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Stochastic Analysis of the Asymptotic Kinetics of Multi-particle Spurs

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Analyses are presented of the long-time asymptotic kinetics of spur reactions in the absence of scavenger, and of the asymptotic concentration dependence of the scavenging yield. The results show no dependence on the initial spatial distribution of the particles apart from that inherent in the escape yield. However, the asymptotics are shown to provide further information about the probability distribution of the numbers of particles escaping, and hence to provide an indirect probe of the initial number distribution.

1. Introduction

The flash photolysis or electron pulse radiolysis of a liquid results in the formation of a non-homogeneous spatial distribution of highly reactive free radicals and ions.[1] Flash photolysis generally produces particles in geminate pairs,[2] whereas high-energy electrons give a distribution of clusters resulting from the dissociation of one or more solvent molecules.[3] The kinetics that follow the light or electron pulse give the most direct window currently available on the initial conditions. A major aim in photochemistry and radiation chemistry has been to utilize the transient kinetics to extract this information. The two aspects of most interest are the spatial distributions of the radicals and ions produced, and (in radiation chemistry) the probability distribution of the numbers of particles in the clusters. Towards this end two main types of experiment have been performed: direct spectroscopic or conductimetric measurement of the time dependence of the space-averaged concentrations of certain reactants,[4–8] and competition experiments in which the recombination of the reactive particles competes with scavenging.[9–11] The former approach has the advantage of measuring the kinetics directly, but is limited to transients which absorb strongly enough to be observed. Furthermore, while short-pulse lasers are readily available, there are very few electron irradiation facilities that can produce radiation pulses short enough and with high enough flux for this type of experiment. The latter approach is more generally applicable, but suffers from the disadvantage that it is an indirect probe of the kinetics.

In both types of investigation, although there are exceptions, the most readily accessible kinetics correspond to the long-time tail of the time dependence, or the low concentration dependence of the scavenging yield. In this regime three parameters may be obtained: a long-time asymptotic escape yield, a power of time with which the asymptote is approached, and a parameter governing the rate of approach to the asymptote. Three related parameters can be extracted from the low-concentration dependence of the scavenging yield: the low-concentration limit, which should be identical to the asymptotic escape probability, a power law for the approach to the limit, which is the negative of the power describing the time-dependent asymptotics, and a proportionality parameter, whose relationship to the corresponding parameter for the time dependence is more complicated.

The only information about the initial spatial distribution that is available from the asymptotics of geminate recombination or scavenging kinetics is contained in the escape yield.[12,13] The power law and the constant of proportionality provide no further information about the spatial distribution. The aim of this study is to investigate whether this is also true for larger clusters, where information is sought not only on the spatial distribution of the particles but also on the numbers of particles in the clusters. In Section 2 the problem of geminate recombination is analysed in detail in order to explain why the long-time asymptotics are independent of the initial distribution (except through the escape yield). In Section 3 master equation descriptions are set up for model reaction schemes in which only one reaction is possible, and the asymptotics of the solutions are investigated with the aim of discovering whether they contain any additional information. Finally, in Section 4 a more general reaction scheme is considered and it is shown how the method can be applied to realistic systems.

2. Geminate Recombination

The long-time asymptotic behaviour of the geminate pair survival probability is well known.[14] Explicit solutions are known for some potentials, but the asymptotic behaviour can be obtained for any physically realistic, spherically symmetrical, potential energy of interaction. The asymptotic form of the Green's function for the time-dependent survival probability is always of the form[12–15]

$$\Omega(r, t) \approx \left(1 - \frac{a_{\rm eff}}{r_{\rm eff}}\right)\left[1 + \frac{a_{\rm eff}}{(\pi D' t)^{1/2}} + O(a_{\rm eff}^2/D't)\right] \qquad (1)$$

in which

$$r_{\rm eff} = \left\{\int_r^\infty x^{-2} \exp[U(x)]\, dx\right\}^{-1}$$

$$a_{\rm eff} = \left\{(1 + \delta) \int_a^\infty x^{-2} \exp[U(x)]\, dx\right\}^{-1}$$

$$\delta = \frac{D' \exp[U(a)]}{va^2 \int_a^\infty x^{-2} \exp[U(x)]\, dx}$$

where r is the initial pair separation, a the encounter distance, $U(r)$ the spherical potential-energy function in units of kT, D' the relative diffusion coefficient of the pair, and v the 'boundary velocity' which determines the rate of reaction when the pair has encountered.[16]

Since the survival probability in eqn. (1) is the asymptotic form of the Green's function for the problem, a similar asymptotic survival probability can be constructed for an arbitrary probability density for the initial separation. Denoting the density by $f(r)$ the survival probability, $\Pi(t)$, is

$$\Pi(t) = \Pi(\infty)\left[1 + \frac{a_{\rm eff}}{(\pi D' t)^{1/2}} + O(a_{\rm eff}^2/D't)\right] \qquad (2)$$

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where $\Pi(\infty)$ is the long-time limiting asymptotic escape probability. This limiting probability contains some information about the initial spatial distribution of the pair, since it is a linear function of the expectation of the reciprocal of r_{eff}:

$$\Pi(\infty) = 1 - a_{\text{eff}}\langle r_{\text{eff}}^{-1}\rangle \tag{3}$$

However, the rate of approach to the asymptote contains no further information about the initial distribution: the asymptotic power law is always $-\frac{1}{2}$ and the proportionality constant is simply $a_{\text{eff}}/(\pi D')^{1/2}$, and so both are independent of the initial distribution. An equation similar to eqn. (2), with the same rate of approach to the asymptotics is obtained from the prescribed diffusion approximation.[13]

When geminate recombination takes place in the presence of a scavenger which can only react with one of the particles a simple rate equation for the surviving fraction of pairs $\phi(t, s)$ can be set up:[17]

$$\frac{\mathrm{d}\phi}{\mathrm{d}t} = -\lambda(t)\phi(t, s) - s\phi(t, s) \tag{4}$$

Here s is the pseudo-first order rate constant for scavenging, $s = k_s c_s$, and $\lambda(t)$ is an effective transient rate coefficient for the geminate recombination, which is related to $\Pi(t)$ by

$$\lambda(t) = -\frac{\mathrm{d}\ln\Pi}{\mathrm{d}t} \tag{5}$$

The resulting long-time asymptotic scavenging yield $y_s(s)$ is therefore

$$y_s(s) = s\int_0^\infty \exp(-st)\Pi(t)\,\mathrm{d}t \tag{6}$$

which is s times the Laplace transform of the decay in the absence of scavenger. It is therefore possible to use standard theorems of the Laplace transform to relate the asymptotic behaviour of y_s for small s and that of $\Pi(t)$ for large t, giving

$$y_s(s) \approx \Pi(\infty)[1 + a_{\text{eff}}(s/D')^{1/2} + \ldots] \tag{7}$$

Thus there is no information on the spatial distribution from the small s behaviour of the scavenging yield. If both particles in the pair can be scavenged the analysis is slightly more complex, but the results are similar: $y_s(s)$ is still given by eqn. (7), but with s replaced by $2s$ on the right-hand side.[17]

Clearly, in the diffusion approximation at least, there is no information apart from the one moment in the escape yield, $\langle r_{\text{eff}}^{-1}\rangle$, about the initial spatial distribution of the particles in the long-time behaviour of the survival probability or in its Laplace transform. The question addressed in the remainder of this paper is whether this result can be extended to multiple-particle clusters, or whether there is further information to be gleaned from the long-time behaviour in these cases.

3. Single Reaction Schemes

As soon as the cluster of reactants contains more than two particles it is no longer possible to solve the diffusion-reaction equations for the system exactly. However, it has been shown that a stochastic theory based on the independent pairs approximation is very accurate under most conditions,[18–20] and particularly accurate at modelling the long-time behaviour of the surviving fraction.[20] The form of the theory most appropriate for analytical investigations is based on a master equation. In this section two very simple reaction schemes are considered where the master equation can be solved exactly: in one scheme all the particles are considered to be identical; and in the other scheme the cluster contains two species, A and B, but only cross-reactions are possible. The first scheme is a very approximate model of radical–radical reactions,[21] whereas the second scheme is probably a rather good model of ion–ion reactions in clusters induced by radiation in liquids of low permittivity, such as n-hexane.[22]

3.1. Single-species Systems

The master equation for a single-species system has been known for some time, and can be solved exactly.[23] In this system identical particles are supposed to be initially distributed independently and identically according to some model distribution. The marginal density of each of the interparticle distances is identical, and given by $f(r)$. The marginal distribution for the reaction time of each pair (*i.e.* the probability that the pair would survive to time t in the absence of any of the other particles) is denoted $\Pi(t)$, and the transient rate coefficient for recombination is $\lambda(t)$, which is related to $\Pi(t)$ as in Section 2. If $P_n(t)$ is the probability that the cluster contains n particles at time t then in the independent-pairs approximation the probability P_n obeys the master equation[23]

$$\frac{\mathrm{d}P_n}{\mathrm{d}t} = \tfrac{1}{2}(n+2)(n+1)\lambda(t)P_{n+2} - \tfrac{1}{2}n(n-1)\lambda(t)P_n \tag{8}$$

This equation is solved to give the expectation of the number of particles remaining[23,24]

$$\langle N\rangle_t = \sum_{n=m}^{N_0} \frac{(2n-1)\Gamma[N_0+1]\Gamma[\frac{1}{2}(N_0-n+1)]\Pi^{n(n-1)/2}}{2^n\Gamma[N_0-n+1]\Gamma[\frac{1}{2}(N_0+n+1)]} \tag{9}$$

where N_0 is the initial number of particles in the spur and the sum covers alternate values of n, starting either from $m = 2$ or 1, according to whether N_0 is even or odd, respectively.

Eqn. (9) is simply a polynomial in Π, and so it contains no further information about the initial distribution $f(r)$ beyond what is already contained in $\Pi(\infty)$. A graph of $\langle N\rangle$ against Π is shown in Fig. 1 for several different values of N_0. If the initial number of particles is known then the observed kinetics $\langle N\rangle_t$ can be transformed to give the functional form of the underlying geminate kinetics $\Pi(t)$ simply by reading off this graph. It is apparent that although there is no information about the spatial distribution from the approach to the asymptotic escape probability, each value of N_0 gives a different curve, and so it may be possible to extract information about the initial number of particles in the cluster from the form of the asymptotics. Careful examination of the asymptotic behaviour of $\langle N\rangle_t$ is therefore necessary.

Using the same generating function method used to derive eqn. (9),[24] or the more generally applicable method described in ref. 17, it is straightforward to show that the long-time asymptotics of $\langle N\rangle$ are

$$\langle N\rangle_t \approx \langle N\rangle_\infty + \langle N(N-1)\rangle_\infty \frac{a_{\text{eff}}}{(\pi D't)^{1/2}} \tag{11}$$

An asymptotic analysis of the scavenging yield can also be performed using the techniques described in ref. 17, and gives

$$y_s(s) \approx \langle N\rangle_\infty + \langle N(N-1)\rangle_\infty a_{\text{eff}}(2s/D')^{1/2} \tag{12}$$

Note that in the case of a single pair of identical particles $\langle N\rangle_t = \langle N(N-1)\rangle_t = 2\Pi(t)$, and eqn. (11) and (12) reduce to the correct geminate pair solutions. In all other cases $\langle N(N-1)\rangle$ may be calculated from a polynomial similar to eqn. (9),[24]

$$\langle N(N-1)\rangle_t = \sum_{n=m}^{N_0} \frac{n(n-1)(2n-1)\Gamma[N_0+1] \times \Gamma[\frac{1}{2}(N_0-n+1)]\Pi^{n(n-1)/2}}{2^{n+1}\Gamma[N_0-n+1]\Gamma[\frac{1}{2}(N_0+n+1)]} \tag{13}$$

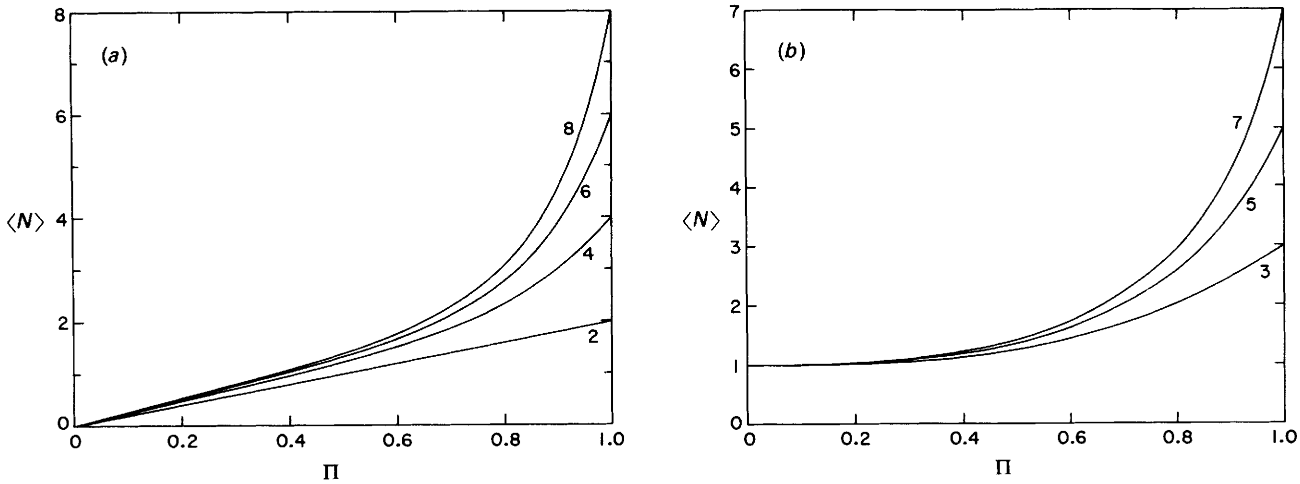

Fig. 1 Survival in single-species spurs: expectation number of particles remaining in a spur as a function of the underlying geminate survival probability $\Pi(t)$. Lines are labelled with the initial number of particles N_0. (*a*) Even values of N_0. (*b*) Odd values of N_0.

where the sum covers alternate values of *n*, *cf.* eqn. (9). The rate of approach to the asymptote therefore gives an estimate of the ratio $\langle N(N-1)\rangle_\infty/\langle N\rangle_\infty$, which is plotted as a function of $\langle N\rangle_\infty$ and Π for several different values of N_0 in Fig. 2. Systems with odd numbers of particles behave in a qualitatively different way from systems with even numbers if Π is small. For those with odd numbers the ratio $\langle N(N-1)\rangle/\langle N\rangle$ approaches zero because a minimum of one particle must always escape, so that $\langle N\rangle$ approaches unity while $\langle N(N-1)\rangle$ diminishes towards zero. However for systems with even numbers if Π is small the ratio of the first two factorial moments approaches one. This is because when Π is small it is most likely that no particles remain, but if any do, then the most likely possibility is that a single pair survives, and for a single pair $\langle N\rangle = \langle N(N-1)\rangle$.

If the asymptotic value $\Pi(\infty)$ is not close to zero, as will

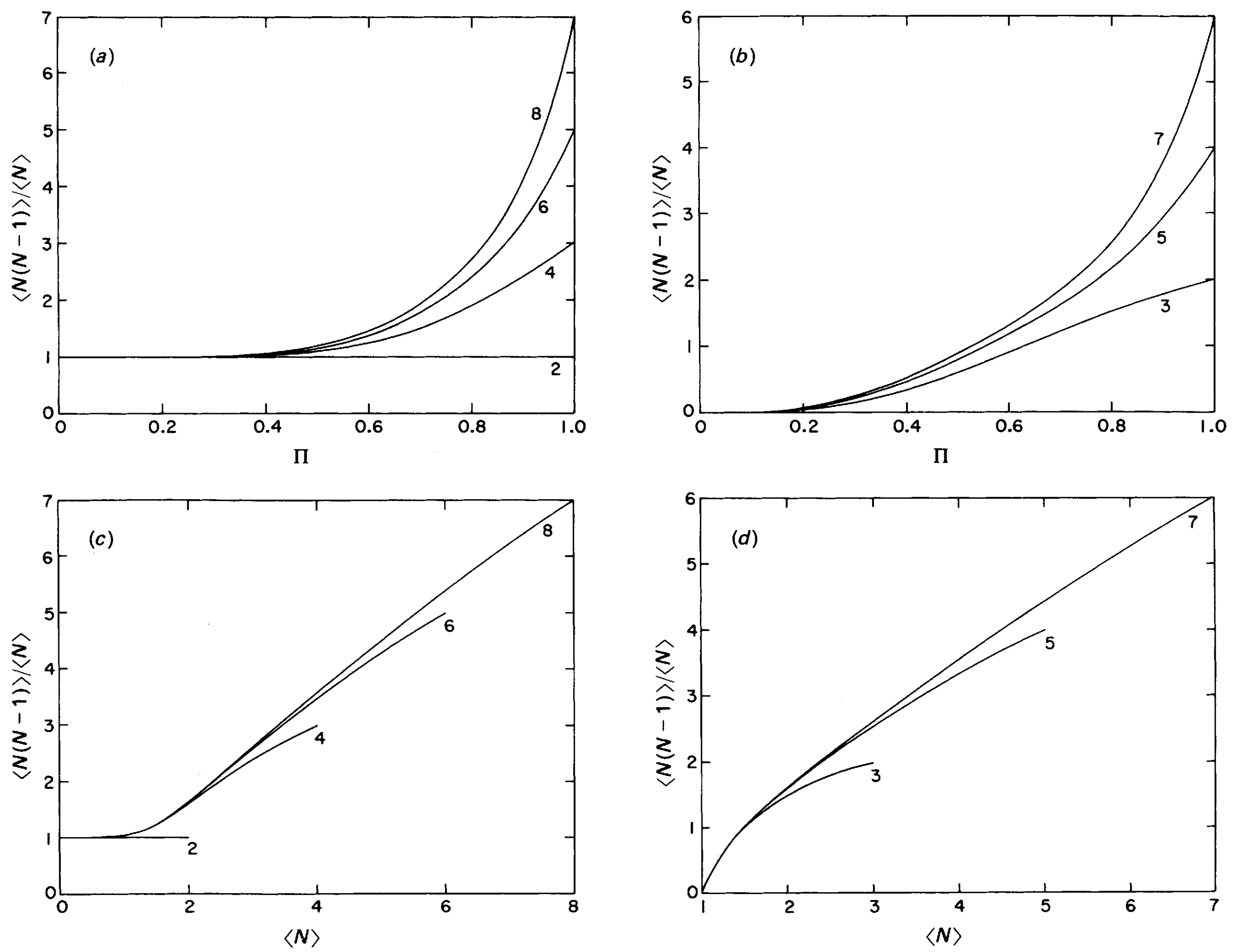

Fig. 2 Survival in single-species spurs: the second factorial moment of the number of particles remaining divided by the mean. Lines are labelled with the initial number of particles. (*a*) Plotted against Π for even N_0. (*b*) Plotted against Π for odd N_0. (*c*) Plotted against $\langle N\rangle$ for even N_0. (*d*) Plotted against $\langle N\rangle$ for odd N_0.

generally be the case in clusters of uncharged particles and in solvents of high permittivity, then the ratio $\langle N(N-1)\rangle/\langle N\rangle$ varies as a function of N_0. Clearly, if all clusters initially contain N_0 particles, then it is possible to work out the initial number of particles in the cluster from the relationship between the asymptotic value of $\langle N\rangle$ and the rate at which this asymptote is approached. However, if the system contains a distribution of initial cluster sizes, then the best that can be done is to calculate the parameter $\langle N(N-1)\rangle/\langle N\rangle$, which gives some insight into the probability distribution of N at long times. For example for a Poisson distribution the ratio is equal to $\langle N\rangle$, for a geometric distribution it is $2\langle N\rangle$, and for any combination of a single pair and nothing it is 1. It is also noteworthy that knowledge of this ratio and the escape yield permits the estimation of the fluctuation of N, $\langle N^2\rangle - \langle N\rangle^2$, which is implicitly assumed to be zero by deterministic theories.[23]

3.2 Cross-reactions Only

A second, and more realistic, scheme where the master equation can be set up and solved explicitly is the scheme in which two species, A and B, are present in the cluster, and only the cross-reaction, A + B, is observed.[22,24] Such a scheme may be realised in experimental systems where clusters of ions are produced in solvents of low permittivity such as hydrocarbons. In such a system the Coulomb forces between the ions are very strong, and encounter of two ions of the same charge is effectively impossible, thus the only reaction observed is between counter-ions. Here we only consider the case where there are equal numbers of cations and anions in the cluster.

The master equation for this system has been discussed previously.[22] If $P_n(t)$ is the probability that the cluster contains exactly n ion pairs at time t, and $\lambda(t)$ has the usual meaning, the master equation is of the form

$$\frac{dP_n}{dt} = (n+1)^2\lambda(t)P_{n+1} - n^2\lambda(t)P_n \tag{14}$$

The solution for the expectation number of pairs remaining is

$$\langle N\rangle_t = \sum_{n=1}^{N_0} \frac{2n[\Gamma(N_0+1)]^2\Pi^{n^2}}{\Gamma(N_0-n+1)\Gamma(N_0+n+1)} \tag{15}$$

Once again, this is a polynomial in Π, and since the asymptotic approach of Π to its long-time limit contains no information about the spatial distribution, neither does $\langle N\rangle_t$.

The long-time behaviour of $\langle N\rangle$ is found to be

$$\langle N\rangle_t \approx \langle N\rangle_\infty + \langle N^2\rangle_\infty \frac{a_{\text{eff}}}{(\pi D't)^{1/2}} \tag{16}$$

and the small-s behaviour of the scavenging yield is

$$y_s(s) \approx \langle N\rangle_\infty + \langle N^2\rangle_\infty\, a_{\text{eff}}(s/D')^{1/2} \tag{17}$$

The second moment of N can also be calculated explicitly

$$\langle N^2\rangle_t = \sum_{n=1}^{N_0} \frac{2n^3[\Gamma(N_0+1)]^2\Pi^{n^2}}{\Gamma(N_0-n+1)\Gamma(N_0+n+1)} \tag{18}$$

The ratio $\langle N^2\rangle/\langle N\rangle$ is plotted as a function of $\langle N\rangle$ in Fig. 3 for a variety of different values of N_0.

If $\langle N\rangle_\infty$ is far from zero the approach to the free-ion yield can be used to extract information about the initial number of particles in the cluster. However, it can be seen from Fig. 3 that if Π is less than *ca.* 0.4, then $\langle N^2\rangle_\infty/\langle N\rangle_\infty$ will be close to unity because of the likelihood that if any particles are left at long times only a single pair will survive. This situation will normally pertain in a solvent of low permittivity since the free-ion yield is usually rather low.[25,26] It will usually be the case, therefore, that $\langle N^2\rangle_\infty \approx \langle N\rangle_\infty$ within a few per cent, and hence the approach to the long-time asymptote or the small s limiting scavenging yield will be indistinguishable from the geminate pair case, *i.e.* eqn. (2) and (7).

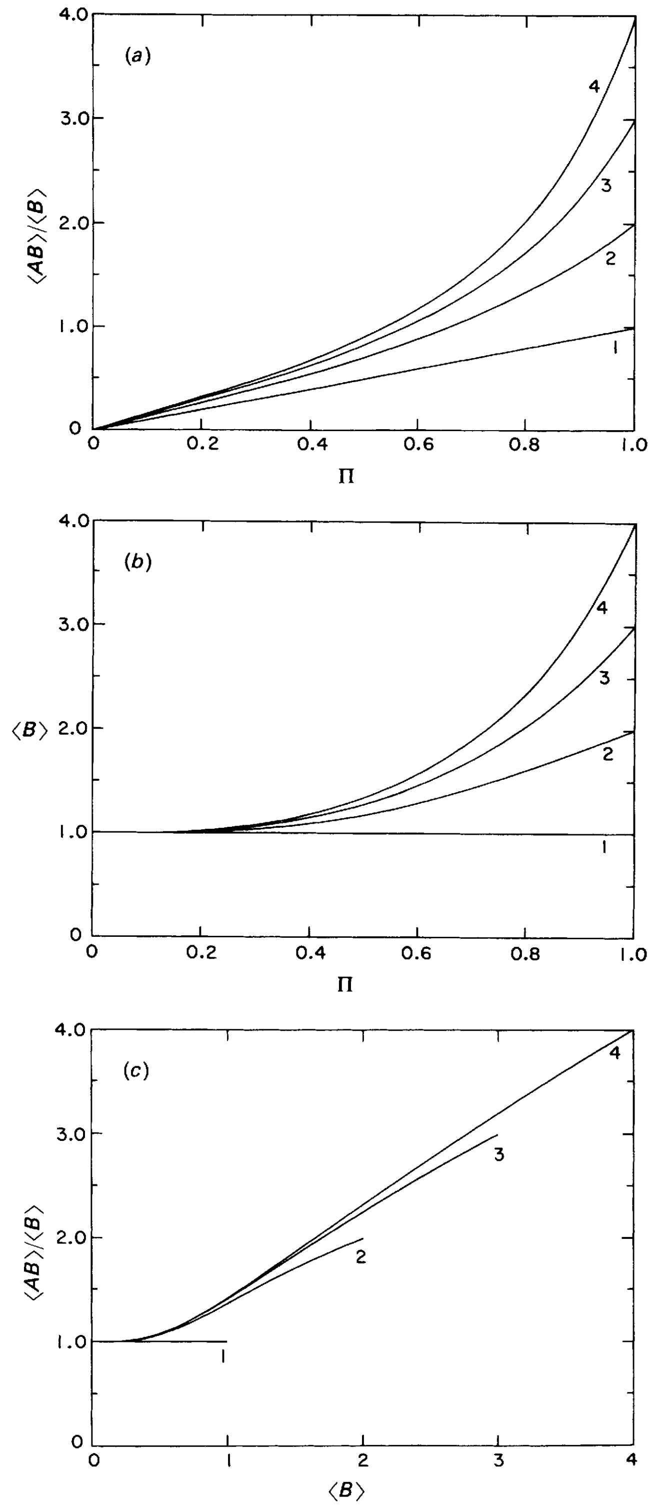

Fig. 3 Survival in two-species spurs: moments of the numbers of pairs remaining in spurs where only cross-reactions are possible. Lines labelled according to the initial number of pairs present. (*a*) Mean number of pairs against Π. (*b*) Mean-square number of pairs divided by the mean against Π. (*c*) Mean-square divided by mean against mean number of pairs remaining.

The manner in which the small-s dependence of the scavenging yield is often parameterized is called into question by this analysis. Experimental scavenging yields are usually fit to an equation with the functional form[27]

$$y_s(s) = \langle N\rangle_\infty + (N_0 - \langle N\rangle_\infty)\frac{(\alpha s)^{1/2}}{1 + (\alpha s)^{1/2}} \quad (19)$$

Other related functions have also been used.[11,28] The parameters used in this fit are N_0 and α. It is clear from the preceding discussion that if only the asymptotic behaviour is observed then no direct information about N_0 can legitimately be extracted. This explains the numerical observation reported previously that this type of fit is very poor at isolating the parameter N_0 unless data are available at least as far as the point of inflexion in the $y_s(s)$ curve.[17] If the fitted function has the correct asymptotics then the parameter α is

$$(\alpha D')^{1/2} = \frac{a_{\text{eff}}\langle N^2\rangle_\infty}{N_0 - \langle N\rangle_\infty} \quad (20)$$

If the free-ion yield is small so that $\langle N^2\rangle_\infty \approx \langle N\rangle_\infty$, and the fraction of ions surviving at long times, $\langle N\rangle_\infty/N_0$ is denoted f, then this can be written

$$(\alpha D')^{1/2} \approx a_{\text{eff}}\frac{f}{1-f} \approx a_{\text{eff}} f \quad (21)$$

Thus the parameter α does not have any simple interpretation in terms of the factors governing the rate of recombination; it is a compound parameter incorporating a measure of the recombination rate, $a_{\text{eff}}/D'^{1/2}$ and a factor measuring the escape yield, $f/(1-f)$. This latter factor appears simply because $(1-f)/f$ has been factored out in the way that the equation has been written. Of course if data are available over a wide range of scavenger concentration then the type of parameterization in eqn. (19) permits a fit which has the correct limit at high scavenger concentrations N_0 and the correct asymptotic behaviour for small values of s. However, the parameter α is a composite and cannot be interpreted simply in terms of the recombination rate.

One corollary of this discussion involves the kinetics inferred from a fit to the scavenging yield such as that discussed above. These are obtained by inverse Laplace transform (ILT) of the fitting function, which gives in the case of eqn. (19)

$$\langle N\rangle_t^{\text{ILT}} = \langle N\rangle_\infty + (N_0 - \langle N\rangle_\infty)\exp(t/\alpha)\text{erfc}[(t/\alpha)^{1/2}] \quad (22)$$

Although the kinetics predicted by the ILT method are governed by the timescale α, and the long-time asymptotics of the decay are correct, it is clear that the α parameter has no wider significance as a fundamental universal parameter governing the rate of the recombination reaction because it is a composite of the rate parameter, moments of the escape yield and the initial number of pairs present. Furthermore, if the free-ion yield is small, α is simply a composite of the rate parameter and the fraction of ions ultimately reacting (or surviving). It therefore depends on the factors that determine N_0, such as the stopping power of the radiation, the radiation quality and the solvent.

4. More Complex Schemes

The schemes dealt with in Section 3 are simplifications of reality, although the second scheme is generally used to describe ion-recombination kinetics in solvents of low permittivity. It is relatively easy to set up the master equation for more complicated reaction schemes in which particles formed in the cluster can undergo several different intra-cluster reactions in addition to the possibility of scavenging.[18,29] If the complete decay is required, the master equation must be solved numerically, however explicit solutions can be obtained for the long-time asymptotics of the decay kinetics, or for the small-s asymptotics of the scavenging yield, by using perturbation methods, as described in ref. 17. For a prototype general reaction scheme

$$A + A \rightarrow AA \quad (I)$$

$$A + B \rightarrow AB \quad (II)$$

$$B + B \rightarrow BB \quad (III)$$

where the effective reaction distance for reaction i is denoted a_i and the relative diffusion coefficient D_i, the long-time asymptotics of the expectation number of B particles are given by

$$\langle B\rangle_t \approx \langle B\rangle_\infty + \langle B(B-1)\rangle_\infty \frac{a_3}{(\pi D_3 t)^{1/2}} + \langle AB\rangle_\infty \frac{a_2}{(\pi D_2 t)^{1/2}} \quad (23)$$

where B denotes the number of B particles and A the number of A particles remaining in the cluster. Similarly, if a scavenger for species B is included, the small-s asymptotics of the scavenging yields are[17]

$$y_s(s) \approx \langle B\rangle_\infty + \langle B(B-1)\rangle_\infty a_3(2s/D_3)^{1/2} + \langle AB\rangle_\infty a_2(s/D_2)^{1/2} \quad (24)$$

These formulae may be extended in an obvious way to schemes in which any arbitrary number of spur species can react with B simply by adding further terms of the same type as the final term in eqn. (23) and (24), one term for each species. In both cases it is clear that the asymptotics contain information about the ratios $\langle B(B-1)\rangle_\infty/\langle B\rangle_\infty$ and $\langle AB\rangle_\infty/\langle B\rangle_\infty$, that is about the variance and the covariance of the numbers of particles of each species remaining in the long-time limit.

Although information about the ratios $\langle B(B-1)\rangle_\infty/\langle B\rangle_\infty$ and $\langle AB\rangle_\infty/\langle B\rangle_\infty$ is present, it is not possible to isolate it from any one given set of experimental data. One possible method for extracting information about the second moments relies on the extra factor of $2^{1/2}$ which appears in the contribution to the scavenging yield from the B + B reaction. In principle the appearance of this factor enables the separation of the two moments $\langle B(B-1)\rangle_\infty$ and $\langle AB\rangle_\infty$ if both the asymptotic time-dependence of $\langle B\rangle$ and the small-s behaviour of y_s are known. Defining ζ and ξ to be the coefficients of $s^{1/2}$ and $1/(\pi t)^{1/2}$ in the limiting behaviour of the scavenging yield and the time-dependent decay respectively, *i.e.*

$$\zeta \equiv \lim_{s\to 0}\frac{y_s(s) - \langle N\rangle_\infty}{s^{1/2}} = \langle B(B-1)\rangle_\infty 2^{1/2}\frac{a_3}{(D_3)^{1/2}} + \langle AB\rangle_\infty \frac{a_2}{(D_2)^{1/2}} \quad (25)$$

and

$$\xi \equiv \lim_{t\to\infty}(\langle N\rangle_t - \langle N\rangle_\infty)(\pi t)^{1/2} = \langle B(B-1)\rangle_\infty \frac{a_3}{(D_3)^{1/2}} + \langle AB\rangle_\infty \frac{a_2}{(D_2)^{1/2}} \quad (26)$$

it is easy to see that these are non-equivalent simultaneous equations for the two second moments, whose resolution gives

$$\langle B(B-1)\rangle_\infty \frac{a_3}{(D_3)^{1/2}} = \zeta - \xi \qquad (27)$$

$$\langle AB\rangle_\infty \frac{a_2}{(D_2)^{1/2}} = \xi\sqrt{2} - \zeta \qquad (28)$$

(Since A and B can only take positive integer values, the two moments $\langle B(B-1)\rangle$ and $\langle AB\rangle$ must be positive.) The parameters a_i and D_i are frequently known in advance, for example from measurements of the steady-state rates of the relevant reactions as a function of temperature.[30] In this case it is clearly possible in principle to estimate $\langle B(B-1)\rangle_\infty$ and $\langle AB\rangle_\infty$. In practice it is not likely that experimental data will be good enough to make this separation.

5. Conclusions

It is well known that the asymptotic approach to the escape probability for a geminate pair contains no information on the initial spatial distribution of the particles. The rate of approach to the asymptote depends only on the quantity $a_{\text{eff}}/(D')^{1/2}$, which is the same quantity that governs the asymptotic decay of the time-dependent rate constant to the steady-state limit in homogeneous systems. The same conclusion is obtained from an analysis of scavenging experiments in the low-concentration limit, because the two are related by a Laplace transform type of relationship.[27,28] This article questions whether the same result is true for systems which contain more than two reactive particles, or whether the asymptotic approach to the escape yield contains further information.

The analysis reported here relies on the independent-pairs approximation, but it has been shown for many systems that this approximation is extremely accurate,[18–20] and in the few systems where it does break down the final approach to the escape yield is still generally accurate.[20] The results of the analysis show that there is no further information about the spatial distribution from either the long-time asymptotics of the time dependence or from the small-s asymptotics of the scavenging yield. Although the time-dependent rate coefficient appropriate for the non-homogeneous recombination reactions, $\lambda(t)$, defined by eqn. (5), depends on the initial distribution, its long-time asymptotics are simply related to those of the geminate survival probability $\Pi(t)$, which are known to be independent of the initial spatial distribution.

While no information is available from the asymptotics on the spatial distribution, it has been shown here that there is some extra information about the variance and covariances of the numbers of particles of each species surviving, and since for a given escape yield these moments depend on the initial number of particles in the cluster, they provide an indirect probe of the initial number distribution. For simple (single) reaction schemes it is straightforward to extract the second moments of interest from either the asymptotic time-dependence or the scavenging yield. However, the only simple scheme likely to be realistic (ion recombination in hydrocarbons) generally has such low yields that the second moment is very close to the expectation number of pairs surviving, and under these conditions, where only a single pair (if anything) survives, the data contain no more information than the geminate recombination experiments. It is shown, in principle, how the fluctuation of the number of scavengable particles remaining can be separated from the cross-products.

All the analysis reported here has used the true analytic asymptotic time-dependence of the recombination probability, which can be obtained from exact or asymptotic solutions to the diffusion equation. However, experiments for systems of ions in solvents of low permittivity indicate that the true asymptotics pertain at such long times that they are not actually experimentally significant. Numerical analysis of the Debye–Smoluchowski equation seems to support this observation, and it also seems that the apparent power law observed in the tail of the time-dependent kinetics or the scavenging yield depends on the initial width of the spatial distribution. If this proves to be the case then at least in hydrocarbons the asymptotic power law may provide information on the initial spatial distribution. This observation is currently under investigation, and results will be reported elsewhere.

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