

APPLICATION OF STOCHASTIC MODELS TO RADIATION CHEMISTRY.



A thesis submitted for the degree of Doctor of Philosophy

by

Simon M. Pimblott.

St. Peter's College, Oxford.

Trinity Term, 1988.

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ABSTRACT.

This thesis addresses one area of major interest in reaction kinetics, the theoretical description of recombination in nonhomogeneous systems. The reaction of the highly reactive particles formed by the passage of ionising radiation through a medium is an important example of this type of system.

Stochastic effects are apparent in every stage of the development of a radiolysis system: in the interaction between the radiation and the medium and in the diffusion and reaction processes that follow. Conventional models for nonhomogeneous kinetics in radiation chemistry are based upon a deterministic analysis. These models are appraised together with an alternative stochastic approach. Three stochastic methods are discussed: a full Monte Carlo simulation of the diffusion and reaction and two approximate models based upon an independent pairs approximation.

It is important that any kinetic model accurately describes the system it purports to represent and this can only be assured by extensive validation. The stochastic models are developed to encompass the diffusion-controlled reactions of ions and radicals and to include the effects of a bulk electrolyte upon the reactions between ions. To model a realistic radiation chemistry reaction scheme, it is necessary to consider reactions that are not fully diffusion-controlled. The radiation boundary condition is introduced and used to extend stochastic modelling to partially diffusion-controlled reactions. Recombination in an anisotropic environment is also considered.

Although a complete analysis of the chemistry of a radiolysis system requires a complex reaction scheme, the scheme can be simplified, in acid and in alkali, by the use of an instantaneous scavenging approximation. In acid, this approximation produces a simple three reaction mechanism based upon five species: H, OH, H₂, H₂O and H₂O₂. The acid system is used to demonstrate the stochastic treatment of realistic kinetics. The instantaneous scavenging approximation is examined in detail and techniques are developed for the explicit modelling of reactions with a homogeneously distributed scavenger.

A stochastic treatment of nonhomogeneous reaction kinetics requires a description of the initial spatial distribution of the reacting particles. A rudimentary Monte Carlo simulation is used to determine a simple distribution of clusters of reactive particles similar to that found along the path of a high energy electron in water. This distribution provides a suitable basis for kinetic simulation. The kinetics of a more detailed idealised track structure are also considered and the stochastic and deterministic kinetics of extended particle distributions are discussed.

For Margaret, my Mother.

ACKNOWLEDGEMENTS.

I would like to thank my friends and colleagues without whom the past three years would have been much less fun. I owe a great deal to several special people:

Mike Pilling, for interest, encouragement and an opportunity to air my views;

Bob Burns, without whom this research project would not have reached fruition;

Asoke Mozumder, who suggested the studies described in chapters III.3 and III.5;

Peter Clifford, a mathematician who understands chemists;

Jay LaVerne, for providing the DOSDs used in the calculations of chapter III.3.

I am grateful to Dr. Pilling's research group for keeping my feet on the ground and providing many interesting discussions. In particular, I acknowledge the assistance of Martin Keiffer and Simon Davies in keeping the staff of Halifax House gainfully employed.

Finally, I would like to thank Nick Green for helpful discussions, numerous arguments and his assistance in the production of this thesis. The studies of chapters II.3 and III.4 were performed in collaboration.

The work presented in this thesis was funded by the U.K.A.E.A., Harwell.

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REFERENCES.

SECTION I : Introduction.

Chapter 1 : The early events in radiation chemistry.

This thesis describes the development of stochastic techniques for modelling nonhomogeneous kinetics. The aim is to introduce a methodology that is suitable for application to the period of fast reaction immediately following the radiolysis of a liquid. In this first chapter, the origins of the nonhomogeneous distribution of reactive particles are discussed and the importance of considering statistical effects is emphasised.

1.1 Radiolysis.

As a high energy particle passes through matter, it loses energy. The electromagnetic field induced by the motion of the particle couples with the fields of the molecular electrons of the medium and the result is a track of discrete energy deposition events marking the path of the primary particle. The characteristics of this energy transfer vary along the track as the energy of the primary radiation particle is reduced. Separations between successive energy losses are random and obey local Poisson statistics (Mozumder et al., 1968). The track itself is a stochastic phenomenon and while in detail each radiation track is different, the statistical properties are determined by the medium and by the velocity and the charge of the radiation (Heckman & Starring, 1967).

The chemical consequences of the transfer of energy from the radiation are ionisation and excitation of the medium, creating highly excited molecular and ionic species and energetic electrons. The track initially consists of a series of ionisation and excitation events (Mozumder & Magee, 1975) in which the identity of

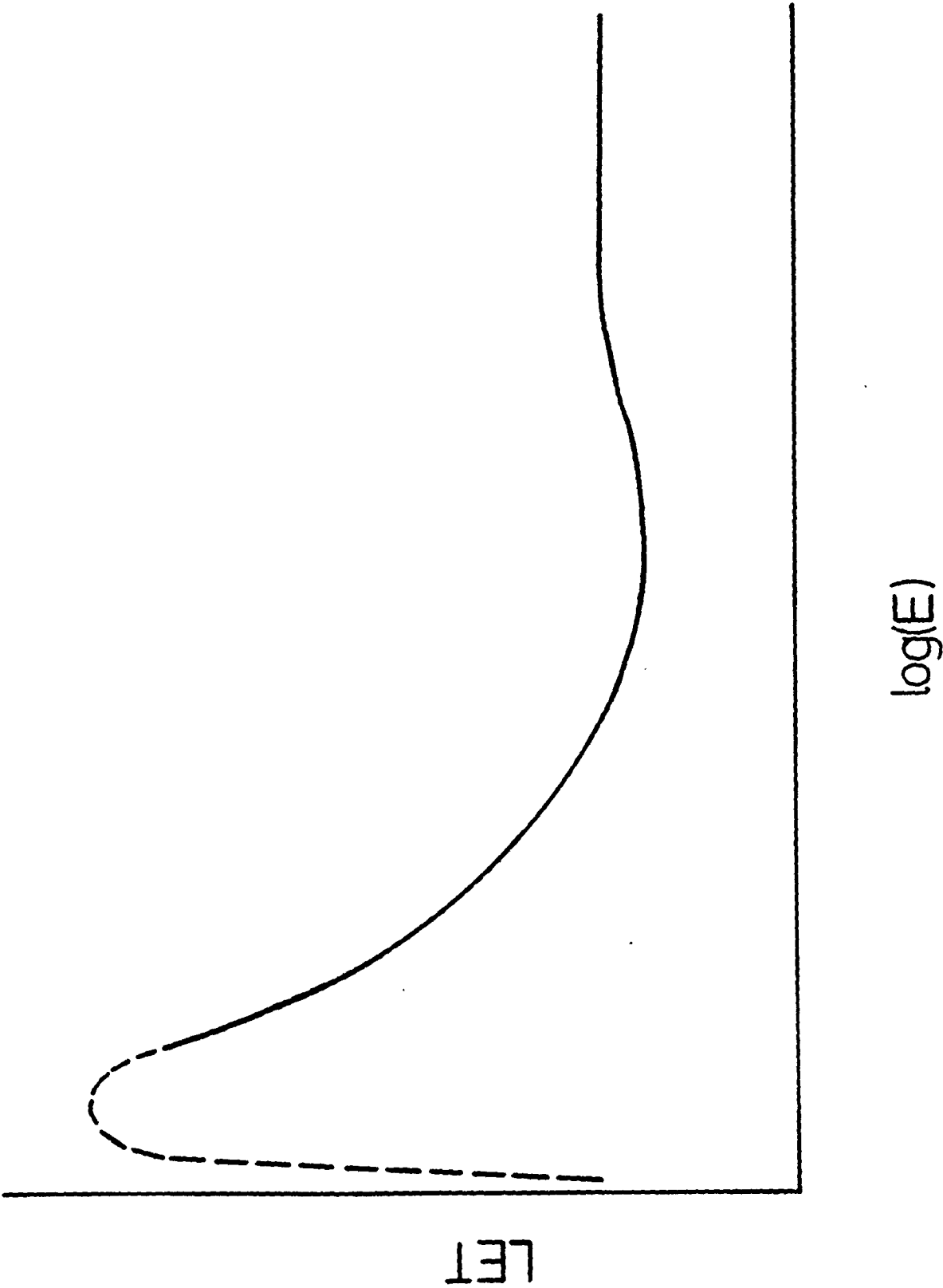
a particular molecular ion or excited molecule and its internal and kinetic energy depend upon the energy lost to the medium in the parent deposition event and upon the phase of the medium (Platzman, 1967). A discrete energy loss may result in either a single ionisation/excitation event or a group of spatially correlated events.

Ionisation and excitation take place on a subfemtosecond timescale (Magee, 1953) and are followed by the fragmentation of the molecular species into 'hot' ions and radicals. These particles rapidly lose their translational energy and thermalise close to the site of the original deposition event. The daughter electrons, produced in ionisations, travel further than their heavier partners and may, given sufficiently high energies, form their own secondary ionisation/excitation tracks, known as delta-rays.

1.2 Radiation quality effects.

The complicated spatial correlations of the distribution of particles along a radiolysis track are determined by the rate at which energy is lost by the radiation to the medium and by the dynamics of the thermalisation and fragmentation processes that follow. The former influence on the distribution is expressed in terms of a radiation quality effect. In chemistry, radiation quality is usually described by the stopping power or Linear Energy Transfer, $LET = - \frac{d\langle E \rangle}{dx}$, of the radiation in the medium. (E is the kinetic energy of the radiation particle and x is the distance travelled.) The behaviour of LET as a function of energy is shown in Fig.I.1.1. Whilst theoretical treatment of energy loss at very low velocities is difficult (LaVerne & Mozumder, 1984), the curve is adequately described from the maximum to the plateau of highly

Fig.I.1.1 Schematic variation of LET with the kinetic energy of an electron.



relativistic particles by the Bethe-Bloch equation (Bethe, 1930, 1932)

$$\frac{d\langle E \rangle}{dx} = - \frac{N z^2 Z}{\beta^2} F(\beta, I) \quad (I.1.1)$$

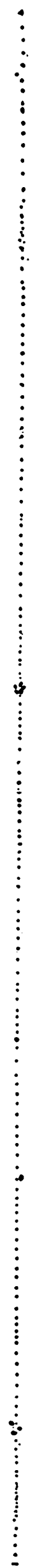
where N and Z refer to the number density of the medium and the number of electrons per molecule and where $F(\beta, I)$ is a function that is dependent on the velocity, $\beta = v/c$, of the radiation particle, whose charge is ze , and upon the ionisation potential, I , of the absorbing material.

For a low LET radiation, e.g. high energy electrons, the mean separation between energy deposition events is large and the resulting particle distribution can be considered to consist of discrete clusters (Kara-Michailova & Lea, 1940). When the distance between energy deposition events is small, that is in the high LET limit of heavy nuclei, for example C^{6+} or Ne^{10+} , the spatial distributions of the molecular fragments from different events overlap and, rather than discrete clusters, a 'cylindrical core' of particles is generated (Christman & Appleby, 1981). As a radiation particle loses energy, its LET increases and the mean separation of successive energy deposition events is reduced, i.e. the particle distribution is affected by the degradation in energy.

Fig.I.1.2 is a schematic picture showing the difference between low and high LET tracks (Allen, 1961). Each dot represents an energy deposition event and the three tracks are for (i) a 40 keV electron, (ii) a 18 MeV deuteron and (iii) a 5.5 MeV alpha particle. On this scale a 1 MeV electron would probably not suffer an energy loss in the length considered.

The use of LET to describe radiation quality is problematical. It is an average measure and, as the name suggests, it does not

40 keV electron in water.



18 MeV deuteron in water.



5.5 MeV alpha particle in water.



10nm

Fig.I.1.1.2 A schematic representation of a radiation track. (Allen, 1961).

provide a 3-dimensional description of the absorbed dose. Radiations with the same LET (e.g. $-\frac{d\langle E \rangle}{dx} \sim 68 \text{ eV/nm}$ for both 750 keV protons and 18 MeV alpha particles in liquid cyclohexane) may result in tracks with different distributions of energy (Miller & West, 1981). There is no allowance for the spatial integrity of delta-rays, which represent regions where the particle distribution is different from that in the main track.

Dose, the total quantity of energy absorbed per unit mass, and dose rate play an important role in determining the relative distribution of reactive particles in radiolysis (Mozumder, 1969). At high dose and high dose rate the density of tracks is large and so the chance of intertrack overlap is considerable. As the dose rate is reduced, the separation between tracks of different primary particles increases and the proximity of tracks becomes less important. The influence on the kinetics of radicals and ions surviving from older tracks must still be considered. It is only in the limit of low dose rate that a radiation track can be thought of as isolated.

1.3 Fragmentation and thermalisation.

While the nature of the radiation influences the distribution of energy loss events along a track, the detailed structure of a cluster is determined by the fragmentation of the excited molecular and ionic species produced by the energy deposition and by the thermalisation of the resulting ions and radicals. For simple molecular gases, the possible fragmentation channels of the molecular and ionic species, created during excitation and ionisation, are complex (Green, 1982). They depend upon the internal state of the molecular ion or excited molecule, upon the energetically available products and upon the shape of the potential energy surfaces. In condensed media, the picture is more

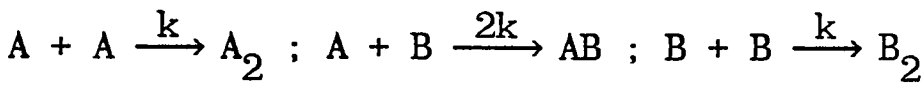
complicated and experimentally less accessible (Quickenden et al., 1980). The thermalisation of the 'heavy' particles is determined by the complicated dynamics of the parent fragmentation and depends upon the local structure of the medium, which is disturbed by the deposition of energy. Thermalisation and solvation of low energy electrons have been studied in depth both theoretically and experimentally (LaVerne & Mozumder, 1984). Frequently, the two processes cannot be considered as separate as they take place on a very short timescale (Migus et al., 1987). The trapping of the electron may take place either before or after thermalisation and the number of pre-existing traps depends critically on the solvent (Funabashi, 1974). Experimentally, trapping has been shown to be particularly important in polar media (Baxendale & Wardman, 1971; Hase et al., 1971) and, in fact, "proper thermalisation" has not been demonstrated, either experimentally or theoretically, in polar liquids (LaVerne & Mozumder, 1984).

A few picoseconds after radiolysis a nonhomogeneous distribution of highly reactive radicals and ions remains, which consists of groups of particles clustered about the initial energy deposition sites. This nonhomogeneous distribution is kinetically very important as its subsequent evolution, by diffusion and reaction, constitutes a significant fraction of the overall chemistry of the system.

1.4 The importance of spatial correlations.

The radicals and ions formed in the physico-chemical stages of radiolysis, described briefly above, are highly reactive. In general, the particles react on encounter so their kinetics are determined by the corresponding first encounter times and are described as diffusion-controlled. The time-dependent behaviour of the reactive particles and the nature of the products formed

depends critically on the number and the distribution of reactive particles. The importance of both factors can be illustrated by considering a simple idealised scheme,



where A and B particles are identical, except in name, and where the rate constants are those for the formation of products. For a homogeneous system, with equal concentrations of A and B, the expected product ratio, $A_2:AB:B_2$, is 1:2:1. This is not the case for discrete isolated clusters of particles. For example, where both species initially have the same spatial distribution, the product ratio depends on the initial numbers, N_A and N_B , of particles in the cluster and is given by

$$^{1/2} N_A(N_A-1) : N_A N_B : ^{1/2} N_B(N_B-1).$$

This effect is shown in Table I.1.1.

Table I.1.1 Statistical Effects on Product Ratios.

N_A, N_B	1,1	2,2	3,3	4,4
Product Ratio, $A_2:AB:B_2$	0:1:0	1:4:1	1:3:1	3:8:3

The homogeneous limit is only reached for clusters containing large numbers of particles, $N_A = N_B > 50$.

The appropriate kinetic description, for the highly reactive systems that are produced by radiolysis, lies somewhere between these simplistic nonhomogeneous and homogeneous limits because the clusters are not isolated for all time. The path of a heavy radiation particle has a concentration profile that is homogeneous in one dimension, but not in the other two, whilst the track of a high energy electron consists of initially discrete and generally

unequal clusters of radicals and ions at its low LET beginning and resembles a heavy ion 'core' at the high LET track-end. Clearly, statistical effects are important in the fast kinetics that occur as the spatial correlations of the particles relax and as these short-time kinetics are the only source of information about such correlations, any kinetic model used to obtain this information must accurately represent the system it describes.

Chapter 2 : Conventional modelling in radiolysis.

This chapter is a brief summary of the conventional techniques used in modelling the kinetics of nonhomogeneous systems. The discussion begins with an examination of the recombination of an isolated pair and then introduces the models employed for larger clusters and extended distributions. Important results and conclusions are presented, but the methodology is not reproduced in detail. (If a model is used in an unorthodox manner at a later stage, a detailed description is included at that point.) The chapter ends with a brief critique of the conventional kinetic methods.

2.1 Geminate recombination.

The simplest possible cluster is a pair of reactive particles isolated in an infinite space. Geminate recombination, as this is known, can be divided into two categories: when at least one reactant is uncharged and when both reactants are ions. In the former case, where there is no electrostatic force, the approach of the pair is governed by their relative diffusive motion and can be described in terms of the probability density, ρ , of the pair being at a separation r , which obeys a diffusion equation

$$\frac{\partial \rho}{\partial t} = D' \nabla^2 \rho + \delta(r-r_0) \delta(t-t_0). \quad (I.2.1)$$

The constant D' is the relative diffusion coefficient of the pair and the second term in the diffusion equation - the product of two delta functions - represents the formation of the pair at time t_0 at a distance r_0 . To calculate the survival probability, Ω , or the reaction probability, W , of the pair, equation (I.2.1) must be solved using the appropriate boundary conditions. In the limit of

diffusion-controlled reaction, i.e. instantaneous reaction on encounter at a separation R , the ultimate probability of reaction is (Crank, 1956)

$$\Omega(r_0, \infty) = 1 - \frac{R}{r_0} \quad (\text{I.2.2})$$

and the time-dependent survival probability is

$$\Omega(r_0, t) = 1 - \frac{R}{r_0} \operatorname{erfc}(\{r_0 - R\} / 2\sqrt{D't}). \quad (\text{I.2.3})$$

The partially diffusion-controlled process has also been treated exactly (Collins & Kimball, 1949). In this case, the rate of reaction at the encounter distance is assumed to be proportional to the probability that the pair exists. This is known as a radiation boundary condition by analogy with heat conduction.

When the reactive particles are charged, the electrostatic force modifies the diffusive trajectories and the appropriate diffusion equation for ρ is (Debye, 1942)

$$\frac{\partial \rho}{\partial t} = \nabla \cdot D' \left[\nabla \rho + \frac{\rho}{k_B T} \nabla U \right] + \delta(r - r_0) \delta(t - t_0). \quad (\text{I.2.4})$$

This is known as the Debye-Smoluchowski equation, U is the electrostatic potential and k_B is the Boltzmann constant. If U is Coulombic and the reaction is diffusion-controlled, the ultimate escape probability of an oppositely charged pair is (Debye, 1942)

$$\Omega(r_0, \infty) = \frac{\exp\left[r_c / r_0\right] - \exp\left[r_c / R\right]}{1 - \exp\left[r_c / R\right]}. \quad (\text{I.2.5})$$

The Onsager distance, r_c , is the separation at which the Coulombic interaction of the particles equals $k_B T$. This 'separation' is negative for an attractive pair and positive for a repulsive pair. If the natural distance scale,

$$r_{\text{eff}} = \frac{-r_c}{1 - \exp\left[r_c / r_0\right]}, \quad (\text{I.2.6})$$

is used, equation (I.2.5) becomes

$$\Omega(r_0, \infty) = 1 - \frac{R_{\text{eff}}}{r_{\text{eff}}} \quad (\text{I.2.7})$$

which has the same form as the ultimate survival probability of a reacting pair in the absence of an interparticle force.

No exact, closed form of the time-dependent survival probability is available and it has been claimed (Delaire et al., 1981) that a closed analytic solution is not possible. An exact (but not closed) analytic formulation of the time-dependent escape probability is available in Laplace transform space (Hong & Noolandi, 1978). This solution is a complicated series. A number of simpler approximations have been published (Pedersen & Sibani, 1981; Raaen & Hemmer, 1982), but even the simplest of these has to be inverted numerically as contour integration does not give a closed formula. At least in terms of kinetic modelling, the inversion of a Laplace transform solution by numerical techniques holds no advantage over direct numerical integration of the Debye-Smoluchowski equation. Typical numerical treatments of the recombination of an ion-pair are those of Ludwig (1969) and Hummel and Infelta (1974).

The search for a closed analytic solution for equation (I.2.4) with $U = r_c/r_o$ has led to the derivation of several approximate formulations for $\Omega(r_o, t)$. Generally these analytic approximations refer to a particular region of interest and are of the form

$$\Omega(r_o, t) = 1 - W_\infty W_* \quad (\text{I.2.8})$$

where W_∞ is the ultimate probability of reaction,

$$W_\infty = \frac{1 - \exp(-r_c / r_o)}{1 - \exp(-r_c / R)} \quad (\text{I.2.9})$$

and W_* is an analytic approximation for the time-dependent reaction probability of a pair that will eventually react. Clifford et al. (1984) presented a detailed "discussion of the approach to approximate solution" and derived two equations describing recombination in high permittivity solvents. The first refers to water ($|r_c| = 7.0 \times 10^{-10}$ m) and the time-dependent approximation for the conditioned reaction probability is

$$W_* = \operatorname{erfc} \left[\frac{r_c}{4\sqrt{D't}} \{ \coth(r_c/2r_o) - \coth(r_c/2R) \} \right]. \quad (\text{I.2.10})$$

In the natural distance scale, equation (I.2.8) is

$$\Omega(r_o, t) = 1 - \frac{R_{\text{eff}}}{r_{\text{eff}}} \operatorname{erfc} \left[\frac{r_{\text{eff}} - R_{\text{eff}}}{2\sqrt{D't}} \right] \quad (\text{I.2.11})$$

which is equivalent to equation (I.2.3) for neutrals. The second

approximation applies to high permittivity solvents from methanol onwards. Here,

$$W_{*}(r_o, t) = \frac{1}{2} \operatorname{erfc}(S(t) - \phi(t)) + \frac{1}{2} \exp(2S(t)\phi(t)) \operatorname{erfc}(S(t) + \phi(t)) \quad (\text{I.2.12})$$

where

$$S(t) = \frac{r_{\text{eff}} - R_{\text{eff}}}{2\sqrt{D't}}$$

and

$$\phi(t) = \frac{(0.50R - 0.45|r_c|)}{2\sqrt{D't}} \quad ; \quad R \leq 0.8|r_c|$$

$$\phi(t) = 0 \quad ; \quad R > 0.8|r_c|.$$

Comparisons of the equations of Clifford et al. with numerical solutions of the Debye-Smoluchowski equation show excellent agreement, within the regions of interest.

A closed analytic approximation for $\Omega(r_o, t)$ in low permittivity solvents has been derived by Mozumder (1968). This solution is based upon the assumption that the probability density of the ion pair is a Gaussian at all times,

$$\Omega(r_o, t) = \exp \left[\frac{r_c}{r_o} \operatorname{erfc} \left[\frac{r_o}{2\sqrt{D't}} \right] \right]. \quad (\text{I.2.13})$$

(Prescribed diffusion, as the assumption of a Gaussian profile is known, is considered in detail later in this chapter.) This equation has the correct long time asymptote ($R \ll |r_c|$),

$$\Omega(r_o, \infty) = \exp(r_c / r_o), \quad (\text{I.2.14})$$

but compares poorly with numerical solution of the Debye-Smoluchowski equation (Clifford et al., 1984).

2.2 Initial recombination.

The period of fast recombination prior to general homogeneous reaction was first recognised by Bragg and Kleeman (1906) in their studies of the radiolysis of molecular gases. They postulated the occurrence of "initial recombination" of the ejected electron and its sibling ion and then went on to examine the dependence of this geminate recombination on the nature of the ionising radiation (Kleeman, 1906). The description of fast radiolysis kinetics in terms of the recombination of geminate pairs is not generally acceptable, although the 'picture' of Bragg and Kleeman is useful when the free ion yield is low. This type of system, where the number of reactive particles escaping to the bulk is small, is typical of the low LET irradiation of a low permittivity medium. Under these circumstances, the Coulombic forces between ions are strong and any multipair cluster will very rapidly degrade to a single pair. However, in modelling radiolysis kinetics it is usually necessary to consider the development of a many particle system.

The first theoretical treatment of an "initial recombination" problem was not made until several years after the studies of Bragg and Kleeman. Following Wilson's experimental demonstration of the columnar nature of a radiolysis track (Wilson, 1911, 1912), Jaffe (1913) modelled the kinetics of recombination in ionisation columns. The general approach outlined by Jaffe in his pioneering study provides the basis for most conventional models of radiolysis kinetics. These models consider a hypothetical average system, which is characterised in terms of a local concentration of each species. Macroscopic laws are used to describe the diffusion of the

particles and reaction is modelled using deterministic kinetics which deal with net changes in the average concentration. The result is a set of coupled macroscopic diffusion-reaction equations that are supposed to describe the nonhomogeneous kinetics. Each equation has the form (Schwarz, 1969):

$$\frac{\partial C_i}{\partial t} = D_i \nabla^2 C_i - \sum_j k_{ij} C_i C_j + \sum_{j,k}' k_{jk} C_j C_k \quad (\text{I.2.15})$$

where D_i and C_i are the diffusion coefficient and concentration of species i , respectively. The first term of the right hand side represents the diffusive contribution to the evolution of C_i , whilst the second and third terms represent, respectively, reactive removal and production of species i . The prime on term 3 implies that the summation only applies to those reactions in which species i is formed. The justification for the use of diffusion-reaction equations of this form has been considered by Monchick, Magee and Samuel (1957), but most studies proceed without any such consideration (Kara-Michailova & Lea, 1940; Samuel & Magee, 1953; Magee, 1955). The coupled set of equations is solved either numerically or by analytic approximation.

2.2.1 Prescribed diffusion.

The most frequently used analytic, approximate models for the fast kinetics following radiolysis are based on an approximation suggested by Jaffe (1913) and known as prescribed diffusion. The initial spatial distribution of particles is assumed to be Gaussian and the kinetic analysis invokes the approximation that reaction only affects the number of particles and not the form of the nonhomogeneous concentration profile which is, therefore, always Gaussian. Jaffe considered an effectively 2-D columnar system and

the approximation was generalised to include clusters by Samuel and Magee (1953). The prescribed diffusion approximation relies upon the Green's function solution for the diffusion equation being a Gaussian whose variance develops as a linear function of time (Einstein, 1926). If the kinetics are nonlinear, this assumption is incorrect (Schwarz, 1969).

When considering the fast kinetics of low LET radiolysis, conventional analytic models describe the system in terms of an isolated, typical cluster, known as a spur (Magee et al., 1965), with an average spherically symmetric Gaussian concentration profile. The concentration profile of species i is

$$C_i(t) = N_i(t) (\pi b_i^2)^{-1.5} \exp(-r^2/b_i^2). \quad (I.2.16)$$

where N_i is the number of i particles in the spur, r is the distance from the centre of the spur and b_i is a length characteristic of the Gaussian. The variable b_i is time dependent, $b_i^2 = 4D_i(t+t_0)$, and includes the initial width of the Gaussian, $\sqrt{2D_i t_0}$. The symmetry constraint greatly simplifies the analysis as it implies that it is only necessary to consider the radial evolution, i.e. in equation (I.2.15)

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r}. \quad (I.2.17)$$

In the studies of Magee and co-workers (Samuel & Magee, 1953; Monchick et al., 1957; Mozumder & Magee, 1966b), the prescribed diffusion approximation was used to examine single species spurs. Later, the methodology was extended to more generalised reaction schemes and to include time-dependent rate coefficients and attempts were made to account for the occurrence of faster reaction

close to the centre of a cluster. This faster reaction is a consequence of the second order kinetics. To retain the simplifying Gaussian profile, a nonlinear time dependence was introduced (Schwarz, 1969; Burns & Curtis, 1972),

$$\frac{d(b_i^2)}{dt} = 4D_i + \beta(t). \quad (I.2.18)$$

The time-dependent variable, $\beta(t)$, is rather arbitrary and depends upon the method by which it is evaluated. It has the form,

$$\beta(t) = \alpha \frac{k N_i(t)}{b_i (2\pi)^{1.5}} \quad (I.2.19)$$

where α is a constant and is different in the two derivations as they are based upon different approximations.

When studying the kinetics of an ionisation column - a high LET track - the concentration profile is usually considered to be cylindrically symmetric,

$$C_i(t) = \frac{N_i(t)}{\pi b_i^2} \exp(-r^2/b_i^2), \quad (I.2.20)$$

where N_i is now the number of particles per unit length of track. The diffusion operator is

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r}. \quad (I.2.21)$$

An alternative treatment of high LET radiolysis was suggested by Ganguly and Magee (1956). This model develops the track as a string of spurs. Each spur has a Gaussian profile throughout its lifetime

and all the spurs have initially the same contents, but the separation between spurs is random with the average spacing depending on the LET of the radiation.

2.2.2 Numerical methods.

Even in the simple one-species studies mentioned above, mathematical approximations are necessary to make analytic solution possible. Numerical integration of the coupled diffusion-reaction equations provides an alternative. This approach was employed by Kupperman (Kupperman & Belford, 1962a, 1962b; Kupperman, 1967) to examine the kinetics of both spherically and cylindrically symmetric systems - low LET spurs and high LET tracks. The non-linear differential equations were simplified by the introduction of "convenient dimensionless variables" and integration was performed by a finite difference method. Recently, Burns et al. (1984) have presented an alternative numerical method. This method relies upon an efficient coupled differential equation solver, FACSIMILE (Chance et al., 1977), and accommodates spatial nonhomogeneity by combining reaction within discrete homogeneous cells with transport between the cells. Burns' method has also been applied to low and high LET systems. Unlike prescribed diffusion models, the numerical methods are not restricted to an initially Gaussian concentration, nor do they impose this profile upon the system as it develops by diffusion and reaction.

2.2.3 Ionic effects.

The techniques discussed above deal with the kinetics of uncharged species. The consequence of radiolysis is a nonhomogeneous distribution of radicals and ions. Even in the limit of low LET radiolysis, the single pair approximation is only valid for low permittivity solvents (Magee & Chatterjee, 1980). Ionic effects in water radiolysis have been studied using macroscopic

diffusion-reaction equations and the prescribed diffusion approximation (Schwarz, 1969). An extra term is added to equation (I.2.15) which becomes,

$$\begin{aligned} \frac{\partial C_i}{\partial t} = & D_i \nabla^2 C_i - \sum_j k_{ij} C_i C_j + \sum_{j,k} k_{jk} C_j C_k \\ & + \frac{1}{k_B T} D_i \nabla \cdot (C_i E) \end{aligned} \quad (I.2.22)$$

where $k_B T$ is the thermal energy and E is the field gradient. Schwarz suggested the assumption that E is proportional to r is justified if the charge density is constant. A change of less than 0.5% in the predicted final yields was found when ionic effects were included and it was concluded that, in aqueous radiation chemistry, these effects can be neglected. This finding is discussed in more detail in chapter II.3.

The kinetics of multiple ion-pair distributions in low permittivity solvents have been considered entirely neglecting the effects of interparticle forces and dealing only with an external field. This treatment has been applied to both cylindrically (Jaffe, 1913) and spherically (Lea, 1934) symmetric distributions. An approximate analytic solution of the multiple pair situation including ionic effects has been presented (Mozumder, 1971). This model is based on the prescribed diffusion approximation and considers the cations:

- i) for a spherical spur to be at the centre of a 3-dimensional Gaussian distribution of electrons
- ii) for a columnar track to be along the axis of a cylinder of electrons with a radially Gaussian concentration profile.

A time-dependent screened potential, defining the electrostatic

force, is introduced to perform the kinetic analysis. For a spherical spur the time-dependent equation for survival is

$$\frac{N}{N_0} = \left[1 + \frac{e^2 N_0}{2\epsilon k_B T \pi^{1.5}} \left[\frac{1}{b_0} - \frac{1}{b} \right] \right]^{-1} \quad (I.2.23)$$

if N is the number of particles in the cluster. This equation is strikingly similar to the equation obtained if inter-ion forces are ignored (Lea, 1934)

$$\frac{N}{N_0} = \left[1 + \frac{e^2 N_0}{\sqrt{8} D' \pi^{1.5}} \left[\frac{1}{b_0} - \frac{1}{b} \right] \right]^{-1} \quad (I.2.24)$$

and the two equations are equivalent if the rate constant is taken to be $2\sqrt{2}D'e^2/\epsilon k_B T$ (Hummel, 1974).

2.3 The validity of conventional methods.

Detailed examination of the conventional models used to describe the fast kinetics that follow radiolysis reveals a number of faults. The problems arise from the deterministic description of the nonlinear kinetics, from the use of rate coefficients relevant to homogeneous kinetics and from the approximations introduced to facilitate analytic solution of the diffusion-reaction equations describing the evolution of the system.

A deterministic rate equation uses the same variable, N , to describe both the (integer) number of particles in the cluster and the expectation value, $\langle N \rangle$, of this quantity. In fact, it is not recognised that N must be an integer. As the kinetics of recombination are nonlinear this approximation is tantamount to assuming that $\langle N^2 \rangle = \langle N \rangle \langle N \rangle$, which is never valid though for very large numbers of particles the relative error becomes small.

This effect gives rise to product ratio anomalies as described in chapter I.1.

In addition to the N versus $\langle N \rangle$ problem, the correct time-dependent rate coefficient to use in the deterministic rate equations is unclear. If kinetics are diffusion-controlled, the rate coefficients should be determined by the evolution of the relative particle distributions and different time-dependent rate coefficients arise from different initial distributions. The correct rate constant for a nonhomogeneous distribution of particles depends on that distribution. The profile, itself, is insufficient to determine the rate coefficient and it is the distribution of separations, i.e. the two body correlation function, that is important. Conventional models of radiolysis kinetics use rate constants measured under steady-state conditions and with time dependences appropriate to an initially homogeneous system. They do not have the correct time dependence for an initially cylindrical or spherical Gaussian distribution. The correct time-dependent rate coefficient for the latter case has been derived by Clifford et al. (1982a).

The difficulty in analytically solving the coupled diffusion-reaction equations describing the development of a system necessitates the use of approximations. In the commonly used prescribed diffusion methods, the particle distributions are assumed to evolve independently of reaction. The limitations of this approximation are well known. The fact that reaction will occur faster closer to the centre of a Gaussian reactant distribution than at its fringes has been recognised and the prescribed diffusion methodology has been modified to make allowance for this. As detailed earlier, a faster than linear expansion of the profile is introduced, however, the resulting

physical picture is still unrealistic. Nonhomogeneous kinetics of this kind ought to cause depletion at the centre of the distribution (Green et al., 1984).

A full critique of the conventional approach to spur kinetics has been presented by Clifford et al. (1982a), but it is clear, even from the brief discussion above, that conventional deterministic kinetics are only accurate for systems of relatively large numbers of particles and where concentrations are, at least initially, locally and microscopically homogeneous.

Initial recombination is critical in the development of an irradiated medium as it represents a significant fraction of the overall reaction and the study of the fast kinetics provides the most direct experimental information about the consequences of the energy deposition events. It is important that the models of radiolysis kinetics accurately represent what they are supposed to describe. The theoretical considerations, presented above, place some doubt upon this accuracy for the conventional models and have recently led to the development of alternative descriptions of radiolysis kinetics.

SECTION II : Stochastic models in radiation chemistry.

Chapter 1 : Stochastic models in chemical kinetics.

In the previous section, the period of fast kinetics that follows radiolysis was introduced and was explained in terms of the diffusion and reaction of a spatially nonhomogeneous distribution of reactive particles. The conventional treatment of these kinetics was presented and criticised. This chapter introduces an alternative, stochastic, approach to reaction kinetics. The stochastic kinetics of homogeneous systems are discussed, then three stochastic methods of modelling the evolution of nonhomogeneous systems are presented. One involves the full simulation of the diffusion and reaction processes and the remaining two are approximate models based upon an independent pairs treatment of the kinetics.

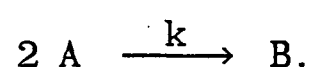
1.1 Stochastic processes.

The theory of stochastic processes deals with the statistics of change and can be applied to a wide range of scientific and technological problems. For a process to be described as stochastic, it must have some random element - observations of the phenomenon, repeated under similar conditions, must have irregular and random variation. Well known examples of stochastic phenomena in the real world include Brownian motion, the growth of a bacterial colony and the fluctuation of the numbers of electrons and photons in a cosmic-ray shower (Bartlett, 1978). These, like most physical examples of stochastic processes, involve change with time, but change with respect to other parameters is possible; for example, the velocity field of a turbulent fluid changes in space as well as with time (Bartlett, 1978).

The behaviour of a stochastic process is usually described by a master equation (Oppenheimer et al., 1977). This is either a set of differential-difference equations or a set of integro-differential equations describing the conditional probabilities of the process. The form of the master equation depends upon the nature of the state space.

1.2 Conventional stochastic kinetics.

The application of stochastic theory to kinetics has been reviewed by McQuarrie (1967) and developed more recently by Hall (1983a, 1983b); a brief summary of this topic is appropriate here. Consider the system defined by the reaction scheme



The kinetics are conventionally expressed using rate equations in terms of the concentration, c_A , of A,

$$\frac{dc_A}{dt} = -k c_A^2 \quad ; \quad c_A(t) = \frac{c_A(0)}{(1 + c_A(0) kt)} \quad (\text{II.1.1})$$

For small systems it is necessary to pay particular attention to the law of mass action and so strictly,

$$\frac{dc_A}{dt} = -kc_A(c_A - K) \quad ; \quad c_A(t) = \frac{Kc_A(0)}{c_A(0) + (K - c_A(0))\exp(-kt)} \quad (\text{II.1.2})$$

where K is a constant representing the removal of one particle from the system. In both sets of equations, c_A , is a continuous function of time, but the actual number of reactants in the system is an integer quantity and reaction removes particles in pairs.

The system $2A \longrightarrow B$ is more fully described in terms of the discrete probability distribution of the integer quantity. If $P_x(t)$ represents the probability that the system has x A particles at time t , and remembering that if there are x particles there are $1/2 x(x-1)$ pairs, then

$$P_x(t+\Delta t) = P_{x+2}(t) [1/2 (x+1) (x+2) k' \Delta t] + P_x(t) [1 - 1/2 (x-1) x k' \Delta t] . \quad (\text{II.1.3})$$

Note the change from concentration to number and the corresponding change from k to k' . From this equation it is obvious that the system is described by a set of coupled differential-difference equations of the form

$$\frac{dP_x}{dt} = 1/2 (x+1) (x+2) k' P_{x+2}(t) - 1/2 (x-1) x k' P_x(t) \quad (\text{II.1.4})$$

which can be solved using a generating function method (McQuarrie, 1967). The expectation number, $\langle x \rangle$, corresponds to the experimental observable and is given by

$$\langle x \rangle = - \sum_{x=i}^{x_0} A_x T_x(t) \quad (\text{II.1.5})$$

alternate

i.e. summation over either odd or even x , where

$$A_x = \frac{(1-2x)}{2^x} \frac{\Gamma(x_0+1) \Gamma(1/2(x_0-x+1))}{\Gamma(x_0-x+1) \Gamma(1/2(x_0-x+1))} \quad (\text{II.1.6})$$

and

$$T_x(t) = \exp(- 1/2 \times (x-1) k' t). \quad (\text{II.1.7})$$

When x_0 , the initial number of particles, is even i is 2 and when x_0 is odd i is 1. The deterministic kinetics described by equations (II.1.1) and (II.1.2) bracket the stochastic model (McQuarrie, 1967).

Differences between stochastic and deterministic theories of homogeneous kinetics are only significant if the number of reactive centres is small, nevertheless, there are such systems in which it is necessary to consider statistical aspects in modelling the kinetics. These include reaction in biological cells (Bartholomay, 1958), aggregation processes (Whittle, 1965) and various aspects of polymer chemistry (Mazur, 1963). Until recently, despite a highly developed mathematical literature (Cox & Miller, 1965; Karlin & Taylor, 1975, 1981), stochastic theories had not been applied to radiation chemical kinetics because of the difficulty in incorporating the important spatial considerations.

1.3 Stochastic effects in radiolysis.

Stochastic effects are apparent in every stage of the development of a radiolysis system: in the interaction between radiation and medium and in the diffusion and reaction processes that follow. The track of energy deposition events marking the path of the primary particle is a quantum-mechanical phenomenon and so is inherently stochastic. Several stochastic simulation techniques (Paretzke et al., 1986; Terrissol, 1978; Zaider et al., 1983) have been developed to model the positions of the energy transfers and the amount of energy lost in each event. Idealised track structure calculations model the trajectory of a primary particle assuming a

local Poisson distribution of inter-event separations. This distribution has a mean path length determined by the energy-dependent total interaction cross section of the particle and by the number density of the medium. The energy lost in each event influences the fragmentation pathway of the excited molecules and ions and hence the form of the cluster. The nature of an interaction and the concomitant energy loss are derived from the ionisation and excitation cross sections that make up the total cross section whilst the direction and velocity of any energetic daughter electrons depend upon the various differential cross sections involved. A detailed description of the spatial distribution of the ions and radicals is not available as the thermalisation/trapping processes of low energy particles are poorly understood (Mozumder, 1969; LaVerne & Mozumder, 1984) and the idealised track structure calculations either do not consider the thermalisation/trapping or they do so by conjecture (Zaider & Brenner, 1984).

1.4 The modelling of nonhomogeneous kinetics.

The kinetics of the thermalised ions and radicals are mostly diffusion-controlled and so depend on the diffusive paths of the particles. The most complete description of these trajectories would be via molecular dynamics and involves solving the classical equations of motion of the molecules in the system. Molecular dynamics provides a detailed description of the motion of all the particles in a liquid/solid and is usually employed for short-time dynamical problems (Rahman, 1964), though some kinetic simulations have been performed (Bergsma et al., 1987). A less detailed approach, which describes diffusive motion as a random 'buffeting' force moderated by a frictional drag, is Brownian dynamics. This technique is used to examine the short-time dynamics and kinetics

of a system when the mechanism for reaction is well known and when there are few reactive particles (Allen, 1980; Nesbitt & Hynes, 1982). Molecular and Brownian dynamics methods are computationally expensive and both provide a more detailed description of short-time/short-distance effects than is necessary for radiolysis kinetics.

In radiation chemistry, the reaction schemes are often complex, an extended timescale (10^{-11} - 10^{-7} s) is considered and a large number of independent realisations of a system are required to provide meaningful kinetics. At the times of interest these kinetics can be adequately described by a diffusion equation - the spreading of the probability density function, p , for a particle is described by the Debye-Smoluchowski equation referred to in chapter I.2 (Debye, 1942)

$$\frac{\partial p}{\partial t} = \nabla \cdot D \left[\nabla p + \frac{p}{k_B T} \nabla (U) \right]. \quad (\text{II.1.9})$$

It has been shown that the trajectories implied by this description are probabilistic (Itô & McKean, 1974) and that their evolution is governed by a stochastic differential equation (Arnold, 1971).

Whilst it is clear that the gross track structure, the fragmentation and thermalisation processes and the diffusion-controlled reactions of the particles can all be described stochastically, this thesis is concerned, primarily, with the evolution of the thermalised system via diffusion and reaction. In all cases the initial distributions are idealised to varying degrees and, as even the particle distributions generated by track structure calculations depend heavily upon conjecture, there is a limit to effective comparison with experiment.

On the level of the diffusion equation, the stochastic modelling of short-time kinetics in irradiated media can be divided into three classes; full time-dependent Monte Carlo simulation of the diffusion-reaction processes, approximate modelling using a first passage time to encounter approach and formulation of a master equation which describes the evolution of the system. A brief description of these methods follows.

1.4.1 Full Monte Carlo simulation.

The use of a diffusion equation in modelling the kinetics of a group of the particles is equivalent to assuming that diffusive motion obeys a stochastic differential equation. These equations are usually written in the (infinitesimal) form,

$$d\underline{R} = \frac{\underline{DF}}{k_B T} dt + \sqrt{2D} d\underline{W}_3 \quad (\text{II.1.10})$$

which describes the change in a particle position $\underline{R}$ under the action of a classical force $\underline{F}$ and a random force. This random force is modelled as the 'derivative' of a prototype diffusion, $\underline{W}_3$, which is known as a Wiener process and is the limit of a simple random walk where the jumps have infinitesimal size and are infinitely frequent (Karlin & Taylor, 1975). Any numerical simulation must represent an approximation to the stochastic differential equation. Convergence to the diffusion limit is shown by comparing simulation with analytic (or converged numerical) solution for a simple physical system and for diffusion-controlled reactions, this is the first encounter of a pair of particles.

The earliest studies of nonhomogeneous kinetics using simulation techniques considered clusters of uncharged reactants. As there are no electrostatic forces in this type of system,

i.e. only random Brownian motion, the stochastic differential equation for the trajectory of a diffusing particle reduces to

$$d\mathbf{R} = \sqrt{2D} d\mathbf{W}_3 \quad (\text{II.1.11})$$

and each trajectory evolves as a scaled Wiener process (Green et al., 1988). In the limit of diffusion-controlled reaction, the kinetics are studied by simulating the encounter times of the particles and the kinetics ought to converge to the solution of the relevant diffusion equation which cannot, at present, be solved exactly if more than two particles are present.

The kinetic analysis of an initially nonhomogeneous distribution of uncharged particles using Monte Carlo simulation methods was first presented by Botár et al. (1976, 1979), who modelled the reactions of isolated two species clusters in the presence of a scavenger. In this model, the radicals perform a 3-D random walk on a cubic lattice and react when they occupy the same site, whilst the scavengers are fixed and uniformly distributed on the lattice and are immediately replenished upon reaction. The Botár approach is clearly a very simple discretisation of the stochastic differential equation and no claims are made as to the quantitative accuracy of the calculated time-dependent combination and scavenging probabilities. Whilst there is no attempt to examine a real radiolysis system, the experimental cube root dependence of product yield on scavenger concentration (Rafi & Sutton, 1965) was observed (Botár, 1980).

A lattice random walk model similar to that of Botár et al. was developed, independently, by Clifford et al. (1982b). This model has a much finer lattice discretisation and a non-zero particle size, thus while reaction in the Botár model requires the

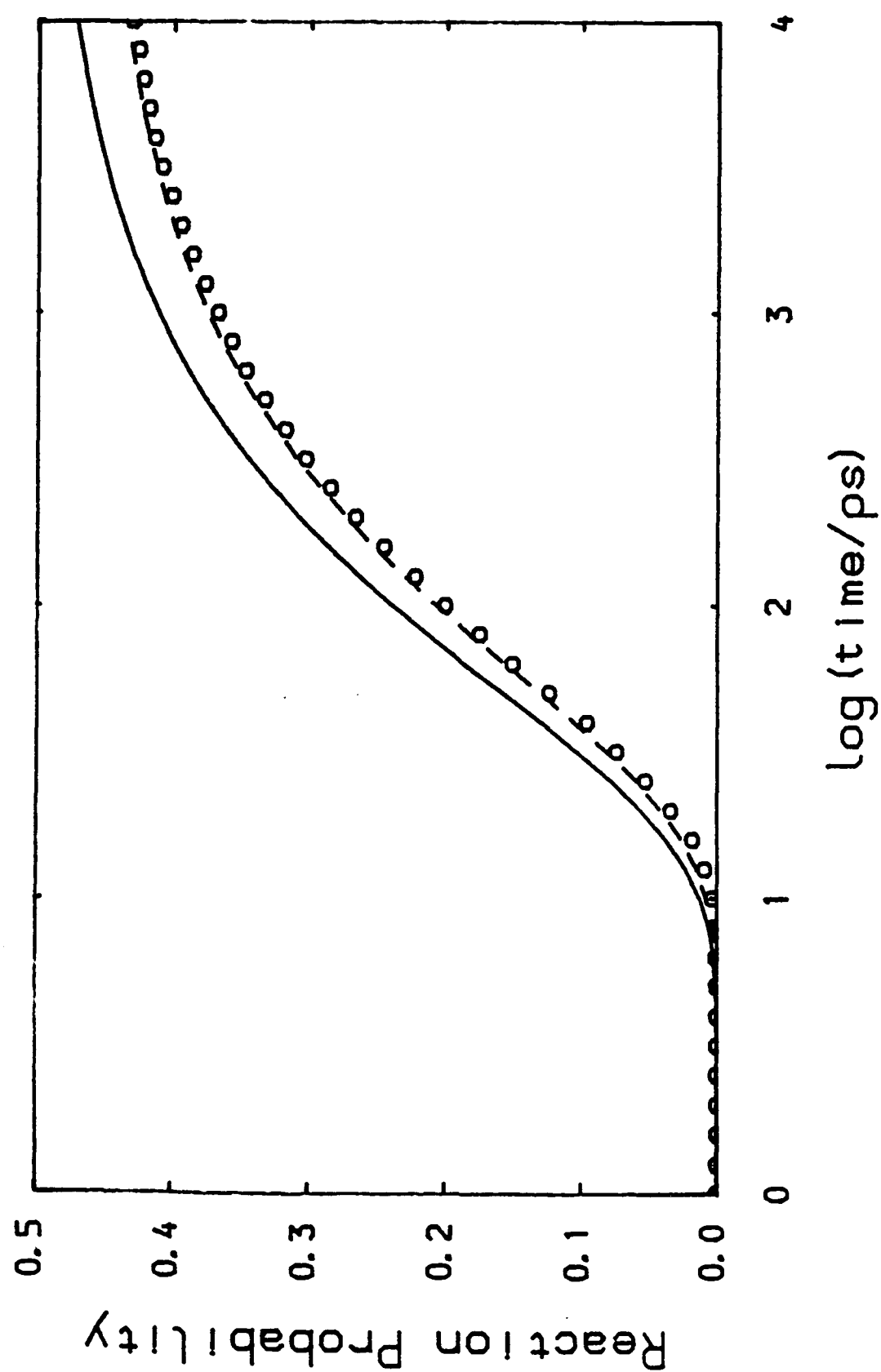
radicals to occupy the same site following a jump, the simulations of Clifford have an encounter separation which is typically ten times the lattice parameter. The latter approach to simulation was applied to single species spurs both in the absence (Clifford et al., 1982b) and in the presence of scavengers (Clifford et al., 1985).

As mentioned previously, exact solution of the diffusion equation for an isolated pair in an infinite space is available. The time-dependent survival probability is compared with the simulation method of Clifford et al. in Fig.II.1.1. Even with this fine lattice, agreement between simulation and analytic solution is imperfect and to obtain agreement it is necessary to use a corrected encounter distance - 9.3 lattice units instead of 10 units. This correction is essentially a discretisation error which can be reduced by decreasing the lattice parameter at the expense of an increase in the computer time required for the simulation. The corrected encounter distance is the average distance of all the lattice points, within a radius R of a central particle, that can be reached, in a single jump, from any lattice point outside R (Green, 1980). An exact fit is still not obtained as this treatment assumes that jumps to all the considered sites inside R are equally likely.

If performed carefully and correctly, the evolution of an initially nonhomogeneous distribution of reactive particles can be modelled using time-dependent Monte Carlo simulation to a precision arbitrarily close to the exact solution of the multiparticle diffusion equation for the system, however, this approach is costly in computational resources and provides more detailed information than is required to evaluate the kinetics.

Fig.II.1.1 Recombination probability of a geminate pair.
Relative diffusion coefficient = $1.0 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$; initial
separation = 2.0 nm.

(—) Analytic solution, $R = 1.0 \text{ nm}$.
(- - -) Analytic solution, $R = 0.93 \text{ nm}$.
(o o o o) Simulation following Clifford et al. (1982b).



1.4.2 First passage time methods.

The only data actually required to produce a kinetic description of the development of a reactive system are the reaction times, i.e. the first passage times from generation to reaction for the reacting pairs, and in diffusion-controlled kinetics these are the first encounter times for the relevant particles. It is only possible to evaluate such a set of times without following the trajectories, by introducing an approximation, but this change brings a large saving in computer processor time. One such method is the Independent Reaction Times (IRT) model of Clifford et al. (1982a). This model is a computer-efficient Monte Carlo technique and depends upon the generation of a random variable from an arbitrary distribution which is discussed in appendix A. The technique is best demonstrated by example and reference to Fig.II.1.2.

Consider a cluster of four particles at given positions. There are six interparticle distances and six potentially reactive pairs. A random reaction time is generated independently for each of the pairs from the correct marginal first passage time distribution for that pair, i.e. as if it were in isolation. As the times are generated independently the resulting ensemble is not a sample from the correct joint probability density function for the times, but, it is assumed to be so - an independent pairs approximation is made. The simulation proceeds by finding the minimum time of the ensemble, which defines the first reacting pair (2+3 in Fig.II.1.2), and the particles are removed from further consideration. As particles 2 and 3 have reacted, the times corresponding to reaction of 1+2, 1+3, 4+2, 4+3 are ignored and the second reaction occurs at the remaining time (1+4), if it is finite. As IRT simulation is much faster to perform than full

Pair	r_{ij}/nm	t_{ij}/ps	Reaction
1+2	1.3	12	x
1+3	2.1	27	x
1+4	1.0	40	2
2+3	1.1	8	1
2+4	1.7	125	x
3+4	1.8	∞	x

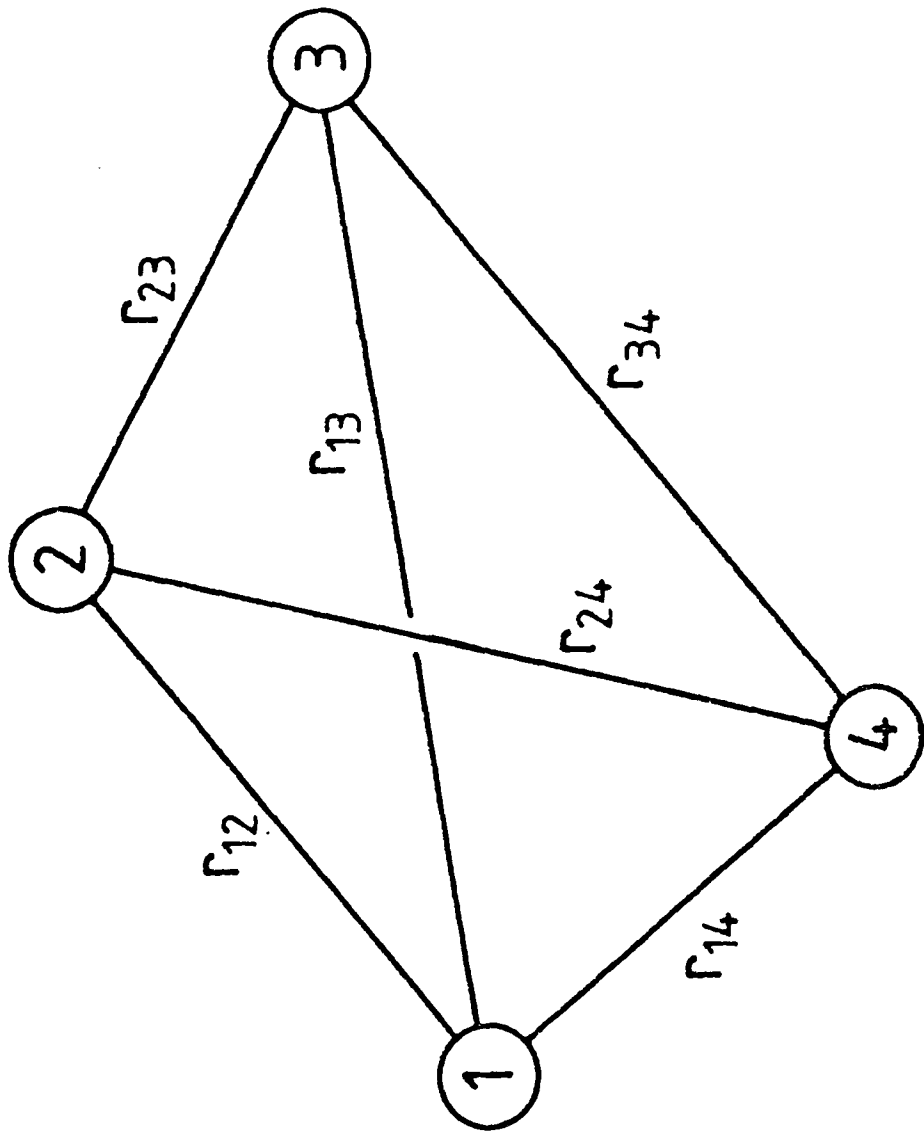


Fig.II.1.1.2 Independent reaction times methodology.

simulation, it is possible to attain much higher statistical precision for the same computational cost. The model appears to be very accurate for the simple systems investigated by Clifford et al. - single species clusters in isolation (1982a) and in the presence of a scavenger (1985) - but the reason for this success is not obvious (Clifford et al., 1987a).

The term *first passage time* is usually used in the chemical literature to imply mean first passage time (Szabo et al., 1980; Weiss, 1981). In an isolated cluster, the mean reaction time of a radical is infinite (even conditioned upon ultimate reaction) and since the isolated spur is assumed to be the model system for low LET radiolysis kinetics a mean first passage time method of analysis is, in the strictest sense, not possible. The introduction of an outer boundary condition depending on the bulk concentration of radicals provides a method for avoiding this problem (Mozumder, 1982). For the diffusion-controlled reaction of a geminate pair of particles, the mean reaction time is

$$\tau = \frac{r^2}{6} \left[\left(\frac{R}{r} \right)^2 (1 - \Omega') + \Omega' \left(\frac{\lambda}{r} \right)^2 - 1 \right] \quad (\text{II.1.11})$$

where $\Omega' = \frac{\lambda}{r} \left[\frac{r - R}{\lambda - R} \right]$ and λ is an outer boundary defined by the dose (λ is proportional to the reciprocal dose). In the limit of zero dose, $\lambda \rightarrow \infty$ and $\tau \rightarrow \infty$ as expected.

1.4.3 Master equation formulation.

In the brief summary of the conventional treatment of radiolysis kinetics presented in chapter I.2, the characterisation of a system in terms of an average concentration profile was criticised and the need to distinguish between the discrete number of particles, x , and the continuous variable expectation number, $\langle x \rangle$, was emphasised. The stochastic treatment of homogeneous

kinetics has already been introduced in this chapter. To extend this analysis to nonhomogeneous kinetics it is necessary to include the spatial aspect of the problem in the formulation. Consider again the $2 A \longrightarrow B$ scheme. The homogeneous kinetics are described by the master equation (II.1.4) and to include the spatial nonhomogeneity it is necessary to replace the steady-state rate constant, k , by a time-dependent coefficient, $\omega(t)$, related to the distribution of interparticle distances, $f(r)$. Thus, assuming $f(r)$ is not altered by the reaction of a pair,

$$\frac{dP_x}{dt} = \frac{1}{2} (x+1) (x+2) \omega(t) P_{x+2}(t) - \frac{1}{2} (x-1) x \omega(t) P_x(t) . \quad (\text{II.1.12})$$

At present many-body problems cannot be solved exactly and it is necessary to introduce an approximation to evaluate ω . One approach is to assume that the evolution of every pair of particles in a cluster is independent, except in reaction (Clifford et al., 1982a). The rate coefficient is then,

$$\omega(t) = - \frac{d}{dt} [\ln(\Pi_R(t))] \quad (\text{II.1.13})$$

where $\Pi_R(t)$ is the survival probability of an isolated pair with the initial distribution of interparticle distances, $f(r)$,

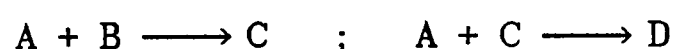
$$\Pi_R = \int_R^\infty f(r) \Omega(r,t) dr . \quad (\text{II.1.14})$$

Clifford et al. (1982a) describe ω as the "intensity of reaction of an isolated pair". They solved the master equation (II.1.12) for initially Gaussian clusters and extended the treatment to include

reaction with a scavenger (1985). Solution of the A+A and the A+A,A+S reaction schemes is very simple, but it is difficult to develop this formulation for more complex systems as each new species introduced increases the state space of the master equation by a further dimension. In consequence, master equation methods have not been widely used in radiation chemistry, although a recent generalisation of the formalism (Green et al., 1988) could result in an increased usage.

1.4.4 Improvements.

The stochastic studies presented thus far, have dealt exclusively with simple one or two species radical systems, both in the absence and in the presence of a scavenger. The models, as formulated, are not sufficiently advanced to deal with realistic kinetics and the extension to more complex systems implies that the models must be developed to encompass, for instance, ionic effects, activation-controlled processes, reactions producing reactive species - c.f. the scheme



and nonhomogeneous distributions with large numbers of reactive centres. The following chapters consider the introduction of some of these effects into the Monte Carlo, the first passage time and the master equation approaches and the third section of the thesis examines the application of the models to a number of realistic radiolysis systems.

Chapter 2 : The short-time kinetics of neutral species.

Chapter II.1 introduced a basic methodology for modelling the kinetics of nonhomogeneous systems using stochastic techniques. The systems were very simple and the methods primitive. In this chapter the full simulation of diffusion and reaction is extended to encompass more complicated reaction schemes. The diffusive motion of the particles is re-examined and an alternative, and superior, random flights approach is presented. Bridging processes to predict the occurrence of reaction during a jump are introduced. The use of random flights diffusion and bridging processes is conceptually more pleasing than the lattice random walk method and it is computationally advantageous. The independent pairs modelling of many species systems is considered. A master equation formulation of this type of system is produced and its solution is considered. The IRT model is extended to include systems where the product of a reaction can undergo reaction itself.

2.1 Random flights simulation.

The time-dependent Monte Carlo techniques of Botár et al. (1976, 1979) and Clifford et al. (1982b) simulate the kinetics of single and two species clusters using a random walk on a cubic lattice. According to this approach if the jumps are always along body diagonals, the diffusion coefficient, D_i , of species i is

$$D_i = \frac{1}{2} v_i \ell_i^2 \quad (\text{II.2.1})$$

where v_i and ℓ_i are the jump frequency and the lattice spacing, respectively, for i , and to model the development of a many species system a different jump frequency or lattice parameter is required for each reactant species. This approach is not completely

satisfactory and if the particles have zero size, c.f. Botár et al., the lattices of species i and j must be coincident.

To avoid the use of different jump frequencies or different lattice spacings, it is necessary to abandon the cubic lattice and employ an alternative technique for modelling the diffusive motion of the particles in real space. One approach, a random flights description of the trajectories, is based upon the solution of the stochastic differential equation describing a trajectory as a scaled Wiener process (in the absence of an electrostatic force). As the transition density of a Wiener process is Gaussian in each dimension, the trajectory of a particle is simulated by letting each Cartesian coordinate change independently by a normally distributed random variable of mean zero and variance $2D\delta t$, where δt is the timestep. The recombination of an A+B pair is shown in Fig.II.2.1.

As with the random walk techniques, agreement with analytic solution is not exact and there is a discretisation error which lessens as the period of the timestep is reduced. The origins of this error lie in the method of modelling reaction. If the kinetics are diffusion-controlled, reactive encounter occurs whenever a pair of particles reaches a separation less than the reaction distance, R . In the simplest random flights formulation, reaction is only registered if the interparticle distance is less than R at the end of a timestep. It is possible, however, for a pair to attain a separation $r \leq R$ during a timestep and then to part during the same timestep (Fig.II.2.2). Reaction ought to have been registered, but within the confines of the simple model this is not the case.

As long as the timestep is short enough that third particles cannot interfere (Green et al., 1988), the problem of reaction during a timestep can be overcome using the correct conditional

Fig.II.2.1 Recombination probability of a geminate pair.
Initial separation = 2.0 nm; reaction distance = 1.0 nm;
relative diffusion coefficient = $1.0 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$.

(—) Analytic solution
(+ + + +) Random flights simulation without bridge.
(o o o o) Random flights simulation using Brownian bridge.

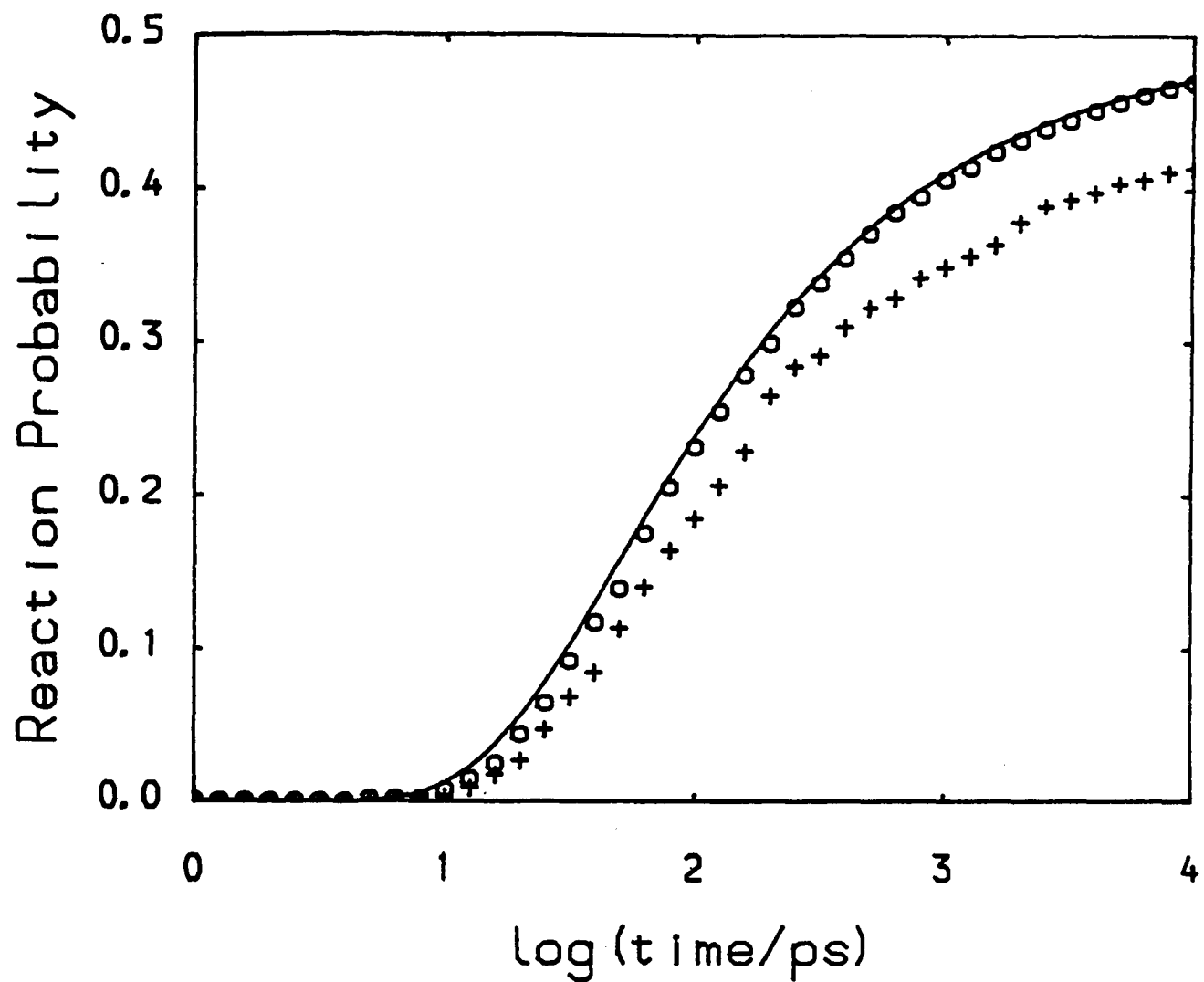


Fig.II.2.2 Encounter during a time step.
A schematic representation of the variation in interparticle separation. Reaction occurs when $r \leq R$.



encounter probability for an interpolating "bridge process" during the timestep. If the separation of a pair of particles both before a jump, x , and afterwards, y , is known, then the probability of encountering at a distance R can be calculated if it is assumed that the development of the pair is unaffected by the other particles in the system - a mild form of the independent pairs approximation. Having established a bridging technique, the efficiency of the simulation can then be improved by incorporating a variable timestep.

2.1.1 Bridging processes.

Two forms of interpolating bridge have been developed; the Brownian bridge (Clifford & Green, 1986) and the Bessel bridge (Green & Pimblott, unpublished work). According to the former process, the probability of encounter during a time period Δt is

$$W_{Br} = \exp \left[- \frac{(x-R)(y-R)}{D' \Delta t} \right]. \quad (II.2.2)$$

The application of a Brownian bridge assumes that the separation of two particles behaves as a Wiener process. (The difference between each of the Cartesian coordinates is a 1-D Wiener process, but not the radial separation.) This approximation is only valid if the radial drift does not change significantly during the timestep, i.e. in the diffusion equation

$$\frac{\partial \rho}{\partial t} = D' \nabla^2 \rho \quad ; \quad \nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \quad (II.2.3)$$

the $\frac{2}{r}$ coefficient in the second term on the right hand side is approximately invariant over the distance jumped in Δt . The effect of including a Brownian bridge in the simulation of geminate

recombination is shown in Fig.II.2.1. Note the agreement with the analytic solution using the same encounter distance, R .

The separation between two diffusing particles, even in the absence of an interparticle force, is not a Wiener process, but a Bessel process (Green, 1980). A Bessel process is the radial component of a multi-dimensional Wiener process. The corresponding interpolating bridge is known as a Bessel bridge and in 3 dimensions, the encounter probability is

$$W_{Be} = \frac{\exp\left[-\frac{(x-R)(y-R)}{D'\Delta t}\right] - \exp\left[-\frac{xy}{D'\Delta t}\right]}{1 - \exp\left[-\frac{xy}{D'\Delta t}\right]}. \quad (\text{II.2.4})$$

The Bessel bridge is derived in appendix B. In one dimension, the Bessel bridge encounter probability is equivalent to W_{Br} . As the Bessel bridge does not make the radial drift assumption of the Brownian bridge, it is applicable to timesteps of any size within the limits of the independent pairs approximation (i.e. as long as there is no third body interference).

2.1.2 Variable timestep simulation.

The full time-dependent Monte Carlo simulation of the diffusion-reaction processes is expensive in terms of computer resources even for a small system, and the development of interpolating bridge processes implies that more efficient modelling is possible, as larger timesteps can be introduced without any loss in accuracy. The implementation of a variable timestep, depending upon the minimum interparticle separation, allows the simulation to proceed quickly by taking larger timesteps when the particles are far apart and more slowly by taking smaller timesteps as the particles approach. A lower limit on possible timesteps, δt_{min} , is employed since if the timestep is allowed

indefinitely to become progressively smaller as particles approach the simulation becomes infinitely inefficient. The Brownian bridge can only be applied when particles are close together and the timestep is small, or the approximation under which the bridging process is derived begins to breakdown. This forces either an upper restriction upon the timestep, $\delta t_{\max}$, or a maximum separation over which the bridge is employed.

A variable timestep method has been developed for radical systems (Pimblott, 1985; Clifford et al., 1986). In this method the length of a jump is the sum of two times; τ_0 , a fixed timestep and τ_m , the minimum of an ensemble of times depending on the interparticle separations,

$$\delta t = \tau_0 + \tau_m. \quad (\text{II.2.5})$$

Each separation, r_i , between potentially reactive particles has a corresponding time in the ensemble, which is calculated according to the prescription

$$t_i = \frac{[(r_i - R_i) / \text{erfc}^{-1}(\delta p)]^2}{4D_i}. \quad (\text{II.2.6})$$

The time-dependent reaction probability of a pair with separation r_i is well known. This probability can be conditioned on ultimate reaction by normalising the long time asymptote to one. t_i is the time at which this conditioned reaction probability first attains a small given value δp , i.e. t_i is the time at which the reaction probability is δp if the pair is ultimately going to react. δp is typically set equal to 0.01. Rather than limiting the maximum size of δt , the bridging process is only applied when a pair is within a fixed distance, $2R$. The complete simulation technique, including

application of the Brownian bridge is summarised in the flow chart, Fig.II.2.3 and the recombination kinetics of a pair modelled by variable time step simulation using a Brownian bridge are shown in Fig.II.2.4. Agreement is significantly better than is found in the absence of an interpolating bridge and there is an enormous saving in computational cost when compared with the fixed timestep simulation.

Full simulation of the diffusion and reaction of a pair of uncharged particles gives an accurate representation of the solution of the correct diffusion equation and as no further approximations are introduced when the number of particles is increased, this technique is believed to be equally accurate for larger and more complicated systems which cannot be solved exactly.

2.2 Independent pairs kinetics of multispecies systems.

The generalisation of the master equation formulation of nonhomogeneous kinetics to many species systems was mentioned in chapter II.1 and requires the extension of the state space of the equation. For instance, if a system consists of A and B reactive particles distributed independently from the same density then the equation becomes

$$\begin{aligned}
 \frac{dP(x_A, x_B)}{dt} = & \frac{1}{2} (x_A+2) (x_A+1) \omega_{AA}(t) P(x_A+2, x_B) \\
 & + (x_A+1) (x_B+1) \omega_{AB}(t) P(x_A+1, x_B+1) \\
 & + \frac{1}{2} (x_B+2) (x_B+1) \omega_{BB}(t) P(x_A, x_B+2) \\
 & - \frac{1}{2} x_A (x_A-1) \omega_{AA}(t) P(x_A, x_B) \\
 & - x_A x_B \omega_{AB}(t) P(x_A, x_B) \\
 & - \frac{1}{2} x_B (x_B-1) \omega_{BB}(t) P(x_A, x_B)
 \end{aligned}
 \tag{II.2.7}$$

where $\omega_{ij}(t) = -\frac{d}{dt}[\ln(\Pi_{ij})]$ (according to the independent pairs

Fig.II.2.3 Flow chart for random flights simulation.

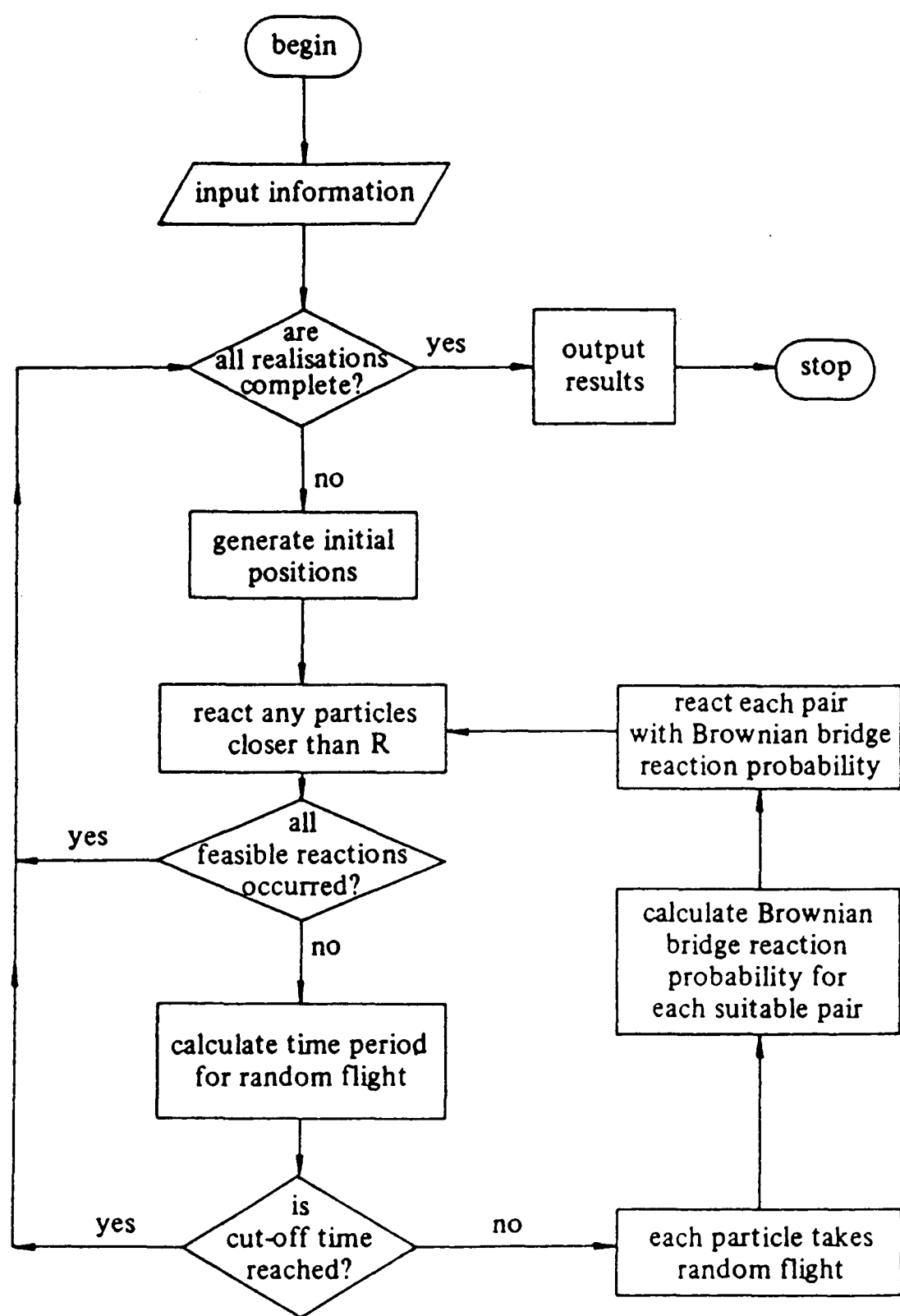
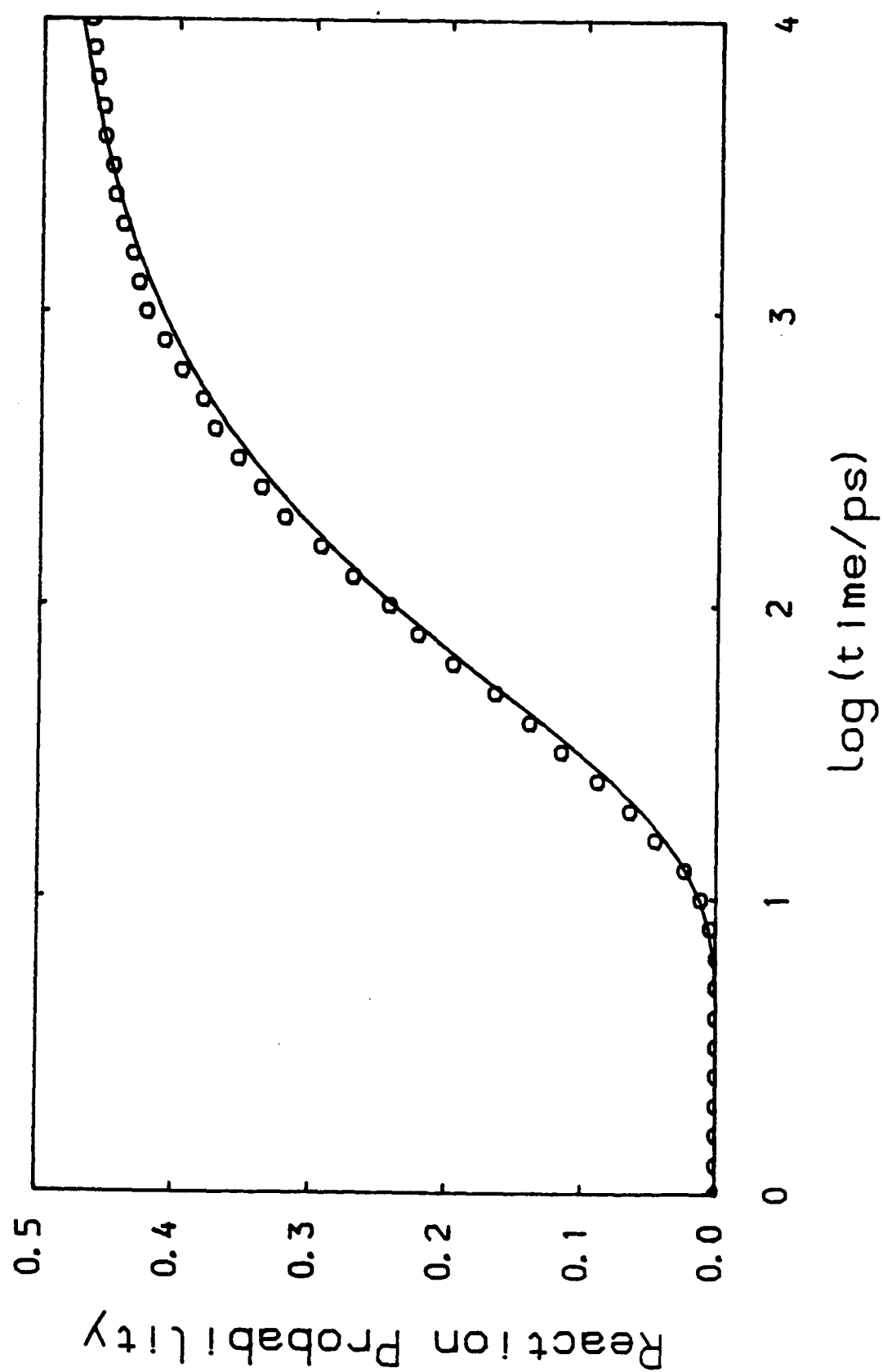


Fig.II.2.4 Recombination probability of a geminate pair.
Initial separation 2.0 nm; reaction distance = 1.0 nm;
relative diffusion coefficient = $1.0 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$.

(—) Analytic solution.
(o o o o) Variable timestep random flights simulation.



approximation) and Π_{ij} is the survival probability for each ij pair given the initial relative distribution of i and j particles. This master equation implies the kinetic equations,

$$-\frac{d\langle x_A \rangle}{dt} = \omega_{AA}(t) \langle x_A(x_A-1) \rangle + \omega_{AB}(t) \langle x_A x_B \rangle \quad (\text{II.2.8})$$

and

$$-\frac{d\langle x_B \rangle}{dt} = \omega_{BB}(t) \langle x_B(x_B-1) \rangle + \omega_{AB}(t) \langle x_A x_B \rangle. \quad (\text{II.2.9})$$

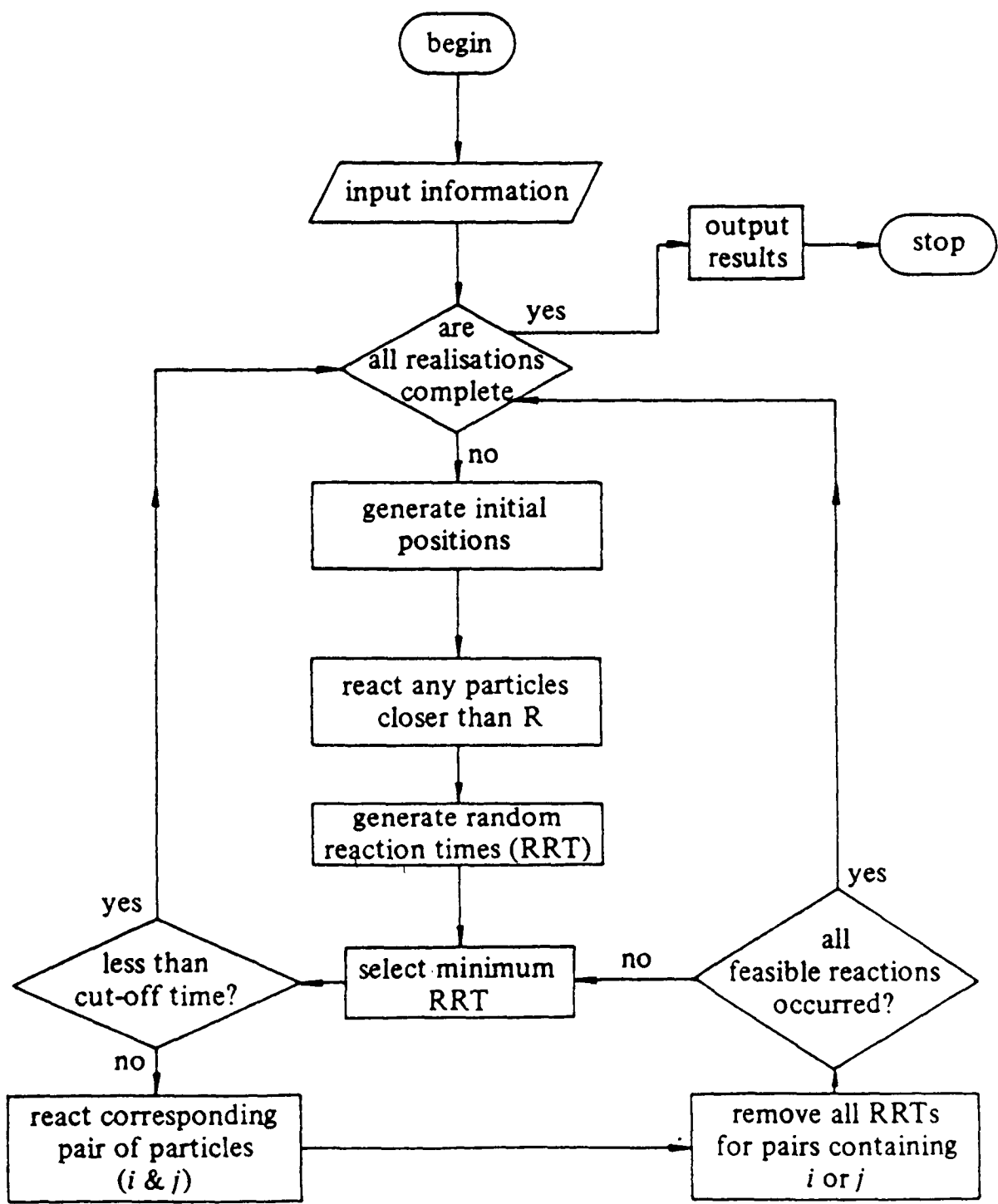
For a simple one reaction scheme, the kinetics are evaluated using a generating function treatment of the master equation. If the scheme is more complicated this approach is no longer possible and the master equation has to be solved numerically, except in special cases.

The IRT simulation of multispecies systems follows the same basic approach as that employed in the single species simulation and is summarised in the flow diagram, Fig.II.2.5.

2.2.1 Many-body interactions.

With the extension of both the full simulation methodology and the IRT model to many species systems, it is necessary to consider the 'ordering' of the particles. At zero time, i.e. when considering the initial configuration of the particles, and during the early period of full simulation the local reactant density is high and there is the possibility of multibody conflicts. A multibody conflict would occur when a particle is simulated to encounter two different partners in the same timestep. These conflicts must be resolved without giving systematic preference to any one reaction over the others. For instance, in a cluster of three particles where more than one pair is close enough to react,

Fig.II.2.5 Flow chart for IRT simulation.

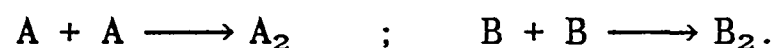


if the order in which the overlap is checked in the program is always the same, then only one type of reactive encounter will be observed. The effect is shown in Fig.II.2.6 (a 2A/B cluster). If A-A distances are always checked before A-B, only A+A reactions are counted. This multi-overlap problem is resolved by randomising the order in which the pairs of particles are checked. In principle other methods of resolution could be used except at zero time, where the problem is most severe.

2.3 Clusters symmetric in two species.

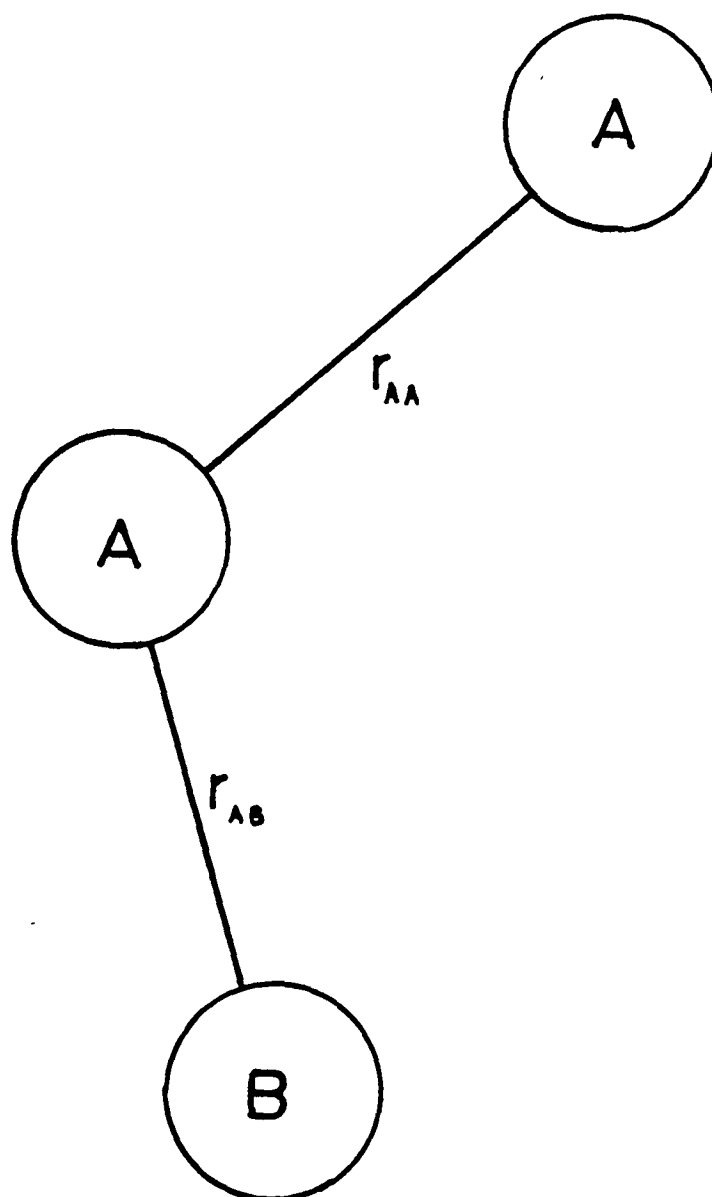
The improvements in the methodology of time-dependent simulation and the application of IRT and master equation techniques to many-species systems have been tested in a number of idealised situations and particular attention has been paid to the study of clusters symmetric in two reactive species (Pimblott, 1985; Clifford et al., 1986). The studies generally consider two types of particle, A and B, that are identical except in name and that have the same spatial distribution, usually Gaussian. Reaction schemes have been examined that test (i) the application of the independent pairs approximation, (ii) the validity of this approximation and (iii) the effect of competition between pairs.

a) The first of these analyses involves the scheme



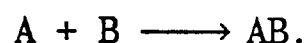
In a 2A/2B cluster, and according to this scheme, there are two truly independent reactive pairs and the master equation treatment is exact. Comparison of the kinetics shows that the three stochastic approaches agree within the 99% confidence limits of the simulation methods. This shows that IRT modelling does treat the pairs correctly and confirms the accuracy of full simulation. It must be remembered that according to this scheme A and B particles can diffuse through each other.

Fig.II.2.6 Many-body overlap.



$$r_{AA} \leq R_{AA} \text{ \& \> } r_{AB} \leq R_{AB}$$

b) The independent pairs approximation is tested using a scheme allowing only cross reaction, i.e.



If x_A and x_B are larger than one, then there are $x_A x_B$ potentially reactive pairs. Pairs with a particle in common do not evolve independently. The deviations between the IRT and master equation techniques and the full simulation of the diffusion-reaction processes are only just outside 99% confidence limits after 10^5 realisations and the approximate models do represent the kinetics accurately.

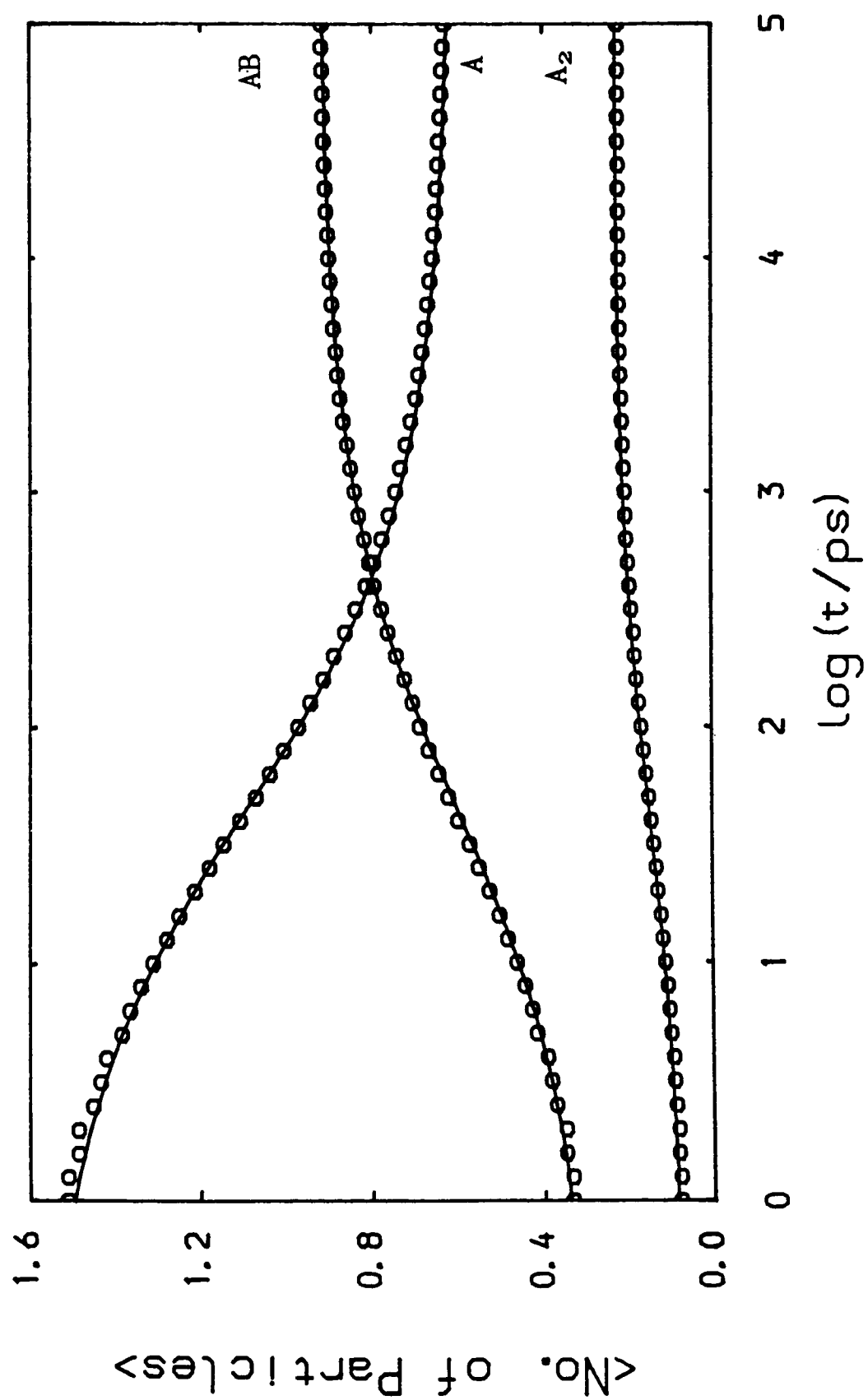
c) To analyse the effects of competition between reactive species, under the independent pairs approximation, the particles must have the potential to react with more than one type of partner. This behaviour is seen if the two reaction schemes above are combined, that is



Agreement between the full and the IRT simulation methods is almost exact, but the master equation treatment makes a small overestimate of the reaction rate. The essential difference between the two approximate models is the extension of the independent pairs approximation to 'zero time' in the master equation formulation, whilst in IRT simulation there is a realisable initial configuration of particles. The error introduced by this difference is only small. The kinetics of the 2A/2B system are shown in Fig.II.2.7. The diffusion coefficients of A and B particles are $5.0 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and all the reaction distances, $R_{A+A} = R_{A+B} = R_{B+B}$, are 1.0 nm. The initial configurations are generated from independent and identically distributed Gaussians of standard deviation 1.0 nm. For the sake of comparison, the kinetics predicted by the conventional prescribed diffusion model of Schwarz (1969) are also

Fig.II.2.7 Kinetics of an idealised 2A/2B cluster.
Initial reactant positions from iid Gaussians of standard deviation 1.0 nm; reaction distances all 1.0 nm; diffusion coefficients (A, B) are $5.0 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$.

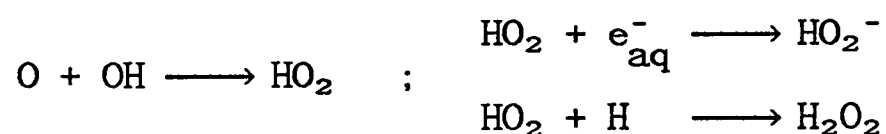
(o o o o) Random flights simulation.
(—) IRT simulation.



included. The large difference between stochastic and conventional kinetics is not unexpected in the light of the discussion of chapter I.2.

2.4 Reactive products.

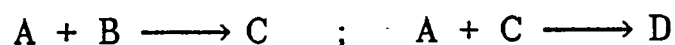
The developments in the stochastic models of nonhomogeneous kinetics described above extend the early work of Clifford et al.^(1982a) to include many species systems, but, as yet, products of a reaction that can undergo further reaction have not been considered, for example in the radiolysis of water



Particles of this type will, henceforth, be referred to as "reactive products".

The treatment of reactive products in the conventional models of nonhomogeneous kinetics is straightforward as these techniques consider the evolution of the nonhomogeneous concentration profile. In the stochastic models, the spatial aspect of the formation of a reactive product is difficult. A particle is produced at a localised point in space and, as the kinetics are determined by encounter, its subsequent behaviour must be treated in exactly the same manner as the initially generated particles.

The full Monte Carlo simulation of nonhomogeneous kinetics models the trajectories of the diffusing reactants and the positions of all the particles are known. Extension to include schemes of the form



is conceptually and practically simple. The new reactive product is simply assigned the position of one of its parents. This is not the

case for the approximate independent pairs models and no successful method of incorporating reactive products in the master equation approach has yet been developed.

In the Independent Reaction Times simulation of nonhomogeneous kinetics the evolution of a system is modelled using reaction times generated from the initial positions of the reactive particles. The only important parameter in the distribution function used to generate a reaction time is the interparticle separation r at time $t = 0$. If a reactive product is formed at time $t = 0$, its position is known and its subsequent reaction times can be generated. However, if the parent reaction takes place when $t > 0$ the positional information required to determine future encounter times is not available. The IRT model, as formulated above, does not follow the diffusive motion of the particles and a supplementary approximation is necessary to provide either new interparticle distances at $t > 0$ or new reaction times without these separations.

Three different methods have been developed for incorporating reactive products into the Independent Reaction Times methodology (Clifford et al., 1986). The first approximation, known as the Position Approach, explicitly determines the positions of the 'parent' particles that form a reactive product and all the other particles at the time of the reaction and is the most computer expensive of the methods. The other two treatments, the Diffusion Approach and the Time Approach, are based upon the independent pairs approximation (the foundation of the IRT model) and do not generate new particle positions. The Diffusion Approach considers the evolution of the interparticle separations, which are assumed to vary independently, and calculates new values of r from which reaction times are generated. This model relies upon the separation of a pair evolving as a Bessel process and so is strictly only

applicable to uncharged particles. Reaction times of a reactive product are derived from the reaction times of its parents in the Time Approach.

These three approximations and their implementation have been described in detail (Pimblott, 1985), but it is worthwhile briefly presenting a hybrid of these techniques that is used in the IRT modelling of reactive products throughout the following studies. For the most part, the reaction times of reactive products are generated according to the Time Approach formulation, but under certain conditions the Diffusion Approach is used.

2.4.1 Reaction times of reactive products.

The hybrid method of generating the reaction times of a reactive product ($t > 0$) is best explained using a simple example: Three particles (a,b,c) have reaction times t_{ab} , t_{ac} and t_{bc} , where $t_{ab} < t_{ac}, t_{bc}$. Particle a 'encounters' b and reacts to form a reactive product d and this new particle replaces one of its parent particles selected at random - let d replace a and let b be removed from further consideration. The separation c-d follows the same 'path' as the distance a-c until the time of the reaction, t_{ab} , and thereafter follows the same trajectory, but with a new diffusion coefficient. The time taken to reach the separation R_{ac} is

$$t(R_{ac}) = t_{ab} + \frac{D'_{ac}}{D'_{cd}} (t_{ac} - t_{ab}). \quad (\text{II.2.10})$$

Clearly, if R_{ac} and R_{cd} are the same this represents the reaction time of the pair cd. When $R_{cd} < R_{ac}$ the reactive product and its partner will not have attained a reactive configuration at $t(R_{ac})$

and they must continue to diffuse until reaching R_{cd} . This time can be approximated by

$$t_{cd} = t_{ab} + \frac{D'_{ac}}{D'_{cd}} (t_{ac}^* - t_{ab}) \quad ; \quad R_{cd} \leq R_{ac} \quad (\text{II.2.11})$$

where t_{ac}^* is the reaction time that would have been generated for the ac pair if its reaction distance had been R_{cd} given the same random number that was used to generate t_{ac} . In the limit $R_{ac} = R_{cd}$ this equation reduces to equation (II.2.10). In cases where $R_{cd} > R_{ac}$ the time t_{ac}^* might be less than t_{ab} and so it is possible that the formulation above would produce a reaction time t_{cd} less than t_{ab} . To avoid this physically unrealistic situation an alternative method is used.

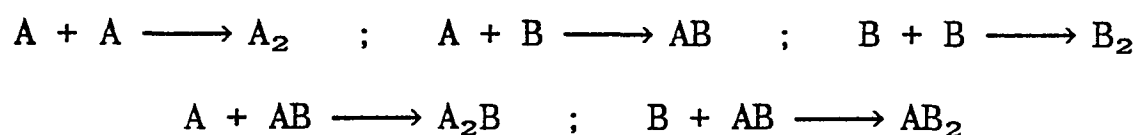
The separation between a diffusing pair is, as mentioned, a Bessel process and the interparticle vector can be expressed in the form,

$$\underline{r} = \underline{r}_0 + N_3[0, 2D'(t-t_0)\underline{1}] \quad (\text{II.2.12})$$

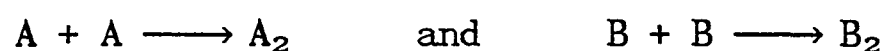
where $\underline{r}_0$ is the vector at time t_0 and N_3 is a normally distributed 3-D random vector whose mean is zero and whose variance/covariance matrix is $2D'(t-t_0)\underline{1}$ ($\underline{1}$ is the identity matrix). The reaction kinetics of a reactive product are based upon the new particle assuming the trajectory of one of its parents. As only the separation of a pair is important in determining its reaction time under the independent pairs approximation, the prescription of equation (II.2.12) can be used to generate separations and, consequently, reaction times for reactive product pairs.

2.4.2 Reaction schemes involving reactive products.

The kinetics of reactive products have been thoroughly examined (Pimblott, 1985) and although the IRT model is less elegant with the inclusion of reactive products, it is possible, using the procedure outlined above, to extend the model and still to maintain a huge computational advantage even over variable timestep simulation. The hybrid reactive products methodology performs at least as well as the Diffusion Approach and the Time Approach from which it is derived and is much better than the Position Approach. The deviation between hybrid IRT simulation and full simulation has never been found to be more than 3%. A typical set of decay and formation curves are shown in Fig.II.2.8. The kinetics are those of a 2A/2B cluster of particles distributed from independent and identically distributed Gaussians and reaction is according to the scheme



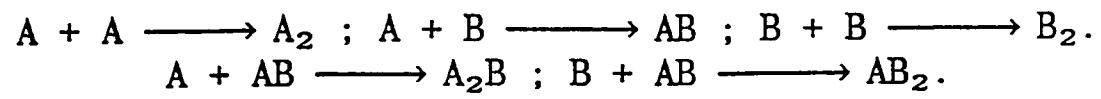
where all the reaction distances are 1.0 nm. The diffusion coefficient of each species is $5.0 \times 10^{-9} \text{ m}^2\text{s}^{-1}$. As no pairs are initially unreactive, this is the simplest possible system for the generation of reaction times for pairs containing reactive products. A much more severe test is provided if the reactions



are removed from the scheme, introducing situations where t_{ab} is potentially greater than t_{ac}^* . Agreement between IRT and full simulation is found to be of the same order as in the simpler case.

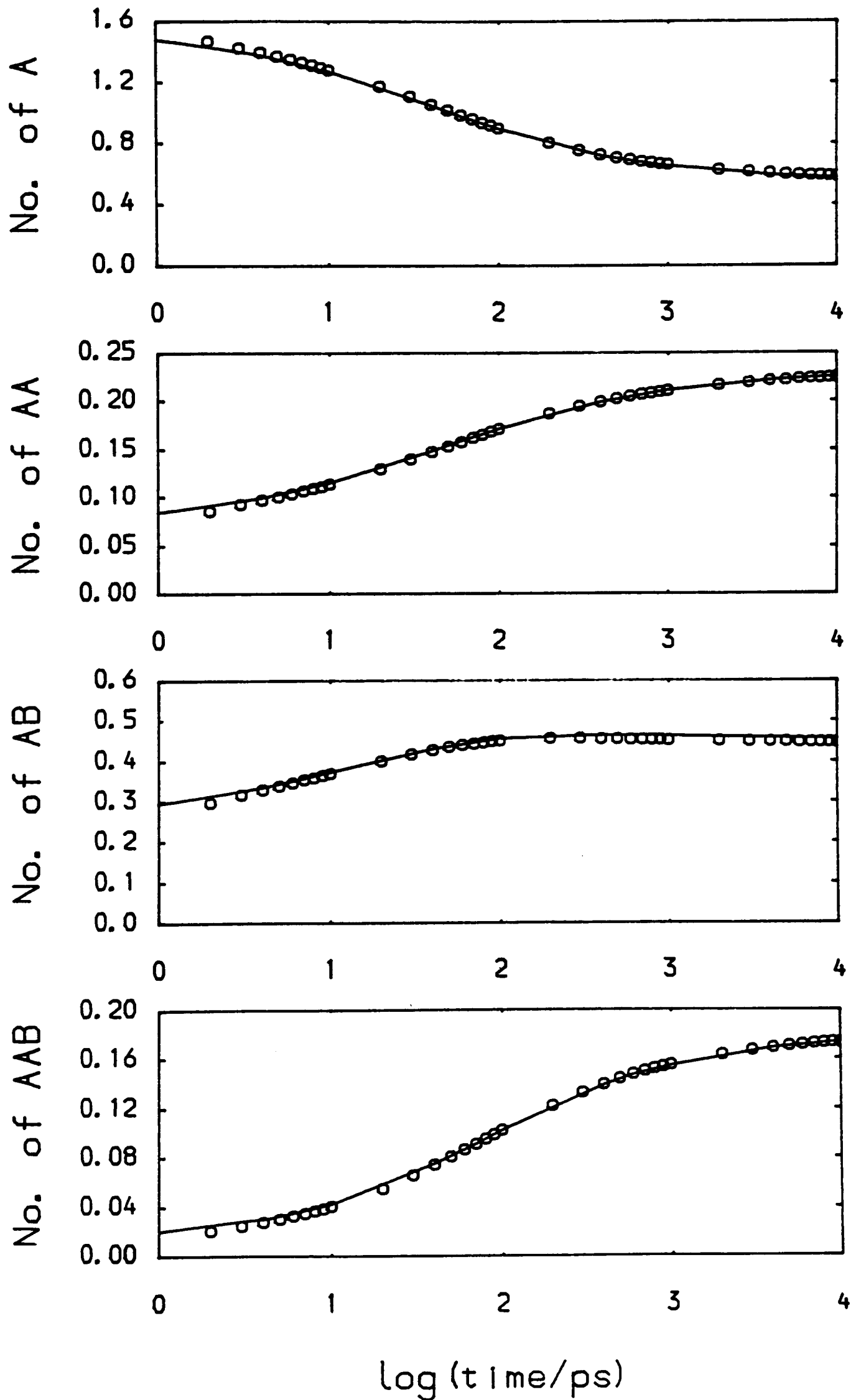
The identical nature of the pathways in both of the reaction schemes above yield superimposable decay curves for A and B and their products. Removing this symmetry and extending the scheme to

Fig.II.2.8 Kinetics of a scheme with reactive products.

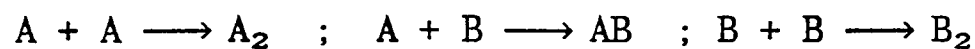


Initially two A and two B are present, distributed from iid Gaussians of standard deviation 1.0 nm; reaction distances all 1.0 nm; diffusion coefficients are $5.0 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$.

(o o o o) Random flights simulation.
(—) IRT simulation.



include the regeneration of one of the initial species, e.g.



also has no effect on the validity of the IRT model and the approximate kinetics correspond to those generated by full simulation (Pimblott, 1985).

2.5 An alternative simulation technique.

The development of the Bessel bridge suggests an alternative approximate stochastic model for the kinetics of nonhomogeneous systems. Like the IRT model of Clifford et al. (1982a) this model, known (somewhat optimistically) as the Great Leap Forward (GLF), is based upon the independent pairs approximation. The kinetics are modelled in the same manner as in the full simulation of the diffusion and reaction processes, but using a fixed, large timestep, τ . The probability of reaction during τ is calculated by independently considering the Bessel bridge for the jump for each pair regardless of separation. The simulated kinetics clearly depend upon the size of τ . At one extreme, small time increments, the kinetics are equivalent to those obtained from full simulation of the diffusion-reaction processes. On the other hand, when the time increments are large, only the escape probability is simulated and the IRT result is obtained. The predicted kinetics would be expected to vary between these two limits as τ is reduced. Surprisingly, this is not always found to be the case.

Consider three particles (1, 2, 3) undergoing Brownian motion. According to the independent pairs approximation, the ultimate probability, S , that the system survives is

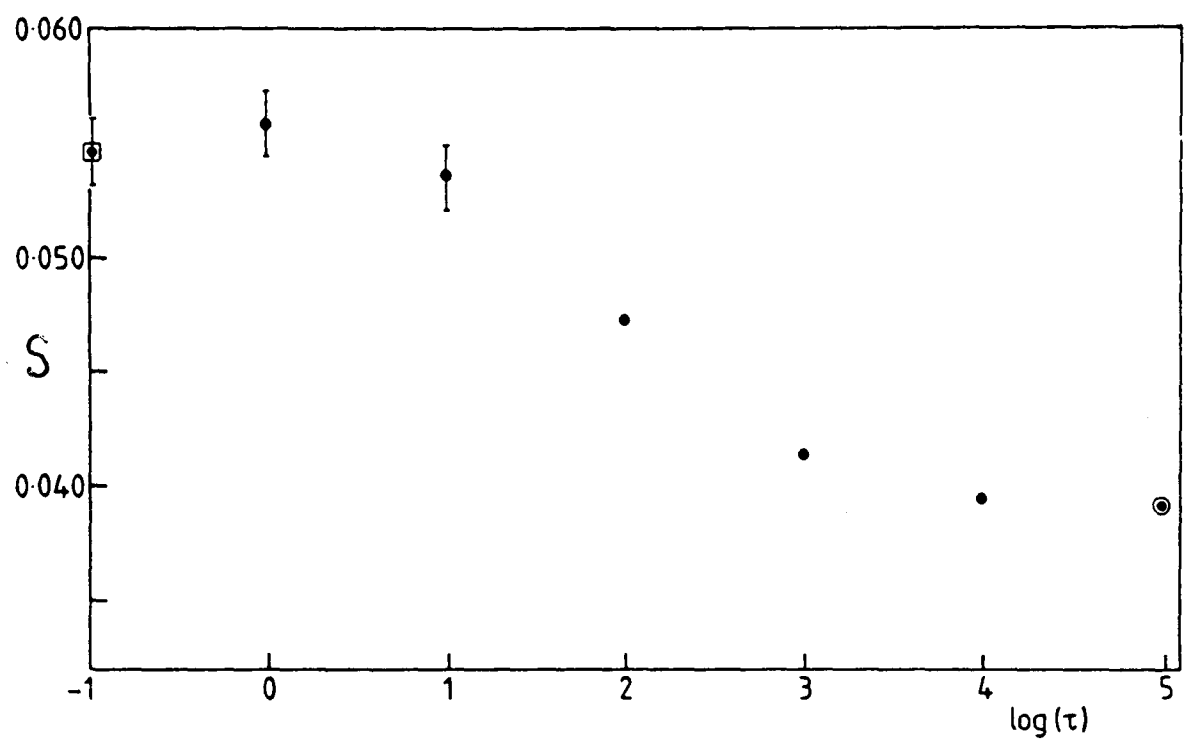
$$S_{\text{IRT}} = \Omega(r_{12}, \infty) \Omega(r_{23}, \infty) \Omega(r_{31}, \infty). \quad (\text{II.2.13})$$

Fig.II.2.9 Survival probability at time 10^{-7} s for a three particle system in three dimensions.
All reaction distances 1.0 nm; all diffusion coefficients $5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$.

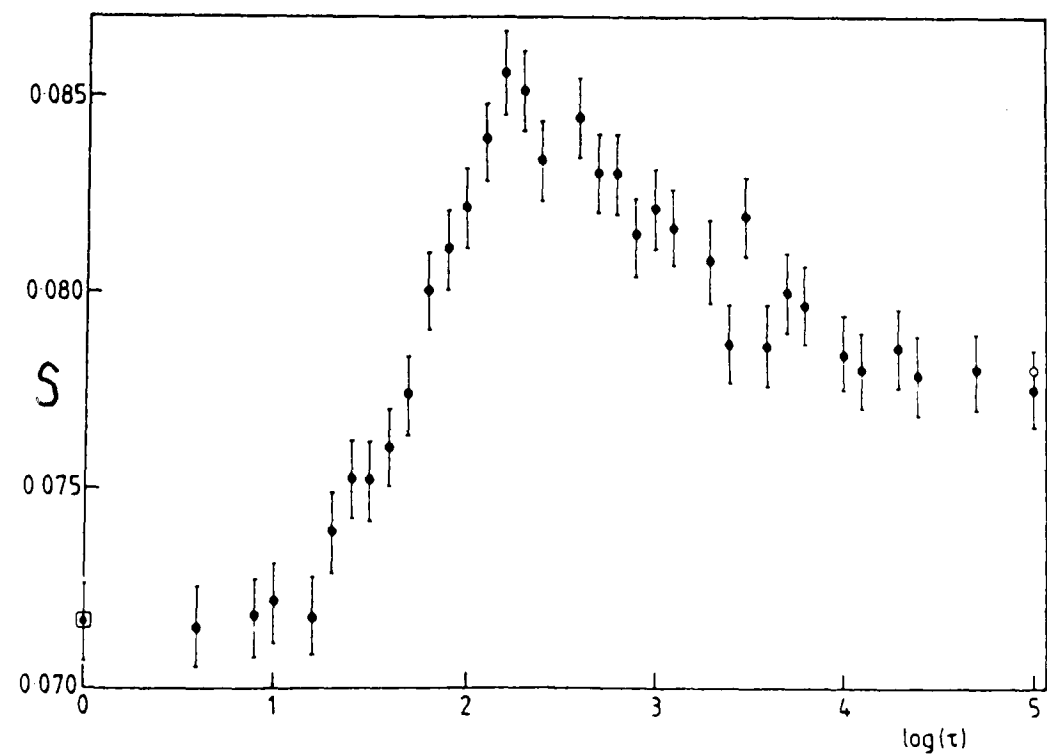
- Variable timestep random flights simulation.
- IRT simulation.
- GLF simulation.

Error bars signify estimated two standard deviations.

Equilateral triangle of side 1.5 nm.



Colinear configuration with two shorter distances 1.5 nm.



where the Ω s are the marginal escape probabilities for each pair. When τ is large S_{GLF} tends to this limit and when τ is small S_{GLF} approaches the full Monte Carlo simulation result, S_{MC} . At values of τ between the two limits the accuracy of S_{GLF} depends upon the initial configuration. This dependence is shown in Fig.II.2.9. The joint survival probability of the three particles initially at the apices of an equilateral triangle behaves in the expected manner, but for a colinear arrangement the deviation of S_{GLF} from S_{MC} is worse for intermediate values of τ than for larger values, and has the opposite sign. This deviation is clearly a breakdown of the independent pairs approximation and contains valuable information about many-body effects. No quantitative explanation of this deviation has been found (Clifford et al., 1987a), although it is probably caused by a correspondence between the time increment, τ , and the timescale for randomisation of the shape of the triangle - the spreading of the distribution is less rapid. As the most probable spatial arrangement for the three particles is an equilateral triangle any deviations caused by a structural relaxation effect would be less obvious for particles initially distributed in this configuration. The GLF, clearly, is of interest and begs further investigation, but is unsuitable for kinetic simulation except in the limits of small and large τ .

Chapter 3 : The influence of charge on recombination kinetics.

About half of the reactants involved in the nonhomogeneous kinetics that immediately follow radiolysis are charged. In this chapter, the effect of the electrostatic interactions upon combination is considered and the influence upon the kinetics is studied. First, the full simulation of the diffusion and reaction processes of ions is discussed and the random flights methodology is extended and validated. Reaction in both low and high permittivity media is considered. Second, using the random flights approach as a 'picture of reality', independent pairs modelling of nonhomogeneous, ionic kinetics is developed. The IRT simulation technique, as presently formulated, requires a closed approximation for the distribution of first passage times to reaction for an isolated pair. An alternative method of generating reaction times, for use when a suitable approximation for $W(r,t)$ is not available, is presented. Finally, the validity of the independent pairs approximation in ionic systems is examined.

3.1 Ionic effects.

Ionic effects are frequently neglected in radiation chemistry (Jaffe, 1913; Schwarz, 1969), but even in high permittivity solvents where the Coulombic forces are weak this assumption is difficult to justify. The interacting charges of the ions influence the diffusion and this effect is non-trivial when more than two ions are present. Even for the single pair case, there is no closed, exact formulation of the time-dependent survival probability. The influence of the interaction between ions is apparent if the geminate problem is examined in detail.

The diffusive motion of an ion in solution and the kinetics of reaction between ions are generally described using the Debye-Smoluchowski equation presented earlier,

$$\frac{\partial \rho}{\partial t} = \nabla \cdot D' \left[\nabla \rho + \frac{\rho}{k_B T} \nabla U \right]. \quad (\text{II.3.1})$$

This equation represents the evolution of the relative spatial density, ρ , of a reactive pair, which is related to the survival probability of the pair by the integral,

$$\Omega(r_0, t) = \int_0^{2\pi} \int_0^\pi \int_0^\infty \rho r^2 \sin\theta \, dr \, d\theta \, d\phi. \quad (\text{II.3.2})$$

The survival probability is independent of the direction of the initial separation vector, $\underline{r}_0$, if the inter-ion force is spherically symmetric and the diffusion is isotropic. Under these conditions equation (II.3.1) simplifies to

$$\frac{\partial \rho}{\partial t} = D' \left[\frac{\partial^2 \rho}{\partial r^2} - \frac{\partial}{\partial r} \left[\frac{\rho(2r+r_c)}{r^2} \right] \right]. \quad (\text{II.3.3})$$

This is a forward equation and describes ρ in terms of the present state of the system. The function ρ also obeys a backward or adjoint equation which expresses the change in ρ with respect to the initial state of the system (Kolmogorov, 1931),

$$\frac{\partial \rho}{\partial t} = D' \left[\frac{\partial^2 \rho}{\partial r_0^2} + \frac{(2r_0+r_c)}{r_0^2} \frac{\partial \rho}{\partial r_0} \right]. \quad (\text{II.3.4})$$

As $\frac{\partial}{\partial r_0}$ does not operate in current space, i.e.

$$\int_{\underline{r}} \frac{\partial \rho}{\partial r_0} \, d\underline{r} = \frac{\partial}{\partial r_0} \int_{\underline{r}} \rho \, d\underline{r}, \quad (\text{II.3.5})$$

the time-dependent survival probability, Ω , and its complement the time-dependent reaction probability, W , also obey the same equation (Goel et al., 1974). The boundary conditions for Ω and W are complementary.

The adjoint equation for Ω and W depends on the physical properties of the system in question through r_c . For a treatment independent of r_c , dimensionless coordinates,

$$x = \frac{2r_0}{r_c} \quad ; \quad \tau = \frac{4D't}{r_c^2} ,$$

are introduced and the equation becomes,

$$\frac{\partial \Omega}{\partial \tau} = \frac{\partial^2 \Omega}{\partial x^2} + \frac{(2x+1)}{x^2} \frac{\partial \Omega}{\partial x} . \quad (\text{II.3.6})$$

This transformation demonstrates the effect that the introduction of an electrostatic force will have upon the kinetics. In radiolysis, the range of separations and the time period that are of interest are generally 10^{-10} to 10^{-8} m and 10^{-12} to 10^{-8} s respectively. In the dimensionless regime, the region of interest is solvent dependent. For water (a high permittivity solvent),

$$0.3 \leq x \leq 30 \quad ; \quad 0.04 \leq \tau \leq 400$$

and for an alkane, typically,

$$7.0 \times 10^{-4} \leq x \leq 0.7 \quad ; \quad 7.0 \times 10^{-5} \leq \tau \leq 0.7.$$

Any complete analytic solution for Ω (or W) has to encompass this entire range - many orders of magnitude of distance and time.

While no closed, exact solution of the Debye-Smoluchowski equation is known, a number of closed approximations exist. If an approximate solution accurately represents the time-dependent problem in a particular region of interest, it can be used to examine whether, or not, charge effects are likely to be important

in recombination. For water, the reaction probability of a geminate pair is accurately described by (Clifford et al., 1987b)

$$W(r_0, t) = \frac{R_{\text{eff}}}{r_{\text{eff}}} \operatorname{erfc} \left[\frac{r_{\text{eff}} - R_{\text{eff}}}{2\sqrt{D't}} \right]. \quad (\text{II.3.7})$$

where the natural distance scale is defined by

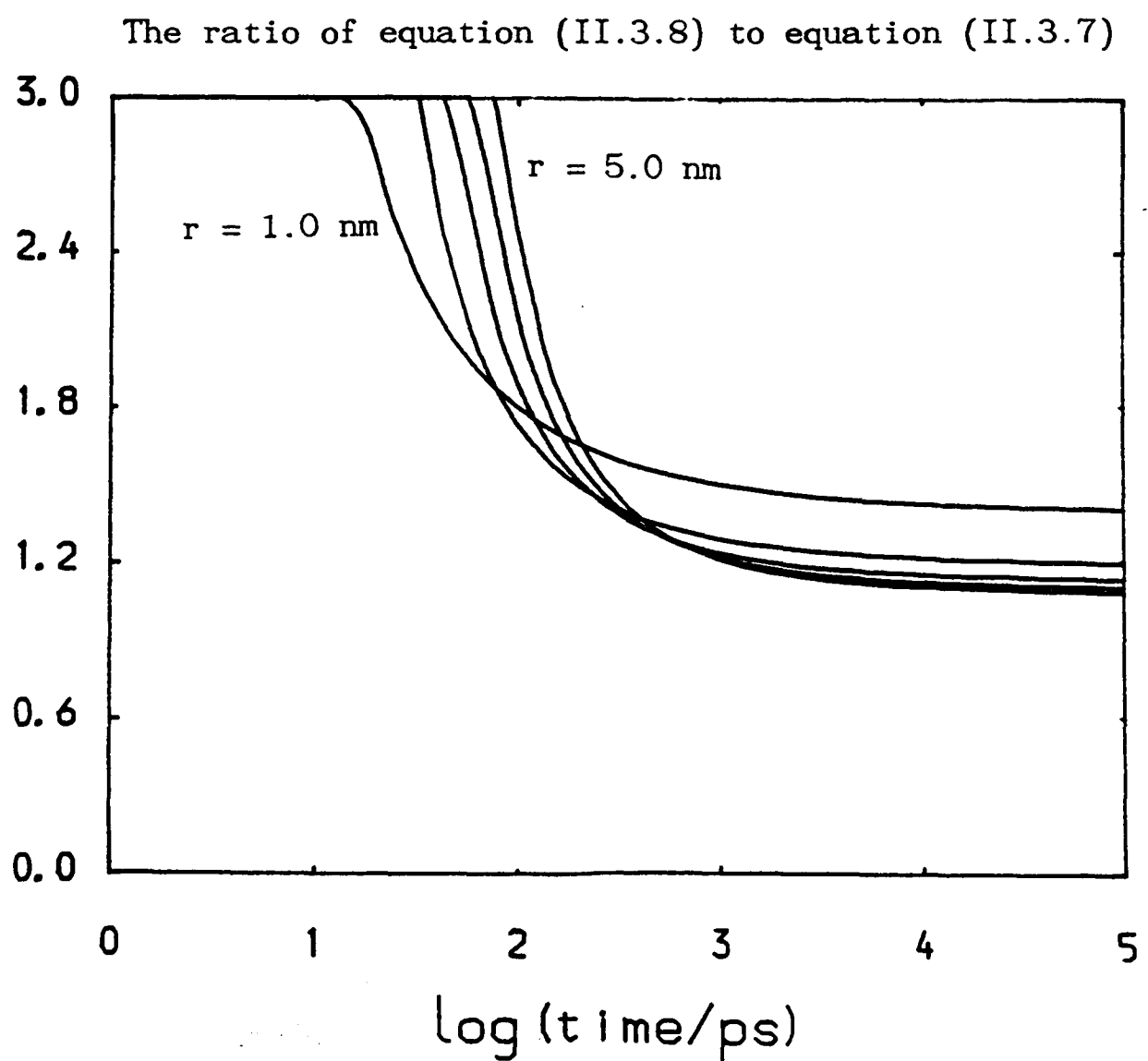
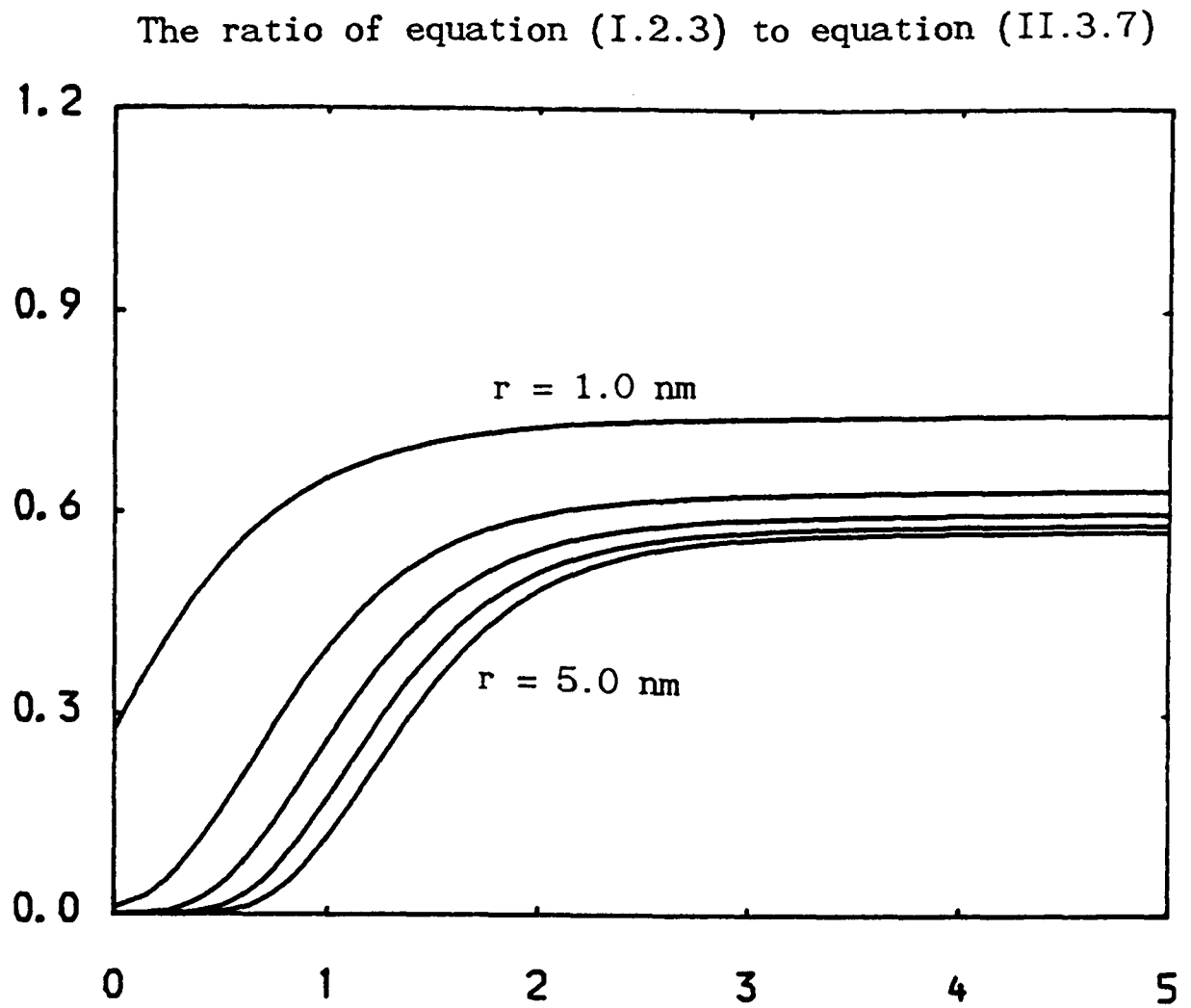
$$x_{\text{eff}} = -r_c / (1 - \exp(r_c/x)).$$

For large r_0 , r_{eff} approaches r_0 asymptotically and so, if r_0 and R are sufficiently large, equation (II.3.7) reduces to the solution for neutrals. Assuming that charge effects can be ignored completely is equivalent to equating r_{eff} with r_0 and R_{eff} with R for all distances. The effect of this approximation is shown in Fig.II.3.1. The time-dependent ratio of equation (I.2.3), the solution for neutrals, to equation (II.3.7) is plotted for an oppositely charged pair at several initial separations. The reaction distance, $R = 0.5 \text{ nm}$, and the relative diffusion coefficient, $D' = 1.0 \times 10^{-8} \text{ m}^2\text{s}^{-1}$, are typical for ions in water. Agreement is poor and reaches a limit as the inter-ion separation increases. This limit is a consequence of r_{eff} approaching r_0 , while R_{eff} is very different from R .

Conventional nonhomogeneous kinetic methods (Schwarz, 1969) frequently neglect the influence of electrostatic forces on the diffusion of the ions, but include, by using experimental rate constants, ionic effects on the effective reaction distance. This is equivalent to using the following time-dependent approximation for W ,

$$W(r_0, t) = \frac{R_{\text{eff}}}{r_0} \operatorname{erfc} \left[\frac{r_0 - R_{\text{eff}}}{2\sqrt{D't}} \right]. \quad (\text{II.3.8})$$

Fig.II.3.1 The effect of ignoring the effects of charge when modelling geminate recombination in water.
 $|r_c| = 0.7 \text{ nm}$; $R = 0.5 \text{ nm}$; $D' = 1.0 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$.



The ratio of this equation to equation (II.3.7) is also shown in Fig.II.3.1. Equation (II.3.8) is asymptotically correct at large initial separations, but there are large errors when r_0 is small - exactly the situation of importance in nonhomogeneous kinetics. Charge effects are clearly important in the recombination of ions and should therefore be considered explicitly in radiolysis kinetics.

3.2 Monte Carlo simulation of the diffusion of ions.

When the random flights analysis is extended to include ionic species a second term specifying the effect of the electrostatic interaction is introduced into the stochastic differential equation describing the trajectory of the particle. If the force is Coulombic, the stochastic differential equation becomes

$$d\mathbf{R}_i = - \sum_j \frac{z_i z_j r_c D_i}{r_{ij}^3} \mathbf{r}_{ij} dt + \sqrt{2D_i} d\mathbf{W}_3 \quad (\text{II.3.9})$$

where r_c is the Onsager distance defined in chapter I.2. The exact Green's function trajectory described by this stochastic differential equation is not known and to simulate the process it is necessary to find a discretisation that will converge to equation (II.3.9) at arbitrarily short timesteps. Several methods of discretisation, and the orders of error incurred, have been discussed in the mathematical literature (Milshtein, 1978; Rumelin, 1982; Pardoux & Talay, 1985). The simplest method (Rumelin, 1982) involves a generalisation of the Euler method for the numerical solution of ordinary differential equations. The stochastic differential equation is discretised to give

$$\delta\mathbf{R}_i = - \sum_j \frac{z_i z_j r_c D_i}{r_{ij}^3} \mathbf{r}_{ij} \delta t + \sqrt{2D_i \delta t} N_3(0, \mathbf{1}) \quad (\text{II.3.10})$$

where N_3 is a 3-D random number of unit variance. This discretisation is adequate if the timestep, δt , is sufficiently small that the infinitesimal mean and variance do not change.

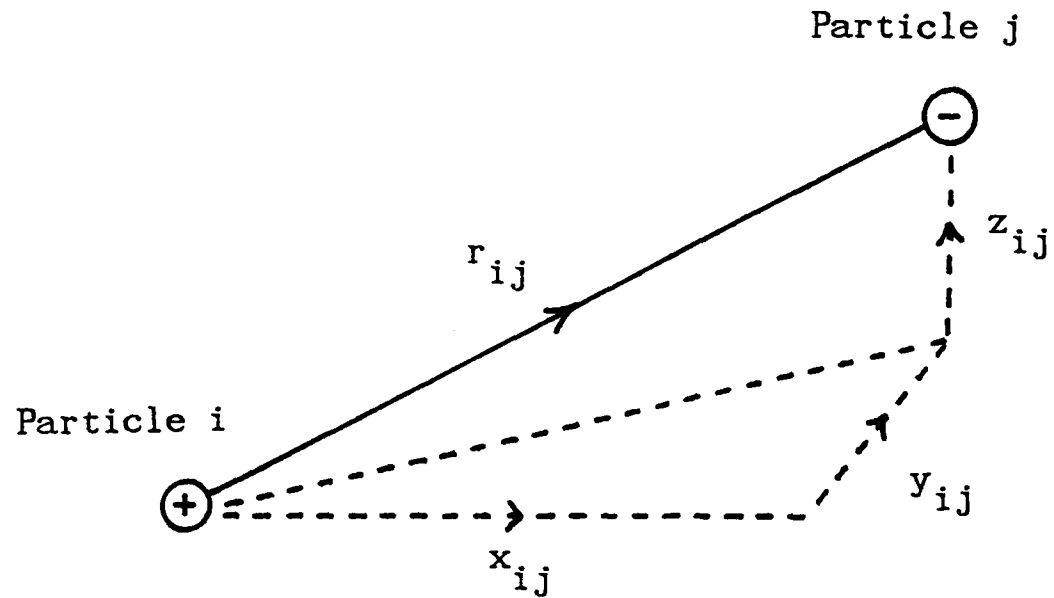
In simulating the diffusion and reaction of neutral particles, the trajectories are sampled using a variable timestep random flights technique and reaction is modelled by encounter or using a bridging process. Extending this treatment to ionic species requires the simulated diffusion to converge to equation (II.3.9). The random flight has two components: one to represent random Brownian motion and a second to include the effect of electrostatic interactions. The former component is modelled in the same manner as in the absence of an interparticle force, while the latter is treated according to the discretisation of the stochastic differential equation describing the diffusive motion - by summing the interactions as if the pairs are in isolation. The net effect is a random flight in which each Cartesian coordinate changes according to

$$\delta x_i = - \sum_j \frac{z_i z_j^r c_i^D}{r_{ij}^3} x_{ij} \delta t + \sqrt{2D_i \delta t} N(0,1). \quad (\text{II.3.11})$$

This is expressed pictorially in Fig.II.3.2.

As the simulated diffusion must converge to the stochastic differential equation (II.3.9), for an accurate representation, the interparticle forces must not change appreciably during a jump. The size of the timestep for a random flight is, in effect, restricted by the change in drift. Rather than place further restrictions on the present method of calculating the timestep for a random flight, a more appropriate approach is to reformulate the calculation of the timestep in terms of a maximum acceptable change in drift. This

Fig.II.3.2 Coordinate system for a random flight under the influence of a Coulomb potential.



$$\delta x_i = - \frac{D_i r_c}{|r_{ij}|^3} x_{ij} t + \sqrt{(2D_i t)} N(0,1)$$

$$\delta x_j = \frac{D_j r_c}{|r_{ij}|^3} x_{ij} t + \sqrt{(2D_j t)} N(0,1)$$

$$\delta y_i = - \frac{D_i r_c}{|r_{ij}|^3} y_{ij} t + \sqrt{(2D_i t)} N(0,1)$$

$$\delta y_j = \frac{D_j r_c}{|r_{ij}|^3} y_{ij} t + \sqrt{(2D_j t)} N(0,1)$$

$$\delta z_i = - \frac{D_i r_c}{|r_{ij}|^3} z_{ij} t + \sqrt{(2D_i t)} N(0,1)$$

$$\delta z_j = \frac{D_j r_c}{|r_{ij}|^3} z_{ij} t + \sqrt{(2D_j t)} N(0,1)$$

type of treatment is applicable to systems of ions and neutral particles.

Consider a group of particles. If the pairs are treated as being in isolation, the diffusion equation describing the evolution of a pair has a drift term with a coefficient proportional to $1/r$. To a first level of approximation the pair with the shortest interparticle distance experiences the greatest change in drift during a diffusive random flight. Analysis of this pair provides a method for calculating the length of a random flight. The timestep is equated to the time for which the drift of the pair has a 95% chance of changing by less than a fraction ϵ (usually 0.10). For a pair of singly charged ions,

$$\delta t = \frac{r_0^4}{D'(2r_0 - r_c)^2} \left[\sqrt{2 + \frac{\epsilon(2r_0 - r_c)^2}{2r_0(r_0 - r_c)}} - \sqrt{2} \right]^2. \quad (\text{II.3.12})$$

(The mathematics are presented in appendix C.) The variation of δt with the inter-ion separation is shown in Fig.II.3.3. Note the discontinuity at separation r_c for the repulsive pair; in the simulation, for the purpose of calculating δt , all pairs are assumed to be oppositely charged. As $\delta t_{+/-} < \delta t_{+/+} = \delta t_{-/-}$, the only effect is a slight reduction in the computer efficiency of the simulation. In the absence of an interparticle force,

$$\delta t = \frac{r_0^2}{2D'} [\sqrt{1+\epsilon} - 1]^2 \quad (\text{II.3.13})$$

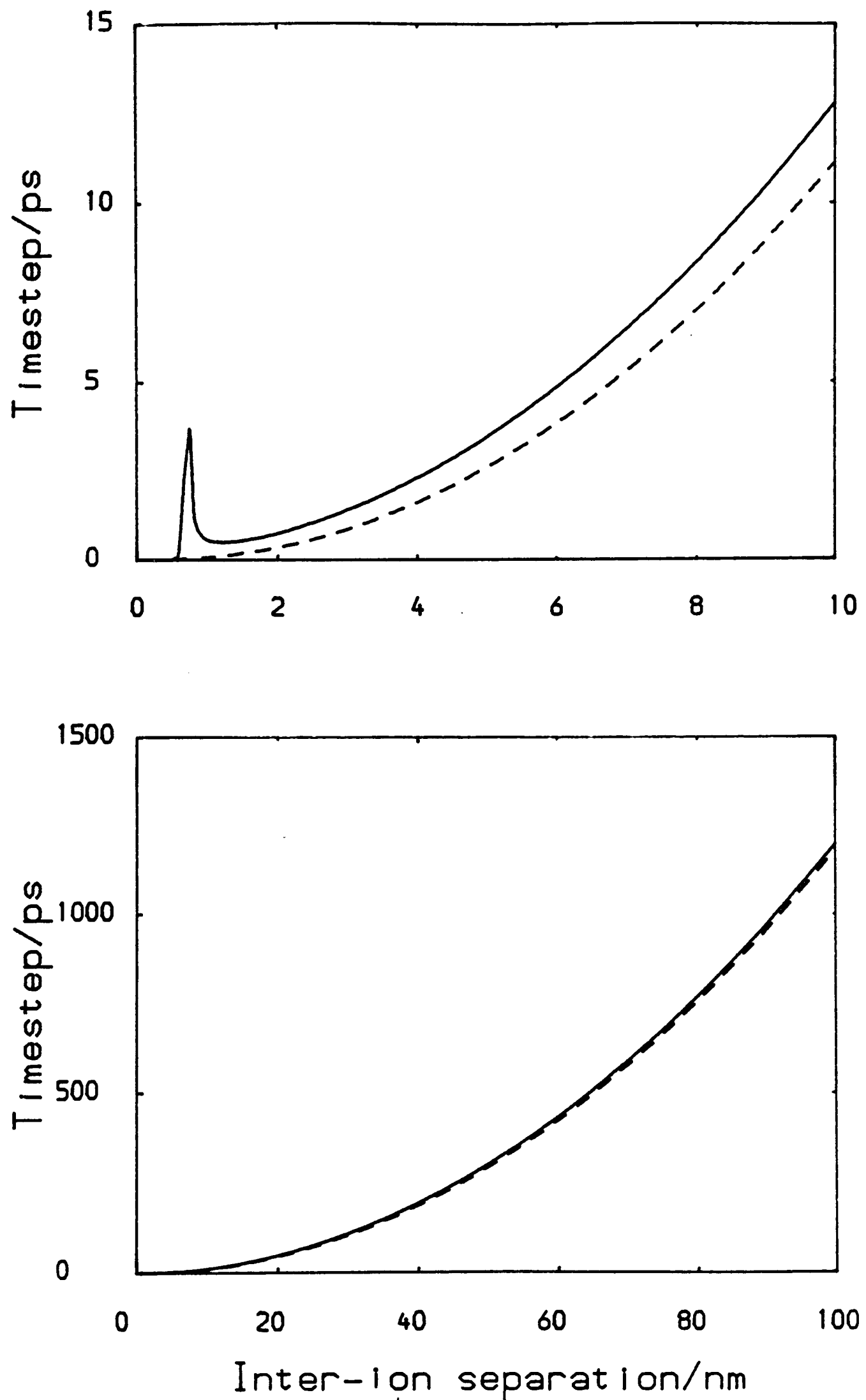
which is the large r_0 asymptote of equation (II.3.12).

In modelling kinetics using full simulation methods, reaction between particles is measured in two ways: either the particles are in a reactive configuration at the end of a timestep or a bridging

Fig.II.3.3 The variation of a random flights timestep with inter-ion separation.

$|r_c| = 0.7 \text{ nm}$; $D' = 1.0 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$; $\epsilon = 0.1$.

(—) Repulsive inter-ion force.
 (---) Attractive inter-ion force.



process is used to estimate the possibility of reaction during a timestep. The inclusion of ionic effects does not invalidate the Brownian bridge, which can be applied without modification. The reformulation of the method for calculating δt in terms of the drift between particles has the additional advantage that it is no longer necessary to limit the application of the bridging process. If the simulation is convergent to the true sample path then, during a timestep, the diffusion process is indistinguishable from a Wiener process with constant drift. This is the assumption made in deriving the Brownian bridge.

To check the discretisation and to confirm that the processes simulated converge to the diffusion of interest, the geminate recombination of an ion-pair is considered. A typical comparison of simulated kinetics and those obtained by numerical solution of the backward equation (II.3.4) is shown in Fig.II.3.4. At times less than 1.0×10^{-12} s the discretisation of the simulation technique is not sufficiently accurate to be a true representation of the kinetics, but on this timescale the use of a diffusion equation method is of questionable validity.

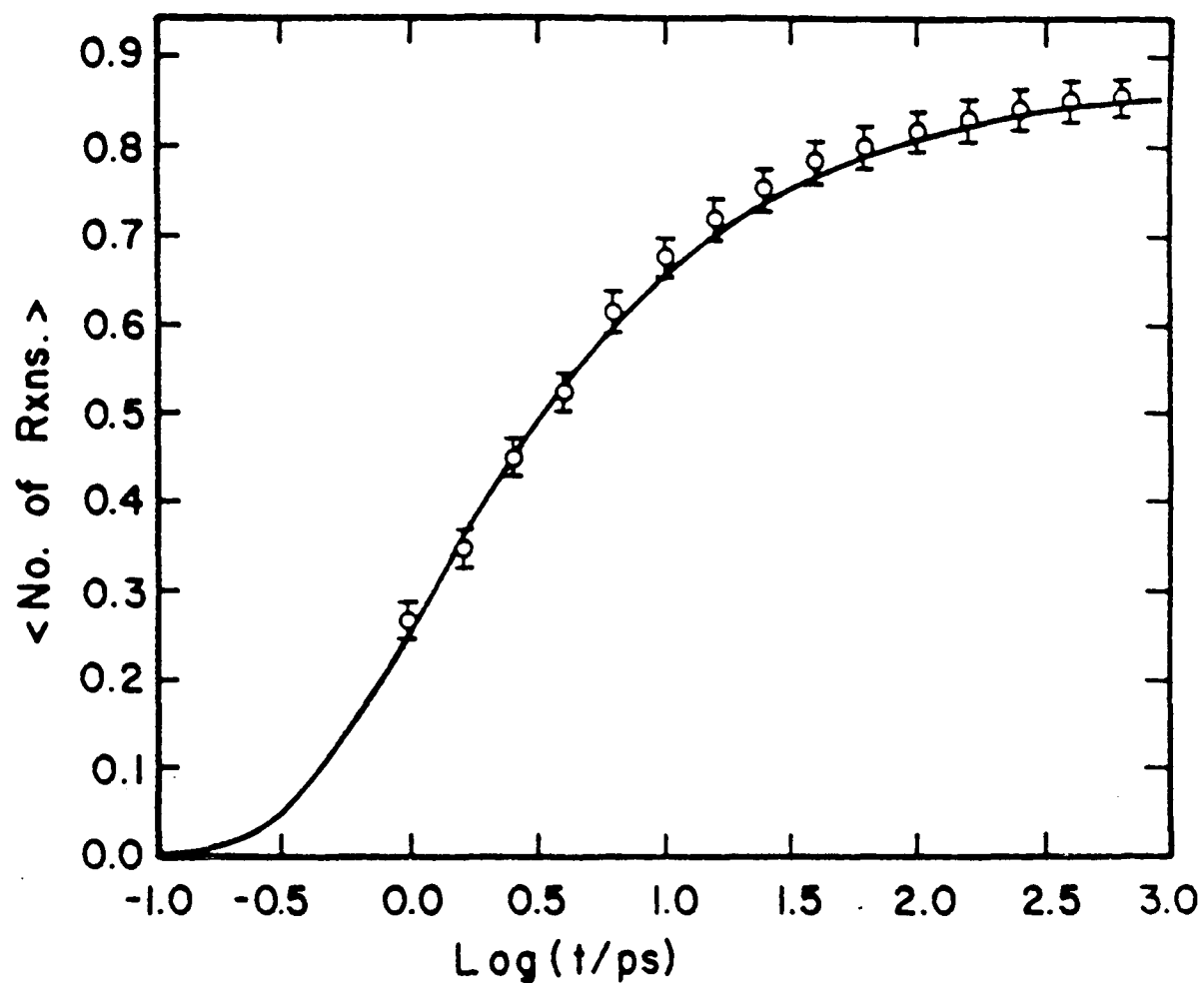
3.3 IRT modelling of the kinetics of ions.

The Independent Reaction Times model explicitly recognises the importance of pair correlation in nonhomogeneous kinetics, but it neglects higher order effects. The model makes an independent pairs approximation and formulates the problem in terms of pair distances. The approximation has been shown to be acceptable, and the model accurately reproduces the kinetics when applied to clusters of neutral particles. In ionic systems, long range forces increase the importance of many-body correlations and the validity of the independent pairs approximation must be re-examined.

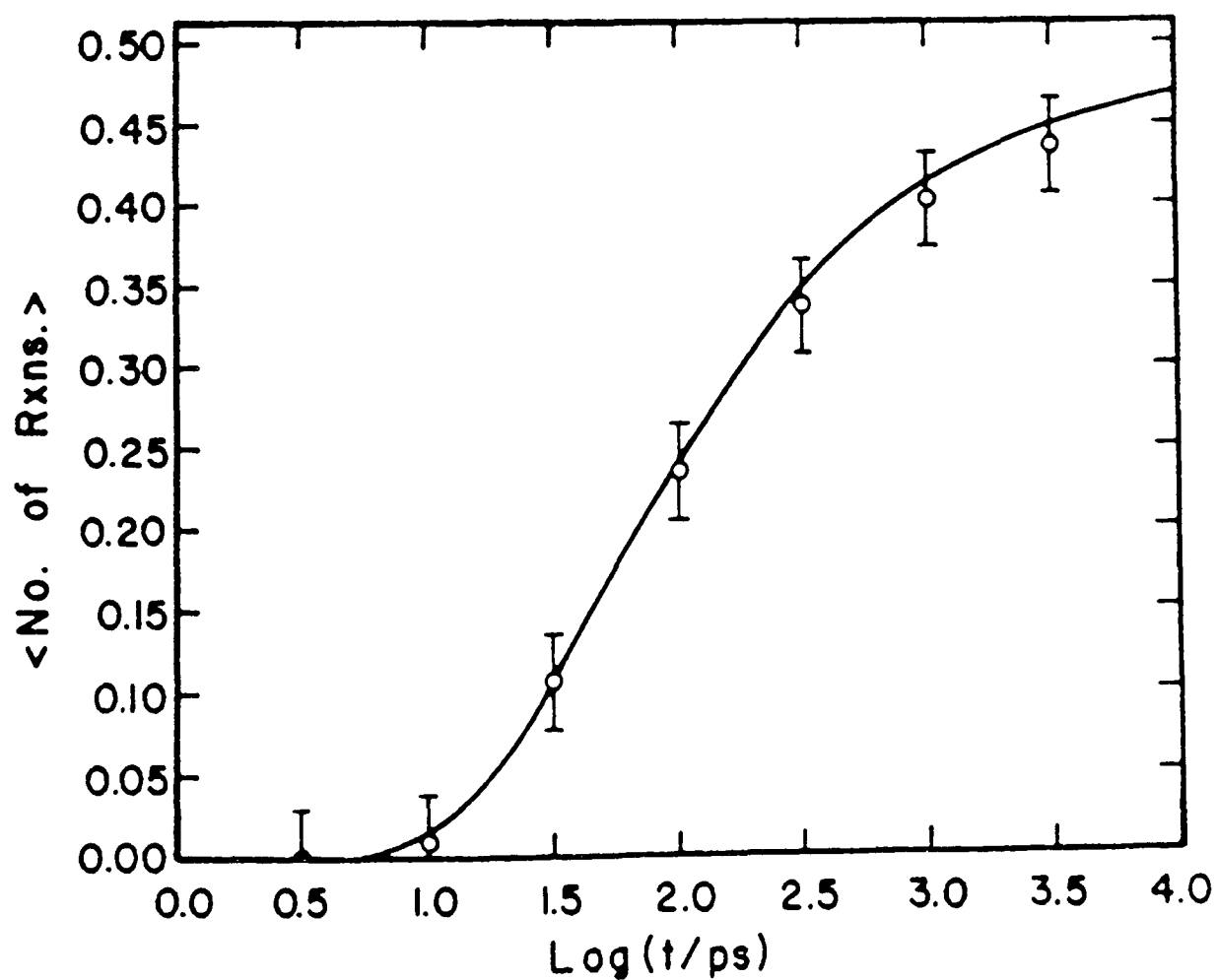
Fig.II.3.4 Geminate recombination of an ion pair.
 $r_c = -0.7$ nm; $D' = 1.0 \times 10^{-8}$ m²s⁻¹; $R = 0.5$ nm.

(—) Numerical solution of backward equation.
 (o o o o) Random flights simulation.

Initial inter-ion separation = 0.65 nm.



Initial inter-ion separation = 1.5 nm.



The IRT model has already been described in detail in chapter II.1. The important step is the generation of a random reaction time for each pair by the inversion of the time-dependent reaction probability of that pair. When dealing with the kinetics of neutrals, this is straightforward, W is closed, exact and easily inverted. A closed, exact solution for W is not available in the presence of an electrostatic force. A number of closed analytic approximations are known, but, these approximations do not always accurately reproduce W even within the limited regions of interest.

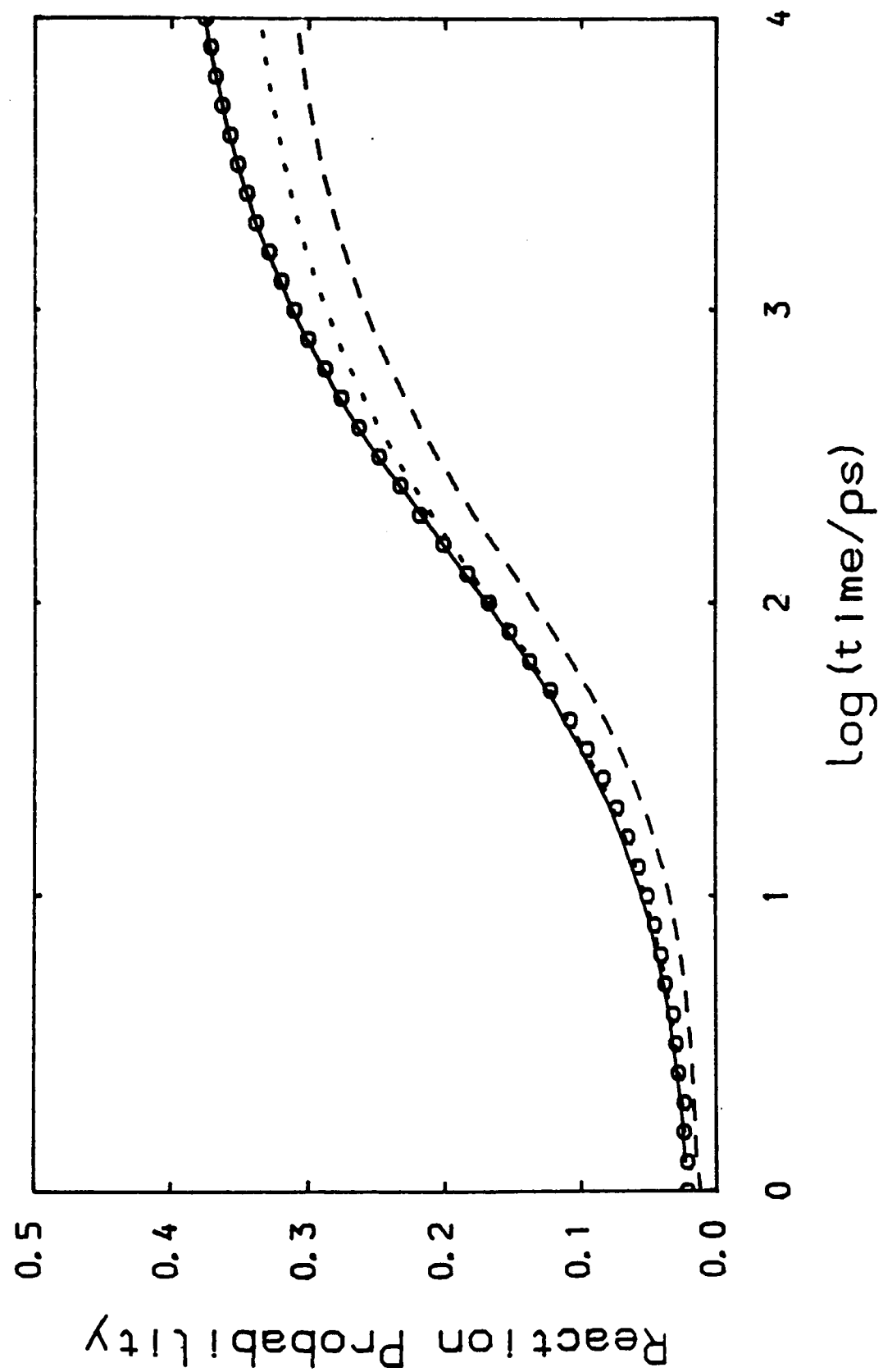
3.3.1 Recombination in water.

One accurate analytic approximation, derived by Clifford et al. (1984) refers to the recombination of ions in water - equation (II.3.7) - and was used earlier in this chapter. When expressed in the natural distance scale of chapter I.2, this approximation has the same form as the exact solution for neutrals and is easily inverted. Inclusion in the IRT methodology is straightforward. To test the validity of the independent pairs approximation in the presence of electrostatic forces, the kinetics of idealised ionic systems are considered. Random flights simulation is taken as 'a model of reality' and it is compared with the corresponding IRT result. For the sake of completeness, the kinetics predicted by the conventional prescribed diffusion model of Schwarz (1969) are also included.

The studies to test the approximations of the IRT model consider two reactive species, A^+ and B^- . Each ion has a diffusion coefficient of $5.0 \times 10^{-9} \text{ m}^2\text{s}^{-1}$ and all reactive pairs have a reaction distance of $1.0 \times 10^{-9} \text{ m}$. The kinetics of a single recombining pair, where ions are positioned from independent and identically distributed (iid) Gaussians of standard deviation 1.0 nm, are shown in Fig.II.3.5. Agreement between full simulation

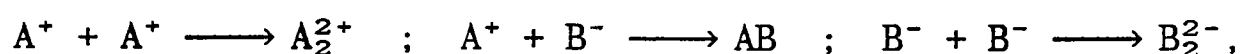
Fig.II.3.5 Comparison of IRT simulation and prescribed diffusion modelling of geminate recombination.
 Ions distributed from iid Gaussians, $\sigma = 1.0$ nm; $R = 0.5$ nm;
 $|r_c| = 0.7$ nm; $D' = 1.0 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$.

(o o o o) Random flights simulation.
 (—) IRT simulation.
 (---) Prescribed diffusion, $k(\infty)$.
 (· · · ·) Prescribed diffusion, $k(t)$.



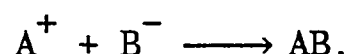
and the IRT model is excellent and this reflects the accuracy of the approximation for the time-dependent reaction probability. Comparison between the model of Schwarz and full simulation shows that the conventional model seriously underestimates the amount of recombination.

The kinetics of two and three pair clusters, governed by the reaction scheme



are considered in Fig.II.3.6. The A^+ and B^- ions are positioned from iid Gaussians of the same width as in the single pair study above. Ionic products are not removed from the full simulation, but allowed to continue diffusing as their charges will affect subsequent diffusion of other ions. The agreement between the two stochastic models is less accurate than for neutrals, showing an error of about 3%. Prescribed diffusion, using a time dependent rate coefficient, performs better than in the neutral case, but it is still inaccurate. Comparison between both the approximate models and the full simulation improves in the three pair case.

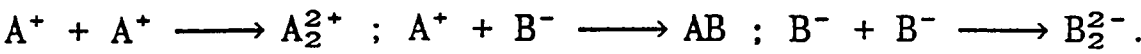
The evolution of similar two and three pair clusters, but under the reaction scheme



is shown in Fig.II.3.7. The same pattern of agreement is observed although prescribed diffusion using a time-dependent rate coefficient shows a significant improvement.

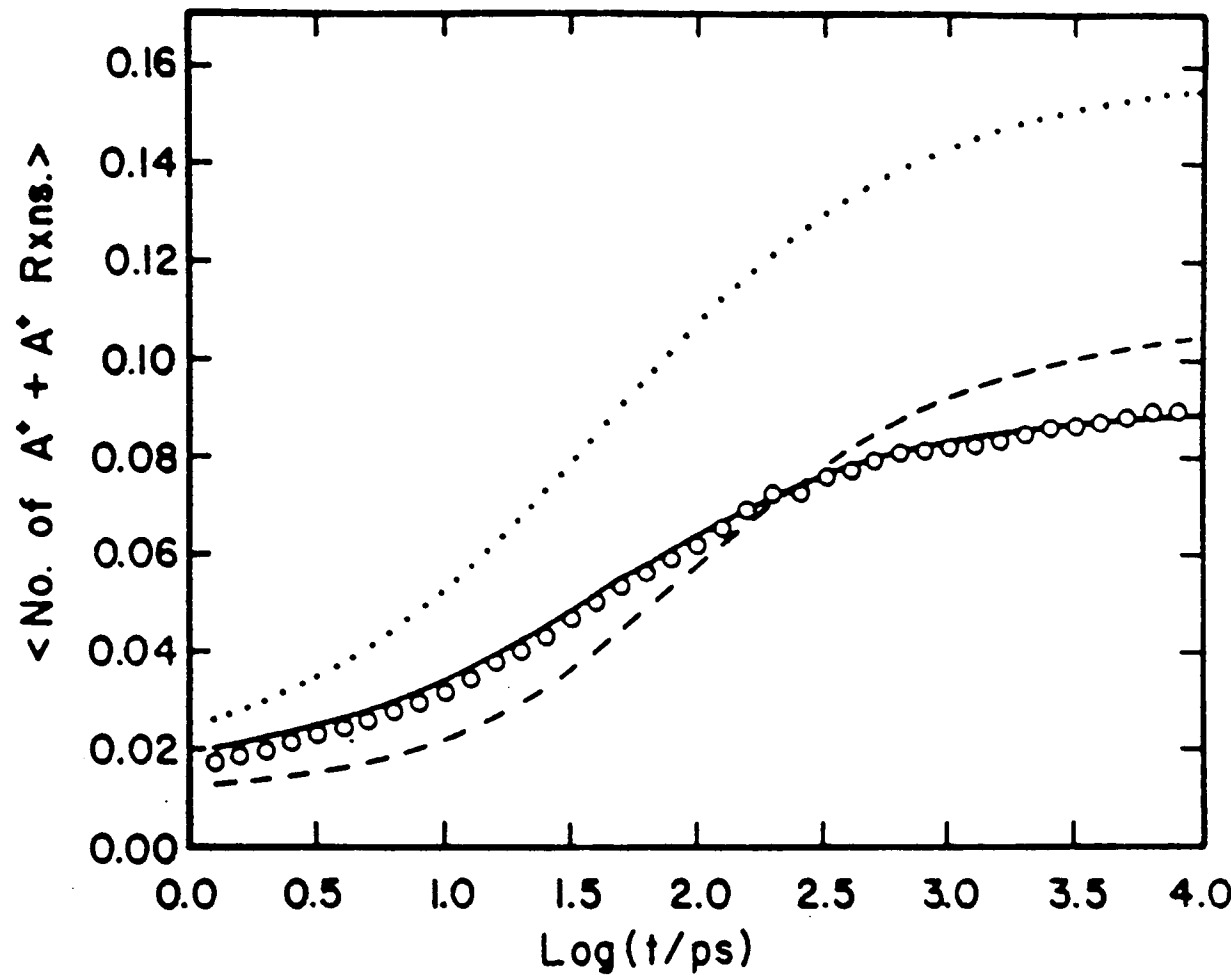
The conventional approximate analytic treatment of nonhomogeneous kinetics using prescribed diffusion methods is restricted to Gaussian systems such as those considered above. The stochastic IRT model can, in principle, deal with any realisable arrangement of particles. For example, the evolution of four ions, two A^+ and two B^- , initially at the vertices of a regular

Fig.II.3.6 Comparison of IRT simulation and prescribed diffusion modelling of the kinetics of multipair clusters.

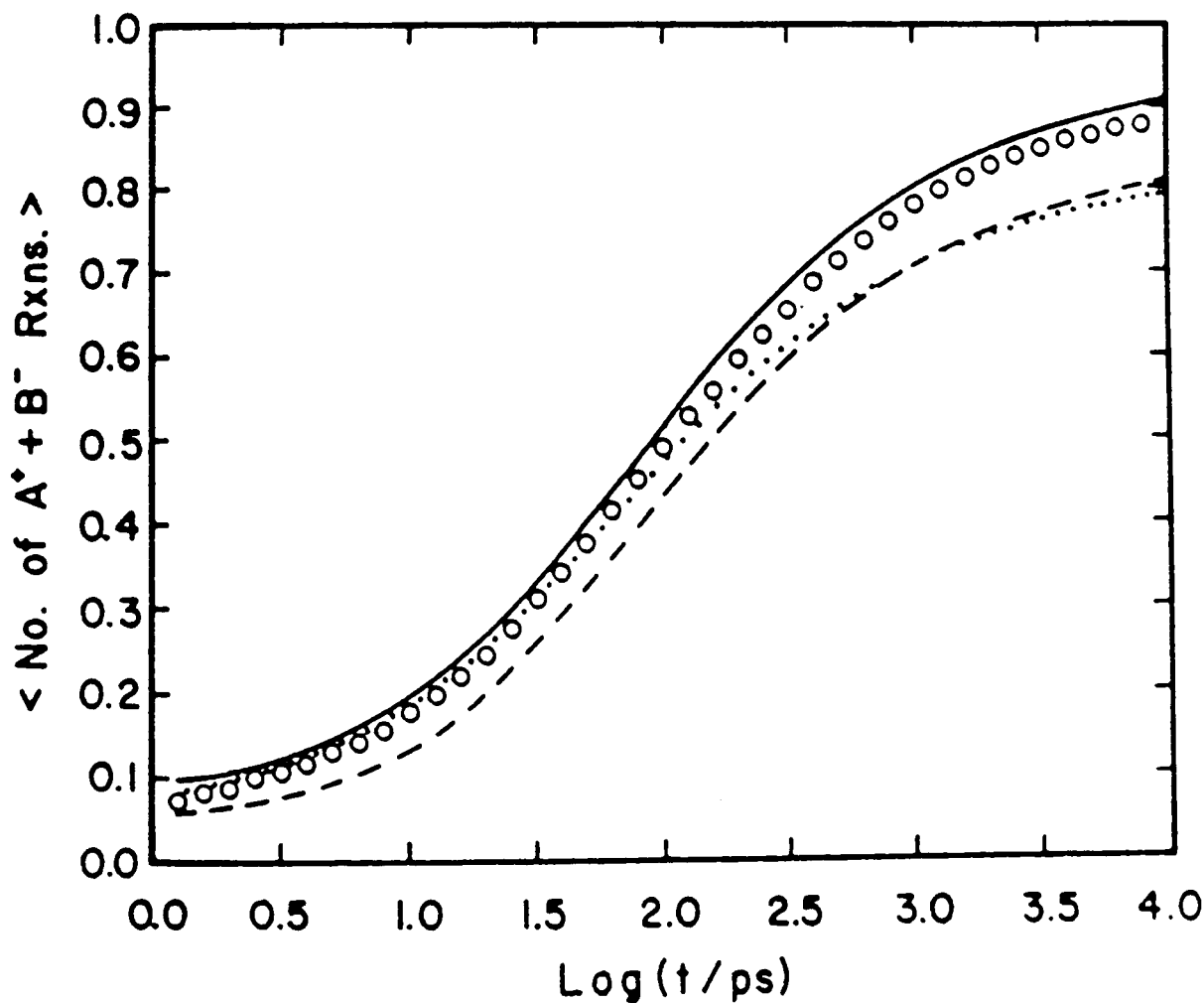


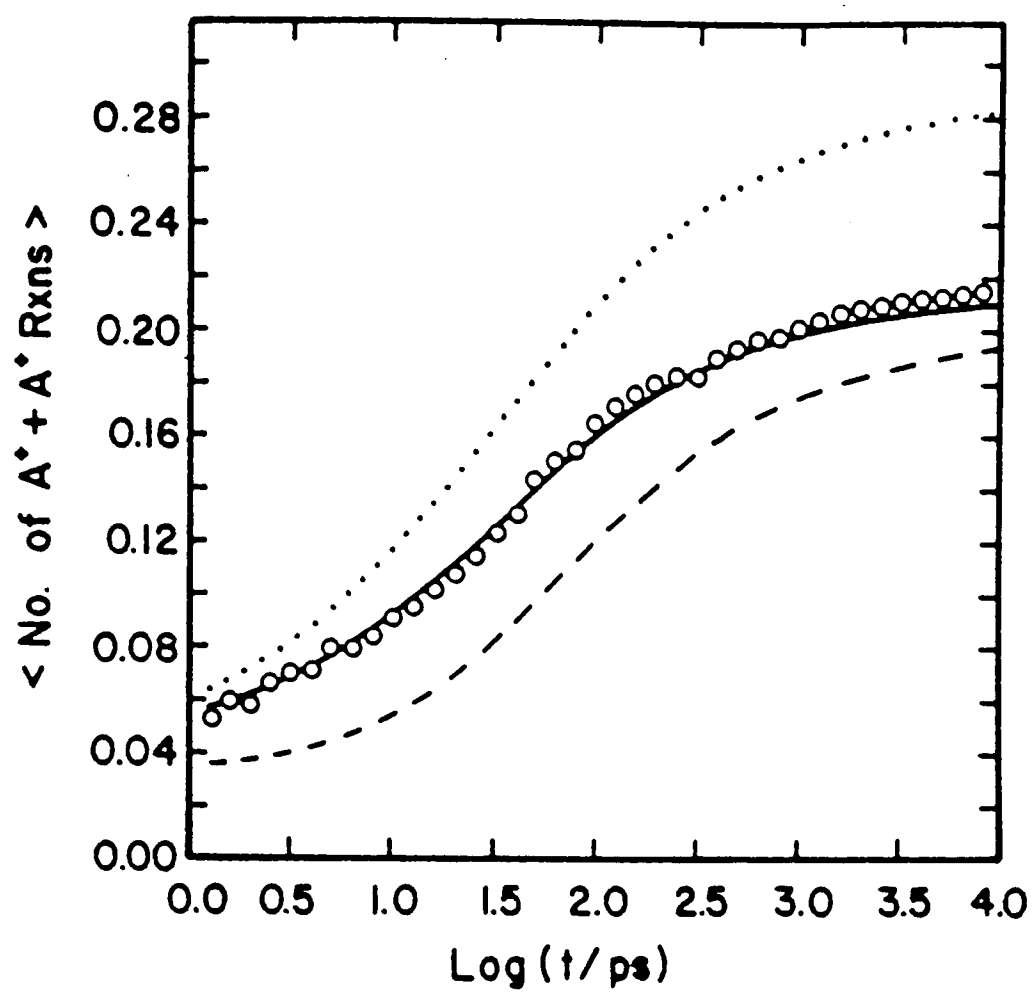
Ions distributed from iid Gaussians, $\sigma = 1.0$ nm; reaction distances all 0.5 nm; diffusion coefficients are $5.0 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$; $|r_c| = 0.7$ nm.

(o o o o) Random flights simulation. (----) Prescribed Diffusion, $k(\infty)$
 (——) IRT simulation. (.....) Prescribed Diffusion, $k(t)$.



(a) Two-pair cluster.





(b) Three-pair cluster.

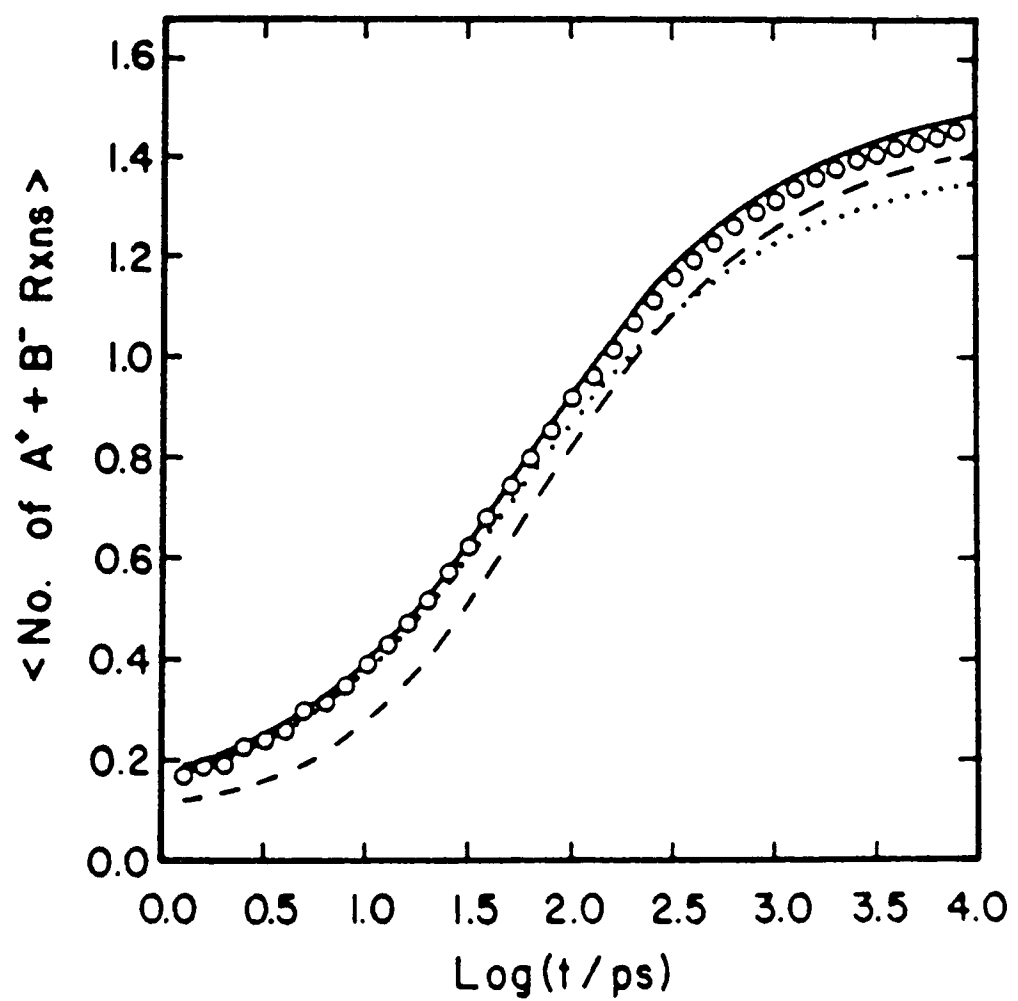
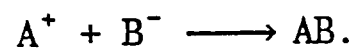


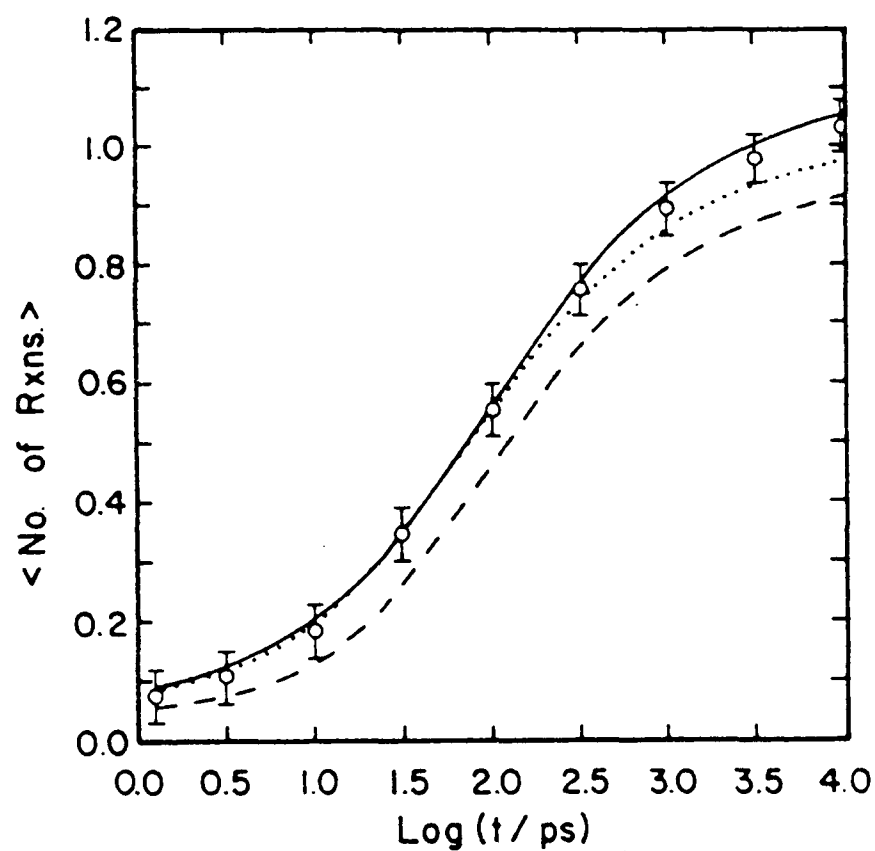
Fig.II.3.7 Comparison of IRT simulation and prescribed diffusion modelling of the kinetics of multipair clusters.



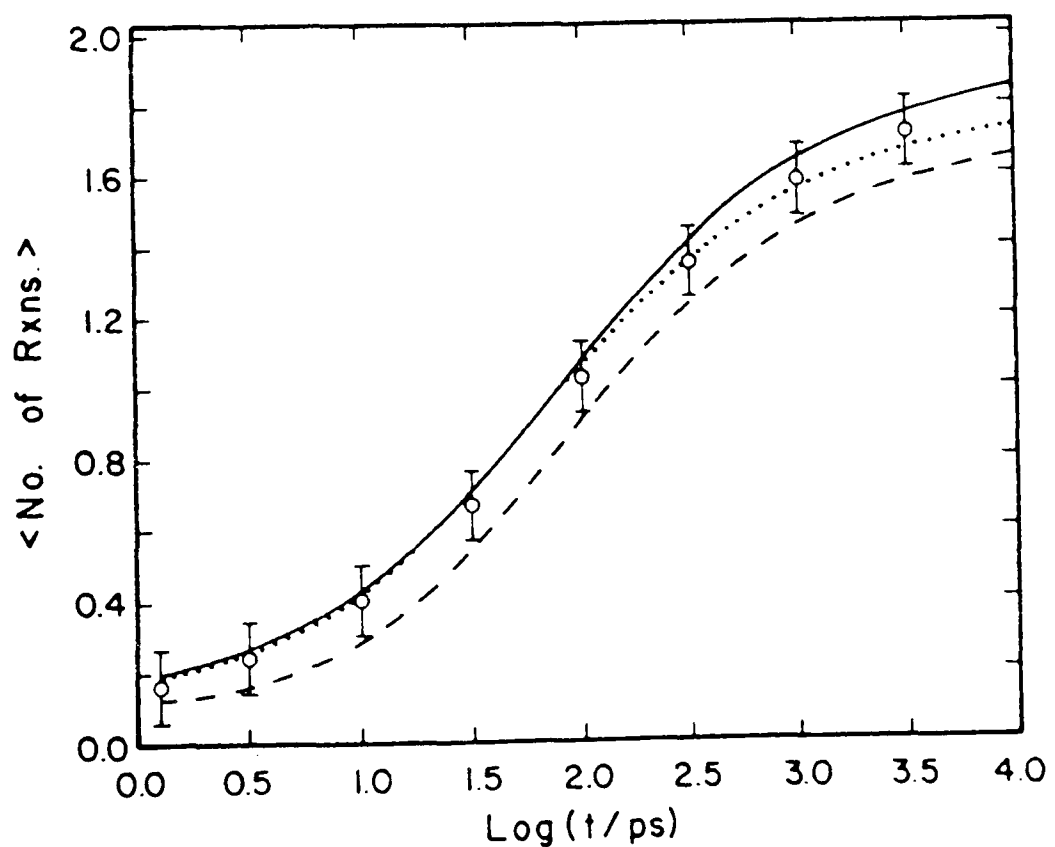
Ions distributed from iid Gaussians, $\sigma = 1.0$ nm; $R = 0.5$ nm; diffusion coefficients are $5.0 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$; $|r_c| = 0.7$ nm.

- (o o o o) Random flights simulation.
- (—) IRT simulation.
- (- - - -) Prescribed diffusion, $k(\infty)$.
- (. . . .) Prescribed diffusion, $k(t)$.

(a) Two-pair cluster.



(b) Three-pair cluster.



tetrahedron of edge $\sqrt{2}$ nm is described in Fig.II.3.8. The ions have the same characteristics as those in the simulations above and the reaction distances are

$$R_{+/+} = R_{+/-} = R_{-/-} = 1.0 \text{ nm.}$$

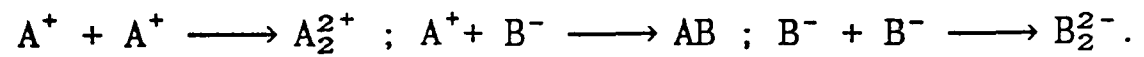
The IRT model is within 4% of the full simulation results. This configuration maximises the effect of competition - all the inter-ion separations are the same and the simulation provides a more stringent test of the independent pairs approximation than the random distributions above.

To show the influence of electrostatic effects upon nonhomogeneous kinetics the kinetics of a two pair Gaussian cluster in which the charge has been 'turned off' are presented in Fig.II.3.9. The same effective reaction distance is used as in the true simulations. This study emphasises the fact that charge effects are very important in the nonhomogeneous kinetics of aqueous solutions, contrary to the generally held view. They alter the product ratios significantly and speed up the timescale of the kinetics slightly.

3.3.2 Low permittivity solvents.

At present, application of the IRT model depends upon the existence of a closed form for the time-dependent reaction probability of a pair under the conditions of interest. Accurate approximations have been presented for the diffusion-controlled recombination of ions in water and other high permittivity solvents, but no approximation of sufficient accuracy, on the timescale and over the distances of interest, has been found for low permittivity solvents such as alkanes. Efficient IRT simulation relies upon the swift inversion of W , where a suitable approximation exists. Numerical inversion of the approximation describing geminate ion recombination in water is possible. Other

Fig.II.3.8 Recombination of tetrahedrally disposed ions.



2 cations, 2 anions; tetrahedron of side $\sqrt{2}$ nm; reaction distances all 1.0 nm; diffusion coefficients are $5.0 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$; $|r_c| = 0.7 \text{ nm}$.

(o o o o) Random flights simulation.

(—) IRT simulation.

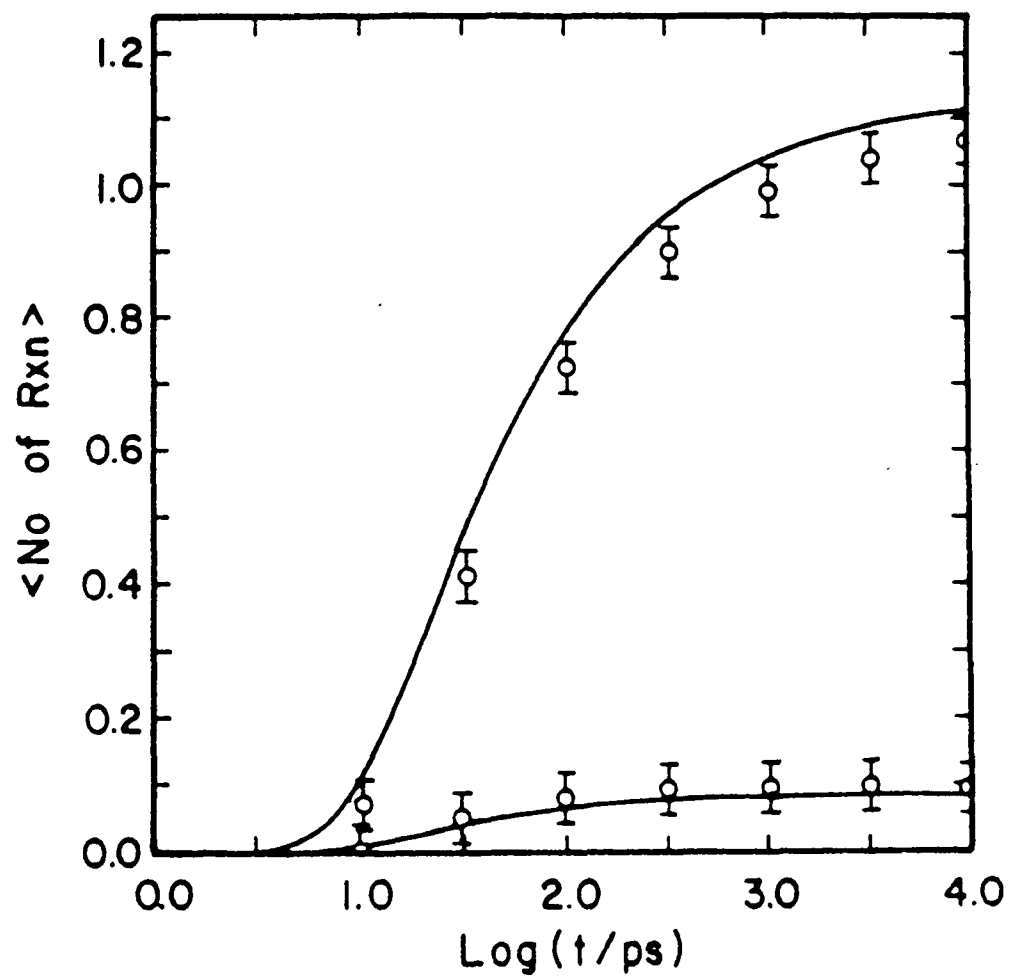
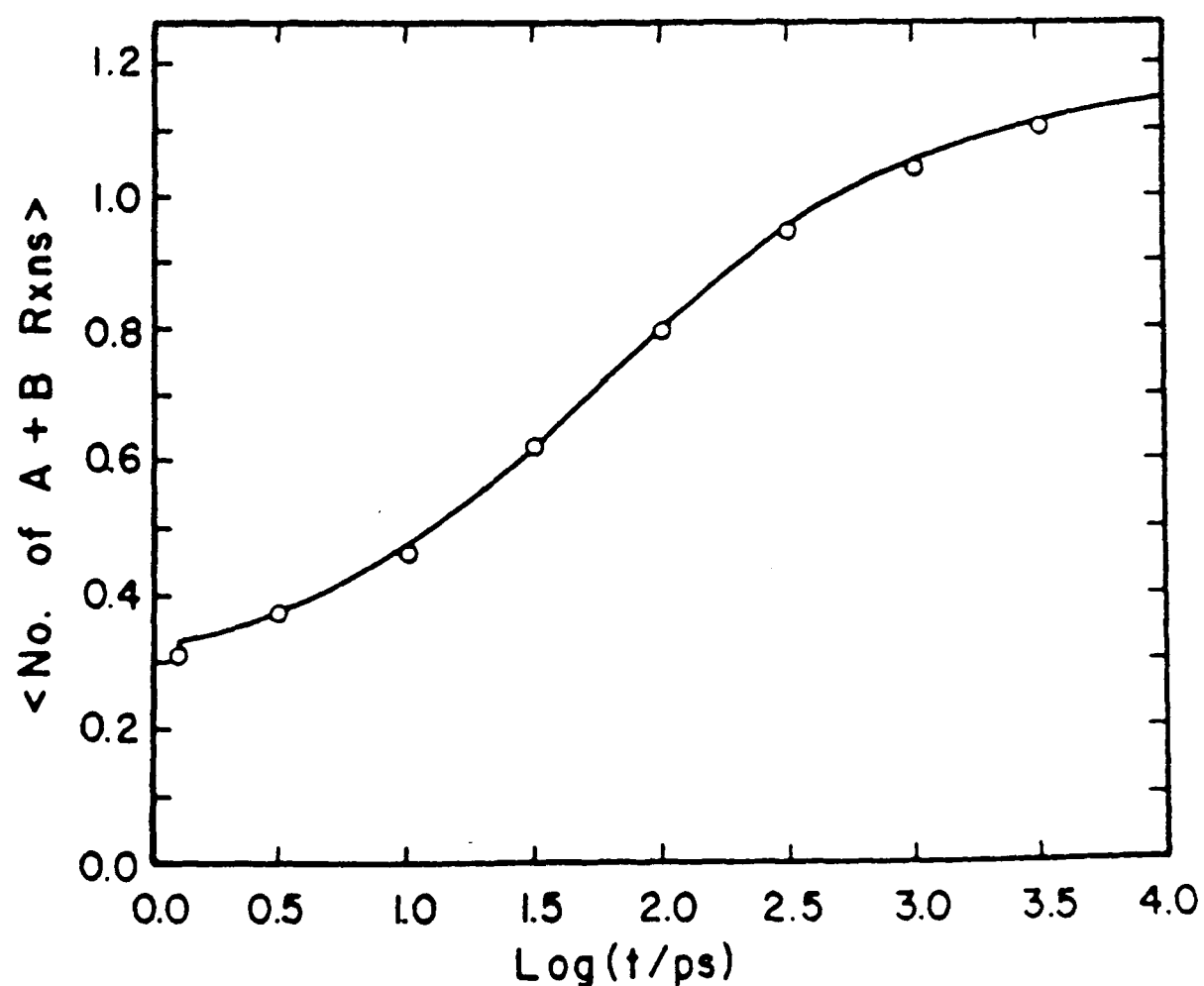
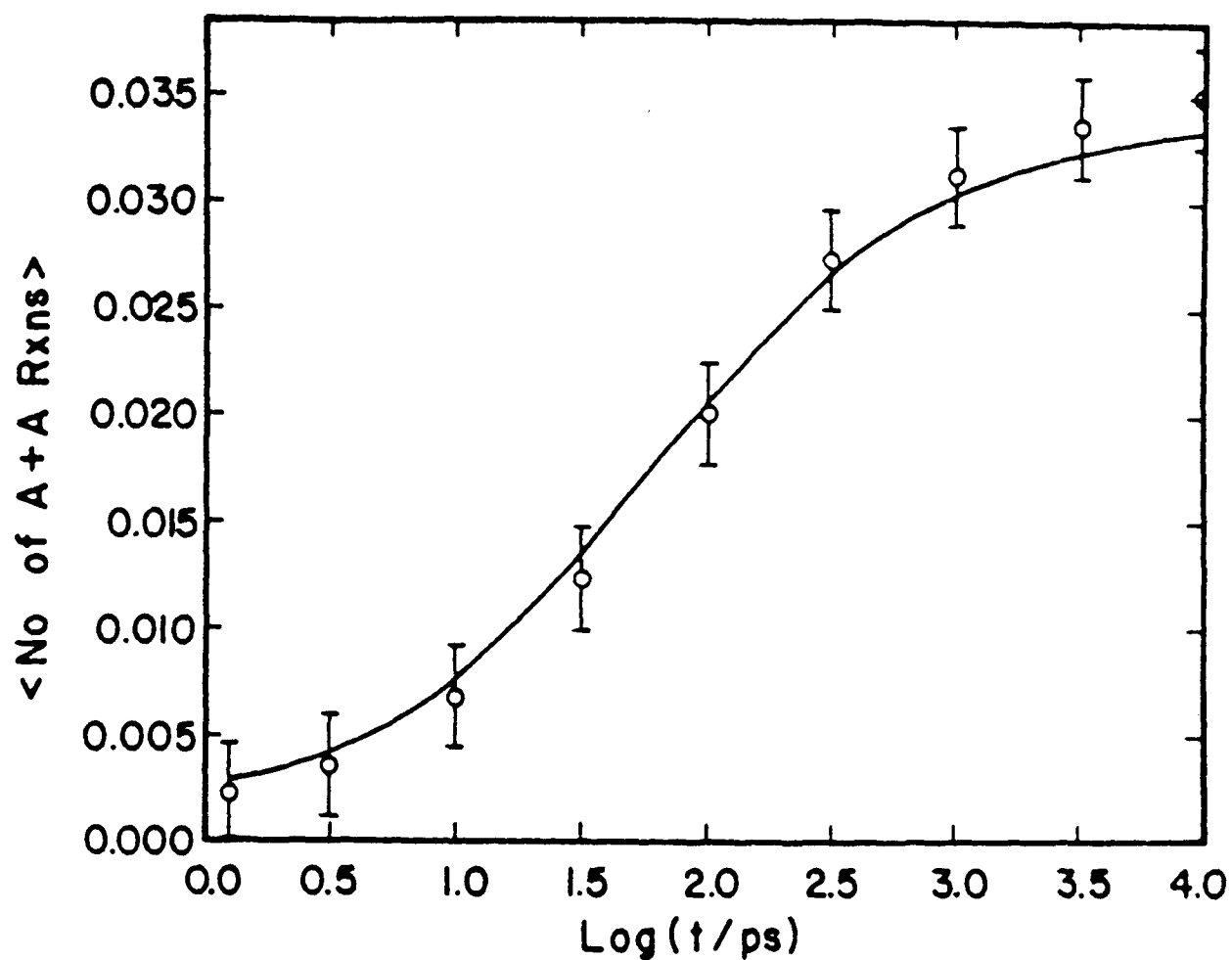


Fig.II.3.9 Recombination of a two-pair neutral cluster.



Particles distributed from iid Gaussians, $\sigma = 1.0$ nm;
 $R(A+A) = R(B+B) = 0.23$ nm; $R(A+B) = 0.93$ nm; diffusion
coefficients are $5.0 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$.

(o o o o) Random flights simulation.
(—) IRT simulation.



more complicated expressions, for instance equation (I.2.12) applying to high permittivity solvents from methanol onwards, have to be inverted by interpolation.

As the IRT model has to rely upon a suitable approximation for W , the model, as formulated, is not general and is only applicable to a limited region, governed by $|r_c|$. For a more general treatment, an alternative method of determining reaction times is required. The backward equation describing the kinetics of recombination of an ion pair has already been transformed into dimensionless coordinates. This conversion allows a numerical solution independent of $|r_c|$. The time-dependent conditioned reaction probability, W_* , - the function describing the time dependence of the recombination of a pair that will ultimately react - obeys a transformed dimensionless backward equation (Clifford et al., 1982c):

$$\frac{\partial W_*}{\partial \tau} = \frac{\partial^2 W_*}{\partial x^2} + \frac{2}{x^2} (x - \coth(1/x)) \frac{\partial W_*}{\partial x}. \quad (\text{II.3.14})$$

Any solution for W_* is equivalent to a whole family of reaction time distributions in real space and condensing the problem in this way suggests an alternative approach to the generation of reaction times - by interpolation from a finely meshed table describing the time-dependent conditioned reaction probability, W_* , as a function of dimensionless separation $x = \frac{2r}{r_c}$, dimensionless reaction distance, $X = \frac{2R}{r_c}$, and dimensionless time, $\tau = \frac{4D't}{r_c^2}$. This is conceptually simple, but accurate and efficient simulation requires a great deal of effort, not least in constructing the finely meshed table - it is necessary to solve the backward equation over a large range of x and X .

The numerical solution of equation (II.3.14) has been discussed by Clifford et al. (1984). The Crank-Nicolson method, a finite-difference technique is suggested as the most suitable for the problem. Solution does require a further transformation of the equation to make the computation more tractable ($u = \ln x$) and this means that careful consideration of the boundaries is necessary. The backward equation for W_* has been solved throughout the region defined by

$$-3.0 \leq \ln(X) \leq 1.5 \quad ; \quad -3.0 \leq \ln(x) \leq 2.0$$

on a mesh with intervals between solutions of $\Delta \ln(x) = 0.5$ and $\Delta \ln(X) = 0.5$. The result is a three dimensional lattice describing conditioned reaction probability percentiles as a function of dimensionless separation and dimensionless reaction distance. This lattice provides the backbone for the interpolation of reaction times. The behaviour outside this region covered is assumed to be well described by the approximate solution of Clifford et al.⁽¹⁹⁸⁴⁾, equation (I.2.12).

To find the reaction time of a pair by interpolation, the dimensionless separation and reaction distance of the pair are calculated. This defines the region of lattice space that contains the reaction time. A random number is generated corresponding to the value of W and is converted into a conditioned probability, $W_* = W/W_\infty$. To obtain the dimensionless time corresponding to the known values of x , X and W_* , the percentiles bracketing W_* are found and the times corresponding to these percentiles at the three nearest lattice points are determined. Linear interpolation in the x - X plane gives the dimensionless reaction time at the appropriate values of x and X and the two bracketing W_* percentiles. From these percentiles the reaction time at the appropriate conditioned reaction probability is determined. In the W_* dimension, t varies

as $\sqrt{W_*}$ except as $W_* \rightarrow 0$ and $W_* \rightarrow 1$ and so a linear interpolation against $\sqrt{W_*}$ is acceptable. Close to 0 and 1 other powers of W_* , that more accurately represent its variation, are used in the linear interpolation.

Two dimensional interpolation in the x - X plane is complicated and a detailed description of the technique used is worthwhile. The x - X mesh is logarithmic and the variation of τ is such that a linear interpolation, of the form

$$\tau = a \ln x + b \ln X + c \quad (\text{II.3.15})$$

is sufficient. The reaction times corresponding to the three nearest points are known and form a triangle about the point of interest:

$$\begin{bmatrix} \tau_1 \\ \tau_2 \\ \tau_3 \end{bmatrix} = \begin{bmatrix} \ln x_1 & \ln X_1 & 1 \\ \ln x_2 & \ln X_2 & 1 \\ \ln x_3 & \ln X_3 & 1 \end{bmatrix} \begin{bmatrix} a \\ b \\ c \end{bmatrix} \quad (\text{II.3.16})$$

or $\underline{\tau} = \underline{M} \underline{a}$. This allows the calculation of the coefficients a , b and c for the triangle of interest from

$$\underline{a} = \underline{M}^{-1} \underline{\tau} \quad (\text{II.3.17})$$

and therefore the reaction times for the bracketing W_* percentiles at (x, X) . As the lattice spacings are fixed, i.e.

$$\Delta \ln x = \Delta \ln X = h,$$

the matrix $\underline{M}^{-1}$ can be simplified considerably. There are two distinct solutions, one for a lower triangle,

$$\underline{M}^{-1} = \begin{bmatrix} h & 0 & -h \\ 0 & -h & h \\ -h(x_1+h) & hy_1 & h(x_1-y_1) \end{bmatrix} \quad (\text{II.3.18})$$

and one for an upper triangle,

$$\underline{M}^{-1} = \begin{bmatrix} 0 & h & h \\ -h & 0 & h \\ h(x_1+h) & -hy_1 & h(x_1+y_1) \end{bmatrix} \quad (\text{II.3.19})$$

where $x_1 = \ln x_1$ and $y_1 = \ln X_1$. The two types of triangle are defined in Fig. II.3.10.

Having obtained a sufficiently finely meshed reaction time lattice, the determination of reaction times during IRT simulation is trivial and is merely a case of developing an efficient interpolation code. In practice, this interpolation method takes little more computer time than direct numerical inversion of a distribution such as equation (II.3.7).

The accuracy of IRT simulation using the interpolation technique has been examined by studying geminate ion recombination in a variety of solvents covering a range of conditions.

Table II.3.1 Solvents and their Onsager distances.

(Pilling, 1975)

Solvent	Onsager distance / nm
Methanol	1.7
Ethanol	2.3
Diethyl Ether	13.0
Hexane	29.0

A selection of typical results are shown in Fig.II.3.11. The kinetics are those of two oppositely charged ions in solvents listed in Table II.3.1. Initially the pair are at a separation of 2.0 nm and the relative diffusion coefficient of the particles is

Fig.II.3.10 Definition of upper and lower triangles.

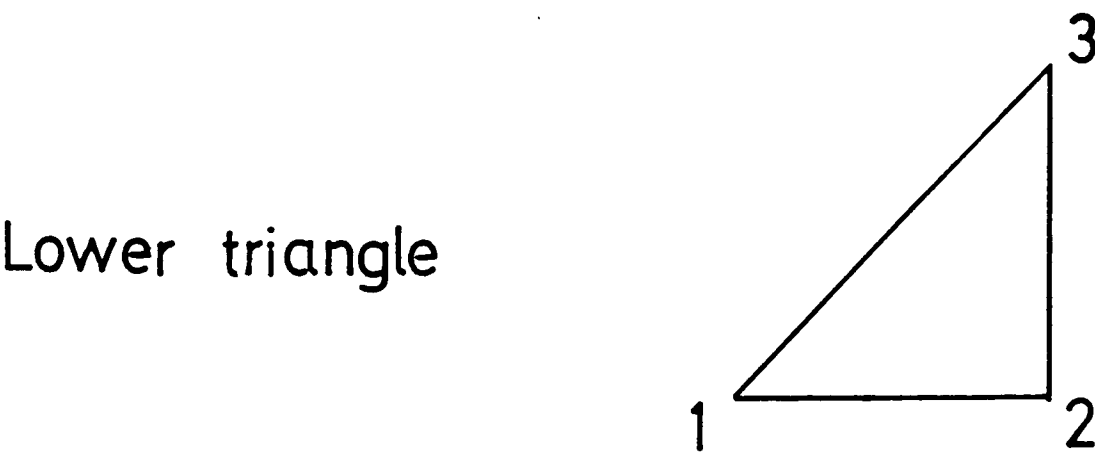
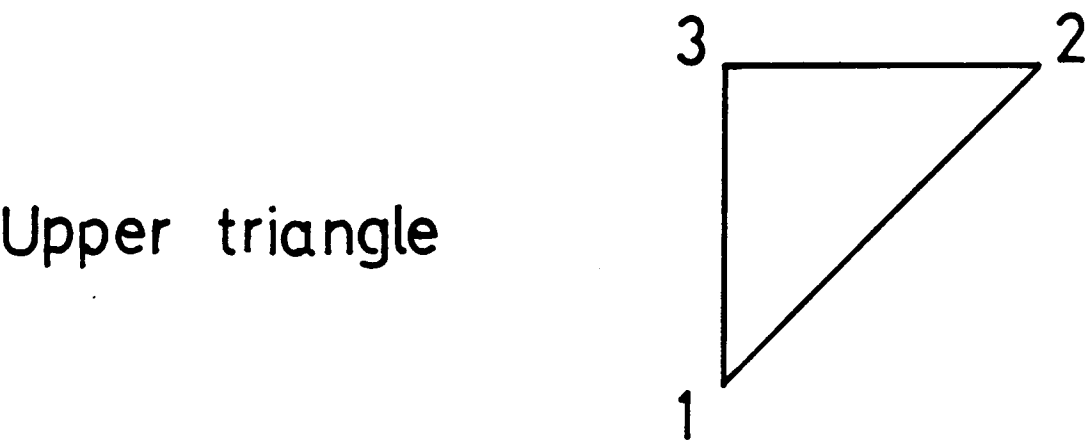
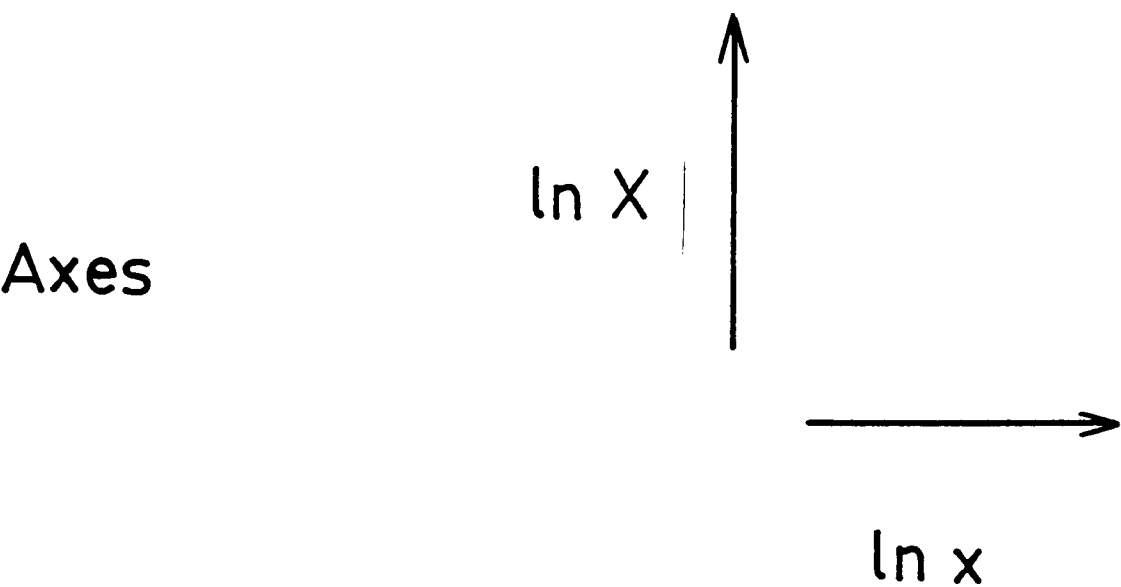
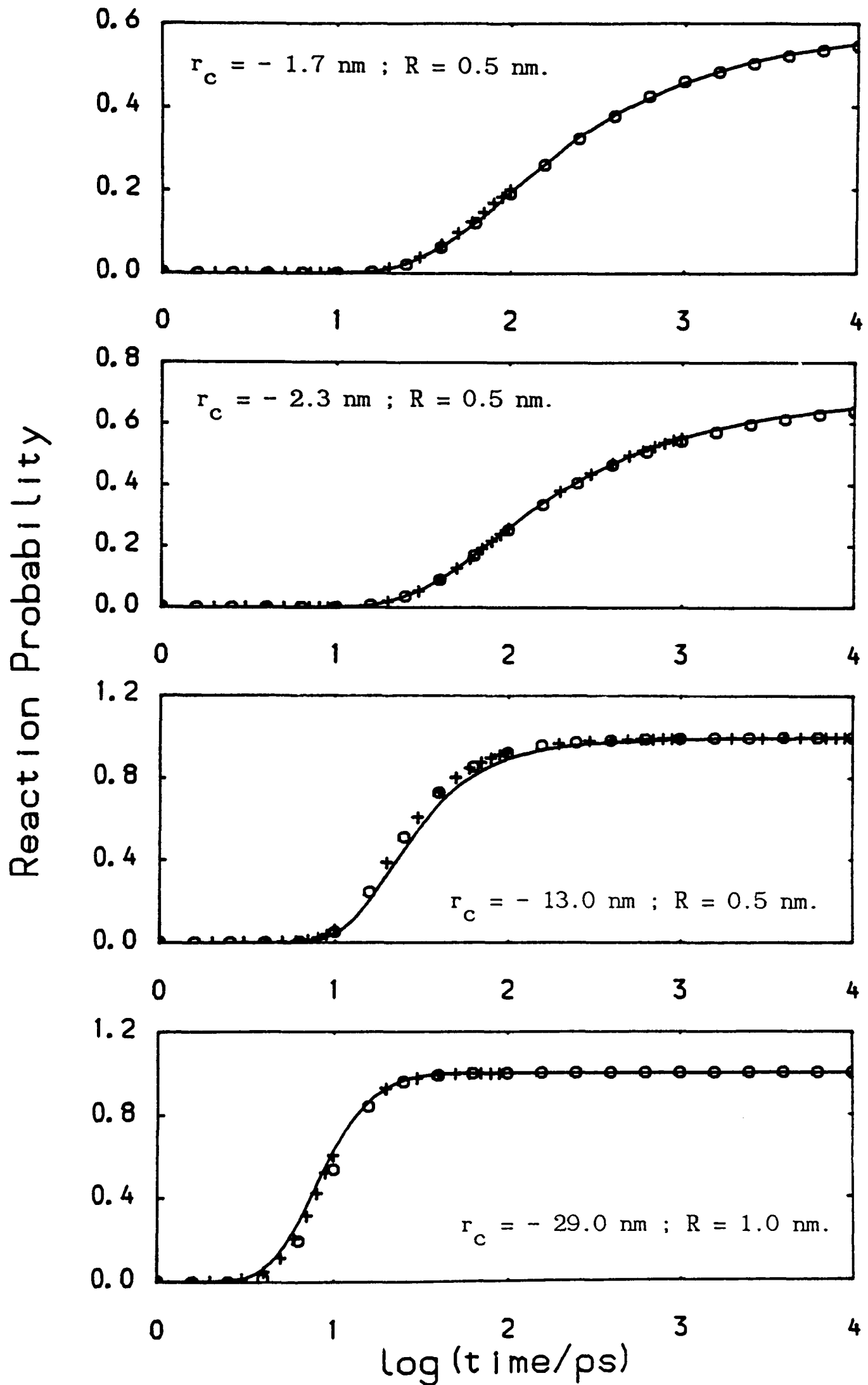


Fig.II.3.11 Geminate recombination in various solvents.
Initial separation = 2.0 nm; $D' = 1.0 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$.

(+ + + +) Numerical solution of backward equation.
(o o o o) Random flights simulation.
(—) IRT simulation.



always $1.0 \times 10^{-9} \text{ m}^2\text{s}^{-1}$. In all the solvents, with the exception of hexane, the reaction distance, $R_{+/-}$, is 0.5 nm and in the hexane study the reaction distance is 1.0 nm, to keep the simulation within the meshed region. In all the solvents the IRT model accurately reproduces the recombination kinetics. A more thorough study of geminate ion recombination in methanol is made in Fig.II.3.12, which presents the IRT simulated kinetics for a number of initial inter-ion distributions. Agreement between approximate modelling and random flight simulation is excellent except when $r_0 \ll |r_c|$. Also included, where the initial separation is fixed, is the approximate solution of Clifford et al., equation (I.2.12). This is clearly less than perfect when r_0 is small.

To test the IRT model and the validity of the independent pairs approximation, upon which it is based, in solvents of differing permittivity, the kinetics of small clusters of ions are considered. Studies made in water have already been described. In intermediate permittivity solvents, like methanol, the effects shown and the conclusions that can be drawn are the same as in water. The combination kinetics of a cluster of two A^+ cations and two B^- anions are shown in Fig.II.3.13. Two reaction schemes are considered: one in which all initially generated pairs are reactive and a second allowing only cross reaction. The IRT model accurately reproduces the kinetics in both cases. This is found to be the case when similar simulations performed on ethanol and diethyl-ether. As the electrostatic forces between ions become stronger, the probability of reaction between like charged particles is reduced and in low permittivity solvents, such as alkanes, it becomes very small. Fig.II.3.14 shows the recombination kinetics of a two-pair cluster in hexane. Only $+/-$ pairs are allowed to react and the reaction distance is 1.0 nm. Two physical situations are

Fig.II.3.12 Geminate recombination in methanol.
 $R = 0.5 \text{ nm}$; $D' = 1.0 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$; $r_c = -1.7 \text{ nm}$.

(o o o o) Random flights simulation.
 (—) IRT simulation.
 (---) Analytic approximation, equation (II.3.7).
 (----) Analytic approximation, equation (I.2.12).

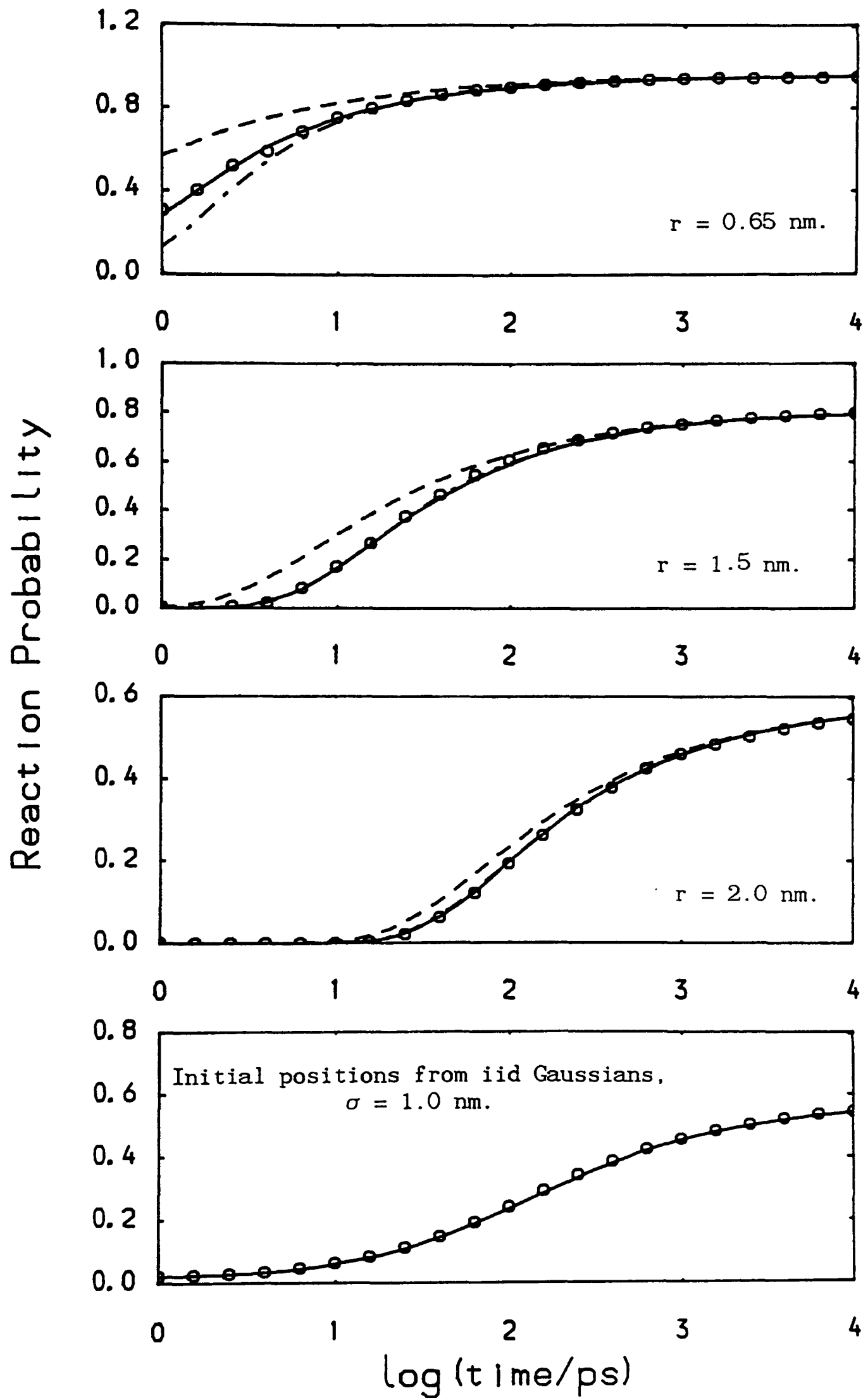
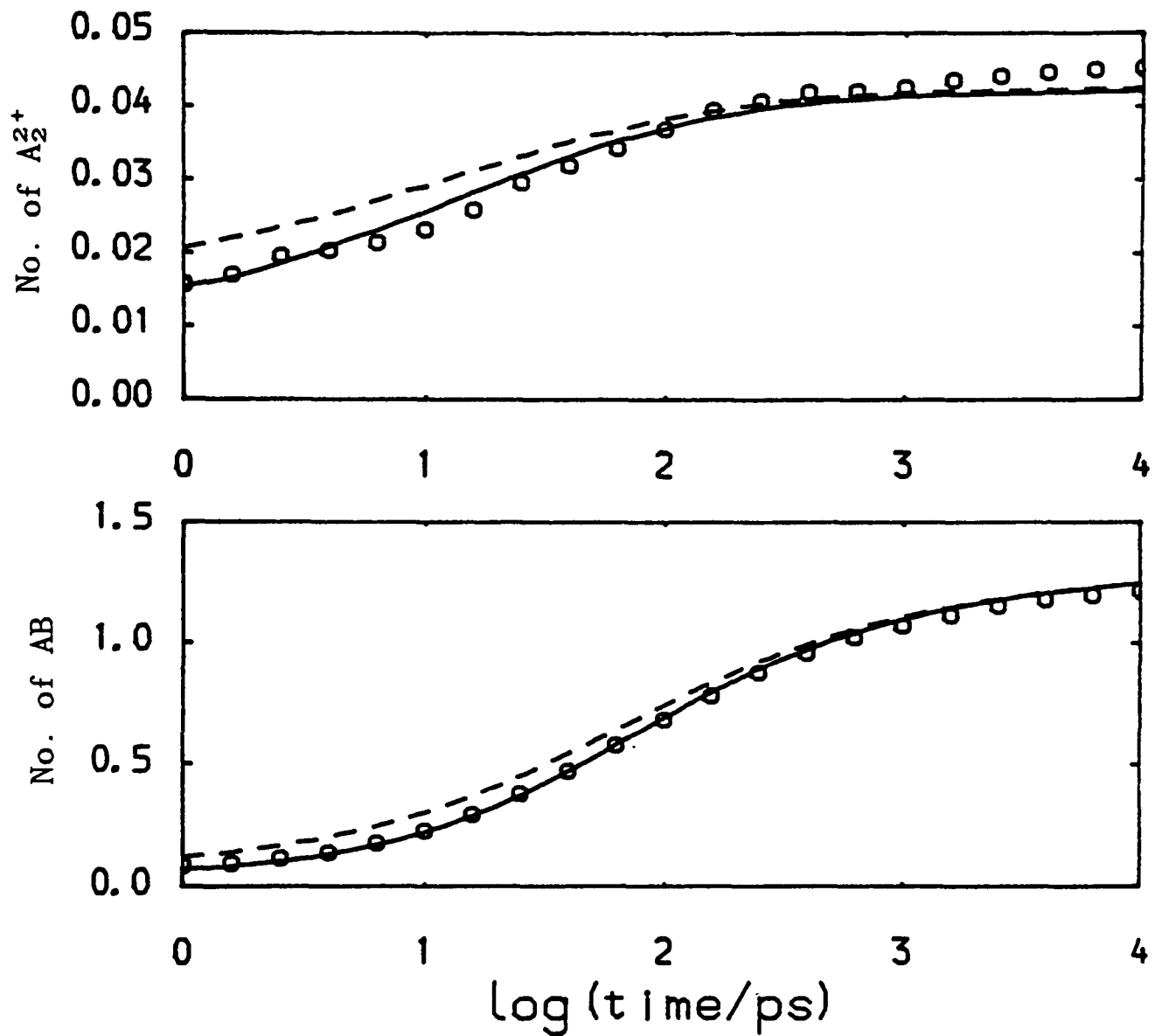
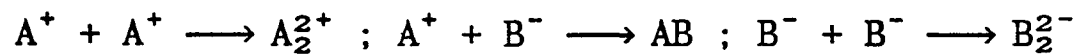


Fig. II.3.13 A two-pair cluster in methanol.
Initial positions from iid Gaussians, $\sigma = 1.0$ nm; reaction distances all 0.5 nm; diffusion coefficients are $5.0 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$; $|r_c| = 1.7$ nm.

(o o o o) Random flights simulation.
(—) IRT simulation using interpolation approach.
(- - -) IRT simulation from equation (I.2.12).

Reaction scheme :



Reaction scheme :

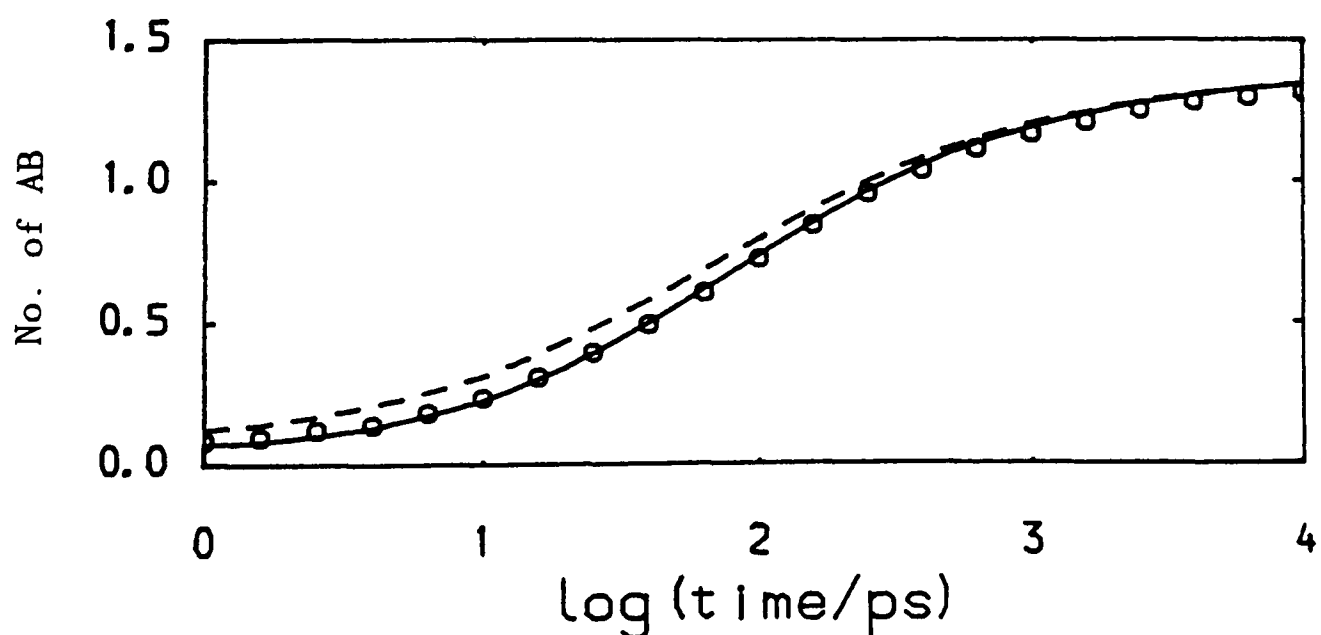
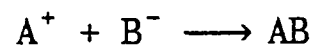
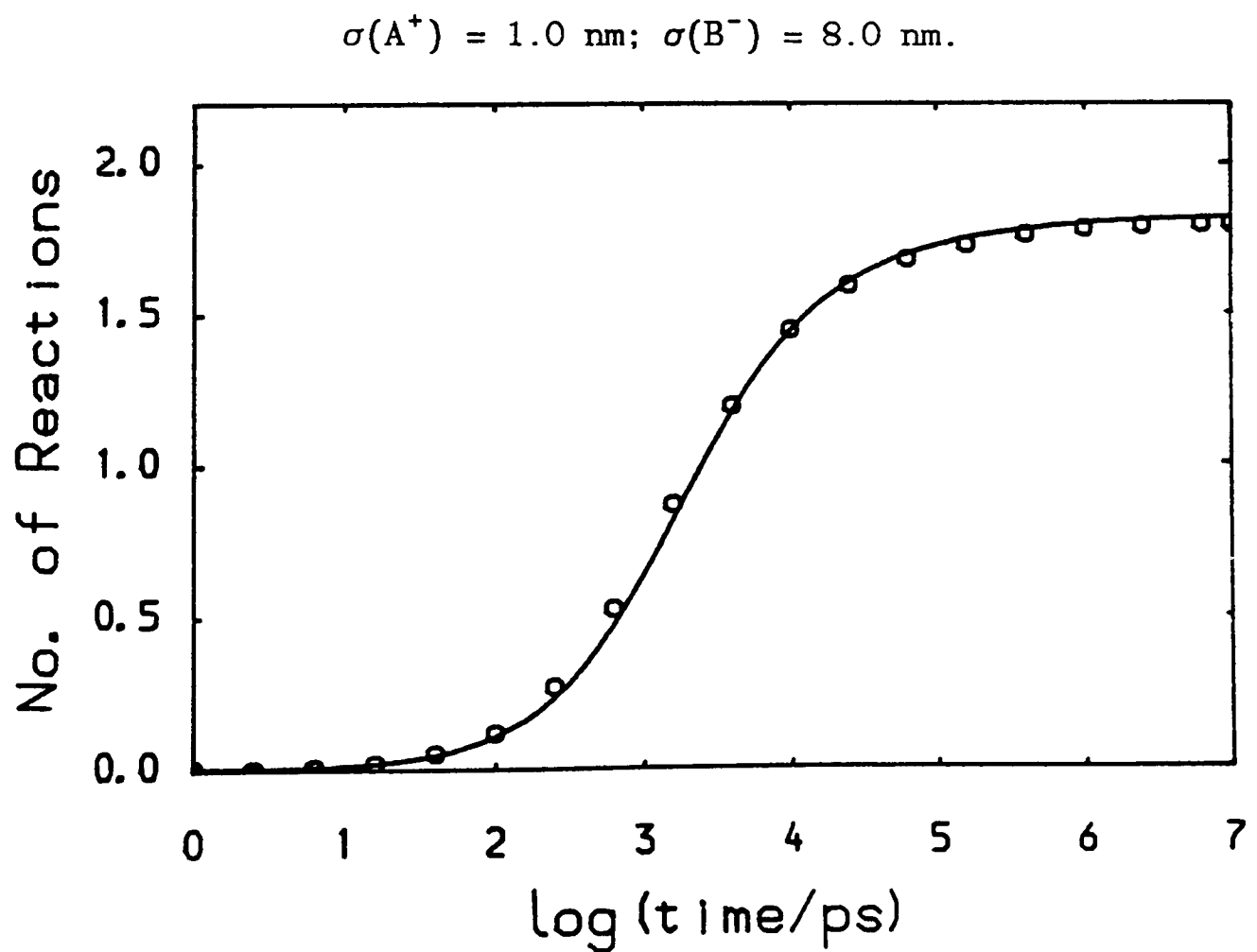
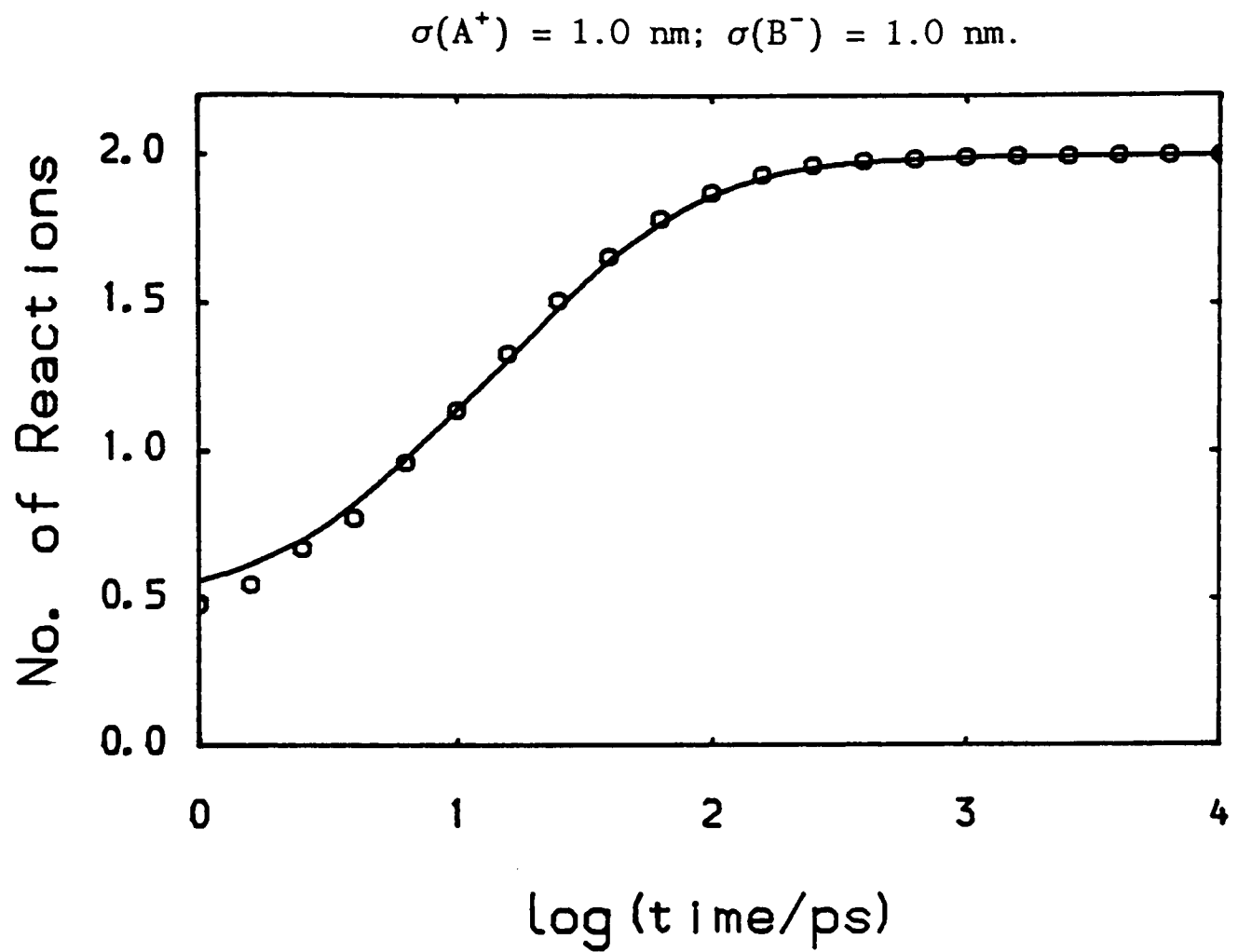


Fig.II.3.14 A two-pair cluster in hexane (a).
Initial positions from iid Gaussians; $R = 1.0$ nm; diffusion coefficients are $5.0 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$; $|r_c| = 29.0$ nm.

(o o o o) Random flights simulation.
(—) IRT simulation.

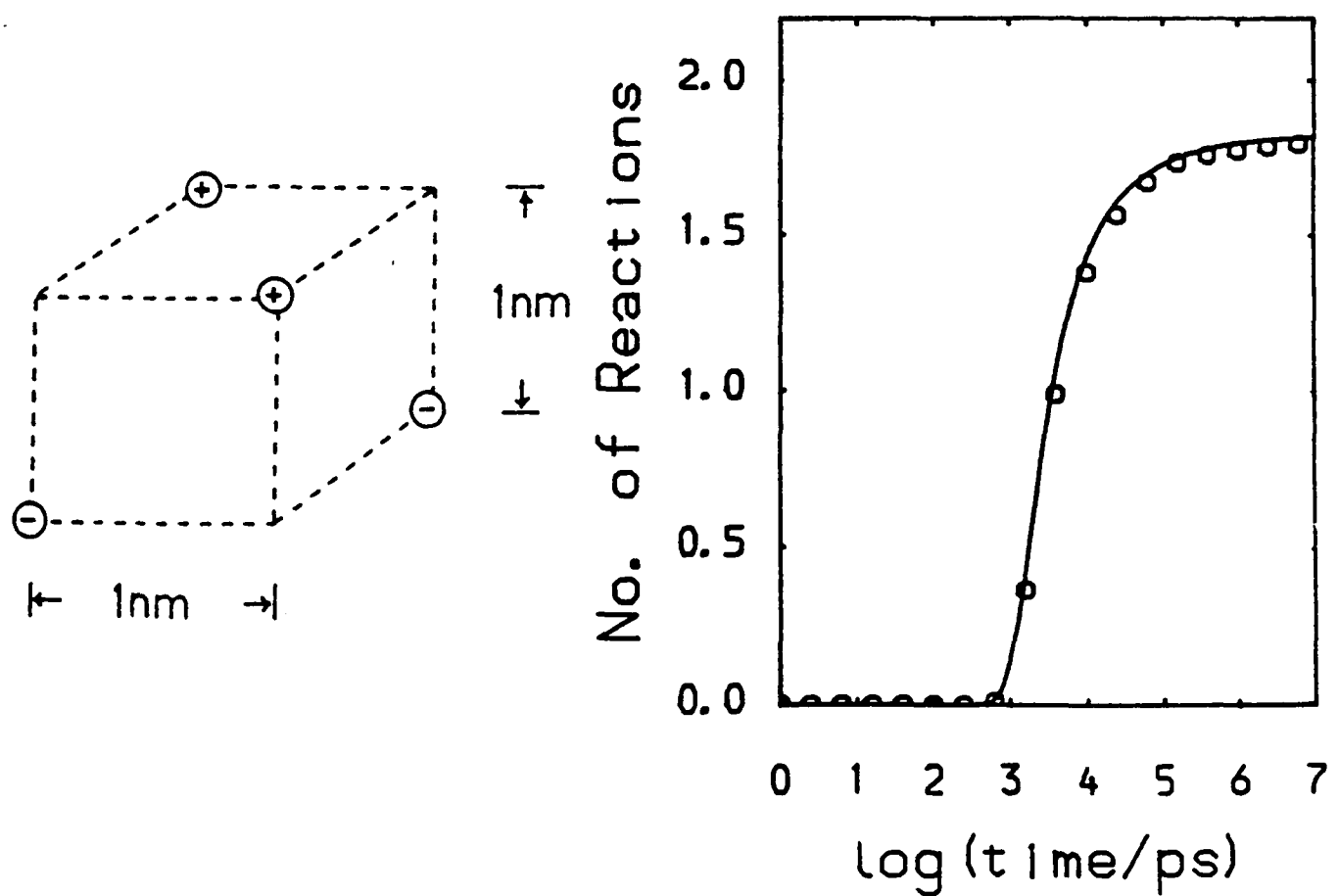
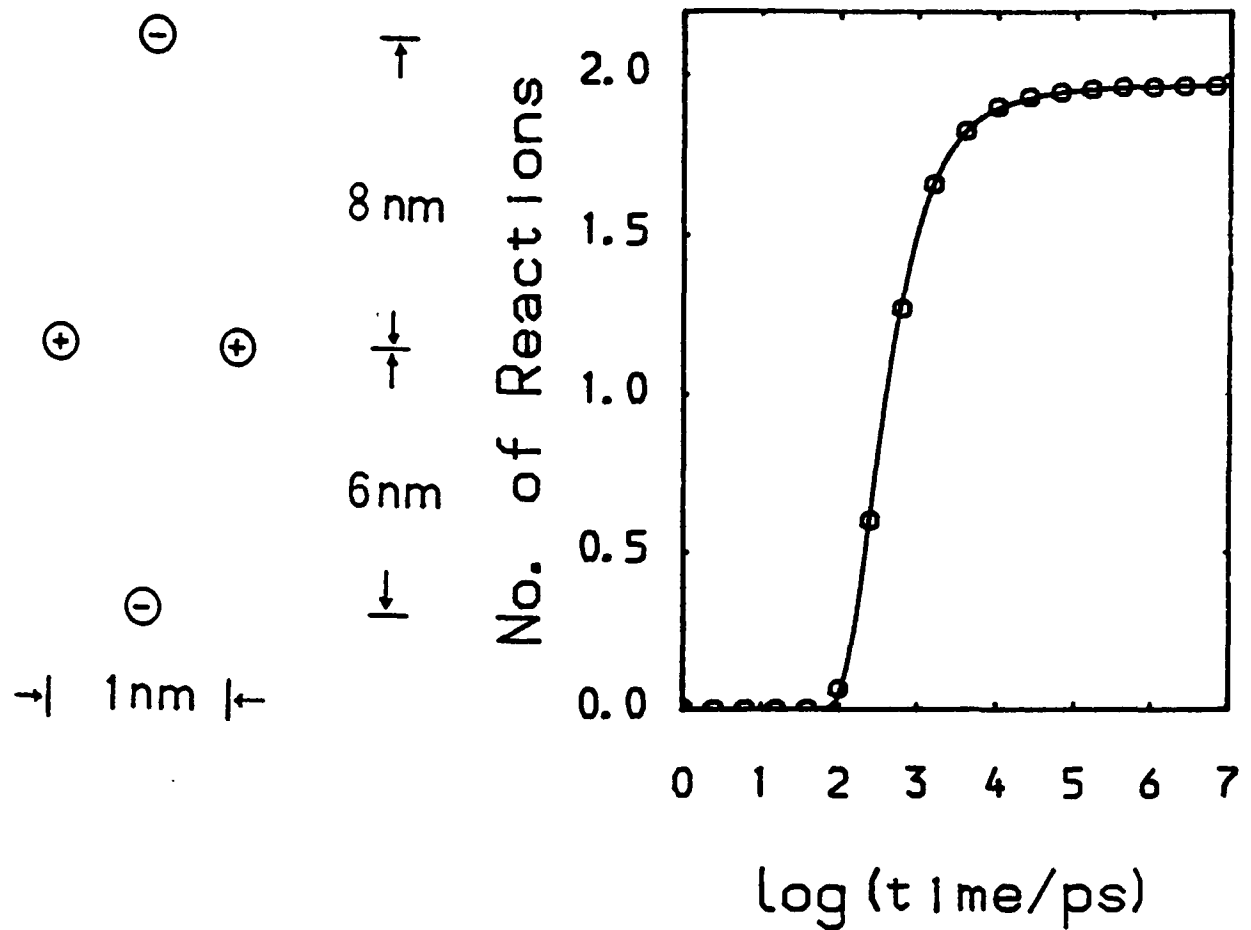


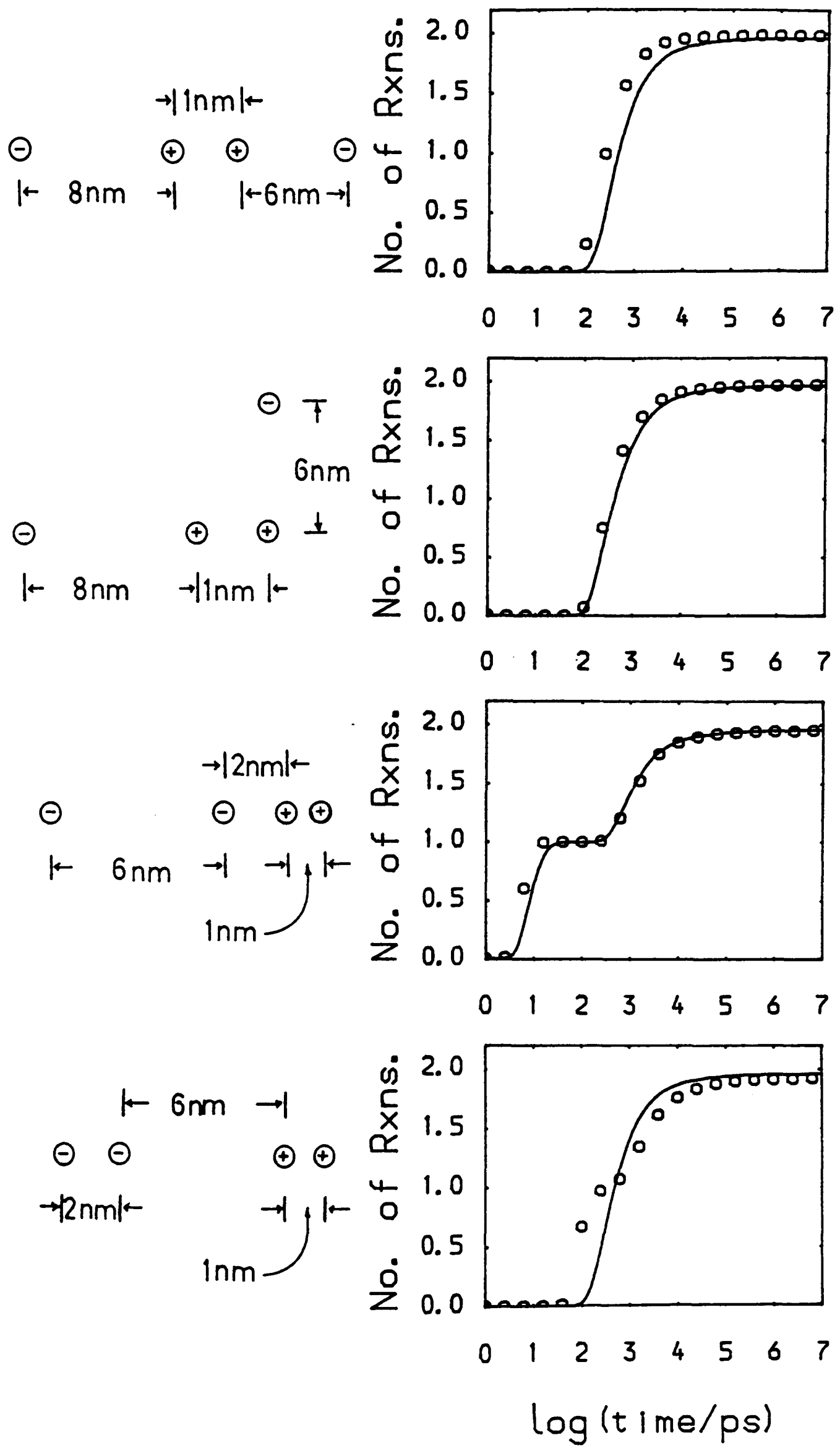
considered: when the cations and anions are tightly grouped and when the distribution of anions is much more diffuse than that of the cations. Increasing the width of the B^- distribution alters both the time dependence of the recombination and the amount of escape. When the cluster of reactants is narrow, the IRT model accurately reproduces the results of full simulation, except on a very short timescale (≤ 2 ps) where it predicts too rapid a recombination. For the wider anion distribution, the IRT kinetics closely resemble those predicted by full simulation, although there is an error in final free-ion yield. A deterministic treatment of these systems using the model of Schwarz (1969) shows major discrepancies in both the time-dependent kinetics and free ion yield. This is not really a fair comparison as the inter-ion forces in low permittivity solvents drastically affect the diffusion and cannot be neglected.

The performance of the independent pairs approximation in low permittivity media is rather surprising. Intuition suggests that, in this type of solvent where interparticle forces are strong, a description of diffusion and reaction in terms of only pairwise interactions should not be accurate. Fig.II.3.15 shows a series of simulations testing the importance of many-body effects. The initial distributions, included in the figure, are non-random and their aim is to maximise electrostatic effects. The IRT modelling of the recombination of ions takes no account of the spatial distribution of the interacting particles, in that it treats each pair with the same separation as equivalent, irrespective of its electrostatic environment. When the spatial distribution of a cluster reinforces the importance of the electrostatic interactions by drawing like charges together, the time dependence and free-ion yield predicted by the IRT simulation are found to be in error. If

Fig.II.3.15 A two-pair cluster in hexane (b).
Initial positions as shown; $R = 1.0 \text{ nm}$; diffusion coefficients are $5.0 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$; $|r_c| = 29.0 \text{ nm}$.

(o o o o) Random flights simulation.
(—) IRT simulation.





the ion distribution is such that the interference of electrostatic forces is less important, IRT simulation reproduces the true kinetics accurately. This type of study deliberately places considerable strain upon the independent pairs approximation and emphasises the surprising accuracy of the IRT model. The non-random distributions considered are highly improbable configurations and are unlikely to occur in a realistic radiation chemistry system. The modelling of this type of non-random system is impossible with conventional models.

3.4 Other stochastic models.

The random flights method of simulation presented in chapter II.2 and modified in this chapter models the Brownian component of a diffusion process as a normally distributed random flight. The basis of this description has been discussed earlier. Recently, Bartczak and Hummel (1986a ,1986b ,1987) have suggested an alternative random flights method in which the Brownian contribution to a jump is uniformly distributed. This discretisation is acceptable as the simulation converges to the relevant stochastic differential equation for small timesteps. Bartczak and Hummel consider the kinetics of idealised clusters of ions in alkane-like solvents. Simulation is based upon a fixed timestep diffusion and reaction is modelled by encounter. The length of a timestep is usually 1.0×10^{-5} to 5.0×10^{-5} in units of r_c^2/D' and this corresponds to about 1 ps to 5 ps in a low permittivity solvent such as hexane if $D' = 1.0 \times 10^{-8} \text{ m}^2\text{s}^{-1}$. No attempt is made to check for reaction during a jump, but as the electrostatic forces between ions are strong in this type of solvent, ions that are sufficiently close to react during a timestep are very likely to be in a reactive configuration at the end of one of the next few timesteps. Bartczak and Hummel tested

their method by comparison with geminate reaction. The recombination kinetics of two centrally located cations and two anions initially positioned from independent and identical Gaussians are shown in Fig.II.3.16. The random flights method described in this chapter and that of Bartczak and Hummel are compared and for the sake of completeness IRT simulation is also included. Both full simulation techniques agree within statistical limits and the recombination predicted by the IRT model is a little too slow.

Schmidt and coworkers (Schmidt, 1983; Sauer et al., 1987) have also carried out simulations on alkane-like systems. They use a fixed timestep of 40ps, which is almost certainly too long to reproduce the nonhomogeneous kinetics accurately. There is no discussion of any tests performed to validate the simulation model in the papers.

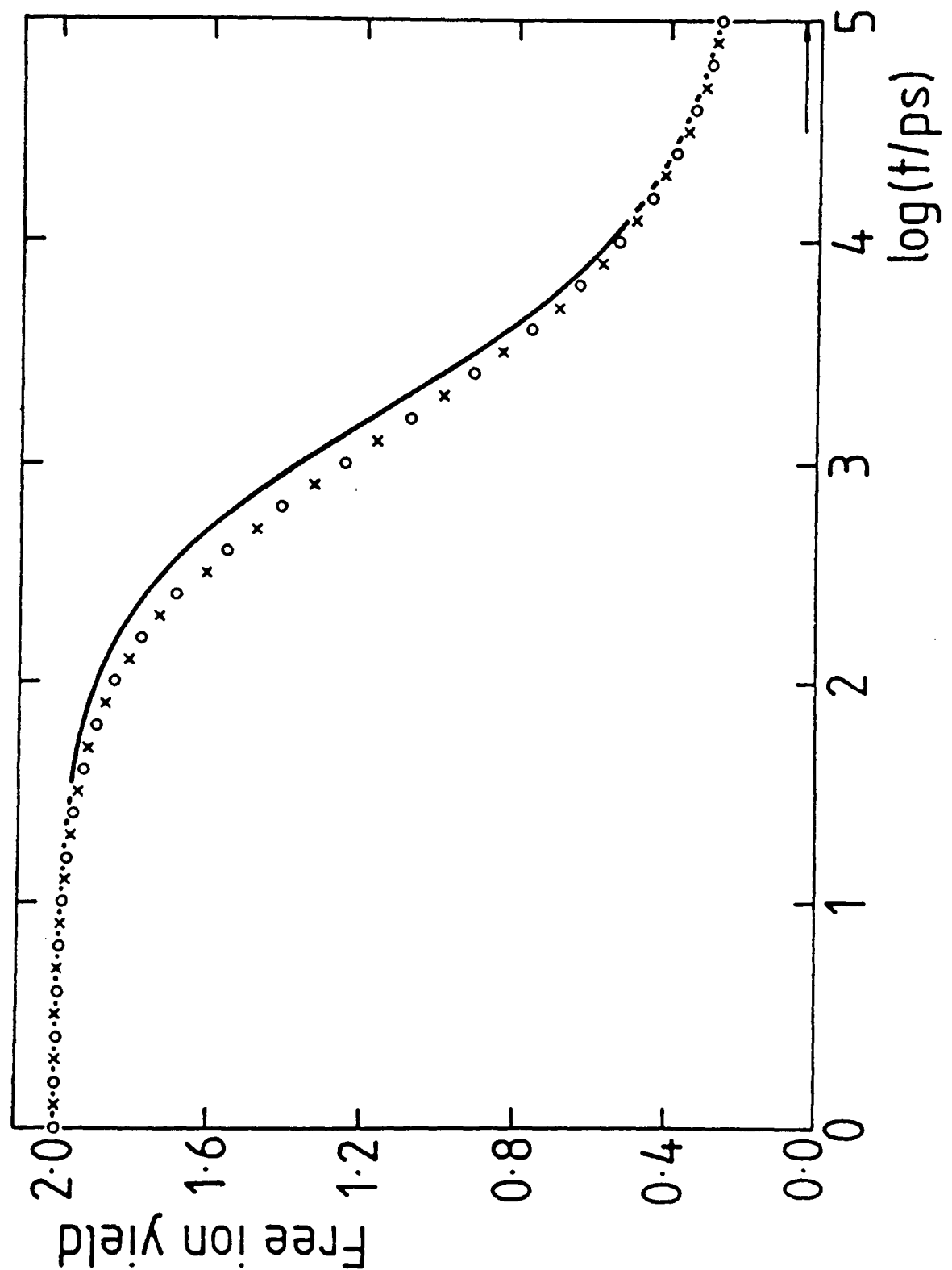
The Independent Reaction Time model is based upon the calculation of first passage times to reaction. One other first passage time technique has been applied to the kinetics of ion recombination. This model, developed by Freeman (1968, 1983), has only been used for^a single pair. The r^3 formula of Williams (1964) is used to estimate the first passage time,

$$t = \frac{\epsilon (r_0^3 - R^3)}{4.32 \times 10^{-7} (u_+ + u_-)} \quad (\text{II.3.19})$$

where ϵ is the dielectric constant of the medium and $u_{\pm}$ is the mobility of the ions. The reaction time is a single valued function of pair separation and for any given initial configuration a single deterministic time is obtained. The only stochastic feature of this model is in the distribution of inter-ion distances. Ludwig (1969)

Fig.II.3.16 Kinetics in low permittivity media.
 Two centrally located cations, A^+ , and two anions, B^- ,
 initial positions from iid Gaussians of standard deviation
 8.0 nm; reaction distance = 1.0 nm; diffusion coefficient
 $(B^-) = 1.0 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$; $|r_c| = 29.0 \text{ nm}$.

- (o o o o) Simulation using normal random flights.
 (x x x x) Simulation using uniform random flights.
 (—) IRT simulation.
 (—→) Free ion yield, Freeman's multipair model.



has shown that the model gives a poor description of kinetics and Freeman, himself, (1983) says that the thermalisation lengths predicted by the model are too large. The generalisation of the model to multispecies clusters has never been made, although a related method to estimate free ion yields from multipair clusters is in the literature (Dodelet & Freeman, 1975). For comparison, the free ion yield predicted by the multipair model is also shown in Fig.II.3.16. The result is a large underestimate according to full simulation.

The ionic systems considered in this chapter are idealised: interparticle forces are assumed Coulombic and reaction is always diffusion-controlled. To model a realistic nonhomogeneous radiation chemical system, it is necessary to consider the influence of a bulk electrolyte and to account for reactions that are not diffusion controlled. All the models discussed in this chapter, and throughout the thesis, are based upon a diffusion equation description of the motion of a particle. The long mean free path of the electron in some non-polar solvents means that this type of analysis is not strictly accurate and requires modification. This problem has been ^daddressed in some detail (Tachiya, 1987, 1988; Tachiya & Schmidt, 1988).

Chapter II.4 : The effect of an electrolyte on recombination.

In the previous chapter the recombination kinetics of small clusters of ions were examined. The analysis was based upon the assumption that the interparticle forces were Coulombic and that the influence of many-body effects and any bulk electrolyte could be neglected. This chapter considers how the recombination of a cluster of ions is modified by the presence of a strong electrolyte. The Coulomb potential of the previous chapter is replaced by a screened Coulomb potential, which treats the electrolyte according to Debye-Huckel theory. An exact solution for the ultimate escape of a pair of ions is derived and various approximations for the conditioned process are discussed. The random flights simulation of diffusion and reaction in ionic solutions is considered.

4.1 The recombination of an ion pair.

The recombination of a pair of ions can be described using the adjoint Debye-Smoluchowski equation (Clifford et al., 1984). This was discussed in the previous chapter, II.3. The equation applies to both the survival probability, Ω , and the reaction probability, of the pair, W , e.g.

$$\frac{\partial \Omega}{\partial t} = D \cdot \left[\frac{\partial^2 \Omega}{\partial r_o^2} + \left[\frac{2}{r_o} - \frac{1}{k_B T} \frac{\partial U}{\partial r_o} \right] \frac{\partial \Omega}{\partial r_o} \right]. \quad (\text{II.4.1})$$

The chance of the pair ultimately surviving is given by the steady-state solution, $\frac{\partial \Omega}{\partial t} = 0$, and for a general potential is

$$\Omega(r_o, \infty) = 1 - \frac{S(r_o)}{S(R)} \quad (\text{II.4.2})$$

where $S(x)$ is the scale function,

$$S(x) = \int_x^{\infty} x^{-2} \exp\left[U(x)/k_B T\right] dx. \quad (\text{II.4.3})$$

Solution of equation (II.4.1) for a Coulomb potential was discussed in the previous chapter. This treatment of the recombination of a pair of ions is only acceptable when the pair is in isolation, or in very dilute solution, otherwise it is necessary to modify the potential to include the screening of the ionic charge by the presence of 'bulk' ions.

The interaction of a pair of ions in dilute solution is usually examined using an exponentially damped Coulomb potential (Debye & Huckel, 1923; Logan, 1966)

$$U = \frac{\gamma r_c}{r} \exp\left[-\frac{r}{r_D}\right] \quad (\text{II.4.4})$$

where γ is a constant. The parameter r_D , usually referred to as the shielding length, is a measure of the thickness of the ionic layer around an ion and determines how strongly the potential is damped. It is related to the ionic strength of the solution, μ , by

$$r_D = (8 \pi |r_c| \mu)^{-1/2}. \quad (\text{II.4.5})$$

The constant γ is a function of the shielding length and of the hydrated radii of the two interacting ions, R_1 and R_2 and its value

depends upon the detailed approximations made. According to Debye and Huckel,

$$\gamma = \frac{1}{2} \left[\frac{\exp\left[R_1/2r_D\right]}{1 + R_2/2r_D} + \frac{\exp\left[R_2/2r_D\right]}{1 + R_1/2r_D} \right]. \quad (\text{II.4.6})$$

Logan suggested weighting the two terms in the ratio of the diffusion coefficients of the ions and the limiting law result is $\gamma = 1$. The choice of the constant, γ , does not affect any of the mathematical discussions that follow. The Debye-Huckel prescription is used in the numerical calculations and, in addition, it is assumed that $R_1 = R_2 = 1/2R$.

4.2 Ultimate reaction probability.

The ultimate survival probability of a pair of ions in dilute solution has been considered by Montroll (1946). He did not attempt to evaluate the scale function $S(x)$, but derived an approximation. His treatment is based upon the assumption that the shielding length, r_D , is large in dilute solutions and, therefore, the expansion of the exponential, $\exp(-r/r_D)$, in the potential can be truncated after its first term in r_D . The scale function is

$$\begin{aligned} S(r) &= \int_r^\infty x^{-2} \exp\left[\frac{\gamma}{x} r_c \left(1 - \frac{x}{r_D}\right)\right] dx \\ &= \frac{1}{\gamma r_c} \exp(-\gamma r_c/r_D) [\exp(\gamma r_c/r) - 1] \end{aligned} \quad (\text{II.4.7})$$

and the resulting approximation for the ultimate survival probability is

$$\Omega(r_0, \infty) = \frac{\exp(\gamma r_c/r_0) - \exp(\gamma r_c/R)}{1 - \exp(\gamma r_c/R)} \quad (\text{II.4.8})$$

The effect of the approximation is to ignore the exponential damping of the potential and to reduce the role of the screening to a constant scaling factor which is greater than one. It is equivalent to merely decreasing the dielectric constant of the solution and it makes the potential stronger, not weaker.

The integral $S(x)$ can be treated exactly, however, the solution is not closed. Consider equation (II.4.3) referring to the general potential, U . This exponential in U is expanded to give

$$S(r) = \int_r^\infty x^{-2} \sum_{i=0}^{\infty} \frac{1}{i!} \left[\frac{U(x)}{k_B T} \right]^i dx. \quad (\text{II.4.9})$$

Since the summation is uniformly convergent, the order of integration and summation can be reversed,

$$S(r) = \sum_{i=0}^{\infty} \int_r^\infty x^{-2} \frac{1}{i!} \left[\frac{U(x)}{k_B T} \right]^i dx. \quad (\text{II.4.10})$$

This equation is exact for any potential. If the screened Coulomb potential described by equation (II.4.4) is substituted for U , then the scale function is

$$S(r) = \sum_{i=0}^{\infty} (\gamma r_c)^i / i! \int_r^\infty x^{-2} \exp \left[- \frac{ix}{r_D} \right] dx. \quad (\text{II.4.11})$$

The integral in this summation can be expressed in terms of the exponential integral, defined by

$$E_n(x) = \int_1^\infty t^{-n} \exp(-xt) dt \quad (\text{II.4.12})$$

and so the scale function is

$$S(r) = \sum_{i=0}^{\infty} (\gamma r_c)^i / i! r^{-i-1} E_{2+i} \left[\frac{ir}{r_D} \right] \quad (\text{II.4.13})$$

This representation of the scale function is exact and can be evaluated accurately using the algorithm of Gautschi (1973). The ultimate survival probability of a pair of ions under the influence of a screened Coulomb force is obtained by substituting into equation (II.4.2) using equation (II.4.13). This is the first exact analytic solution for the ultimate reaction probability.

4.2.1 Comparison of natural distance scales.

The natural distance scale for ~~to~~ a diffusion-controlled reaction is

$$x_{\text{eff}} = 1/S(x) \quad (\text{II.4.14})$$

Fig.II.4.1 compares the natural distance scales for recombination

i) in the absence of an electrostatic force

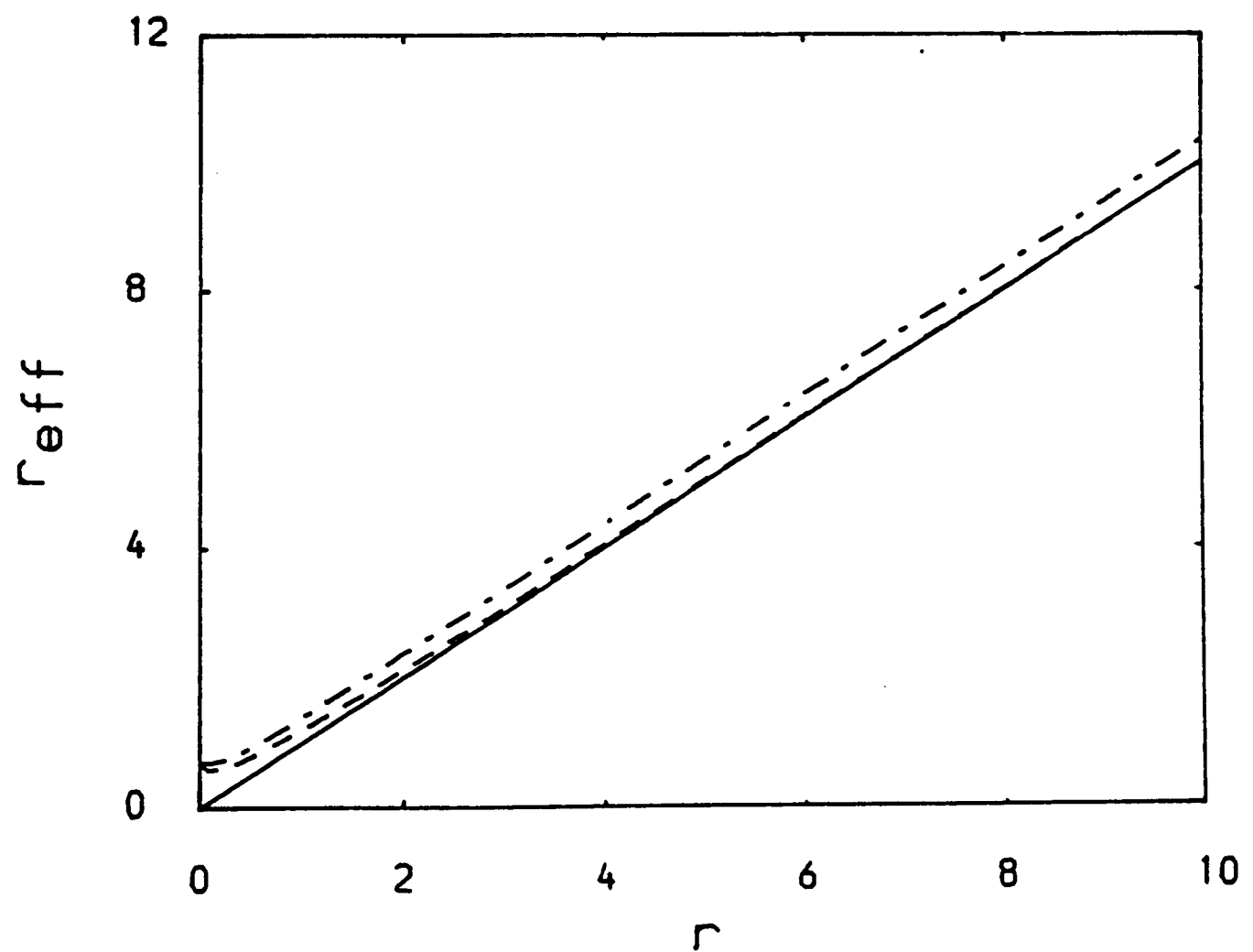
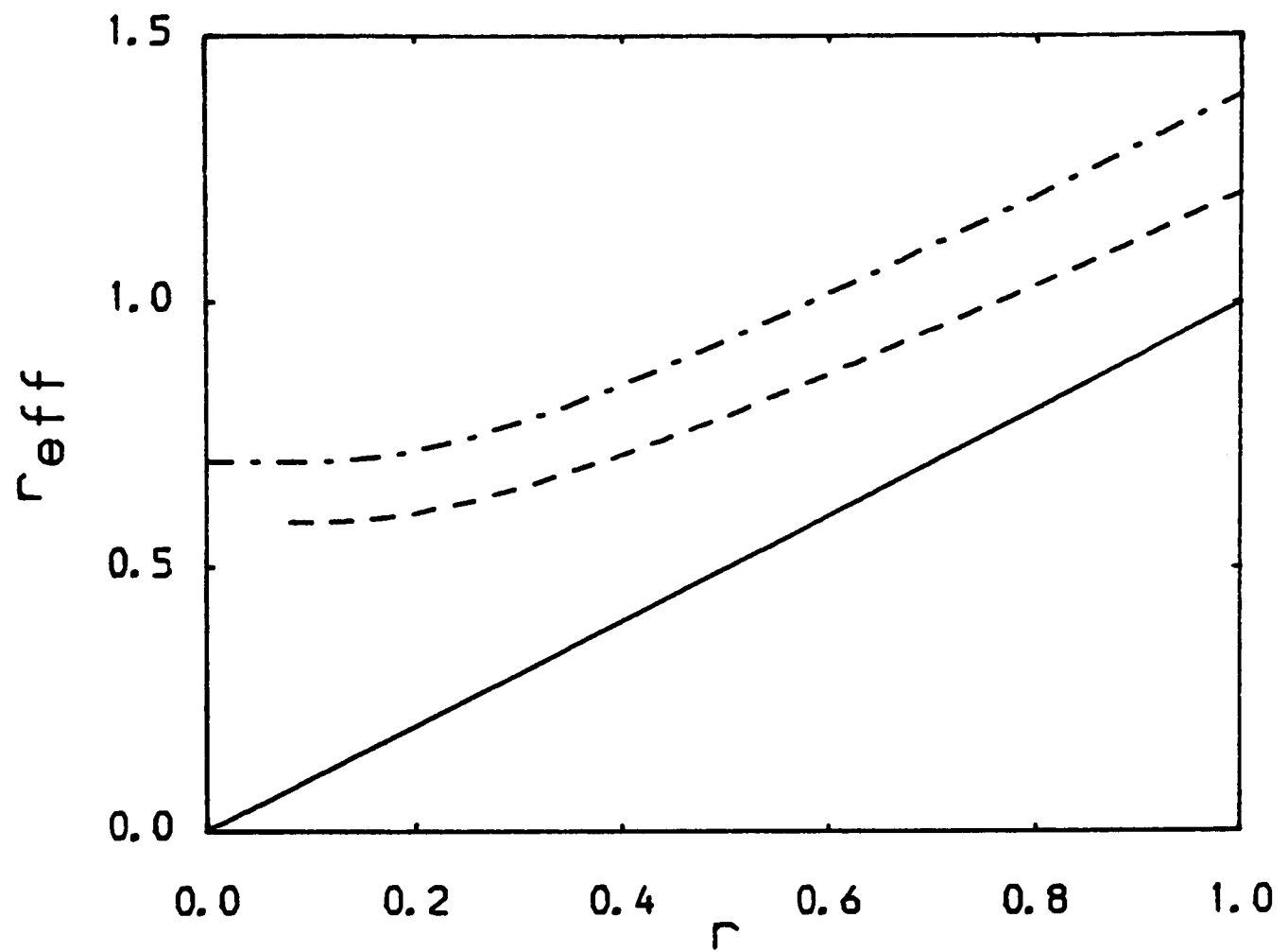
$$x_{\text{eff}} = x \quad (\text{II.4.15})$$

ii) under the influence of a Debye-Huckel screened force

$$x_{\text{eff}} = \left[\sum_{i=0}^{\infty} (\gamma r_c)^i / i! x^{-i-1} E_{2+i} \left[\frac{ix}{r_D} \right] \right]^{-1} \quad (\text{II.4.16})$$

Fig.II.4.1 Comparison of natural distance scales.
 $\gamma r_c = -0.7$ nm; $r_D = 3.0$ nm.

(—) in the absence of an electrostatic force.
 (---) with a Debye-Hückel screened potential.
 (-·-·-) with a Coulomb potential.



iii) under the influence of a Coulomb force

$$x_{\text{eff}} = \frac{-r_c}{1 - \exp\left[r_c/x\right]} \quad (\text{II.4.17})$$

In the limits of small and large x , equation (II.4.16) reduces to equation (II.4.17) and equation (II.4.15) respectively and it is always bounded by the two equations. The change from the unscreened Coulombic scale to the neutral scale is governed by the magnitude of r_D .

4.3 Conditioned reaction probability.

The ultimate probability that a pair of ions will react depends upon the nature of the electrostatic force, i.e. whether it is attractive or repulsive. Clifford et al. (1982c) have shown that, for a Coulomb potential, the time dependence of geminate reaction is independent of the nature of the pair. This is not the case for a screened potential which is not a solution of the Laplace equation $\nabla^2 U = 0$. The conditioned reaction probability of a pair of ions is described by a backward equation. This equation has the form (Clifford et al., 1982c)

$$\frac{\partial W_*}{\partial t} = D \left[\frac{\partial^2 W_*}{\partial r_0^2} - \left[\frac{d}{dr_0} [\ln s(r_0)] + \frac{s(r_0)}{\int_{r_0}^{\infty} s(r) dr} \right] \frac{\partial W_*}{\partial r_0} \right] \quad (\text{II.4.18})$$

where $s(x) = x^{-2} \exp(U/k_B T)$. For a screened potential this equation is

$$\begin{aligned}
\frac{\partial W_{*}}{\partial t} = & D' \frac{\partial^2 W_{*}}{\partial r_0^2} + D' \frac{\gamma r_c}{r_0} \exp\left[-\frac{r_0}{r_D}\right] \left[\frac{1}{r_0} + \frac{1}{r_D} \right] \frac{\partial W_{*}}{\partial r_0} \\
& + \frac{2D'}{r_0} \frac{\partial W_{*}}{\partial r_0} - \frac{2D'}{r_0^2} r_{\text{eff}} \exp\left[\frac{\gamma r_c}{r_0} \exp\left[-\frac{r_0}{r_D}\right]\right] \frac{\partial W_{*}}{\partial r_0} \quad (\text{II.4.19})
\end{aligned}$$

and is clearly asymmetric in r_c . This asymmetry in r_c ~~is~~ emphasises the difference between the attractive and repulsive cases. Equation (II.4.19) is complicated and not amenable to numerical solution as r_{eff} has to be evaluated repeatedly. The adjoint equation for the reaction probability, equation (II.4.1), is much simpler and can be solved numerically using the Crank-Nicolson method. The conditioned reaction probability is obtained merely by dividing by the ultimate reaction probability, for which an exact solution has been derived.

4.3.1 Analytic approximation.

To extend the IRT methodology to include the recombination of ionsⁱⁿ a solution of a strong electrolyte, an approximation for the conditioned reaction probability is required. When the interparticle force is Coulombic, an exact solution for the reaction probability of a pair of ions is not known, however, Clifford et al. (1984) have derived an acceptable approximation for solvents of high permittivity. The conditioned reaction probability is

$$W_{*} = \text{erfc}\left[\frac{r_{\text{eff}} - R_{\text{eff}}}{2\sqrt{D't}}\right] \quad (\text{II.4.20})$$

where the distance scale is that of equation (II.4.17). By analogy,

a similar expression, but with the distance scale defined by equation (II.4.16), might be expected to apply when the recombination is influenced by a screened potential.

The time dependence of the recombination of a pair in the absence of an electrostatic force is

$$W_{*} = \operatorname{erfc}\left[(r-R)/2\sqrt{D't}\right] \quad (\text{II.4.21})$$

i.e. equation (II.4.20) with the true distance scale, equation (II.4.15). Montroll (1946) examined the recombination of an ion pair under the influence of a Coulomb and a screened Coulomb potential. He derived an approximation for W_{*} for the unscreened potential with two terms: the transient solution for neutrals, equation (II.4.21), and a complicated integral only important when the inter-ion separation is small. The second term is small compared to the first and Montroll suggested that equation (II.4.21) ought to be a good approximation for the conditioned reaction probability of a pair under the influence of a screened Coulomb potential.

The suitability of equation (II.4.20) and the distance scales defined by equations (II.4.15) and (II.4.16) as approximations for W_{*} is determined by comparison with numerical solution. It is necessary to examine the behaviour of W_{*} as R , r_0 and r_D change. An acceptable approximation should show a reasonable time dependence and the correct long time asymptote under all conditions. The recombination kinetics of an ion pair, under the conditions listed in Table II.4.1, are shown in Figs. II.4.2, II.4.3 and II.4.4.

Fig.II.4.2 Conditioned reaction probability of a geminate pair with a Debye-Hückel screened potential (a)

(——) in the absence of an electrostatic force.
(---) with a Debye-Hückel screened potential.
(- - - -) with a Coulomb potential.

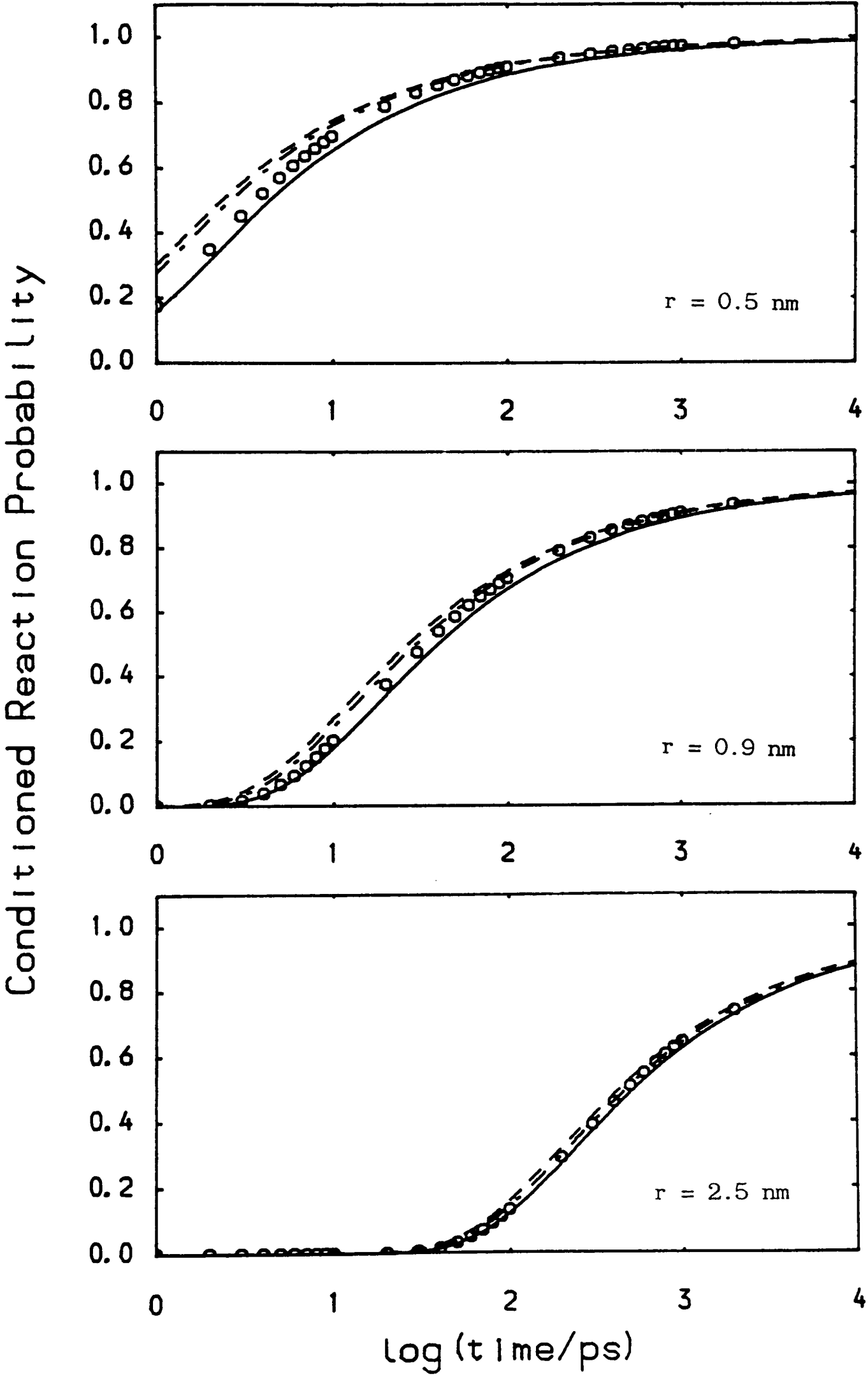


Fig.II.4.3 Conditioned reaction probability of a geminate pair with a Debye-Hückel screened potential (b)

(——) in the absence of an electrostatic force.
 (---) with a Debye-Hückel screened potential.
 (-·-·-·-) with a Coulomb potential.

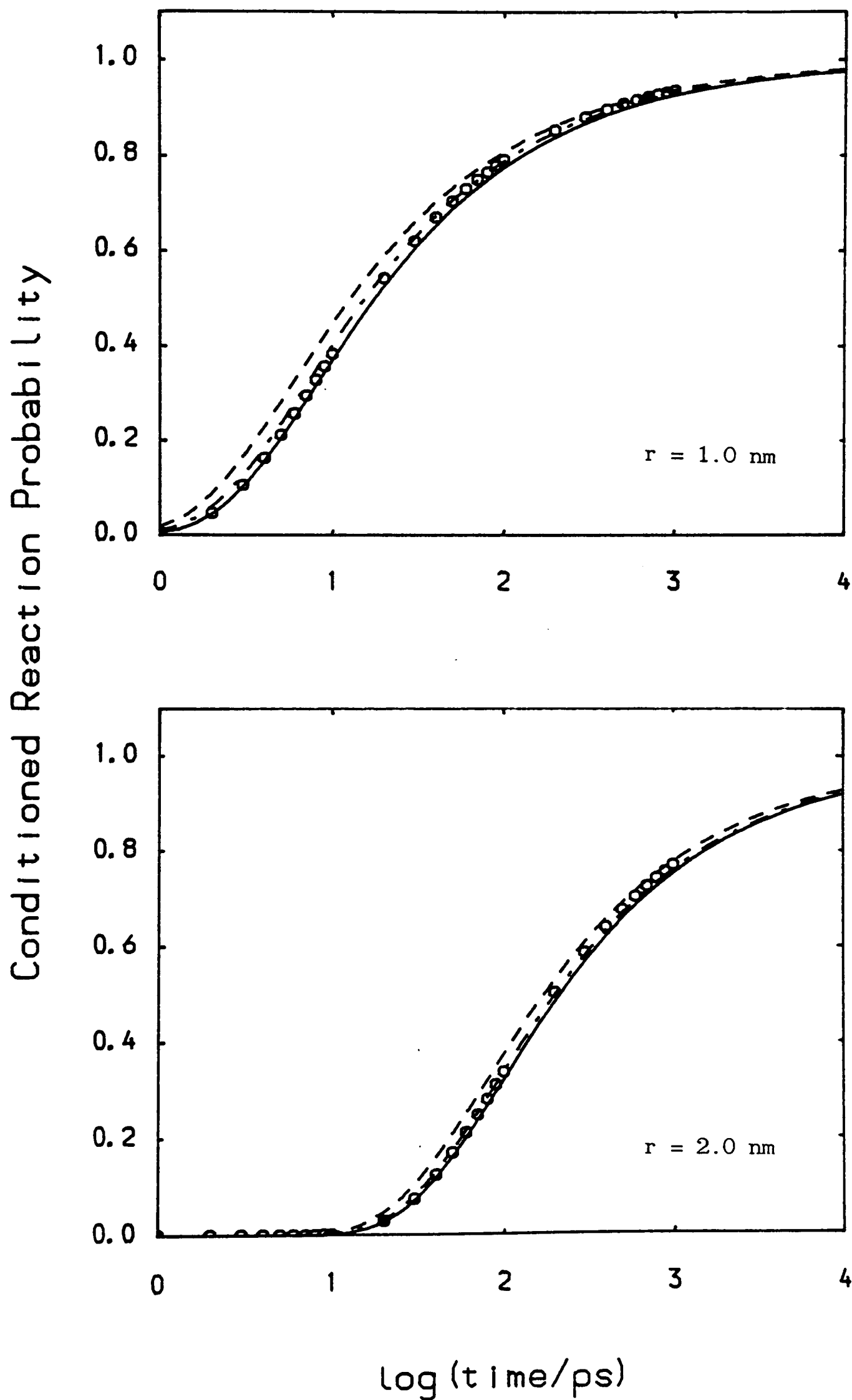


Fig.II.4.4 Conditioned reaction probability of a geminate pair with a Debye-Hückel screened potential (c)

(—) in the absence of an electrostatic force.
 (---) with a Debye-Hückel screened potential.
 (-·-·-) with a Coulomb potential.

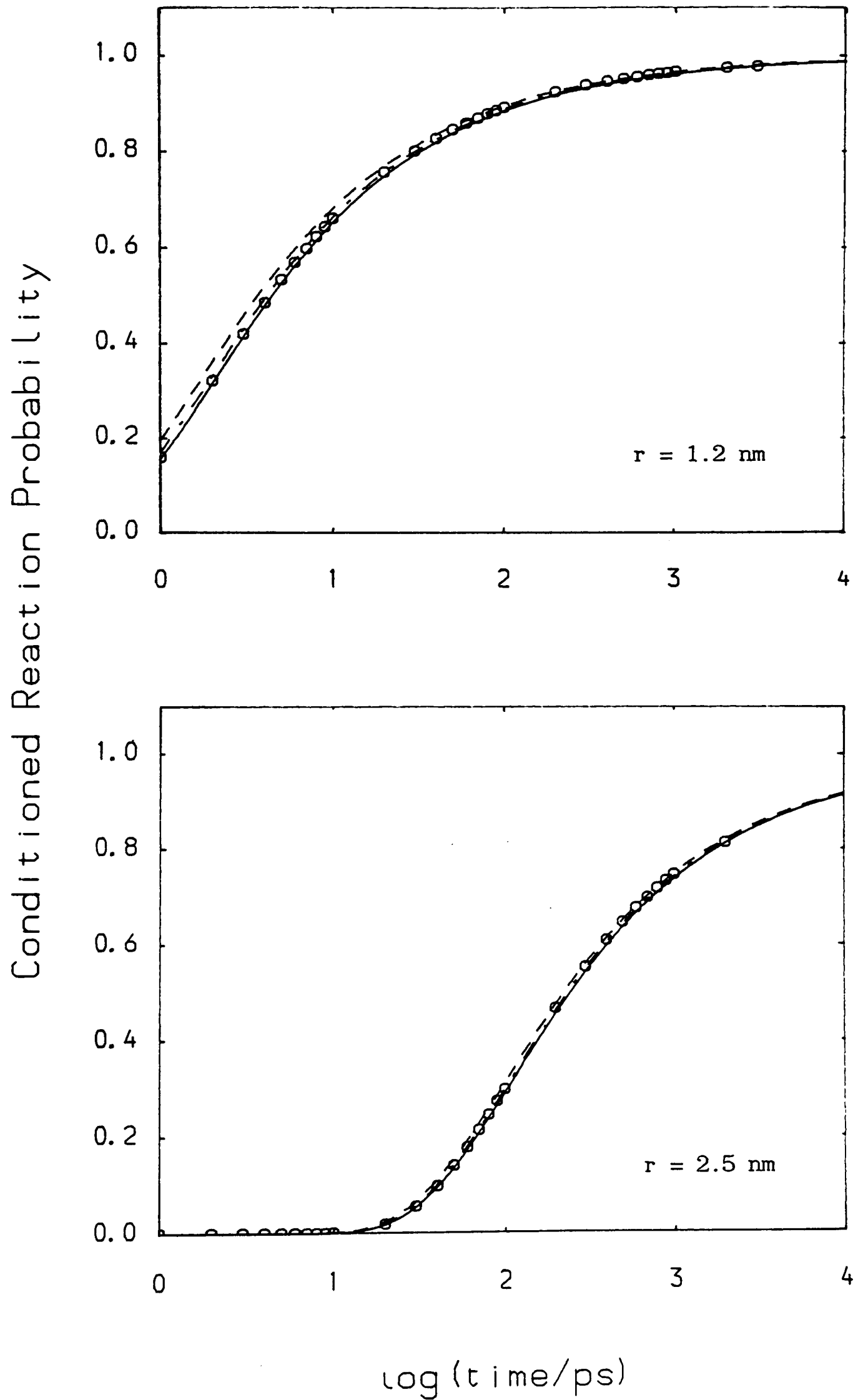


Table II.4.1 Recombination of a geminate pair of ions.

Fig.	electrolyte concentration / mol dm ⁻³ .	r_D /nm	R /nm	$R_1 = R_2$ /nm	r_0 /nm
II.4.2	0.001	9.6	0.3	0.15	0.5, 0.9, 2.5
II.4.3	0.01	3.0	0.6	0.3	1.0, 2.0
II.4.4	0.1	0.96	1.0	0.5	1.2, 2.5

Each figure contains the numerical solution for W_* and the time dependences predicted by equation (II.4.20) with the two distance scales suggested above and the 'Coulombic' scale, equation (II.4.17).

Detailed examination of these figures and other comparisons reveals that, except when both R and r_0 are very small, the Coulombic approximation most closely represents W_* . The natural distance scales described by equations (II.4.16) and (II.4.17) both accurately reproduce the long time asymptote, but the former approach predicts too rapid a reaction. When the reaction distance and the inter-ion separation are small, the short time recombination kinetics are represented by the solution for neutrals, equation (II.4.21), however, this approximation becomes less accurate at longer times. Under these conditions, the time dependence of the reaction probability is most accurately reproduced by the approximation of Clifford et al. (1984) describing recombination in methanol, equation (I.2.12).

It is apparent from this study that the most acceptable approximation for the reaction probability of a pair of ions in a

strong electrolyte is

$$W(r_o, t) = \frac{R_\infty}{r_\infty} \operatorname{erfc} \left[\frac{r_t - R_t}{2 \sqrt{D' t}} \right] \quad (\text{II.4.22})$$

where the distance scales of the ultimate and conditioned processes are different and are given by equation (II.4.16) and equation (II.4.17) respectively. This approximation is compared with the numerical solution of the backward equation in Fig.II.4.5. Also included are the predictions of Montroll's full approximation,

$$W(r_o, t) = \frac{1 - \exp(\gamma r_c / r_o)}{1 - \exp(\gamma r_c / R)} \operatorname{erfc} \left[(r_o - R) / 2 \sqrt{D' t} \right] \quad (\text{II.4.23})$$

and Montroll's time dependence with the correct ultimate reaction probability,

$$W(r_o, t) = \frac{R_{\text{eff}}}{r_{\text{eff}}} \operatorname{erfc} \left[\frac{r_o - R}{2 \sqrt{D' t}} \right] \quad (\text{II.4.24})$$

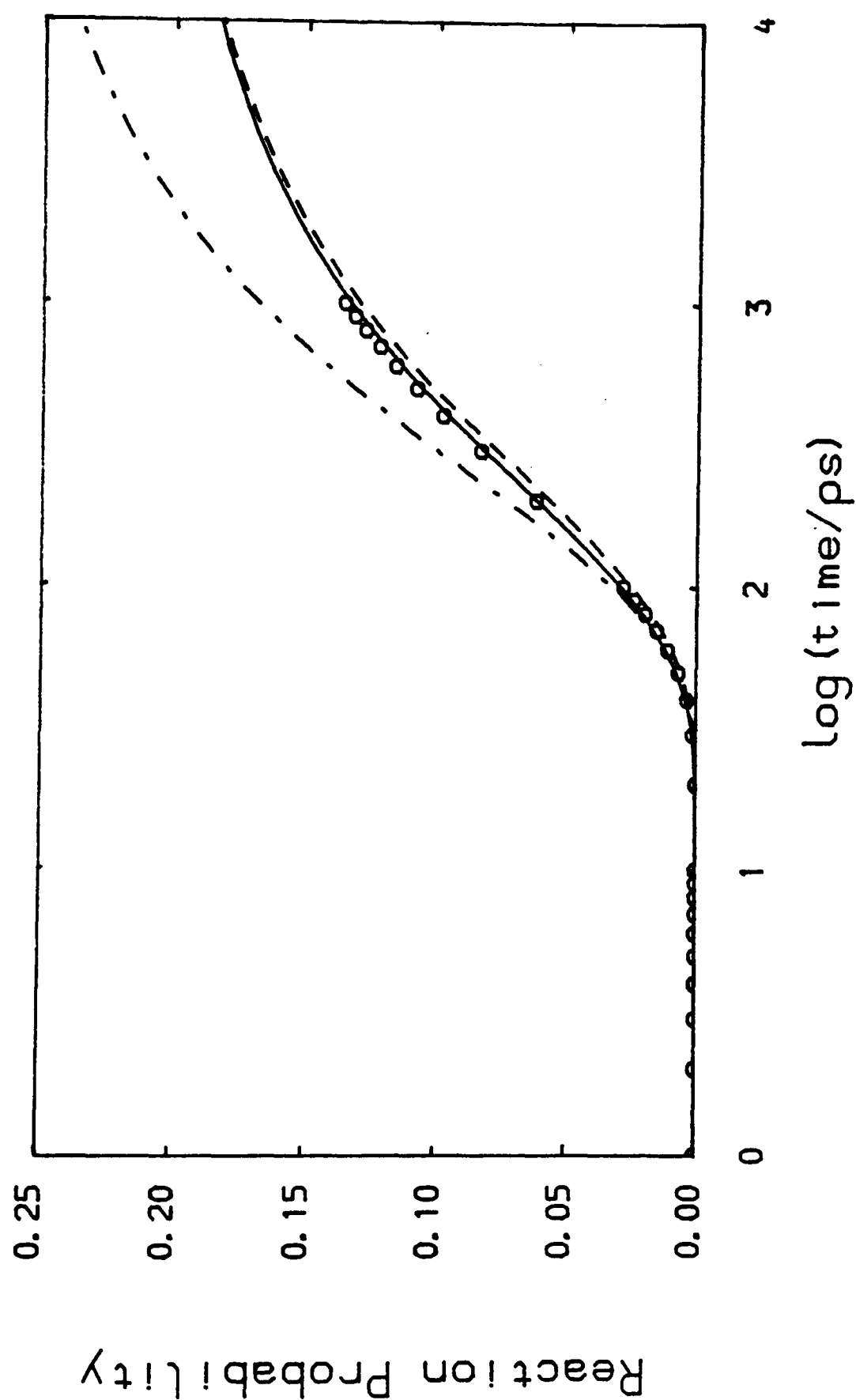
The first approximation is never acceptable, but the second reproduces the correct kinetics when the inter-ion separation and the reaction distance are large.

The success of the Coulombic description of the time dependence in equation (II.4.20) is rather surprising, but can be understood, if not explained, by referring to the backward equation describing the conditioned reaction probability, equation (II.4.19). Any adjoint diffusion equation has the form (Clifford et al., 1982c)

$$\frac{\partial \varphi}{\partial t} = \frac{1}{2} \sigma^2(r) \frac{\partial^2 \varphi}{\partial r^2} + \mu(r) \frac{\partial \varphi}{\partial r} \quad (\text{II.4.25})$$

Fig.II.4.5 Recombination of a geminate ion pair under the influence of a screened Coulomb potential.
 $D' = 1.0 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$; $R = 0.3 \text{ nm}$; $r = 2.5 \text{ nm}$;
 $\gamma r_c = -0.7 \text{ nm}$; $r_D = 0.96 \text{ nm}$.

(o o o o) Numerical solution of backward equation.
 (—) Analytic approximation using equation (II.4.22).
 (- - -) Analytic approximation using equation (II.4.24).
 (-·-·-·-) Analytic approximation using equation (II.4.23).



where σ and μ are said to be the infinitesimal parameters of the equation and the latter is described as the infinitesimal drift. For a Coulomb potential, c.f. chapter II.3,

$$\mu_{*} = \frac{D'}{r^2} \left[2r - r_c \coth\left(\frac{r_c}{2r}\right) \right] \quad (\text{II.4.26})$$

and for a screened potential, c.f. equation (II.4.19),

$$\begin{aligned} \mu_{*} = \frac{D'}{r^2} \left[\gamma r_c \exp\left[\frac{-r}{r_D}\right] \left(1 + \frac{r}{r_D}\right) \right. \\ \left. + 2r - 2r_{\text{eff}} \exp\left[\frac{\gamma r_c}{r} \exp\left[\frac{-r}{r_D}\right]\right] \right] \end{aligned} \quad (\text{II.4.27})$$

The two equations appear to be very different, but when they are plotted as a function of r they are almost indistinguishable, see Fig.II.4.6. The backward equations for W_{*} for an unscreened and a screened Coulomb potential are effectively identical. Fig.II.4.7 compares the numerical (and approximate) solutions for the reaction probability of an ion pair under the influence of the two different potentials. In the study shown, the initial inter-ion separation is such that it is necessary to use the more complex approximation for W_{*} , equation (I.2.12).

Having obtained an accurate approximation for the reaction probability of an ion pair recombining under the influence of a screened potential, inclusion in the IRT methodology is straightforward. The kinetics of multipair clusters are simulated in the manner as described in the previous chapters, but using the appropriate reaction time distribution function, equation (II.4.22).

Fig.II.1.0 Variation in drift of the conditioned process with separation.

(—) Screened Coulomb potential.
 (+ + + +) Coulomb potential.

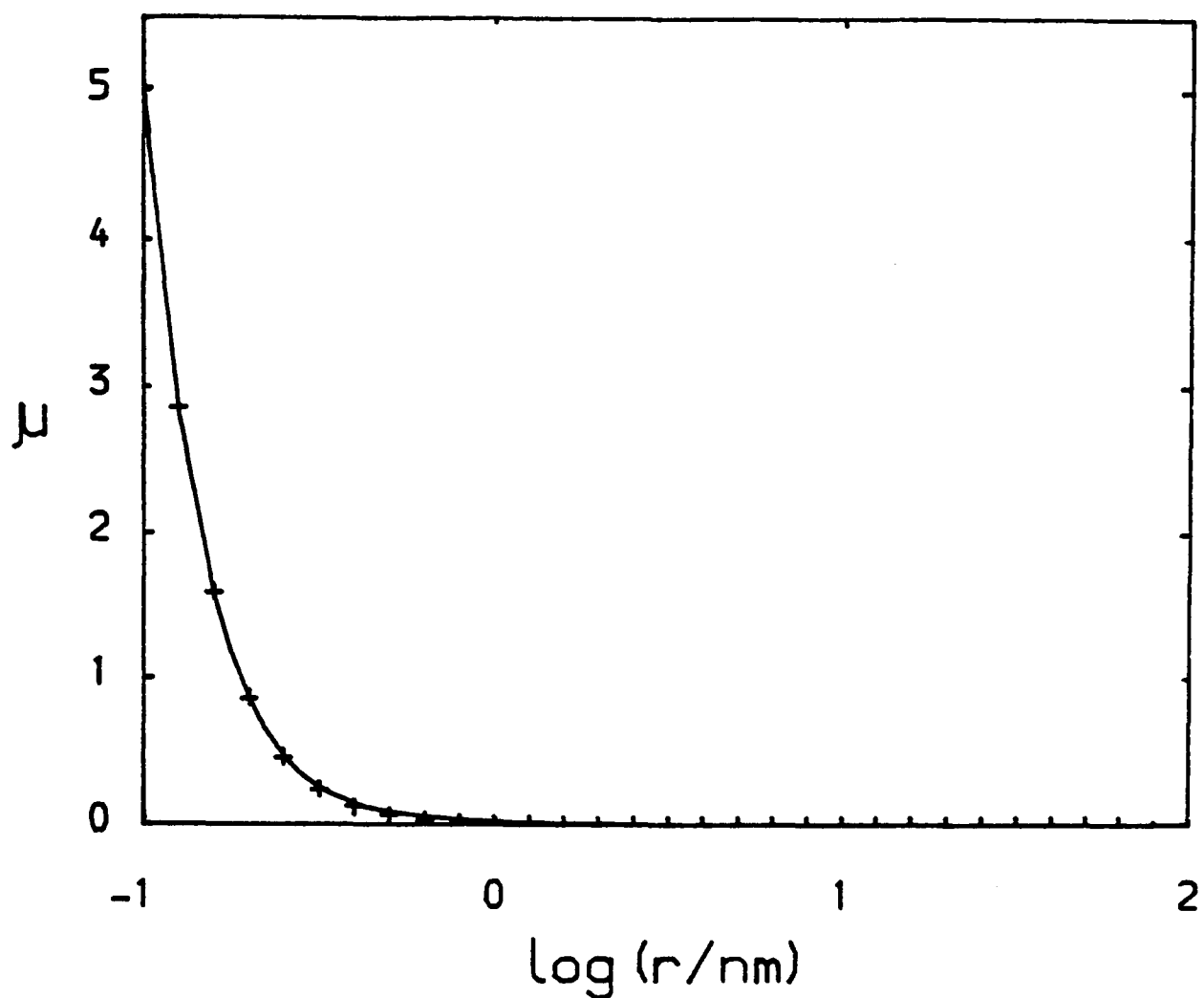
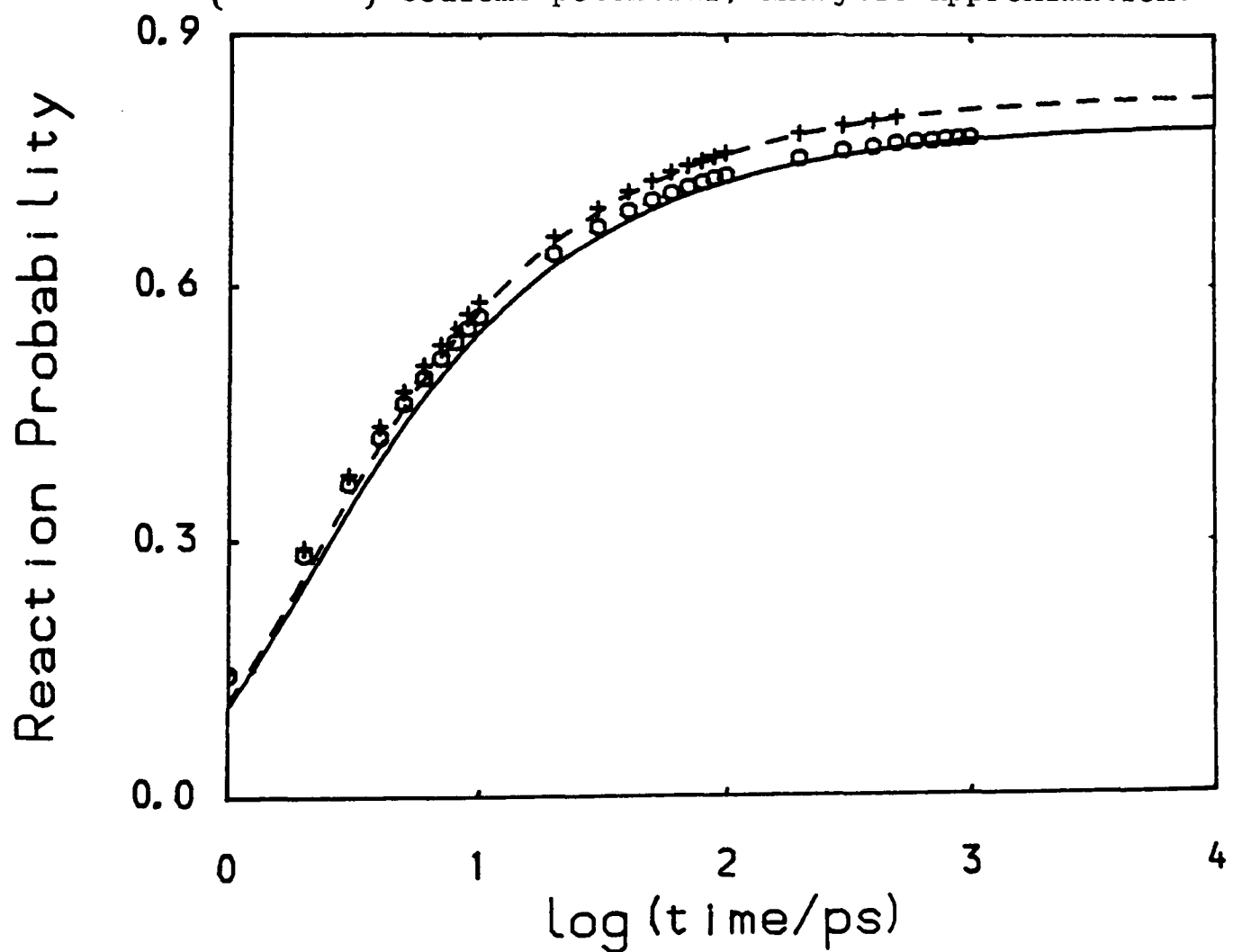


Fig.II.4.7 Recombination of a geminate ion pair.
 $D' = 1.0 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$; $R = 0.3 \text{ nm}$; $r = 0.5 \text{ nm}$;
 $r_c = -0.7 \text{ nm}$; $r_D = 0.96 \text{ nm}$.

(o o o o) Screened potential, numerical solution.
 (—) Screened potential, analytic approximation.
 (+ + + +) Coulomb potential, numerical solution.
 (---) Coulomb potential, analytic approximation.



4.4 Random flights simulation of recombination.

Full random flights simulation of the evolution of a cluster of interacting particles follows the individual trajectories of the particles. The diffusive motion of an ion is described in terms of a two component flight. The first component represents the random buffeting of the ion and the second the drift under the electrostatic influence of other ions. In modelling the kinetics of a cluster of ions in an ionic solution it is necessary to consider the effect of the ions of the bulk. For a purely kinetic study, it is sufficient to use a screened potential that takes into account the shielding of the charges of the interacting ions. According to the discretisation introduced in the previous chapter, the random flight of one member of a geminate pair is

$$\delta \underline{r} = -D \frac{\nabla U}{k_B T} \delta t + \sqrt{2 D \delta t} N_3(0,1). \quad (\text{II.4.28})$$

where, for a Coulomb potential,

$$\frac{\nabla U}{k_B T} = \frac{r_c}{r^3} \underline{r} \quad (\text{II.4.29})$$

and for a screened potential

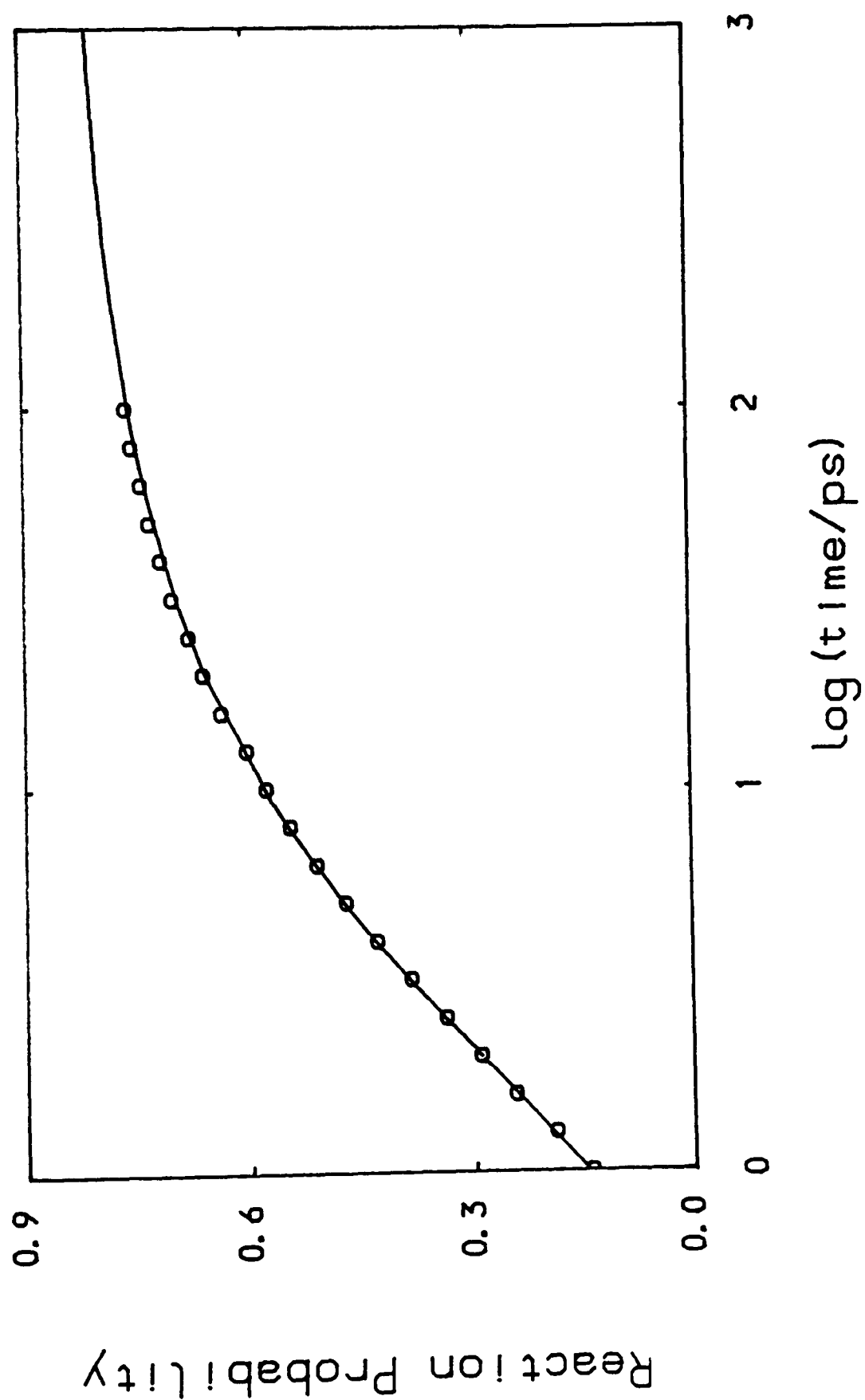
$$\frac{\nabla U}{k_B T} = \frac{r_c}{r^3 r_D} (r + r_D) \exp\left[-\frac{r}{r_D}\right] \underline{r}. \quad (\text{II.4.30})$$

The extension to a cluster of ions is trivial.

The length of a timestep in the variable timestep random flights model is determined by consideration of the drift a pair of ions. The calculation is discussed in chapter II.3 and appendix C. It is not necessary to reconsider the prescription for δt ,

Fig.II.4.8 Recombination of a geminate ion pair under the influence of a screened Coulomb potential.
 $D' = 1.0 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$; $R = 0.3 \text{ nm}$; $r = 0.5 \text{ nm}$;
 $r_c = -0.7 \text{ nm}$; $r_D = 0.96 \text{ nm}$.

(o o o o) Random flights simulation.
 (—) Numerical solution of backward equation.



equation (II.4.12), when a screened Coulomb potential is used. The force between two ions is

$$F = - \frac{\partial U}{\partial r} \quad (\text{II.4.31})$$

and, since $\gamma \simeq 1$, is stronger for a Coulomb potential than a screened Coulomb potential except when r is very small. The timestep for a Coulomb potential is always less than that for a screened potential. Fig.II.4.8 shows the recombination of a pair of ions simulated using the variable timestep random flights method. The simulated kinetics are in excellent agreement with numerical solution of the corresponding backward equation.

A complete simulation of recombination in an ionic solution requires the explicit modelling of the electrolyte. This involves a complicated treatment of long range electrostatic effects and necessitates the simulation of reflecting trajectories. This has not been attempted.

Chapter 5 : Partially diffusion-controlled ionic reactions.

The studies reported in the earlier chapters of this thesis have been concerned with idealised systems in which the kinetics are diffusion-controlled. This chapter considers reactions that are partially diffusion-controlled. There is a brief introduction to this type of reaction and the recombination of a geminate pair is considered. IRT modelling of the kinetics of partially diffusion-controlled reactions is analysed in detail and the random flights simulation of the diffusion and reaction processes is discussed.

5.1 Reaction in the absence of an interparticle force.

Collins and Kimball (1949) examined partially diffusion-controlled reaction in the absence of an interparticle force. The reaction of an encounter pair was assumed to occur at a rate proportional to the probability that the pair exists. According to this approach, the rate of reaction of a pair with separation R is

$$\rho(R) k_{\text{act}} = 4 \pi R^2 D \left. \frac{\partial \rho}{\partial r} \right|_R \quad (\text{II.5.1})$$

where ρ is the probability density function of separation. This is known as a radiation boundary condition by analogy with heat conduction. An alternative measure of the reaction rate at the boundary can be used; the 'velocity of reaction' is related to k_{act} by

$$k_{\text{act}} = 4 \pi R^2 v. \quad (\text{II.5.2})$$

If the reaction is diffusion-controlled then v is very large (strictly infinite). Solving the diffusion equation describing the evolution of a pair of particles using a radiation boundary

condition gives a reaction probability $W = W_{\infty} W_{*}$ where the probability of ultimate reaction is

$$W_{\infty} = \frac{vR^2}{r(D'+vR)} \quad (\text{II.5.3})$$

and the conditioned reaction probability is

$$W_{*} = \text{erfc}(y) - \exp(x^2 + 2xy) \text{erfc}(x + y), \quad (\text{II.5.4})$$

a function of the time-dependent variables

$$x = \frac{Rv+D'}{R} \sqrt{\frac{t}{D'}} \quad (\text{II.5.5})$$

and

$$y = \frac{(r-R)}{2\sqrt{D' t}} \quad (\text{II.5.6})$$

Equation (II.5.3) can be used to define an effective reaction distance,

$$R_{\text{eff}} = \frac{vR^2}{D'+vR} \quad (\text{II.5.7})$$

which links R , v and the steady-state rate constant for reaction,

$$k_2 = \frac{4 \pi D' R^2 v}{(Rv + D')} = 4 \pi D' R_{\text{eff}} \quad (\text{II.5.8})$$

5.2 Reaction under the influence of a Coulombic force.

Green (1984) has considered the partially diffusion-controlled reactions of ions in high permittivity solvents and derived an

approximation that provides a good description of recombination in water, assuming the electrostatic forces are Coulombic. The conditioned probability has the same form as equation (II.5.4) but with the time-dependent variables

$$x = \frac{4R^2\alpha\sqrt{t}}{r_c^2\sqrt{D'}} \sinh^2 \left[\frac{r_c}{2R} \right] \quad (\text{II.5.9})$$

and

$$y = \frac{r_c \left[\coth \left[\frac{r_c}{2r} \right] - \coth \left[\frac{r_c}{2R} \right] \right]}{4 \sqrt{D' t}} \quad (\text{II.5.10})$$

where

$$\alpha = v + \frac{r_c D'}{R^2 [1 - \exp(-r_c/R)]} \quad (\text{II.5.11})$$

To obtain the reaction probability W , W_* is multiplied by

$$W_\infty = \frac{R_{\text{eff}}}{r_{\text{eff}}} \quad (\text{II.5.12})$$

where r_{eff} is the inter-ion separation in the natural distance scale of chapter I.2,

$$r_{\text{eff}} = r_c / [\exp(r_c/r) - 1] \quad (\text{II.5.13})$$

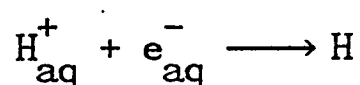
and R_{eff} is the effective reaction distance

$$R_{\text{eff}} = \frac{-r_c}{1 - \exp\left[\frac{r_c}{R}\right] \left[1 + \frac{D'r_c}{vR^2}\right]} \quad (\text{II.5.14})$$

which is related to the steady-state rate constant by an equation with the same form as equation (II.5.8). Table II.5.1 summarises the distance scales and reaction time distribution functions of diffusion-controlled and of partially diffusion-controlled reactions. Some of the expressions have been rearranged to aid comparison.

5.3 IRT simulation of partially diffusion-controlled kinetics.

For the most part, partially diffusion-controlled reactions are not very important in nonhomogeneous radiation chemistry and the quality of the approximation W_* is not critical. There is one major exception, the reaction of the hydrated electron and the hydrated hydrogen ion,



$$k_2 = 2.4 \times 10^{10} \text{ dm}^3\text{mol}^{-1}\text{s}^{-1} \quad R_{\text{eff}} = 2.35 \times 10^{-10} \text{ m.}$$

The partially diffusion-controlled nature of the $\text{H}_{\text{aq}}^+ + \text{e}_{\text{aq}}^-$ reaction is well known (Schwarz, 1964; Anbar, 1965). If a rate constant were estimated, assuming reaction were diffusion-controlled and using the sum of the 'ionic radii' of H_{aq}^+ and e_{aq}^- as a reaction distance, a value of four to five times the experimentally observed k_2 would be predicted (Baxendale et al., 1965; Matheson, 1965). Similar calculations for reactions between e_{aq}^- and hydrated metal ions show little discrepancy between the calculated and the experimental rate constant (Matheson, 1965). Experimental evidence for the partially diffusion-controlled nature of the reaction has been provided by examining the effect of solvent permittivity upon the rate

Table II.5.1 Summary of distance scales and survival probabilities for geminate recombination.

a) Diffusion-controlled reactions.

	No interparticle force	Coulombic force
R_{eff}	R	$-r_c / [1 - \exp(r_c/R)]$
r_{eff}	r	$-r_c / [1 - \exp(r_c/r)]$
W_∞	$R_{\text{eff}} / r_{\text{eff}}$	$R_{\text{eff}} / r_{\text{eff}}$
W_*	$\text{erfc} \left[\frac{r_{\text{eff}} - R_{\text{eff}}}{2 \sqrt{D' t}} \right]$	$\text{erfc} \left[\frac{r_{\text{eff}} - R_{\text{eff}}}{2 \sqrt{D' t}} \right]$

b) Partially diffusioncontrolled reactions.

	No interparticle force	Coulombic force
R_{eff}	$vR^2 / (Rv + D')$	$-r_c \left[1 - \exp(r_c/R) \left(1 + r_c D' / vR^2 \right) \right]^{-1}$
r_{eff}	r	$-r_c / [1 - \exp(r_c/R)]$
W_∞	$R_{\text{eff}} / r_{\text{eff}}$	$R_{\text{eff}} / r_{\text{eff}}$
x	$\frac{Rv}{R_{\text{eff}}} \sqrt{\frac{t}{D'}}$	$\frac{R^2 v}{R_{\text{eff}}} \sqrt{\frac{t}{D'}} \frac{[1 - \exp(-r_c/R)]}{r_c}$
y	$\frac{r_{\text{eff}} - R_{\text{eff}}}{2 \sqrt{D' t}}$	$\frac{r_{\text{eff}} + r_c / (1 - \exp(r_c/R))}{2 \sqrt{D' t}}$
W_*	$\text{erfc}(y) - \exp(x^2 + 2xy) \text{erfc}(x+y)$	$\text{erfc}(y) - \exp(x^2 + 2xy) \text{erfc}(x+y)$

constant. Barat et al. (1973) studied the variation in k_2 in a series of water/ethanol mixtures. The rate constant hardly changes ($\approx 20\%$) where Bronsted theory suggests a relative increase of 10 to 100. This behaviour contrasts with that of reactions involving other ionic electron scavengers.

5.3.1 Estimation of parameters.

Although the steady-state rate constant, k_2 , and the relative diffusion coefficient, D' , are frequently known, they are not the parameters required for the IRT simulation of nonhomogeneous reaction kinetics; R and v are needed. There is insufficient information in k_2 to determine both the encounter distance, R , and the velocity of reaction at this separation. For the highly reactive particles created by radiolysis it is usually acceptable to assume that the kinetics are diffusion-controlled and therefore $R = R_{\text{eff}}$ and v is infinite. When a pair of ions are of opposite charge and the Onsager distance is negative, a reaction can only be ~~is~~ diffusion-controlled if $R_{\text{eff}} \geq |r_c|$. If this condition is not met, the reaction is not diffusion-controlled and must be treated using a radiation boundary condition.

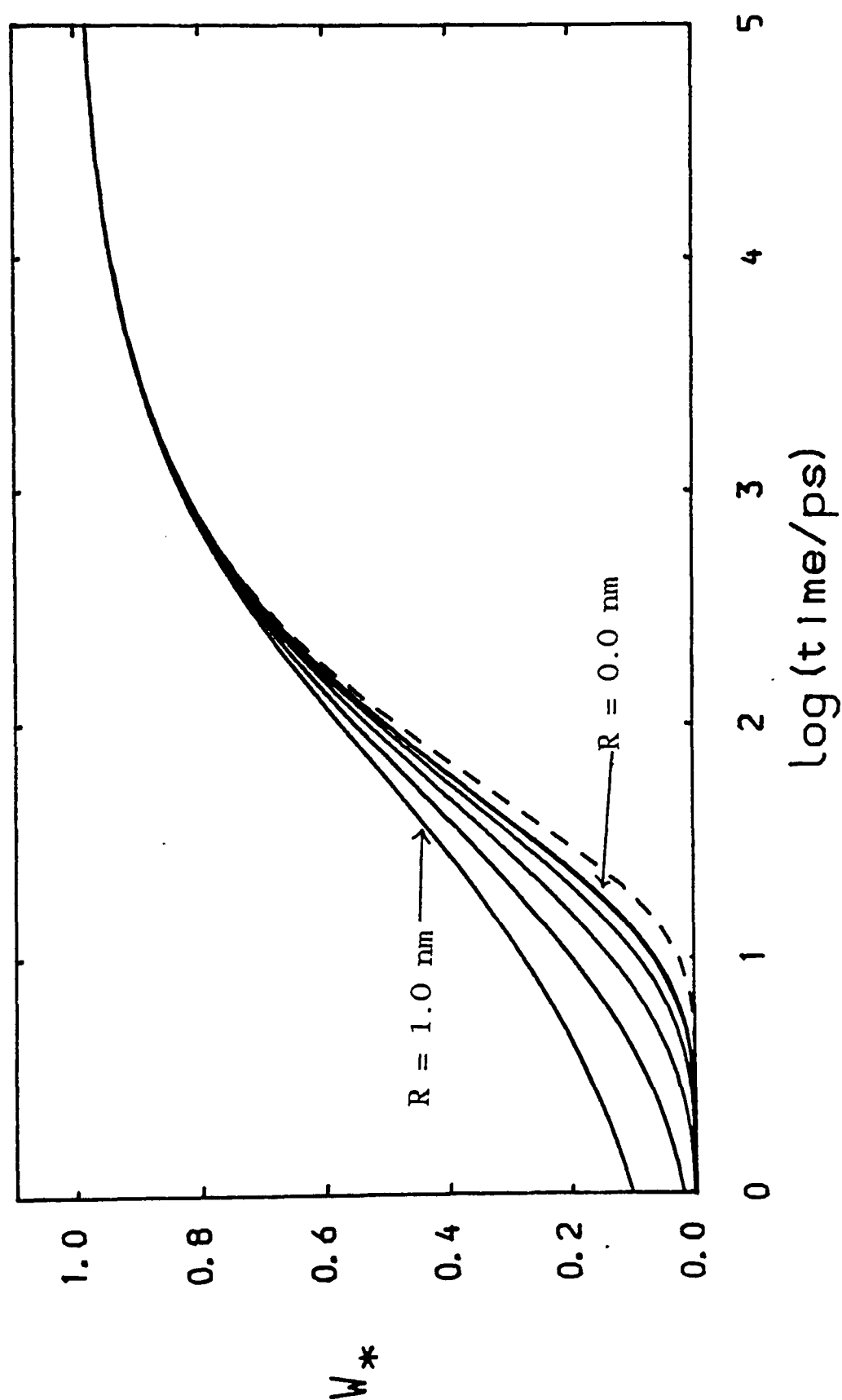
5.3.2 Modelling the $\text{H}^+ + \text{e}^-$ reaction.

To model the recombination of a hydrated hydrogen ion - hydrated electron pair, acceptable estimates for the reaction distance and the reaction velocity are required. Whilst the ultimate reaction probability of a $\text{H}_{\text{aq}}^+/\text{e}_{\text{aq}}^-$ pair is unaffected by the choice of R and v (equation (III.5.12)), the time dependence of the recombination of the pair does depend upon the values selected. This variation in the conditioned reaction probability is illustrated in Fig.II.5.1, which shows the effect of varying R in the range 0.0 to 1.0 nm upon the conditioned reaction probability for a pair initially separated by 1.0 nm. (v is varied in such a

Fig.II.5.1 Variation of W_* with R and v .

$k = 2.4 \times 10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$; $r = 1.0 \text{ nm}$; $D' = 1.35 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$;
 $r_c = -0.7 \text{ nm}$.

(- - - -) Error function approximation, equation (II.5.15).
 (—) Approximate solution of Green ($R = 0.0 \text{ nm}$ to 1.0 nm in steps of 0.2 nm).



way as to keep R_{eff} constant.) A relative diffusion coefficient of $1.35 \times 10^{-8} \text{ m}^2\text{s}^{-1}$ is assumed (Schwarz, 1969). The variation of v as a function of R is shown in Fig. II.5.2. The function, $v(R)$, has a maximum at $R = 3.3 \text{ nm}$, $v = 4.95 \text{ ms}^{-1}$.

Hart and Anbar (1970) calculated the reaction distance for twenty-two different reactions of e_{aq}^- with ionic species. The values range from 0.34 to 0.75 nm (NO_2^- and $\text{S}_2\text{O}_8^{2-}$ respectively) and have a mean of 0.53 nm. On this basis, an acceptable estimate for the reaction distance of a $\text{H}_{\text{aq}}^+/\text{e}_{\text{aq}}^-$ pair is 0.50 nm. The corresponding reaction velocity is 4.19 ms^{-1} . The conditioned reaction probability of a pair, predicted using these parameters, is shown in Fig. II.5.3.

The equation describing the time dependence of partially diffusion-controlled reactions between ions is too complex to invert using the procedures described in chapter II.1 and appendix A. To include this type of reaction in the IRT methodology a simpler approximation for W_* is required. Fig. II.5.3 compares the approximation of Green (equation (II.5.4) with x , y and α defined by equations (II.5.9), (II.5.10) and (II.5.11)) with the solution for a diffusion-controlled reaction in the absence of an electrostatic force and with the approximate distribution function

$$W_* = \text{erfc} \left[\frac{(r_{\text{eff}} - R_{\text{eff}})}{2\sqrt{D't}} \right] \quad (\text{II.5 15})$$

where r_{eff} is the initial separation in the distance scale defined by equation (II.5.13) and R_{eff} is the effective reaction distance described by equation (II.5.14). The approximation of equation (II.5.15) is suggested ^{by} analogy with the studies in chapter I.2 and chapter II.3. The recombination predicted by the solution for neutrals is very different from the correct kinetics. However,

Fig.II.5.2 The relationship between reaction velocity and reaction distance for $k = 2.4 \times 10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$.
 $D' = 1.35 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$; $r_c = -0.7 \text{ nm}$.

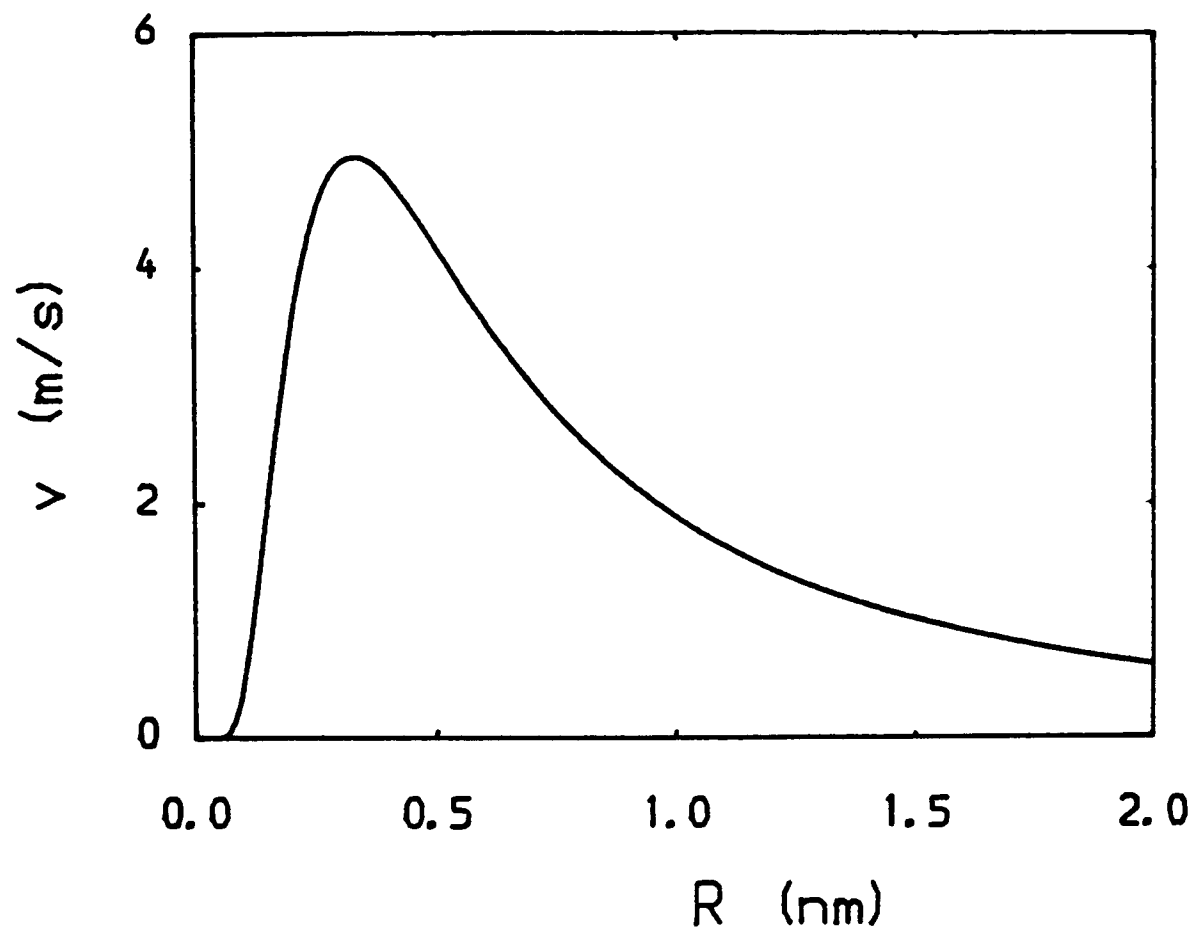
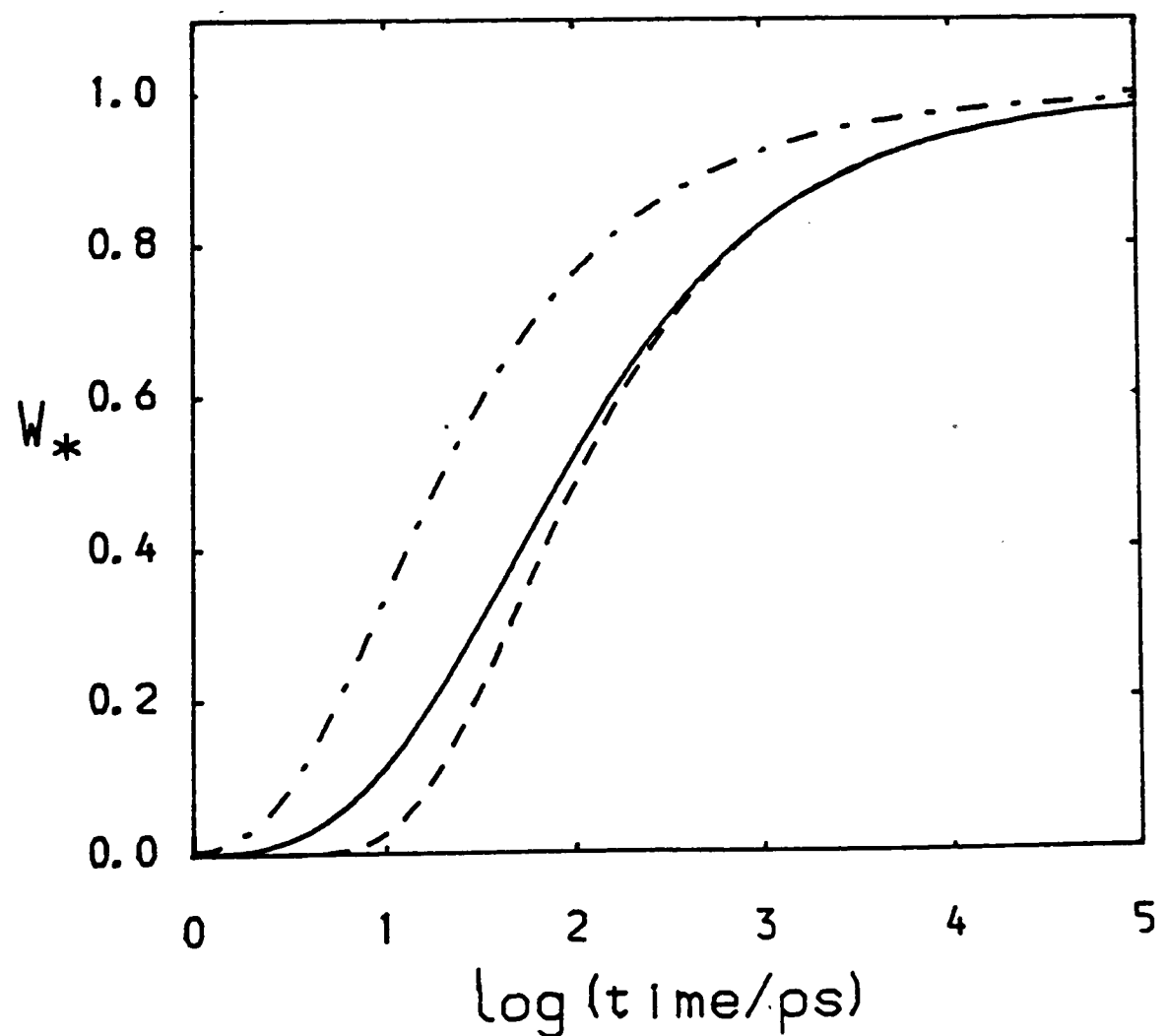


Fig.II.5.3 Comparison of approximations for W_* .
 $D' = 1.35 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$; $r = 1.0 \text{ nm}$; $v = 4.19 \text{ m s}^{-1}$;
 $R = 0.5 \text{ nm}$; $r_c = -0.7 \text{ nm}$.

(—) Approximation of Green, equation (II.5.4).
 (---) Error function approximation, equation (II.5.15).
 (-·-·-·-) Solution for neutrals.



equation (II.5.15) has the correct long time asymptote and is generally an acceptable approximation for W_* except when the initial separation of the ions is small where the approximation underestimates the rate at which the conditioned reaction probability increases.

5.3.3 Zero time reaction.

If equation (II.5.15) is used to describe the time dependence of the reaction of a hydrated electron-hydrated hydrogen ion pair, then the separation at which reaction occurs is important - when r is equal to R , r_{eff} is greater than R_{eff} . This reflects the fact that particles in contact do not necessarily react. If the IRT model is applied in the same manner as for diffusion-controlled systems then zero time reaction occurs when $r \leq R$ and some pairs with $r_{\text{eff}} \geq R_{\text{eff}}$ will have reacted. It is necessary to rationalise this problem. As v is finite at time $t = 0$ as well as $t > 0$, the obvious approach is to allow zero time reaction when $r_{\text{eff}} \leq R_{\text{eff}}$. However, if one of the reacting particles is a hydrated electron, the encounter involves the thermalisation/trapping of the electron by the other particle and the possible states formed by the aggregate ought to be considered. A pair forming an aggregate in a bound state, or a state that relaxes to a bound state, should be treated as having reacted and a reaction time should be generated in all other cases. This approach is complicated and a more approximate treatment is needed. For the reaction $e_{\text{aq}}^- + H_{\text{aq}}^+$, modelling reaction at $r = R$ is likely to be acceptable.

5.3.4 An alternative approximation for W_* .

The error function description of the time dependence of a partially diffusion-controlled reaction, equation (III.5.15), was suggested by analogy with diffusion-controlled reaction. An acceptable approximation must have the correct asymptote and

accurately represent the time dependence. The asymptote is

$$W_{*}(r, \infty) \longrightarrow \operatorname{erfc} \left[\frac{r_{\text{eff}} - R_{\text{eff}}}{2\sqrt{D' t}} \right] \longrightarrow 1 - \frac{r_{\text{eff}} - R_{\text{eff}}}{2\sqrt{D' t}}.$$

One of the more familiar transcendental functions is the incomplete Gamma function,

$$\Gamma(a, y) = \int_y^{\infty} x^{a-1} \exp(-x) dx. \quad (\text{II.5.16})$$

This function covers a family of other functions including the exponential, the error function and the exponential integral. It has a range of arguments from zero to infinity and is a natural function to consider for a distribution of times.

The incomplete Gamma function can be expressed as the sum (Erdelyi, 1953)

$$\Gamma(a, y) = \Gamma(a) - \sum_{n=0}^{\infty} \frac{(a)_n y^{a+n}}{n! (a+n)} \quad (\text{II.5.17})$$

where $(a)_0 = 1$ and $(a)_n = \Gamma(a+n)/\Gamma(a)$. In the limit of small y

$$\frac{\Gamma(a, y)}{\Gamma(a)} = 1 - \frac{1}{\Gamma(a)} \frac{y^a}{a} \quad (\text{II.5.18})$$

which can be compared with the limit of W_{*} above. Defining

$$x = \frac{r_{\text{eff}} - R_{\text{eff}}}{2\sqrt{D' t}}, \quad (\text{II.5.19})$$

W_* can be approximated by the family of curves

$$W_* = \frac{\Gamma(a, [2 \Gamma(a+1) x / \sqrt{\pi}]^{1/a})}{\Gamma(a)} \quad (\text{II.5.20})$$

all of which have the correct long time asymptotic behaviour. Fig.II.5.4 shows this approximation for the conditioned reaction probability of a pair with initial separation 1.0 nm. When $a = 0.8$, the approximation gives a good approximation to the correct time dependence and long time asymptote.

An accurate description of W_* using an incomplete Gamma function depends upon the selection of a suitable value for a . This is determined by examining the best fit value as r and R are varied. For the reaction $H_{aq}^+ + e_{aq}^-$ the empirical relationship

$$a = 0.702 \exp(-0.162\{r-R\}) + 0.5 \quad (\text{II.5.21})$$

provides excellent agreement with the fuller description of equation (II.5.4). Fig.II.5.5 demonstrates the use of the approximation.

5.3.5 Application to nonhomogeneous kinetics.

The simulation of kinetics using IRT techniques involves the determination of reaction times from a suitable distribution. The inversion of a distribution of the form $W_* = \text{erfc}(x)$ was discussed in appendix A. The generation of a reaction time from the family of curves described by equation (II.5.20) is not quite as straightforward and requires sampling from a Gamma distribution. The calculation of a reaction time involves the consideration of whether the pair will ultimately react. Reaction is assumed to occur if a uniformly distributed random number in the range (0,1) is less than W_∞ . If reaction is found to occur, a reaction time is

Fig.II.5.4 Incomplete gamma function approximation for conditioned reaction probability.

$D' = 1.35 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$; $r = 1.0 \text{ nm}$; $v = 4.19 \text{ m s}^{-1}$;
 $R = 0.5 \text{ nm}$; $r_c = -0.7 \text{ nm}$.

- (—) Approximate solution of Green.
 (---) Incomplete Gamma function approximation ($a = 0.4$ to 1.4 in steps of 0.2).

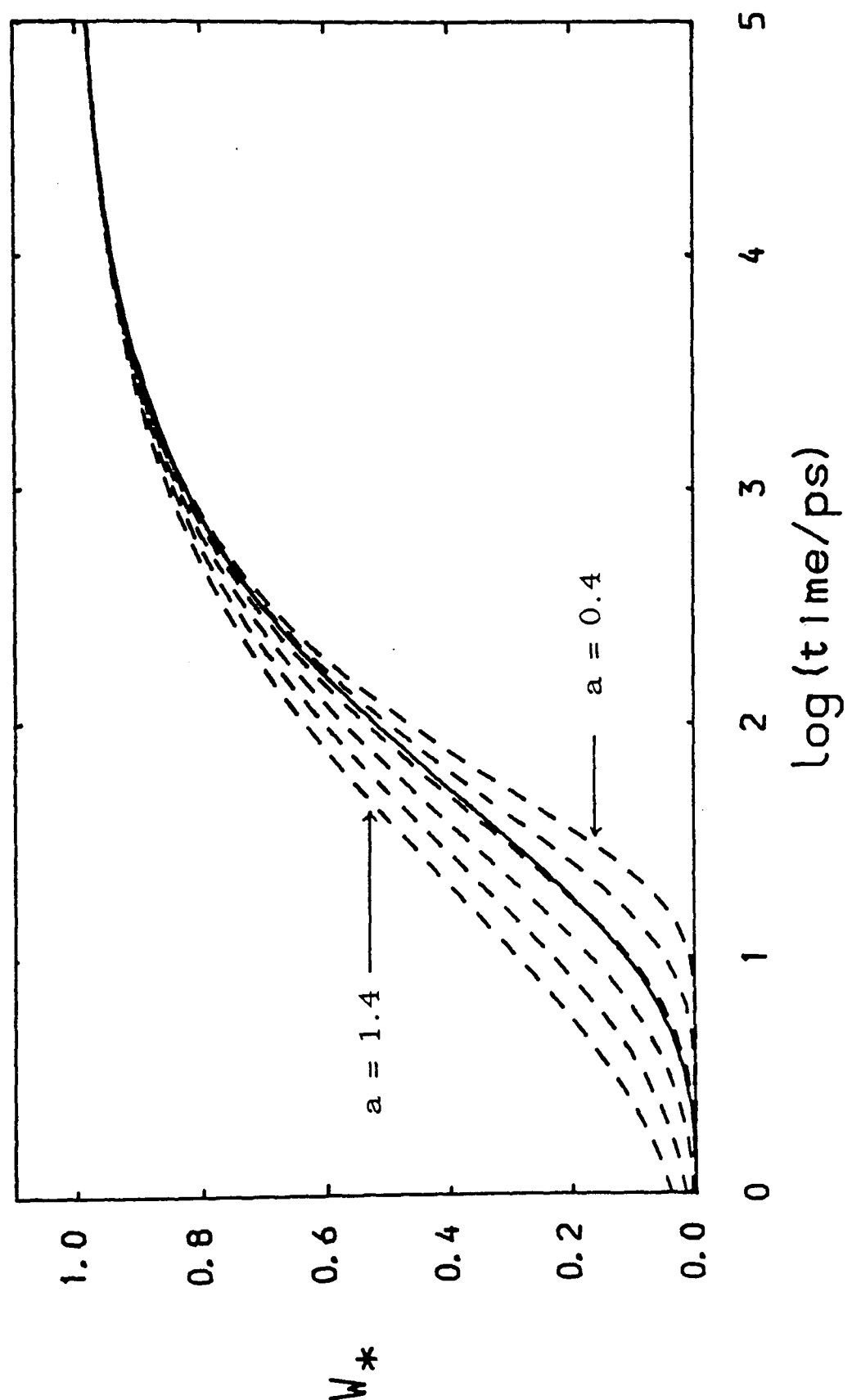
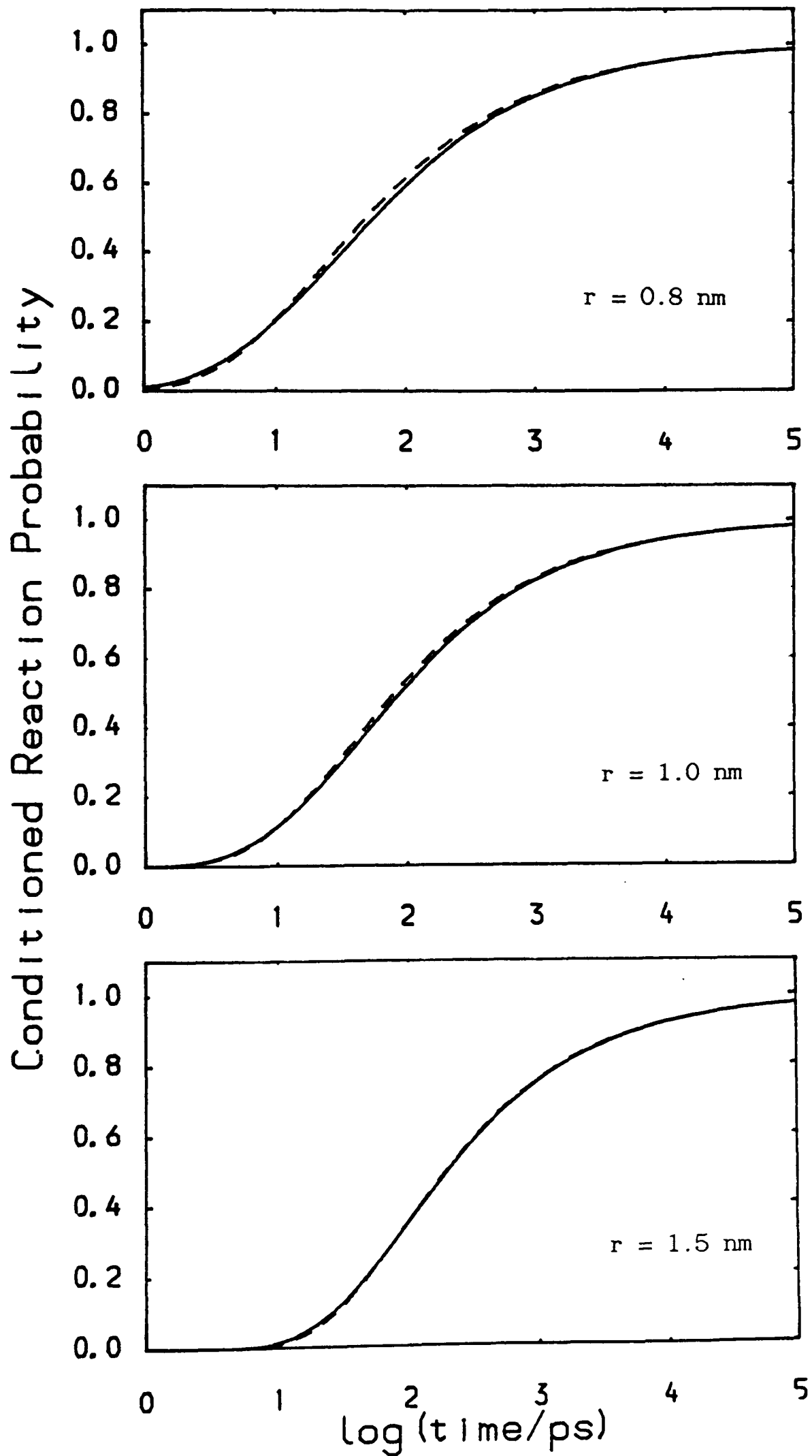


Fig.II.5.5 The best fit incomplete Gamma function approximation for W_* .

$D' = 1.35 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}; \quad R = 0.5 \text{ nm}; \quad v = 4.19 \text{ m s}^{-1};$
 $r_c = -0.7 \text{ nm}.$

(——) Approximate solution of Green.
(- - - -) Incomplete Gamma function approximation.



sampled from the correct gamma distribution. Gamma variates can be generated using a modified rejection technique (Ahrens et al., 1983) and a suitable algorithm has been published in CACM (No.599). This method is much slower than the inversion of the error function.

The three simple approximations for the conditioned reaction probability of a H_{aq}^+/e_{aq}^- pair, the solution for neutrals, equation (II.5.15) and equation (II.5.20) with equation (II.5.21), can be compared by examining the kinetics of idealised clusters of hydrated electrons, hydrated hydrogen ions and hydroxyl radicals. Reaction is governed by the scheme in Table II.5.2, which also includes steady-state rate constants and the reaction distances calculated using the diffusion coefficients listed in Table II.5.3. The kinetics of a two dissociation cluster are shown in Fig.II.5.6. The H^+ and OH are positioned from independent and identical Gaussian distributions of standard deviation 0.4 nm and the hydrated electrons are drawn from Gaussians of standard deviation 0.75 nm. The kinetics predicted using the three approximations for $W_*(H^+ + e^-)$ are, for the most part, similar and the results of equation (II.5.15) and equation (II.5.20) agree almost exactly. One exception is the behaviour of the hydrogen atom. When the influence of interparticle forces upon the time dependence of the reaction $H^+ + e^-$ is neglected, the decay/formation trace predicted shows a much faster production and a much higher final yield than is the case for the other two approximations. Modelling the $H^+ + e^-$ reaction using equation (II.5.15) suggests initial decay from the zero time yield of H followed by a later period of production. This is an artefact introduced by the zero time reaction problem discussed earlier and is only apparent when the spatial distributions of the hydrated electron and the hydrated hydrogen

Table II.5.2 The reaction scheme for the $H_{aq}^{+}/OH/e_{aq}^{-}$ system.

(Burns & Marsh, 1981)

Reaction	$k/10^{10}\text{mol}^{-1}\text{dm}^3\text{s}^{-1}$	R / nm	v / ms^{-1}
$e^{-} + e^{-} \longrightarrow 2\text{OH}^{-} + \text{H}_2$	0.5	0.34	4.19
$e^{-} + \text{H}^{+} \longrightarrow \text{H}$	2.4	0.50	
$e^{-} + \text{H} \longrightarrow \text{OH}^{-} + \text{H}_2$	2.5	0.29	
$e^{-} + \text{OH} \longrightarrow \text{OH}^{-}$	3.0	0.54	
$e^{-} + \text{H}_2\text{O}_2 \longrightarrow \text{OH}^{-} + \text{OH}$	1.2	0.29	
$\text{H} + \text{H} \longrightarrow \text{H}_2$	1.0	0.19	
$\text{H} + \text{OH} \longrightarrow \text{H}_2\text{O}$	2.0	0.27	
$\text{H}^{+} + \text{OH}^{-} \longrightarrow \text{H}_2\text{O}$	14.3	1.23	
$\text{OH} + \text{OH} \longrightarrow \text{H}_2\text{O}_2$	0.45	0.21	

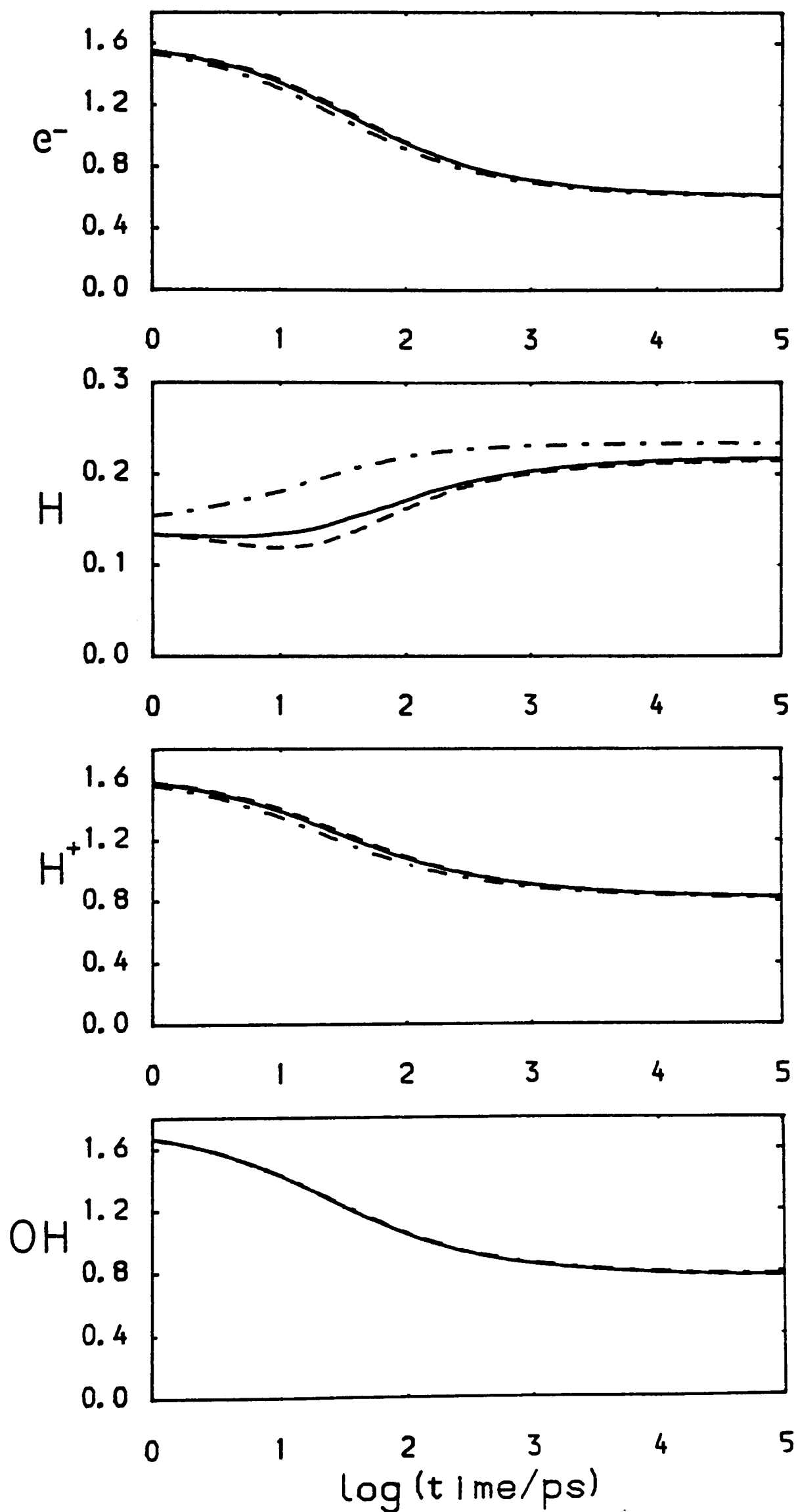
Table II.5.3 Cluster species and their diffusion coefficients.

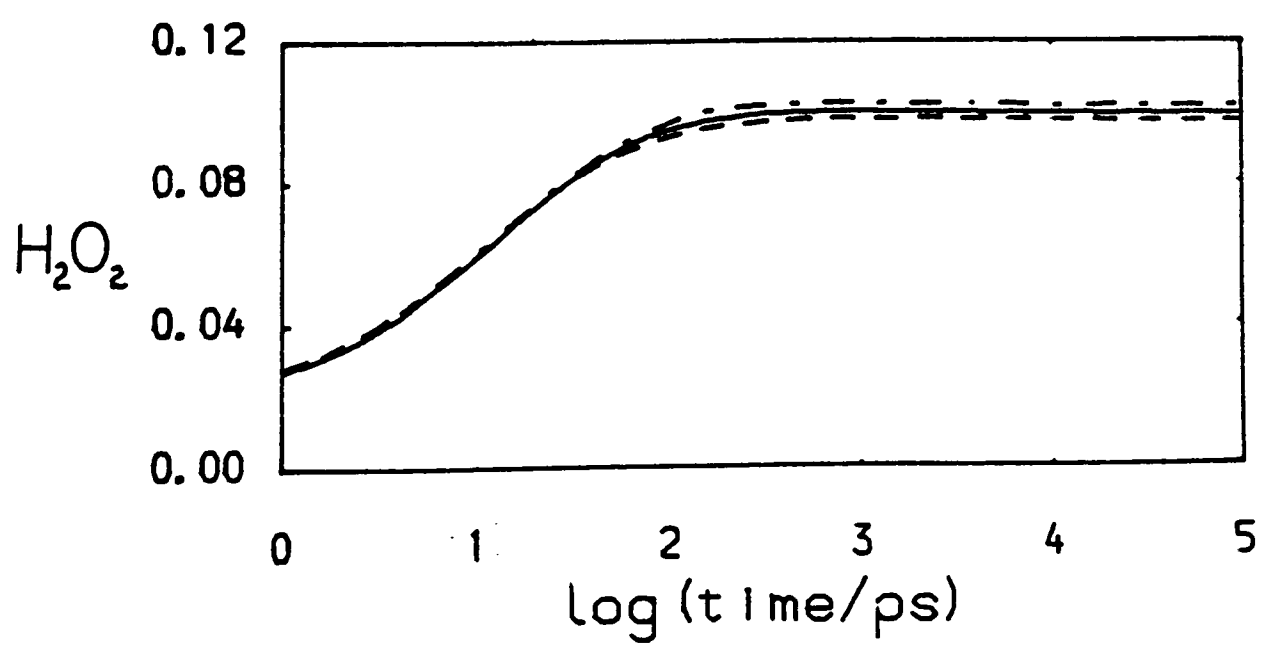
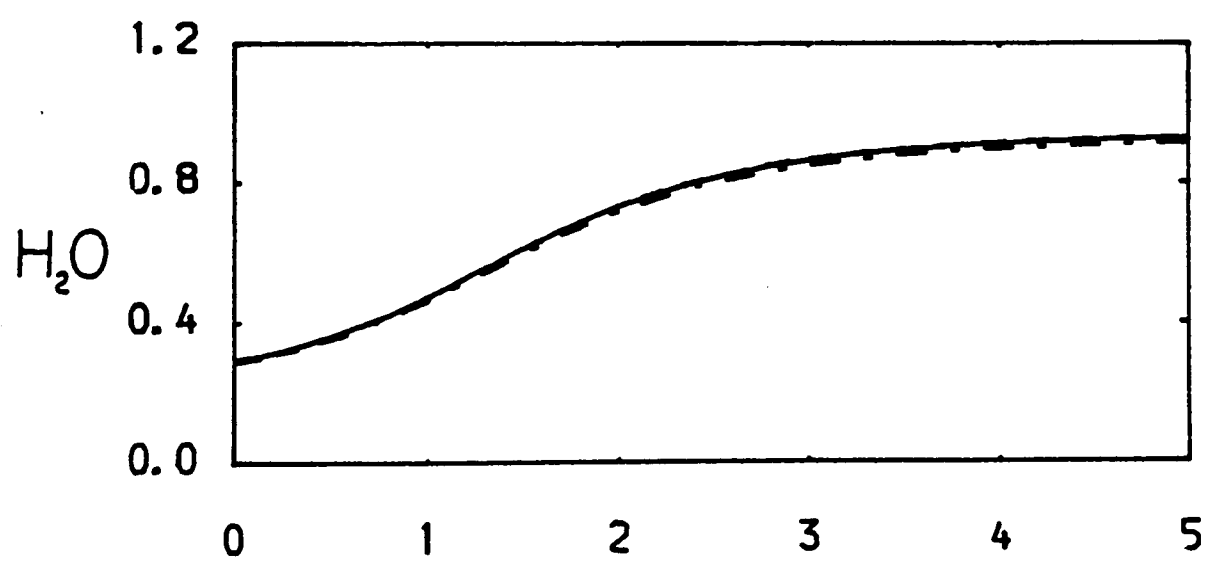
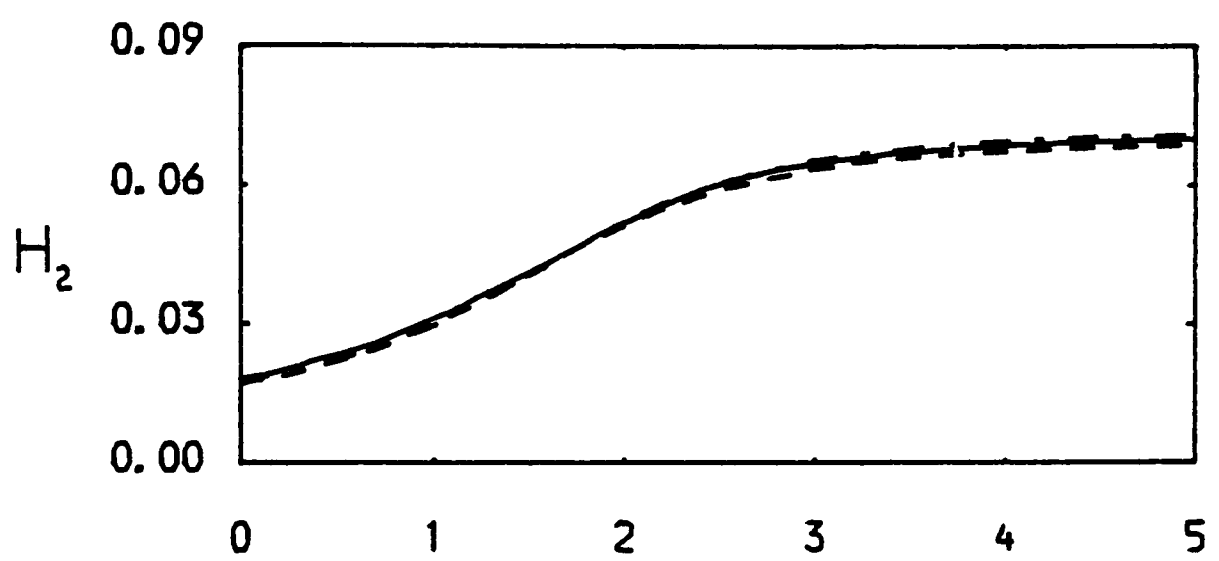
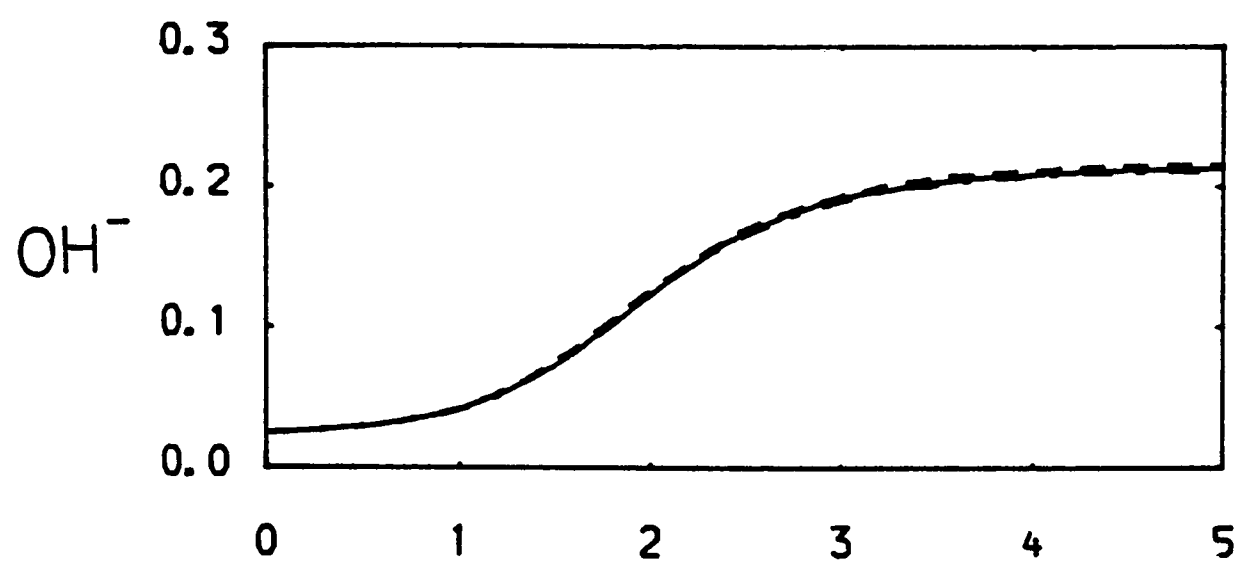
(Trumbore, 1967; Schwarz, 1969; Am.Inst.Physics Handbook, 1967)

Species	D / $10^{-9}\text{m}^2\text{s}^{-1}$
e^{-}	4.5
H	7.0
H^{+}	9.0
OH	2.8
OH^{-}	5.0
H_2	5.0
H_2O	2.8
H_2O_2	1.4

Fig.II.5.6 Kinetics of a two dissociation cluster.
Initial positions from iid Gaussians, $\sigma(e^-) = 0.4$ nm,
 $\sigma(H^+) = \sigma(OH) = 0.75$ nm; $|r_c| = 0.7$ nm.

(—) Gamma function approximation for $H^+ + e^-$ reaction.
(- - -) Error function approximation for $H^+ + e^-$ reaction.
(-·-·-·-) Neutral approximation for $H^+ + e^-$ reaction.





ion are tight. For a two dissociation cluster with $\sigma_{H^+} = \sigma_{OH} = 0.95$ nm and $\sigma_{e^-} = 2.9$ nm (the widths predicted by Schwarz (1969) using prescribed diffusion) the kinetics are unaffected by the choice of equation (II.5.15) or equation (II.5.20) to model the time dependence of the $H^+ + e^-$ reaction.

5.3.6 Discussion.

The kinetics of partially diffusion-controlled reactions can be modelled using IRT techniques despite there being insufficient information in an experimental steady-state rate constant to provide a unique solution for both the reaction distance and the velocity of reaction. As the two parameters are related, it is necessary to make an educated guess for one and adjust the other accordingly. Two approximate methods of generating the time of a partially diffusion-controlled reaction are available: by inversion of a family of incomplete gamma functions or inversion of an error function. The first approach requires the determination of an empirical prescription to describe the family of functions, but is accurate under all conditions. The second method underestimates the speed of reaction if the ions are initially very close together. In general, both methods of generating reaction times are acceptable, but the error function inversion has the advantages of being easier to implement and faster.

5.4 Random flights simulation using a reflecting boundary.

The full simulation of partially diffusion-controlled reaction is a non-trivial project. It has been considered by Green et al. (1987), but has not been published in detail. The random flights technique used throughout this thesis allows unreactive pairs to diffuse "through" one another, but the trajectories ought to be modified to account for reflection on encounter. The imposition of

a reflecting boundary condition modifies a diffusive trajectory $X(t)$ according to (Green, 1988)

$$X_{\text{ref}}(t) \begin{cases} = X(t) & M(t) > R \\ = X(t) + R - M(t) & M(t) \leq R \end{cases} \quad (\text{II.5.22})$$

where $M(t)$ is the infimum of $X(t)$ and can be simulated subject to known values of $X(0)$ and $X(t)$ (Green, 1988). The kinetic effect of considering reflective trajectories when examining the diffusion-controlled reactions of a small cluster of particles may be negligible, but this is not the case when studying larger systems where the reduction in free volume will be important. Partially diffusion-controlled reactions are simulated by modelling the diffusive trajectories of the system taking into account the effects of reflection and then considering the probability of a reflecting encounter being reactive. The bridging process for a reflected sample path has been derived by Green (unpublished) and depends upon the local drift, in contrast to bridging processes referring to paths without reflection.

No detailed comparisons between the random flights approach and the IRT model have been made for systems including particles whose reactions are partially diffusion-controlled.

SECTION III

The kinetics of realistic radiation chemistry systems.

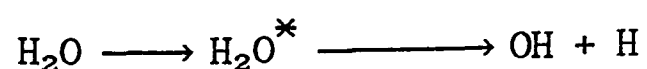
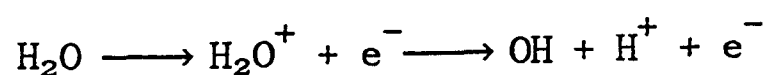
Chapter 1 : A simple atom-radical system.

The previous section described an alternative approach to the traditional treatment of nonhomogeneous kinetics in radiation chemistry. Two approximate methods, the IRT model and a master equation formulation, were introduced and developed. The stochastic models were shown to reproduce accurately the kinetics predicted by a full random flights simulation of the diffusion and reaction processes. Comparisons were made with conventional models and the differences between deterministic and stochastic models of kinetics were emphasised.

This chapter extends the comparison of stochastic and deterministic methods to a more realistic system. Clusters of hydrogen atoms and hydroxyl radicals are selected as a hypothetical model to represent the kinetics occurring in the radiolysis of acid solutions with high energy electrons. This system has the advantage that the kinetics are dominated by the reaction of neutral species.

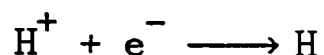
1.1 The H/OH system.

The aim of this study is to examine the kinetics of irradiated aqueous acid. Radiolysis was discussed in chapter I.1. The track of a high energy electron can be described in terms of a series of well separated energy deposition events. An energy loss may result in either ionisation or excitation of the medium,



In aqueous acid, the half life of a solvated electron is short and

for this simple study it is assumed that the reaction



occurs instantaneously. The chemistry of this simple system is based upon five species; two reactants (hydrogen atoms and hydroxyl radicals) and three products (molecular hydrogen, water and hydrogen peroxide). Reaction is summarised in the scheme,



where k_1 , k_2 and k_3 are the experimental steady-state rate constants (Burns & Marsh, 1981). All the reactions are assumed to be diffusion-controlled, even though the formation of hydrogen is believed not to be (Brocklehurst, 1984).

The rate constant for a diffusion-controlled reaction is related to the reaction distance of a pair of particles. For the reaction $\text{A} + \text{B} \longrightarrow \text{products}$,

$$k = 4 \pi D' R. \quad (\text{III.1.1})$$

and if the reacting particles are identical, i.e. $2\text{A} \longrightarrow \text{products}$, then

$$k = 2 \pi D' R. \quad (\text{III.1.2})$$

Calculation of the reaction distances needed in this study requires a knowledge of the diffusion coefficients of the hydrogen atom, D_{H} , and the hydroxyl radical, D_{OH} . Schwarz (1969) used the values

$$D_{\text{H}} = 7.0 \times 10^{-9} \text{ m}^2\text{s}^{-1} \quad ; \quad D_{\text{OH}} = 2.8 \times 10^{-9} \text{ m}^2\text{s}^{-1}$$

when he examined the radiolysis kinetics of aqueous solutions. The diffusion coefficient of H is an estimate from the experimental

value for He and that for OH is calculated, using Stokes' method, from the self diffusion coefficient of water. The reaction parameters calculated using these diffusion coefficients are listed in Table III.1.1.

Table III.1.1 Parameters used in simulation.

Reaction	Reaction distance / 10^{-10} m.	Relative Diffusion Coefficient / 10^{-8} m ² s ⁻¹
H + H → H ₂	1.89	1.40
H + OH → H ₂ O	2.70	0.98
OH + OH → H ₂ O ₂	2.12	0.56

The conventional models of low LET radiolysis kinetics generally consider the clusters of reactive particles that initially constitute the system to have a Gaussian profile. This assumption is fundamental to the prescribed diffusion approximation that is the basis of most approximate treatments, but is not essential to a numerical approach. A Gaussian particle distribution is not totally without foundation, but does not take into account the detailed dynamics of the fragmentation and thermalisation processes that take place prior to solvation. In the absence of a better approximation and to facilitate fair comparison between stochastic and deterministic models the Gaussian initial particle distribution has been assumed in the following studies.

1.2 Clusters containing two radical pairs.

First, the time dependence of the product yields of clusters containing two hydrogen atoms and two hydroxyl radicals is considered. The kinetics of particles positioned from independent and identical Gaussian distributions (of standard deviation

0.95 nm) are summarised in Fig.III.1.1. This cluster width, $0.75 \times N^{1/3}$ nm, is predicted by a comparison of prescribed diffusion and experimental product yields (Schwarz, 1969). The figure includes the results of full random flights simulation, approximate IRT simulation and modelling according to the deterministic methods of Schwarz (1969) and Burns et al. (1984). The two conventional treatments seriously overestimate the yield of H_2 and H_2O_2 , as is anticipated in the discussions of chapter I.2, but the performance of the approximate stochastic model is more than satisfactory. Product yields, at 100 ns, are listed in Table III.1.2. Also included are the predictions of a master equation solution of the problem. In the master equation formulation the initial state probabilities of the cluster system are calculated by simulation. The initial configuration of a cluster is generated and the interparticle distances are checked for overlap. This defines the initial state of the cluster. Realisation of many independent clusters gives a simulated probability for each state, which converges to the correct initial state probability when the number of clusters sampled is sufficiently large.

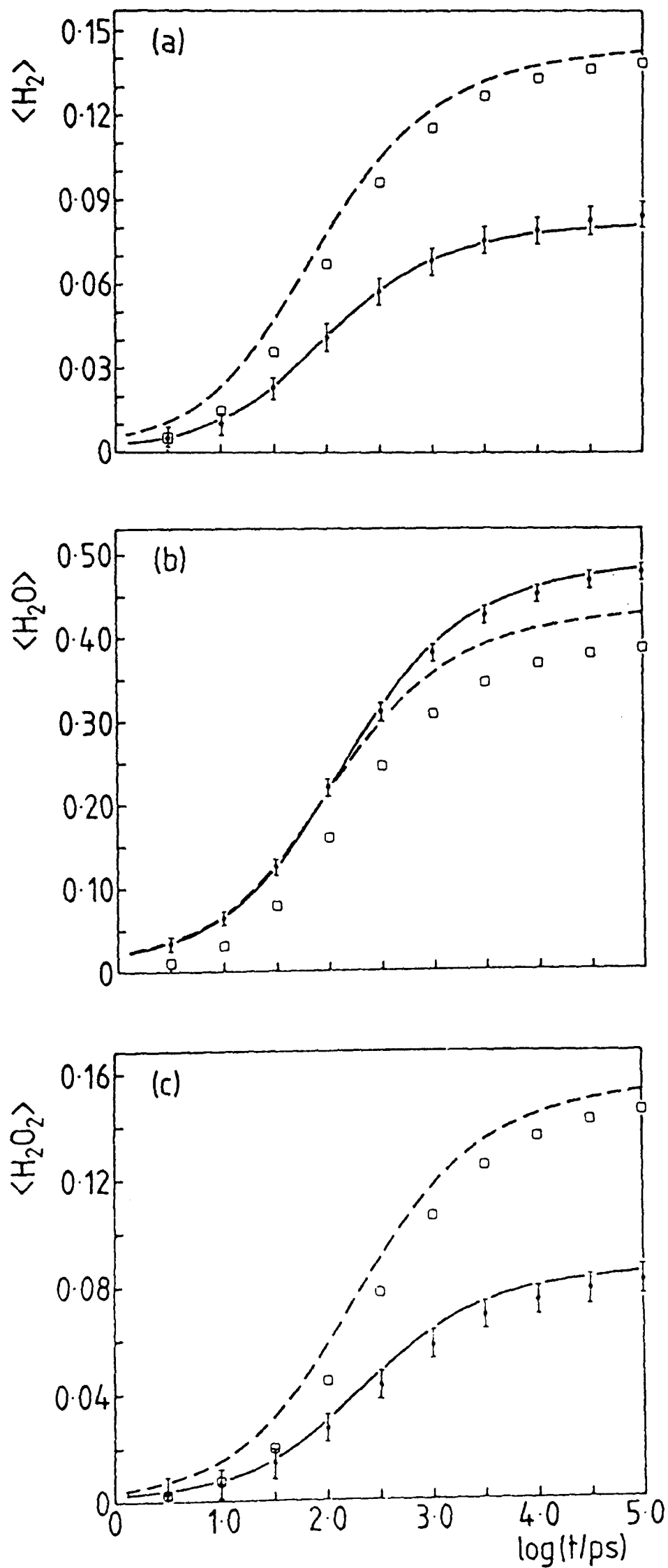
Table III.1.2 Predicted product yields at 100 ns for a 2H and 2OH Gaussian cluster of standard deviation 0.95 nm.

Approach	Expectation value of no. of product molecules.		
	H_2	H_2O	H_2O_2
Full simulation	0.084(6)	0.479(9)	0.082(6)
IRT simulation	0.081	0.483	0.085
Master equation	0.082	0.487	0.086
Prescribed diffusion	0.143	0.429	0.153
Numerical solution	0.135	0.386	0.145

Figures in brackets represent two standard errors of the mean in the third decimal place for the number of simulations performed.

Fig.III.1.1 Time-dependent product yields for Gaussian clusters initially containing two H and two OH radicals.
Cluster standard deviation, $\sigma = 0.95$ nm.

- (. . . .) Random flights simulation.
 (————) IRT simulation.
 (— — — —) Conventional modelling using prescribed diffusion.
 (□ □ □ □) Conventional modelling using Burns model.



1.3 Clusters with a distribution of initial contents.

Realistic low LET radiation chemical systems are composed of a distribution of clusters containing different numbers of pairs. Mozumder and Magee (1966c), using a Monte Carlo simulation method, obtained the size distribution in Table III.1.3.

Table III.1.3 Cluster size distribution.

No. of H/OH pairs, N	Fraction of clusters with N radical pairs.
1	0.486
2	0.351
3	0.097
4	0.035
5	0.019
6	0.011

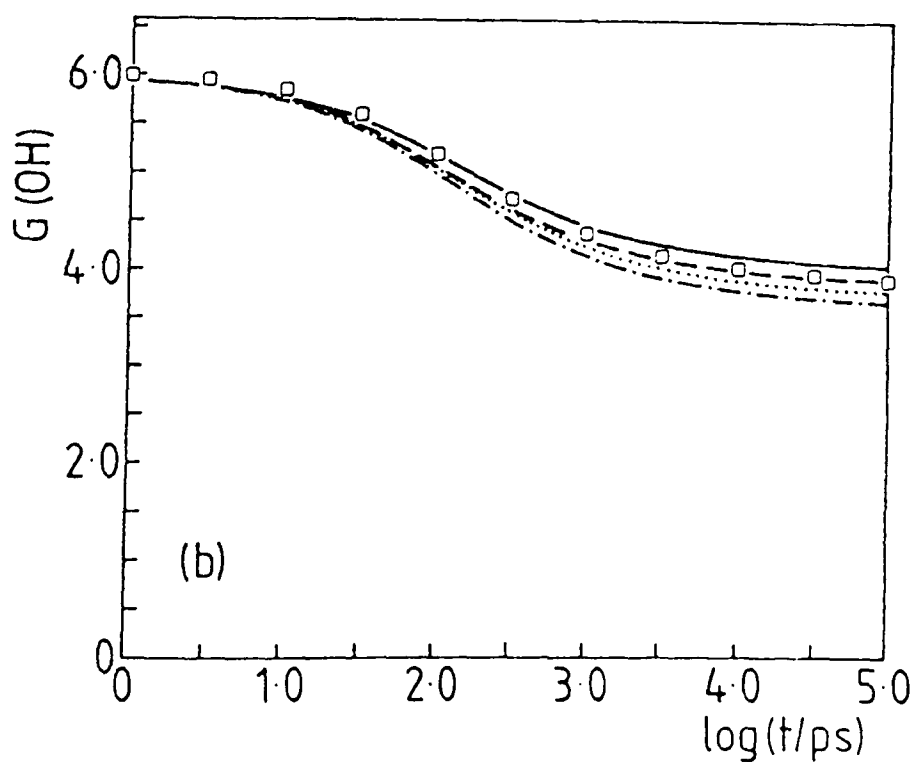
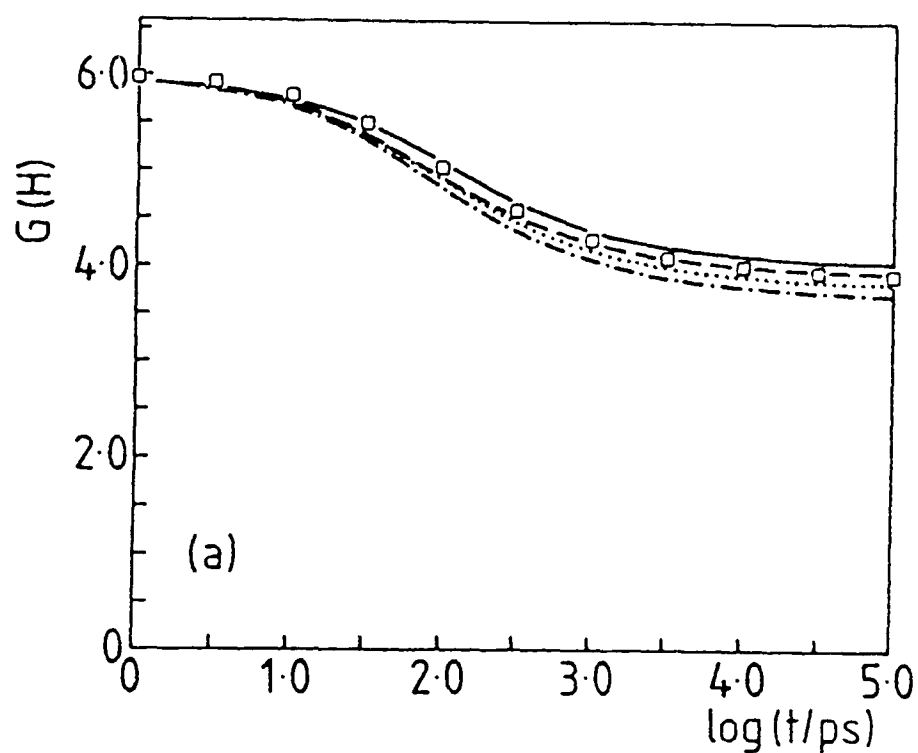
This distribution ~~of~~ represents the radiolysis of water with 1 MeV electrons and describes the relative abundance of clusters with less than six reactive pairs. To model the kinetics of the distribution of clusters a description of the dependence of the cluster volume on the number of pairs, N, is required. A cube root relationship between radius and N is usually used to keep the mean density of particles approximately constant (Samuel & Magee, 1953), i.e.

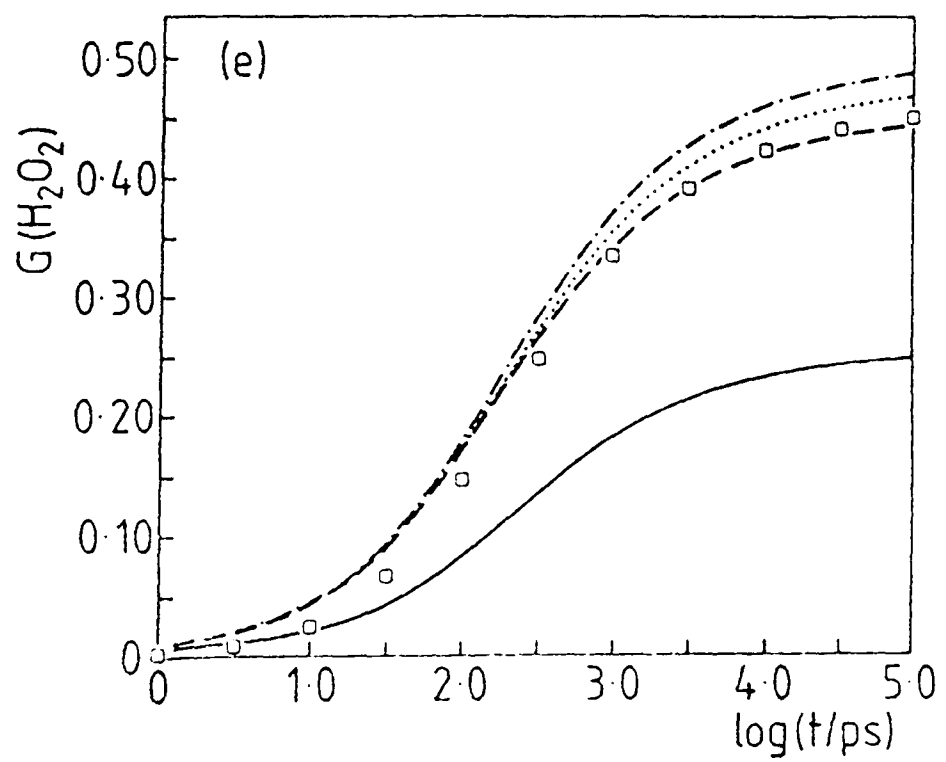
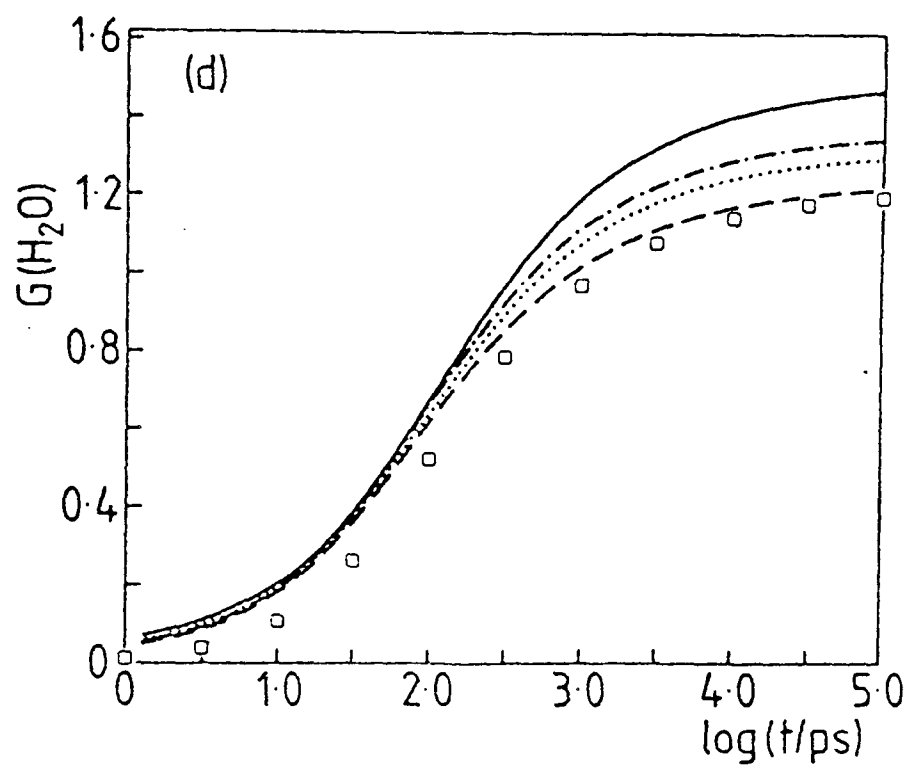
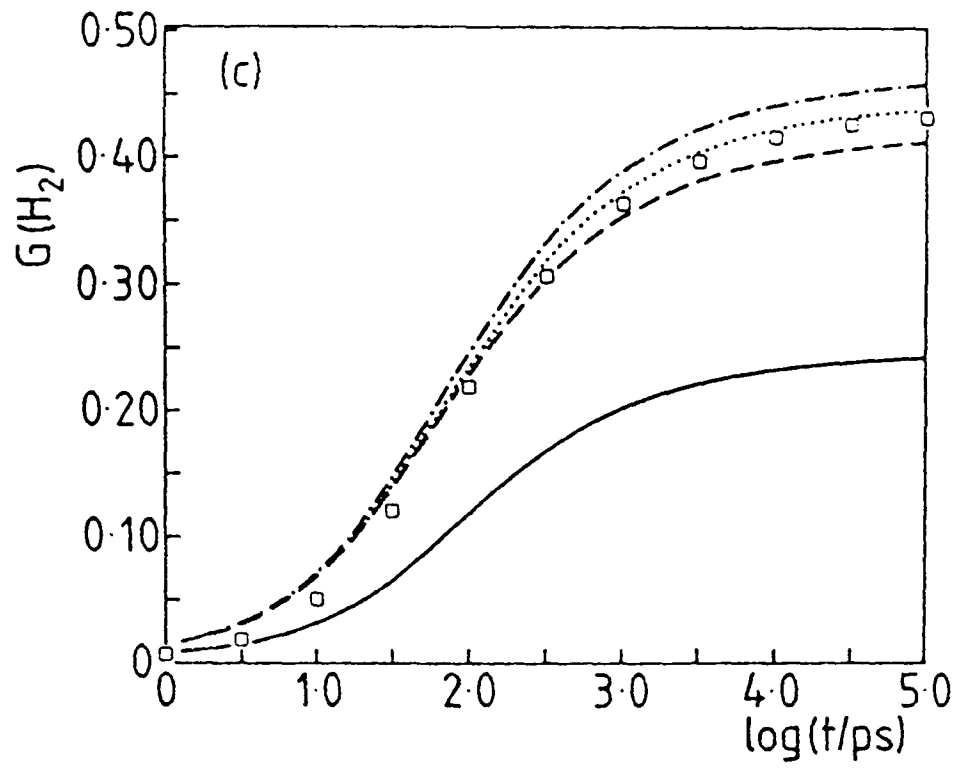
$$\sigma = \sigma_0 N^{1/3} \quad (\text{III.1.3})$$

where σ is the standard deviation of the Gaussian cluster and σ_0 refers to a single pair (the 'unit cluster'). Fig.III.1.2 examines the kinetics of the Mozumder and Magee distribution for $\sigma_0 = 0.75$ nm, using stochastic and deterministic methods. G values

Fig.III.1.2 Kinetics of a distribution of cluster sizes.

- (——) IRT simulation.
- (- - - -) Prescribed diffusion, averaged over distribution.
- (□ □ □ □) Numerical modelling, averaged over distribution.
- (- - - -) Prescribed diffusion, number averaged spur.
- (• • • •) Prescribed diffusion, energy averaged spur.





are the number of particles produced per 100 eV of energy deposited by the radiation. The evolution of the individual clusters, $N = 1$ to 6, are modelled then averaged according to the weights of Table III.1.3. Both numerical and approximate deterministic models are included. This approach to the conventional modelling of the system is not according to ^{the} spirit of the original methodology, which considered a typical average cluster. A cluster can be described by the number of pairs it contains or the amount of energy deposited. The distribution of Mozumder and Magee, listed in Table III.1.3, is in terms of the number of pairs and the average cluster obtained from this distribution is described as number averaged. A distribution in terms of the energy deposited would give a different, energy averaged cluster. If there are six dissociations per 100 eV of energy deposited then, according to the distribution of Mozumder and Magee, a number averaged cluster contains 1.8 pairs and 30 eV of energy. If the number distribution is replaced by the corresponding energy distribution, an energy averaged cluster of 2.4 pairs and 40 eV is predicted. Fig.III.1.2 also shows the kinetics of these two typical clusters modelled using prescribed diffusion.

Stochastic simulation gives very different predictions from the conventional methods. These differences are most obvious in the final molecular product yields, H_2 and H_2O_2 . The stochastic kinetics, which have already been shown to be the most realistic, predict only about half the final molecular yield forecast by a deterministic approach. The 100 ns yields are presented in Table III.1.4.

Table III.1.4 Modelled G values at 100 ns.

Method	G values at 100 ns.		
	H ₂	H ₂ O	H ₂ O ₂
Number averaged cluster:			
Prescribed diffusion	0.4131	1.2209	0.4434
Energy averaged cluster:			
Prescribed diffusion	0.4573	1.3453	0.4873
Averaging over distribution:			
Prescribed diffusion	0.4386	1.2997	0.4680
Numerical solution	0.4327	1.2002	0.4502
IRT simulation	0.2469	1.4866	0.2541
Master equation	0.2424	1.4375	0.2481

Radius of the unit cluster, $\sigma_0 = 7.5 \times 10^{-10}$ m.

The stochastic models are in close agreement, but there is a significant difference from the deterministic calculations for the H₂ and H₂O₂ yields. This difference is important as it implies that the parameters obtained fitting experimental results using deterministic models are not reliable in systems where the clusters of reactive particles are isolated.

1.4 The effect of the initial H and OH distributions.

Experimental product yields for the radiolysis of aqueous acid by 1 MeV electrons (Anbar, 1968) are listed in Table III.1.5. Comparison with the results of the stochastic and deterministic theories suggests initial spatial distributions of the two reactive species, H and OH, that are not the same. The unit widths used in the previous calculations were derived for the heavy fragments of water dissociation, H⁺ and OH, from experimental product yields using the prescribed diffusion model by Schwarz (1969). In acid solution the two reactive species ought to be positioned from distributions of different width as the majority of hydrogen atoms are produced by the fast reaction between secondary electrons and

the homogeneously distributed hydrogen ions of the acid. The electron trapping length is much larger than those of the heavier water fragments (Konovalov et al., 1984).

Table III.1.5 Experimental yields and stochastic predictions.

Approach	G values at 100ns			
	H	OH	H ₂	H ₂ O ₂
Experimental	3.65	2.95	0.45	0.80
IRT simulation ¹	3.17	2.27	0.38	0.73
ME solution ¹	3.08	2.25	0.30	0.72
IRT simulation ²	4.05	4.04	0.24	0.25
ME solution ²	4.03	4.01	0.25	0.25
IRT simulation ³	5.15	4.66	0.09	0.33
ME solution ³	5.12	4.64	0.10	0.34

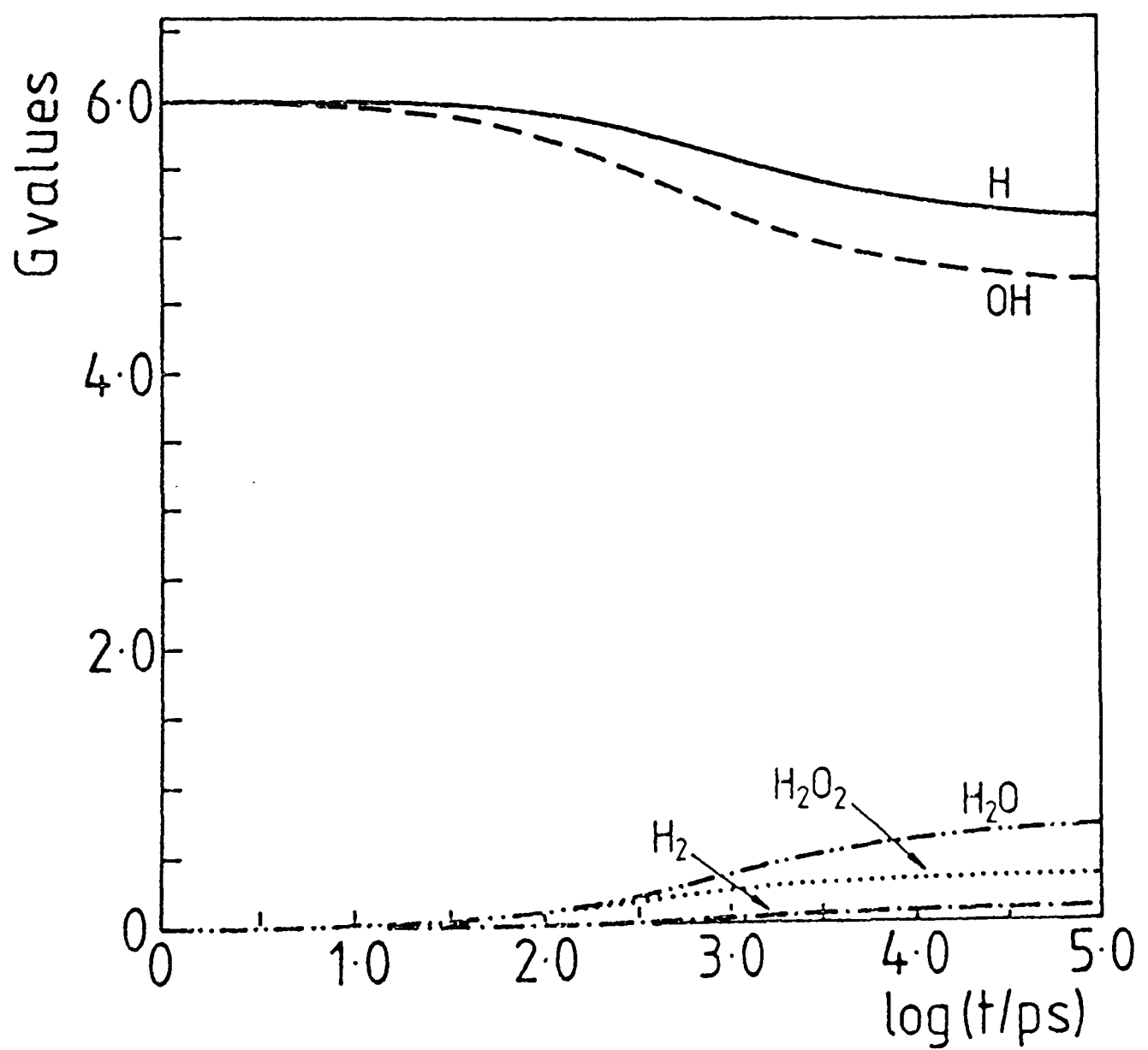
¹ $r_o(H) = 0.44 \text{ nm}$, $r_o(OH) = 0.19 \text{ nm}$.
² $r_o(H) = r_o(OH) = 0.75 \text{ nm}$.
³ $r_o(H) = 2.30 \text{ nm}$, $r_o(OH) = 0.75 \text{ nm}$.

Fig.III.1.3 shows the evolution of the H/OH system when the hydrogen and hydroxyl unit standard deviations are 2.3 nm and 0.75 nm respectively. The value for H is that predicted by Schwarz for the electron. The molecular hydrogen and the hydrogen peroxide yields now show the correct order, $H_2 < H_2O_2$, which suggests that agreement with experiment can, in principle, be obtained by adjustments of this kind.

1.5. Comparisons with experiment.

The stochastic simulations above used cluster widths estimated from prescribed diffusion calculations. Stochastic and deterministic kinetics are not equivalent and it is not, therefore,

Fig.III.1.3 The IRT simulation of the time evolution of the H/OH system.
Initial positions from iid Gaussians: $\sigma_0(\text{H}) = 2.30$ nm;
 $\sigma_0(\text{OH}) = 0.75$ nm.



surprising that experiment and stochastic simulation do not agree using these cluster widths. If stochastic modelling is to reproduce the experimental yields, the clusters considered must be much smaller. To obtain the correct widths, the modelled yields of H, OH, H₂ and H₂O₂ have been optimised. The recombination yield, H₂O, is not available experimentally. This optimisation involves the minimisation of the sum of the residuals,

$$X = \sum_i \left[\frac{G(i)_{\text{stoch}} - G(i)_{\text{expt}}}{G(i)_{\text{expt}}} \right]^2 \quad (\text{III.1.4})$$

where $G(i)_{\text{stoch}}$ and $G(i)_{\text{expt}}$ are the stochastic and experimental G values of species i ($= \text{H, OH, H}_2, \text{H}_2\text{O}_2$) at 100 ns which is assumed to be the end of the nonhomogeneous stage of the kinetics. The most efficient method of performing this calculation is with a master equation. The smallest residuals are generated for the unit radii of

Hydrogen atoms : $\sigma_0 = 4.41 \times 10^{-10} \text{ m}$

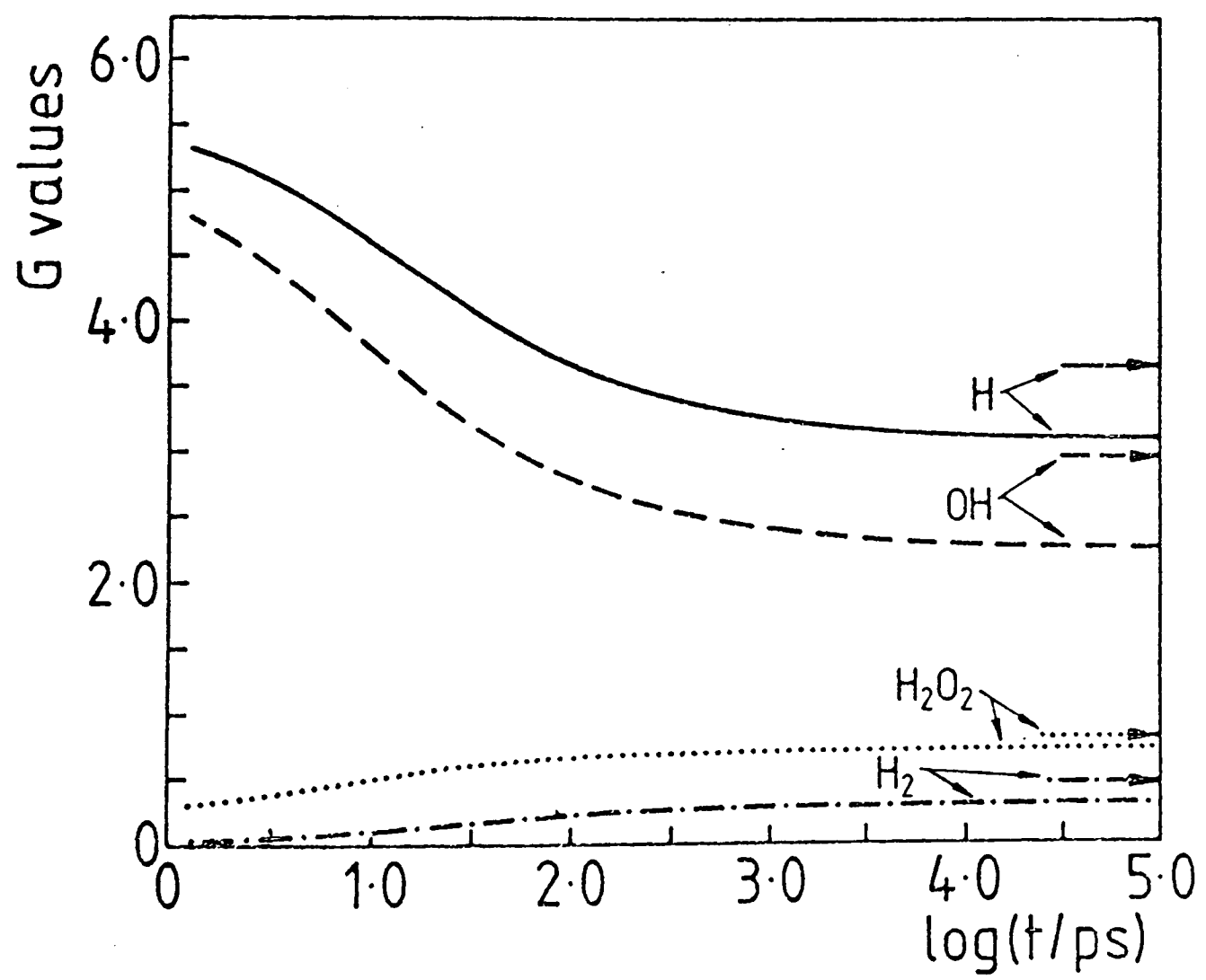
Hydroxyl radicals : $\sigma_0 = 1.94 \times 10^{-10} \text{ m}$

for the Mozumder and Magee cluster distribution. These values are approximately a quarter of those suggested by a conventional treatment and this demonstrates the potential for errors in the deterministic models. The time-dependent kinetics of the optimised system are shown in Fig.III.1.4. There is still some disagreement with experimental yields, but this is expected as a number of unrealistic approximations have been introduced into this 'real' system.

1.6 Discussion of results.

The importance of a stochastic treatment of nonhomogeneous kinetics in radiation chemistry has been emphasised. Standard

Fig.III.1.4 Optimised master equation simulation of the time evolution of the H/OH system.
Initial spatial distributions are iid Gaussians.
Arrows refer to experimental product yields.



deterministic models do not recognise stochastic effects and this fault can cause significant errors in the interpretation of experimental results. It is also necessary to stress that the stochastic results presented are not claimed to be correct. The kinetics are based upon a number of assumptions and the analysis contains a number of simplifications.

The spatial distribution of particles in a cluster is determined by the energy released in fragmentation and the subsequent energy loss processes. A Gaussian initial distribution is the basis of the prescribed diffusion approach to nonhomogeneous kinetics, and for stochastic modelling this approximation has the advantage of being easily applicable, but when applied to experimental systems this profile does not properly account for the real spatial correlations of the particles and for the dynamics of the fragmentation. The width of the Gaussian distribution is assumed proportional to $N^{1/3}$. While intuition suggests that 'volume' of a cluster will increase with the number of particles, neither this increase nor the cube root relationship can be demonstrated experimentally. It has even been proposed that the volume of a cluster is reduced as N increases (Magee & Chatterjee, 1980), because of electrostatic effects.

Like the spatial distribution of particles within a cluster, the initial distribution of cluster sizes is not experimentally available. The Mozumder and Magee distribution is discussed in detail in chapter III.3, but the calculation is very approximate. Even without any deficiencies in the original calculation, the distribution, as used, is truncated at six radical pairs (Schwarz, 1969). The small fraction of clusters containing a larger number of particles is neglected. It is precisely these clusters that give

product yields close to the deterministic values. This omission is important although the total number of radicals is small ($\leq 10\%$).

The stochastic IRT model and master equation do not make any provision for spin correlation and relaxation. Spin correlation effects have been discussed in detail by Brocklehurst (1985). The relaxation of the OH radical is very fast and any spin correlation effect is lost in its reaction, however, relaxation of the hydrogen atom is slower and cannot take place during encounter. Combination of two H atoms on a triplet surface can only take place by separation, relaxation and then re-encounter. Brocklehurst suggests that, nevertheless, spin effects in aqueous systems will be unimportant. The problem of the reaction distance for the $\text{H} + \text{H} \longrightarrow \text{H}_2$ combination still remains. The steady-state rate constant refers to random encounters on singlet and triplet surfaces and the value of R calculated is an effective reaction distance which is likely to be an underestimate for encounters on the singlet surface. No encounter on the triplet surface is successful.

The kinetics predicted by any model depend upon any uncertainties in the experimental parameters. In particular, diffusion coefficients of atoms and radicals are not known accurately. For example, Benderskii et al. (1980) recently reported a diffusion coefficient for the hydroxyl radical almost three times smaller than that used here. The effect is to slow the spreading of the OH distribution and to increase the yield of H_2O_2 . With the Benderskii diffusion coefficient, the optimised value of σ_0 for OH is 0.67 nm and that for H is virtually unchanged.

Under the experimental conditions considered, pH 0 - 2, the generation of hydrogen atoms from secondary electrons is not

necessarily instantaneous. There may be competition with reactions in the cluster. This problem is the subject of the following chapter.

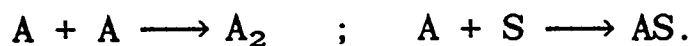
Chapter 2 : Reaction with a homogeneously distributed reactant.

Chapter III.1 considered the evolution of clusters of hydrogen atoms and hydroxyl radicals. Clusters of this type were used to model the kinetics that follow the high energy electron radiolysis of aqueous acid. This treatment makes the implicit assumption that thermalised electrons are scavenged immediately by the hydrated hydrogen ions of an acid and this 'instantaneous scavenging approximation' is introduced to simplify kinetic modelling. The studies of the previous chapter included a comparison of modelled and experimental yields. The experiments were performed in acid concentrations of 10^{-2} to 1 mol dm^{-3} . Under these conditions the half-life of an electron is of the order of 1 ns. This chapter considers the effect of a homogeneously distributed reactant upon the reactions occurring in a cluster of water fragments. Techniques are developed to model reaction with a scavenger and these methods are used to include, explicitly, the presence of an acid or of an alkali. This treatment allows analysis of the importance of the different reactions in a complex scheme and of the validity of the instantaneous scavenging approximation.

2.1 Modification of the simulation techniques.

The stochastic modelling of reaction with a scavenger is problematic. The inclusion of a homogeneously distributed species means that the system under examination is effectively indefinite in amount and extent. Reaction with a scavenger has been considered by Botár and Vidóczy (1979) and by Clifford et al. (1985) and was mentioned in passing in chapter II.1. Both groups discussed the kinetics of simple idealised clusters using random walk techniques. Clifford et al. also described the IRT simulation and the master

equation formulation of the problem for the reaction scheme



Any stochastic simulation method in which discrete scavenger particles are localised can only consider a system of finite size. When a scavenger is included in the reaction scheme, it is necessary to define the system in terms of a region which is small enough to allow efficient modelling, and yet sufficiently large that there is only a small probability of one of the radicals of interest 'escaping' before the cut-off time. The size of this 'region of interest' will depend upon the period of the simulation, $t_{\max}$, and upon the transport properties of the particles. In their single-species studies, Clifford et al. considered a spherical region defined by the radius

$$r_{\max} = 3.4 \sqrt{2D(t_{\max} + t_0)}. \quad (\text{III.2.1})$$

D is the diffusion coefficient of an A particle and $2Dt_0$ is the variance of the initial spatial distribution of the idealised cluster. This region is the sphere that would contain, with 99% probability, a single radical whose probability density function was a Gaussian with variance $2D(t_{\max} + t_0)$. A particle leaving this sphere was assumed to have escaped reaction within the cluster.

The concept of a region of interest is useful both in IRT simulation and in a Monte Carlo treatment of diffusion and reaction processes. In the former it restricts the actual number of particles in the system and in the latter it limits the effective number in the system. This study deals with multispecies clusters, i.e. $H^+/OH/e^-$, and it is necessary to clarify the prescription by taking D to be the maximum value encountered in the reaction scheme.

2.1.1 The IRT modelling of scavenger kinetics.

Having defined a system by the imposition of an outer boundary, the IRT simulation of reaction with a scavenger is straightforward. The kinetics are modelled in the same manner as when dealing with an isolated cluster:

- i) the positions of the reactive particles (i.e. cluster and scavenger) are generated
- ii) the interparticle separations are checked for overlap and zero time reaction
- iii) reaction times are generated for potentially reactive pairs
- iv) etc.

The cluster of hydrated electrons, hydrated hydrogen ions and hydroxyl radicals is located at the centre of the sphere and the scavenger particles are positioned from a uniform Hertzian distribution throughout the sphere. The number of scavenger particles in the sphere should have a Poisson distribution with mean

$$\langle n_s \rangle = \frac{4}{3} \pi c_s r_{\max}^3 \quad (\text{III.2.2})$$

For the purpose of simulation, the number of scavenger particles is assumed to be $n_s = \text{NINT}(\langle n_s \rangle)$ and $r_{\max}$ is re-evaluated accordingly. The total number of pairs is $\frac{1}{2}(n_c + n_s)(n_c + n_s - 1)$ where n_c is the number of cluster particles, however, it is not necessary to consider reaction between scavenger particles and the number of potentially reactive pairs is much smaller than suggested above,

$$n_{\text{pairs}} = \frac{1}{2} n_c (n_c - 1) + n_c n_s. \quad (\text{III.2.3})$$

Since reaction between scavenger particles is not considered, it is

necessary to 'site' any reactive product formed in the reaction of a cluster particle and a scavenger on the cluster particle. Usually, when two cluster particles react the reactive product is sited randomly, c.f. chapter II.2.

2.1.2 Random flights simulation.

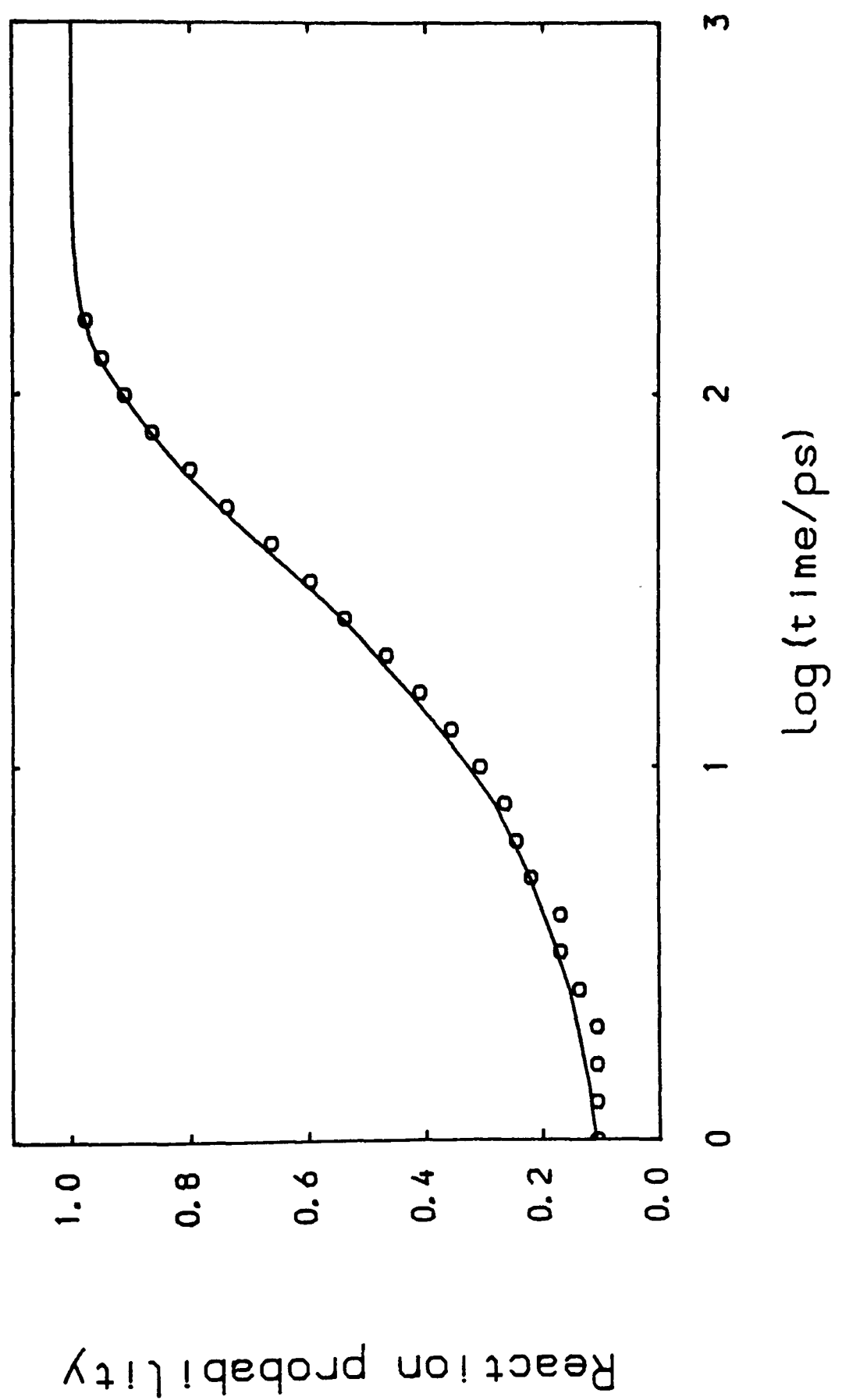
The diffusion and reaction of a homogeneously distributed species can be modelled using the same techniques that were applied to small clusters of particles in the previous discussions, but it is imperative to modify the methodology so as to limit the size of the system. The most obvious approach is the use of a periodic boundary for the scavenger particles, but the details of the application must be considered carefully. Depletion of the scavenger will occur in the vicinity of the cluster of reactive particles and this will not be the case elsewhere. The simplest application of a periodic boundary considers a cube centred on the cluster of interest. It allows scavengers passing through one face to return through the opposite face and is equivalent to surrounding the cube by twenty-six identical cubes (save for the absence of the cluster). If the spherical region of interest, defined by Clifford et al.⁽¹⁹⁸⁵⁾, is employed, then a scavenger passing through the surface of the sphere returns through a point diametrically opposite. The most straightforward solution to the problem of depletion is to continue modelling the trajectory of a scavenger after it has reacted. If the image of the scavenger reaches the periodic boundary it is replaced by a scavenger.

Fig.III.2.1 compares the random flights simulation and the IRT modelling of the reaction of a lone particle in a 1.0 mol dm⁻³ scavenger solution. The reaction distance is 0.25 nm and the two reactive species have the same diffusion coefficient

$$D_A = D_S = 5.0 \times 10^{-9} \text{ m}^2\text{s}^{-1}.$$

Fig.III.2.1 Simulation of reaction with a scavenger.
 $R = 0.25 \text{ nm}$; diffusion coefficients are $5.0 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$.

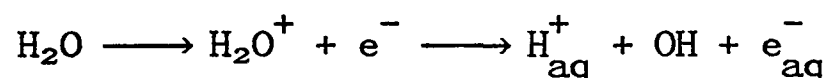
(o o o o) Random flights simulation.
 (—) IRT simulation.



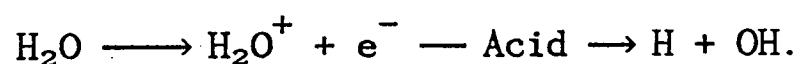
The random flights simulation is performed using the spherical prescription. The predictions of the approximate IRT model and of full random flights simulation agree almost exactly.

2.2 The instantaneous scavenging approximation.

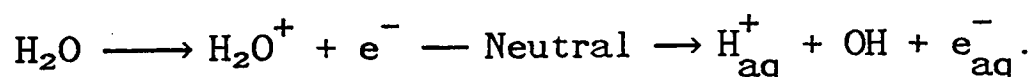
This chapter examines the effect of a homogeneously distributed scavenger upon the recombination within a cluster of reactive radicals and ions. The cluster chosen arises from the fragmentation



There are up to eight species involved in the resulting chemistry and these are listed, with their diffusion coefficients, in Table III.2.1. To study the instantaneous scavenging approximation, three model systems are considered. The first was introduced in the previous chapter and is a model for a cluster in aqueous acid. It is assumed that hydrated electrons react instantaneously with the hydrated hydrogen ions of an acid,



The second system represents neutral water and contains the fragmentation products,



This model does not use the instantaneous scavenging approximation, but is included for completeness. The final system describes a cluster in aqueous alkali. The hydroxide ions of the alkali are assumed to scavenge the hydrated hydrogen ions of a cluster instantaneously,



The reaction schemes of the three model systems are compared in Table III.2.2.

The extension of kinetic modelling to $\text{H}^+/\text{OH}/\text{e}^-$ clusters requires the use of the new techniques developed in section II. It

Table III.2.1 Cluster species and their diffusion coefficients.
(Trumbore, 1967; Schwarz, 1969; Am.Inst.Physics Handbook, 1967)

Species	D / 10 ⁻⁹ m ² s ⁻¹
e ⁻	4.5
H	7.0
H ⁺	9.0
OH	2.8
OH ⁻	5.0
H ₂	5.0
H ₂ O	2.8
H ₂ O ₂	1.4

Table III.2.2 The reaction scheme for the H⁺_{aq}/OH/e⁻_{aq} system.
(Burns & Marsh, 1981)

Reaction	k/10 ¹⁰ mol ⁻¹ dm ³ s ⁻¹	R / nm	v / ms ⁻¹	Systems a b c
e ⁻ + e ⁻ → H ₂ +2OH ⁻	0.5	0.34	4.19	✓ ✓
e ⁺ + H ⁺ → H	2.4	0.50		✓
e ⁻ + H → H ₂ + OH ⁻	2.5	0.29		✓
e ⁻ + OH → OH ⁻	3.0	0.54		✓ ✓
e ⁻ +H ₂ O ₂ → OH ⁻ + OH	1.2	0.29		✓ ✓
H + H → H ₂	1.0	0.19		✓ ✓
H + OH → H ₂ O	2.0	0.27		✓ ✓
H ⁺ + OH ⁻ → H ₂ O	14.3	1.23		✓
OH+ OH → H ₂ O ₂	0.45	0.21		✓ ✓ ✓

a, cluster in acid; b, cluster in water; c, cluster in alkali.

Table III.2.3 Estimated half-lives.

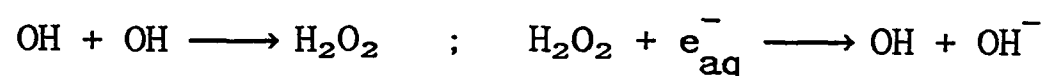
Scavenger concentration / mol dm ⁻³	Half-life / s	
	e ⁻ _{aq} in acid	H ⁺ _{aq} in alkali
0.01	2.9 x 10 ⁻⁹	4.9 x 10 ⁻¹⁰
0.1	2.9 x 10 ⁻¹⁰	4.9 x 10 ⁻¹¹
1.0	2.9 x 10 ⁻¹¹	4.9 x 10 ⁻¹²

$$k(e^-_{aq} + H^+_{aq}) = 2.4 \times 10^{10} \text{ mol}^{-1}\text{dm}^3\text{s}^{-1}$$

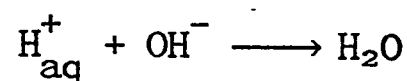
$$k(H^+_{aq} + OH^-) = 1.43 \times 10^{11} \text{ mol}^{-1}\text{dm}^3\text{s}^{-1}$$

is necessary to consider

i) reactive products, e.g.



ii) reactions of ions, e.g.



iii) partially diffusion-controlled reactions, e.g.

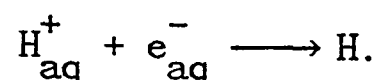


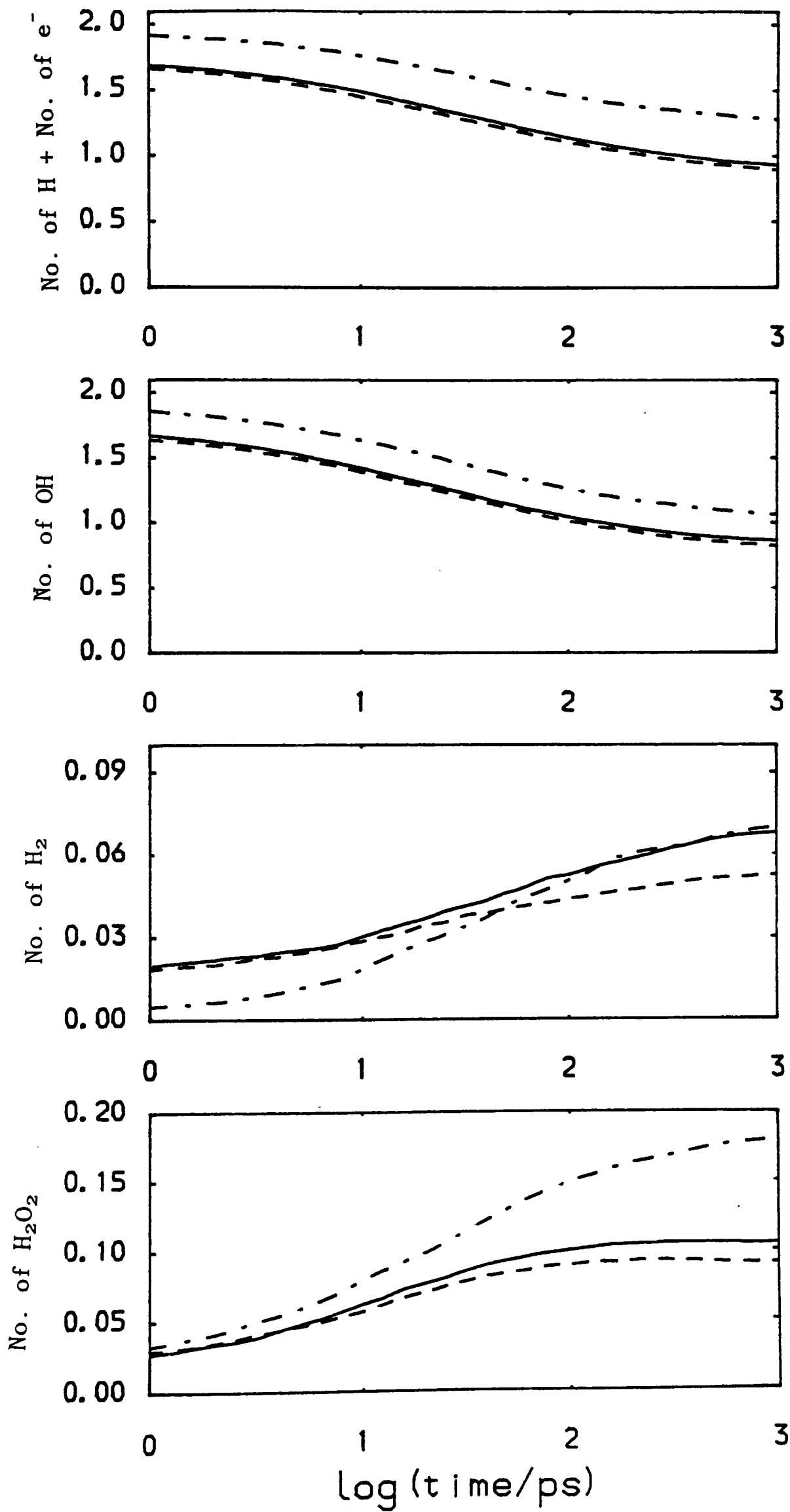
Fig.III.2.2 shows the IRT simulated kinetics of a two dissociation cluster under acidic, neutral and alkaline conditions. The initial positions of the reactive particles are generated from independent and identically distributed Gaussians. The reducing species, H and e_{aq}^- , originate from Gaussians of standard deviation 0.75 nm and their siblings, H_{aq}^+ and OH, are positioned from distributions of width 0.40 nm. The aim of the simulation is to produce results that can be compared with more realistic simulation to test the instantaneous scavenging approximation. The simulations shown in Fig.III.2.2 are the results of 10^4 realisations. They suggest a reduction in the final yield of the molecular products H_2 and H_2O_2 as the pH is increased, but there is an increase in the amount of recombination to H_2O (not shown). This change is a consequence of the change in the 'route' to the various products as the initial constituents of the cluster are altered. The three reactions, of the scheme listed in Table III.2.2, that produce molecular hydrogen are



Under the instantaneous scavenging approximation, only one route is possible; reaction (a) in aqueous alkali and reaction (c) in aqueous acid. In the neutral system, H_2 is produced by all three

Fig.III.2.2 The kinetics of a two dissociation cluster under the instantaneous scavenging approximation.

(- · - ·) Aqueous acid
(————) Neutral water
(- - - -) Aqueous alkali.

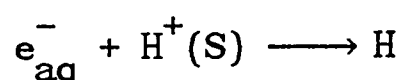


reactions, but only routes (a) and (b) are significant. Fig.III.2.3 shows the importance of reactions (a), (b) and (c) in the three model systems.

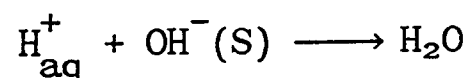
The hydrogen atom/ hydroxyl radical and the hydrated electron/ hydroxyl radical pictures of a cluster in aqueous acid and in aqueous alkali are major simplifications and are introduced to make kinetic modelling straightforward. However, the validity of the instantaneous scavenging approximation, upon which the model systems are based, is questionable. Consider the 'half life' defined by

$$\tau_{1/2} = \ln(2) / k_s c_s \quad (\text{III.2.4})$$

where k_s and c_s are the steady-state rate constant for the reaction of a reactant A with a scavenger S and the concentration of the scavenger respectively. The values of $\tau_{1/2}$ for a hydrated electron and a hydrated hydrogen ion are listed in Table III.2.3 for a variety of scavenger concentrations. These results suggest that the reaction



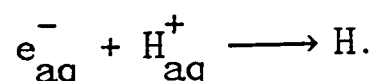
is not instantaneous, although the reaction



may well be. The label (S) signifies a scavenger particle. A detailed study explicitly modelling the reactions of the homogeneous species is therefore necessary.

2.3 Kinetics of a realistic system.

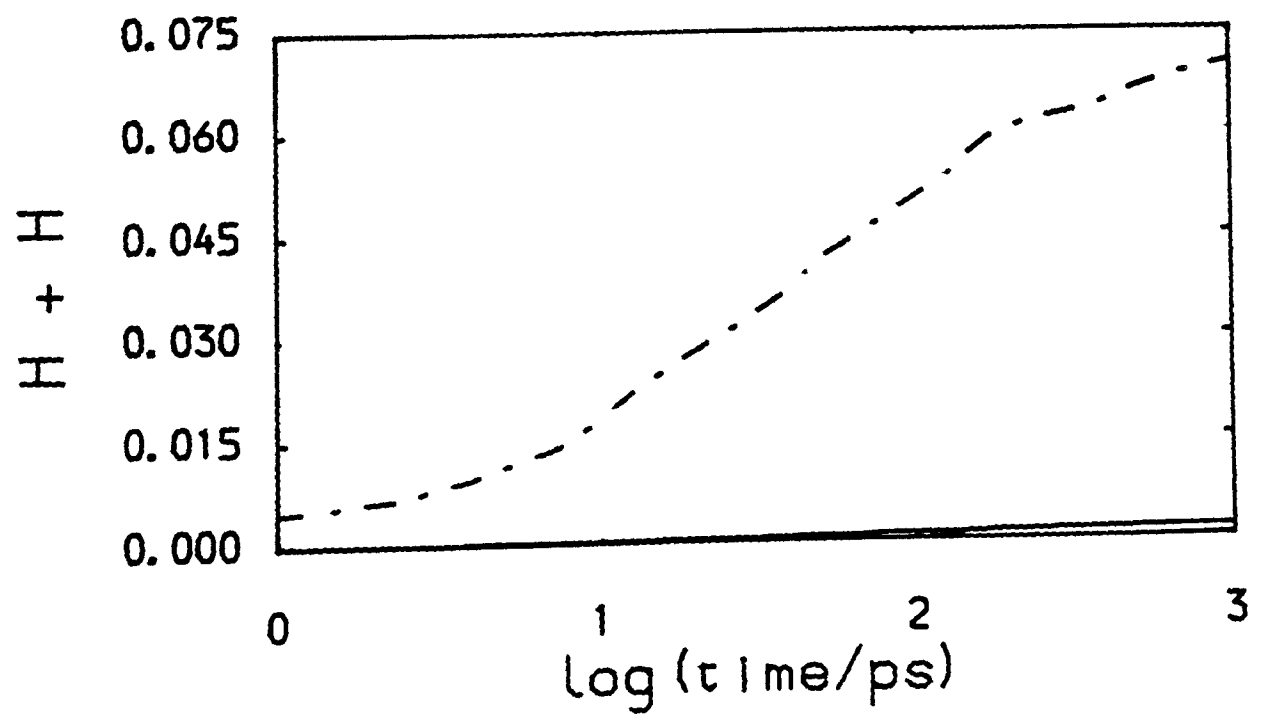
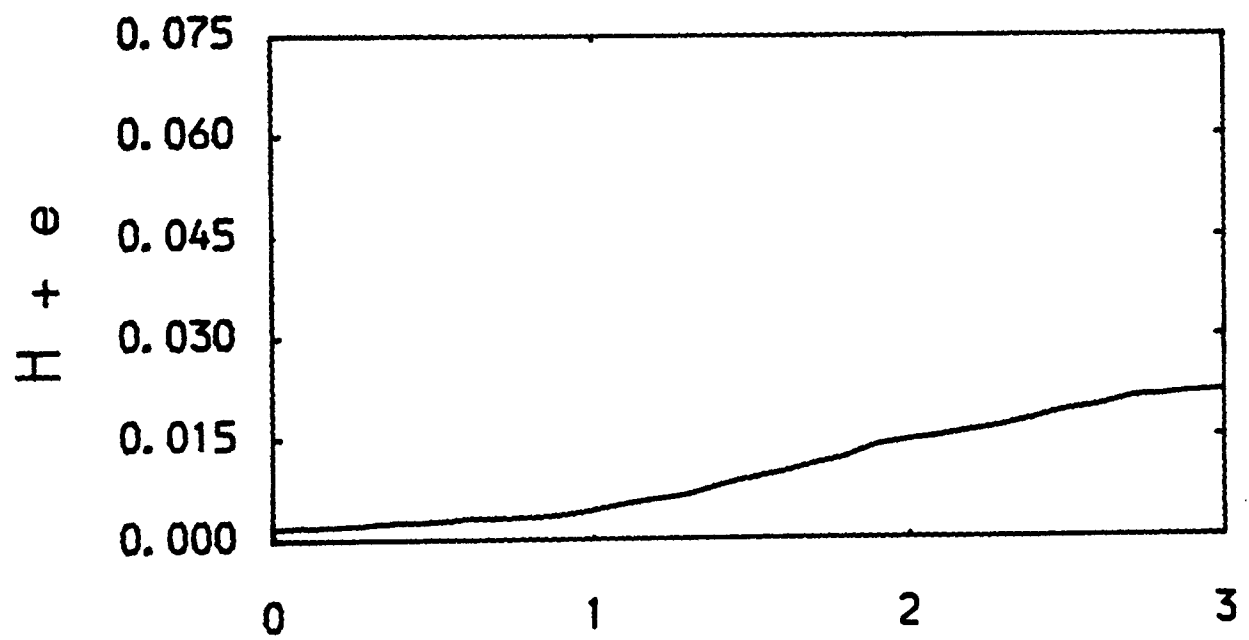
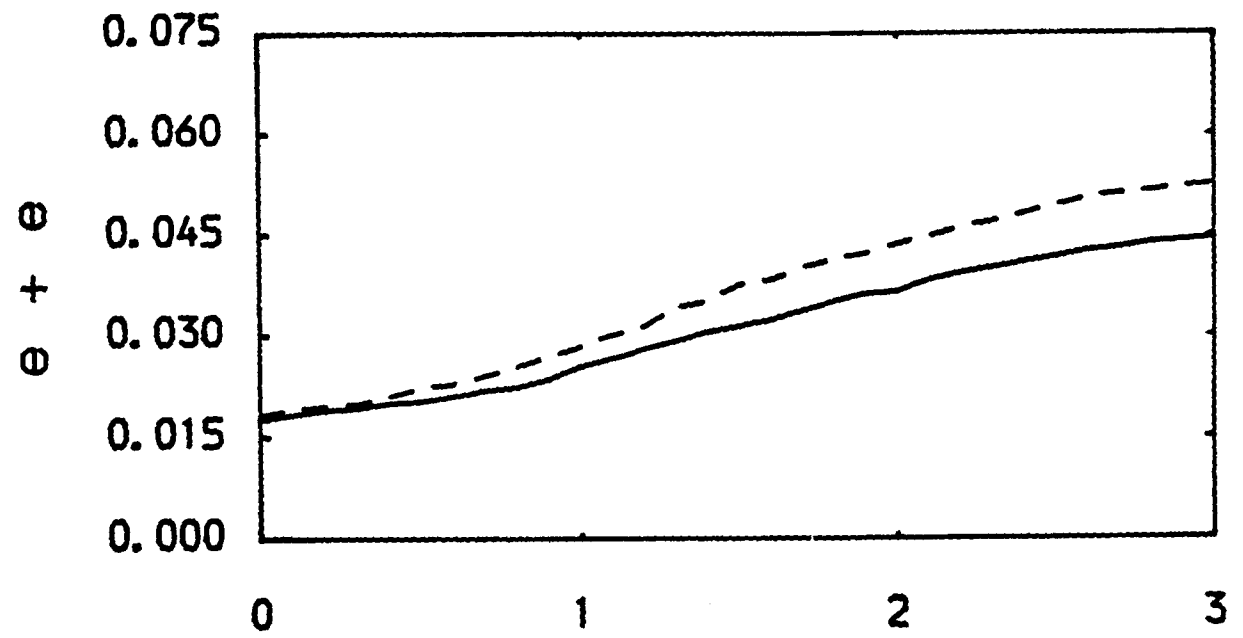
Modelling the effects of pH upon recombination of a cluster of water fragments is complicated by the reaction



This reaction is not diffusion-controlled and the product, H, is

Fig.III.2.3 Reactions producing molecular hydrogen.

(- · - ·) Aqueous acid.
 (—) Neutral water.
 (- - -) Aqueous alkali.



reactive. The cost, in computer resources, of a full random flights treatment of this problem is too high to be acceptable and the following simulations refer solely to an IRT treatment.

2.3.1 The scavenging of a lone electron.

Fig.III.2.4 shows the kinetics of a lone electron in 1.0 mol dm^{-3} acid. The IRT simulation of partially diffusion-controlled reactions was discussed in chapter II.5 and two alternative reaction time distributions were presented: an error function, equation (II.5.15), and an incomplete Gamma function, equation (II.5.20). The predictions of both models are shown in the figure along with the kinetics suggested by an approximate analytic treatment.

The reaction of a single reactive particle in an infinite homogeneous scavenger can be modelled analytically as it is possible to evaluate both the probability that the particle and one of the scavenger ions initially overlap and the time dependence of the reaction of a surviving electron. Reaction at time $t = 0$ occurs if the reactive particle is within a distance R of a scavenger. The presence of a scavenger within a sphere of radius R is a Poisson process and the probability that there is no scavenger in this sphere depends upon the volume of the sphere and the concentration of the scavenger, c_s . The initial survival probability of the particle, $\Omega(0)$, is

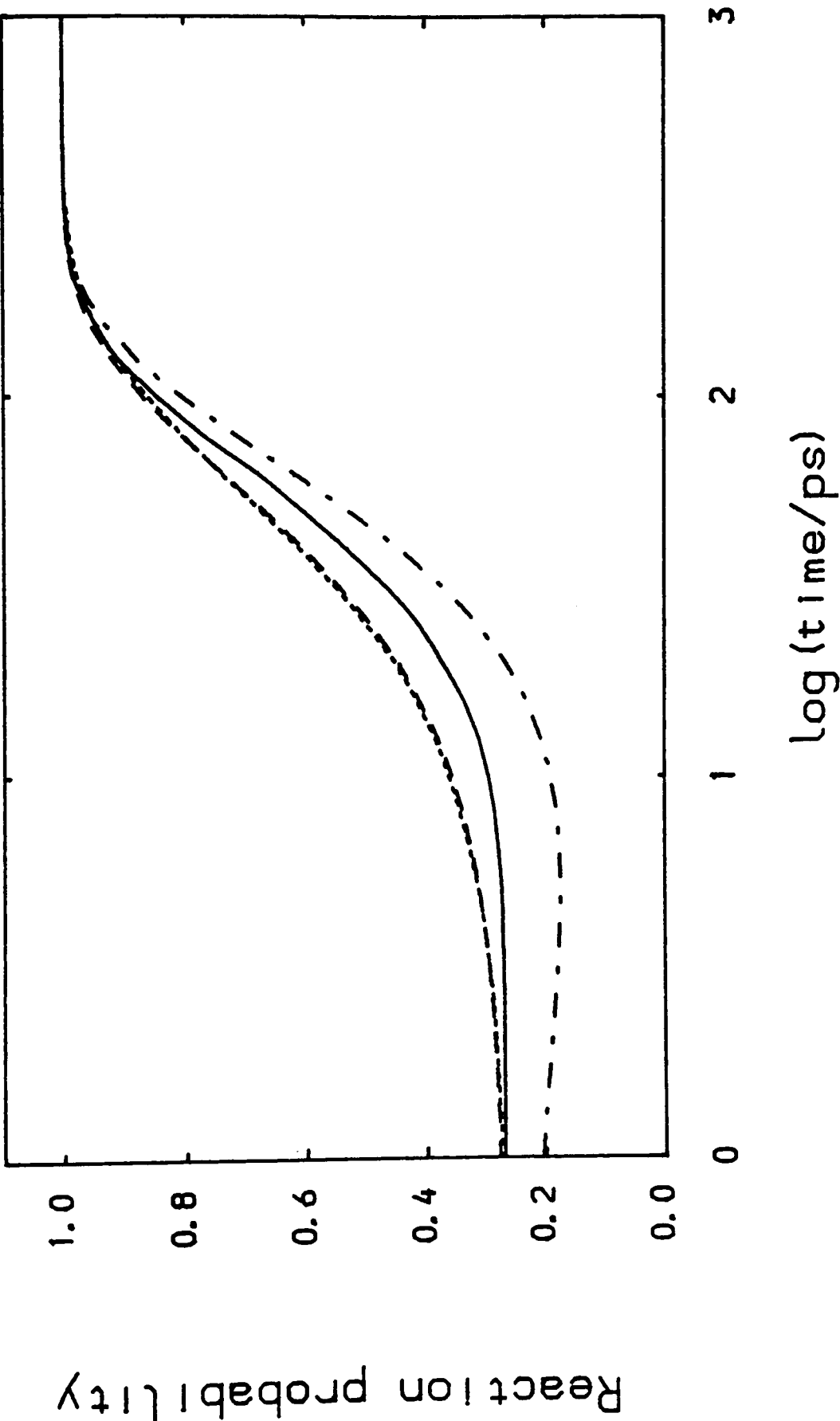
$$\Omega(0) = \exp \left[- \frac{4\pi}{3} R^3 c_s \right]. \quad (\text{III.2.5})$$

The time-dependent survival probability of a particle is governed by the rate equation

$$\frac{d}{dt} \Omega(t) = - k(t) c_s \Omega(t) \quad (\text{III.2.6})$$

Fig.III.2.4. Scavenging of a lone electron.
 Concentration of hydrogen ions = 1.0 mol dm⁻³.

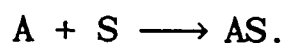
IRT simulation :
 (————) Error function approximation for H⁺ + e⁻ reaction.
 (• • • •) Gamma function approximation for H⁺ + e⁻ reaction.
 Analytic approximation :
 (- • - •) Equation III.2.10.
 (- - - -) Equation III.2.12.



whose solution is

$$\Omega(t) = \Omega(0) \exp \left[- c_s \int_0^t k(u) du \right], \quad (\text{III.2.7})$$

where $k(t)$ is the time-dependent second order rate coefficient for the reaction



Substituting for $\Omega(0)$ in equation (III.2.7) gives the analytic solution for the survival probability,

$$\Omega(t) = \exp \left[- c_s \left[\frac{4\pi}{3} R^3 + \int_0^t k(u) du \right] \right]. \quad (\text{III.2.8})$$

This result is perfectly general within the independent pairs approximation.

The reaction of a hydrated electron and a hydrated hydrogen ion is partially diffusion-controlled and the time-dependent rate coefficient of the reaction is given by (c.f. appendix F)

$$k(t) = 4\pi \int_R^\infty r^2 \left. \frac{\partial W}{\partial t} \right|_R dr. \quad (\text{III.2.9})$$

W is the reaction probability of a pair at separation r . Rice et al. (1979) derived an approximate rate coefficient for a partially diffusion-controlled reaction between ions,

$$k(t) = 4\pi D' R_{\text{eff}} \left[1 + \frac{R_{\text{eff}} + r_c}{\sqrt{\pi D' t}} \right] \quad (\text{III.2.10})$$

where R_{eff} is the effective reaction distance defined in chapter II.5,

$$R_{\text{eff}} = \frac{-r_c}{1 - \exp\left[\frac{r_c}{R}\right] \left[1 + \frac{D'r_c}{vR^2}\right]} \quad (\text{III.2.11})$$

Butler(1978) compared this equation with numerical solution of equation (III.2.9) and showed that the approximation is inaccurate at short times where it can even predict negative rate coefficients. The behaviour is especially poor when v is small. Green (1984) suggested an alternative approximation, based upon the approximate W discussed in chapter II.5,

$$k(t) = 4\pi D'R_{\text{eff}} \left[1 + \left[\frac{vR^2}{D'R_{\text{eff}}} - 1 \right] \exp(\beta^2 t) \operatorname{erfc}(\beta\sqrt{t}) \right] \quad (\text{III.2.12})$$

where R_{eff} is given by equation (III.2.11) and

$$\beta = \frac{vR^2(1 - \exp(-r_c/R))}{r_c R_{\text{eff}} \sqrt{D'}}. \quad (\text{III.2.13})$$

In the long time limit, equation (III.2.12) reduces to equation (III.2.10). Equation (III.2.12) shows excellent agreement with numerical solution.

Both approximations for $k(t)$ can be integrated over the range $t = 0$ to $t = t$ and substitution into equation (III.2.8) gives two analytic approximations for $\Omega(t)$. For the approximation of Rice et al.,

$$\Omega(t) = \exp \left[-\frac{4\pi}{3} R^3 c_s - 4\pi D'R_{\text{eff}} c_s \left[t + 2\sqrt{t} \frac{R_{\text{eff}} + r_c}{\sqrt{\pi D'}} \right] \right] \quad (\text{III.2.14})$$

and for Green's solution

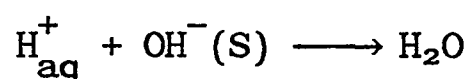
$$\Omega(t) = \exp \left[- \frac{4\pi}{3} R^3 c_s - 4\pi D' R_{\text{eff}} c_s \left[t + \frac{1}{\beta^2} \left(\frac{vR^2}{D' R_{\text{eff}}} - 1 \right) \left[\exp(\beta^2 t) \operatorname{erfc}(\beta \sqrt{t}) - 1 + 2\beta \sqrt{\frac{t}{\pi}} \right] \right] \right].$$

(III.2.15)

When applied to the reaction of a single hydrated electron with homogeneously distributed hydrated hydrogen ions, the two analytic approximations for $\Omega(t)$ suggest very different kinetics. Equation (III.2.14) has a maximum. This is physically unrealistic and is a consequence of equation (III.2.10) predicting negative values at short times. Fig.III.2.4 compares the approximations for the kinetics of a hydrated electron in 1.0 mol dm^{-3} acid with the predictions of IRT simulation. The two IRT simulation techniques suggest different kinetics. When the reaction time distribution function for an $\text{H}^+ + \text{e}^-$ pair is approximated by a family of incomplete Gamma functions, the simulation agrees almost exactly with the analytic approximation derived using equation (III.2.12). Using an error function description for the time dependence of the $\text{H}^+ + \text{e}^-$ pair leads to an underestimate of the initial rate of reaction. This underestimate is a consequence of the inadequacy of the error function approximation when the reacting pair are initially close together. The accuracy of the error function treatment improves as the concentration of scavenger is reduced and the mean H^+/e^- separation increases.

2.3.2 The recombination of water fragments in aqueous alkali.

The simulation of a cluster of water fragments (H_{aq}^+ , OH , e_{aq}^-) in aqueous alkali is primarily concerned with the influence of the scavenger reaction



upon the overall kinetics. The product of the reaction does not take any further part in the chemistry of the system and this simplifies the modelling. Fig.III.2.5 shows the simulated kinetics of a two dissociation cluster for hydroxide concentrations of 0.01, 0.1 and 1.0 mole dm^{-3} . The predictions of the instantaneous scavenging approximation discussed in §2.2 are also included. The ultimate yields predicted depend upon the concentration of OH^- , but the short-time kinetics appear to be unaffected. As the concentration of hydroxide is increased the predictions of the explicit simulations approach those of the model system, suggesting that it is an accurate representation of the limiting case.

2.3.3 The recombination of a cluster in aqueous acid.

When modelling the kinetics of the $\text{H}_{\text{aq}}^+/\text{OH}/\text{e}_{\text{aq}}^-$ system in aqueous acid, the product of the scavenger reaction is reactive. The effect of varying the acid concentration is shown in Fig.III.2.6. The yields and the kinetics are not strongly influenced by the presence of the acid and the predictions of explicit simulation differ markedly from those of the model H/OH system introduced in chapter III.1. This difference can be clarified by investigating the origins of the molecular hydrogen yield. Under the instantaneous scavenger approximation all the hydrogen originates from the reaction $\text{H} + \text{H}$. Fig.III.2.7 shows that if the scavenger reaction is considered explicitly other routes to H_2 are significant. This figure demonstrates the timescales of the different reactions.

Fig.III.2.5. A two dissociation cluster in alkali.

(—) Instantaneous scavenging approximation.
 (---) 1.0 mol dm⁻³ alkali.
 (-·-·-·-) 0.1 mol dm⁻³ alkali.
 (· · · ·) 0.01 mol dm⁻³ alkali.

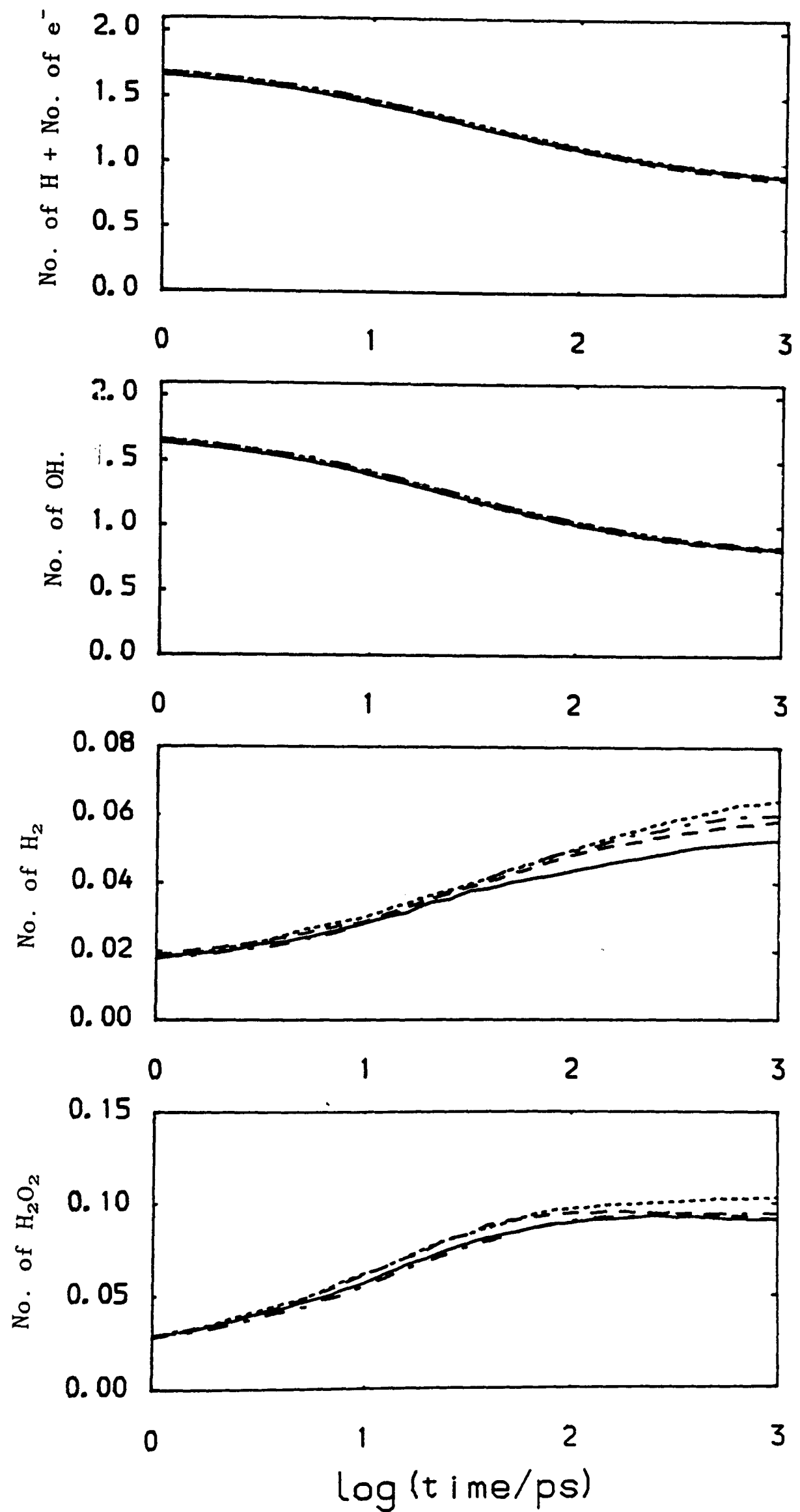


Fig.III.2.6 A two dissociation cluster in acid.

(—) Instantaneous scavenging approximation.
 (---) 1.0 mol dm⁻³ acid.
 (-·-·-) 0.1 mol dm⁻³ acid.
 (· · · ·) 0.01 mol dm⁻³ acid.

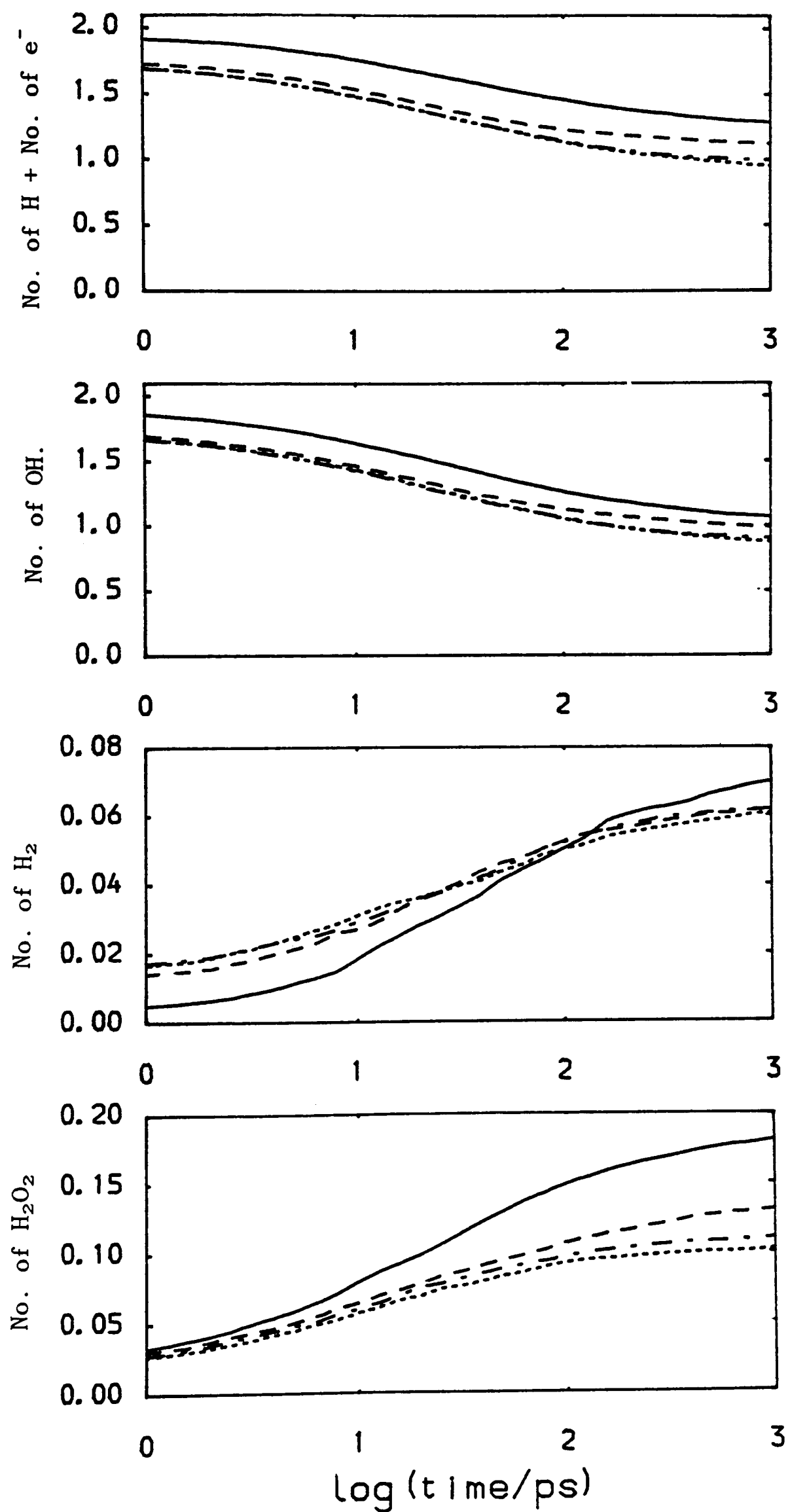
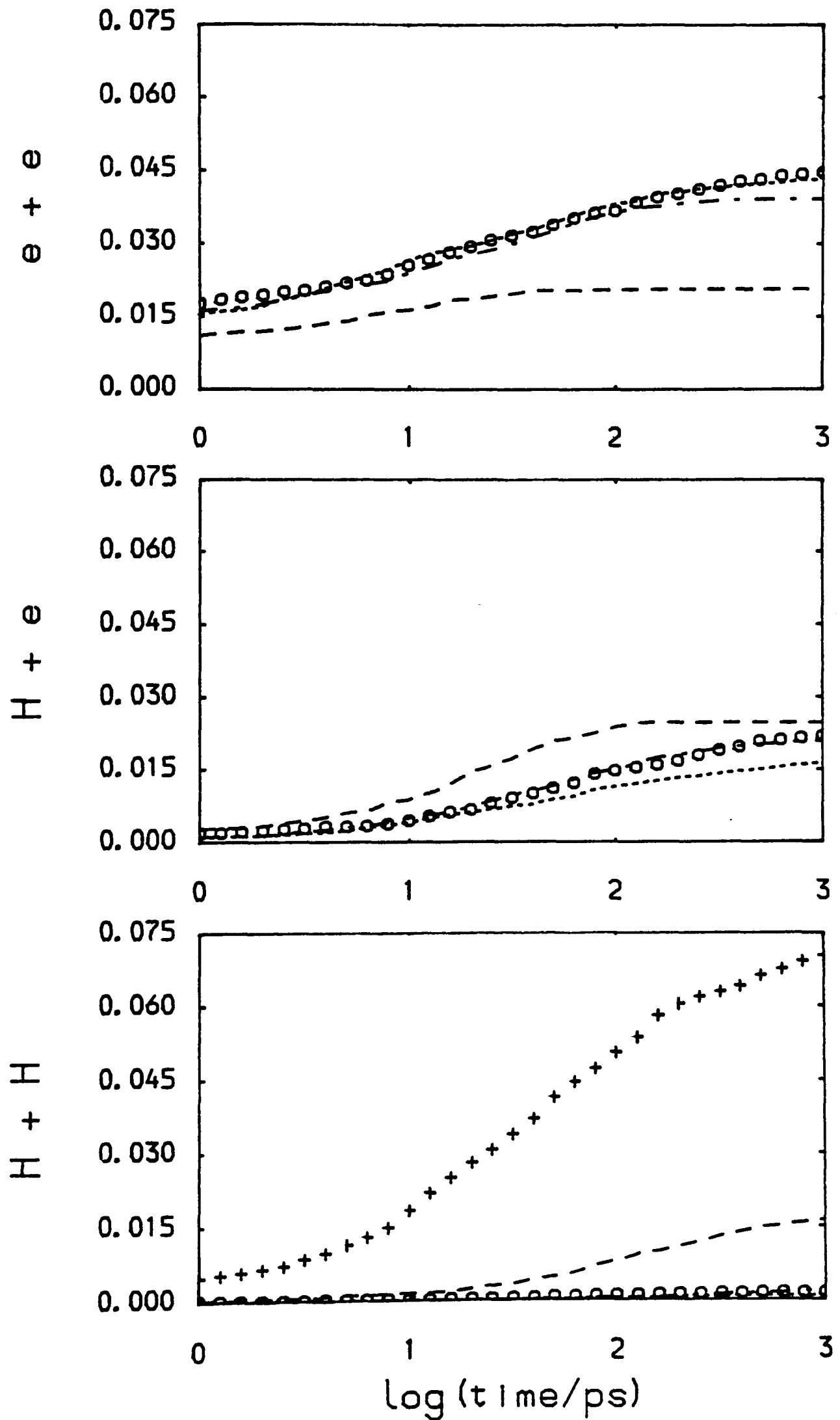


Fig.III.2.7 The production of H_2 under acidic conditions.

(+ + +) Instantaneous scavenging approximation.
 (- - -) 1.0 mol dm^{-3} acid.
 (- . - . -) 0.1 mol dm^{-3} acid.
 (. . . .) 0.01 mol dm^{-3} acid.
 (o o o) Neutral water.



2.4 Scavenger reaction as a decay.

The IRT modelling of nonhomogeneous kinetics considers, explicitly, the reaction of each particle in the system. When the concentration of scavenger is high, the number of reactive particles in the system is large, therefore, even with an efficient technique, like the IRT model, the computational cost of modelling is high. A less expensive method of simulating the reaction of a particle with a homogeneous reactant is desirable. One alternative is to treat reaction with the scavenger as a decay governed by the rate equation (III.2.6). As with explicit simulation, it is necessary to consider:

i) the modelling of reaction at time $t = 0$.

Zero time scavenging in a cluster of particles can be approximated by treating the particles as if they are in isolation. The probability of reaction between an isolated particle and a scavenger at time $t = 0$ is the complement of equation (III.2.5).

ii) the generation of reaction times.

If the reaction of a particle with a scavenger is treated as a decay, the scavenging time is obtained by inverting the solution of the integral equation (III.2.7) with $\Omega(0) = 1$ as the particle must exist at time $t = 0$ if a reaction time is required. The inversion of equation (III.2.7) depends on the form of the integral $\int_0^t k(t) dt$. If $k(t)$ has a simple dependence on t , the generation of a reaction time is straightforward, however, if $k(t)$ is complicated the probability distribution function derived from equation (III.2.7) has to be inverted numerically.

The reaction time distribution derived from equation (III.2.7)

and the approximate rate coefficient of Rice et al. (1979) is

$$\Omega(t) = \exp \left[- 4\pi D' R_{\text{eff}} c_s \left[t + 2 \sqrt{t} \frac{R_{\text{eff}} + r_c}{\sqrt{\pi D'}} \right] \right]. \quad (\text{III.2.16})$$

This can be inverted using the techniques outlined in appendix A. As the function is not monotonic, the inversion will only generate times in the $\Omega < 1$ limb of the function and so, apart from zero time reaction, no reaction can occur until $\Omega \leq 1$. Fig.III.2.8 shows the kinetics predicted by this method for a single hydrated electron in 1.0 mol dm⁻³ acid. The figure also includes the analytic solutions described earlier in the chapter. The unrealistic minimum of Fig.III.2.4 is not apparent in the IRT simulation, but the kinetics obtained by treating the $\text{H}^+ + \text{e}^-$ reaction as a decay do reproduce the corresponding analytic approximation after about 10 ps. With an accurate time-dependent rate coefficient, this type of simulation does reproduce the prediction of explicit simulation. Fig.III.2.9 shows the kinetics of a lone hydrated hydrogen ion in aqueous 0.1 mol dm⁻³ alkali. This clearly demonstrates that the problems of the previous figure lie in the time-dependent rate coefficient. Fig.III.2.10 describes the evolution of a two dissociation cluster in aqueous alkali. IRT simulation treating the scavenging of the hydrated hydrogen ions as a decay agrees almost exactly with explicit IRT simulation. When the kinetics of a cluster in acid are considered there is a small difference between the predictions of the explicit and decay methods of modelling the $\text{e}_{\text{aq}}^- + \text{H}_{\text{aq}}^+$ scavenging reaction. This difference is demonstrated in Fig.III.2.11. The decay time approach to the IRT simulation of scavenger reaction times is an accurate method of modelling the kinetics of an isolated particle, but when

Fig.III.2.8 Scavenging of a hydrated electron.
Concentration of hydrogen ions = 1.0 mol dm^{-3} .

- (—) Full IRT simulation.
 (· · · ·) IRT simulation treating scavenging as a decay.
 (- · - ·) Analytic approximation, equation III.2.10.
 (- - - -) Analytic approximation, equation III.2.12.

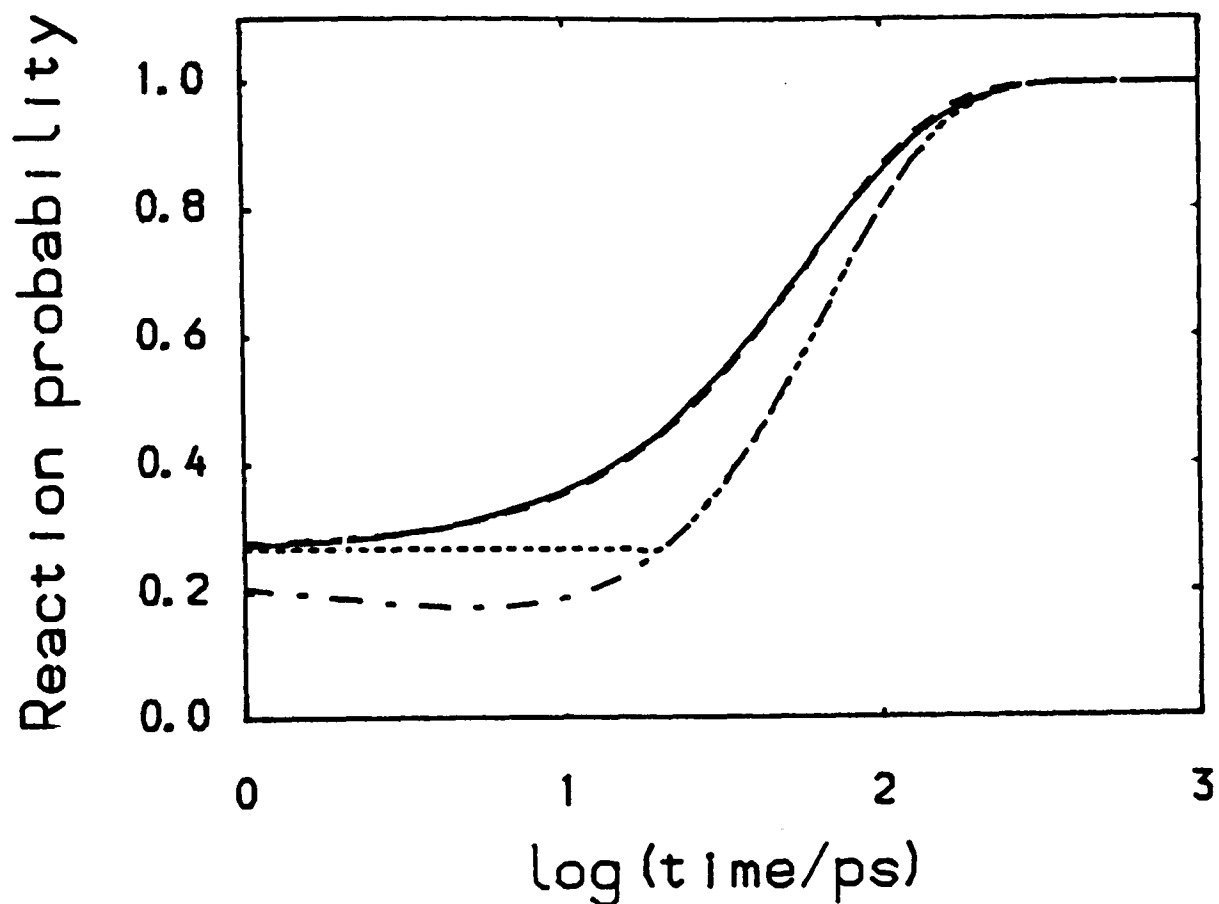


Fig.III.2.9 Scavenging of a hydrated proton.
Concentration of hydroxide ions = 0.1 mol dm^{-3} .

- (—) Full IRT simulation.
 (· · · ·) IRT simulation treating scavenging as a decay.
 (- - - -) Analytic approximation.

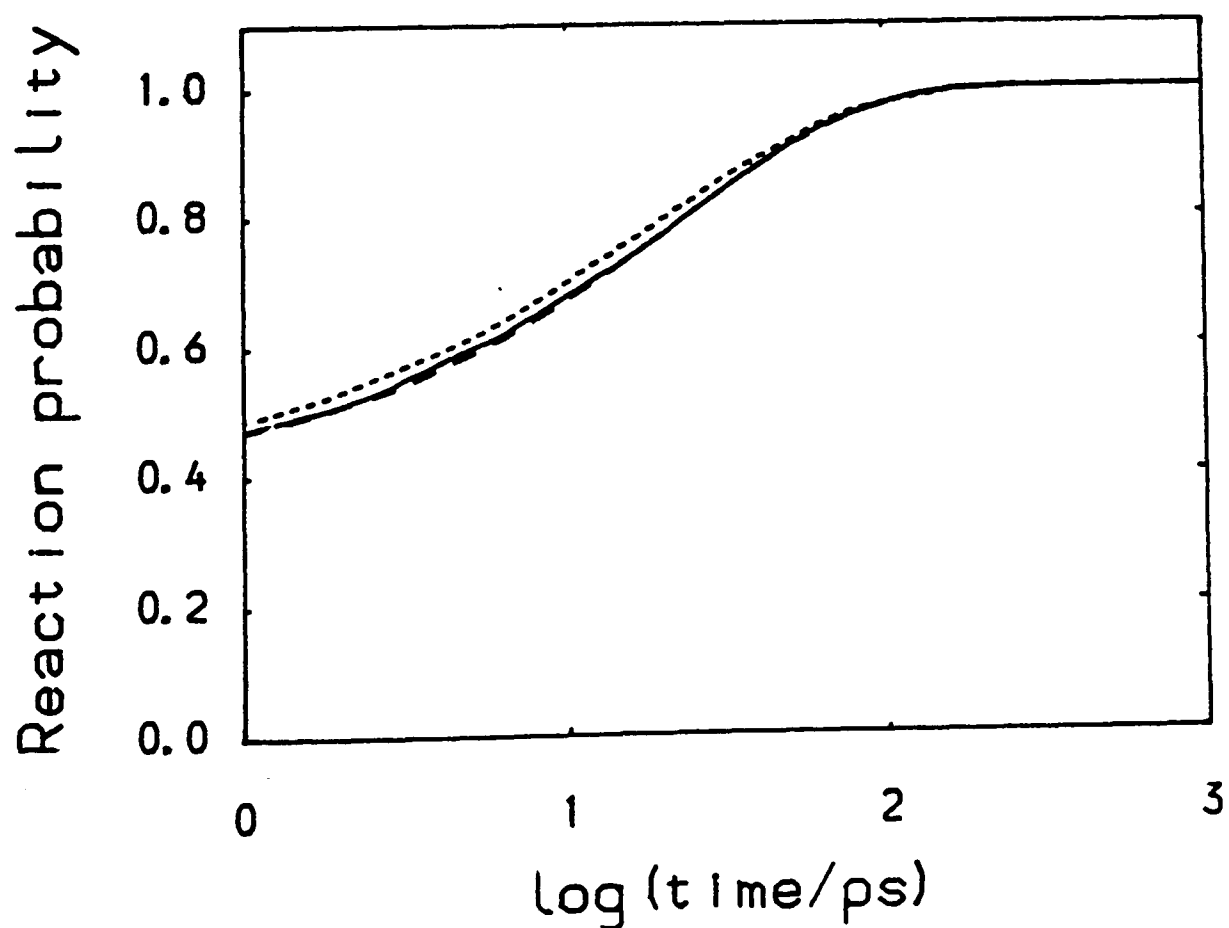


Fig.III.2.10 A two dissociation cluster in alkali.
Concentration of hydroxide ions = 0.1 mol dm^{-3} .

(—) Full IRT simulation.
(· · · ·) IRT simulation treating scavenging as a decay.

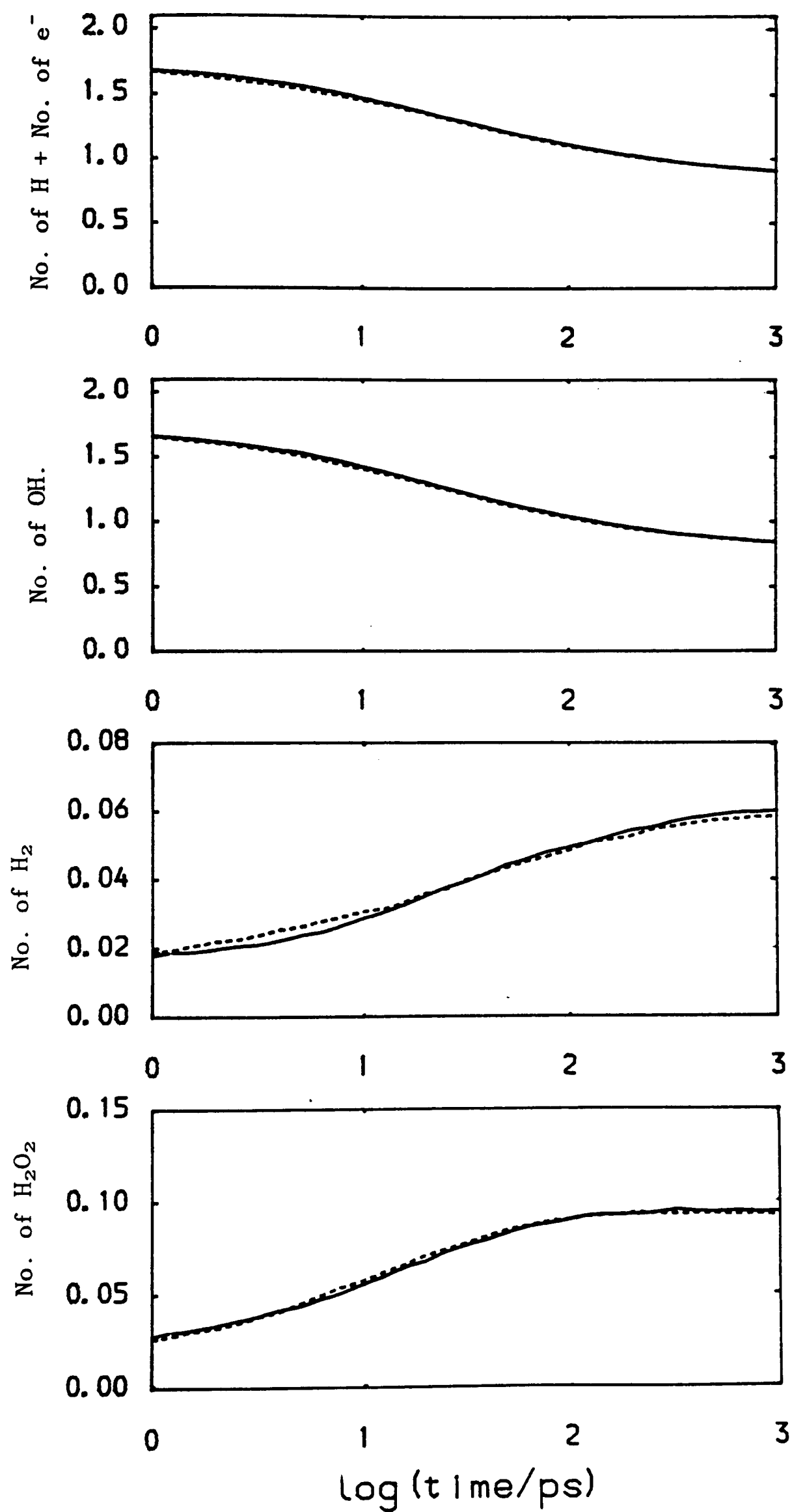
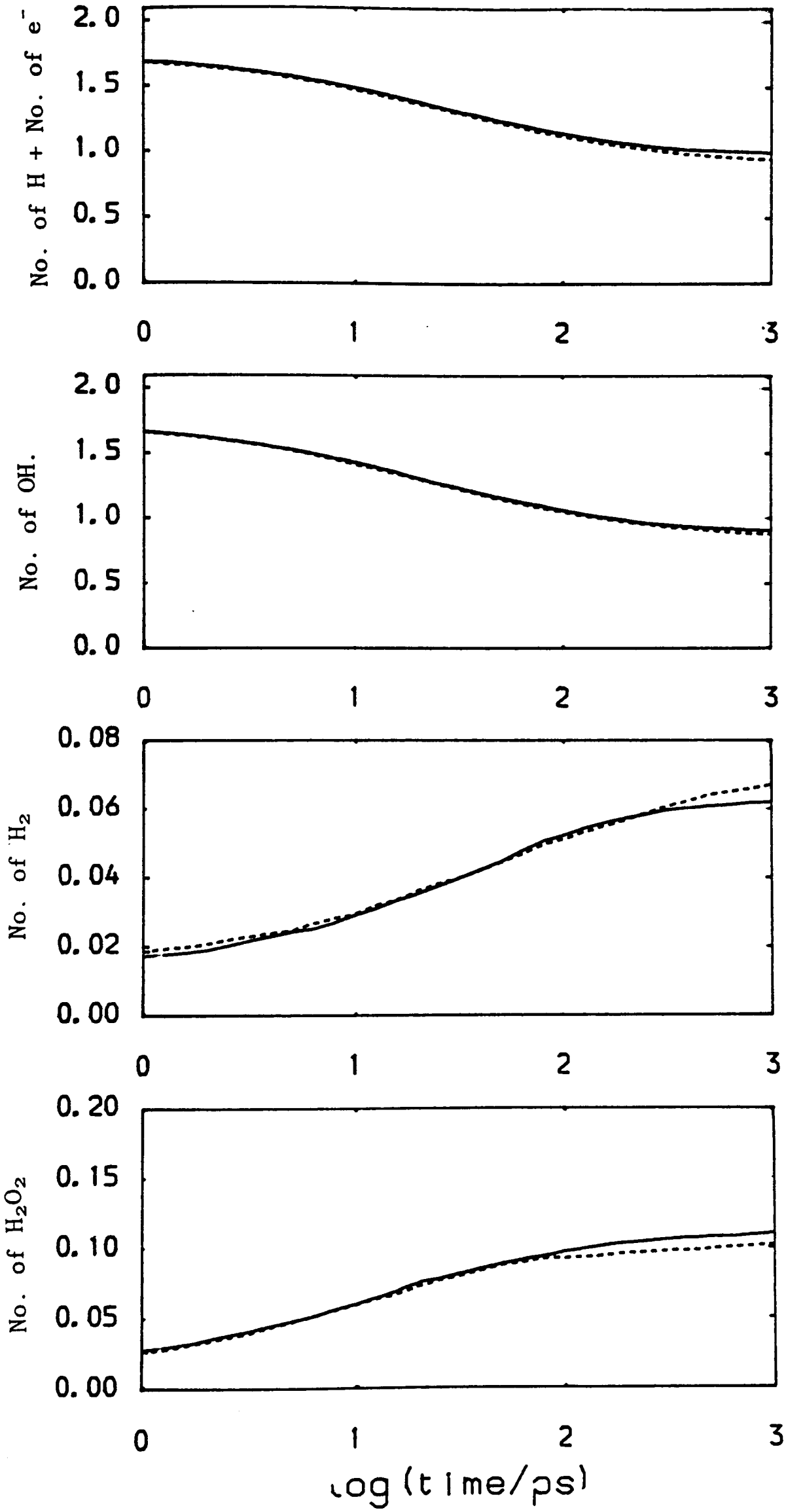


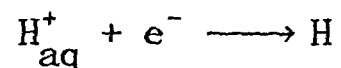
Fig.III.2.11 A two dissociation cluster in acid.
Concentration of hydrated protons = 0.1 mol dm⁻³.

(——) Full IRT simulation.
(· · · ·) IRT simulation treating scavenging as a decay.



the scavenger concentration is small, ~~but~~ the application to cluster kinetics is questionable. Under these conditions the scavenger is depleted in the region of the cluster.

The instantaneous scavenging approximation was introduced in the previous chapter to facilitate the kinetic modelling of realistic radiation chemistry systems. The scavenging of a hydrated hydrogen ion by alkali is rapid and immediate reaction can be considered as a limiting case. The assumption that a thermalised electron reacts instantaneously with the hydrated hydrogen ions of an acid is not acceptable. The reaction



is not fully diffusion-controlled and the reactions of the hydrated electron play a significant role in the development of the chemical system produced by the radiolysis of an aqueous acid.

Chapter 3 : A simple model of an electron track.

The first chapter of this section considered the kinetics of a distribution of clusters containing hydrogen atoms and hydroxyl radicals and the aim was to model the chemistry of a high energy electron track. The distribution of cluster sizes was calculated by Mozumder and Magee (1966b) using a Monte Carlo simulation technique. This chapter describes the original study and discusses some of the approximations made. An improved simulation technique is presented which incorporates a more acceptable description of the energy loss processes. Dipole oscillator strength distributions (DOSDs) with an experimental basis are included in the new approach. Calculations are performed to examine the effect of phase on the distribution of energy loss events. The conversion of an energy deposition distribution into a cluster size distribution is considered. The analyses of chapter III.1 are repeated with the new cluster distribution and the influence of the improved distribution upon the kinetics of the hydrogen atom - hydroxyl radical system is studied.

3.1 Monte Carlo modelling of a radiation track.

At about 10 ps, the track of a high energy electron can be described as a random string of isolated clusters of highly reactive particles and the distribution of cluster sizes is important in modelling the kinetics of the particles. Mozumder and Magee calculated the distribution from "an elementary point of view" using a very simple Monte Carlo model that dealt with only inelastic scattering events. This approach is based upon the differential cross-section describing the inelastic interaction cross-section as a function of energy loss, $\frac{d\sigma}{d\epsilon}$. The actual

calculations require the cumulative cross-section, $\sigma(\epsilon, E)$

$$\sigma(\epsilon, E) = \int_{\epsilon} \left. \frac{d\sigma}{d\epsilon} \right|_E d\epsilon. \quad (\text{III.3.1})$$

This cross-section depends upon upon the the energy of the primary electron, E , and is used to evaluate both the position and the amount of energy lost in an interaction.

The technique of Mozumder and Magee (1966c) simulates the separation between energy deposition events and the energy lost in each interaction. The distance travelled between energy loss events is exponentially distributed with a mean

$$\bar{\ell} = 1/n \sigma(E) \quad (\text{III.3.2})$$

where n is the number density of the medium and $\sigma(E)$ is the total inelastic cross-section,

$$\sigma(E) = \sigma(1/2 E, E). \quad (\text{III.3.3})$$

Distances may be simulated from the required distribution by generating a uniform random number, U , in the range (0,1) and setting the simulated distance equal to $-\bar{\ell} \ln(U)$. The maximum energy loss is limited to half the primary energy as the primary and ejected electron are indistinguishable. The energy transferred between radiation and medium during an interaction is calculated by normalising the cross-section to unity,

$$Y(\epsilon, E) = \sigma(\epsilon, E) / \sigma(E) \quad (\text{III.3.4})$$

inverting the function Y for ϵ numerically and using ^auniform random

number between zero and one. Repeating the inversion procedures for distance travelled and energy lost produces a track of events. As the primary electron slows down its mean free path, $\bar{\ell}$, and the normalised cross-section $Y(\epsilon, E)$ change and must be re-evaluated.

Mozumder and Magee (1966a) divided energy loss events into four categories: spurs, blobs, short tracks and branched tracks. Spurs and blobs are isolated deposition events and any secondary electron does not escape the influence of its sibling ion. Energy loss is in the range 0 to 100 eV for a spur and 100 to 500 eV for a blob. A short track is defined as an energy loss of between 500 and 5000 eV. The physical consequence of such a large energy deposition event is a track in which the interactions of the secondary electron are close together and cannot be modelled using the simple approach of Mozumder and Magee. The model does not take into account elastic scattering or angular effects in the inelastic scattering and the energy loss events along a short track are sufficiently close together to overlap. Energy transfers of greater than 5 keV are called branched tracks. These large energy loss events produce secondary electrons of such an energy that the daughter tracks resemble the primary and the progress of these electrons can be modelled using the same technique as for the main track, but with the appropriate inelastic cross-section.

Monte Carlo track simulation depends upon the availability of a suitable inelastic cross-section. Mozumder and Magee (1966c) used a cumulative cross-section obtained by numerical integration of approximations for the differential cross-section of glancing and head-on collisions (Magee, 1961). The differential cross-section for a glancing collision was derived from Bethe's quantum

mechanical treatment of energy loss (Bethe, 1930)

$$\frac{d\sigma}{d\epsilon} = \frac{2\pi e^2}{mv^2} \frac{f(\epsilon)}{\epsilon} \ln \left[\frac{2mv^2}{\epsilon} \right] \quad (\text{III.3.5})$$

and the cross-section for a head-on collision based upon a classical approach

$$\frac{d\sigma}{d\epsilon} = \frac{2\pi e^2}{\epsilon^2 mv^2} \int_{\epsilon} f(\epsilon) d\epsilon. \quad (\text{III.3.6})$$

The constants m , and v refer to the mass and velocity of the electron. These approximate cross-sections rely upon the differential oscillator strength distribution, $f(\epsilon)$, for which Mozumder and Magee constructed a "reasonable function empirically". The function $f(\epsilon)$ satisfied a sum rule describing the number of electrons, excluding K electrons, in a molecule of the water

$$Z = \int_{\epsilon} f(\epsilon) d\epsilon \quad (\text{III.3.7})$$

and agreed with the definition of the mean ionisation energy of water, I ,

$$\ln(I) = \frac{1}{Z} \int_{\epsilon} \ln(\epsilon) f(\epsilon) d\epsilon. \quad (\text{III.3.8})$$

Repeated realisation of the track simulation generates a distribution of energy deposition events. In their original study, Mozumder and Magee (1966a) considered the effect of the energy of the primary electron on the partition of energy between the three track entities: spurs, blobs and short tracks. As each primary track must end in a short track, decreasing the primary energy

reduces the fraction of energy lost in spurs and increases that lost in short tracks. The fraction of energy lost in the range 100 to 500 eV goes through a maximum for a primary electron of 50 keV energy.

A discussion of high energy electron radiolysis kinetics requires the spatial distribution of the reactants and not merely the positions of the energy deposition events. To calculate the distribution of reactive particles Mozumder and Magee considered the track of a low LET electron to be linear and they assumed the length of a short track to be small compared to the average inter-event distance. Under these approximations, track entities are isolated and a simple "rule of correspondence" can be used to convert each energy loss into the corresponding number of reactive particles. Mozumder and Magee (1966b) considered two alternative rules for conversion from energy to number. The first rule was by direct proportionality. Assuming a total yield of six dissociations per 100 eV, a cluster was considered to contain one pair if the parent energy loss was less than 17 eV, two pairs if $17 \text{ eV} \leq \epsilon \leq 33 \text{ eV}$, etc. The second empirical rule attempted to include the second ionisation energy of water; one pair was produced if $\epsilon \leq 20 \text{ eV}$, two pairs if $20 \text{ eV} \leq \epsilon \leq 35 \text{ eV}$ and so on. The difference between the two resulting distributions was not significant. According to the Mozumder and Magee distribution, about 90% of the dissociations of a 1 MeV primary electron and its daughters result from energy loss events less than 100 eV. The distribution of energy loss events smaller than 100 eV is not expected to vary significantly with the primary energy and the distribution for a 1 MeV electron is commonly used in conventional deterministic models of spur kinetics (Schwarz, 1969).

3.2 An experimentally based energy distribution.

The cluster size distribution of Mozumder and Magee does not provide a satisfactory basis for modelling the nonhomogeneous kinetics that follow fast electron radiolysis as it is based on a conjectured DOSD. To derive a more accurate distribution, the empirical DOSD and the approximations for the differential inelastic cross-sections, equation (III.3.5) and equation (III.3.6), must be discarded and replaced with currently available, accurate and experimentally based alternatives.

3.2.1 Inelastic differential cross-sections.

The theory of energy loss by electrons was derived quantum mechanically, within the Born approximation, by Bethe (1930, 1932). Application of Bethe theory can only be made by approximation. Energy loss by an electron in water was considered by Bethe and by Lea (1955). These treatments are accurate at high energies, but somewhat inadequate at low energies. Several approximate models have been derived, applying Bethe theory in this region. One, presented by Ashley (1982), considers energy loss in terms of the dielectric response function of the medium. This treatment has recently been reformulated (LaVerne & Mozumder, 1983) who replaced the dielectric function with its exact equivalent in terms of the dipole oscillator strength. The reformulation is only strictly valid for the gas phase, but the description ought to be adequate for rudimentary calculations in the condensed phase. The approximation for the differential cross-section is (LaVerne & Mozumder, 1986),

$$\frac{d\sigma}{d\epsilon} = \frac{\pi e^4}{E} \frac{f(\epsilon)}{\epsilon} \left[\ln \left[\frac{4E}{\epsilon} \right] - \left[\frac{\epsilon}{E} \right] \ln \left[\frac{4E}{\epsilon} \tilde{e}^{7/4} \right] \right] \quad (\text{III.3.9})$$

where $\tilde{e}$ is the base of natural logarithms. Equation (III.3.9) does

not take into account relativistic effects, but within this limitation the differential cross-section has the advantage that

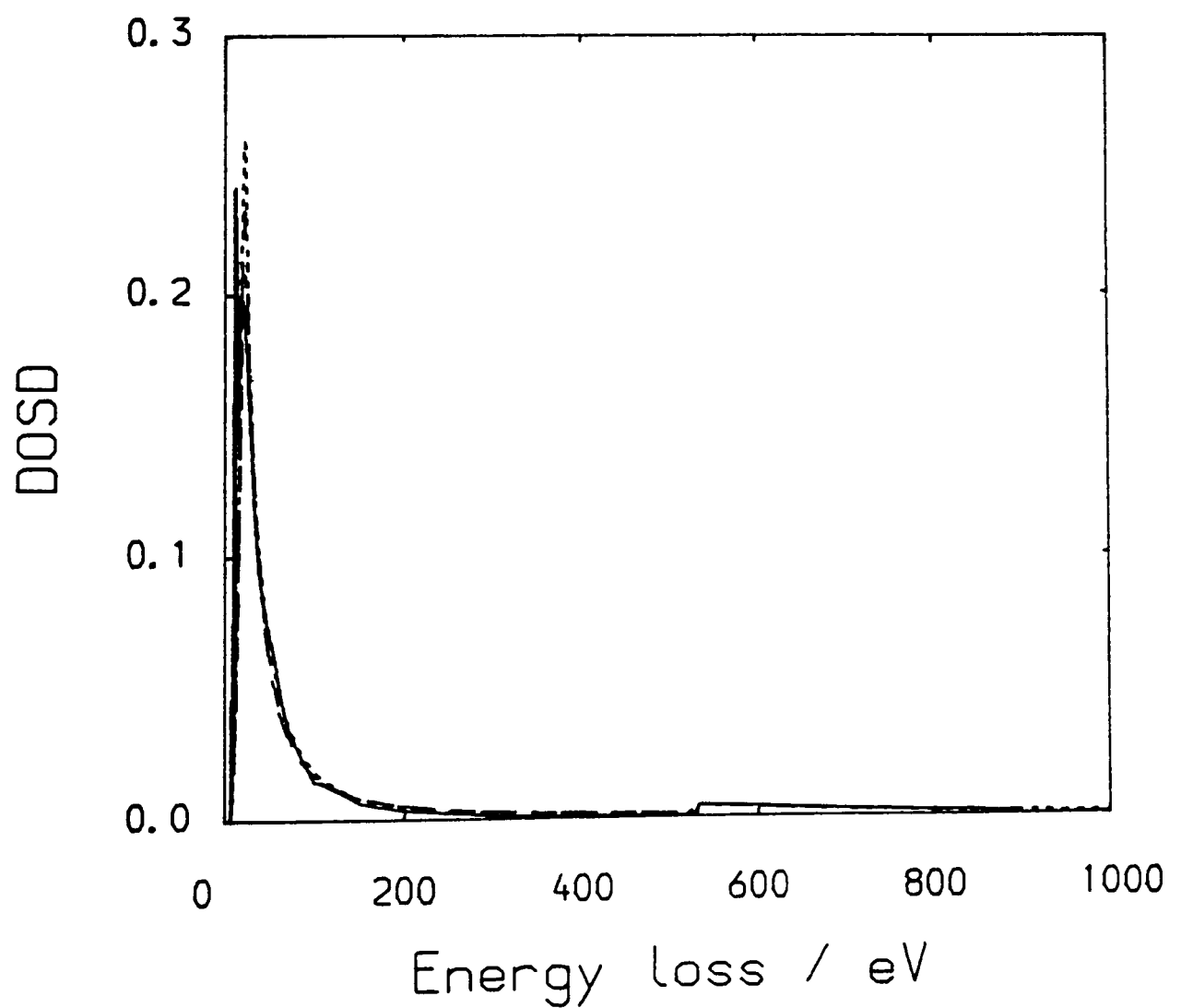
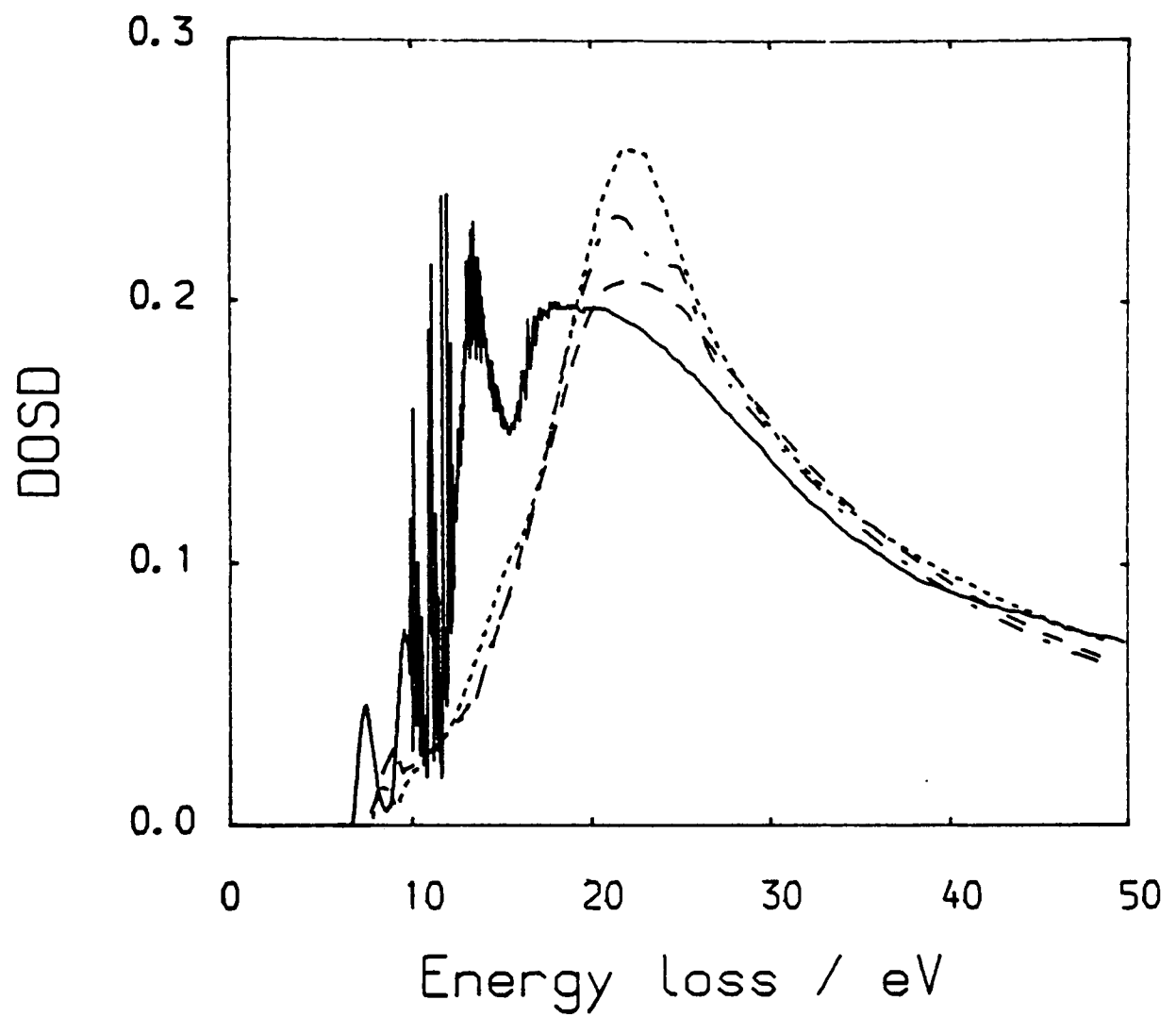
- i) it is applicable over the entire range of incident energy
- ii) it requires the dipole oscillator strength as the only nontrivial molecular parameter
- iii) it agrees with Bethe's equation for LET and the modified Rutherford cross-section (Massey & Burhop, 1969) in their respective limits.

3.2.2 Experimentally based DOSDs.

An accurate DOSD is essential for satisfactory Monte Carlo simulation of the energy deposition distribution. For water in the vapour phase, an acceptable distribution is available and is shown in Fig.III.3.1. It is derived from experimental and theoretical photoabsorption and photoionisation cross-sections (Zeiss et al., 1975). Condensed phase DOSDs can be obtained indirectly from uv-reflectance measurements. For water these measurements are limited to energies below about 26 eV (Heller et al., 1974) and an extrapolation is required above this limit. The complex dielectric constant of a medium can be described using model insulator theory (Ashley, 1982) and the imaginary part is related to the dipole oscillator strength. LaVerne and Mozumder (1986) used this relationship to derive an acceptable DOSD for water. Their predicted spectrum is in close agreement with the experiments of Heller et al. (1974). LaVerne and Mozumder also derived approximate numerical DOSDs for hexagonal and amorphous ice and made comparisons with experimental uv-reflectance spectra. The DOSDs for the condensed phases of water are included in Fig.III.3.1. The gas phase and condensed phase distributions differ in two important ways that will influence the results of energy deposition simulations: there is a shift of the maximum excitation energy and

Fig.III.3.1 Phase effect on the DOSD of water.

(—) vapour; (· · · ·) liquid; (- · - ·) hexagonal ice;
(- - - -) amorphous ice.



a general loss of structure in the condensed phases.

As the experimentally based DOSDs are not analytic, the cumulative inelastic cross-section required for simulation has to be calculated numerically from equation (III.3.9). The discretisation of the DOSD is sufficiently fine that integration using a trapesium rule is acceptable. More refined integration techniques based upon curve fitting are inappropriate as the DOSD may have a detailed fine structure at low energies. The normalised cross-sections for 5.5 keV, 10 keV, 100 keV and 1 MeV electrons in water vapour are shown in Fig.III.3.2. The curves appear indistinguishable, but for intermediate energy losses this is not the case. Notice the discontinuity introduced by the K shell electrons of the oxygen atom.

3.2.3 Simulation of energy loss.

The variation of the normalised inelastic cross-section with ϵ is important in the simulation of an energy deposition distribution. The distribution Y defines the energy lost in each event and an accurate method of inverting Y is critical. A linear least squares cubic spline is fitted through ϵ as a function of Y and then, following the approach defined in appendix A, a uniformly distributed random number in the range (0,1) is used to calculate the size of an energy loss event. This technique has been tested by comparing generated values of ϵ with the original numerical distribution, $Y(\epsilon)$.

Rudimentary Monte Carlo simulation of the energy deposition of a fast electron, and its daughters, in water vapour produces the distribution of energy depicted in Fig.III.3.3. The interactions have been divided according to the prescription of the original work: spurs, blobs and short tracks. When compared with the original simulations, a much larger fraction of the total energy

Fig.III.3.2 Normalised cross-section for water vapour.

(- - - -) $E = 5.5$ keV; (- · - ·) $E = 10.0$ keV;
 (· · · ·) $E = 0.1$ MeV; (————) $E = 1.0$ MeV.

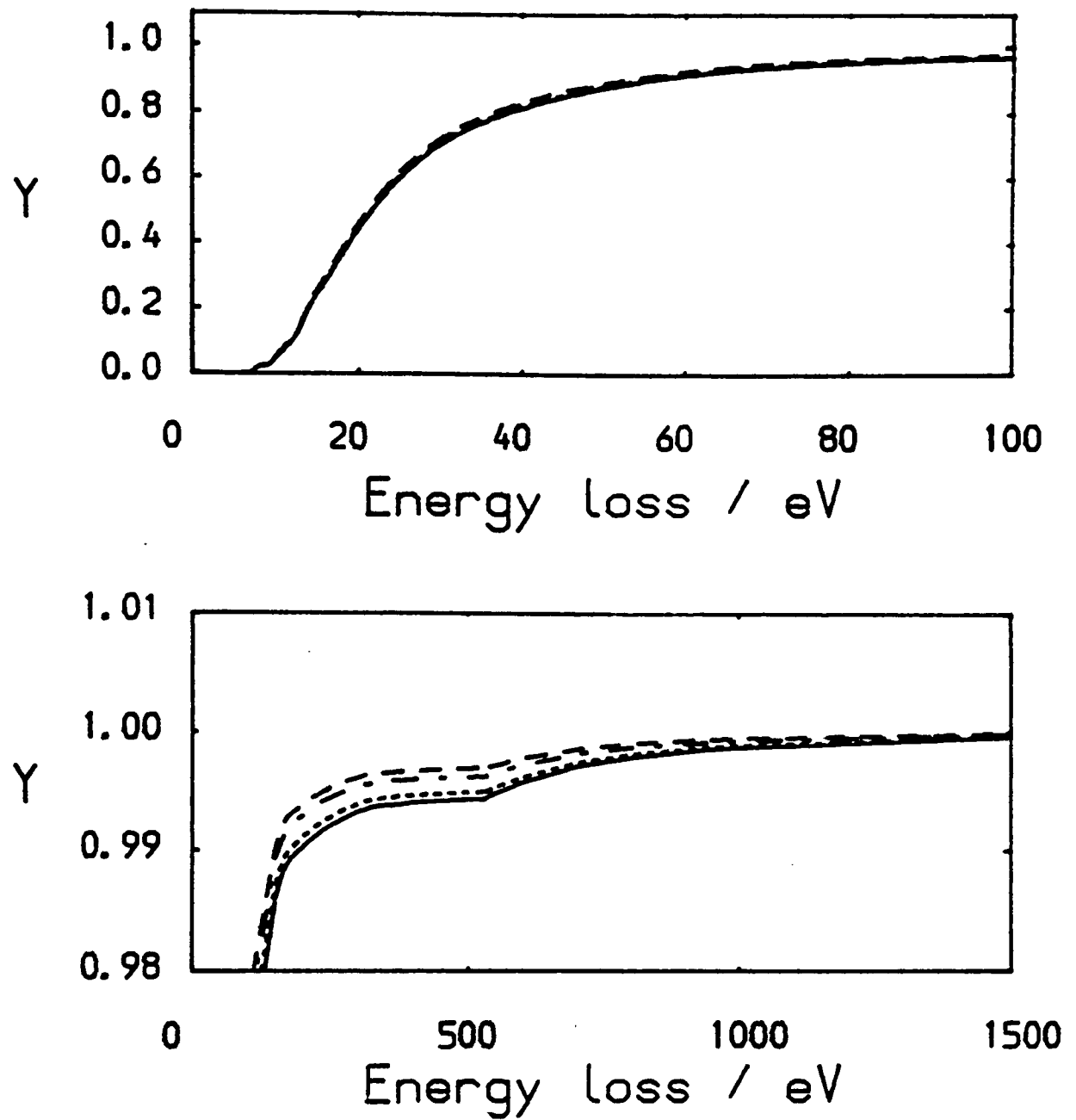
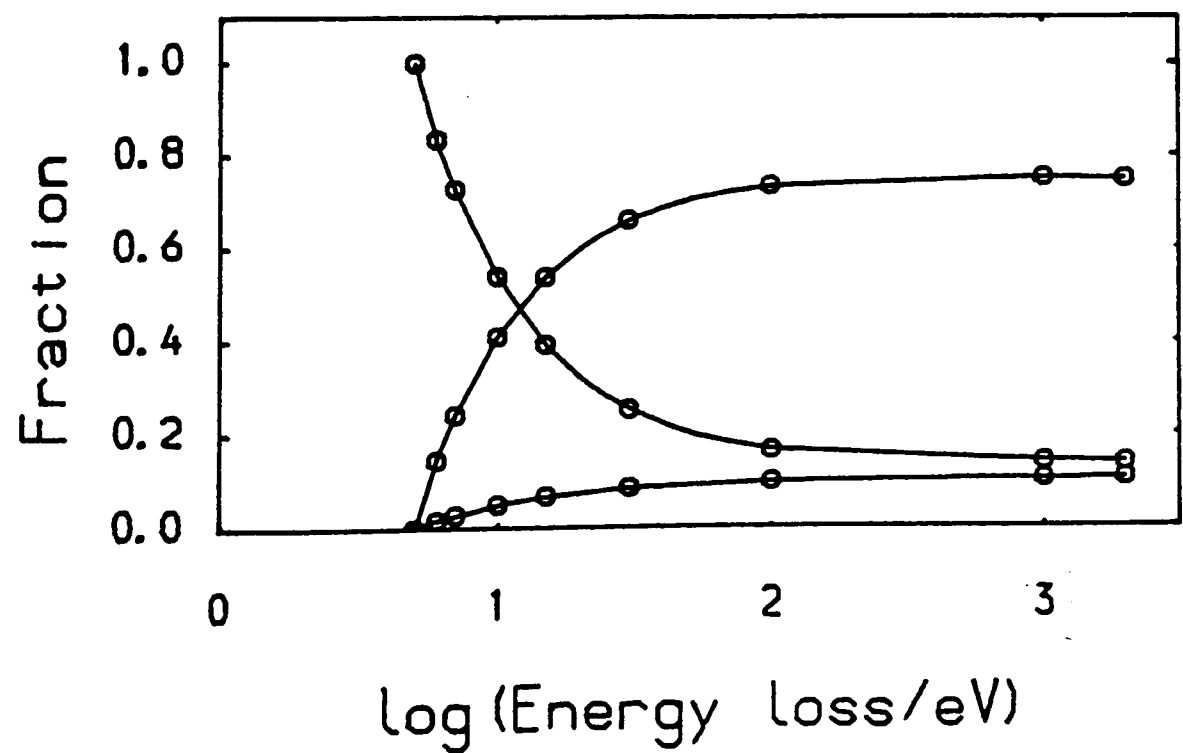


Fig.III.3.3 Distribution of energy loss events for a 1 MeV primary electron in water vapour.



deposited appears as spurs rather than blobs and short tracks. This represents a significant increase in the number of interactions.

The distribution of energy deposition events within the three loss categories is described in Fig.III.3.4. The simulation refers to the degradation of a 1 MeV electron. Comparison with study of the study of Mozumder and Magee (1966c) shows the maximum of the distribution has shifted to higher energy both in terms of frequency and total energy lost. The incident electron energy has no substantial effect on the distribution of energy losses in the spur region as is shown in Fig.III.3.5 for electrons with energy 5.5 keV, 10 keV, 100 keV and 1 MeV. This reflects the slow change in the value of the normalised cross-section with ϵ .

3.2.4 Infrequent energy loss events.

In any simulation, the frequency of large energy loss events is small. This type of event is particularly important when examining the character of the main, or primary, track. To obtain acceptable statistics in this region of the energy deposition distribution requires extensive simulation and the majority of this effort is expended in modelling small energy deposition events. To extend the distribution efficiently and accurately to high energy loss interactions an alternative approach is necessary.

An approximate treatment of the problem is possible. If the primary track is considered, then the probability that a given energy loss is in the range ϵ to $\epsilon + \Delta\epsilon$ is

$$P = \int_{\epsilon}^{\epsilon+\Delta\epsilon} p(\epsilon) d\epsilon \quad (\text{III.3.10})$$

where $p(\epsilon)$ is the probability density function of energy loss events. Neglecting the contribution of branched tracks to the

Fig.III.3.4 Frequency of energy loss events for a 1 MeV primary electron in water vapour.

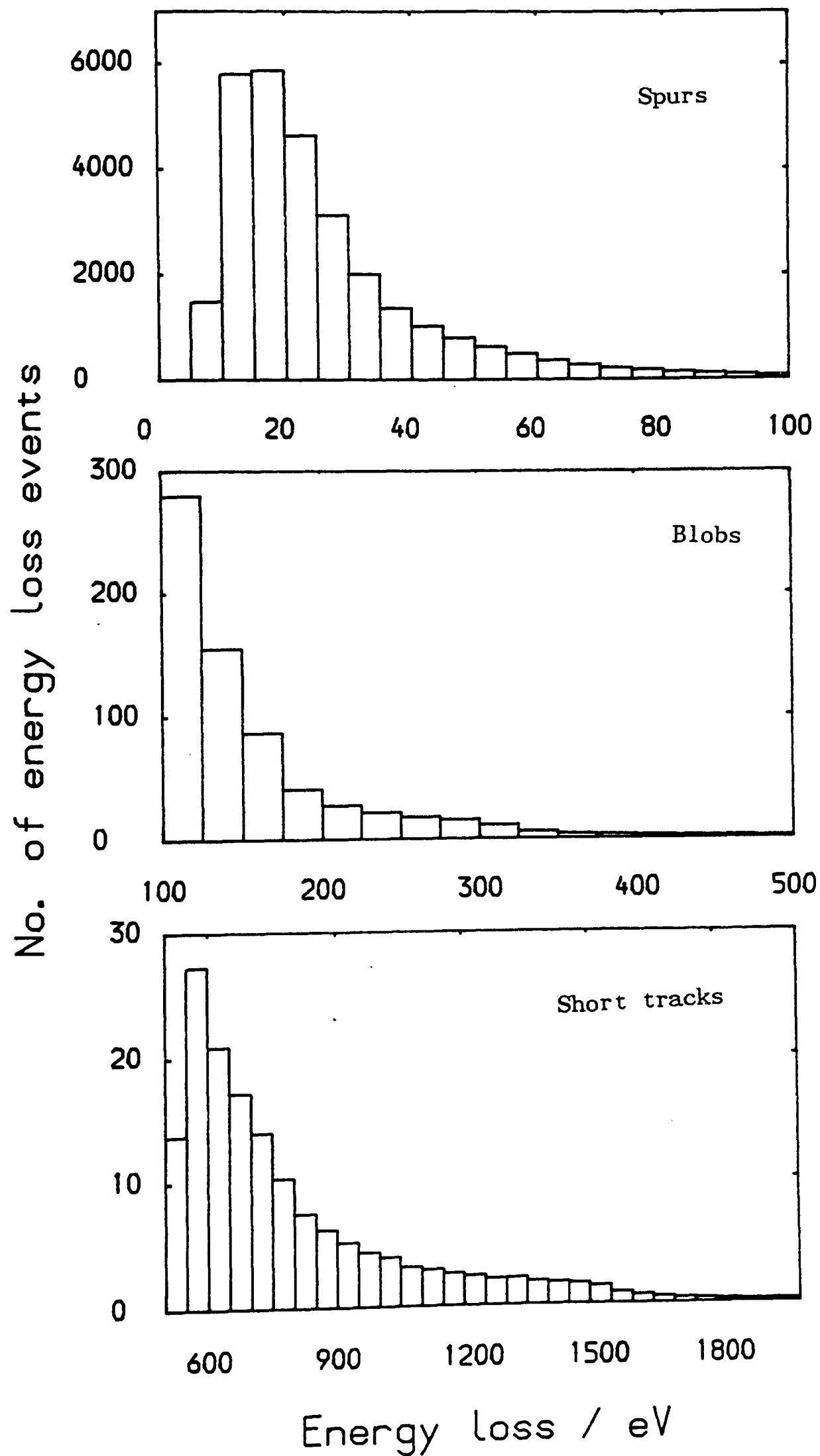
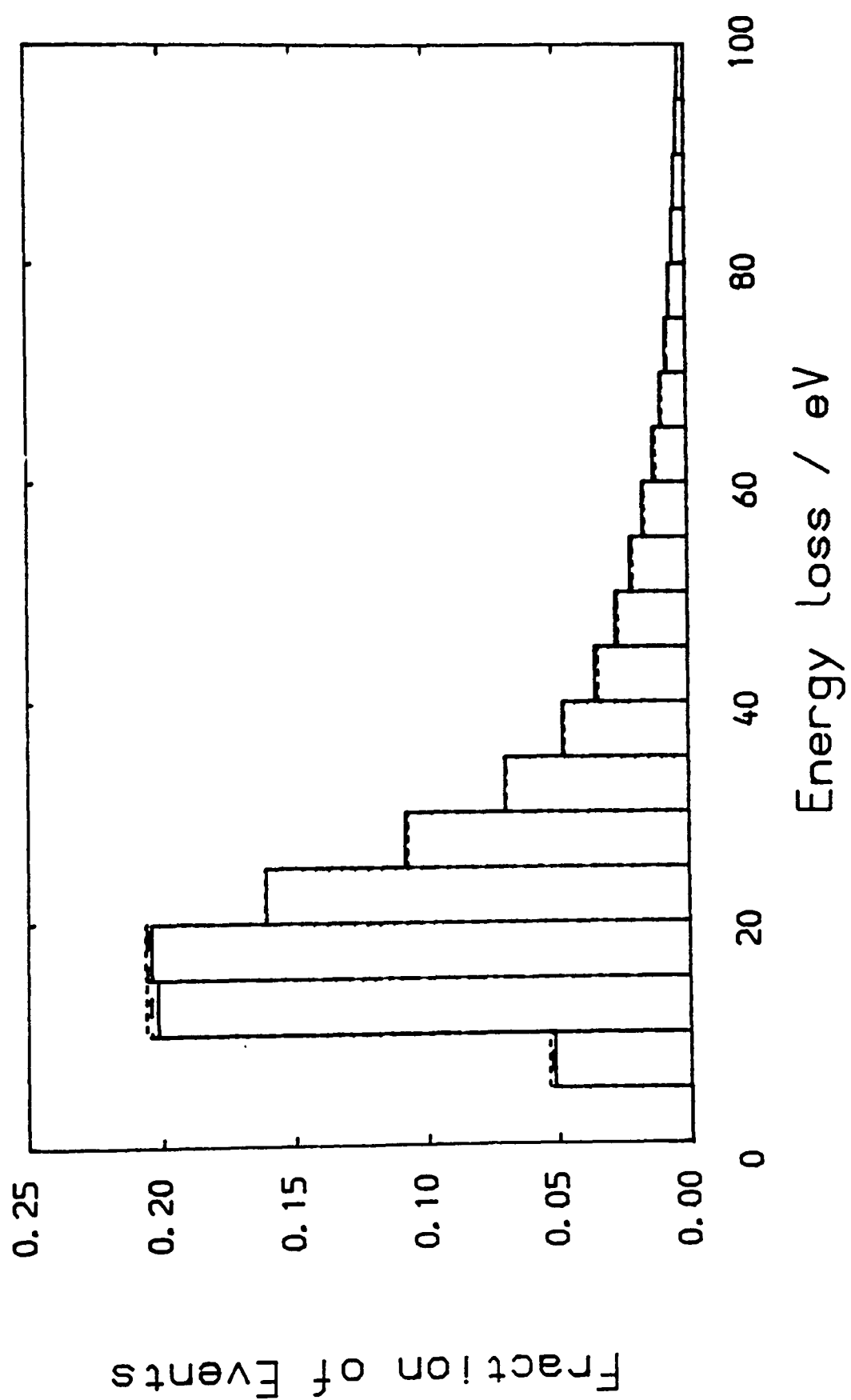


Fig.III.3.5 Effect of primary energy upon energy loss.

(. . . .) $E = 30.0$ keV; (— — —) $E = 0.1$ MeV;
 (————) $E = 1.0$ MeV.



distribution of interactions and neglecting any variation in Y with primary energy,

$$P \propto \frac{1}{\sigma(E)} \int_{\epsilon}^{\epsilon+\Delta\epsilon} \left[\frac{d\sigma}{d\epsilon} \right]_E d\epsilon. \quad (\text{III.3.11})$$

The ratio of the number of energy losses in the range ϵ_i to $\epsilon_i+\Delta\epsilon_i$ to that in the range ϵ_j to $\epsilon_j+\Delta\epsilon_j$ is the ratio of the probabilities P_i and P_j ,

$$Q = \frac{\int_{\epsilon_i}^{\epsilon_i+\Delta\epsilon_i} \left[\frac{d\sigma}{d\epsilon} \right] d\epsilon}{\int_{\epsilon_j}^{\epsilon_j+\Delta\epsilon_j} \left[\frac{d\sigma}{d\epsilon} \right] d\epsilon} \quad (\text{III.3.12})$$

If the differential cross-section is sensibly constant within each of the ranges then this ratio can be approximated by

$$Q \simeq \frac{\Delta\epsilon_i \left[\frac{d\sigma}{d\epsilon} \right]_{\epsilon_i}}{\Delta\epsilon_j \left[\frac{d\sigma}{d\epsilon} \right]_{\epsilon_j}} = \frac{\Delta\epsilon_i f(\epsilon_i) \epsilon_j g(\epsilon_i, E)}{\Delta\epsilon_j f(\epsilon_j) \epsilon_i g(\epsilon_j, E)} \quad (\text{III.3.13})$$

where

$$g(\epsilon, E) = \ln \left[\frac{4E}{\epsilon} \right] - \left[\frac{\epsilon}{E} \right] \ln \left[\frac{4E\tilde{\epsilon}^{7/4}}{\epsilon} \right]. \quad (\text{III.3.14})$$

When ϵ_i and ϵ_j are large, but still less than the maximum energy loss ($\frac{1}{2}E$), $g(\epsilon_i, E)/g(\epsilon_j, E)$ approaches unity and the ratio of events

in the two ranges tends to

$$Q = \frac{\Delta\epsilon_i f(\epsilon_i) \epsilon_j}{\Delta\epsilon_j f(\epsilon_j) \epsilon_i}. \quad (\text{III.3.15})$$

Using this ratio it is possible to calculate the relative distribution of events in the high energy region where the simulation statistics are poor. The predictions of this analytic approximation and Monte Carlo simulation are compared in Fig.III.3.6. The histogram refers to a 1 MeV electron and considers energy loss events of greater than 1550 eV.

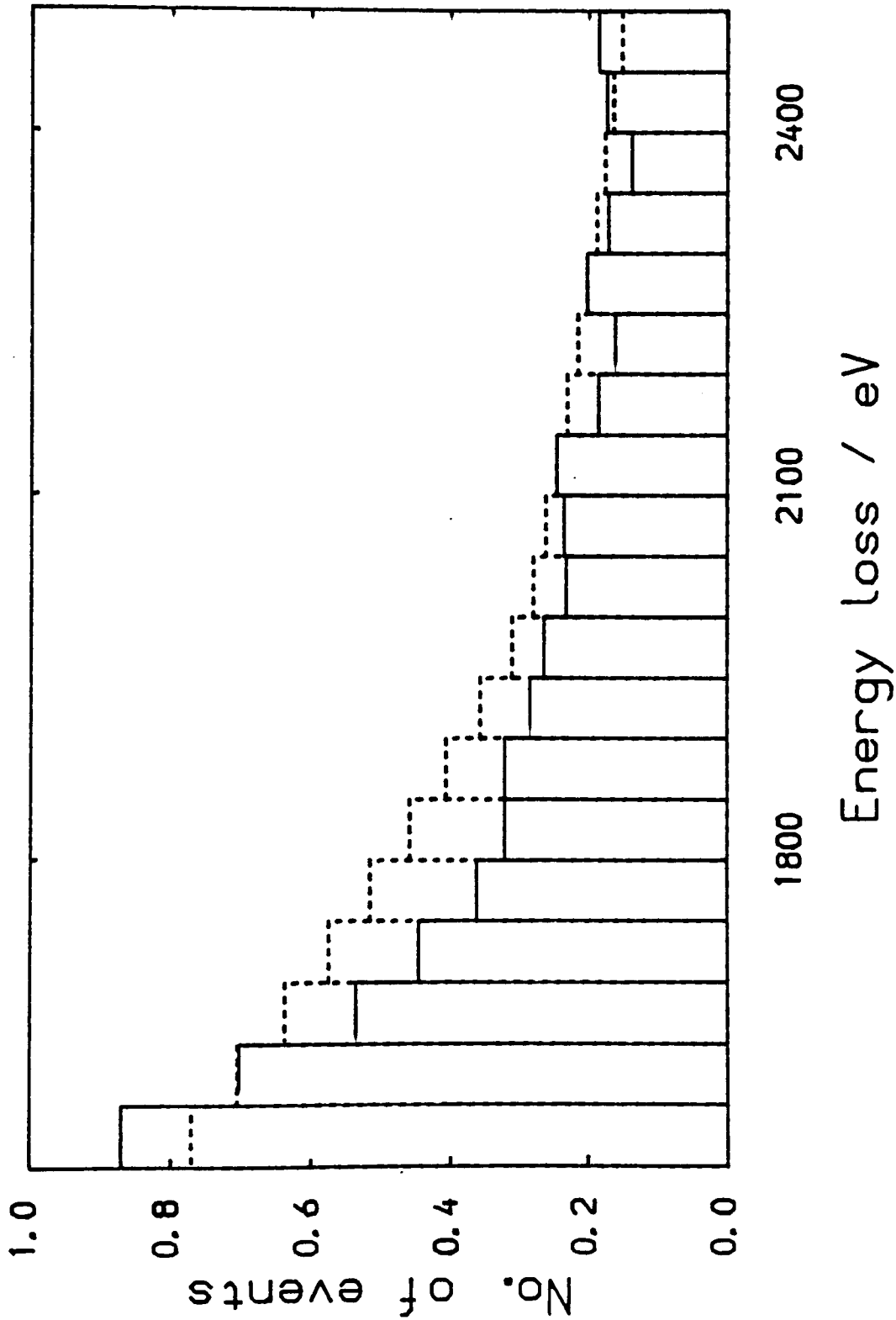
If a detailed and accurate description of the energy distribution of deposition events is required, an alternative rigorous treatment of the infrequent event problem is necessary. The use of a recurrence relationship describing the distribution of events for a primary with energy $E+\Delta E$, $F(\epsilon, E+\Delta E)$, in terms of the distribution for a primary with energy E , $F(\epsilon, E)$, is possible and the relationship is derived in appendix D. This approach is based upon the simulation of a series of energy deposition distributions. First, the energy loss distribution of a primary of relatively low energy, $E_1 \simeq 50$ keV, is modelled. This simulation includes any branched tracks. Secondly, the distribution representing the degradation of a primary from $E_2 = E_1 + \Delta E$ to E_1 is considered. Similar calculations referring to higher energies are performed and the result is a series of linked distributions,

$$\longrightarrow E_{i+1} \longrightarrow E_i \longrightarrow E_{i-1} \longrightarrow \dots \longrightarrow E_3 \longrightarrow E_2 \longrightarrow E_1.$$

The complete distribution for a primary of energy E is constructed using the recurrence relationship, starting from the complete distribution referring to the relatively low energy, E_1 . This approach greatly reduces the computational cost involved and is really only necessary when dealing with very high energy electrons,

Fig.III.3.6 Distribution of infrequent events.
(Energy loss by a 1 MeV electron in water vapour.)

(——) Simulation.
(. . . .) Analytic approximation.



3.2.5 The effect of phase upon the energy loss spectrum.

DOSDs are available for water in four phases: vapour, liquid, amorphous ice and hexagonal ice. The effect of phase upon the energy deposition distribution of a 1 MeV electron is shown in Fig.III.3.7. The histogram also includes the distribution of Mozumder and Magee (1966c). The new distributions are very different from the original. They have a much smaller number of the events in the region 5 eV to 20 eV and the condensed phase distributions exhibit a greater shift than the vapour. The effect of phase upon the energy deposition spectrum corresponds to the differences shown in the DOSDs, c.f. Fig.III.3.1.

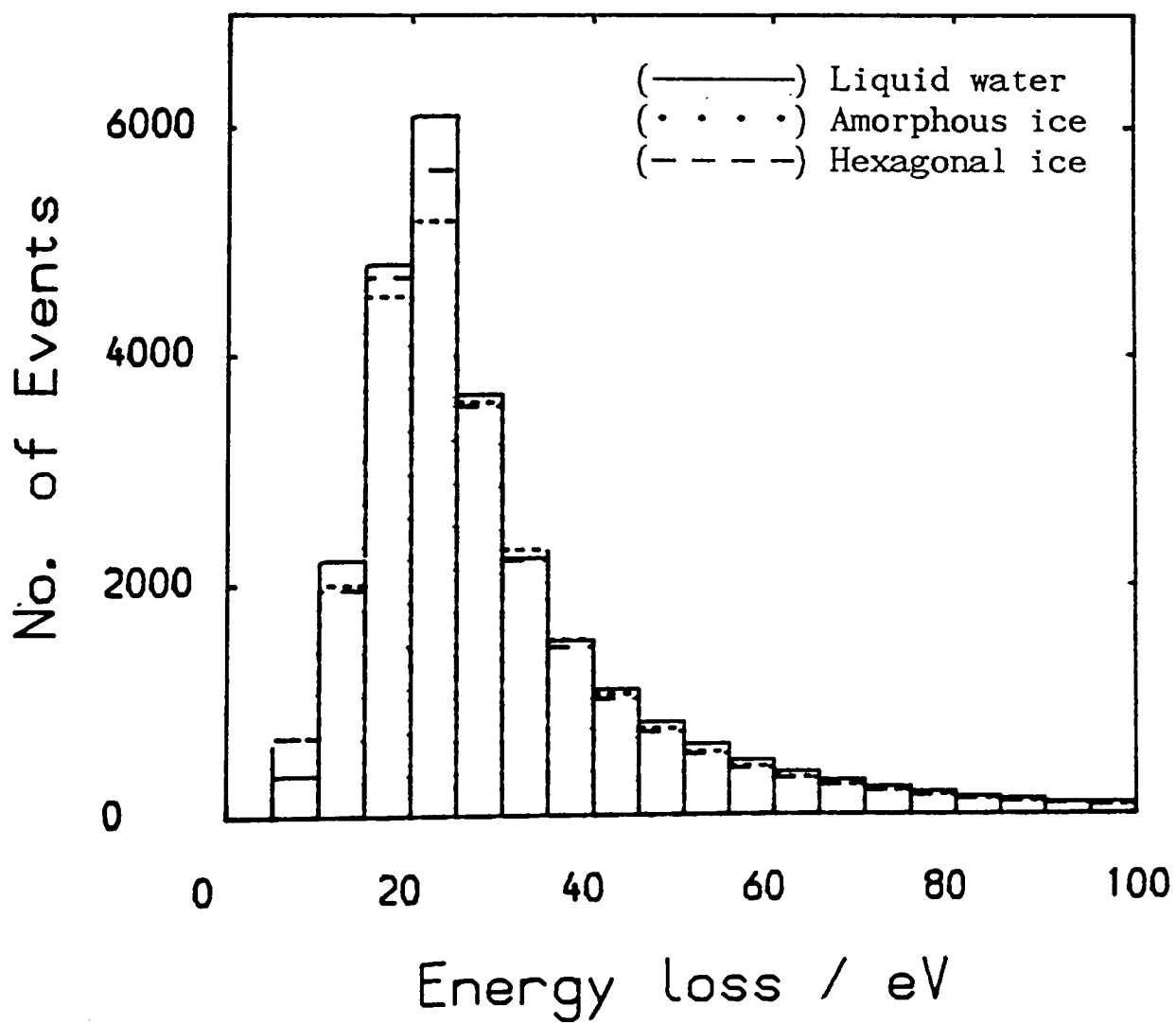
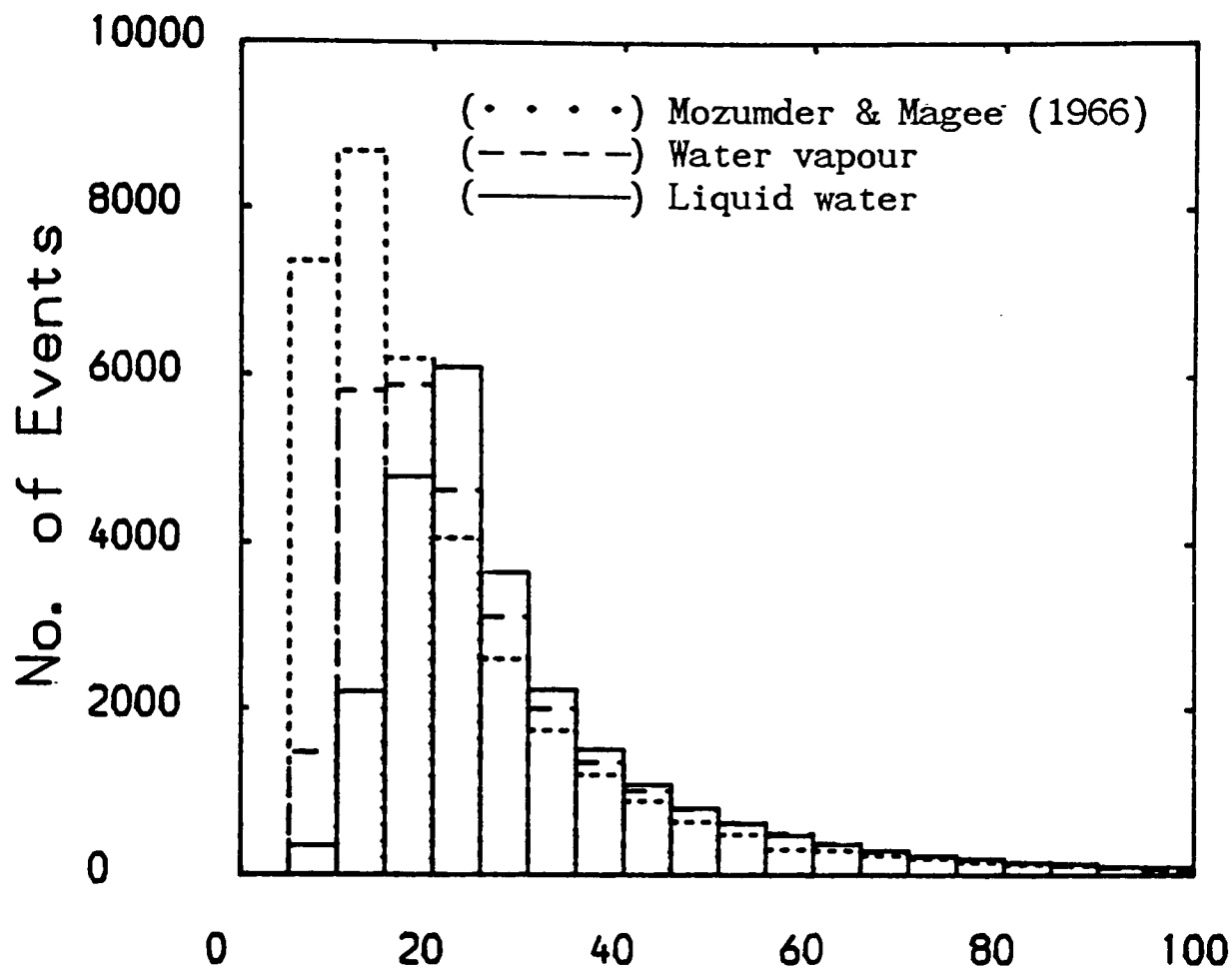
3.3 A distribution in terms of contents.

In modelling the nonhomogeneous kinetics of an electron track, a distribution of cluster sizes, rather than energy losses, is required. If the energy content of a cluster is assumed directly proportional to the number of dissociations (Mozumder & Magee, 1966b) then the number distribution referring to energy loss events smaller than 100 eV is that listed in Table III.3.1. This distribution is for a 1 MeV electron in liquid water, but Fig.III.3.5 suggests that varying the primary energy will have little effect. A number average spur has 2.3 dissociations and contains 38 eV of energy.

Table III.3.1 Cluster size distribution.

No. of dissociations, N	Fraction of clusters with N dissociations.
1	0.1635
2	0.5668
3	0.1634
4	0.0613
5	0.0291
6	0.0159

Fig.III.3.7 Effect of phase upon energy loss.



The adoption of this new cluster size distribution will affect the predicted kinetics. Returning to the simple hydrogen atom and hydroxyl radical system of chapter III.1 and repeating the master equation optimisation with the experimental yields for H, OH, H₂ and H₂O₂ gives a unit cluster width (standard deviation) of 5.80×10^{-10} m for H and 2.72×10^{-10} m for OH and the kinetics of Fig.III.3.8. This optimisation does not include an experimental yield for H₂O, which is experimentally inaccessible. In deriving the cluster size distribution an initial dissociation yield of $G = 6.0$ is assumed, and this implies that, allowing for the experimentally available G values, the recombination yield should be $G_{\text{expt}}(\text{H}_2\text{O}) = 1.45$. If this 'yield' is included in the optimisation then the predicted unit cluster widths are 7.57×10^{-10} m and 2.86×10^{-10} m for hydrogen atoms and hydroxyl radicals respectively. The kinetics are shown in Fig.III.3.9. There is a distinct difference between the kinetic predictions derived using the improved cluster size distribution presented here and those using the cluster size distribution of Mozumder and Magee; agreement with experiment has improved and the unit widths suggested are markedly larger. Table III.3.2 compares the results of the kinetic studies based on the different cluster size distributions.

Table III.3.2 Experimental yields and optimised ME predictions.

Approach	Unit radii / nm.		G values				
	$r_0(\text{H})$	$r_0(\text{OH})$	H	OH	H ₂	H ₂ O	H ₂ O ₂
Experiment			3.65	2.95	0.45	'1.45'	0.80
ME solution ¹	0.44	0.19	3.08	2.25	0.30	2.32	0.72
ME solution ²	0.58	0.27	3.33	2.48	0.33	2.32	0.72
ME solution ³	0.76	0.29	3.76	2.71	0.29	1.66	0.81

¹ Cluster distribution of Mozumder & Magee (1966b).

² Cluster distribution of Table III.3.1.

³ Cluster distribution of Table III.3.1, optimisation including recombination yield (H₂O).

Fig.III.3.8 Optimised master equation kinetics of Gaussian H/OH clusters. Arrows refer to experimental yields.

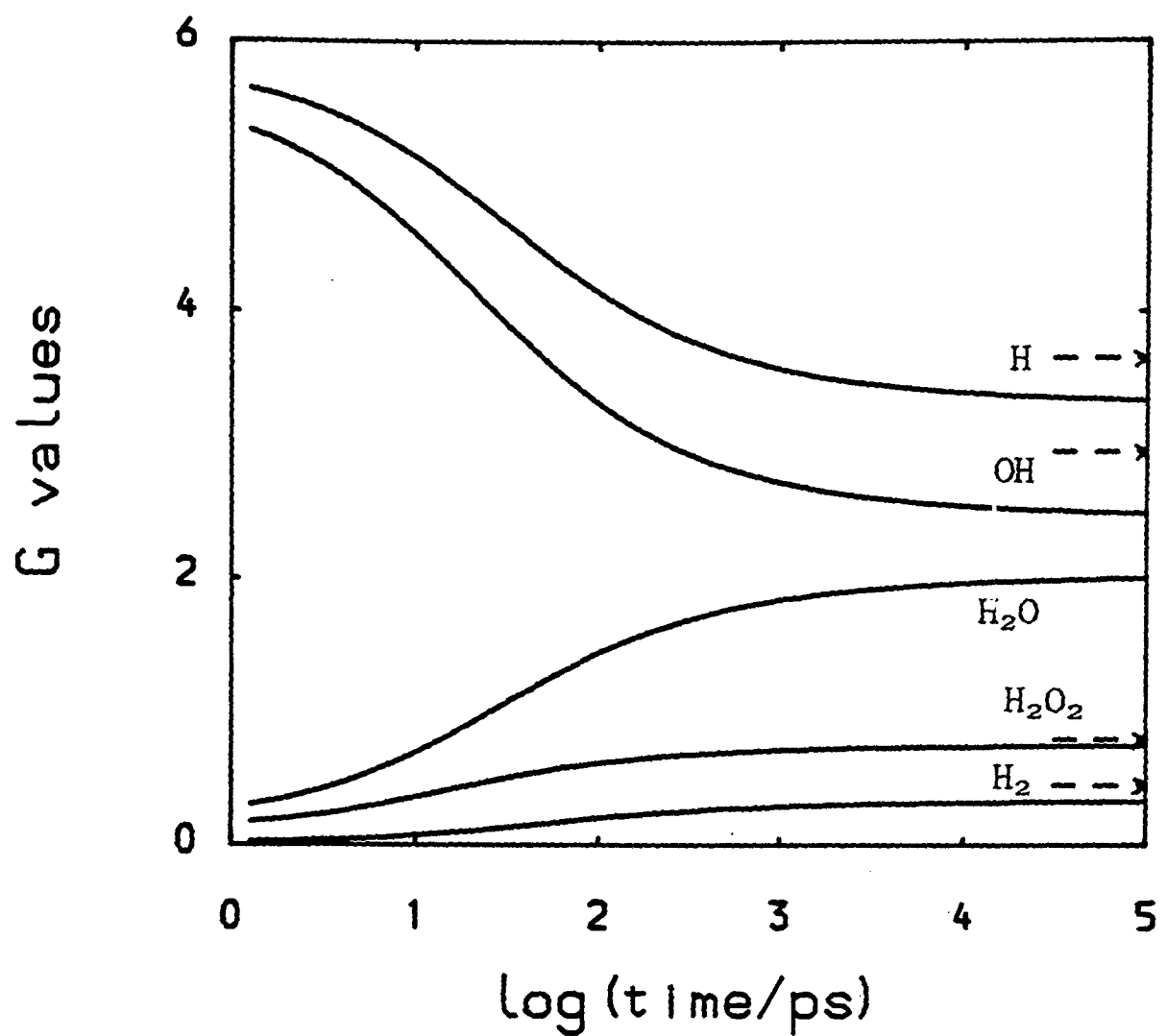
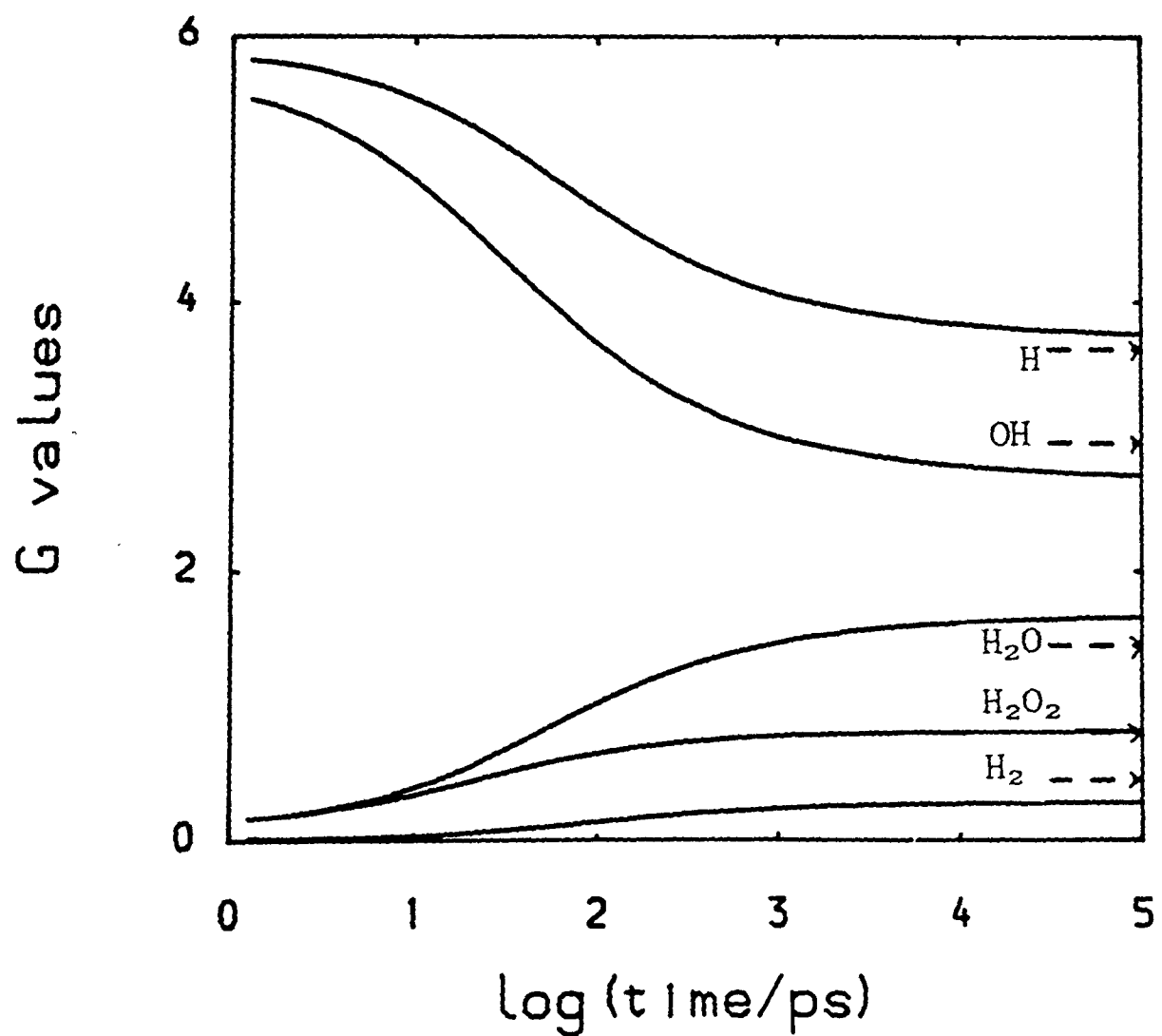


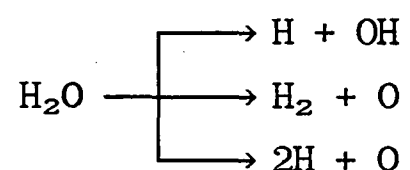
Fig.III.3.9 Optimised master equation kinetics of Gaussian H/OH clusters. Optimisation includes deduced H₂O yield. Arrows refer to experimental yields.



3.3.1 Criticism of a rule of correspondence.

The conversion of an energy deposition size distribution into a cluster size distribution using a rule of correspondence is not really satisfactory. The approach is very simplistic and takes no account of the energy deposition and fragmentation processes. This treatment makes no distinction between ionisation and excitation events. The two processes occur with different probability depending upon the size of ϵ and they yield clusters of different chemical compositions. Energy deposition events smaller than the ionisation energy of the medium can only result in excitation and ionisation dominates when ϵ is large. Any cluster distribution ought to take into account the different decomposition pathways available following an energy deposition event.

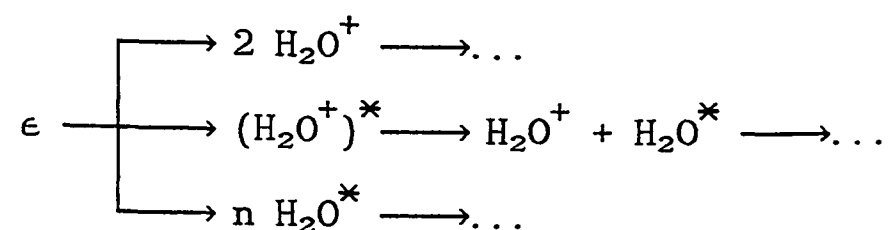
The fragmentation of an excited molecule depends upon its electronic state and is related to the size of the parent energy deposition event. The possible dissociations for water include



The dissociation of water has been reviewed by Andresen and Schinke(1987) and it is possible to assign the various bands in the DOSD of water vapour, see Fig.III.3.10. The absorption continuum, X_1 , of water vapour corresponds to a transition leading to ground state $\text{H} + \text{OH}$ particles and the excitation regions X_2 and X_3 , containing both sharp and continuous bands, result in $\text{H} + \text{OH}^*$ and $\text{H}_2 + \text{O}$ fragments, respectively, but this approach is not possible in the condensed phases where the DOSD is less accurate and has less structure and where the fragmentation patterns are not so well characterised.

When the energy deposited is sufficiently large as to allow more than one dissociation, the fate of the transferred energy is

important and influences the reactive particles produced. For instance if ϵ is about twice the ionisation energy then

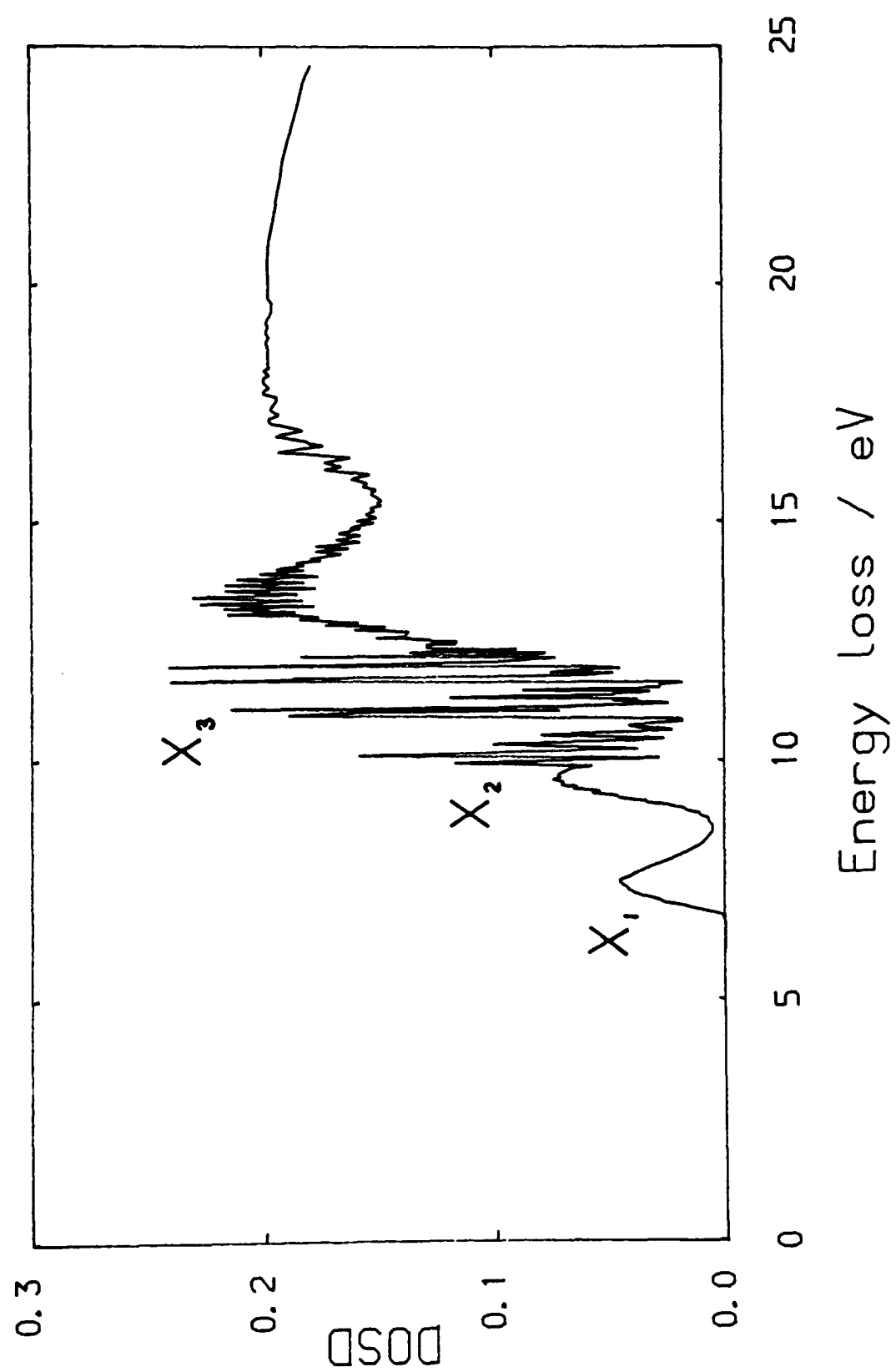


Furthermore, in the gas phase if ϵ is large the emission of a K electron is possible. The resulting molecular ion may lose a second, or Auger, electron and leave an unstable doubly charged species. This type of process is poorly understood in the condensed phases. In the liquid phase it is unlikely that ionisation will take place even at the ionisation energy, I . Superexcited states will be formed from which there is competitive decomposition into ionisation and dissociation pathways (Platzman, 1967; de Heer, 1975). It has been suggested that superexcitation is the main route to excitation in high energy radiolysis (Markarov et al., 1970).

The accurate description of the radiolysis of water vapour in terms of a distribution of clusters of reactive particles is complicated and in the condensed phase the problem is more complex. A more rigorous treatment of the transition from energy distribution to cluster size distribution than the Mozumder and Magee rule of correspondence is possible in the gas phase, but extension to water and ice is fraught with danger. The different conditions under which energy is lost affects the division between excitation and ionisation and the energies of the different processes. The change in local environment increases the importance of superexcited states in the condensed phase and a large part of the DOSD is undoubtedly due to this type of species (Platzman, 1967).

This chapter considered the description of a high energy electron track as a distribution of reactive particles in a series

Fig.III.3.10 DOSD of water vapour.



of isolated clusters, which for the purpose of kinetic modelling are assumed to be Gaussian. The following chapter introduces a more detailed treatment in which the spatial distribution of the reactive particles is represented by an idealised track structure.

Chapter 4 : The kinetics of a low LET electron track.

Most studies of nonhomogeneous kinetics in radiation chemistry consider a model distribution. The conventional treatments usually deal with a typical average cluster or an extended cylinder. The stochastic kinetics of the former type of system were considered in chapter III.1 and, in particular, the development of a distribution of clusters, similar to that found along the track of a high energy electron, was examined. Detailed experimental information about the distribution of the reactive particles along a radiation track is not available. However recent advances in the modelling of the energy deposition processes of fast electrons and other heavier radiation particles have enabled the modelling of idealised track structures that can provide the basis for kinetic simulations. The major aim of this chapter is to establish the methodology for - and to demonstrate the feasibility of - modelling realistic kinetics from a realistic track structure. A stochastic treatment of the kinetics of a radiation track requires, as input parameters, the identity and the thermalised positions of all the reactive particles produced by the energy deposition along the track. The kinetics are not governed by a simple reaction scheme, c.f. chapter III.1, but by an extended mechanism linking the many different species produced during radiolysis and the subsequent chemical phase. It is not sufficient to know the diffusion coefficients and charges of the particles and the rate coefficients of the reactions. The nature of a reaction, i.e. whether or not it is diffusion-controlled, is important in stochastic simulation and it is necessary to know encounter distances and reaction velocities, when the reactions are not diffusion-controlled (c.f. chapter II.5).

At present, track structure calculations must be viewed with caution and cannot be considered entirely realistic, especially in the liquid phase. To this extent the kinetics described in this chapter are unrealistic. The purpose of this study is not to make a comparison with experimental results, but to demonstrate a suitable approach to simulation for use when acceptable track structure calculations are available.

4.1 Realistic aqueous systems.

The Monte Carlo simulation of the structure of a radiation track is discussed in detail in appendix E. This type of calculation provides a detailed picture of the energy deposition by a high energy particle as it passes through a medium. It assigns each energy deposition event an exact position and an energy loss and predicts the velocity of any ejected secondary electron. The attenuation of a secondary electron is followed in the same way as the primary radiation particle. The codes usually follow the degradation of secondaries down to about 10 eV.

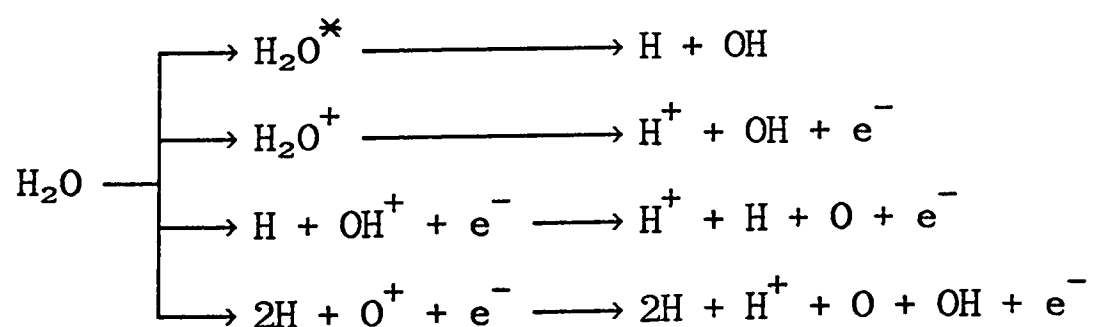
Stochastic modelling of radiolysis kinetics is based upon the initial spatial distribution of reactive particles remaining after radiolysis. This distribution depends upon the dynamics of the fragmentation of the molecular ions and excited molecules produced at each energy deposition site. At present, Monte Carlo track simulations either do not consider this problem or treat it by conjecture (Turner et al., 1983; Zaider & Brenner, 1984). Heavy fragments are assumed to lose energy rapidly and are located, in an arbitrary manner, close to the site of the original energy deposition event. Secondary electrons are usually followed until their energy has degraded to about 10 eV (subexcitation level), but then a distribution of trapping distances is assumed. In the absence of a better approximation, a Gaussian prescription is

generally used to describe the fragmentation and thermalisation distributions.

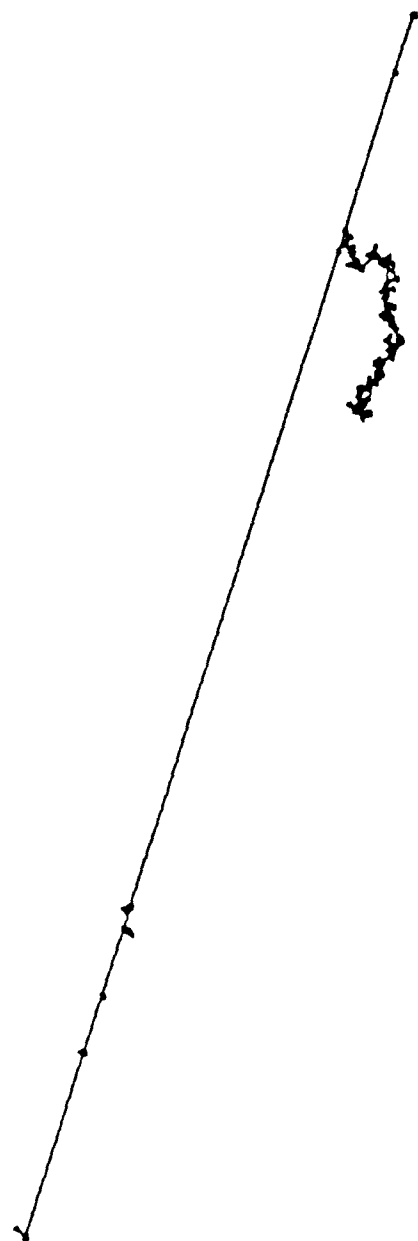
In this chapter the kinetics of a typical section of idealised track are considered. The track calculation was performed by Zaider and Brenner using their code DELTA (Zaider et al., 1983) and the simulation represents the initial 2.5×10^{-4} m of a 22 MeV electron track. There are about 750 primary deposition events which account for a degradation of about 40 keV of the incident electron energy and the largest delta-ray has an energy of 10 keV. Fig.III.4.1 shows a short section of the main track and the 10 keV delta ray. The axial scale is reduced by a factor of ten to show the meandering path of secondary electrons and to separate deposition events along the secondary tracks. A more precise demonstration of the differences between the main track and the delta ray is found in Fig.III.4.2, the cumulative distribution of inter-event separations.

A comparison between the track structure calculation and the simulations of the previous chapter is shown in Fig.III.4.3. The histogram describes the relative distribution of energy deposition events in the range 0 to 100 eV. The distribution of events predicted by the rudimentary Monte Carlo method has little resemblance to that of either the main track or the delta ray.

The fragmentation pathways of the excited molecules and molecular ions formed in the high energy electron radiolysis of water are complicated. The track structure calculation of Zaider and Brenner considers only four possible interactions,



Section of track of
primary electron.



Delta ray.

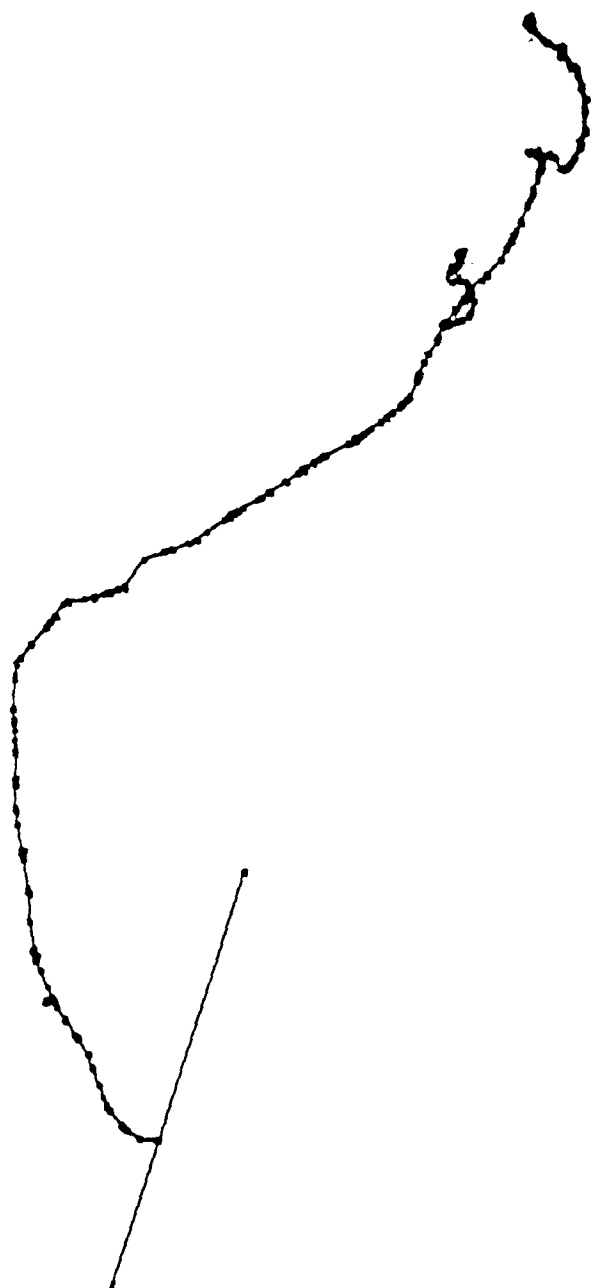


Fig.III.4.1 Sections from an idealised track structure.

Fig.III.4.2 Distribution of inter-event separations.

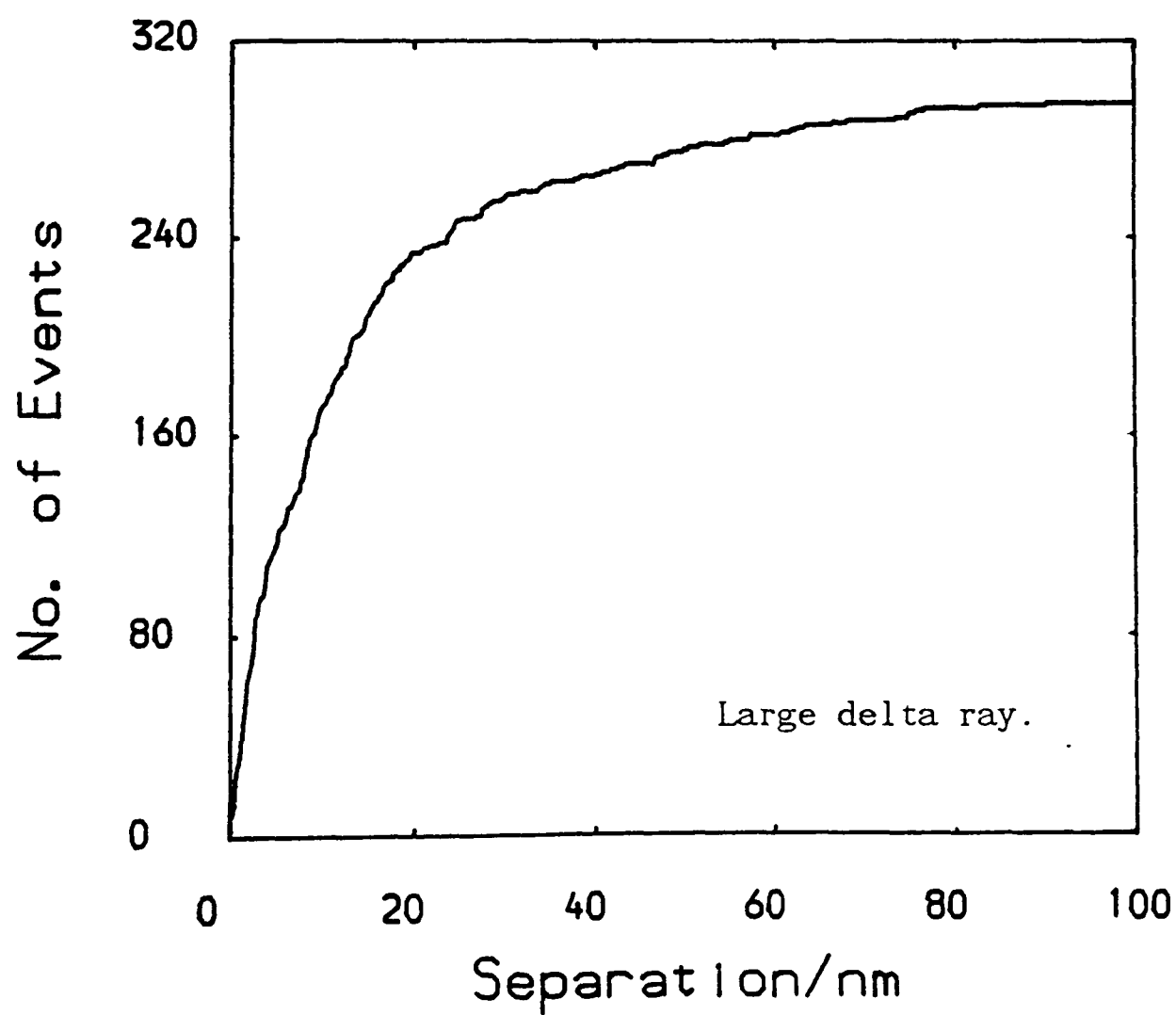
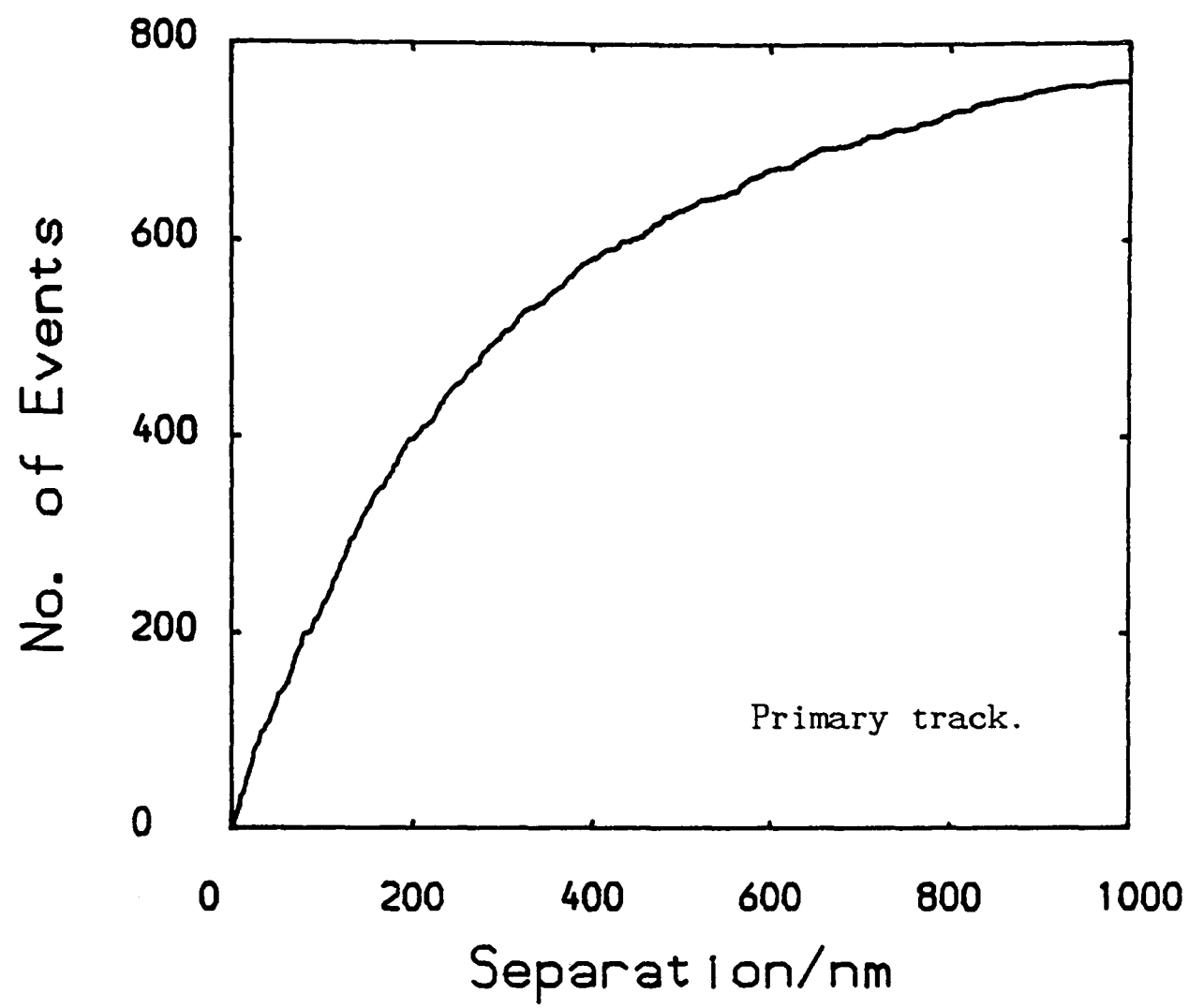
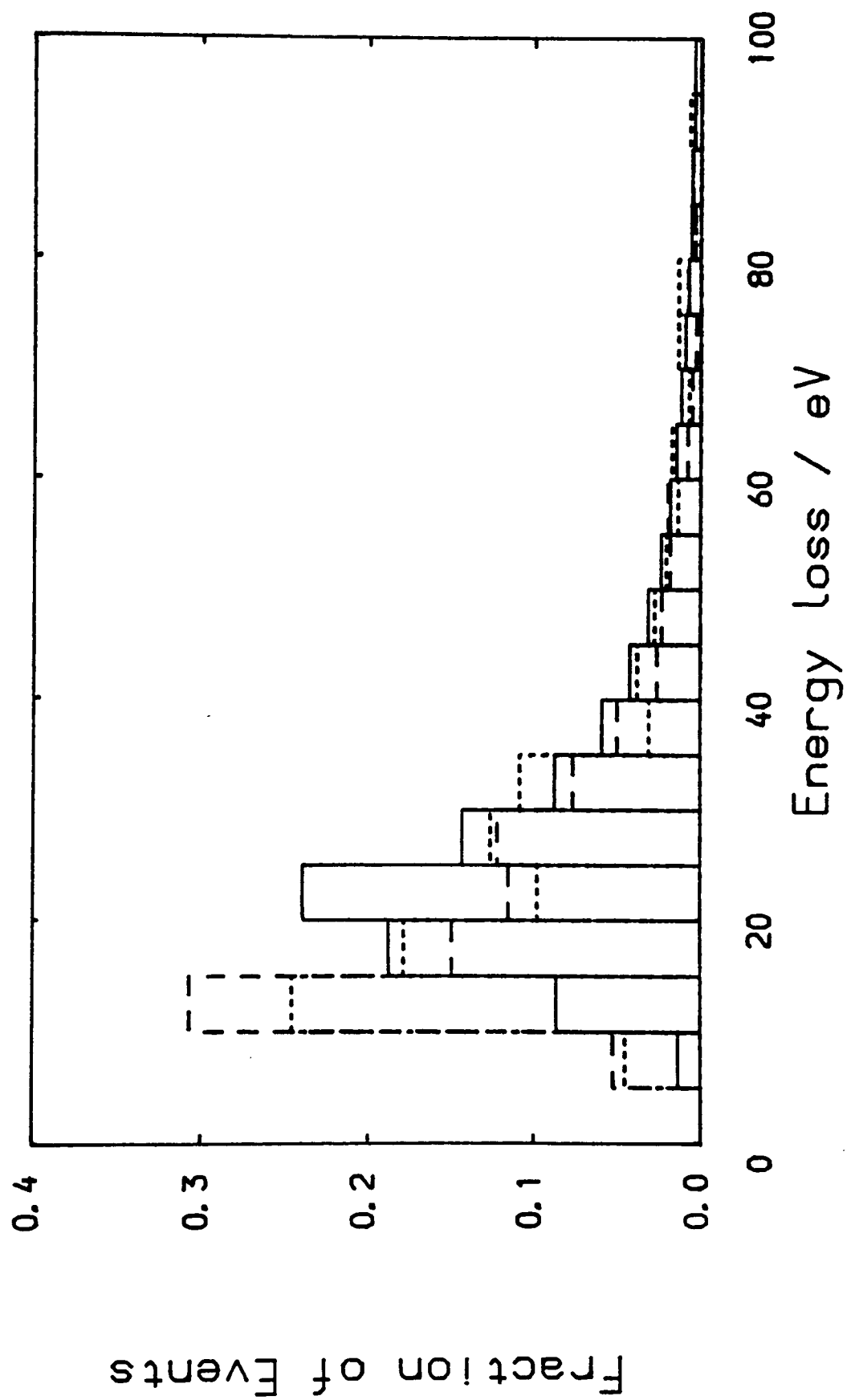


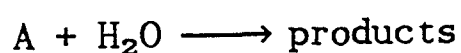
Fig.III.4.3 Frequency of loss events smaller than 100 eV.

(- - - -) Primary track; (· · · ·) Delta ray;
(————) Rudimentary modelling, chapter III.3.



On a picosecond timescale, the 2.5×10^{-4} m track section consists of approximately 9000 reactive particles. In the following study, the chemistry of the track is based upon twelve reactive species (e_{aq}^- , H_{aq}^+ , H, O, OH, OH^- , O_2 , O_2^- , HO_2 , HO_2^- , H_2 , H_2O_2) and the solvent, H_2O , and a scheme of twenty-two reactions. The simulation parameters are listed in Tables III.4.1 and III.4.2. The first table contains estimates of the diffusion coefficients of the reactive particles and the second the parameters required for modelling reaction: steady-state rate constant, encounter distance and reaction velocity. Only reactions with R greater than 0.1 nm are included. Previous calculations (Pimblott, 1985) have shown that encounters between pairs with a ~~smaller~~ reaction distance smaller than 0.1 nm are highly unlikely and can be neglected.

While this kinetic scheme includes the important reactions between the twelve reactive species, solvolysis has been ignored. Water is the most abundant reactant in the radiolysis system and its reactions are potentially very important, however, the rate constants for the reactions



are orders of magnitude smaller than for reactions included in Table III.4.2 and so despite a concentration of approximately 55 mol dm^{-3} the probability of a solvolysis reaction is low. The reaction of a single reactive particle with the bulk solvent is shown in Fig.III.4.4; the decay is exponential. The IRT techniques developed in the previous chapter could be used to extend the reaction scheme to include solvolysis, but the very slow decay of Fig.III.4.4 suggests that, in the case of water, no significant reaction would be registered on the timescale of interest.

Table III.4.1 Track species and their diffusion coefficients.

(Burns & Marsh, 1981; Am.Inst.Physics Handbook, 1967)

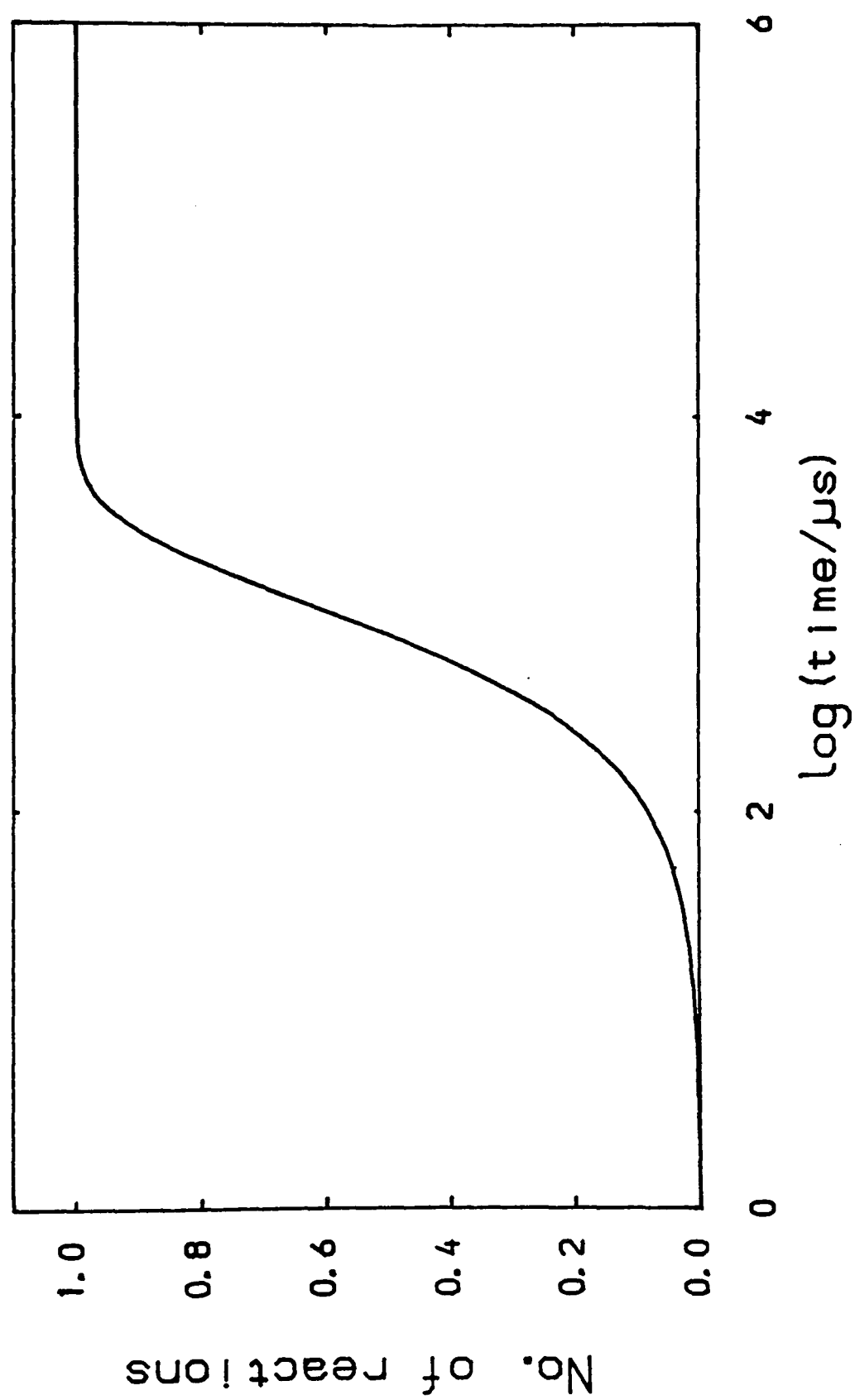
Species	D / 10 ⁻⁹ m ² s ⁻¹
e ⁻	4.5
H	7.0
H ⁺	9.0
O	2.0
OH	2.8
OH ⁻	5.0
H ₂	5.0
O ₂	2.1
O ₂ ⁻	2.1
H ₂ O	2.8
HO ₂	2.0
HO ₂ ⁻	1.4
H ₂ O ₂	1.4

Table III.4.2 The reaction scheme for the radiolysis of water.

(Burns & Marsh, 1981)

Reaction	k/10 ¹⁰ mol ⁻¹ dm ³ s ⁻¹	R / nm	v / ms ⁻¹
e ⁻ + e ⁻ → 2 OH ⁻ + H ₂	0.5	0.34	4.19
e ⁻ + H ⁺ → H	2.4	0.50	
e ⁻ + H → OH ⁻ + H ₂	2.5	0.29	
e ⁻ + OH → OH ⁻	3.0	0.54	
e ⁻ + O ₂ → O ₂ ⁻	1.9	0.38	
e ⁻ + O ₂ ⁻ → OH ⁻ + HO ₂ ⁻	1.3	0.54	
e ⁻ + HO ₂ → HO ₂ ⁻	2.0	0.41	
e ⁻ + H ₂ O ₂ → OH ⁻ + OH	1.2	0.29	
H + H → H ₂	1.0	0.19	
H + O → OH	2.0	0.29	
H + OH → H ₂ O	2.0	0.27	
H + O ₂ → HO ₂	1.9	0.28	
H + O ₂ ⁻ → HO ₂ ⁻	2.0	0.29	
H + HO ₂ → H ₂ O ₂	2.0	0.29	
H ⁺ + OH ⁻ → H ₂ O	14.3	1.23	18.12
H ⁺ + O ₂ ⁻ → HO ₂	5.0	0.50	
O + O → O ₂	2.2	1.46	
O + OH → HO ₂	2.0	0.55	
O + HO ₂ → OH + O ₂	2.0	0.66	
OH + OH → H ₂ O ₂	0.45	0.21	
OH + O ₂ ⁻ → OH ⁻ + O ₂	1.2	0.32	
OH + HO ₂ → O ₂ + H ₂ O	1.2	0.33	

Fig.III.4.4 Solvolysis of an electron.
 $k(e_{\text{aq}}^- + \text{H}_2\text{O}) = 16.0 \text{ mol}^{-1}\text{dm}^3\text{s}^{-1}$.

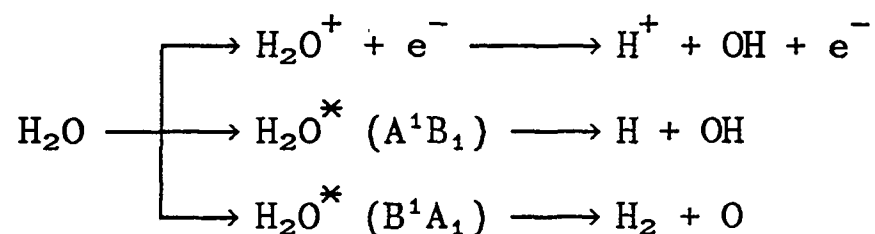


4.2 Kinetic simulation.

The radiation chemistry of aqueous systems is of considerable interest and there is a large amount of experimental information available. Chapter III.1 discussed the modelling of a high energy electron track in terms of isolated clusters and a number of the problems encountered were considered in chapters III.2 and III.3. Modelling the evolution of a realistic radiation track provides an alternative approach to radiation kinetics.

4.2.1 Previous studies.

Turner et al. (1983) have considered the kinetics of an idealised track structure using a random walk technique in which the timescale of the jumps, the size of the particles and the probability of reaction is changed at a number of points in time. Modelling begins at 10^{-14} s with an initial distribution of reactive particles outlined by a track structure and based upon the fragmentation scheme



Analysis of the recombination of a geminate hydrogen atom/ hydroxyl radical pair shows that the scale changes of this simulation method introduce unacceptable artefacts into the predicted kinetics (Green et al., 1988). This example demonstrates the dangers of carrying out extensive simulations without the necessary validation of the method. Terrissol and co-workers have performed similar simulations using a random walk technique (Terrissol et al., 1987). The studies

of both groups make no allowance for any modification of the diffusion and reaction processes by electrostatic forces.

The full random walk simulation of the kinetics of a radiation track is a major computational task and the modelling of such a large system requires a more efficient approach. The IRT model has been shown to reproduce the kinetics of nonhomogeneous distributions of reactive particles accurately and is many times more efficient than full simulation, both in terms of computational cost and use of memory resources.

4.2.2 IRT simulation.

IRT simulation characterises a nonhomogeneous system in terms of the interparticle separations and provides one method of modelling track kinetics. The methodology is sufficiently advanced, following the work presented in this thesis, to consider a realistic radiolysis reaction scheme, but it is necessary to reformulate the simulation program in light of the large number of reactive particles involved. It is not computationally feasible, on any save the largest machines, to consider the possibility of reaction between every reactive pair in the system; nor is it necessary to do so. A very significant fraction of the reaction takes place between reactants generated in the same or proximate energy deposition events and the probability of reaction between widely separated particles is small.

Simulating the kinetics of N reacting particles using the IRT model as formulated in the previous chapters would involve the analysis of $\frac{1}{2}N(N-1)$ times. As the number of particles increases, this becomes prohibitively expensive in computational resources. Many of these times would be infinite, or greater than the simulation cut-off time, and these pairs need not be considered. If any pairs are to be neglected, the conditions under which they are

neglected must be sufficiently stringent that the resulting kinetics are not affected in any way. Rather than consider each particle in turn the fact that the particles are initially located close to their parent energy deposition is used; thus the timescale for encounters between particles arising from different events is considered. Reactions between particles arising from two events separated by a distance x will take place at times longer than that predicted on the basis of the conditioned reaction probability:

$$W_{*}(x, t) = \operatorname{erfc} \left[\frac{(x-X)}{2\sqrt{D' t}} \right] \quad (\text{III.4.1})$$

where X is the largest possible reaction distance and D' is the largest possible relative diffusion coefficient permitted by the reaction scheme. These maximum values are used to make the criterion as stringent as possible, although they do not in general belong to the same reaction. Setting $t = t_{\max}$ gives an upper bound to the conditioned probability that particles arising from two events at a separation x will have met within the cut-off time, $t_{\max}$. If this probability is sufficiently small, typically 0.01, than all the pairs originating from the two events can be ignored. In practice, all events separated by distances x , where

$$x \leq X + 2 \sqrt{D' t_{\max}} \operatorname{erfc}^{-1}(U), \quad (\text{III.4.2})$$

must be considered. This prescription has the advantage that if the evolution of the same energy deposition track is modelled many times, the spatial distribution of deposition events is the same for each realisation of the kinetics and so it is only necessary to perform any restricting calculation once. If the distribution of reactive particles rather than energy deposition events is

considered, a restricting calculation is required for each realisation of the kinetics.

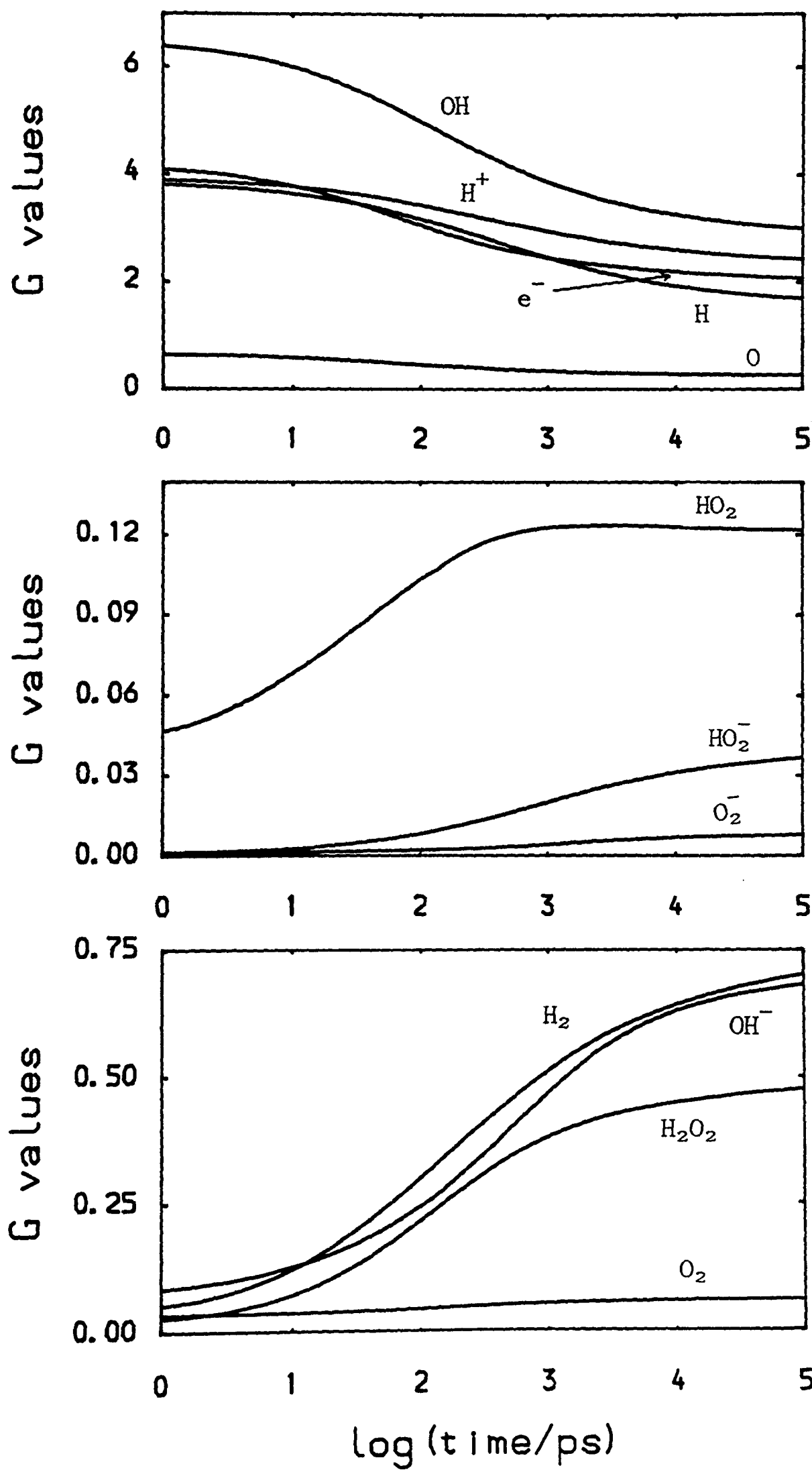
The efficiency of the simulation can be improved further by dividing the time period of simulation, $t_{\max}$, into sections and treating each section in the manner above. For instance, consider the division

$$0 \longrightarrow t_1 \longrightarrow t_2 \longrightarrow t_{\max}.$$

Up to time t_1 , the reactants from a particular energy deposition site can react with particles from any other event within a distance $x_1 = X + 2\sqrt{D't_1} \operatorname{erfc}^{-1}(U)$ and similarly for t_2 , $x_2 = X + 2\sqrt{D't_2} \operatorname{erfc}^{-1}(U)$, and $t_{\max}$. Clearly, $x_1 < x_2 < x_{\max}$ but the actual number of potentially reactive pairs to be considered does not increase greatly as the simulation passes from one time period to the next, since a high proportion of the particles react in each period to form products that cannot undergo further reaction. The program efficiency depends upon the choice of t_1 , $t_2, \dots$, but the simulated kinetics must not. The time divisions must be chosen with care to ensure that $x_1, x_2, \dots$ are larger than the 'width' of the fragmentation distributions.

The kinetics of a radiolysis track depend critically upon the distribution of the reactive particles produced by the fragmentation of the molecular ions and excited molecules formed in the inelastic track events. A detailed description of this distribution is not available so in the absence of a better approximation, a Gaussian prescription has been used in the following calculations. The kinetics presented in Fig.III.4.5 are for fragmentation distributions with a standard deviation of 0.75 nm. This width was taken from the prescribed diffusion calculations of Schwarz (1969). The simulations of chapters III.1 and III.3 suggest a tighter distribution. Experimental radiolysis

Fig.III.4.5 Simulated kinetics of an idealised track.



yields are listed in Table III.4.3.

Table III.4.3 Experimental radiolysis yields.
(Schwarz et al., 1954; Anbar, 1968;
Draganic et al., 1969; Pikaev et al., 1972)

Species	e ⁻	H	H ⁺	OH	H ₂	H ₂ O ₂
Yield	2.70	0.60	3.15	2.85	0.45	0.75

Zaider and Brenner have also performed IRT simulations of reaction in electron (Zaider & Brenner, 1984) and proton (Brenner & Zaider, 1985) tracks. They grafted an early version of the model onto track structure calculations, but did not report how the problems of reactive products, charged species and partially diffusion-controlled reactions are treated. It is not therefore possible to assess the reliability of their results.

The results of Fig.III.4.5 agree only qualitatively with experimental yields. However, the aim of the calculations was not to reproduce experimental results, but to demonstrate the applicability of the IRT methodology to an idealised track structure. The kinetics obtained depend upon the initial particle distribution and therefore also upon the validity of the track structure calculation and the fragmentation patterns used. Track structure calculations, at present, have to be regarded with some caution, see appendix E. It is difficult to justify the treatment of a liquid as a dense gas even with modifications introduced to make allowance for many-body effects (Paretzke et al., 1982; Kaplan et al., 1986). The simple analytic distributions used to locate the reactive particles produced by an energy deposition event are approximations and do not account for the processes of

fragmentation and thermalisation. Despite these qualifications, this study suggests that accurate kinetic modelling is possible.

Chapter 5 : Recombination in an anisotropic medium.

In a variety of condensed media, the kinetics that follow low LET radiolysis can be described in terms of the recombination of a geminate pair. This problem has already been discussed in passing, chapters I.2 and II.3. This chapter presents a fuller treatment. Chapters I.2 and II.3 considered the recombination of an ion pair under the influence of a spherically symmetric potential and under conditions where diffusion is isotropic. When the diffusion and the potential are anisotropic, the treatment must be extended. This chapter considers the solution of the anisotropic problem. The adjoint diffusion equation describing the recombination probability is reduced to a form where the solution can be represented by a family of two parameters and a numerical technique for solving the adjoint equation is developed. This new treatment is used to study the recombination of an electron-hole pair in crystalline anthracene and particular reference is made to the analysis of experimental estimates of the escape probability. The adjoint equation describing recombination in an anisotropic medium is extended to include the influence of an external field and the numerical solution of the resulting reduced equation is considered.

5.1 Geminate recombination of ions.

Onsager's theory (1938) describes the calculation of the probability of geminate escape under the influence of diffusion and a Coulombic interparticle force. The treatment is based upon the solution of an isotropic diffusion equation and in the limit $R \ll r_c$ the ultimate survival probability is

$$\Omega_{iso} = \exp\left[r_c/r\right] \quad (III.5.1)$$

A closed, exact solution for the time-dependent survival probability is not known. The escape predicted by equation (III.5.1) compares favourably with experimental free ion yields measured in liquid hydrocarbons (Schmidt & Allen, 1968), but in crystals the treatment is not valid. In this case the diffusion of the recombining ions and the interparticle forces are anisotropic. One example is photoionisation in crystalline anthracene, where even though the Onsager theory is not valid, experimental results have been analysed using this formulation (Batt et al., 1968; Chance & Braun, 1973; Kato & Braun, 1980)

The ultimate fate of a geminate ion pair in an isotropic environment is governed by the backward equation (Onsager, 1938)

$$\nabla \cdot [\exp(U/k_B T) \nabla \Omega] = 0 \quad (\text{III.5.2})$$

where U is the electrostatic potential. This equation is readily generalised to anisotropic media (Tachiya, 1978)

$$\nabla \cdot [\exp(U/k_B T) \underline{D} \cdot \nabla \Omega] = 0. \quad (\text{III.5.3})$$

$\underline{D}$ is the diffusion tensor and is related to the experimental mobility tensor, $\underline{\mu}$, by the Nernst-Einstein relationship,

$$\underline{\mu} = \frac{e}{k_B T} \underline{D}. \quad (\text{III.5.4})$$

The boundary conditions for solving equations (III.5.2) and (III.5.3) are the same, $\Omega = 0$ at the origin and $\Omega = 1$ at infinity. The mutual electrostatic potential in the anisotropic equation is given by (Landau & Lifshitz, 1960)

$$U = \frac{e^2}{(\underline{r}^T \underline{E} \underline{r})^{1/2}} = \frac{e^2}{4\pi \epsilon_0 |\epsilon|^{1/2} (\underline{r}^T \underline{\epsilon}^{-1} \underline{r})^{1/2}} \quad (\text{III.5.5})$$

where $\underline{r}$ is the vector describing the separation of the ions, $\underline{E}$ is a symmetric dielectric matrix

$$\underline{E} = (4\pi \epsilon_0)^2 |\epsilon| \underline{\epsilon}^{-1} \quad (\text{III.5.6})$$

and $\underline{\epsilon}$ is the dielectric tensor. The superscript T signifies the transpose of a matrix.

5.1.1 Reformulation of the anisotropic problem.

No analytic solution of the anisotropic backward equation (III.5.3) is known and the problem has to be treated numerically. The backward equation can be expanded explicitly to give

$$\nabla \cdot \underline{D} \cdot \nabla \Omega - \frac{1}{k_B T} \nabla \Omega \cdot \underline{D} \cdot \nabla U = 0. \quad (\text{III.5.6})$$

First consider the orthogonal transformation that diagonalises the symmetric diffusion tensor

$$\underline{D} = \underline{Q}^T \text{diag}(\lambda_i) \underline{Q} \quad (\text{III.5.7})$$

and defines a transformed space

$$\underline{s} = \underline{Q}^T \text{diag}(\lambda_i^{-1/2}) \underline{Q} = \underline{D}^{-1/2} \underline{r} \quad (\text{III.5.8})$$

Under this transformation the backward equation reduces to

$$\nabla \cdot \nabla \Omega - \frac{e^2}{k_B T} \frac{\nabla \Omega \cdot \underline{M} \underline{s}}{(\underline{s}^T \underline{M} \underline{s})^{1.5}} = 0 \quad (\text{III.5.9})$$

where the ∇ operators now refer to $\underline{s}$ space and the symmetric matrix $\underline{M}$,

$$\underline{M} = \underline{D}^{1/2} \underline{E} \underline{D}^{1/2} . \quad (\text{III.5.10})$$

contains all the required information of the diffusion and dielectric tensors. After making a second transformation that diagonalises $\underline{M}$,

$$\underline{M} = \underline{P}^T \text{diag}(m_i) \underline{P}, \quad (\text{III.5.11})$$

the backward equation becomes

$$\nabla \cdot \nabla \Omega - \frac{e^2}{k_B T} \frac{\nabla \Omega \cdot \text{diag}(m_i) \underline{t}}{(\underline{t}^T \text{diag}(m_i) \underline{t})^{1.5}} = 0 \quad (\text{III.5.12})$$

where the differential operators now refer to $\underline{t}$ space, $\underline{t} = \underline{P} \underline{s}$. The equation can be further simplified by making the linear transformation

$$\underline{u} = \underline{c} \underline{t} ; \quad c^2 = \left[\frac{k_B T}{e^2} \right]^2 \sum_1^3 m_i . \quad (\text{III.5.13})$$

This gives

$$\sum_1^3 \frac{\partial^2 \Omega}{\partial u_i^2} - \left[\sum_1^3 u_i^2 p_i \right]^{-3/2} \sum_1^3 p_i u_i \frac{\partial \Omega}{\partial u_i} = 0 \quad (\text{III.5.14})$$

where $p_i = m_i / \sum m_i$ and $\sum p_i = 1$. The series of transformations converting $\underline{r}$ to $\underline{t}$ space is equivalent to a rotation, a stretch and finally a reflection.

5.1.2 Determination of the anisotropic survival probability.

Equation (III.5.14) governs the ultimate survival probability of a geminate pair in an infinite space. To facilitate numerical solution, this space is expressed in spherical polar coordinates (u, θ, ϕ) and transformed to a finite space by letting $w = \exp\left[-\sqrt{3}/u\right]$. The polar and azimuthal angles are unaltered by the transformation, but the infinite u space is mapped onto a unit sphere with boundary conditions $\Omega(w \rightarrow 0) = 0$, $\Omega(w \rightarrow 1) = 1$. Numerical solution of the differential equation is achieved using a finite difference method and, because of the D_{2h} symmetry of the solution, it is only necessary to consider a single octant. The finite difference equation is

$$\begin{aligned}
 & 2 \left[3w^2 + \frac{12}{\pi^2 (\ln w)^2} \left[\frac{1}{\sin^2 \theta} + 1 \right] \right] \Omega_{\text{calc}}(w, \theta, \phi) \\
 &= \left[3w^2 \Sigma_w + \frac{12}{\pi^2 (\ln w)^2} \left[\frac{\Sigma_\phi}{\sin^2 \theta} + \Sigma_\theta \right] \right] \\
 &+ \frac{h}{2} \left[3w \Delta_w \left[1 - \frac{1}{\mathcal{A}\sqrt{3}} \right] - \frac{2\sqrt{3} \sin \phi \cos \phi}{\pi \mathcal{A}^3 (\ln w)} (p_2 - p_1) \Delta_\phi \right. \\
 &\quad \left. + \frac{2}{\pi} \Delta_\theta \left[\frac{3 \cot \theta}{(\ln w)^2} + \frac{\sqrt{3} \sin \theta \cos \theta \mathcal{B}}{\mathcal{A}^3 (\ln w)} \right] \right] \quad (\text{II.3.15})
 \end{aligned}$$

where $\Omega_{\text{calc}}(w, \theta, \phi)$ is the survival probability at the point (w, θ, ϕ) calculated from the n th estimate of the probability, Ω_n , at the surrounding points,

$$\mathcal{A} = (p_1 \sin^2 \theta \cos^2 \phi + p_2 \sin^2 \theta \sin^2 \phi + p_3 \cos^2 \theta)^{1/2} \quad (\text{III.3.16})$$

$$\mathcal{B} = p_1 \cos^2 \phi + p_2 \sin^2 \phi - p_3 \quad (\text{III.3.17})$$

$$\Sigma_w = \Omega_n(w+h, \theta, \phi) + \Omega_n(w-h, \theta, \phi) \quad (\text{III.3.18})$$

and

$$\Delta_w = \Omega_n(w+h, \theta, \phi) - \Omega_n(w-h, \theta, \phi) \quad (\text{III.3.19})$$

The sum and difference terms in θ and ϕ (Σ_θ , Σ_ϕ , Δ_θ , Δ_ϕ) have the same form as the corresponding equations in w . Examination of equation (III.5.15) suggests a problem in evaluating Ω at the pole, $\theta = 0$, as $\sin \theta \rightarrow 0$. The equation considers only the six nearest neighbours in evaluating Ω_{calc} . Close to the pole, the discretisation of the (w, θ, ϕ) lattice is very fine and there are a large number of points in close proximity. $\Omega_{\text{calc}}(w, 0, \phi)$ is calculated by taking an average of all the neighbouring points.

The convergence of Ω_{calc} to an acceptable value depends upon the size of the (w, θ, ϕ) lattice and even a coarse $10 \times 10 \times 10$ lattice, which gives a poor estimate of Ω , requires the solution of 1000 linear equations. For an efficient and accurate solution, it is of primary importance to maximise the rate of convergence. The rate at which Ω_{calc} approaches Ω can be increased using a relaxation technique, which accelerates the motion of Ω_{n+1} in the direction of change. Rather than setting

$$\Omega_{n+1}(w, \theta, \phi) = \Omega_{\text{calc}}(w, \theta, \phi)$$

the $n+1$ 'th estimate of the survival probability is assumed to be

$$\Omega_{n+1}(w, \theta, \phi) = r_x \Omega_{\text{calc}}(w, \theta, \phi) + (1-r_x) \Omega_n(w, \theta, \phi) \quad (\text{III.5.20})$$

where r_x is the relaxation coefficient. This coefficient is set as large as possible to maximise the rate of convergence and is usually assumed to be

$$r_x = 2 - 1/N \quad (\text{III.5.21})$$

where N is the lattice parameter. The use of a relaxation method requires a stable problem and a starting solution close to the final solution. For extreme cases, it is necessary to approach the problem through a succession of relaxation coefficients, using a partial solution of one as the initial solution for another.

The simplest method of measuring the convergence of Ω_n is to follow the total absolute convergence of all the points of the lattice,

$$X = \sum_w \sum_\theta \sum_\phi |\Omega_n(w, \theta, \phi) - \Omega_{\text{start}}(w, \theta, \phi)|. \quad (\text{III.5.22})$$

The finite difference method and the relaxation technique for increasing the rate of convergence have been tested by considering the isotropic problem, $p_1 = p_2 = p_3 = 1/3$, for which the analytic solution is known

$$\Omega(w, \theta, \phi) = w. \quad (\text{II.5.23})$$

Agreement depends upon the size of the lattice mesh and can be improved at the cost of an increase in computer time, but a discrepancy of less than 1 part in 10^5 is easy to achieve.

The construction of the reduced backward equation (III.5.14) requires the ratios p_i and not the absolute constants, m_i . As it is not necessary to calculate the absolute value of the diagonal

matrix $\text{diag}(m_i)$, the tensors $\underline{E}$ and $\underline{D}$ can be replaced by $\underline{\epsilon}^{-1}$ and $\underline{\mu}$ respectively and it is sufficient to evaluate

$$\text{diag}(m'_i) = \underline{P} \underline{Q}^T \text{diag}(\mu_i'^{1/2}) \underline{Q} \underline{\epsilon}^{-1} \underline{Q}^T \text{diag}(\mu_i'^{1/2}) \underline{Q} \underline{P}^T, \quad (\text{III.3.24})$$

where $\underline{\mu} = \underline{Q}^T \text{diag}(\mu'_i) \underline{Q}$, since $p_i = m_i / \sum m_i$. Any reasonable, continuous function is acceptable as the starting point, Ω_{start} , for numerical solution. The simplest form of Ω_{start} is

$$\Omega_{\text{start}} = \exp(U/k_B T). \quad (\text{III.5.25})$$

where U is an isotropic potential. This is the Onsager solution for an isotropic system and in (w, θ, ϕ) coordinate system is given by equation (III.5.23). An alternative starting point is the exact analogue of equation (III.5.25) with the potential referring to the anisotropic medium. This estimate is not spherically symmetric and contains initial anisotropy. This starting equation for Ω is

$$\Omega_{\text{start}}(w, \theta, \phi) = \exp \left[\left[\sum p_i / (\ln w_i)^2 \right]^{-1/2} \right] \quad (\text{III.5.26})$$

where $w_1 = w \sin \theta \cos \phi$, $w_2 = w \sin \theta \sin \phi$ and $w_3 = w \cos \theta$.

5.1.3 General comments on anisotropic recombination.

Solving the reduced equation and observing the behaviour of Ω as the ratios p_i are varied allows several observations.

i) If one of the p_i is zero, then the solution is zero for any initial position. Consider the limiting case where $p_1 = p_2 = 0$ and $p_3 = 1$. The potential is infinite in the w_1 - w_2 plane rather than just at the point $w = 0$. The inter-ion vector will diffuse freely, attracted by the w_1 - w_2 plane until it lies in that plane. Once the

vector reaches this plane it is trapped by the infinite potential and the only remaining process is lateral diffusion in the plane. This is a 2-D Wiener process and so the diffusion covers the whole of the plane (Ito & McKean, 1974). The vector must eventually reach $w = 0$ and the pair recombines. As the inter-ion vector reaches the $w_3 = 0$ plane in a finite time, whatever its initial value, the ultimate survival probability of a pair of ions is always zero. A similar explanation applies when only one of the p_i is zero, but in this case there is an axis of infinite potential and the particle is first trapped on this axis and then undergoes a 1-D Wiener process along it until it meets the origin. This discussion is only true for an attractive force.

ii) For most cases, the solution for an anisotropic medium is less than or equal to the isotropic solution

$$\Omega_{\text{aniso}}(w, \theta, \phi) \leq \Omega_{\text{iso}}(w, \theta, \phi)$$

and the two solutions approach one another as $w \rightarrow 1$.

iii) The only case where

$$\Omega_{\text{aniso}}(w, \theta, \phi) \geq \Omega_{\text{iso}}(w, \theta, \phi)$$

is when one of the p_i is close to $1/3$ and the positive deviation always occurs close to the axis corresponding to the smallest p_i . The combination of p_i ratios with maximum positive deviation is (0.235, 0.333, 0.432).

5.2 The recombination of an electron-hole pair in anthracene.

An experimental estimate of the escape probability of an electron-hole pair in anthracene is available from photoionisation studies. Using X-rays, Kepler and Coopage (1966) and Hughes (1971) found that approximately 3 keV are required to produce a pair of charge carriers. The energy required for ionisation is 30 eV (Chance & Braun, 1976). This suggests an escape probability of about 0.01. Chance and Braun (1976) predicted between 0.1% and 0.7%

survival from an indirect study with uv radiation, but rationalised an escape probability of 0.01 from an analysis of the quantum yield for photogeneration. Pope and Swenberg (1982) have analysed these results using uncorrected Onsager theory and they predict an initial separation of 5.0 nm which is independent of direction. Chance and Braun have suggested that a survival probability of 0.01 is representative of a distribution of electron-hole separations of between 1.0 and 7.0 nm depending upon the wavelength of the radiation.

5.2.1 An anisotropic treatment of recombination in anthracene.

The anthracene crystal is monoclinic (Sinclair et al., 1950) and its crystallographic axes are labelled as shown in Fig.III.5.1.

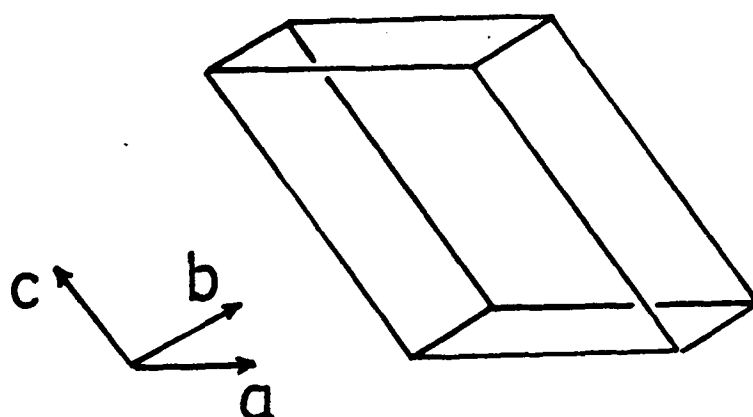


Fig.III.5.1 Crystallographic axes of anthracene.

Experimental determinations and theoretical predictions of the dielectric tensor (Munn et al., 1973) and the mutual electron-hole

mobility tensor (Thaxton et al., 1962; Katz et al., 1963) in this coordinate system (a,b,c') are

$$\underline{\epsilon} = \begin{bmatrix} 2.90 & 0 & -0.57 \\ 0 & 2.94 & 0 \\ -0.57 & 0 & 3.84 \end{bmatrix} \quad (\text{III.5.27})$$

$$\underline{\mu} = \begin{bmatrix} 2.70 & 0 & -0.0458 \\ 0 & 3.00 & 0 \\ -0.0458 & 0 & 1.20 \end{bmatrix} \quad (\text{III.5.28})$$

Errors of less than 4% are estimated in the values in $\underline{\epsilon}$, but there are considerable uncertainties in the elements of $\underline{\mu}$ and its interpretation. The matrices (III.5.27) and (III.5.28) give the p_i ratios (0.135, 0.444, 0.421) and substituting into the reduced equation (II.5.14) allows a numerical solution for the survival probability of an electron-hole pair in anthracene. Fig.III.5.2 shows contour plots of the $\phi = 0$ and the $\phi = \pi/2$ plane. The contours represent closed curves of equal probability. The plots show the importance of considering the influence of anisotropy. Onsager theory predicts contours that are concentric circles, i.e. it is only the inter-ion separation that is important and not the direction. When the spherically symmetric potential of the Onsager solution is replaced with the anisotropic potential, c.f. equation (III.5.26), the direction dependent survival probability shown in Fig.III.5.3 is obtained. Clearly neither Onsager probability is an acceptable approximation for Ω . Since an approximation for the survival probability is desirable it is worth considering a linear combination of the two Onsager probabilities, that is,

$$\Omega_{\text{approx}} = (1-\lambda) w + \lambda \exp \left[\left[\sum p_i / (\ln w_i)^2 \right]^{-1/2} \right]. \quad (\text{III.5.29})$$

Fig.III.5.2 Contour plot of escape probability of a geminate electron-hole pair in anthracene. Contours represent closed curves of equal probability: 0.01 then 0.02(0.02)0.20. Each division on the axes represents 0.02 dimensionless units. Closed curve (a) denotes the escape probability of a pair with a separation of 5.0 nm in crystallographic space.

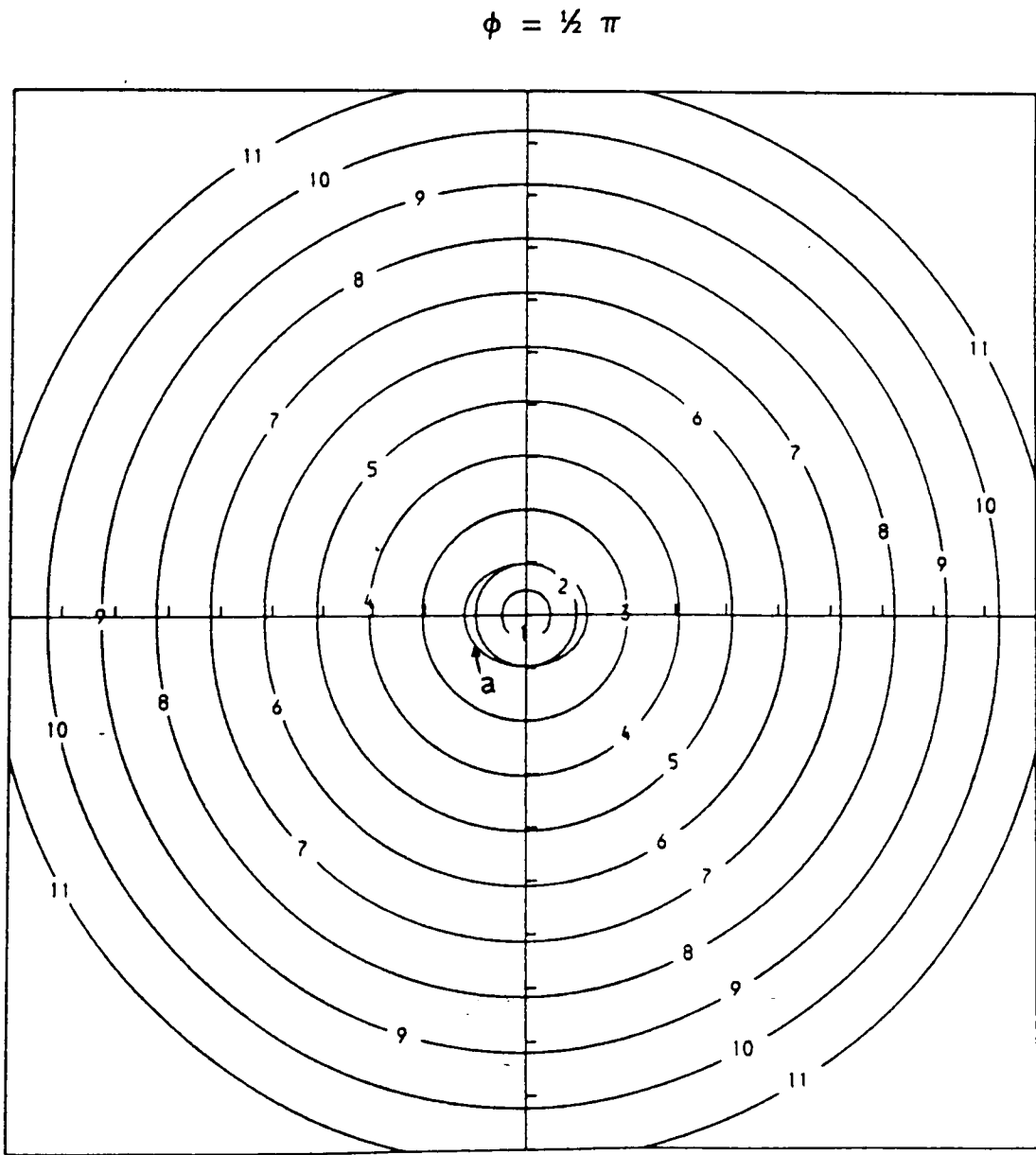
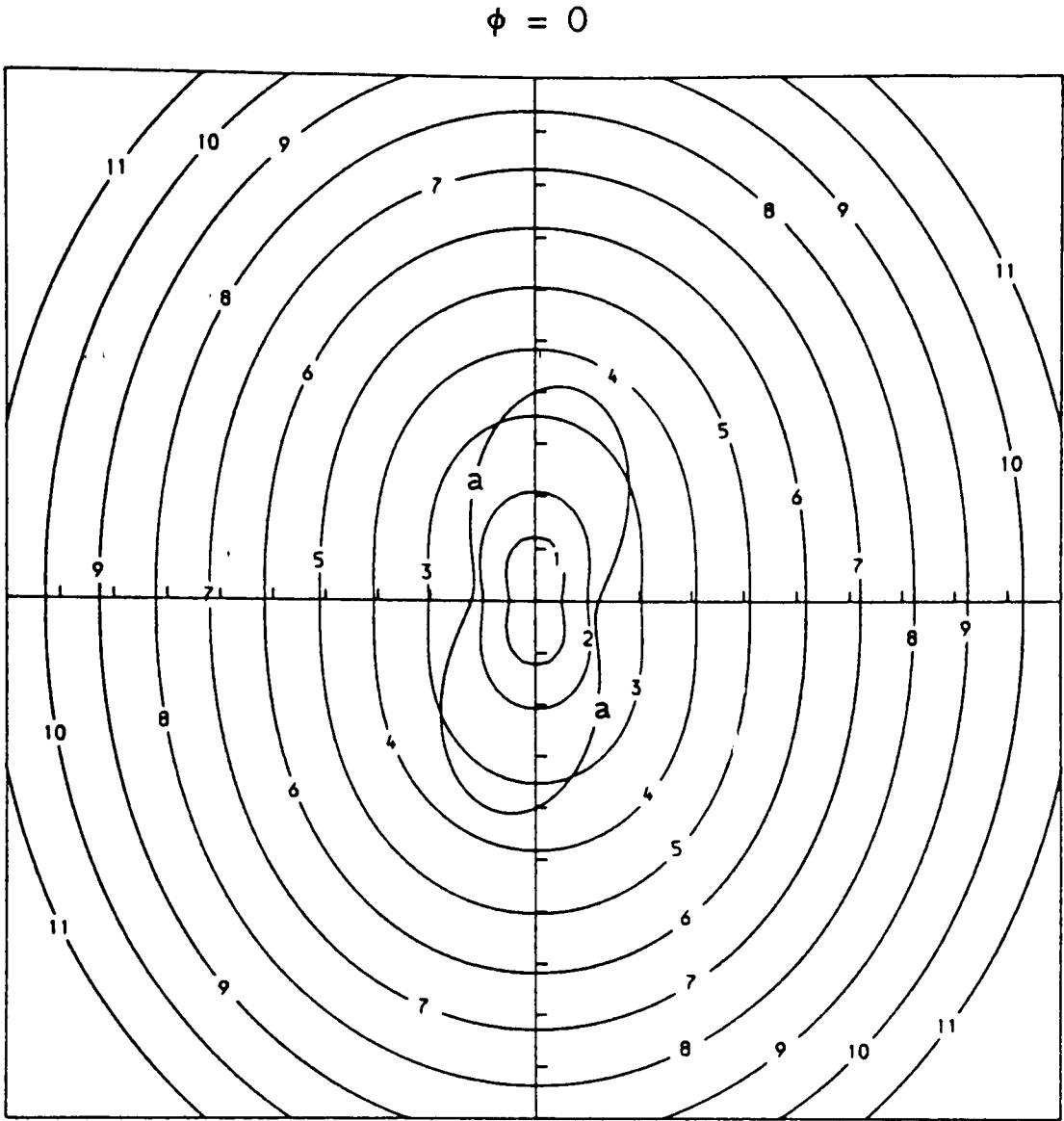
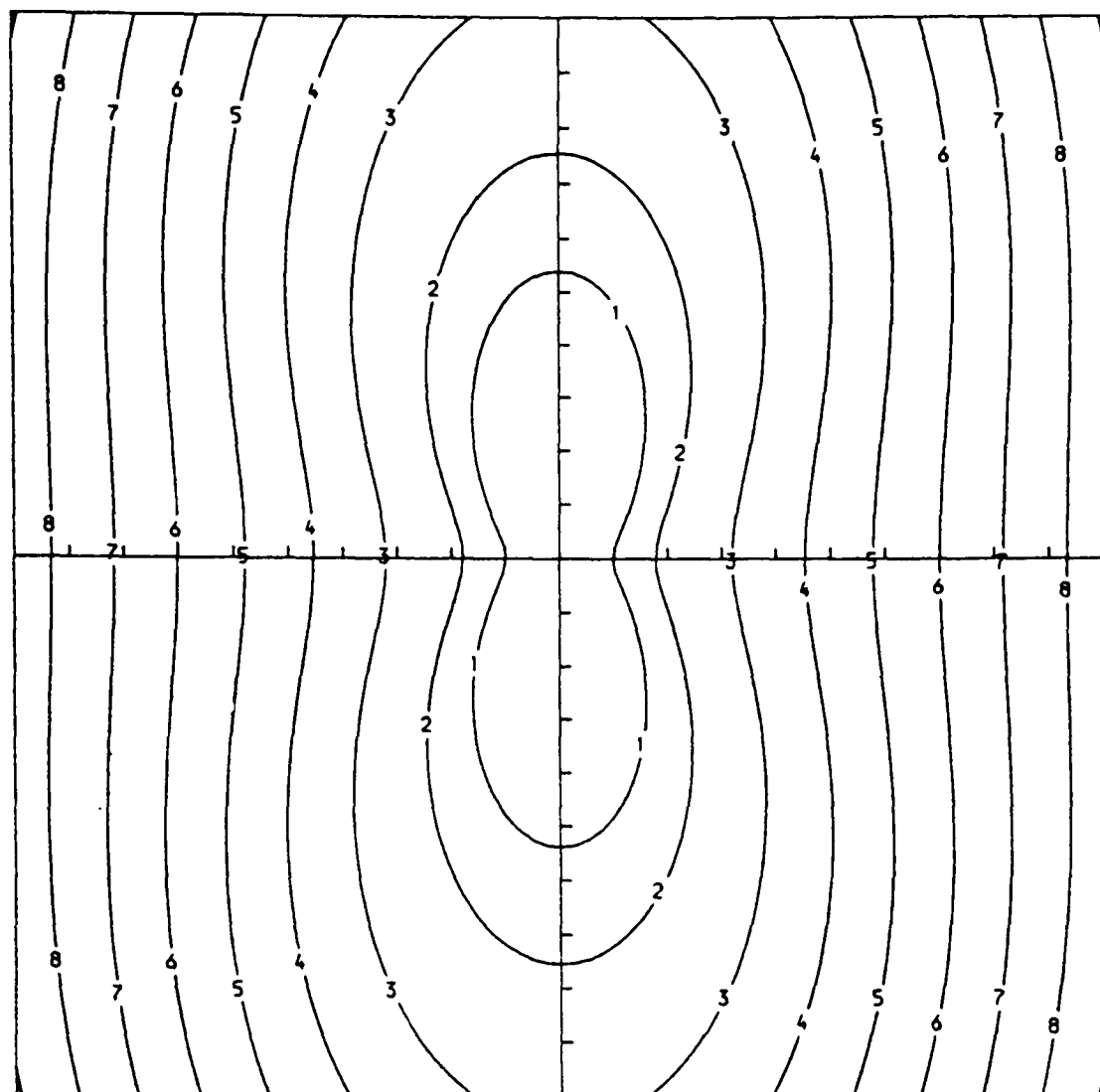
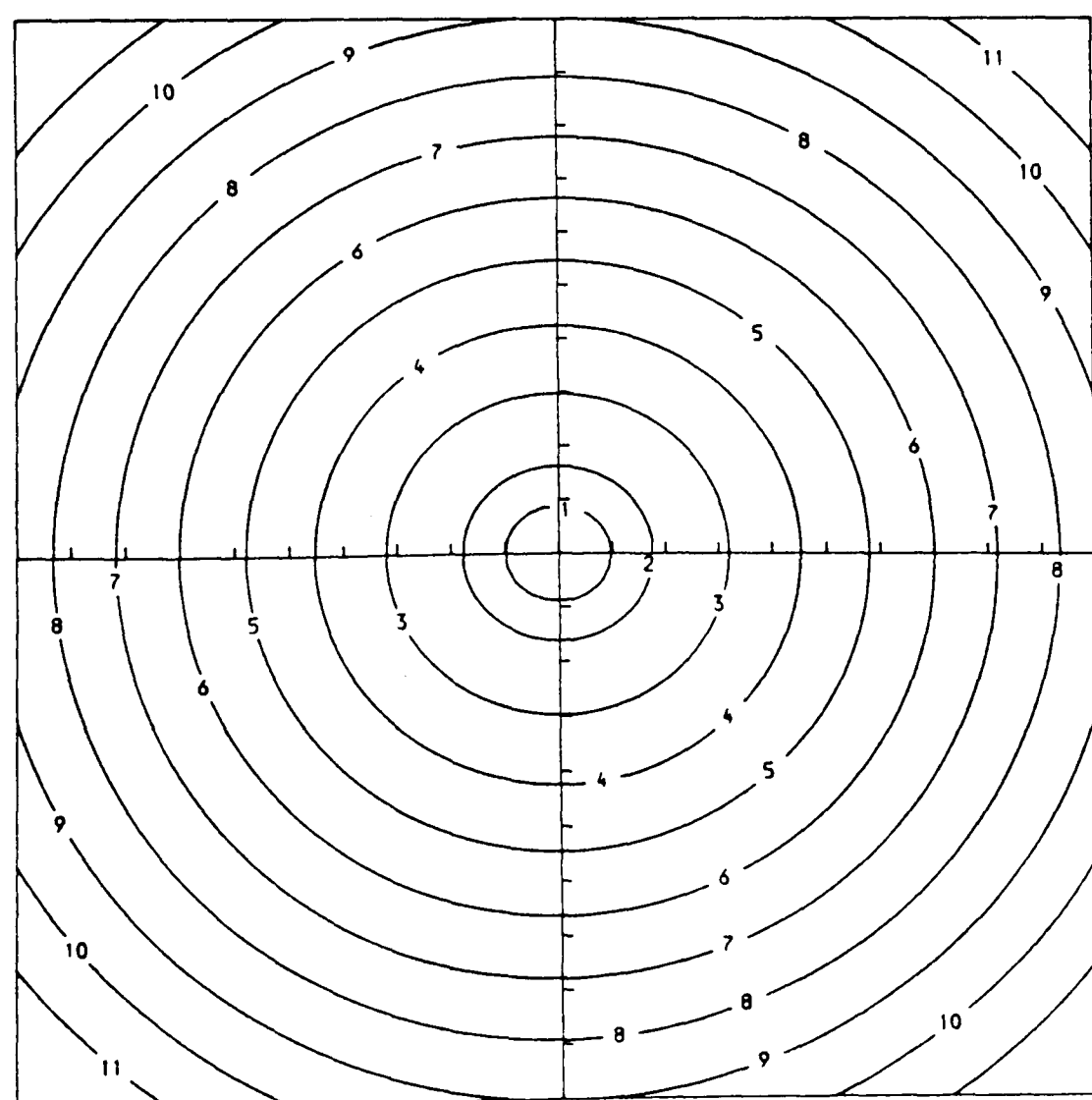


Fig.III.5.3 Contour plot of Onsager escape probability with spherically symmetric potential replaced by anisotropic potential.

$$\phi = 0$$



$$\phi = \frac{1}{2} \pi$$



The best fit of Ω_{approx} to Ω is obtained for $\lambda = 0.142$ and the contour plots are shown in Fig.III.5.4. Comparison with Fig.III.5.2 shows that the approximation is not very good and emphasises the importance of the correct treatment for detailed predictions.

5.2.2 Analysis of the anisotropic solution.

To extract information from the numerical solution for Ω , it is necessary to transform back into real space. It is not sufficient to deal solely with $\text{diag}(m'_i)$ and $\underline{D}$, $\underline{E}$, and $\text{diag}(m_i)$ must be considered. Fig.III.5.2 also includes a curve representing an escape probability of an electron-hole pair with a separation of 5.0 nm in crystallographic space. A sphere of radius $\mathcal{A}$ in this space is, in matrix notation,

$$\underline{r}^T \underline{r} = (x,y,z) \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \mathcal{A}^2 \quad (\text{III.5.30})$$

This is transformed into an ellipsoid in $\underline{u}$ space,

$$\underline{u}^T (\underline{S}^T)^{-1} \underline{S}^{-1} \underline{u} = (X,Y,Z) \begin{bmatrix} \alpha & 0 & -\beta \\ 0 & \gamma & 0 \\ -\beta & 0 & \delta \end{bmatrix} \begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = c^2 \mathcal{A}^2 \quad (\text{III.5.31})$$

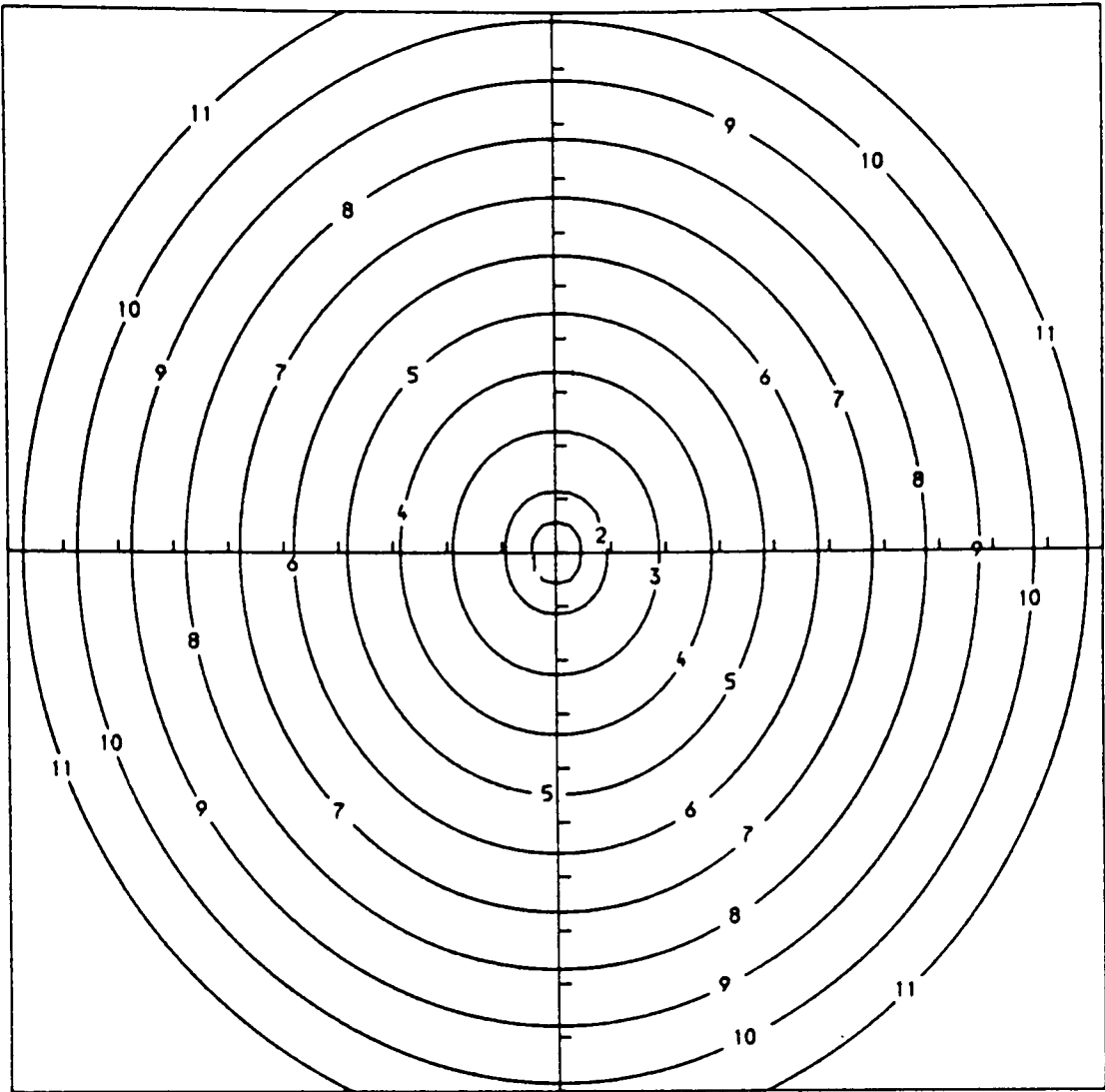
where

$$\underline{S} = \underline{P} \underline{Q}^T \text{diag}(\lambda^{-1/2}) \underline{Q} \quad (\text{III.5.32})$$

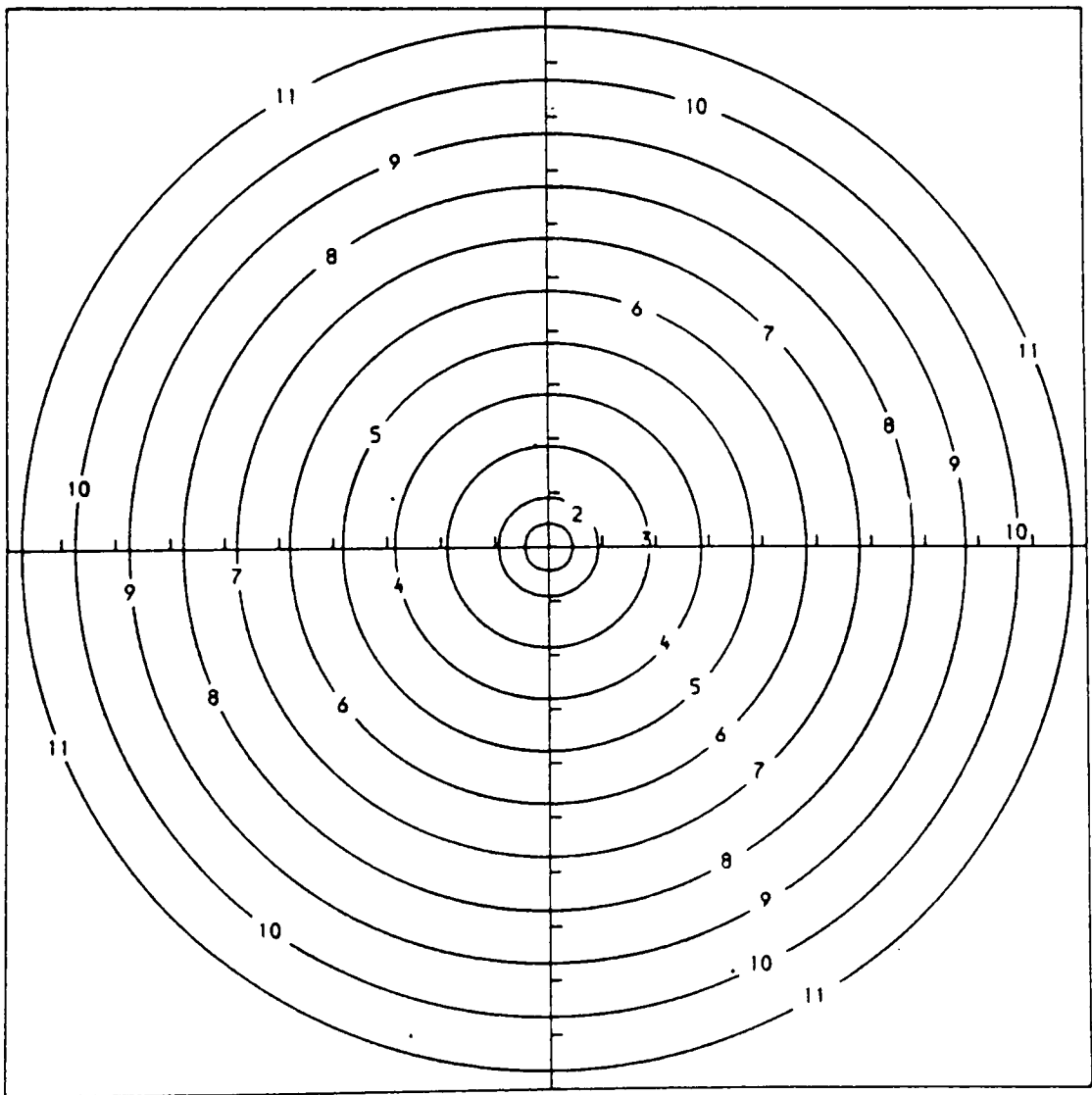
and the matrix $(\underline{S}^T)^{-1} \underline{S}^{-1}$ has the form shown because of the nature of the tensors $\underline{D}$ and $\underline{e}$. In (w,θ,ϕ) space the equation of the closed

Fig.III.5.4 Contour plot of the best fit approximation, equation (III.5.29). $\lambda = 0.142$.

$\phi = 0$



$\phi = \frac{1}{2} \pi$



surface corresponding to the original sphere is

$$c^2 \mathcal{A}^2 (\ln w)^2 = 3 (\alpha \sin^2 \theta \cos^2 \phi + \gamma \cos^2 \theta + \delta \sin^2 \theta \sin^2 \phi - 2 \beta \sin \theta \cos \theta \cos \phi) \quad (\text{III.5.33})$$

The constants α , β , γ and δ have the values 1.234, 0.228, 2.666 and 3.000 in units of $4\pi\epsilon_0$. Similar methods can be applied to any point or locus in any of the transformed coordinate spaces.

A full analysis, using the theory described above and the dielectric and mobility tensors given in equation (III.5.27) and equation (III.5.28), yields a direction dependent result. For an escape probability of 0.01 this approach predicts initial separations of 4.0 nm, 4.0 nm and 3.2 nm along the crystallographic axes a , b and c' .

5.2.3 Analysis of experimental predictions.

The experimental survival probability is an average value. It does not correspond to a single electron-hole separation, but a range of distances. If the distribution of interparticle separations is $f(\underline{r})$ then the measured probability, Ω_{expt} represents

$$\Omega_{\text{expt}} = \int f(\underline{r}) \Omega(\underline{r}) d\underline{r}. \quad (\text{III.5.34})$$

A realistic treatment of the recombination of an electron-hole pair requires integration of the numerical solution for $\Omega(\underline{r})$ over a suitable distribution of separations, $g(\underline{r})$.

$$\Omega_{\text{calc}} = \int g(\underline{r}) \Omega(\underline{r}) d\underline{r}. \quad (\text{III.5.35})$$

As the integration has to be performed numerically there is little

advantage in an analytic formulation for $g(\underline{r})$. The logarithmic transformation, $w = \exp(-\sqrt{3}/u)$, in the numerical treatment of Ω means that it is necessary to perform the integration for Ω_{calc} in the coordinate space of the distribution as the discretisation of $\Omega(w, \theta, \phi)$ causes errors if the typical separation is small or large. Integrating in the space of the distribution of separations requires the interpolation of Ω . The numerical solution $\Omega(w, \theta, \phi)$ does not vary rapidly with w , θ or ϕ so with a finely discretised solution a Lagrangian form of linear interpolation (Gerald, 1978) is acceptable. The numerical integration for Ω_{calc} is based upon the basic difference method of Grenz and Malik (1980) and is performed using NAG algorithm D01FCF. This technique does not require any assumptions about the form of the integrand.

The accuracy of this method of calculating the survival probability of an electron-hole pair with a distribution of separations can be tested by consideration of the isotropic case. An exact solution exists for a number of simple analytic distributions. If the relative positions of a pair are exponentially distributed

$$g(\underline{r}) = \frac{\lambda^3}{8\pi} \exp(-\lambda r), \quad (\text{III.5.36})$$

then the survival probability is

$$\Omega = \frac{\lambda^3}{2} \int_0^\infty r^2 \exp\left[-\lambda r - \frac{\beta}{r}\right] dr \quad (\text{III.5.37})$$

where λ is a parameter describing the 'width' of the distribution and β is a constant depending on the coordinate space of the

solution. The integral (III.5.37) has an exact and closed solution,

$$\Omega = (\lambda\beta)^{3/2} K_3(2\sqrt{\lambda\beta}). \quad (\text{III.5.38})$$

K_3 is a Bessel function of imaginary argument. The survival probability of a pair with a Gaussian distribution of relative positions is

$$\Omega = \frac{4\pi}{(\pi b)^{1.5}} \int_0^\infty r^2 \exp\left[-\frac{r^2}{b} - \frac{\beta}{r}\right] dr. \quad (\text{III.5.39})$$

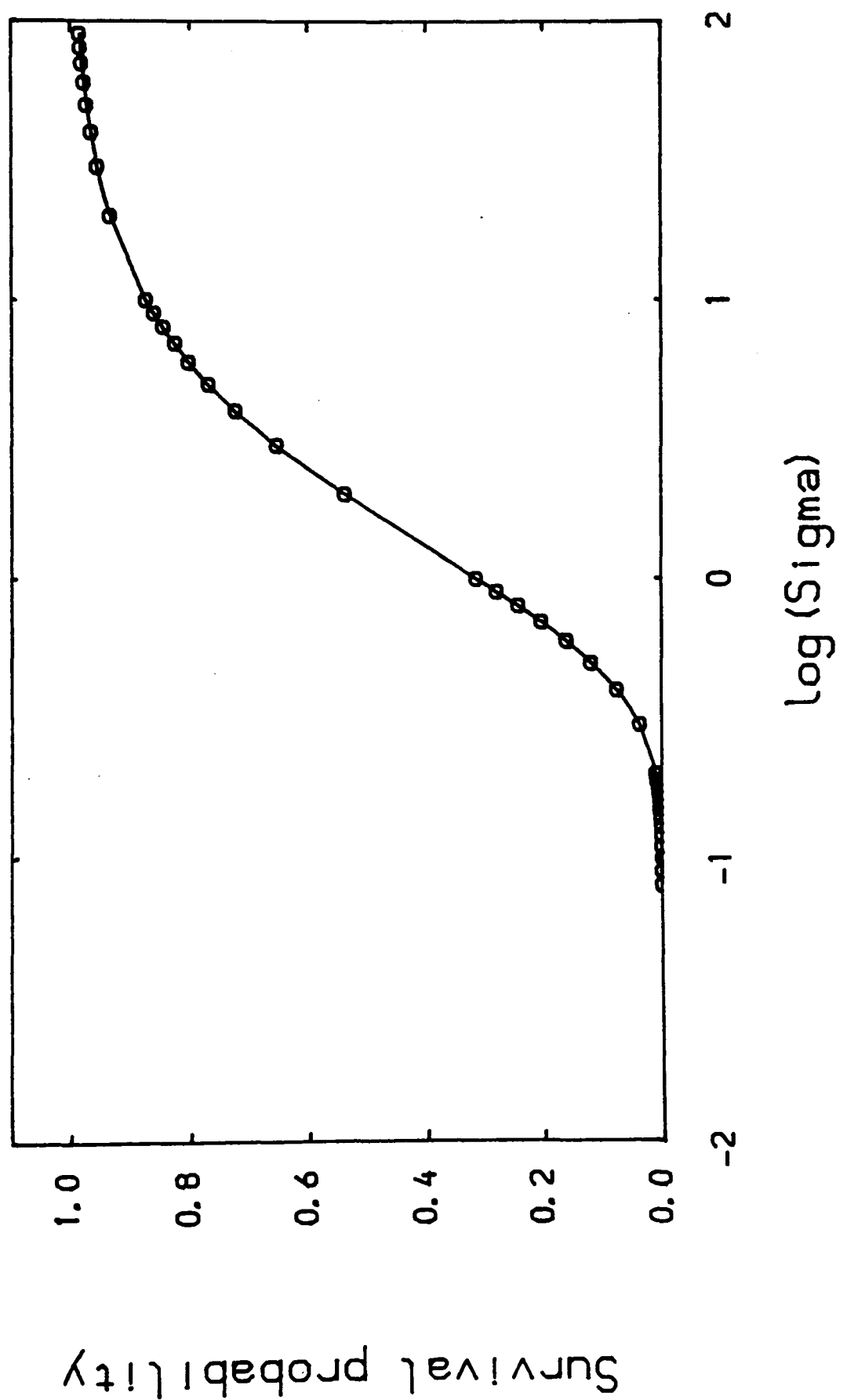
In this equation, b is twice the variance of the distribution and β has the same meaning as in equation (III.5.37). This integral does not have a closed solution, but can be split into two convergent sums,

$$\begin{aligned} \Omega = \frac{4\pi}{(\pi b)^{1.5}} & \left[\sum_i^\infty \left[-\frac{1}{\beta}\right]^i \frac{\beta^{3+2i}}{i!} \Gamma(-3-2i, \beta/y) \right. \\ & \left. + \frac{1}{2} \sum_i^\infty \frac{(-\beta)^i}{i!} b^{(3-i)/2} \Gamma(\frac{1}{2}(3-i), y^2/b) \right] \quad (\text{III.5.40}) \end{aligned}$$

y is the point in space at which the integral is split and its value only affects the rate of convergence of the sums. Fig.III.5.5 compares analytic and numerical solutions. It shows the variation of survival probability as the standard deviation of the Gaussian distribution is varied. The particular example refers to (u, θ, ϕ) space, but conversion to crystallographic space merely involves a scaling. Agreement between the two methods is excellent except when the free ion yield is very small, less than 5×10^{-4} . In this

Fig.III.5.5 Escape probability of electron-hole pair in an isotropic medium.
Relative separation has a Gaussian distribution in (u, θ, ϕ) space; $\epsilon = 3.17$.

($\circ \circ \circ \circ$) Numerical solution.
(—) Analytic solution, equation (III.5.40).



region the computation of the summation of the analytic' treatment begins to break down.

When considering an anisotropic system, the coordinate space, in which the integration is performed, is important. Fig.III.5.6 shows the escape probability of a Gaussian distribution of relative positions in (u, θ, ϕ) space and a Gaussian distribution in crystallographic space. The two distributions are not related. Also included in the figure are the predictions of uncorrected Onsager theory. A mean dielectric constant of 3.17 is used. This is obtained from the determinant of $\underline{\epsilon}$ and compares well with experimental measurements which range from 3.20 to 3.24 (e.g. Nakada, 1962; Karl et al., 1971; Chance & Braun, 1976).

5.3 The effect of an applied field.

The recombination of an electron-hole pair in a low mobility medium is influenced not only by the mutual Coulombic field, but also any applied field. In the isotropic case, the escape probability in the presence of an external field E is (Onsager, 1938)

$$\Omega(r, \theta) = 1 - S_- \left[\exp \left[\frac{r_c}{r} - \zeta(1 + \cos \theta) \right] \right] \quad (\text{III.5.41})$$

where θ is the angle between E and the initial separation vector and $\zeta = eEr/2k_B T$. The function S_- is a Laurent expansion containing only negative powers of r . For small initial separations and low electric fields this treatment predicts a linear increase in Ω with increasing field,

$$\Omega(r, \theta) = 1 - \frac{r_c}{r} [1 - \exp\{\zeta(1 + \cos \theta)\}] + O(\zeta^2). \quad (\text{III.5.42})$$

Mozumder (1974a, 1974b) used isotropic Onsager theory in a detailed

Fig.III.5.6 Escape probability of an electron-hole pair
in anthracene.
Relative separation has a Gaussian distribution.

(o o o o) Numerical solution.
(- - - -) Analytic solution for isotropic case.

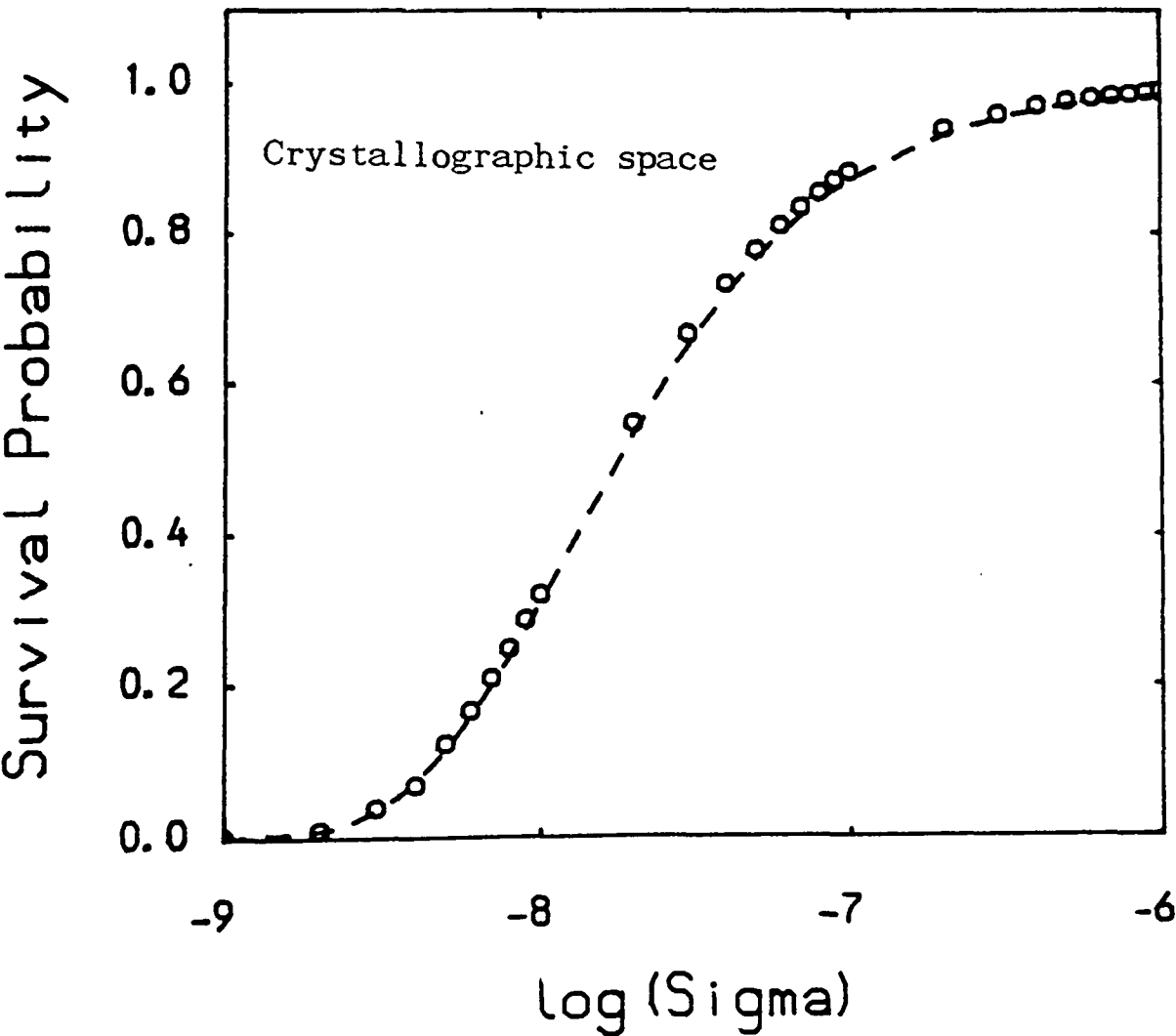
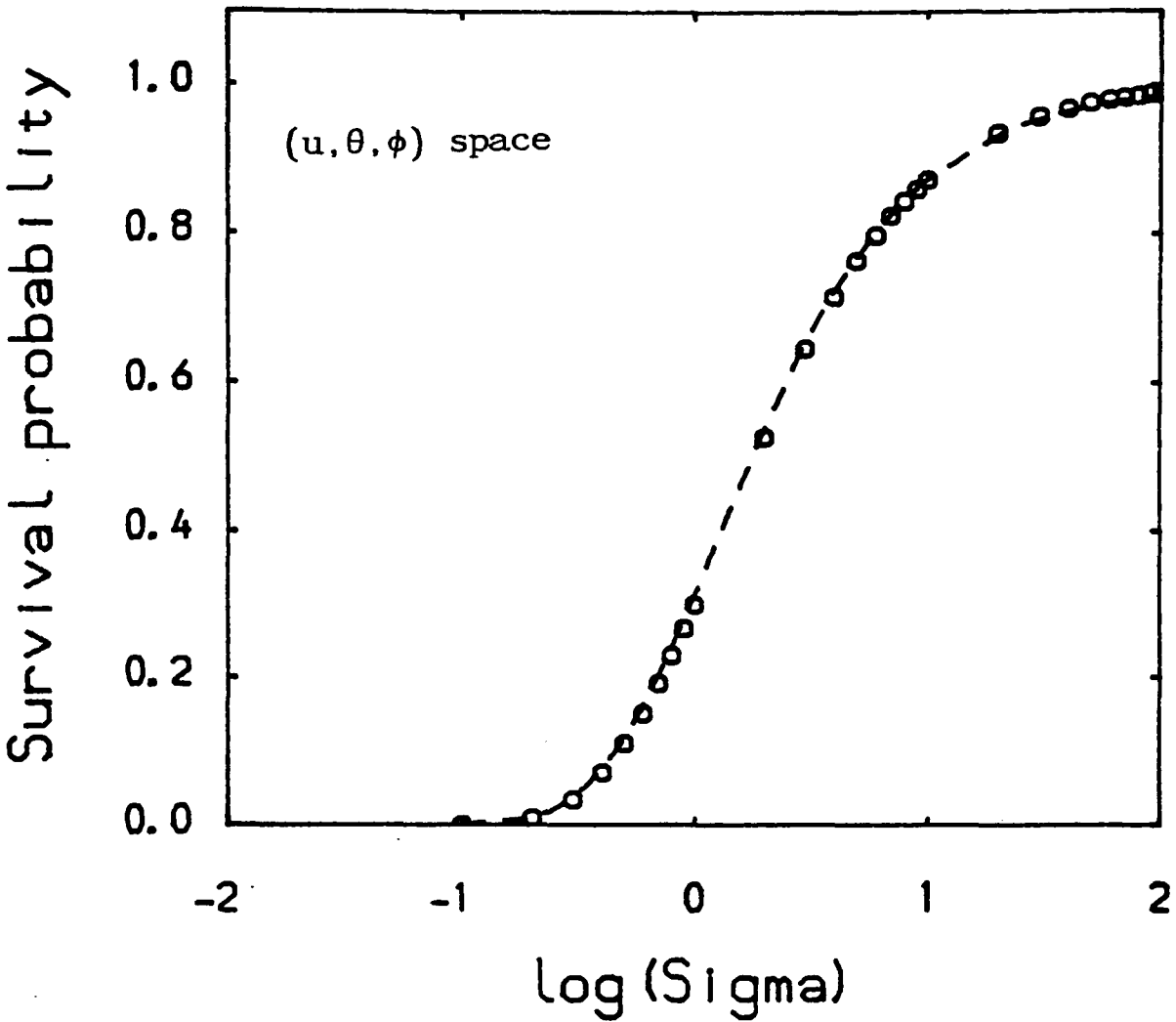
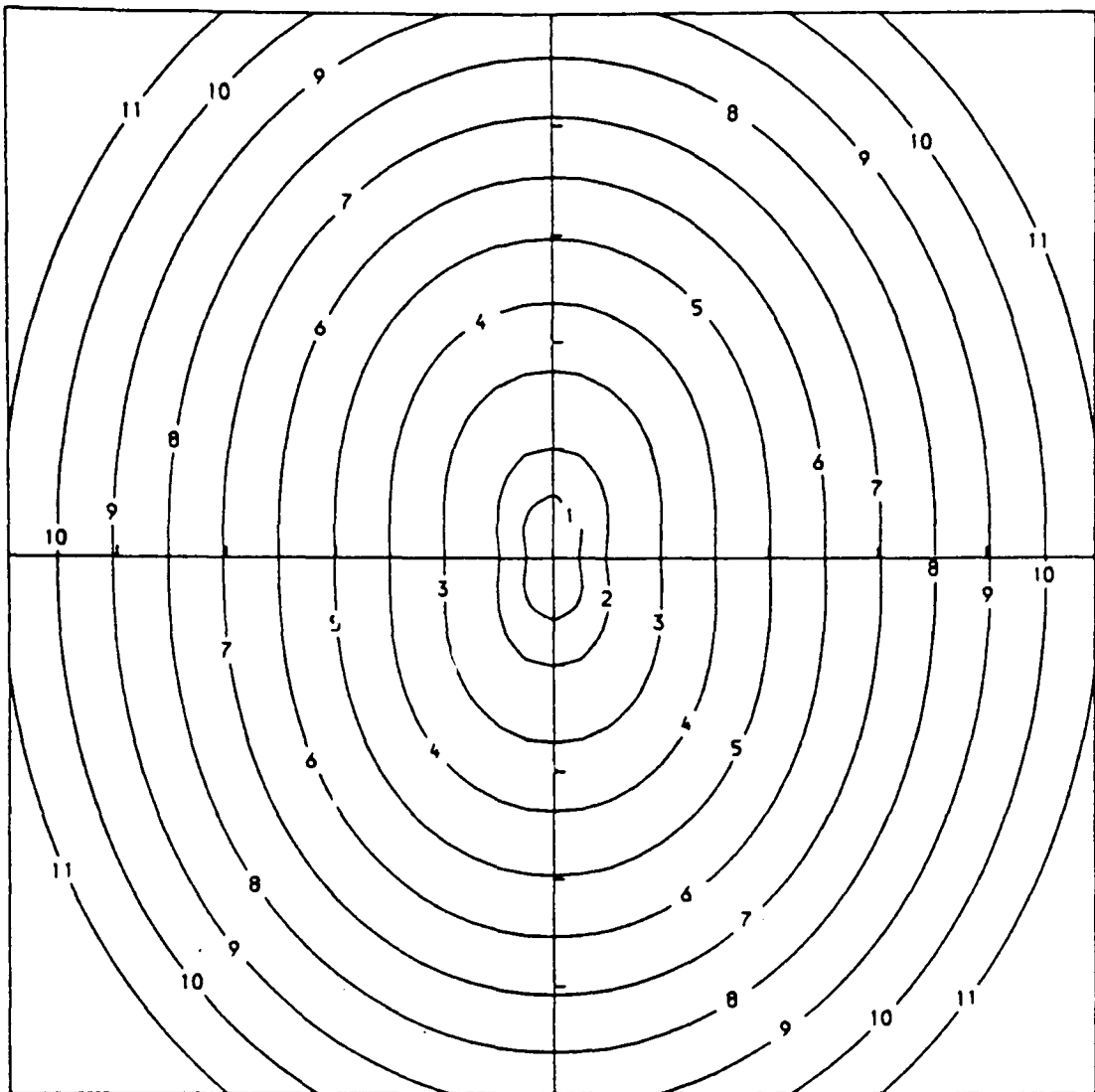
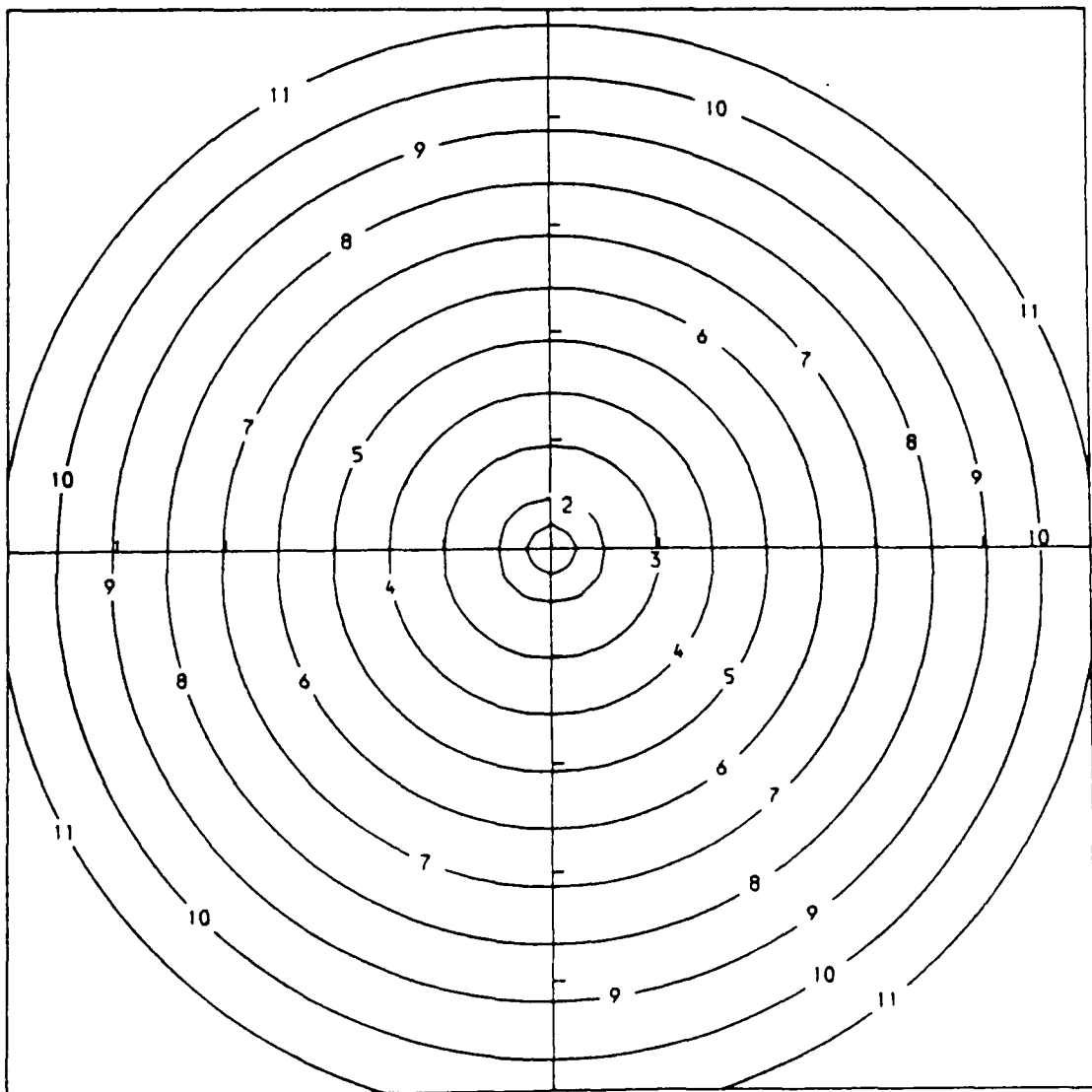


Fig.III.5.7 Effect of external electric field on escape probability of a geminate electron-hole pair in anthracene. $E = 100 \text{ keV/cm}$ along the b crystallographic axis.

$$\phi = 0$$



$$\phi = \frac{1}{2} \pi$$



study of the effect of an external field on the yield of free ions.

The presence of an external field influences the escape probability of a pair of ions in an anisotropic medium. In this case the adjoint diffusion equation describing the survival probability of the pair is

$$\nabla \cdot D \cdot \nabla \Omega - \frac{1}{k_B T} \nabla \Omega \cdot D \cdot [\nabla U + \nabla V] = 0. \quad (\text{III.5.43})$$

∇V is a vector representing the vector sum of the forces derived from the external field, i.e. $\nabla V = -\underline{F}$. Performing the same series of transformations as in the absence of an external field yields the reduced equation

$$\sum_1^3 \frac{\partial^2 \Omega}{\partial u_i^2} - \left[\sum_1^3 u_i^2 p_i \right]^{-3/2} \sum_1^3 p_i u_i \frac{\partial \Omega}{\partial u_i} + \frac{e^2}{(\sum m_i)^{1/2}} \sum f_i \frac{\partial \Omega}{\partial u_i} = 0 \quad (\text{III.5.44})$$

where $\underline{f} = \underline{p} \underline{D}^{1/2} \underline{F}$. This equation can be solved numerically in the same manner as equation (III.5.14), but cannot be described purely in terms of the ratios p_i . The solution does not have the D_{2h} symmetry shown in the absence of an external field and so it is necessary to solve the equation for the whole sphere. This loss of symmetry increases the computational cost of solution and reduces the accuracy of the result obtained as a coarser meshed lattice has to be used. The effect of an external field is shown in Fig.III.5.7. This diagram refers anthracene and an external field of 100 keV/m along the b crystallographic axis. To make comparisons with experiment, it is necessary to solve equation (III.5.44) varying the external field and to examine the effect of this variation on the escape probability of an electron-hole pair with some specific distribution.

SECTION IV : Extended Distributions.

Chapter 1 : The kinetics of overlapping clusters.

Section I introduced the period of fast kinetics that immediately follows radiolysis of a medium. The production of a nonhomogeneous distribution of reactive particles was described and the conventional methods of modelling the evolution were discussed. Section II presented an alternative stochastic approach to nonhomogeneous kinetics. The full random flights simulation of diffusion and reaction was introduced and two approximate models, based upon an independent pairs approximation, were developed. These new techniques were tested by examining the kinetics of small idealised clusters of reactive particles. Section III considered the stochastic modelling of realistic radiolysis kinetics. The chemistry of a low LET electron track was modelled using a distribution of cluster sizes and an idealised track structure. In principle, the kinetics of any radiolysis system can be modelled given a detailed description of the nonhomogeneous particle distribution, but the computational expense means that, practically, this is not the case. Track structure calculations and kinetic simulation of the resulting particle distribution are non-trivial undertakings. This chapter considers more acceptable methods of modelling extended nonhomogeneous systems similar to those encountered in high LET radiolysis. Conventional deterministic models are examined and improved. The correct time-dependent rate coefficient for modelling is discussed. The stochastic modelling of an extended distribution is considered.

1.1 Extended distributions.

The isolated cluster is the traditional model used in evaluating the kinetics of low LET radiolysis systems. For higher LET radiation, this description will not suffice and the spatial distribution of the reactive particles is more appropriately expressed in terms of either enlarged clusters or a cylindrical core (depending upon the conditions). The conventional modelling of all nonhomogeneous kinetics is based upon the solution, by numerical or approximate techniques, of a set of coupled diffusion-reaction equations that describe the evolution of the system, c.f. chapter I.2

$$\frac{\partial C_i}{\partial t} = D_i \nabla^2 C_i - \sum_j k_{ij} C_i C_j + \sum_{j,k} k_{jk} C_j C_k. \quad (\text{IV.1.1})$$

The concentration profile, C_i , of each species depends upon the physical picture of the nonhomogeneous system that is used.

In examining the stochastic kinetics of nonhomogeneous systems the diffusive and reactive development of the constituent particles is modelled. Statistical effects have been shown to be very important in the small clusters, but the influence that these effects will have on the kinetics of extended systems is not obvious. The kinetic simulation of small clustered systems is computationally expensive if a full treatment of the diffusion and reaction processes is required and even approximate IRT modelling becomes costly if the number of particles is excessive. To examine extended systems using stochastic techniques a reformulation of the problem using new boundary conditions may be necessary to avoid the need for excessive computer resources. Any such development must be

tested rigorously to ensure that the accuracy of the simulated kinetics is not affected.

1.2 Deterministic kinetics.

In the conventional modelling of high LET radiolysis kinetics, two descriptions for the radiation track have been suggested; a column which has an axially homogeneous concentration, but a radial concentration profile (Jaffe, 1913) and a linear arrangement of spherically symmetric clusters (Samuel & Magee, 1953; Ganguly & Magee, 1956). The cylindrical system, because of its symmetry and the resultant simplifications in the mathematics, has received a great deal more attention than the 'string of beads' description, but both types of track are amenable to approximate analytic and numerical analysis.

The recombination kinetics, $A + B \longrightarrow AB$, of a cylindrical system were considered analytically in Jaffe's paper. Assuming a prescribing Gaussian profile - the prescribed diffusion approximation - and no interparticle forces, the number of particles surviving per unit length of track, N , is

$$\frac{N}{N_0} = \left[1 + \frac{kN_0}{8\pi D} \ln \left(\frac{b}{b_0} \right) \right]^{-1} \quad (\text{IV.1.2})$$

where

$$b^2 = 2(\sigma^2 + 2Dt) \quad ; \quad b_0^2 = 2\sigma^2 = 4Dt_0 \quad (\text{IV.1.3})$$

and σ^2 is the variance of the radial Gaussian distribution. An analytic treatment of the recombination kinetics of a linear arrangement of clusters has not been presented, but modification of the approach used by Ganguly and Magee to study recombination in the presence of a scavenger is straightforward. If the track is an

arrangement of n initially identical clusters and each has $v(\tau)$ particles in a spherically symmetric Gaussian distribution, the diffusion-reaction equation describing the kinetics is

$$\frac{\partial C}{\partial t} = D \nabla^2 C - k C^2 \quad (\text{IV.1.4})$$

and the concentration profile of A and B in cylindrical polar coordinates is

$$C(r, z, \tau) = (4\pi D \tau)^{-1.5} \exp\left[-\frac{r^2}{4D\tau}\right] \sum_{i \neq j}^n v_i(\tau) \exp\left[-\frac{(z-z_i)^2}{4D\tau}\right] \quad (\text{IV.1.5})$$

where $\tau = t + t_0$ and z_i is the centre of the i th cluster. If it is assumed that $v_i(\tau)$ is the same in every cluster, then integrating equation (IV.1.4) over all space gives the kinetic equation

$$\begin{aligned} \frac{dN}{dt} &= k \int_V C^2 dV \\ &= \frac{kN^2}{n(8\pi D \tau)^{1.5}} \left[1 + \frac{1}{n} \sum_{i \neq j}^n \exp\left[-\frac{(z_i - z_j)^2}{8D\tau}\right] \right] \end{aligned} \quad (\text{IV.1.6})$$

where $N = \sum_{i=1}^n v_i(\tau) = n v(\tau)$. The number of particles surviving at time t is,

$$\frac{N}{N_0} = \left[1 + \frac{kN_0}{n(8\pi D)^{1.5}} \int_{t_0}^{t+t_0} \tau^{-1.5} \left[1 + \frac{1}{n} \sum_{i \neq j}^n \exp\left[-\frac{(z_i - z_j)^2}{8D\tau}\right] \right] d\tau \right]^{-1} \quad (\text{IV.1.7})$$

This is equivalent to Ganguly and Magee's equation (10). If the separations between clusters are Poisson distributed with mean $\langle \ell \rangle$ and the total length of the track is $n\langle \ell \rangle$, then the integral becomes

$$\frac{N}{N_0} = \left[1 + \frac{kN_0}{8\pi Dn} \left[\sqrt{\frac{2}{\pi}} \left(\frac{1}{b_0} - \frac{1}{b} \right) + \langle \ell \rangle \ln \left(\frac{b}{b_0} \right) \right] \right]^{-1} \quad (\text{IV.1.8})$$

The parameter b now refers to the width of the spherically symmetric Gaussian clusters rather than the cylindrically symmetric Gaussian core in the equation (IV.1.2). This formulation reduces to the Jaffe equation for a cylinder as $\langle \ell \rangle$ becomes small and to the equation of Lea for an isolated cluster, equation (I.2.24) when n is one and $\langle \ell \rangle$ (obviously) is infinite. The kinetics of many-species tracks have been modelled using the prescribed diffusion approximation assuming both a cylindrical (Schwarz, 1969) and a 'string of beads' structure (Burns & Curtis, 1972).

Numerical treatment of the recombination kinetics of a cylindrical track was performed by Kupperman and Belford (1962a, 1962b) and this approach has been extended to more complicated reaction schemes, the most recent numerical model being that of Burns et al. (1984). This model divides the reaction space into a number of cells. Initially each cell contains the number of reactants prescribed by the spatial profile, but the concentration within the cell is homogeneous. The development of the nonhomogeneous system is modelled by allowing reaction within the cells and diffusion between cells according to macroscopic rules. The precision with which this numerical model represents the

conventional nonhomogeneous kinetics is determined by the size of the cells used.

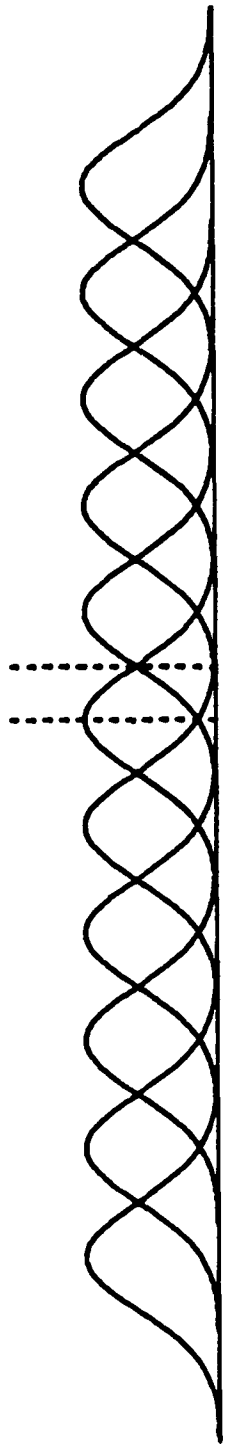
Modelling the kinetics of a linear arrangement of randomly spaced clusters using numerical methods is not straightforward. The increase in difficulty, over the cylindrical track, is a consequence of the loss of axial homogeneity. Numerical modelling requires a specific spatial distribution of clusters and to obtain the conventional kinetics of a truly random distribution of separations requires either the analysis of an extended series of clusters or the averaging of the kinetics of numerous small, and different, track sections. Neither approach is entirely satisfactory. The axial discretisation of a large track section is subject to significant discretisation error and the resulting nonhomogeneous kinetics are inaccurate. Averaging a number of small track sections is expensive in terms of computer resources and may introduce edge effects if unacceptable boundary conditions are used.

The conventional kinetics of a linear arrangement of clusters can be modelled using numerical methods if the symmetry of the system is increased. If the clusters along the track are assumed to be equidistant and identical, then a repeating unit is introduced. This is shown schematically in Fig.IV.1.1. For a chain of $2n+1$ clusters, the concentration at the centre of the track is

$$C_i(r, z, \tau) = \frac{C_0}{(4\pi D\tau)^{-1.5}} \exp\left[-\frac{r^2}{4D\tau}\right] \exp\left[-\frac{z^2}{4D\tau}\right] \\ \times \left[2 \sum_{i=1}^n \exp\left[-\frac{(il)^2}{4D\tau}\right] \cosh\left[\frac{ilz}{2D\tau}\right] + 1 \right] \quad (\text{IV.1.9})$$

(This relationship applies to every cluster if the track is

Equidistant repeating clusters.



Half spur.

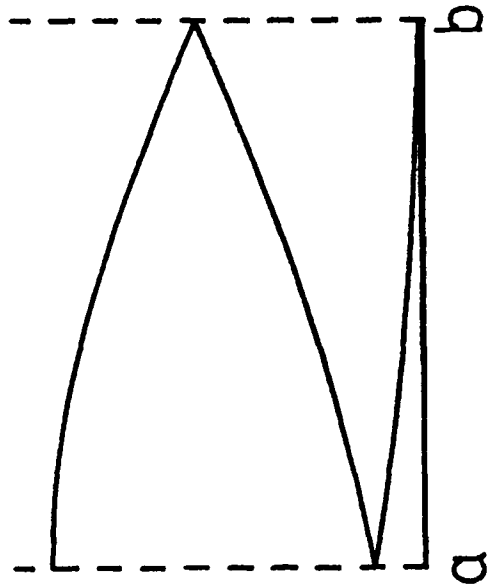


Fig. IV.1.1.1 Schematic representation of a series of equidistant repeating clusters and a half spur.

infinite.) To model the conventional kinetics of the track, it is only necessary to consider the 'half spur' region ab and enforce a reflecting boundary condition at a and b. The evaluation of the kinetics has been reduced to a restricted two dimensional problem and numerical modelling is possible using an extension of the techniques suggested by Burns et al. (1984). First, the half spur is divided into (p x q) zones prescribed by the radial mesh

$$r_j = h_r(K^j - 1) \quad ; \quad j = 0, 1, 2, \dots, p-1, p \quad (\text{IV.1.10})$$

and the axial mesh

$$z_k = kh_z \quad ; \quad j = 0, 1, 2, \dots, q-1, q \quad ; \quad b - a = qh_z \quad (\text{IV.1.11})$$

where h_r , h_z and K are constants that determine the discretisation of the problem (h_r and h_z) and the radial width of the system (h_r and K). The amount of reactant i in a cell is therefore

$$n_i(j,k) = C_i(r'_j, z'_k, \tau) V_{jk}, \quad (\text{IV.1.12})$$

the product of the concentration at its effective centre (r'_j, z'_k)

$$r'_j = (K^{(j-1/2)} - 1) h_r \quad ; \quad z'_k = (k - \frac{1}{2}) h_z \quad (\text{IV.1.13})$$

and its volume

$$V_{jk} = \pi (r_j^2 - r_{j-1}^2) h_z. \quad (\text{IV.1.14})$$

As diffusion between cells is assumed to obey Fick's law the flux

across a radial boundary is

$$f_{i,j}^r = \frac{2D_i r_j}{(r_{j+1}' - r_j')} \left[\frac{n_i(j,k)}{(r_j^2 - r_{j-1}^2)} - \frac{n_i(j,k+1)}{(r_{j+1}^2 - r_j^2)} \right] \quad (\text{IV.1.15})$$

and across an axial boundary is

$$f_{i,k}^a = \frac{2D_i}{h_z^2} \{ n_i(j,k) - n_i(j,k+1) \} \quad (\text{IV.1.16})$$

The boundaries z_0 and z_q are reflecting and there is only mass transfer in the directions $z_0 \rightarrow z_1$ - and $\rightarrow z_{q-1} \rightarrow z_q$. A similar restriction is enforced at r_0 , but at r_p reactants escape to the bulk and there is no replenishment - an absorbing boundary.

The recombination kinetics, $A + B \rightarrow AB$, of an 'infinite' string of 2A/2B clusters are shown in Fig. IV.1.2. The kinetics predicted by the approximate prescribed diffusion formulation for this string of clusters, equation (IV.1.2), is also included. Agreement between the two models is acceptable. This is not a test of the validity of the deterministic treatment, only of the consistency within the limitations of a conventional approach. The following diagram, Fig. IV.1.3 compares the kinetics of the cylindrical and string of beads descriptions of a radiation track. For fair comparison, the average reactant density is the same for both systems, i.e.

$$N_0(\text{cylinder}) = \frac{N_0(\text{string})}{n\langle\ell\rangle}.$$

The agreement between the two approaches depends upon the parameters selected.

1.2.1 Time-dependent rate coefficients.

The deterministic treatment of nonhomogeneous kinetics was discussed critically in chapter I.2. One of the deficiencies cited

Fig.IV.1.2 String of two-pair clusters.



Initial profile of reactant within a cluster is an iid Gaussian, $\sigma = 1.0$ nm; $\langle \ell \rangle = 2.0$ nm; $R = 1.0$ nm; diffusion coefficients are $5.0 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$.

(—) Prescribed diffusion.
(o o o o) Numerical solution.

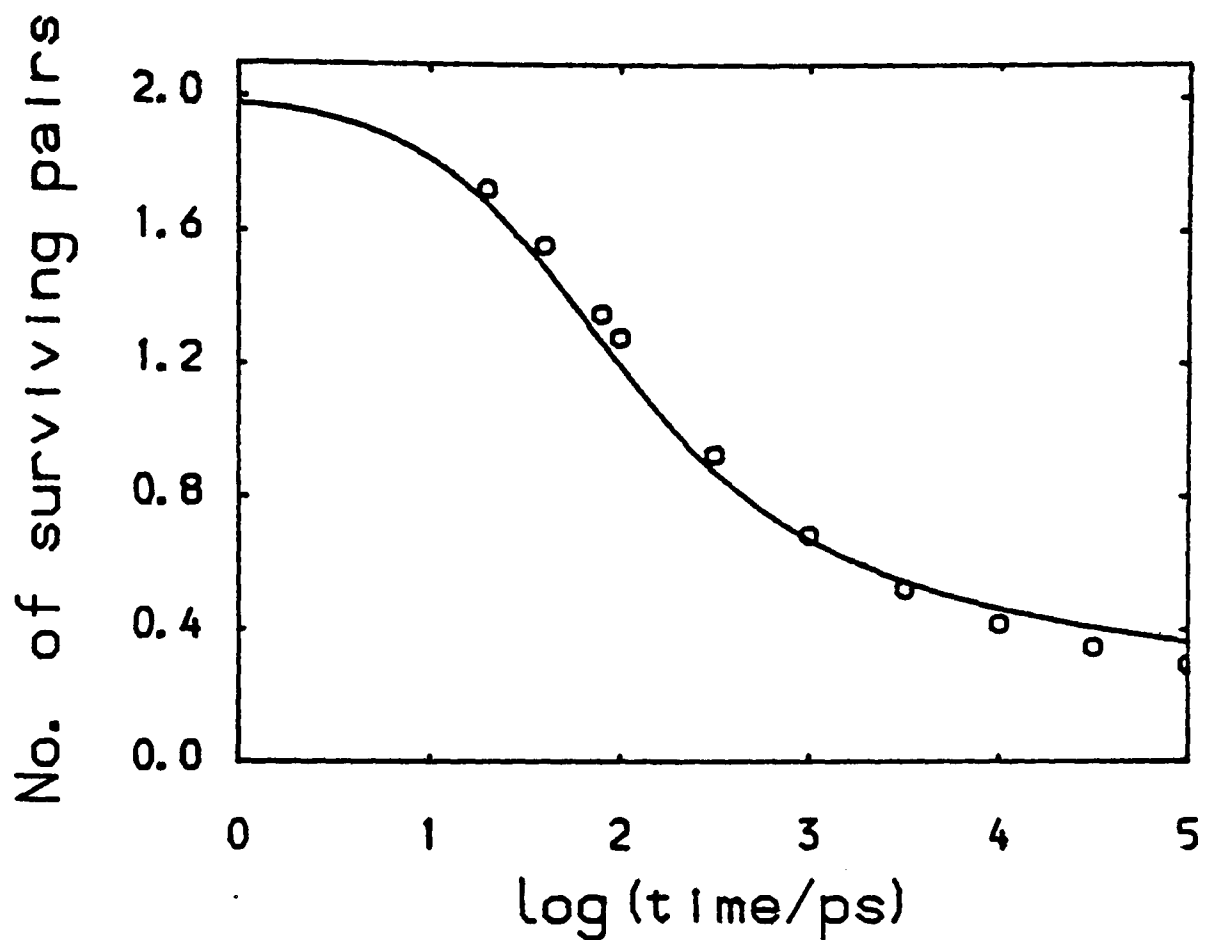
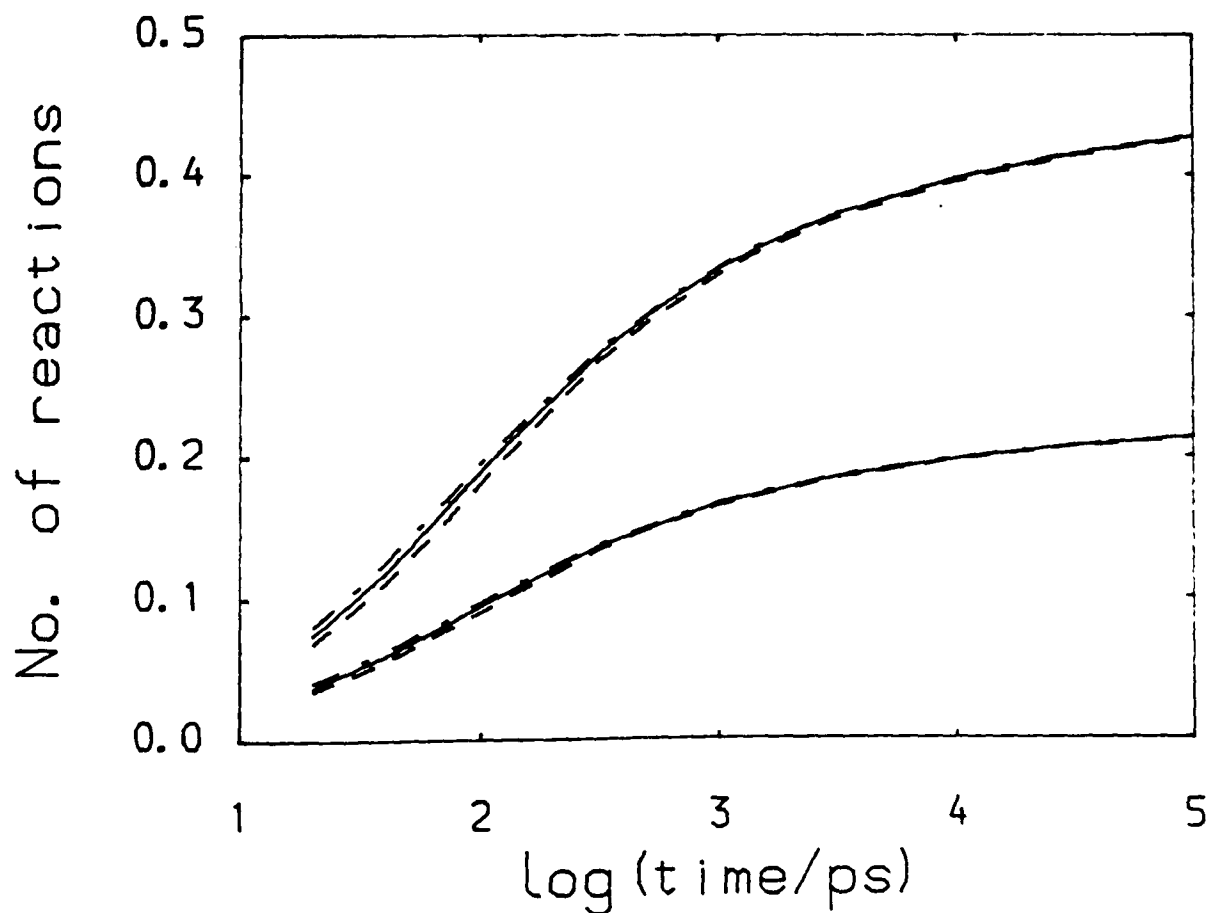


Fig.IV.1.3 Deterministic kinetics of an extended distribution.



Axial particle density is 5×10^8 pairs per m; reaction distances all 1.0 nm; diffusion coefficients are $5.0 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$.

(—) Cylindrical description.
(---) String of clusters with $\langle \ell \rangle = 2.0$ nm and $N = 1$.
(- · - ·) String of clusters with $\langle \ell \rangle = 4.0$ nm and $N = 2$.



was the use of rate constants measured under steady-state conditions and with time dependences appropriate to homogeneous distributions. In principle, the correct time-dependent rate coefficient for any distribution is accessible as the reaction probability of a pair of particles is related to the rate constant through the independent pairs assumption (Steinberg & Katchalski, 1968). Green (1982) has shown that

$$k(t) = \int_{\underline{r}} g(\underline{r}) \frac{\partial}{\partial t} W(\underline{r}, t) d\underline{r} \quad (\text{II.3.17})$$

where $W(\underline{r}, t)$ is the time-dependent probability that a pair with initial separation $\underline{r}$ will react and $g(\underline{r})$ is the ratio of the 'local' to 'bulk' concentration. When applied to a uniform concentration, the rate coefficient

$$k(t) = k_2 \left[1 + \frac{R}{\sqrt{\pi D' t}} \right] \quad (\text{IV.1.18})$$

is obtained. This is the time dependence conventionally used in deterministic modelling (Schwarz, 1969) and was originally derived by Smoluchowski (1917).

The correct time-dependent rate coefficient for use with an isolated Gaussian cluster has been derived (Clifford et al., 1982a), but no consideration has been given to the rate constants applicable to the extended systems used in modelling high LET kinetics. For a cylindrical track, the ratio $g(\underline{r})$ has the form

$$g(\underline{r}) = \mathcal{A} \exp \left[- \frac{x^2 + y^2}{2\sigma^2} \right] = \mathcal{A} \exp \left[- \frac{r^2 \sin^2 \theta}{2\sigma^2} \right] \quad (\text{IV.1.19})$$

where $\mathcal{A}$ is a constant and the rate coefficient is described by the integral

$$k(t) = \mathcal{A} \int_R^\infty \int_0^\pi \int_0^{2\pi} \frac{\partial W}{\partial t} \exp\left[-\frac{r^2 \sin^2 \theta}{2\sigma^2}\right] r^2 \sin \theta \, d\phi \, d\theta \, dr. \quad (\text{IV.1.20})$$

An analytic solution of this equation has not been found even for the diffusion-controlled reaction of uncharged particles, though in this simple case the integral does simplify to

$$k(t) = \mathcal{A} R \pi \sqrt{\frac{8\pi}{D' t^3}} \int_0^\infty r \exp\left[-\frac{r^2}{4D' t}\right] F\left[\frac{r+R}{\sigma\sqrt{2}}\right] dr \quad (\text{IV.1.21})$$

which can be evaluated numerically using the algorithm of Gautschi (1969) for Dawson's Integral, $F(x)$,

$$F(x) = e^{-x^2} \int_0^x e^{z^2} dz = \frac{1}{2} \sqrt{\pi} e^{-x^2} \gamma^*(1/2, -x^2). \quad (\text{IV.1.22})$$

This integral behaves as (Lebedev, 1972)

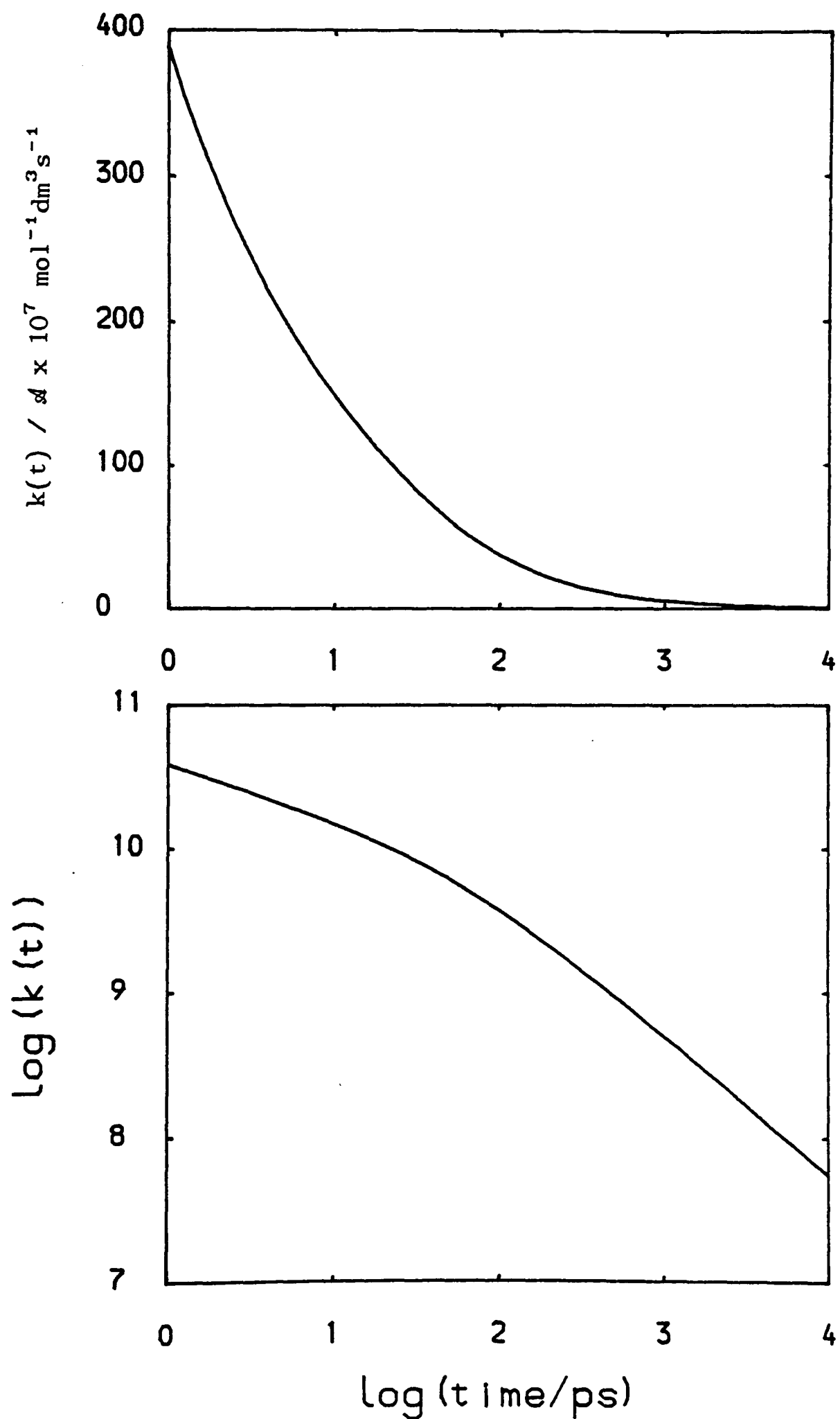
$$F(x) \simeq x \quad \text{for small } x$$

$$F(x) \simeq \frac{1}{2x} \quad \text{for large } x$$

No exact, or simple approximate, solution of equation (II.3.21) has been found. The behaviour of $k(t)$ for a system of recombining particles, $A + B \longrightarrow AB$, is shown in Fig. IV.1.4. The short and long time behaviour are proportional to $1/\sqrt{t}$ and $1/t$ respectively the asymptotes of the integral.

Treating the string of beads description of a radiation track in the same manner as the axially homogeneous cylinder yields an

Fig.IV.1.4 Time-dependent rate coefficient for an initially cylindrical concentration profile.
 $R = 0.5 \text{ nm}$; $D' = 1.0 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$.



analytic expression for $k(t)$, which is derived in appendix F. For $2n$ equidistant and identical clusters arranged in a line, the rate coefficient is a sum of exponentials and error functions,

$$k(t) = \mathcal{A}' \nu \frac{R\sigma^2}{A} \sqrt{\frac{\pi}{D't^3}} \sum_{i=0}^n \frac{1}{z_i} \left[e^{-C} \left[1 - B \sqrt{\pi} e^{B^2} \operatorname{erfc}(B) \right] - e^{-E} \left[1 - D \sqrt{\pi} e^{D^2} \operatorname{erfc}(D) \right] \right] \quad (\text{IV.1.23})$$

where

$$A = \frac{\sigma^2 + 2D't}{4D't\sigma^2}$$

$$B = \frac{R-z_i}{\sigma} \sqrt{\frac{D't}{\sigma^2 + 2D't}} \quad ; \quad C = \frac{(R-z_i)^2}{2\sigma^2}$$

$$D = \frac{R+z_i}{\sigma} \sqrt{\frac{D't}{\sigma^2 + 2D't}} \quad ; \quad E = \frac{(R+z_i)^2}{2\sigma^2}$$

and z_i is the centre of the i th cluster,

$$z_i = (i + 1/2) \ell.$$

$\mathcal{A}'$ is a constant fulfilling the same role as $\mathcal{A}$ in equation (IV.1.19). The inclusion of time-dependent rate coefficients in conventional kinetic models for high LET radiation chemistry is not simple. The expression for $k(t)$ for a cylindrical track is an integral that has to be evaluated numerically and the coefficient for a string of clusters track is a complicated summation. It is necessary to evaluate $k(t)$ as a function of time or to introduce a simple approximation for the time dependence.

1.3 Stochastic kinetics.

In principle, the stochastic simulation of the kinetics of an extended nonhomogeneous distribution of reactive particles is straightforward and it is only a matter of increasing the size of the system. Whilst conceptually simple, this approach is of limited practical use as the cost in terms of both central processor time and virtual memory requirement soon becomes excessive. The kinetic simulation of an idealised track was considered in chapter III.4. This study referred specifically to the IRT model. Full random flights modelling is only computationally feasible if the nonhomogeneous system can be simplified in some way. This simplification might be the application of some form of periodic boundary or the division of the original system into a group of subsystems.

The cylinder and string of beads pictures of a high LET radiolysis track, used in the conventional studies described previously, contain very little spatial information and rely upon a 'continuum' description of the nonhomogeneous concentration profile. A stochastic treatment of the kinetics of an extended system requires precise spatial information. The distribution used must have the same properties as its conventional equivalent: LET, initial concentrations and so on. An approximate particle distribution can be generated solely to match the macroscopic properties - a simple core of particles with the axial coordinate generated from a uniform distribution and the initial radial positions determined by a nonhomogeneous prescription. This makes no allowance for the microscopic detail of the energy deposition processes and takes no account of the spatial correlations between sibling particles generated from the same fragmentation. These effects can be included to some extent by treating the track as a

series of clusters. Obviously, the most complete description of a radiation track is in terms of an idealised track structure calculation which attempts to describe , in full, the deposition of energy and the thermalisation/trapping of the reactive particles whose kinetics are under consideration.

1.3.1 Full simulation of an extended distribution.

The random flights modelling the diffusion and reaction processes of a nonhomogeneous system provides detailed information about the kinetics and the spatial evolution of the system as the trajectories of the particles are known. If the distribution of particles in a high LET radiation track is considered at its crudest level, modelling a section of track and employing periodic boundary conditions at its axial limits provides an acceptable discretisation of the system. The full track is, in effect, described as a series of repeating units. A particle leaving a track section through one face 'returns' through the other face. This is shown schematically in Fig.IV.1.5. Edge effects are introduced by the imposition of a periodic boundary, but are negligible if the initial number of reactive particles is sufficiently large. This 'repeating cell' approach to simulation can be applied to the string of clusters description of a radiation track, although in this case the optimum size of the track section is larger. As the complexity of the nonhomogeneous distribution of reactive particles is increased, the size of the repeating unit must necessarily increase to account for statistical effects in the spatial distribution.

Fig.IV.1.6 shows the recombination kinetics of a simple idealised string of equidistant clusters. The separation between adjacent clusters is 2.0 nm and each cluster initially contains an A/B pair. Within a cluster the particles are distributed from

Fig.IV.1.5 Use of a periodic boundary in simulation.

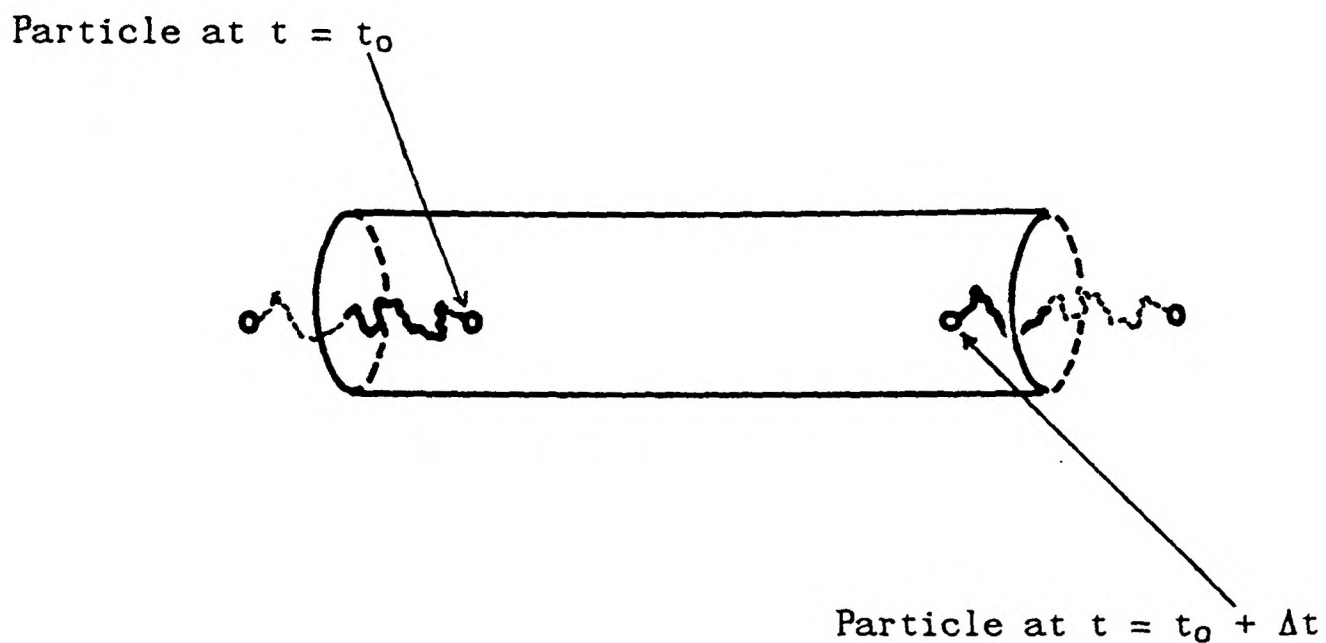
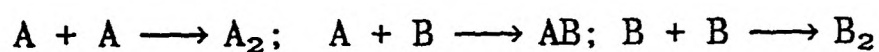
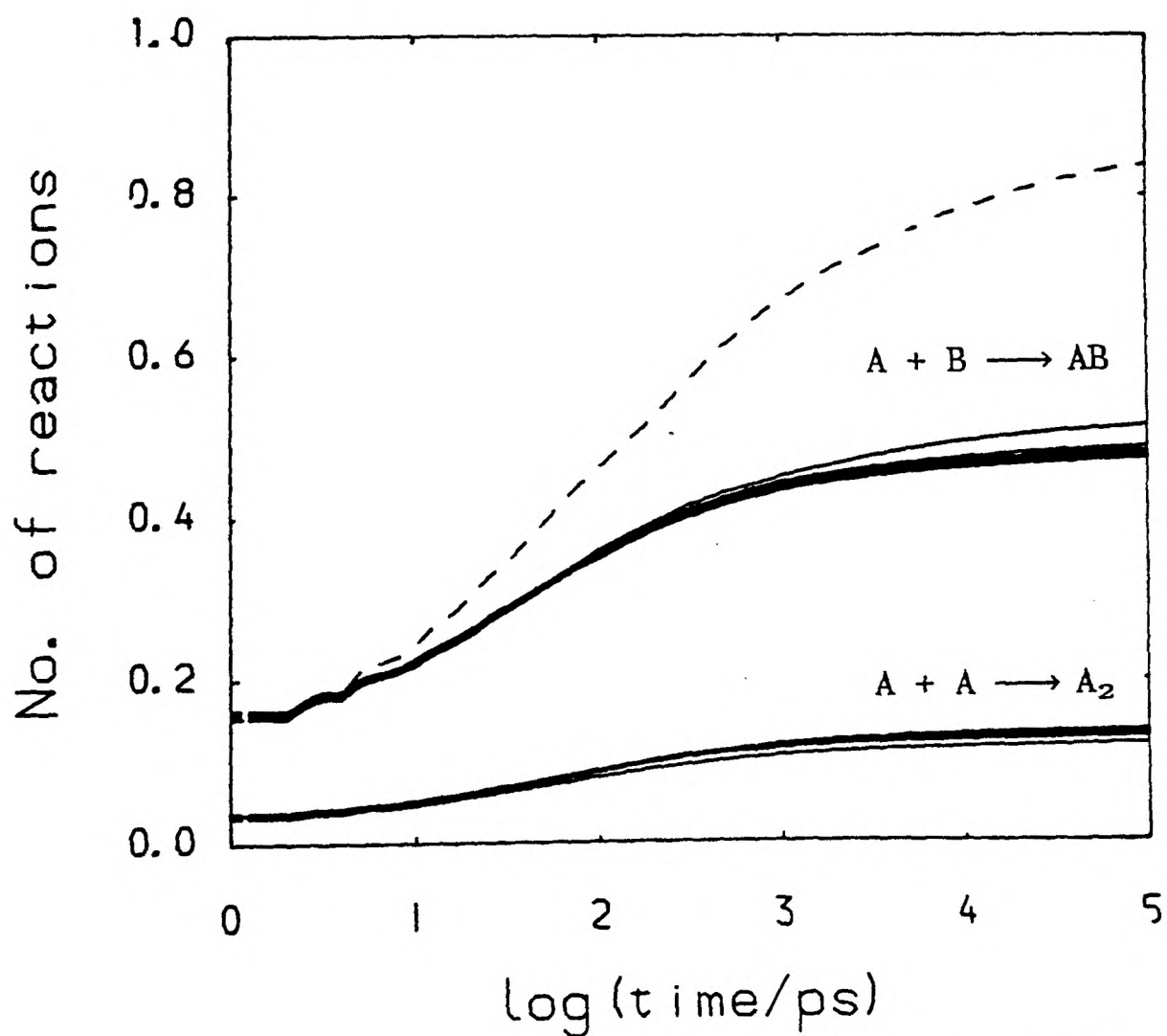


Fig.IV.1.6 String of A/B clusters.

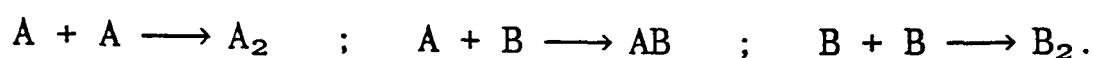


Initial positions within cluster from iid Gaussians, $\sigma = 1.0$ nm; $\langle \ell \rangle = 2.0$ nm; reaction distances all 1.0 nm; diffusion coefficients are $5.0 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$; repeating unit length is $n\langle \ell \rangle$.

(---) Random flights simulation with $n = 1$.
 (—) Effect upon simulated kinetics as n is increased ($n = 2(1)7$).



identical and independent Gaussians of standard deviation 1.0 nm. The two reactive species have the same diffusion coefficient, $D_{A,B} = 5 \times 10^{-9} \text{ m}^2\text{s}^{-1}$, and the particles react according to the scheme,



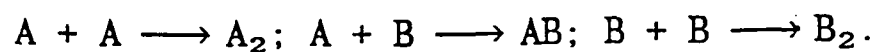
at a common reaction distances of 1.0 nm ($R_{A+A} = R_{A+B} = R_{B+B}$). When the length of the repeating unit is the intercluster separation no $A + A$ and $B + B$ combination is observed. This is a direct consequence of the periodic boundary as the system consists of one particle of each species. The kinetics of this system are not, however, those of an isolated cluster. As the length of the repeating unit is increased and the number of particles in the system grows, the influence of the periodic boundary upon the kinetics is reduced.

The stochastic kinetics of the repeating string of A/B clusters are compared with the corresponding deterministic kinetics in Fig.IV.1.7. Agreement between the two different methods is poor and suggests the the discrete nature of reactive particles is important even in extended distribution. As the density of particles increases and the intercluster separation is reduced, the discrepancy between the deterministic and stochastic treatments becomes small. The kinetics of an equidistant series of 2A/2B clusters are compared in Fig.IV.1.8.

1.3.2 Independent pairs modelling of large systems.

The approximate independent pairs methods used to model the kinetics of nonhomogeneous systems do not explicitly follow the positions of the reactive particles as they diffuse and react. Independent Reaction Times simulation characterises the system in terms of the interparticle separations, which are assumed to evolve independently, and models the kinetics by considering the first

Fig.IV.1.7 Deterministic and stochastic kinetics (a).



Initial clusters have a Gaussian profile; 1 A/B pair per cluster; $\langle \ell \rangle = 2.0$ nm; reaction distances all 1.0 nm; diffusion coefficients are $5.0 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$.

(o o o o) Deterministic treatment.
(—) Stochastic simulation, $n = 6$.

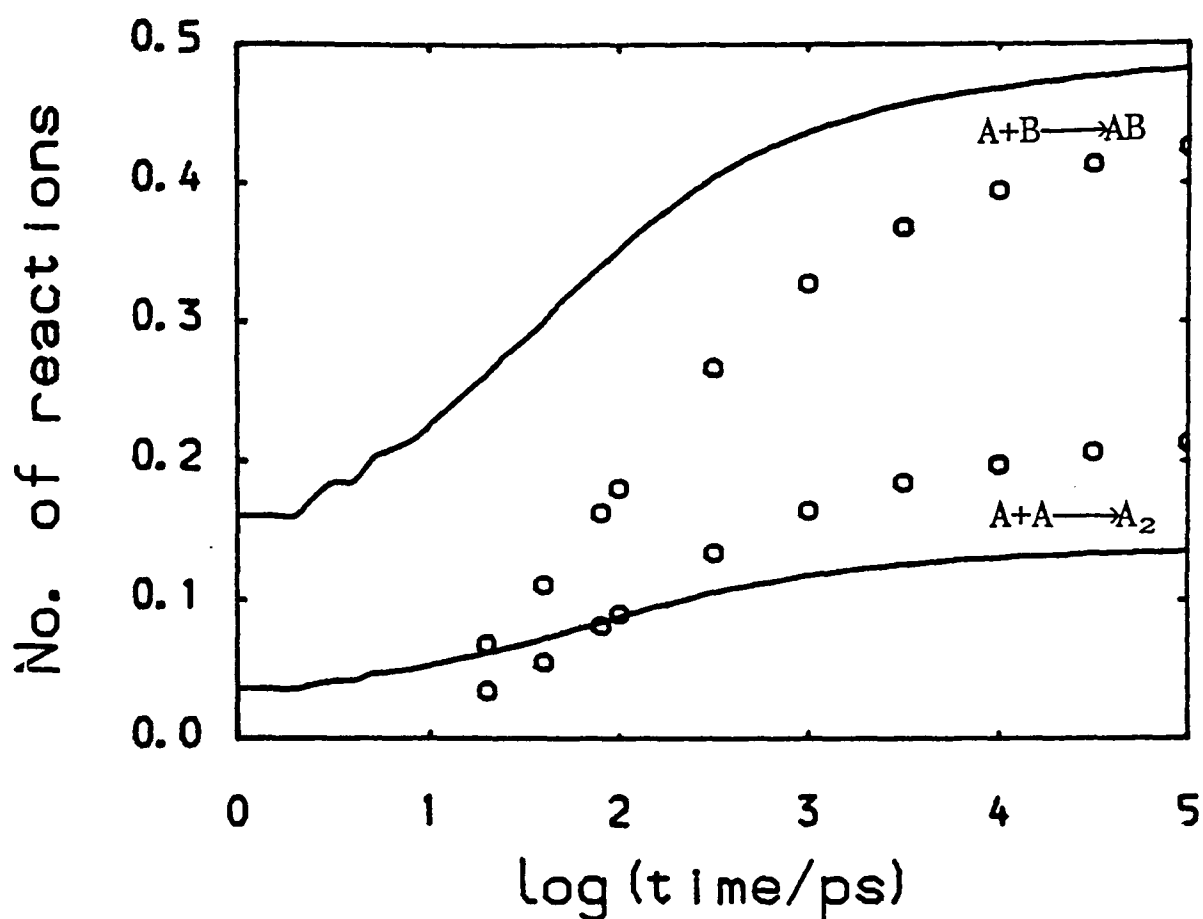
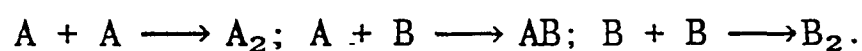
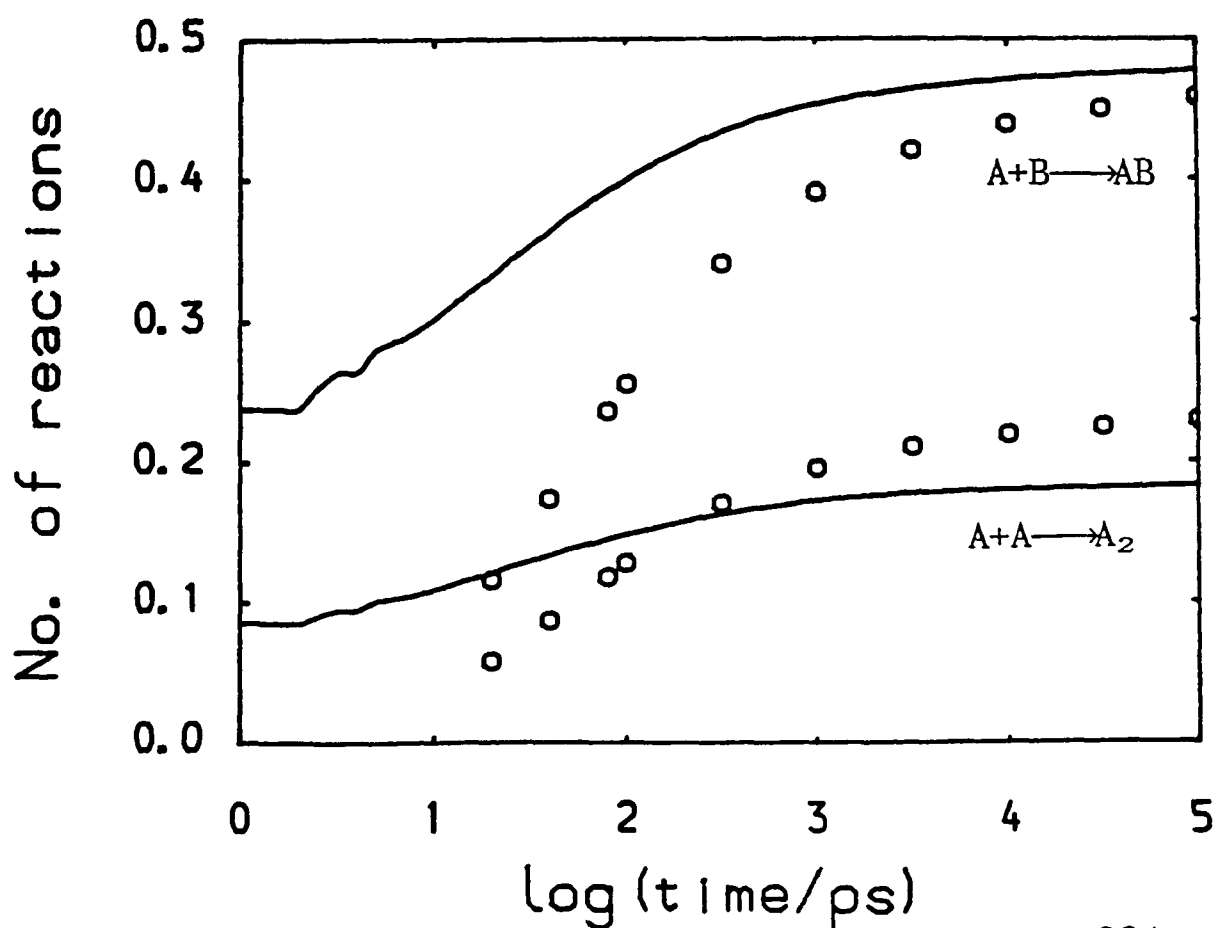


Fig.IV.1.8 Deterministic and stochastic kinetics (b).



Initial clusters have a Gaussian profile; 2 A/B pairs per cluster; $\langle \ell \rangle = 2.0$ nm; reaction distances all 1.0 nm; diffusion coefficients are $5.0 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$.

(o o o o) Deterministic treatment.
(—) Stochastic simulation, $n = 6$.



passage times to reaction. The imposition of a periodic boundary, as in the full random flights simulation, is difficult and the kinetics of a complete distribution have to be addressed. Treating sections of a track as if they are in isolation will influence the kinetics as reactions with particles outside the region of interest are not considered and this will introduce edge effects. The importance of the edge effects depends upon the length of the track section and the density of reactive particles. IRT simulations of idealised strings of clusters have been performed by Green (unpublished). As the number of particles is increased the influence of edge effects upon the kinetics is reduced and eventually becomes negligible. The simulations of Green consider an extended distribution in the same way that a small isolated cluster is treated by the IRT model. A method for dealing with the kinetics of very large distributions was presented in chapter III.4 where the modelling of an idealised high energy electron track is discussed.

The master equation formulation of the nonhomogeneous kinetics of an extended distribution requires the evaluation of the correct rate constant for the corresponding distribution of interparticle separations, $\omega(t)$. This constant is related to the rate constant, $k(t)$, that ought to be used in a conventional treatment by

$$\omega(t) = - \frac{d}{dt} [\ln(\Pi(t))] = \frac{\text{Const.}}{\Pi(t)} k(t) \quad (\text{IV.1.24})$$

where $\Pi(t) = \int_{\underline{r}} (1-W(r_0, t)) f(\underline{r}) d\underline{r}$. In principle the form of $\omega(t)$ is unimportant and may be analytic or numerical, but the former is clearly preferable. Master equation techniques have not been applied to particle distributions found in high LET radiolysis, but such studies are planned.

APPENDICES.

Appendix A

The generation of a random number from an arbitrary distribution.

Consider a strictly increasing probability density function defined by

$$W(t) = \Pr(T \leq t).$$

The probability that a uniformly distributed random number, U , in the range $(0,1)$ is less than x , where x is an element in the interval $(0,1)$ is given by

$$\Pr(U \leq x) = x \quad (x \in (0,1)).$$

Therefore

$$\Pr(U \leq W(t)) = W(t).$$

$W(t)$ is a strictly increasing function, so

$$U \leq W(t) \iff W^{-1}(U) \leq t$$

which means that

$$\Pr(W^{-1}(U) \leq t) = W(t).$$

By definition $\Pr(T \leq t) = W(t)$, therefore, $W^{-1}(U)$ is a random variable with the same distribution as T . This is a perfectly general result.

Examples :

i) First reaction time distribution functions frequently have the form

$$W(t) = W_{\infty} \operatorname{erfc}(S(D,r,R) / \sqrt{t}) .$$

In this case

$$T = W^{-1}(U) \begin{cases} = \infty & U \geq W_{\infty} \\ = \left[\frac{S(D', r, R)}{\operatorname{erfc}^{-1}(U/W_{\infty})} \right]^{-1} & U < W_{\infty} \end{cases}$$

ii) The pseudo-first order reaction time distribution for a single particle is

$$W(t) = 1 - \exp(-k_1 t) .$$

Here

$$T = W^{-1}(U) = - \frac{\ln(1-U)}{k_1} .$$

Appendix B.

Reaction on a bridge.

Consider a diffusion $X(t)$ with transition density $p(x,y,t)$. The probability of the separation attaining a value R in the time interval $(0,t)$ is equivalent to the reaction probability

$$\Pr(t_R \leq t | X(0)=x) = W(x,t) \quad (x > R, t > 0)$$

Now the probability of having attained the separation R conditioned upon being at y at t is

$$\Pr(t_R \leq t | X(0)=x, X(t)=y) = W^*(x,y,t).$$

According to standard probability theory,

$$\Pr(t_R \leq t | X(0)=x, X(t)=y) = \frac{\Pr(t_R \leq t \text{ \& } X(t)=y | X(0)=x)}{\Pr(X(t)=y | X(0)=x)}.$$

The denominator of this equation is the transition density of the diffusion and the numerator is the probability of two successive events; first passage to R at t_R followed by transition from R to y in the remaining time interval. If the first passage time density function is $w(x,t)$ then

$$\Pr(t_R \leq t | X(0)=x, X(t)=y) = \frac{g(x,y,t)}{p(x,y,t)}$$

where

$$g(x,y,t) = \int_0^t w(x,u) p(R,y,t-u) du.$$

Taking the Laplace transform of g gives

$$\tilde{g}(x,y,s) = \tilde{w}(x,s) \tilde{p}(R,y,s).$$

By definition

$$W(x,t) = \int_0^t w(x,u) du$$

and so

$$\tilde{w}(x,s) = s \tilde{W}(x,s) - W(0) = s \tilde{W}(x,s).$$

Substituting for $\tilde{w}$ gives

$$\tilde{g}(x,y,s) = s \tilde{W}(x,s) \tilde{p}(x,y,s).$$

Green (1986) has shown that

$$W(x, t) = \varphi^{-1} \left[\frac{1}{s} \frac{\tilde{p}(R, y, s)}{\tilde{p}(R, R, s)} \right]$$

and therefore

$$\tilde{g}(x, y, s) = \frac{\tilde{p}(x, R, s) \tilde{p}(R, y, s)}{\tilde{p}(R, R, s)}.$$

The transition density of a d dimensional Bessel process is (Itô & McKean, 1974)

$$p(x, y, t) = \frac{x}{t} \left[\frac{y}{x} \right]^{d/2} \exp(-[x^2 + y^2]/2t) I_{\frac{1}{2}d-1}(xy/t)$$

where $I_\nu(z)$ is a modified Bessel function of the first kind. When $x \geq y$

$$\tilde{p}(x, y, s) = 2 \times \left[\frac{y}{x} \right]^{d/2} K_{\frac{1}{2}d-1}(x\sqrt{2s}) I_{\frac{1}{2}d-1}(y\sqrt{2s})$$

and when $x \leq y$

$$\tilde{p}(x, y, s) = 2 \times \left[\frac{y}{x} \right]^{d/2} K_{\frac{1}{2}d-1}(y\sqrt{2s}) I_{\frac{1}{2}d-1}(x\sqrt{2s})$$

where $K_\nu(z)$ is a modified Bessel function of the third kind.

Substituting for $\tilde{p}$ gives

$$\tilde{g}(x, y, s) = 2 \times \left[\frac{y}{x} \right]^{d/2} K_{\frac{1}{2}d-1}(x\sqrt{2s}) K_{\frac{1}{2}d-1}(y\sqrt{2s}) \frac{I_{\frac{1}{2}d-1}(R\sqrt{2s})}{K_{\frac{1}{2}d-1}(R\sqrt{2s})}.$$

Inversion of $\tilde{g}$ yields g and therefore the Bessel bridge reaction probability. (If the transition density of a Wiener process is used in place of the density for a Bessel process, the Brownian bridge results.)

Example : $d = 3$.

By definition (Abramowitz & Stegun, 1970)

$$I_{\frac{1}{2}}(z) = \frac{1}{2} \sinh(z) \quad ; \quad K_{\frac{1}{2}}(z) = \sqrt{\frac{\pi}{2z}} \exp(-z).$$

Therefore

$$p(x, y, t) = \frac{y}{x\sqrt{2\pi t}} \left[\exp(-[x-y]^2/2t) - \exp(-[x+y]^2/2t) \right]$$

and

$$\tilde{g}(x, y, s) = \frac{y}{x\sqrt{2s}} \left[\exp(-[x+y-2R]\sqrt{2s}) - \exp(-[x+y]\sqrt{2s}) \right].$$

Inversion of $\tilde{g}$ gives

$$g(x,y,t) = \frac{y}{x\sqrt{2\pi t}} \left[\exp(-[x+y-2R]^2/2t) - \exp(-[x+y]^2/2t) \right].$$

The Bessel bridge in three dimensions is

$$w^* = \frac{\exp(-2[x-R][y-R]/t) - \exp(-2xy/t)}{1 - \exp(-2xy/t)}.$$

Appendix C.

Calculation of the timestep for random flights simulation.

Consider a pair of particles. The change in the interparticle separation during a random flight is

$$\delta r = |\mu(r)| \delta t + \sqrt{2D'\delta t} N_3(0,1) \quad (C.1)$$

where $\mu(r)$ is the drift. Now during a random flight of duration δt the drift is allowed to change by less than a small amount, ϵ ,

$$\epsilon \geq \left| \frac{\mu(r+\delta r) - \mu(r)}{\mu(r)} \right|. \quad (C.2)$$

For a sufficiently small change δr ,

$$\epsilon \geq \left| \frac{\mu(r+\delta r)}{\mu(r)} - 1 \right| = \left| \delta r \left[\frac{d}{dr} \ln \mu(r) \right] \right| \quad (C.3)$$

and

$$|\delta r| \leq \epsilon f(r) \quad (C.4)$$

where

$$f(r) = \left[\left| \frac{d}{dr} \ln[\mu(r)] \right| \right]^{-1}. \quad (C.5)$$

Substituting the inequality (C.4) into equation (C.1) gives

$$\epsilon f(r) \geq |\mu(r)| \delta t + \sqrt{2D'\delta t} |N|. \quad (C.6)$$

where N is a normally distributed random number with mean zero and variance one. If a 95% confidence limit is applied to the Brownian component of the jump, $|N| = 2$, and so

$$\epsilon f(r) \geq |\mu(r)| \delta t + 2 \sqrt{2D'\delta t}. \quad (C.7)$$

A timestep, $\delta t'$, is defined such that

$$\epsilon f(r) = |\mu(r)| \delta t' + 2 \sqrt{2D'\delta t'}. \quad (C.8)$$

which gives

$$\sqrt{\delta t'} = \frac{1}{|\mu|} \left[-\sqrt{2D'} + \sqrt{2D' + \epsilon f(r)\mu} \right] \quad (C.9)$$

The inequality (C.7) is a strictly increasing function of $\delta t'$ and is therefore obeyed for all $\delta t \leq \delta t'$. The time period $\delta t'$ is a suitable estimate for use in simulation.

Important cases:

i) No interparticle force, $\mu = \frac{2D'}{r}$.

$$\delta t' = \frac{r^2}{2D'} [\sqrt{1+\epsilon} - 1]^2$$

ii) Coulombic interparticle force, $\mu = \frac{D'}{r^2} (2r-r_c)$

$$\delta t' = \frac{r^4}{D' (2r-r_c)^2} \left[\sqrt{2 + \frac{\epsilon(2r-r_c)^2}{2r(r-r_c)}} - \sqrt{2} \right]^2$$

Appendix D.

A recurrence relationship for infrequent track events.

Consider the distribution of energy loss events, $F(\epsilon, E)$, along the track of an electron with incident energy E . If the distribution refers to all events along the main track and any daughter tracks then

$$N \int_{\epsilon_0}^{\epsilon_1} F(\epsilon, E) d\epsilon = 1.$$

where N is a normalisation constant and ϵ_1 is the lowest energy producing a branched track, i.e. 5 keV according to the classification of Magee et al. (1965). Now the mean energy of a deposition event is

$$\langle \epsilon \rangle = N \int_{\epsilon_0}^{\epsilon_1} \epsilon F(\epsilon, E) d\epsilon$$

and the mean number of events is $\langle N \rangle = E / \langle \epsilon \rangle$. Let $E + \Delta E$ be some energy for which $F(\epsilon, E + \Delta E)$ is significantly different from $F(\epsilon, E)$. If $\langle \Delta v(\epsilon, E) \rangle$ is the mean number of events in the interval ϵ to $\epsilon + \Delta \epsilon$ created by the degradation of the primary from $E + \Delta E$ to E and if $v(\epsilon, E)$ is the mean number of events for the complete degradation from E , then

$$v(\epsilon, E + \Delta E) \simeq \langle \Delta v(\epsilon, E) \rangle + v(\epsilon, E)$$

and

$$\langle N(E) \rangle = \int_{\epsilon_0}^{\epsilon_1} v(\epsilon, E) d\epsilon.$$

Thus

$$\begin{aligned} \langle N(E + \Delta E) \rangle &= \int_{\epsilon_0}^{\epsilon_1} v(\epsilon, E + \Delta E) d\epsilon \\ &\simeq \int_{\epsilon_0}^{\epsilon_1} \langle \Delta v(\epsilon, E) \rangle d\epsilon + \langle N(E) \rangle. \end{aligned}$$

Clearly,

$$\begin{aligned}
 F(\epsilon, E+\Delta E) &= \frac{v(\epsilon, E) + \langle \Delta v(\epsilon, E) \rangle}{\langle N(E) \rangle + \int_{\epsilon_0}^{\epsilon_1} \langle \Delta v(\epsilon, E) \rangle d\epsilon} \\
 &= \frac{F(\epsilon, E) + \langle \Delta v(\epsilon, E) \rangle / \langle N(E) \rangle}{1 + \frac{1}{\langle N(E) \rangle} \left[\int_{\epsilon_0}^{\epsilon_1} \langle \Delta v(\epsilon, E) \rangle d\epsilon \right]}
 \end{aligned}$$

which links $F(\epsilon, E+\Delta E)$ and $F(\epsilon, E)$.

Appendix E.

Track structure calculations.

In the discussions of chapter II.1. the deposition of energy along a radiation track was presented as a stochastic phenomenon. The statistical nature of the track makes Monte Carlo modelling a natural choice and several such techniques (e.g. Paretzke et al., 1986; Zaider et al., 1983) have been developed to simulate the deposition of energy and the types of process occurring. These models follow the progress of an ionising particle and its daughter electrons through the medium, recording the location and size of each the energy loss event. Approximate analytic calculations, of a more limited scope, have been used to derive expressions for the number of ionisations and the energy distribution of the secondary particles (Pagnamenta & Marshall, 1986).

The transport calculations provide a detailed picture of the idealised track, in that they assign each event an exact position and energy loss and they predict the velocity of any ejected secondary electron. Unfortunately, with few exceptions (e.g. Olivero et al., 1972), the actual protocol of the calculations is omitted from the literature. The basic model considers the primary particle to have a straight line trajectory and assumes the separations between adjacent events to be exponentially distributed with a mean depending upon the total interaction cross-section of the radiation particle in the medium. The type of interaction and the amount of energy lost is determined by the constituent ionisation and excitation cross-sections that make up the total cross-section, and the velocity of any secondary electron is derived from the differential ionisation cross-section. The program

codes usually follow the attenuation of secondary electrons down to about 10 eV.

The validity of the results obtained by the Monte Carlo transport calculations depends upon the accuracy with which the cross-sections for the elementary processes are known. This information is available for water in the vapour phase (e.g. Vroom & de Heer, 1969; Bose & Stoka, 1973; Beenakker et al., 1974; Mark & Egger, 1976) and, at high energies, where the experimental data is not available, extrapolation is possible. The condensed phase is of most interest in radiation chemistry and radiation biology and there is a distinct lack of information. Most track structure simulations describing the radiolysis of a liquid consider the liquid merely as a dense gas, i.e. by scaling the number density of the scattering molecules. This is a crude approximation that ignores the interactions between the molecules in the condensed phase. The influence of these interactions is important. It causes the lowering of the ionisation potential, typically $\Delta I \simeq 1$ to 2.5 eV (Kaplan, 1983), and changes in the energy loss spectrum (Kaplan & Miterov, 1987; Marsolais et al., 1987) and the oscillator strength distribution (LaVerne & Mozumder, 1986). These effects will alter the yields and energies of the molecular ions and excited molecules formed in radiolysis.

Some attempt has been made to account for specific features of the condensed phase (e.g. Kutcher & Green, 1976; Paretzke et al., 1982; Kaplan et al., 1986), but agreement between the different calculations is only qualitative. There has been no consideration of the distribution of energy over the quantum states in a liquid nor of the existence of collective excited states. Despite these improvements and extensive comparisons between gas and liquid phase simulations, condensed phase track structure calculations must be regarded with caution.

Appendix F.

The time-dependent rate constant for a linear arrangement of clusters.

The rate constant of a diffusion-controlled reaction and the reaction probability of a pair are related through the independent pairs assumption (Steinberg & Katchalski, 1968). Green (1984) has shown that

$$k(t) = \int_{\underline{r}} g(\underline{r}) \left[\frac{\partial W}{\partial t} \right] d\underline{r} \quad (F.1)$$

where $g(\underline{r})$ is the ratio of the "local" to the "bulk" concentration. If the initial particle distribution is a linear arrangement of clusters, then

$$g(\underline{r}) = \mathcal{A} \sum_{i=1} v_i \exp \left[- \frac{(x^2+y^2)}{2\sigma_i^2} \right] \exp \left[- \frac{(z-z_i)^2}{2\sigma_i^2} \right] \quad (F.2)$$

where $\mathcal{A}$ is a constant, z_i is the axial coordinate of the centre of the i th cluster which contains v_i pairs and has a standard deviation of σ_i . The reaction probability of a pair of particles, in the absence of an interparticle force is

$$W(r, t) = \frac{R}{r} \operatorname{erfc} \left[- \frac{(r-R)}{2\sqrt{D't}} \right] \quad (F.3)$$

and therefore

$$\frac{\partial W}{\partial t} = \frac{R(r-R)}{2r\sqrt{\pi D't^3}} \exp \left[- \frac{(r-R)^2}{4D't} \right] \quad (F.4)$$

Substituting into equation (F.1) and integrating over the polar and azimuthal angles gives

$$k(t) = 2\pi\mathcal{A} \int_R^\infty \frac{\partial W}{\partial t} r S(r) dr \quad (F.6)$$

where $S(r)$ is the sum

$$S(r) = \sum_{i=1} v_i \frac{\sigma_i^2}{z_i} \left[\exp \left[- \frac{(r-z_i)^2}{2\sigma_i^2} \right] - \exp \left[- \frac{(r+z_i)^2}{2\sigma_i^2} \right] \right].$$

Making the transformation $x = r - R$,

$$k(t) = \mathcal{A}R \sqrt{\frac{\pi}{D't^3}} \int_0^\infty x \exp\left[-\frac{x^2}{4D't}\right] S'(x) dx \quad (F.7)$$

with

$$S'(x) = \sum_{i=1} v_i \frac{\sigma_i^2}{z_i} \left[\exp\left[-\frac{(x+R-z_i)^2}{2\sigma_i^2}\right] - \exp\left[-\frac{(x+R+z_i)^2}{2\sigma_i^2}\right] \right].$$

Now the integral $\int_0^\infty x \exp(-Ax^2 - Bx) dx$ is given by Erdelyi (1953) and taking this solution,

$$k(t) = \mathcal{A}R \sqrt{\frac{\pi}{D't^3}} \sum_{i=1} v_i \frac{\sigma_i^2}{z_i} \frac{I(t)}{A(t)} \quad (F.8)$$

where the functions $A(t)$ and $I(t)$ are

$$A(t) = \frac{\sigma_i^2 + 2D't}{2D't\sigma_i^2}$$

and

$$I(t) = \exp(\frac{1}{4}B^2 - C^2) D_{-2}(B) - \exp(\frac{1}{4}E^2 - C^2) D_{-2}(E)$$

and $D_v(x)$ is a Whittaker parabolic cylinder function and for $v = -2$ is given by (Erdelyi, 1953)

$$\begin{aligned} D_{-2}(x) &= -\sqrt{\pi} \exp(-\frac{1}{4}x^2) \frac{d}{dx} \left[\exp(\frac{1}{4}x^2) \operatorname{erfc}(x/\sqrt{2}) \right] \\ &= \sqrt{\frac{\pi}{2}} x \exp(\frac{1}{4}x^2) \operatorname{erfc}(x/\sqrt{2}) - \exp(-\frac{1}{4}x^2). \end{aligned}$$

The parameters B , C , E and F are

$$B = \frac{(R-z_i)}{\sigma_i} \sqrt{\frac{2D't}{\sigma_i^2 + 2D't}} \quad ; \quad C = \frac{(R-z_i)}{\sqrt{2}\sigma_i}$$

$$D = \frac{(R+z_i)}{\sigma_i} \sqrt{\frac{2D't}{\sigma_i^2 + 2D't}} \quad ; \quad E = \frac{(R+z_i)}{\sqrt{2}\sigma_i}$$

Equation (F.8) is exact and applies to any linear string of clusters.

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