustrating the multi-radical correlation effect. The red curve is taken from Fig. 1 at time t_2 based on Smoluchowski theory. The green curve is how the profile should be if the multi-radical correlation effect is considered, where the ratio ρ is supposed to rise to unity slower than expected based on Smoluchowski theory.

simulations is observed to increase with N_0. As N_0 increases, the value of the function f increases, the value of the complementary error function approaches closer to the steady-state limit and the value of ρ decreases. Now if eqn (8) is used instead of eqn (4) to calculate the reaction rate (eqn (5) and (6)), the following corrected rate constant is found

$$k(t) = 4\pi a D'\left(1 + \frac{a}{f(N_0)\sqrt{\pi D' t}}\right) \tag{9}$$

As discussed in the next part, the correction f is approximately given as follows

$$f(N_0) = 1 + \beta(N_0 - 1) \quad \beta \approx 0.5 \tag{10}$$

And so $f(N_0 = 1) = 1$ as required. The use of eqn (9) and (10) in the hybrid simulations gives the results shown in Fig. 8–10 for the case of $N_0 = 6$ (other examples are available as ESI†). It is clear from these results that the above correction seems to be a significant improvement, although it is not exact.

5.2. Justification

It is shown in this part how eqn (9) and (10) can be justified based on the approximation of independent pairs. This method of obtaining the reaction rate coefficient has been described in detail elsewhere before.[8,22–24,42] The justification of eqn (9) and (10) is in two steps. The first step considers the special case of one radical (the Smoluchowski case), and the second step develops the general case of N_0 radicals.

5.2.1. Smoluchowski rate constant. Consider the case of one radical R located at the centre of a large sphere of radius Q, and one scavenger S where the R–S distance is r ($r < Q$). The survival probability of the pair Ω_{pair} is well known, and given as follows[4,17]

$$\begin{aligned}\Omega_{\text{pair}} &= \Omega_{\text{pair}}(t, r; a) = 1 - W(t, r; a) \\ &= 1 - \frac{a}{r}\operatorname{erfc}\left(\frac{r-a}{\sqrt{4D't}}\right)\end{aligned} \tag{11}$$

where W is the reaction probability of the pair, a is the encounter distance of the two particles, D' is their relative diffusion coefficient, erfc is the complementary error function and where the reaction is assumed to be fully diffusion-controlled. Assuming that the single scavenger molecule S has a probability density that is spread uniformly inside that sphere of radius Q, the survival probability $\Omega_{\text{pair,u}}$

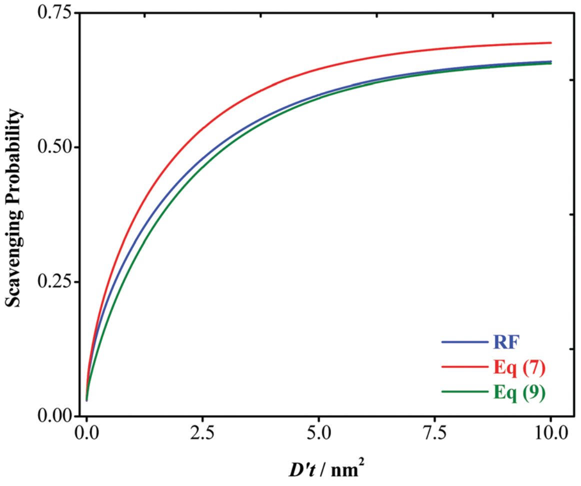

Fig. 8 The effects of the correction on the scavenging probability in the S1 scheme (scavenging and recombination). The number of radicals $N_0 = 6$. The RF refers to RF simulations. Eqn (7) refers to the hybrid simulations where eqn (7) is used. Eqn (9) refers to the hybrid simulations where eqn (9) is used.

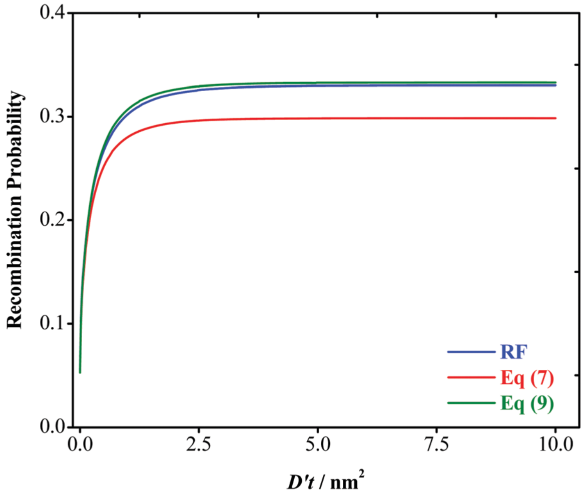

Fig. 9 The effects of the correction on the recombination probability in the S1 scheme (scavenging and recombination). The number of radicals $N_0 = 6$. The RF refers to RF simulations. Eqn (7) refers to the hybrid simulations where eqn (7) is used. Eqn (9) refers to the hybrid simulations where eqn (9) is used.

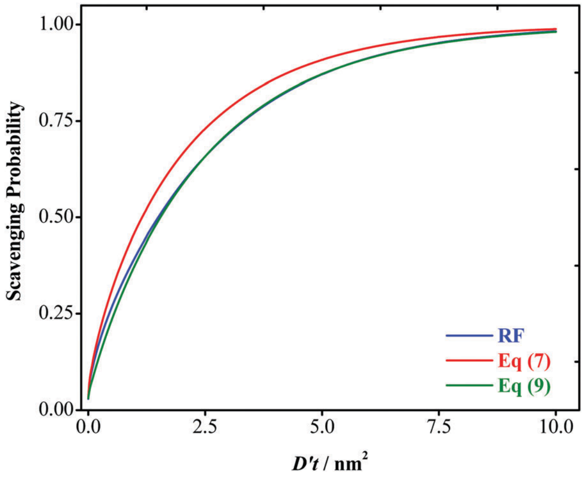

Fig. 10 The effects of the correction on the scavenging probability in the S2 scheme (scavenging only). The number of radicals $N_0 = 6$. The RF refers to RF simulations. Eqn (7) refers to the hybrid simulations where eqn (7) is used. Eqn (9) refers to the hybrid simulations where eqn (9) is used.

becomes[8,41–44]

$$\Omega_{\text{pair,u}} = \frac{4\pi}{V}\int_a^Q \Omega_{\text{pair}} r^2 \mathrm{d}r = \frac{4\pi}{V}\int_a^Q \left[1-\frac{a}{r}\operatorname{erfc}\left(\frac{r-a}{\sqrt{4D't}}\right)\right] r^2 \mathrm{d}r \tag{12}$$

where V is the volume of the sphere of radius Q. It is straightforward to perform the integral in the last equation, using the Laplace transform method for example, and so

$$\Omega_{\text{pair,u}} = \frac{4\pi}{3V}\left(Q^3 - a^3 - 6a^2\sqrt{\frac{D't}{\pi}} - 3aD't\right) \tag{13}$$

The last equation applies to one radical and a single scavenger in the sphere of radius Q. However, the number of scavengers in the sphere of radius Q is an integer-valued random variable M which follows a Poisson distribution to a good approximation as follows

$$\Pr\{M = m\} = \frac{(C_0 V)^m}{m!}\exp(-C_0 V) \tag{14}$$

where C_0 is the concentration of S. Applying the approximation of independent pairs and using the last two equations, Ω, the probability that the radical has survived the scavenging reaction by time t, is written as follows

$$\begin{aligned}\Omega &= \sum_m \frac{(C_0 V)^m}{m!}\exp(-C_0 V)\Omega^m_{\text{pair,u}} \\ &= \exp\left(-\frac{4}{3}\pi a^3 C_0\right)\cdot\exp\left(-4\pi a D' C_0\left(t + 2a\sqrt{\frac{t}{\pi D'}}\right)\right)\end{aligned} \tag{15}$$

where the limit $Q \to \infty$ is considered. The first exponential term in the last equation represents the probability of surviving "zero-time" reaction, *i.e.* the probability that the radical does not overlap a scavenger in the initial configuration. The second exponential term is the decay kinetics of the survival probability of the radical. Using the last equation in the following, well-known relationship between the time-dependent rate constant k and the survival probability Ω

$$k(t) = -\frac{1}{N_0 C_0}\frac{\mathrm{d}(\ln \Omega)}{\mathrm{d}t} \tag{16}$$

where N_0 is the number of radicals considered (in this case $N_0 = 1$), gives eqn (7). The same method described above was applied to the case of two radicals.[8] The rate constant in this case was found to be[8]

$$k(t) = 4\pi a D'\left(1 + \frac{a}{\sqrt{2\pi D't}}\right) \tag{17}$$

The generalization of these results is considered next.

5.2.2. General case. Consider a system of N_0 radicals in a sphere of radius Q and one scavenger molecule S uniformly distributed inside that sphere. To simplify the problem, assume that all the initial R–S distances are equal (denoted r), and also that the only possible reaction in the system is the scavenging reaction R + S. The probability that the radicals have survived to time t is given as follows[42]

$$\Omega_{N_0} = \frac{4\pi}{V}\int_a^Q \Omega^{N_0}_{\text{pair}} r^2 \mathrm{d}r = \frac{\eta}{V} \quad \eta = 4\pi\int_a^Q \Omega^{N_0}_{\text{pair}} r^2 \mathrm{d}r \tag{18}$$

where Ω_{pair} is given in eqn (11). Consider m scavenger molecules inside the sphere of radius Q; repeating the Poisson weighting (eqn (14)), the total survival probability, the probability that all the radicals have survived all the scavengers, is then

$$\Omega = \sum_m \frac{(C_0 V)^m}{m!}\exp(-C_0 V)\left(\frac{\eta}{V}\right)^m \tag{19}$$

and, taking the limit $Q \to \infty$, if the last equation is used in eqn (16), the time-dependent rate coefficient is found to be

$$k(t) = 4\pi a D'\left\{1 + \frac{a}{\sqrt{\pi D't}}[1 - 2I(N_0)]\right\} \tag{20}$$

where

$$\begin{aligned} I(N_0) \;&=\; \sum_{n=1}^{N_0-1}\left\{\frac{(N_0-1)!}{(N_0-n-1)!n!}\right. \\ &\quad \left.\times\left[\int_0^\infty x\left(\frac{-\alpha}{\alpha+x}\right)^{n-1}(\operatorname{erfc}(x))^n \exp\left(-x^2\right)\mathrm{d}x\right]\right\}, \end{aligned} \tag{21}$$

and

$$\alpha = \frac{a}{\sqrt{4D't}} \tag{22}$$

Eqn (20) explicitly points out, if compared with the Smoluchowski rate coefficient (eqn (7)), that the time-dependent term (or the transient part) of the rate coefficient is always a function of N_0, the number of radicals at the start of the reaction, and that the steady-state rate constant is unaffected. It is worth noticing that the above equation includes the two cases where the solution is already known ($N_0 = 1$ in eqn (7) and $N_0 = 2$ in eqn (17)), discussed above. Eqn (21) vanishes for $N_0 = 1$, and for $N_0 = 2$ it results in the following known integral[45]

$$I(2) = \int_0^\infty x \operatorname{erfc}(x)\exp\left(-x^2\right)\mathrm{d}x = \frac{1}{2}\left(1 - \frac{1}{\sqrt{2}}\right) \tag{23}$$

which, if used in eqn (20), gives eqn (17). Unfortunately, the integrals in eqn (21) do not seem to be known in general when $N_0 \geq 3$.[45–47] Therefore, it is only possible to investigate eqn (20) and (21) numerically when $N_0 \geq 3$. Before the numerical calculations are considered, the asymptotics of the rate constant will be discussed.

It is normal to concentrate on the long-time asymptotics, corresponding to the approach to the steady state. This corresponds to the small α asymptotics of the integral I. In this limit the solution can be found analytically for the rate coefficient and is

$$k(t) = 4\pi a D'\left\{1 + \frac{a}{\sqrt{\pi D't}}\left[1 - (N_0 - 1)\left(1 - \frac{1}{\sqrt{2}}\right)\right]\right\} \tag{24}$$

These asymptotics are compared with the rate constant calculated from a numerical integration of eqn (21) to evaluate I for a

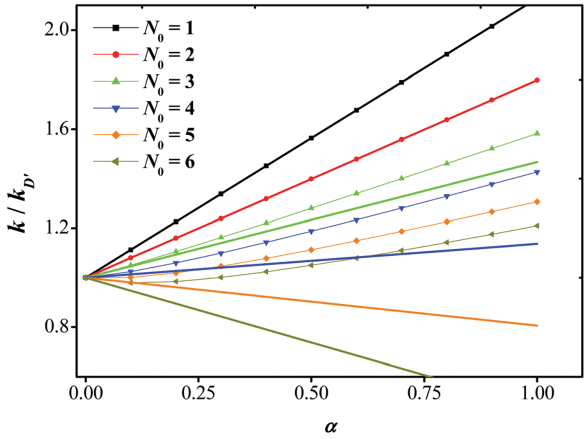

Fig. 11 The ratio of the time-dependent rate coefficient calculated from eqn (20) to the steady state rate constant, compared with the long-time asymptotics. For each number of radicals (certain colour), line and symbol refers to numerical integral, and line only refers to asymptotic behaviour (eqn (24)).

number of different values of N_0 (Fig. 11). It will be noted that the case $N_0 = 1$ and 2 are in perfect agreement, but thereafter the asymptotic behaviour represents a rapidly decreasing part of the time-dependence, going catastrophically wrong by the time $N_0 = 6$. Clearly, relying on the long-time asymptotics is not reliable.

It seems from Fig. 11 that the rate constant should increase linearly with α, and this is borne out by an asymptotic analysis of the integral I

$$\lim_{\alpha\uparrow\infty}\frac{k(t)}{\alpha} = 4\pi a D'\frac{4}{\sqrt{\pi}}\int_0^\infty x\,\exp\left(-x^2\right)[\mathrm{erf}(x)]^{N_0-1}\mathrm{d}x \qquad (25)$$

This integral is known for the cases $N_0 = 1$ to 4, which are tabulated below[45,47]

$$N_0 = 1:\ \frac{4}{\sqrt{\pi}}\int_0^\infty x\exp\left(-x^2\right)\mathrm{d}x = \frac{2}{\sqrt{\pi}}$$

$$N_0 = 2:\ \frac{4}{\sqrt{\pi}}\int_0^\infty x\exp\left(-x^2\right)\mathrm{erf}(x)\mathrm{d}x = \frac{2}{\sqrt{2\pi}}$$

$$N_0 = 3:\ \frac{4}{\sqrt{\pi}}\int_0^\infty x\exp\left(-x^2\right)[\mathrm{erf}(x)]^2\mathrm{d}x = \frac{4}{\sqrt{2\pi}}\frac{2}{\pi}\tan^{-1}\left(\frac{1}{\sqrt{2}}\right)$$

$$N_0 = 4:\ \frac{4}{\sqrt{\pi}}\int_0^\infty x\exp\left(-x^2\right)[\mathrm{erf}(x)]^3\mathrm{d}x = \frac{6}{\sqrt{2\pi}}\frac{2}{\pi}\tan^{-1}\left(\frac{1}{2\sqrt{2}}\right),$$

resulting in values of the time-dependent part of the rate constant in good agreement with eqn (9) and (10). Beyond $N_0 = 4$, it is easy to calculate the integral numerically as the integrand approaches zero rapidly.

To finish the current part of the study, it should be noted that the main region of interest is where the time-dependent term of the rate constant is large relative to the steady-state part (or the time-independent part). From eqn (7) and (9), this region corresponds to the asymptotics of small times and therefore large α of eqn (22). In this limit, it is straightforward to show analytically that the integral $I(N_0)$ is independent of α.[30]

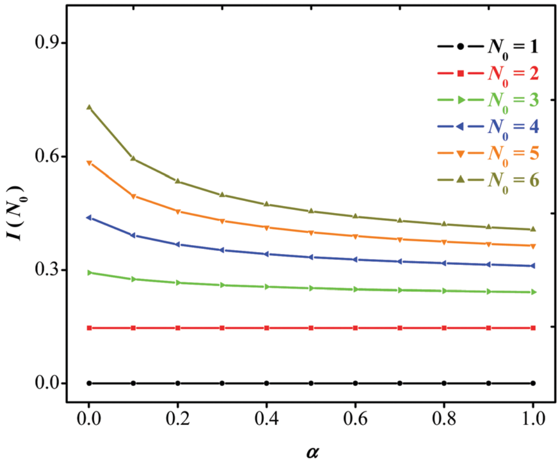

Fig. 12 The integral $I(N_0)$ as a function of α for different values of N_0.

The full dependence is shown in Fig. 12, the integral $I(N_0)$ as a function of α for different values of N_0. As discussed above, when $N_0 = 1$ and $N_0 = 2$, the integral is independent of α, demonstrated by straight lines with a zero slope. For higher values of N_0, the integral depends on α, but only when α is small where as α increases, the tangents to the curves tend to zero. Therefore, when considering the asymptotics of large α (small times), it is possible to assume that the integral is independent of α. Eqn (21) was numerically calculated using Matlab, where $N_0 = 3$–12, and the results were fit to the following function, proposed in the last section as a simple correction,

$$\psi(N_0) = C_1 + \frac{C_2}{N_0 + 1} \qquad (26)$$

The fit for the calculated limiting values are shown in Fig. 13, where the values for the coefficients c_1 and c_2 obtained from fitting are 0.474 and −1.012 respectively. The fit is very good ($R^2 = 0.999$). Therefore

$$I(N_0) \approx \psi(N_0) = c_1 + \frac{c_2}{N_0 + 1} \qquad (27)$$

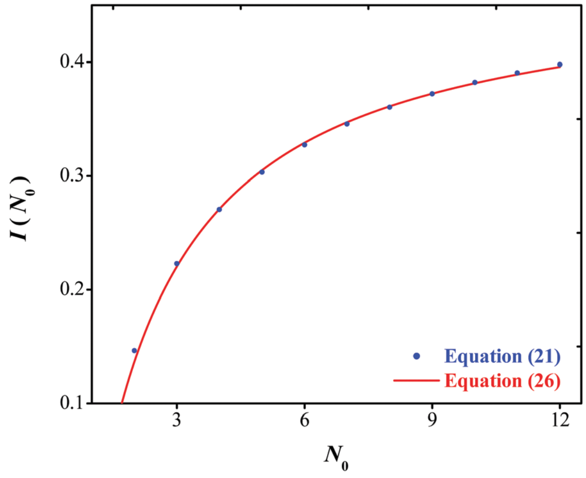

Fig. 13 The numerical calculation of eqn (21) under the asymptotic condition $t \to 0$. The function used for fitting (eqn (26)) is also shown.

If the approximate values for the coefficients $c_1 \approx 0.5$ and $c_2 \approx -1$ are used in the last equation and then the result is inserted in eqn (20), eqn (9) (with eqn (10)) is obtained. This provides a theoretical justification of eqn (9), the main aim of the current part of this study.

5.3. More tests

The correction proposed here has been tested under a variety of different conditions. This includes cases where different initial distributions for the radicals were used. For example, broadening the Gaussian distribution to a standard deviation of 1.5 nm (instead of 1 nm in the above simulations), and using a uniform distribution in the center cube. It was found that the proposed correction continues to be an important improvement compared to the original in eqn (7). Similarly, the number of scavengers in the simulation box were also changed, *i.e.* the scavengers' concentration, between 10–80 and it was found that the correction continues to hold.

The case of a spur containing two types of radicals A and B with the following scheme (S3)

$$A + A \rightarrow A_2$$

$$B + B \rightarrow B_2$$

$$A + B \rightarrow AB$$

$$A + S \rightarrow AS$$

was also considered, where the scavenger S can react with the radical A only. In this case, 60 scavenger particles were included in the box, and the radical coordinates were generated from a Gaussian with a standard deviation of 1 nm. In Fig. 14 and 15, the number of radicals in the spur is 6, 3 of A and 3 of B, and $N_0 = 3$ was used in the correction. Even with this small number of each radical, the effect of the correction is still clear.

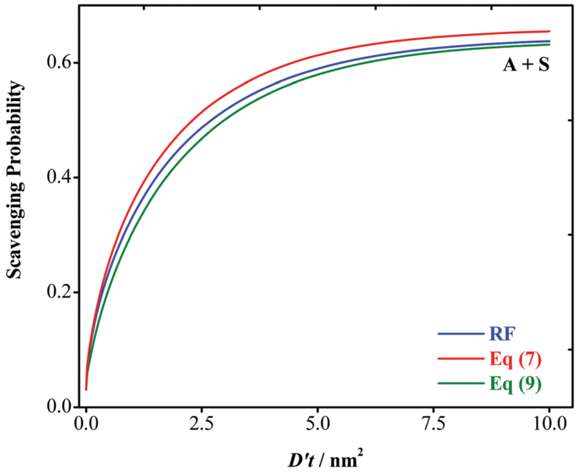

Fig. 14 The scavenging probability in the S3 scheme. The notations are similar to those of the previous figures.

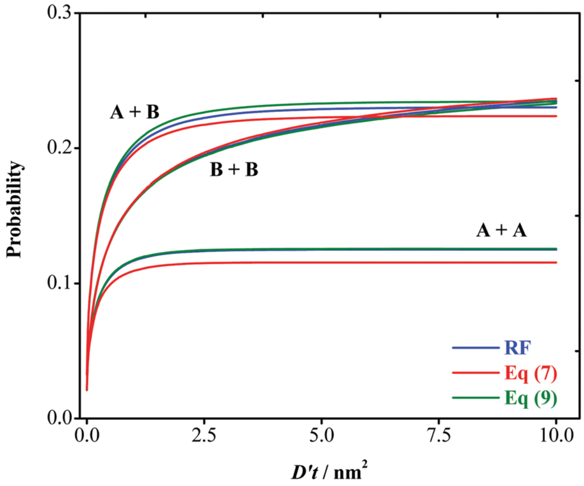

Fig. 15 The probabilities of the other reactions in the S3 scheme.

6. Monte Carlo IRT simulations

This section discusses how the IRT theory can be modified to simulate the competition between scavenging and recombination in a spur.

Briefly, the IRT method to simulate radiation chemical kinetics was first proposed in 1982.[43,48,49] It has been discussed in detail in many places, and will only briefly be described here for electrically neutral reactants and diffusion-controlled reactions. Since the only necessary parameter to obtain the chemical kinetics is the sequence of reaction times, the IRT method is constructed to generate the reaction times without having to monitor the trajectories of the reactants (in contrast to the RF simulations). It is therefore a computationally efficient method when compared to the full RF simulations. Consider a system of two neutral spherical particles separated initially by a distance r, the probability W that the particles have reacted by time t is well known (eqn (11))[4,17] which indicates that

$$t = \frac{1}{4D'}\left[\frac{r-a}{\operatorname{erfc}^{-1}(\lambda)}\right]^2 \qquad \lambda = \frac{r}{a}W(t,r;a) \tag{28}$$

where erfc^{-1} is the inverse of the complementary error function. The last equation can be used to generate a reaction time for the two particles in Monte Carlo simulations where W is replaced by a uniformly distributed random number between 0 and 1 (provided that r is known, and the function erfc^{-1} can be computed). If $\lambda > 1$ then no encounter of this pair takes place. This is known as the inverse function method for generating non-uniform random numbers.[38] The IRT method then employs the independent pairs approximation to obtain the reaction times in systems of more than two particles, *i.e.* it generates a reaction time for each pair present as described above, ignoring the presence of any other particles, and then sorts the reactions out in order of reaction times and taking account of the surviving particles. One of the strengths of the IRT theory is that, in some cases, it can give an analytic solution to the problem of interest. This is because the independence approximation substantially simplifies the mathematics of the problem. For example, as shown above in 5.2, the time-dependent Smoluchowski rate constant can be derived using the IRT method.

6.1. General description

In a spur, the radicals have a random, non-homogenous distribution of some sort, and they are surrounded by a large number of uniformly distributed scavenger molecules. A radical can react with another radical (recombination reaction), or it can react with a scavenger molecule (scavenging reaction). As simulation is expanded to include more scavenger molecules, further away from the center of the spur, the simulation becomes rapidly more expensive for little gain because the reaction probabilities become much smaller (due to the large distances) and the effect on the short-term transient kinetics is negligible: these far-off scavengers contribute mainly to the steady-state rate constant. Therefore, the difficulty in developing an IRT model for the problem lies in dealing with the scavengers that are far away from the center of the spur almost all of which will generate infinite reaction times. In this study, an alternative method is proposed for s spherical spur (Fig. 16): the scavengers close to the center of the spur are dealt with explicitly in the simulations and those far away are dealt with using a ‘‘continuum region’’. For a typical radical, a separate scavenging time is generated for each scavenger in the central sphere, and a single scavenging time is generated for reaction with the continuum.

Consider a radical R at a distance z from the centre of the spur, which is also the centre of a sphere of radius b, enclosing the spur, as shown in Fig. 16. Inside the sphere scavengers are explicitly located as samples from a uniform distribution. Outside the sphere the scavenger S is taken to be a continuum with a radial distribution function g that satisfies the following

$$g(r) = \begin{cases} 0 & r < b \\ 1 & b \le r \le Q \end{cases} \tag{29}$$

The continuum region has an inner radius b and an outer radius Q, which will be considered to be infinitely large later. For the purposes of analysis the radical is placed on the z-axis for convenience, but because of the spherical symmetry of the system this has no consequence. For an S particle with spherical polar coordinates r, θ and φ, the distance R–S is

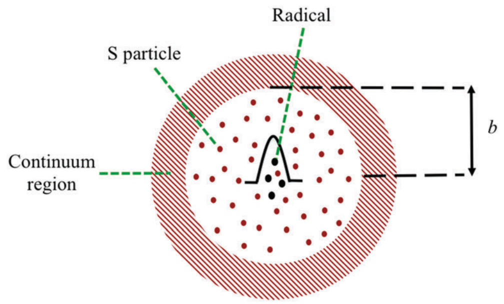

Fig. 16 The IRT simulations. The radicals are sampled from a Gaussian distribution and they are surrounded by a large number of scavenger molecules. The scavengers away from the center of the spur are considered as a continuum region.

$$q = \sqrt{r^2 + z^2 - 2rz\cos\theta} \tag{30}$$

The survival probability for reaction with a typical scavenger averaged over the outer scavenging continuum is then[4,6,8,41–44]

$$\begin{aligned} \Omega_{\mathrm{pair,u}} &= \frac{1}{V}\int_0^Q\int_0^\pi\int_0^{2\pi} g(r)\Omega_{\mathrm{pair}} r^2 \sin\theta \mathrm{d}r\mathrm{d}\theta\mathrm{d}\varphi \\ &= \frac{2\pi}{V}\int_b^Q\int_0^\pi \left[1 - \frac{a}{q}\mathrm{erfc}\left(\frac{q-a}{\sqrt{4D't}}\right)\right] r^2 \sin\theta \mathrm{d}r\mathrm{d}\theta \end{aligned} \tag{31}$$

where

$$V = 4\pi\int_0^Q r^2 g(r)\mathrm{d}r = 4\pi\int_b^Q r^2\mathrm{d}r = \frac{4}{3}\pi\left(Q^3 - b^3\right) \tag{32}$$

Following the same procedures as in the last section (Poisson weighting and independence of pairs) gives

$$\Omega = \sum_m \frac{(C_0 V)^m}{m!}\exp(-C_0 V)\Omega^m_{\mathrm{pair,u}} = \exp(-C_0 V)\cdot\exp\left(C_0 V \Omega_{\mathrm{pair,u}}\right) \tag{33}$$

Therefore, the time-dependent rate coefficient for scavenging with the continuum region $k_{\mathrm{b}}(t)$ is

$$k_{\mathrm{b}}(t) = -2\pi\frac{\mathrm{d}}{\mathrm{d}t}\int_b^Q\int_0^\pi\left[1 - \frac{a}{q}\mathrm{erfc}\left(\frac{q-a}{\sqrt{4D't}}\right)\right] r^2 \sin\theta \mathrm{d}r\mathrm{d}\theta \tag{34}$$

The integral in the last equation can be performed using the Laplace transform method as described in detail in ref. 38. The final result is

$$\begin{aligned} k_{\mathrm{b}}(t) &= \frac{2\pi a D'}{z}\left[(z+a)\mathrm{erfc}\left(\frac{b-z-a}{\sqrt{4D't}}\right) + (z-a)\mathrm{erfc}\left(\frac{b+z-a}{\sqrt{4D't}}\right)\right. \\ &\quad \left. + \sqrt{\frac{4D't}{\pi}}\left(\exp\left(\frac{-(b-z-a)^2}{4D't}\right) - \exp\left(\frac{-(b+z-a)^2}{4D't}\right)\right)\right] \end{aligned} \tag{35}$$

It should be noted that k for the special case $z = 0$ was shown to be given as follows[42]

$$k_{b,z=0}(t) = 4\pi a D'\left[\mathrm{erfc}\left(\frac{b-a}{\sqrt{4D't}}\right) + \frac{b}{\sqrt{\pi D't}}\exp\left(\frac{-(b-a)^2}{4D't}\right)\right] \tag{36}$$

The reaction probability for scavenging with the continuum H is

$$H(t) = 1 - \Omega(t) = 1 - \exp\left(-C_0\int_0^t k_{\mathrm{b}}(t)\mathrm{d}t\right) \tag{37}$$

The difficulty now is that the above equation cannot be used directly in the course of Monte Carlo simulations to generate a reaction time for scavenging with the continuum. This is because the mathematical formula cannot be inverted for t analytically. Fortunately, the following probability density function h

$$h(t) = \frac{\mathrm{d}}{\mathrm{d}t}H(t) = C_0 k_{\mathrm{b}}(t)\exp\left(-C_0\int_0^t k_{\mathrm{b}}(t)\mathrm{d}t\right) \tag{38}$$

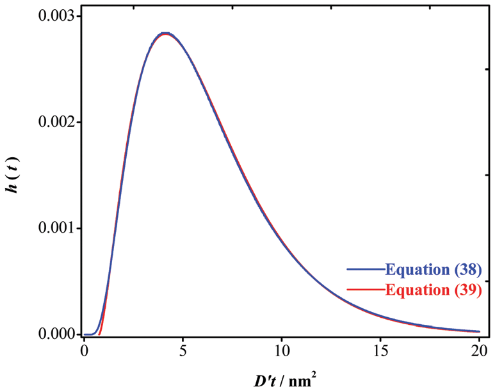

Fig. 17 The probability density function for scavenging with the continuum. This is for z = 1 nm, a = 0.5 nm and b = 5 nm. D' is the relative diffusion coefficient and t is the time.

is similar to a gamma density function of the following form (Fig. 17)

$$\zeta_{\alpha\beta\gamma}(t) = \frac{1}{\beta^{\alpha}\Gamma(\alpha)}(t-\gamma)^{\alpha-1}\exp\left(\frac{-(t-\gamma)}{\beta}\right) \tag{39}$$

where each of the coefficients α, β and γ was found by fitting to be approximated by a simple, second-order polynomial function of z as follows

$$\lambda = \rho z^2 + \sigma z + \upsilon \tag{40}$$

where λ is α, β or γ, and the coefficients ρ, σ and υ are obtained from fitting process as described in detail in ref. 38. (Briefly, calculations for several value of z are produced. For each value of z, a fit similar to that of Fig. 17 is obtained, which gives values for α, β and γ of eqn (40) as functions of z. These values of α, β and γ are then fit to equation 41 to obtain ρ, σ and υ). The key conclusion of the current part of this study is that eqn (40) can be used to generate a reaction time for the scavenging with the continuum region in Monte Carlo simulations.

6.2. Procedures of the simulations

This section describes how the simulation program works using the method developed in 6.1. At zero time, the space is divided into two regions. The first is the inside of a sphere of radius b and it contains the radicals, whose coordinates are sampled from a Gaussian distribution in this study, and explicit, uniformly distributed scavenger molecules with the appropriate density (see Fig. 16). In this region, the reaction times (for both recombination and scavenging reactions) are generated using the independent pair approximation (eqn (29)). The second region is the outside the sphere of radius b, and is the ''continuum region''. For each radical in the spur, a reaction time for scavenging with the continuum region is generated using eqn (40). The reaction times are then ordered from small to large. After an appropriate time increment, the program checks if a reaction has occurred (this is limited of course to the particles that have survived so far) and makes the necessary changes (count a reaction and remove the particles that have reacted *etc.*) Then another time increment is added and the process is repeated until such time that either all the radicals in the spur have reacted or a cut off time (maximum waiting time) is reached. These procedures are repeated a very large number of times (realizations), typically 10^5 times, and the kinetics are obtained at the end.

6.3. Results

Simulations for several values of N_0, the number of radicals in the spur at zero time, were obtained and the results of these simulations were all consistent. Examples are shown in Fig. 18 and 19 where in Fig. 18 the scavenging probability is shown (for N_0 = 5) and in Fig. 19 the recombination probability is shown. The radius b was 5 nm. The coordinates of the radical were sampled from a Gaussian distribution with a standard deviation of 1 nm. The number of the explicit scavenger molecules in the sphere of radius b corresponds to C_0 = 0.06 scavenger per nm^3 (about 0.1 mol dm^{-3}). The reaction distance for both R + S and R + R reactions was 0.5 nm. The results of the three methods (RF, IRT and hybrid where eqn (9) is used to generate

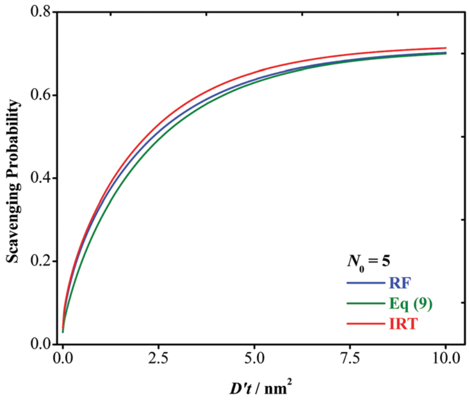

Fig. 18 The scavenging probability for N_0 = 5. RF refers to random flight simulations. Eqn (11) refers to the simulations where eqn (11) is used. IRT refers to independent reaction time simulations. Statistical errors are (±0.002) at 5 nm^2 and the number of realizations is 10^5.

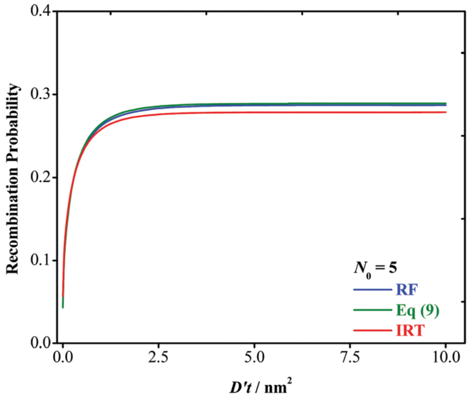

Fig. 19 The recombination probability for N_0 = 5. RF refers to random flight simulations. Eqn (11) refers to the simulations where eqn (11) is used. IRT refers to independent reaction time simulations. Statistical errors are (±0.002) at 5 nm^2 and the number of realizations is 10^5.

scavenging times for the radicals) are in a reasonable agreement with each other within statistical variation.

7. Conclusions and future work

The rate coefficient for a fully diffusion-controlled reaction is time-dependent. Smoluchowski theory describes this time-dependence under certain assumptions.[10,12] Practically, these assumptions are accurate when the radicals are isolated, and the problem is that in a radiation-generated spur a radical cannot normally be considered isolated from the other radicals as the radical recombination is in competition with scavenging. In this study, a simple correction to the Smoluchowski rate constant (eqn (9) with eqn (10)) to include this multi-radical correlation effect has been proposed, justified (using the approximation of independent pairs) and tested by simulation. This correction seems to be a significant improvement under conditions where the recombination and scavenging are in competition. In practice, a correction of this type is likely to be important in high LET tracks, where the density of radicals is high because spur overlap increases the number of radicals close to one another. It will be interesting to generalize the results to geometries other than spherical for this reason, as well as testing whether the same corrections can be used when reactions are not fully diffusion-controlled and when the effects of ionic charge are included. Finally, it will be important to run more tests for this correction. The correction is expected to break down when the radical distribution is wide, as the effect of the overlap of the concentration gradients will be reduced, but under these conditions the recombination is slow and there will be little competition between the recombination and the scavenging. It is also likely that the correction will break down at times short relative to the recombination time, before the interference of the concentration gradients can be set up and here the Smoluchowski theory should apply. It is for these reasons that a new method for the simulation of scavenging in the IRT approximation has been introduced, where the scavengers close to the spur are explicitly included and the scavengers further away are treated as a continuum. This should allow the IRT method to be used efficiently in such a way that the initial correlations between radical-scavenger distances are taken into account, and that it is no longer necessary to generate huge numbers of IRTs for scavengers far-off, most of which will be infinite. This method has the potential to be useful in future track simulations, but at present the time for reaction with the outer continuum region has to be generated by a parametric method, and it has been shown how these parameters can be found in general. However, it would be very useful to investigate whether there are any conditions where an analytical approach could be used here, avoiding the problems of fitting parameters described above. The IRT method realised in this way is in excellent agreement with both the random flight simulation method and the Smoluchowski theory when the correction proposed before is included.

Future work will include cases of more than one spur and more realistic reaction schemes, for example including the effects of charge, and comparing the proposed correction with experimental data when possible. Since the uncorrected Smoluchowski theory works satisfactorily at short times, future work might consider introducing a switching function into the correction, so that the normal Smoluchowski theory operates at short times and switches smoothly to the corrected version on timescales where recombination can take place and the concentration gradients overlap.

References

1 A. Mozumder, *J. Phys. Chem. Lett.*, 2011, **2**, 2994.
2 K. Noda and T. Kamada, in *Cancer Therapy with Heavy-Ion Beams*, ed. Y. Hatano, Y. Katsumura and A. Mozumder, Charged Particle and Photon Interactions with Matter, CRC Press, Taylor & Francis Group, Boca Raton, 2011.
3 A. Mozumder, in *Interaction of Fast Charged Particles with Matter*, ed. A. Mozumder and Y. Hatano, Charged Particle and Photon Interactions with Matter, Marcel Dekker Inc., New York, 2004.
4 S. M. Pimblott and N. J. B. Green, in *Recent Advances in the Kinetics of Radiolytic Processes*, ed. R. G. Compton and G. Hancock, Research in Chemical Kinetics, Elsevier Science BV., Amsterdam, 1995, vol. 3.
5 I. Plante, *Radiat. Environ. Biophys.*, 2011, **50**, 389.
6 S. M. Pimblott and A. Mozumder, in *Modeling of Physicochemical and Chemical Processes in the Interactions of Fast Charged Particles with Matter*, ed. A. Mozumder and Y. Hatano, Charged Particle and Photon Interactions with Matter, Marcel Dekker Inc., New York, 2004.
7 N. J. B. Green and S. M. Pimblott, *Res. Chem. Intermed.*, 2001, **27**, 529.
8 V. M. Bluett and N. J. B. Green, *J. Phys. Chem. A*, 2006, **110**, 6112.
9 M. W. Chevalier and H. El-Samad, *J. Chem. Phys.*, 2014, **141**, 214108.
10 S. A. Rice, in *Diffusion-Limited Reactions*, ed. C. H. Bamford, C. F. H. Tipper and R. G. Compton, Comprehensive Chemical Kinetics, Elsevier Science Publishers B. V., Amsterdam, 1985, vol. 25.
11 A. Einstein, *Ann. Phys.*, 1905, **17**, 549.
12 M. Smoluchowski, *Z. Phys. Chem.*, 1917, **92**, 129.
13 K. Enomoto, J. A. LaVerne and S. M. Pimblott, *J. Phys. Chem. A*, 2006, **110**, 4124.
14 J. A. LaVerne, K. Enomoto and M. S. Araos, *Radiat. Phys. Chem.*, 2007, **76**, 1272.
15 S. Yamashita, M. Taguchi, G. Baldacchino and Y. Katsumura, in *Radiation Chemistry of Liquid Water with Heavy Ions: Steady-State and Pulse Radiolysis Studies*, ed. Y. Hatano, Y. Katsumura and A. Mozumder, Charged Particle and Photon Interactions with Matter, CRC Press, Taylor & Francis Group, Boca Raton, 2011.
16 N. J. B. Green, *Chem. Phys. Lett.*, 1984, **107**, 485.

17 P. Clifford, N. J. B. Green, M. J. Pilling and S. M. Pimblott, *J. Phys. Chem.*, 1987, **91**, 4417.

18 C. E. Bolton and N. J. B. Green, *J. Phys. Chem. A*, 1999, **103**, 4446.

19 S. M. Pimblott and N. J. B. Green, *J. Phys. Chem.*, 1992, **96**, 9338.

20 A. Hummel, in *Kinetics in Radiation Chemistry*, ed. Farhataziz and M. A. J. Rodgers, Radiation Chemistry Principles and Applications, VCH Publishers, Inc., New York, 1987.

21 F. C. Collins and G. E. Kimball, *J. Colloid Sci.*, 1949, **4**(4), 425.

22 I. Z. Steinberg and E. Katchalski, *J. Chem. Phys.*, 1968, **48**(6), 2404.

23 M. Tachiya, *J. Chem. Phys.*, 1978, **69**(6), 2375.

24 M. Tachiya, *Radiat. Phys. Chem.*, 1983, **21**, 167.

25 K. Joohyun, J. Younjoon, J. Jonggu, S. K. Joe and L. Sangyoub, *J. Chem. Phys.*, 1996, **104**, 5784.

26 S. G. Fedorenko and A. A. Kipriyanov, *Chem. Phys. Lett.*, 2006, **428**, 200.

27 S. G. Fedorenko, A. A. Kipriyanov and A. B. Doktorov, *Chem. Phys. Lett.*, 2007, **436**, 104.

28 M. D. Donsker and S. R. S. Varadhan, *Comm. Pure Appl. Math.*, 1975, **28**, 525.

29 P. Clifford and N. J. B. Green, in *Contemporary problems in statistical physics*, ed. G. H. Weiss, SIAM press, 1994, ch. 1.

30 N. J. B. Green, *Mol. Phys.*, 1988, **65**(6), 1399.

31 N. J. B. Green, M. J. Pilling, S. M. Pimblott and P. Clifford, *J. Phys. Chem.*, 1989, **93**, 8025.

32 P. Clifford, N. J. B. Green and M. J. Pilling, *J. R. Stat. Soc.: Ser. B*, 1987, **43**(3), 266.

33 S. M. Pimblott, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 3533.

34 S. M. Pimblott and J. A. LaVerne, *J. Phys. Chem. A*, 1997, **101**, 5828.

35 S. M. Pimblott, *J. Phys. Chem.*, 1992, **96**, 4485.

36 S. M. Pimblott, *J. Phys. Chem.*, 1991, **95**, 6946.

37 S. M. Pimblott and J. A. LaVerne, *Radiat. Res.*, 1990, **122**, 12.

38 L. Devroye, *Non-Uniform Random Variate Generation*, Springer-Verlag, New York, 1986.

39 R. M. Noyes, *Prog. React. Kinet.*, 1961, **1**, 129.

40 V. M. Bluett and N. J. B. Green, *J. Phys. Chem. A*, 2006, **110**, 4738.

41 S. M. Pimblott, M. J. Pilling and N. J. B. Green, *Radiat. Phys. Chem.*, 1991, **37**(3), 377.

42 E. H. Al-Samra, DPhil thesis, University of Oxford, 2015.

43 P. Clifford, N. J. B. Green and M. J. Pilling, *J. Phys. Chem.*, 1982, **86**, 1322.

44 N. J. B. Green and S. M. Pimblott, *J. Phys. Chem.*, 1989, **93**, 5462.

45 A. P. Prudnikov, Y. A. Brychkov and O. I. Marichev, *Integrals and Series*, Gordon and Breach Science Publishers, New York, 1992, vol. 2.

46 H. B. Dwright, *Tables of Integrals and Other Mathematical Data*, The Macmillan Company, New York, 4th edn, 1968.

47 A. P. Prudnikov, Y. A. Brychkov and O. I. Marichev, *Integrals and Series*, Gordon and Breach Science Publishers, New York, 1992, vol. 1.

48 P. Clifford, N. J. B. Green and M. J. Pilling, *J. Phys. Chem.*, 1982, **86**, 1318.

49 N. J. B. Green, M. J. Oldfield, M. J. Pilling and S. M. Pimblott, *J. Chem. Soc., Faraday Trans. 1*, 1986, **82**, 2673.