Chapter 6

Episode II

On the Smith–Ewart Equations and RAFT/Emulsion

A mathematician is a machine for converting coffee into theorems.

– Alfréd Rényi (1921–1970)

6.1 Kinetics of Particle Growth

It was established in Chapter 5 that c and k_pC_p are of similar magnitude in many RAFT-containing systems and that zero-one kinetics therefore become inapplicable (see also Chapter 4); therefore, it is either pseudo-bulk kinetics are applicable or, alternatively, the kinetics may be described by neither the pseudo-bulk nor zero-one limits. In Chapter 4, an overview of the zero-one and pseudo-bulk limits for the kinetics of particle growth was given, showing that, in the case where ($\rho/c \approx 1$ or $k/c \approx 1$) and ($\rho/c \not\gg 1$ and $k/c \not\gg 1$), the kinetics are not well-described by either of these limits. Moreover, it will be shown in Chapter 7 that all three of the Smith–Ewart parameters (ρ, k and c) are of similar magnitude. Thus, it is necessary to consider particle growth kinetics more closely.

In dealing with the exit of radicals from particles, their fate in the aqueous-phase and the additional entry and termination processes, it is instructive to examine the roots of both the zero-one and pseudo-bulk limits. The common roots for these kinetic schemes are the seemingly simple Smith–Ewart equations.

6.2 The Smith–Ewart Equations

In an emulsion polymerization in which particle formation does not occur and termination is chain-length *independent*, the population of particles with i radicals, N_i, is determined by the rate coefficients for the processes that change the number of radicals in a particle and the initial conditions of the system. In particular, intra-particle termination is described by the pseudo-first-order rate coefficient for the destruction of two radicals, c, radical entry by a first-order rate coefficient, ρ, and the loss of a single radical from a particle by the first-order rate coefficient, k. Physical processes that may correspond to ρ, k and c are the entry of an aqueous phase radical into a particle (ρ), the desorption of a monomeric radical formed by a transfer to monomer reaction (k) and termination (c). These processes are shown for an N_i particle in Fig. 6.1.

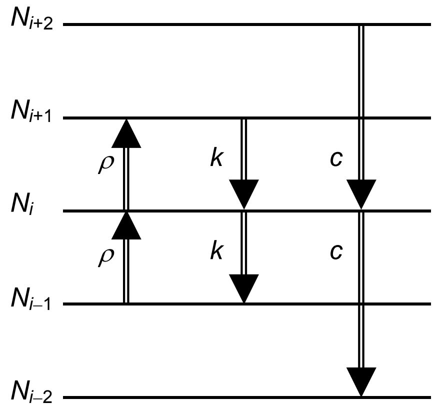

Figure 6.1: A schematic of the events changing the number of radicals in the particles containing *i* radicals.

The processes shown in Fig. 6.1 may be reduced to a time-evolution equation for the population of N_i-type particles, the infinite set of which comprise the Smith–Ewart equations:[1]

$$\frac{\mathrm{d}N_i}{\mathrm{d}t} = \rho\left[N_{i-1} - N_i\right] + k\left[(i+1)N_{i+1} - iN_i\right] + c\left[(i+2)(i+1)N_{i+2} - i(i-1)N_i\right] \tag{6.1}$$

Note that, since a particle with *i* radicals in it may have any one of the *i* radicals exit (through whatever mechanism is involved in that exit), the rate coefficient for exit per particle (as opposed to per radical) is also proportional to *i*; similarly, the rate coefficient for termination per particle is proportional to $i(i-1)$.

While these equations provide insight into the population balances of radicals in the particles and their importance should not be underestimated, they provide no direct means of understanding the kinetics of the system. The work of Hawkett *et al.*[2] provided a suitable means of solving these equations using eigenvectors. The zero-one limit emerged from the Smith–Ewart equations by truncating the infinite series of equations in such a way that if a radical entered an N_1 particle, pseudo-instantaneous termination would result not in an N_2 particle but in an N_0 particle.[3] An alternate closure relation was found by Ballard *et al.*,[4] assuming that $\overline{n^2} - \overline{n} = \overline{n}^2$ (the case if the N_i follow a Poisson distribution[5]), leading to pseudo-bulk kinetics.

It is recognized that the treatment of emulsion polymerization kinetics in terms of the Smith–Ewart equations is a simplification that removes the chain-length dependence of the termination reaction. Deviations from the Smith–Ewart equations have been observed,[6,7] and in general the chain-length dependence of termination cannot be ignored. However, as will be discussed in Section 6.2.2, under certain circumstances the Smith–Ewart equations are applicable; moreover, some of the conclusions based on a chain-length independent treatment should be semi-quantitatively applicable to systems where this chain-length independence assumption is inadmissible.

Consideration of the Smith–Ewart equations and the origins of the zero-one and pseudo-bulk limits is a necessary step in developing a simplified model for RAFT/emulsion systems. In Section 6.3, a method whereby average Smith–Ewart parameters may be calculated from the full chain-length dependent kinetics is presented.

6.2.1 Exited Radicals and the Smith–Ewart Equations

Incorporating the fate of the exited radicals into the original Smith–Ewart equations (Eq. 6.1) can often be done trivially by rewriting the Smith–Ewart equations in terms of ρ_t (where the subscript denotes “total) instead of ρ. A fate parameter $\alpha \in [-1,1]$ may then be introduced, making ρ_t a function of the true, initiator derived radical flux ρ and the average number of radicals per particle, $\bar{n}$:[4,8]

$$\rho_t = \rho + \alpha k\bar{n} \tag{6.2}$$

However, the use of the fate parameter is problematic in that, for fates other than the limiting cases of $\alpha \in \{-1, 0, 1\}$, α itself is a function of $\bar{n}$. For this reason, the treatment here will be confined to a brief overview of the use of α when it falls into one of these limits; other cases require the full treatment of the aqueous-phase kinetics to estimate the fate of the exited radicals in the aqueous phase.

The fate of the exited radicals in zero-one kinetics gives five separate limits depending on the efficiency of the initiator, whether or not complete aqueous-phase termination occurs and whether a re-entering radical will stay in a particle that it re-enters or desorb once more.[5,9] The limiting values of α (*i.e.* -1, 0, 1) correspond to the following fates (showing the exited radical as $E^\bullet$), which in the case of zero-one kinetics have been ascribed names as shown:[5,9]

- $\alpha = +1$:
  - complete re-entry (and no subsequent re-escape) of the exited species (Limit 2a).
- $\alpha = 0$:
  - complete aqueous-phase *homo*termination (*e.g.* $E^\bullet + E^\bullet$) of the exited species (Limit 1a), or
  - complete aqueous-phase termination (*e.g.* $E^\bullet + IM_i^\bullet$ or $E^\bullet + E^\bullet$) with an initiator of low efficiency (Limit 1c), or
  - continual re-entry and re-escape of the exited species until termination in a particle (*e.g.* $E^\bullet + P^\bullet$) occurs (Limit 2b).
- $\alpha = -1$:
  - complete aqueous-phase *hetero*termination (*e.g.* $E^\bullet + IM_i^\bullet$) of the exited species with an initiator of otherwise high-efficiency (Limit 1b).

While there is great aesthetic appeal in using the fate parameter α, there are difficulties in its application. In addition to α itself being a function of $\bar{n}$ except in the limiting cases above, ρ_t may now be a function of $\bar{n}$, making the differential equations considerably more difficult to solve. Given these difficulties with the use of α, it will not be used in this work except for the purposes of mathematical convenience and to highlight the particular form of Eq. 6.2 being used.

In an uncompartmentalized system, the complete re-entry of the exited species (with no re-escape) is equivalent to $\alpha = 1$ in Eq. 6.2; this approximation makes the system somewhat easier to solve, giving the familiar pseudo-bulk equation:[4]

$$\frac{\mathrm{d}\bar{n}}{\mathrm{d}t} = \rho - 2c\bar{n}^2 \tag{6.3}$$

It must be noted that, for the purposes of clarity, the formulation here is slightly different from that shown elsewhere. In particular, there is often confusion between whether ρ is ρ_t or ρ_i (initiator-derived radicals), especially when considering conditions such as $\rho/c \gg 1$. Here and in the subsequent treatment of the Smith–Ewart equations and the zero-one and pseudo-bulk limits, ρ will always be used to represent only the entry of initiator-derived radicals, with the re-entry of other radicals being denoted with alternate subscripts where appropriate.

6.2.2 Full Treatment of Polymer Kinetics

The occurrence of desorption requires taking into account the fate of exited free radicals, which can be implemented by extending the Smith–Ewart equations to differentiate particles containing one or more monomeric radicals (which can desorb) from particles containing the same number of longer radicals (which cannot desorb).[9] It is also essential to note that the Smith–Ewart equations do not take chain-length dependent (CLD) termination into account; therefore, they are only semi-quantitative for all except zero-one systems and systems where termination is independent of chain length (*e.g.* where termination by reaction-diffusion is dominant).[10]

When the effects of CLD termination are taken into account, one can still apply the Smith–Ewart equations, but in general all the rate coefficients (ρ, k and c) will not be constant, but will depend on the instantaneous radical distribution and the number of radicals in each particle.[10] Explicitly, c is a function of the number of radicals in the particle, i, and also of the overall instantaneous distributions of all the $G_i(N)$ (chain-length distributions of growing chains within that particle), the instantaneous distributions of all the $D_i(N)$ (chain-length distributions of dormant chains within that particle) and ρ is a function of the overall number of monomeric radicals within all particles. In general, these dependencies can only be found by a solution of the more complete system where explicit account is taken of the distributions of the lengths of each chain in each particle. This forms an extremely complex set of hierarchical equations replacing Eq. 6.1:[10]

$$\begin{aligned}\frac{\mathrm{d}N_i}{\mathrm{d}t} &= \rho_{i-1}(N)\big[N_{i-1} - N_i\big] + k\big[(i+1)N_{i+1} - iN_i\big] \\ &\quad + c_{i+2}\big(G_{i+2}(N), D_{i+2}(N)\big)\big[(i+2)(i+1)N_{i+2}\big] - c_i\big(G_i(N), D_i(N)\big)(i-1)N_i \qquad (6.4)\end{aligned}$$

In Section 6.3, a method is described whereby the "instantaneous" Smith–Ewart rate coefficients can be determined from the full CLD kinetics for the direct interpretation of experimental data.

6.2.3 Solution of the Smith–Ewart Equations

Along with the pseudo-bulk limit of the Smith–Ewart equations, Ballard *et al.*[4] also reported a simple method of finding approximate solutions to the full Smith–Ewart equations (Eq. 6.1) using a recursive approach. A brief summary of this process is as follows.

Ballard *et al.*[4] made use of a physical limit of the N_i particles as their closure relation:

$$\lim_{i\to\infty} N_i = 0 \qquad (6.5)$$

Thus, by selecting a sufficiently large $i = n$ and setting all $N_i = 0$ for $i > n$, the infinite set of equations described by Eq. 6.1 is reduced to a more manageable set of n equations. The accuracy of this artificial truncation procedure was verified by Ballard *et al.*[4] against alternative solution methods presented by Stockmayer[11] and O'Toole.[12]

Solving the truncated set of equations in steady state then yields the following set of equations that are readily solved starting with N_n set to an arbitrary value. Strictly, the value selected for N_n will determine the normalization of the population distribution but this is readily renormalized after all calculations have been performed; however, care must be taken to prevent numerical overflows in the computation of the other N_i.

$$N_{n-1} = \frac{1}{\rho}\left\{\left[\rho + nk + n(n-1)c\right]N_n\right\} \tag{6.6}$$

$$N_{n-2} = \frac{1}{\rho}\left\{\left[\rho + (n-1)k + (n-1)(n-2)c\right]N_{n-1} - \left[\rho + nk\right]N_n\right\} \tag{6.7}$$

$$N_i = \frac{1}{\rho}\left\{\left[\rho + (i+1)k + i(i+1)c\right]N_{i+1} - (i+2)kN_{i+2} - (i+3)(i+2)cN_{i+3}\right\} \tag{6.8}$$

A minimum value of n required for a reasonable approximation for the population distribution was estimated by Ballard *et al.*[4] to be $5(\bar{n} + 1)$, where $\bar{n}$ is estimated from the steady-state solution of Eq. 6.3. (In the case of a zero-one system where the true value of $\bar{n}$ is around ½, the value of n so calculated is around 5, which is sufficient for the zero-one system.)

It may be noted from Eq. 6.1 that the population distribution (and hence $\bar{n}$) is dependent only on the values of ρ/c and k/c; these three parameters may thus be reduced to two when considering the value of $\bar{n}$ that describes a system. Repeating the above process for the calculation of $\bar{n}$ over a range of values of ρ/c and k/c produces a surface of $\bar{n}$ values that describes various systems, shown in Fig. 6.2. Note the plateau in the surface caused by the highly compartmentalized systems that follow zero-one kinetics.

In the case where exiting radicals have some kinetic effect after exit (*i.e.* $\alpha \neq 0$ in the vernacular of Eq. 6.2), their effect must also be incorporated into this solution method. In the limiting cases where α itself is not a function of $\bar{n}$ (*i.e.* −1, 1), this may be done in a straightforward (albeit computationally inefficient) method by first preparing an estimate for $\bar{n}$ using Eq. 6.6 to 6.8 and the truncation method described above, then using Eq. 6.2 to determine a new value of ρ to be used once more in Eq. 6.6 to 6.8.[4] This procedure may be repeated until the value of $\bar{n}$ is of sufficient accuracy. In practice, this technique converges quite quickly to the actual value of $\bar{n}$. In the case of complete re-entry and no re-escape (which corresponds to the limiting case $\alpha = 1$), the surface of $\bar{n}$ *vs* ρ/c and k/c is shown in Fig. 6.3.

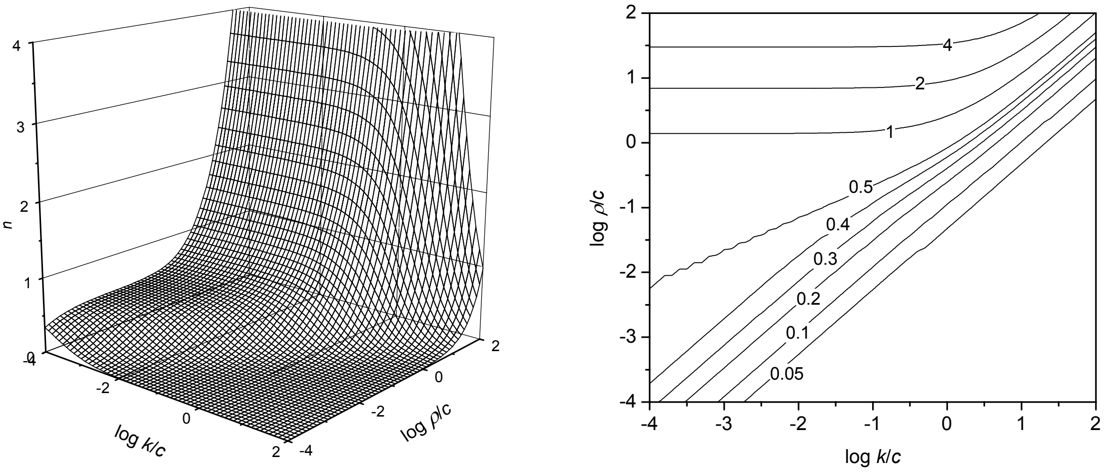

Figure 6.2: The 3D surface and contour plot of $\bar{n}$ *vs* ρ/c and k/c described by the Smith–Ewart equations in steady state where exited radicals have no subsequent kinetic effect. Note the zero-one plateau at $\bar{n} = ½$.

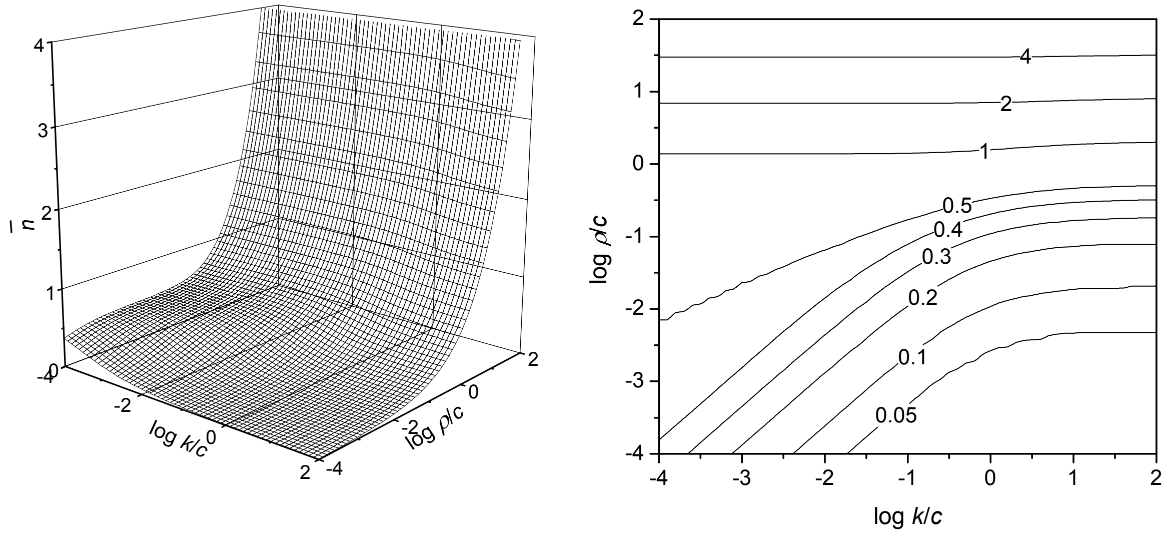

Figure 6.3: The 3D surface and contour plot of $\bar{n}$ *vs* ρ/c and k/c described by the Smith–Ewart equations in steady state with complete re-entry and no subsequent re-escape.

6.2.4 Limits of the Smith–Ewart Equations

The applicability of the zero-one and pseudo-bulk limits to the Smith–Ewart equations has already been discussed, with various conditions in terms of the relative magnitudes of ρ, k and c being devised. In particular, it was noted that, in the case where ($\rho/c \approx 1$ or $k/c \approx 1$) and ($\rho/c \not\gg 1$ and $k/c \not\gg 1$), neither of these limits would appear to hold. However, it is possible that, while neither limit may be rigorously derived under such conditions, the values for $\bar{n}$ that result from one or other of these limits may still provide useful approximations to the value of $\bar{n}$.

As it has previously been shown that the limit of complete re-entry and no re-escape is suitable for the emulsion polymerization of styrene,[5,13] the discussion presented here will be restricted to this limit. It is noted that the treatment presented here is for the steady state $\bar{n}$ of the systems. The error in the value of $\bar{n}$ calculated by the various approximations to the Smith–Ewart equations presented here is, thus, only one facet of these approximations; the accuracy of these limits in estimating the relaxation kinetics and the molecular weight distributions is an area for further work outside the scope of this study.

6.2.4.1 Zero-One Kinetics

In the case of zero-one kinetics, complete re-entry with minimal re-escape corresponds to Limit 2a. This limit has the steady state solution for $\bar{n}$:[5,9]

$$\bar{n} = -\frac{\rho}{2k} + \frac{1}{2}\left[\left(\frac{\rho}{2k}\right)^2 + 2\frac{\rho}{2k}\right]^{1/2} \tag{6.9}$$

It is thus possible to map out $\bar{n}$ in the ρ/c and k/c space as before, as well as looking at the relative error between the zero-one approximation and the numerical solution of the Smith–Ewart equations. Fig. 6.4 shows the surface described by the (Limit 2a) zero-one equations. Note that the surface described in this way has the same plateau as that shown by the Smith–Ewart equations in Fig. 6.3, but that, due to the exaggerated compartmentalization of the “zero-one” assumption, as ρ/c increases, the system remains at $\bar{n} = ½$.

A contour-plot comparison of the relative error between the zero-one solution and the numerical solution to the full Smith–Ewart equations presented above is shown in Fig. 6.5. When $\rho/c \ll 1$ and $k/c \ll 1$, this error is quite small; however, when either $\rho/c \gg 1$ or $k/c \gg 1$, this error becomes more substantial.

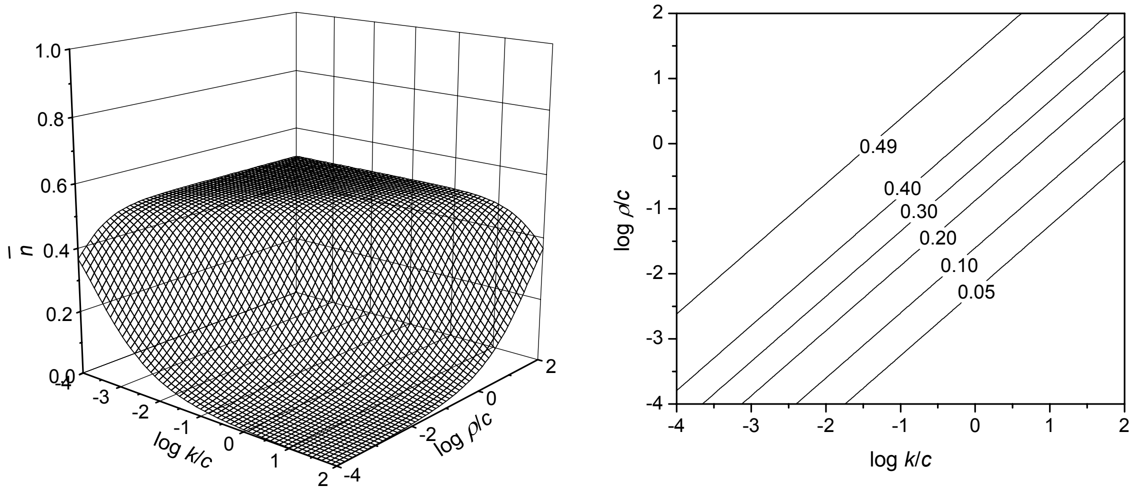

Figure 6.4: The 3D surface and contour plot of $\bar{n}$ *vs* ρ/c and k/c described by the zero-one equations with complete re-entry and minimal re-escape.

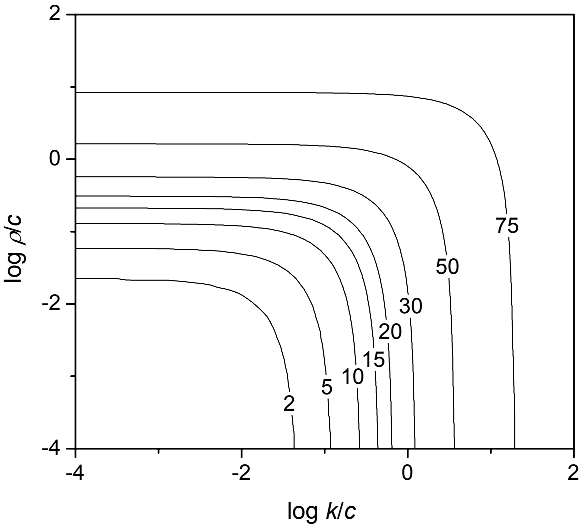

Figure 6.5: Percentage error in the calculation of $\bar{n}$ using zero-one kinetics as a function of ρ/c and k/c with complete re-entry and minimal re-escape.

6.2.4.2 Pseudo-Bulk Kinetics

In the case of an uncompartmentalized system, complete re-entry and minimal re-escape corresponds to pseudo-bulk kinetics.[4] The differential equation describing the time-evolution of $\bar{n}$ (Eq. 6.3) has the steady state solution:

$$\bar{n} = \left(\frac{\rho}{2c}\right)^{1/2} \qquad (6.10)$$

Once more, it is possible to map out $\bar{n}$ and the error in $\bar{n}$ from pseudo-bulk calculations as a function of ρ/c and k/c. These are shown in Fig. 6.6 and 6.7, showing that, for either $\rho/c \gg 1$ or $k/c \gg 1$, the correspondence between the pseudo-bulk approximation and the numerical solution to the Smith–Ewart equations is quite good.

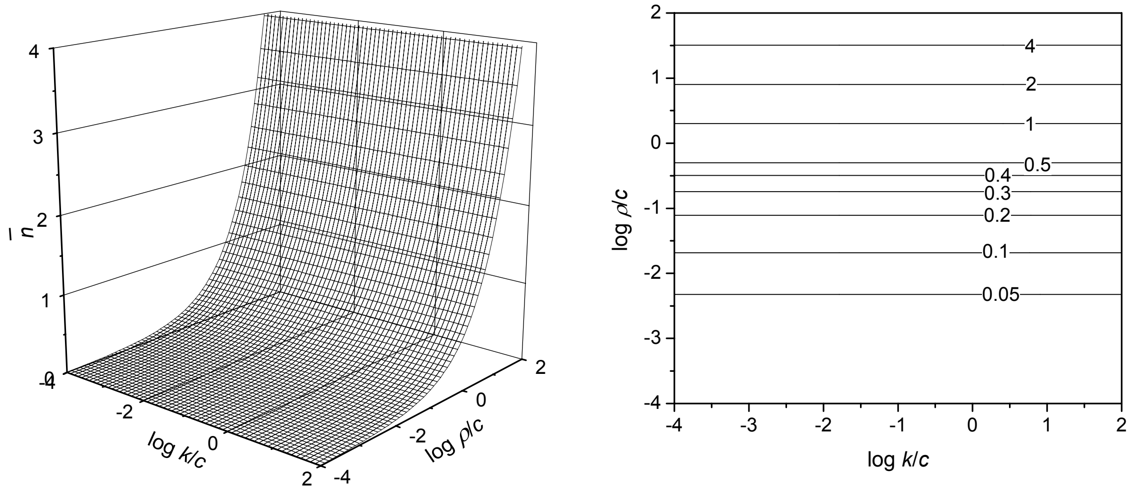

Figure 6.6: The 3D surface and contour plot of $\bar{n}$ *vs* ρ/c and k/c described by the pseudo-bulk equation.

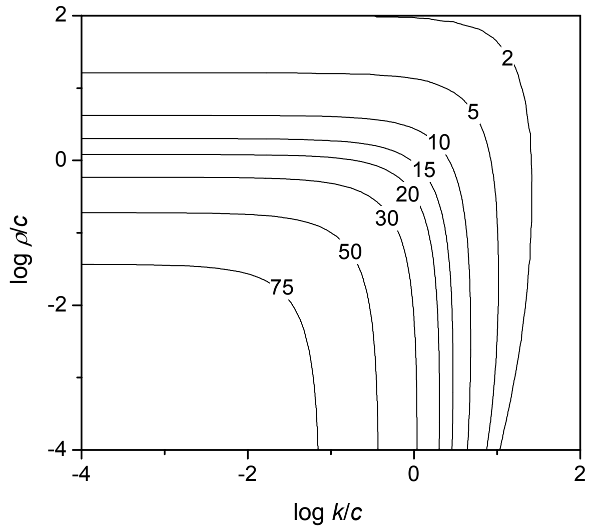

Figure 6.7: Percentage error in the calculation of $\bar{n}$ using pseudo-bulk kinetics as a function of ρ/c and k/c.

6.2.4.3 Zero-One-Two Kinetics

It would be remiss not to briefly mention the work of Lichti *et al.*[6] and zero-one-two kinetics in this discussion. While this limit was principally designed to be used with chain-length independent termination rate coefficients to generate molecular weight distributions for zero-one systems, it provides an alternate solution of the Smith–Ewart equations through a different closure relation. It also provides a means of expressing the chain-length dependence of termination, which, although very cumbersome, is rigorous. Moreover, this limit (with CLD termination) is expected to provide better quantitative accuracy for the difficult region in which the conditions for neither zero-one nor pseudo-bulk limits are satisfied. The zero-one-two equations are obtained from the full Smith–Ewart equations using a closure relation: entry of a radical into an N_2 particle produces an N_1 particle rather than an N_3 particle.

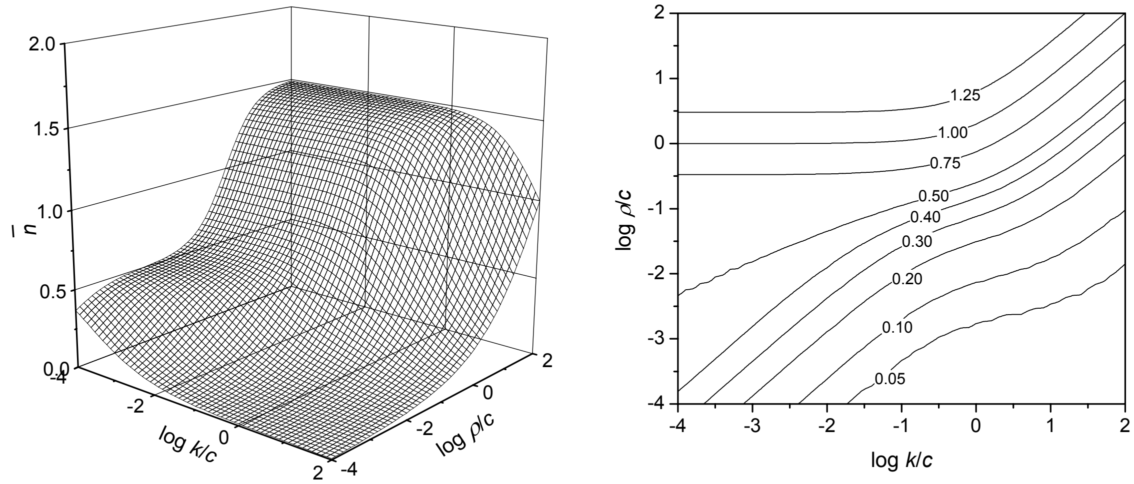

Figure 6.8: The 3D surface and contour plot of $\bar{n}$ *vs* ρ/c and k/c described by the zero-one-two equations with complete re-entry and minimal re-escape.

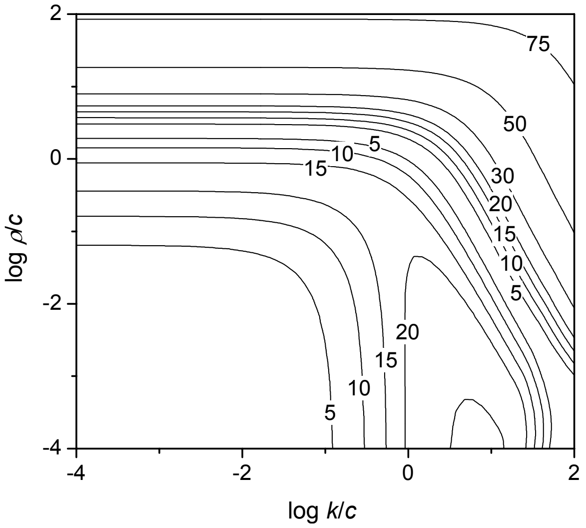

Figure 6.9: Percentage error in the calculation of $\bar{n}$ using zero-one-two kinetics as a function of ρ/c and k/c with complete re-entry and minimal re-escape.

These kinetics are considerably more difficult to solve than those of the zero-one or pseudo-bulk limits; moreover, once ρ becomes a function of $\bar{n}$ (*i.e.* exited radicals have subsequent kinetic effects, when $\alpha \neq 0$), it becomes simpler to solve these equations using the iterative technique described above for use with the Smith–Ewart equations. Unfortunately, despite the added complexity of the zero-one-two system, the approximation to the complete Smith–Ewart equations is only marginally better than for the zero-one and pseudo-bulk equations in the critical ($\rho/c \approx 1$ or $k/c \approx 1$) and ($\rho/c \not\gg 1$

and $k/c \not\gg 1$) regions, as shown in Fig. 6.8 and 6.9. While it would appear that the use of zero-one-two kinetics are unjustified in calculating steady-state values of $\bar{n}$ with chain-length *independent* termination, the zero-one-two model will be used as a basis for calculating suitable average values of the pseudo-first-order rate coefficient for termination in Section 6.3.

6.2.4.4 Approximations to the Smith–Ewart Equations

In this section, the scope of the discussion is once more limited to zero-one and pseudo-bulk kinetics, as Fig. 6.9 suggests that the added complexity of zero-one-two kinetics would appear largely unjustified for steady-state calculations. It is possible to construct a diagram of the best approximation to $\bar{n}$, calculated from the limit (zero-one or pseudo-bulk) with the lowest (absolute) percentage error in the calculation of $\bar{n}$. This is shown as a contour plot in Fig. 6.10, with contours of constant percentage error in $\bar{n}$. The region $\rho/c \ll 1$ and $k/c \ll 1$ is well described by zero-one kinetics, while the region $\rho/c \gg 1$ or $k/c \gg 1$ is well described by pseudo-bulk kinetics.

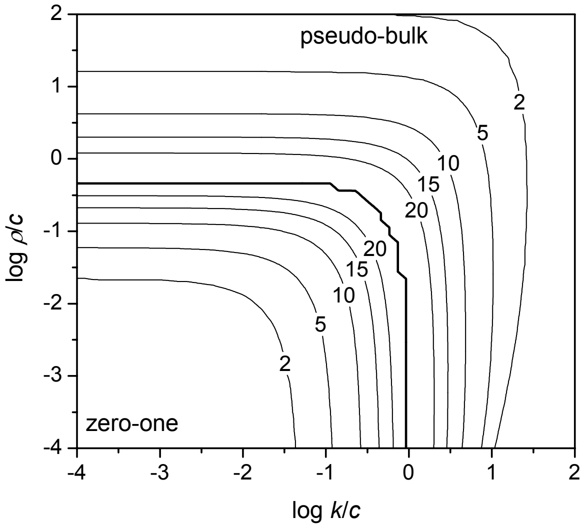

Figure 6.10: The best fit to $\bar{n}$ over the $(\rho/c, k/c)$-space with complete re-entry and minimal re-escape, taking $\bar{n}$ from either zero-one or pseudo-bulk kinetics (selecting on basis of minimum relative error). Contours are of constant percentage error in $\bar{n}$. The thick line indicates the boundary between zero-one and pseudo-bulk kinetics being the best fit.

The regions for which pseudo-bulk and zero-one kinetics are valid do not overlap. Fig. 6.5 and 6.7 indicate that there is significant error (20−30%) in the region between zero-one and pseudo-bulk kinetics. This is borne out in Fig. 6.10; the region where ($\rho/c \approx 1$ or $k/c \approx 1$) and ($\rho/c \not\gg 1$ and $k/c \not\gg 1$) may be described by either zero-one or pseudo-bulk kinetics only to an error of up to 30% in $\bar{n}$. Therefore, great care must be taken in interpreting the modeling result of either zero-one or pseudo-bulk kinetics in this region.

6.3 Chain-Length Dependence and Smith–Ewart Kinetics

The Smith–Ewart equations[1] have been used to describe emulsion polymerization kinetics in many systems, as they account for the compartmentalization of the radicals in the system. In the formalism developed by Smith and Ewart,[1] intra-particle termination is described by the (average) chain-length independent, pseudo-first-order rate coefficient for the destruction of two radicals, c. The treatment of emulsion polymerization kinetics in terms of the Smith–Ewart equations is, thus, a simplification that removes the chain-length dependence of the termination reaction.

Deviations from the Smith–Ewart equations due to CLD termination were described by Lichti *et al.*[6] and Adams *et al.*[7] Ignoring the chain-length dependence of termination is valid for zero-one systems and for pseudo-bulk systems at high weight-fractions of polymer, w_p, when the dominant termination mode becomes reaction-diffusion termination, which is independent of chain length. As noted above, some of the conclusions based on a chain-length independent treatment should be semi-quantitatively applicable to systems where this chain-length independence assumption is inadmissible.

As noted earlier, the occurrence of desorption requires taking into account the fate of exited free radicals, which can be implemented by extending these equations to differentiate particles containing one or more monomeric radicals (which can desorb) from particles containing the same number of longer radicals (which cannot desorb).[9]

When both CLD termination and radical desorption are taken into account, one can still apply the Smith–Ewart equations, but in general all the rate coefficients (ρ, k and c) will not be constant. Rather, they will depend on the instantaneous radical distribution and on the number of radicals in each particle.[10] Explicitly, c is a function of the number of radicals in the particle, i, and also of the overall instantaneous distributions of all the $G_i(N)$ (chain-length distributions of growing chains within that particle) and ρ is a function of the overall number of monomeric radicals within all particles. These dependencies can in general only be found by a solution of the more complete system where explicit account is taken of the distributions of the lengths of each chain in each particle.[10]

Various limits and approximations to the Smith–Ewart equations have been proposed, with the aim of variously describing the rate of polymerization or the molecular weight distribution of the polymer formed. Commonly used limits have included the zero-one limit[3,5] (where entry of a radical into a particle already containing a growing radical leads to pseudo-instantaneous termination) and the pseudo-bulk limit[4] (where there is no compartmentalization and the system polymerizes like the "equivalent" bulk system). The zero-one-two model,[14] where entry of a third radical into a particle leads to pseudo-instantaneous termination, has also been used to account for the molecular weight distributions.

In a compartmentalized system such as an emulsion polymerization, the effect of CLD termination is difficult to include, with the generalized kinetic scheme resulting in significant complexity. Even in the zero-one-two simplification with CLD termination, the full expressions include coupled partial integrodifferential equations with three independent variables (time and the length of the two radicals) that are generally intractable.

The application of the Smith–Ewart equations to systems in which CLD termination important is thus fraught with difficulties. Here, a method of taking account of the chain-length dependence of termination will be demonstrated to generate appropriate chain-length *independent* (average) parameters that may be used in the Smith–Ewart equations. The method presented here will firstly be shown for the zero-one-two limit[14] of the Smith–Ewart equations, with a generalization to systems containing more radicals being subsequently presented.

6.3.1 Overall Strategy

In the case of zero-one-two kinetics, it is first shown that the rate of loss of particles with two radicals in them (N_2 particles) is determined by the *time-dependent* pseudo-first-order rate coefficient for termination. Suitable physical models may be used to analytically describe termination or alternate numerical methods implemented. Once the loss of N_2 particles has been described, it is shown that this may be related to an *average* termination rate coefficient that is applicable to the quasi-steady-state in which the calculations were performed.

The notation used here is that of the distinguished particle equations of Lichti *et al.*[14] Here, the overall reaction time since the steady state was reached is denoted t, while the time since the first (distinguished) radical entered the particle under consideration is t'. The time for which two (distinguished) radicals have been in a particle is denoted t'' and the proportion of particles that have two distinguished radicals in them is thus $N_2''(t, t', t'')$ or simply $N_2''(t'')$. The pseudo-first-order rate coefficient for termination depends on the weight fraction of polymer in the system, $w_p(t)$, and the lengths of the two radicals in the particle; it is thus written as $c(t, t', t'')$ or simply $c(t'')$. The objective of the derivations presented here is to offer methods for obtaining $\overline{c}(t)$, the time-dependent rate coefficient for termination averaged over the current population distribution of radicals to account for CLD termination.

6.3.2 Average Termination Rate Coefficient in Zero-One-Two Kinetics

In a system where zero-one-two kinetics are applicable (*e.g.* ρ, $k \lesssim c$), the primary means of loss of N_2'' particles is termination between the two radicals. The following relation is thus found for the population balance $N_2''(t'')$:[14]

$$\frac{\mathrm{d}N_2''(t'')}{\mathrm{d}t''} = -\,2c(t'')N_2''(t'') \tag{6.11}$$

Solution of this differential equation gives $N_2''(t'')$ as a function of $c(t'')$:

$$N_2''(t'') = C_1(t)\exp\left(-2\int c(t'')\,\mathrm{d}t''\right) \tag{6.12}$$

where $C_1(t)$ is a constant of integration determined using the value of $N_2''(0)$; $N_2''(t'')$ is a monotonic decreasing function. Methods by which Eq. 6.12 may be solved are presented in subsequent sections.

It will now be shown that this result for $N_2''(t'')$ may be related back to the zero-one-two limit[14] of the Smith–Ewart equations,[1] where intra-particle termination is described by the *t*-dependent pseudo-first-order rate coefficient for the destruction of two radicals, $c = \overline{c}(t)$, averaged over t'' to account for CLD termination. Rewriting Eq. 6.11 in terms of $\overline{c}(t)$, one has:

$$\frac{\mathrm{d}N_2''(t'')}{\mathrm{d}t''} = -\,2\overline{c}(t)N_2''(t'') \tag{6.13}$$

where $\overline{c}(t)$ is *independent* of t''. This expression is integrated over t'' from $t'' = 0$ to the limit as $t'' \to \infty$. Noting that the limit as $t'' \to \infty$ of $N_2''(t'')$ is 0 (eventually all radicals must terminate), it is found that:

$$\overline{c}(t) = N_2''(0)\left[2\int_0^\infty N_2''(t'')\,\mathrm{d}t''\right]^{-1} \tag{6.14}$$

To obtain values for $\overline{c}(t)$, Eq. 6.12 must now be solved. In some cases, this may be done analytically, as will be shown in the next section, while in other cases it is more convenient to use numerical simulations to estimate this quantity.

6.3.2.1 Population Integral

It has been established experimentally[15,16] and through theoretical arguments[17] that the rate coefficient for termination between an *m*-meric and *n*-meric radical, k_t^{mn}, is determined by the mutual diffusion coefficient of the two radicals. In the case of the termination of a long chain and a short chain, this diffusion coefficient is (to a good approximation) that of the short chain, with the diffusion of the long chain making an insignificant contribution to the mutual diffusion of the chain ends.[17] If the short chain is the *m*-meric chain, the termination rate coefficient, k_t^{mn}, may be written in terms of a Smoluchowski diffusion reaction:[17]

$$k_t^{mn} \approx 4\pi D_m p^{mn} \sigma N_A \tag{6.15}$$

where D_m is the diffusion coefficient of the *m*-meric radical, p^{mn} the probability of reaction occurring during a collision (for radical-radical termination reactions, $p^{mn} = \frac{1}{4}$ due to spin multiplicity, except at high conversion[18,19]) and σ is the interaction radius (for styrene,[20] $\sigma \approx 0.7$ nm).

Since $c(t'')$ is the pseudo-first-order rate coefficient for termination per radical, it may be written in terms of the concentration of *m*-meric radical in the particle, $1/N_A V_s$, where V_s is the swollen volume of the particle:

$$c(t'') = k_t^{mn}(t'')/N_A V_s \tag{6.16}$$

Experimental studies of diffusion and termination have indicated that a power law relationship between the diffusion coefficient and the length of the short chain may be appropriate.[16,21] One may then write:

$$D_m(w_p) = D_1(w_p)\, m^{-\beta(w_p)} \tag{6.17}$$

where $D_1(w_p)$ is the diffusion coefficient of the monomer in the polymer matrix and $\beta(w_p)$ is the scaling exponent. (It is noted that, in other work, α has been used as the exponent for the chain-length dependence;[22] for clarity, β is used here to differentiate from the fate parameter described in Section 6.2.1.)

Both D_1 and β are dependent on the weight fraction of polymer, w_p, in the system, with previous studies providing empirical relations for these quantities; in many cases (such as in a γ-relaxation experiment), the dependence of D_1 and β on w_p can be neglected as the experiment is conducted over a relatively narrow range of values of w_p. Estimates for D_1 have been published for various monomers[21,23] and expressions for β have been found for systems below c^*,[16] and also well above c^{**}.[21]

Following the notation of Lichti *et al.*,[14] the length of the entering radical may be expressed as a function of the time since entry, t''. However, the length of the radical is not simply proportional to t'', as the radical already has a length z (where z is the critical degree of polymerization for entry[24]) on entry. It is convenient to introduce a parameter $t_z = z/(k_p C_p)$, giving the following expression for m:

$$m = \left[t'' + t_z\right] k_p C_p \tag{6.18}$$

where k_p is the second-order rate coefficient for propagation and C_p is the concentration of monomer in the particle.

It is then possible to express $c(t'')$ as a function of D_m, noting that $c(t'')$ is also a function of t due to the dependence on w_p:

$$c(t'') = c_0(t) \left[t'' + t_z\right]^{-\beta(t)} \tag{6.19}$$

where

$$c_0(t) = 4\pi p^{mn} \sigma V_s^{-1} D_1(t) [k_p C_p]^{-\beta(t)} \tag{6.20}$$

In considering the solution of Eq. 6.12 and then subsequently Eq. 6.14, it is necessary to break the solution into different cases according to the value of β. Physically reasonable values of β are [0,2], with $\beta = 0$ indicating no chain-length dependence and

$\beta = 2$ giving the reptation limit.[25] In the cases detailed below where Eq. 6.14 is not convergent, a more suitable model for $c(t'')$ must be chosen; in particular, once reaction diffusion (where chain ends move by propagation) provides a significant contribution to the diffusion of the radicals and when transfer to monomer is significant, the simple scaling law of Eq. 6.19 is inapplicable.

Case 0 < β < 1:

Returning to Eq. 6.12, it is possible to analytically evaluate this expression given the power law relation for $c(t'')$ shown in Eq. 6.19:

$$N_2''(t'') = C_1(t)\, N_2''(0)\, \exp\!\left(\frac{-2c_0(t)}{1-\beta(t)}\, \left[t'' + t_\mathrm{z}\right]^{1-\beta(t)}\right) \tag{6.21}$$

with $C_1(t)$ being evaluated using $N_2''(0)$:

$$C_1(t) = \exp\!\left(\frac{2c_0(t)}{1-\beta(t)}\, \left[t_\mathrm{z}\right]^{1-\beta(t)}\right) \tag{6.22}$$

Evaluation of Eq. 6.14 is once again possible analytically, given the power law dependence assumed here:

$$\overline{c}(t) = \frac{\left[\beta(t)-1\right] \left[\frac{2c_0(t)}{1-\beta(t)}\right]^{\frac{1}{1-\beta(t)}}}{2C_1(t)\Gamma\!\left(\frac{1}{1-\beta(t)}, \frac{2c_0(t)\, t_\mathrm{z}^{\,1-\alpha(t)}}{1-\beta(t)}\right)} \tag{6.23}$$

where $\Gamma(b, z)$ is the incomplete Γ-function:

$$\Gamma(b, z) = \int_z^{\infty} t^{b-1} e^{-t}\, \mathrm{d}t \tag{6.24}$$

Case β = 1:

The integral shown in Eq. 6.12 takes quite a different form when $\beta = 1$, giving:

$$N_2''(t'') = C_1(t)\, \left[t'' + t_\mathrm{z}\right]^{-2c_0(t)} \tag{6.25}$$

with $C_1(t)$ given by:

$$C_1(t) = N_2''(0)\,[t_z]^{-2c_0(t)} \tag{6.26}$$

It is now possible to evaluate $\overline{c}(t)$ using Eq. 6.14 in some circumstances, depending on the value of $c_0(t)$. In the case where $\beta = 1$, Eq. 6.20 gives $c_0(t) \approx c^{1L}/k_pC_p$, where c^{1L} is the pseudo-first-order rate coefficient for termination of the monomeric radical under the short-long assumption used here. When $c_0(t) > ½$, it is found that:

$$\overline{c}(t) = \frac{C_1(t)}{(2c_0(t)-1)t_z^{2c_0(t)-1}} \tag{6.27}$$

However, for $c_0(t) < ½$, the integral in Eq. 6.14 is divergent giving the unphysical result $\overline{c}(t) = 0$. The value of $c_0(t)$ may cross the value of ½ during the course of a reaction: the ratio between termination (*i.e.* diffusion) and propagation rate coefficients determines the behavior of the system with $c_0 \propto D_1/(k_pV_s)$. Larger particles also tend to decrease $c_0(t)$ as termination is less likely.

Case 1 < β < 2:

In the case where $\beta > 1$, $N_2''(t'')$ and $C_1(t)$ are given by Eq. 6.21 and 6.22; however, the integral over all t'' to find $c(t'')$ (Eq. 6.14) is divergent. In this case, it is not possible to calculate $\overline{c}(t)$ from a simple power law expression for $c(t'')$. The divergence of the integral is unphysical, but easily understood given the assumptions of the model for termination used here. Note also that the work of Griffiths *et al.*[21] indicates that emulsion polymerizations would normally have $\beta > 1$, making this shortcoming quite significant.

6.3.2.2 Population Integral with Reaction Diffusion and Transfer to Monomer

An alternate model for $c(t'')$ incorporating both reaction diffusion and chain transfer to monomer permits the calculation of $N_2''(t'')$. With physically reasonable assumptions, these two additions add equivalent complexity to the mathematics of the system; hence, it is convenient to discuss them both together. However, the expression obtained for $N_2''(t'')$

with either reaction-diffusion or transfer to monomer does not permit $\overline{c}(t)$ to be obtained analytically. Recourse to numerical methods is quite feasible in this case.

Incorporating reaction diffusion, the model for the diffusion of the terminating radicals is as follows. The mutual diffusion coefficient may be constructed from the center-of-mass diffusion coefficients for each species, D_m^{com} and D_n^{com}, and the reaction-diffusion coefficient for each chain, D_m^{rd} and D_n^{rd}:[20]

$$D_{mn} = D_m^{\mathrm{com}} + D_n^{\mathrm{com}} + D_m^{\mathrm{rd}} + D_n^{\mathrm{rd}} \tag{6.28}$$

As before, the center-of-mass diffusion coefficient for the longer *n*-meric species may be neglected. Additionally, the reaction-diffusion term will be independent of chain-length,[20] giving:

$$D_m = D_m^{\mathrm{com}} + 2D^{\mathrm{rd}} \tag{6.29}$$

where D^{rd} is given by:

$$D^{\mathrm{rd}} = k_{\mathrm{p}}C_{\mathrm{p}}a^2/6 \tag{6.30}$$

Here, *a* is the root-mean-square end-to-end distance per square root of the number of monomer units in the polymer chain. Values for *a* for various monomers are given by Russell *et al.*[20]

The rigorous inclusion of transfer to monomer is quite difficult. However, it was shown by Clay *et al.*[22] that the pseudo-first-order rate coefficient for transfer to monomer was of similar magnitude to the pseudo-first-order average rate coefficient for termination; moreover, approximately equal numbers of chains were stopped by transfer and termination.[22] One may conclude that the most probable fate for a monomeric radical is termination with another radical, since the termination rate coefficient for a monomeric radical is significantly greater than that of a longer chain, as noted in the experiments of Adams *et al.*[7] Working with this physically reasonable assumption that all monomeric radicals terminate, a lower limit on the pseudo-first-order termination rate coefficient $c(t'')$ is the transfer frequency, $k_{\mathrm{tr}}C_{\mathrm{p}}$.

Once again, using a power law relationship for the chain-length dependence of the center-of-mass diffusion, an expression for $c(t'')$ may be obtained:

$$c(t'') = c_0(t)\,\left[t'' + t_{\mathrm{z}}\right]^{-\beta(t)} + c_{\mathrm{rd}} + c_{\mathrm{trM}} \tag{6.31}$$

where $c_0(t)$ is defined as before (Eq. 6.20). The contribution of reaction-diffusion to termination is $c_{\mathrm{rd}}(t)$ (p^{mn} being dependent[26] on w_{p} and C_{p} being dependent on t):

$$c_{\mathrm{rd}}(t) = \frac{4\pi p^{mn}\sigma k_{\mathrm{p}}C_{\mathrm{p}}a^2}{3V_{\mathrm{s}}} \tag{6.32}$$

The contribution of transfer to monomer to termination, $c_{\mathrm{trM}}(t)$, is t-dependent as the transfer reaction has been shown to have a dependence on w_{p} at high conversion[22,26] and C_{p} varies throughout Interval III:

$$c_{\mathrm{trM}}(t) = k_{\mathrm{tr}}C_{\mathrm{p}} \tag{6.33}$$

As before, this expression may be integrated to give an expression for $N_2''(t'')$. For example, in the case where $\beta \neq 1$,

$$N_2''(t'') = C_1(t)\,\exp\!\left(\frac{-2c_0(t)}{1-\beta(t)}\,\left[t'' + t_{\mathrm{z}}\right]^{1-\beta(t)} - 2c_{\mathrm{rd}}t'' - 2c_{\mathrm{trM}}t''\right) \tag{6.34}$$

with $C_1(t)$ being the same as defined in Eq. 6.22.

In general, it is not possible to integrate $N_2''(t'')$ as given in Eq. 6.34 over all t'', thus $\overline{c}(t)$ cannot be obtained analytically from Eq. 6.19 and 6.34. However, numerical computation of the integral over all $N_2''(t'')$ is relatively inexpensive, permitting this method to be used to calculate a value of $\overline{c}(t)$ that suitably takes account of the chain-length dependence of termination in the Smith–Ewart equations.

6.3.2.3 Probabilistic Method

Analytic expressions for the probability that radicals will propagate j or more steps in a two radical environment were used by Maeder and Gilbert[27] to estimate the applicability of zero-one kinetics to the polymerization of butyl acrylate. More recently, Monte Carlo models were used by Prescott[28] to estimate radical lifetimes in RAFT-mediated emulsion polymerizations (although this technique could be equally well used with non-RAFT systems). The inclusion of reaction-diffusion and transfer to monomer is quite simple in these models, permitting the kinetics of the system to be more accurately modeled.

The probability that the two radicals in a particle will consume j or more monomer units is denoted by $P_j(t)$, noting that this will be a function of $w_\mathrm{p}(t)$. It will first be shown that the area under the $P_j(t)$ *vs* j curves, constructed according to the method of Prescott[28] (or alternatively $P_j(t)$ *vs* $2j$ if using the method of Maeder and Gilbert[27]), provides a measure of the average number of monomer units consumed before termination in a particle, $\overline{\Delta_\mathrm{m}}(t)$, and that this, in turn, permits the evaluation of $\overline{c}(t)$.

Consider a $P_j(t)$ *vs* j curve generated by sequentially assessing N test-particles, each originally containing 2 radicals. By definition, $P_j(t)$ is the proportion of systems that consumed *j or more* monomer units before a termination reaction occurred. Thus, NP_j is equal to the number of systems that consumed j or more monomer units and $N(P_j - P_{j+1})$ is the number of systems that consumed precisely j monomer units. The (number) average number of monomer units consumed in a system, $\overline{\Delta_\mathrm{m}}$, is then given by:

$$\overline{\Delta_\mathrm{m}} = \frac{N(P_1 - P_2) + 2N(P_2 - P_3) + 3N(P_3 - P_4) + \ldots}{N} \tag{6.35}$$

which simplifies to:

$$\overline{\Delta_\mathrm{m}} = \sum_{j \geq 0} P_j \tag{6.36}$$

This may be reduced to an integral form through a discrete-to-continuous approximation for j:

$$\overline{\Delta_{\mathrm{m}}} = \int_0^\infty P_j \, \mathrm{d}j \tag{6.37}$$

It will now be shown that $\overline{\Delta_{\mathrm{m}}}(t)$ may be related back to $\overline{c}(t)$. The time taken for j monomer units to be consumed in a particle with two radicals, t'', is:

$$t'' = j/2k_{\mathrm{p}}C_{\mathrm{p}} \tag{6.38}$$

Changing the variable of integration in Eq. 6.37 from j to t'' using Eq. 6.38 yields the following integral over time for the number of monomer units consumed in the system:

$$\overline{\Delta_{\mathrm{m}}}(t) = 2k_{\mathrm{p}}C_{\mathrm{p}} \int_0^\infty N_2''(t'') \, \mathrm{d}t'' \tag{6.39}$$

In the probabilistic formulation described here, $N_2''(0) = 1$. This result for $\overline{\Delta_{\mathrm{m}}}(t)$ provides a method for evaluating $\overline{c}(t)$ using Eq. 6.14, without the need to solve the differential equation shown in Eq. 6.12:

$$\overline{c}(t) = \frac{k_{\mathrm{p}}C_{\mathrm{p}}}{\overline{\Delta_{\mathrm{m}}}(t)} \tag{6.40}$$

6.3.3 Average Termination Rate Coefficients in Generalized Smith-Ewart Systems

The above method described for zero-one-two kinetics may now be extended to generalized Smith–Ewart kinetics. Restricting the discussion once more to the termination reaction between two radicals, the following relation is found for the population balance N_i:

$$\frac{\mathrm{d}N_i}{\mathrm{d}t} = -\, i(i-1)\overline{c}(t)N_i \tag{6.41}$$

where $\overline{c}(t)$ is once again the effective chain-length independent *average* coefficient for second-order radical loss (which is invariant over the timescale of the lifetime of one radical). Integrating over time from $t = 0$ to the limit as $t \to \infty$ (and writing $N_i(t{=}0)$ as N_i^0) gives:

$$-N_i^0 = -\,i(i-1)\bar{c}(t)\int_0^\infty N_i\,\mathrm{d}t \tag{6.42}$$

Rearranging yields:

$$\bar{c}(t) = \frac{N_i^0}{i(i-1)\int_0^\infty N_i(t)\,\mathrm{d}t} \tag{6.43}$$

where the integral in Eq. 6.43 is ultimately a function of the chain-length dependent $c(t, t', t'', i)$, as previously described for the zero-one-two case. However, $c(t'')$ will also now be a function of the chain lengths of the other i–2 radicals not under consideration. It is reasonable to approximate the termination reaction as occurring between the most recently entered radical and one other radical, in which case the mutual diffusion coefficient will be dominated by the diffusion of the shortest species and $c(t'')$ may be estimated from t'' alone. Under such conditions, it is possible to calculate $\bar{c}(t)$ from Eq. 6.43 using the previously illustrated analytic or numeric methods.

To make use of the probabilistic method for calculating $\bar{c}(t)$ shown above, the time coordinate must be related to the number of monomer units consumed using the frequency of propagation (including the number of radicals present, i), $ik_\mathrm{p}C_\mathrm{p}$. This yields the required transform:

$$t = \frac{j}{ik_\mathrm{p}C_\mathrm{p}} \tag{6.44}$$

$$\frac{\mathrm{d}t}{\mathrm{d}j} = \frac{1}{ik_\mathrm{p}C_\mathrm{p}} \tag{6.45}$$

which may be used as a change of variable for the integral w.r.t. t (Eq. 6.43):

$$\bar{c}(t) = \frac{k_\mathrm{p}C_\mathrm{p}N_i^0}{(i-1)\int_0^\infty N_i(j)\,\mathrm{d}j} \tag{6.46}$$

As before, one sees that $P_{j,i} = N_i(j)/N_i^0$, where $P_{j,i}$ is the probability P_j, now also dependent on i. The average number of monomer units consumed in a particle before a termination reaction occurs is a function of i and denoted $\overline{\Delta_{\mathrm{m},i}}$; Eq. 6.37 then provides the necessary relation to permit $\overline{c}(t)$ to be calculated from probabilistic data, such as a Monte Carlo simulation, as follows:

$$\overline{c}(t) = \frac{k_{\mathrm{p}} C_{\mathrm{p}}}{(i-1)\overline{\Delta_{\mathrm{m},i}}} \tag{6.47}$$

6.4 Principles of γ-Relaxation

As it is now feasible to extract suitable average Smith–Ewart parameters from the full chain-length dependent kinetic scheme, it is useful to briefly revisit the principles of the experimental technique available for extracting these kinetic parameters.

As discussed in Chapter 1, dilatometry measures the volume change of the reaction at frequent intervals, allowing conversion *vs* time data to be obtained from these volume changes using the difference in density between the monomer and polymer. From these data, a steady state value of $\overline{n}$ may be obtained, providing one kinetic parameter for the system.

In a γ-relaxation, the system is permitted to come to a (quasi-) steady state before the dilatometer is removed from the proximity of the γ-source, thus ceasing external initiation (see Chapter 1 for a schematic of the ^{60}Co shielding and elevator mechanism).[29] Once external initiation has been switched off, the system will move to a new steady state; the new value of $\overline{n}$ and the time-constant for the relaxation provide two additional kinetic parameters, in theory permitting three physical kinetic parameters to be determined from the data. In practice, the relaxation is dependent on the kinetic model followed (*e.g.* the assumed fate of the exited radicals) and thus additional information is required to completely specify the behavior of the system.[5]

While UV radiation is sufficient to initiate bulk and solution polymerization experiments, an emulsion polymerization has significant turbidity, preventing uniform initiation throughout the latex with UV radiation. In contrast, γ-initiation is able to pass through the latex with little attenuation, producing radicals homogeneously throughout the reaction mixture.[5]

Previous well-documented uses of γ-initiation in RAFT-mediated polymerizations include verifying that a polymerization follows RAFT-mediated kinetics rather than "iniferter" kinetics[30] and investigations of radical storage effects in the RAFT mechanism.[31] It has also been used for the creation of novel materials by initiating grafting to substrates.[32] Kinetic investigations using γ-relaxations have been performed on emulsion polymerizations of monomers including styrene,[29] methyl methacrylate,[33] and vinyl acetate.[34]

The numerical treatment of the dilatometry data with reference to possible mechanisms for radical loss is described in Chapter 7, with additional information about the mass-balance and model-independent kinetics used to treat the raw data contained in the Appendices.

6.5 References

(1) Smith, W. V.; Ewart, R. H. *J. Chem. Phys.* **1948**, *16*, 592.

(2) Hawkett, B. S.; Napper, D. H.; Gilbert, R. G. *J. Chem. Soc. Faraday Trans. 1* **1977**, *73*, 690.

(3) Hawkett, B. S.; Napper, D. H.; Gilbert, R. G. *J. Chem. Soc. Faraday Trans. 1* **1980**, *76*, 1323.

(4) Ballard, M. J.; Gilbert, R. G.; Napper, D. H. *J. Polym. Sci., Polym. Letters Edn.* **1981**, *19*, 533.

(5) Gilbert, R. G. *Emulsion Polymerization: A Mechanistic Approach*; Academic: London, 1995.

(6) Lichti, G.; Gilbert, R. G.; Napper, D. H. *J. Polym. Sci., Part A: Polym. Chem.* **1980**, *18*, 1297.

(7) Adams, M. E.; Russell, G. T.; Casey, B. S.; Gilbert, R. G.; Napper, D. H.; Sangster, D. F. *Macromolecules* **1990**, *23*, 4624.

(8) Ugelstad, J.; Hansen, F. K. *Rubber Chem. Technol.* **1976**, *49*, 536.

(9) Casey, B. S.; Morrison, B. R.; Maxwell, I. A.; Gilbert, R. G.; Napper, D. H. *J. Polym. Sci. A: Polym. Chem.* **1994**, *32*, 605.

(10) Clay, P. A.; Gilbert, R. G. *Macromolecules* **1995**, *28*, 552.

(11) Stockmayer, W. H. *J. Polym. Sci.* **1957**, *24*, 314.

(12) O'Toole, J. T. *J. Appl. Polym. Sci.* **1965**, *9*, 1291.

(13) Morrison, B. R.; Casey, B. S.; Lacík, I.; Leslie, G. L.; Sangster, D. F.; Gilbert, R. G.; Napper, D. H. *J. Polym. Sci. A: Polym. Chem.* **1994**, *32*, 631.

(14) Napper, D. H.; Lichti, G.; Gilbert, R. G. In *ACS Symp. Series - Emulsion Polymers and Emulsion Polymerization*; Bassett, D. R., Hamielec, A. E., Eds.; American Chemical Society: Washington D.C., 1981; Vol. 165.

(15) de Kock, J. B. L.; Klumperman, B.; van Herk, A. M.; German, A. L. *Macromolecules* **1997**, *30*, 6743.

(16) de Kock, J. B. L.; van Herk, A. M.; German, A. L. *J. Macromol. Sci., Polym. Rev.* **2001**, *C41*, 199.

(17) Russell, G. T. *Aust. J. Chem.* **2002**, *55*, 399.

(18) Clay, P. A.; Christie, D. I.; Gilbert, R. G. In *ACS Symp. Series - Advances in Free-Radical Polymerization*; Matyjaszewski, K., Ed.; American Chemical Society: Washington D.C., 1998; Vol. 685.

(19) Clay, P. A.; Gilbert, R. G.; Russell, G. T. *Macromolecules* **1997**, *30*, 1935.

(20) Russell, G. T.; Napper, D. H.; Gilbert, R. G. *Macromolecules* **1988**, *21*, 2133.

(21) Griffiths, M. C.; Strauch, J.; Monteiro, M. J.; Gilbert, R. G. *Macromolecules* **1998**, *31*, 7835.

(22) Clay, P. A.; Gilbert, R. G. *Macromolecules* **1995**, *28*, 552.

(23) Scheren, P. A. G. M.; Russell, G. T.; Sangster, D. F.; Gilbert, R. G.; German, A. L. *Macromolecules* **1995**, *28*, 3637.

(24) Maxwell, I. A.; Morrison, B. R.; Napper, D. H.; Gilbert, R. G. *Macromolecules* **1991**, *24*, 1629.

(25) de Gennes, P. G. *J. Chem. Phys.* **1971**, *55*, 572.

(26) Casey, B. S.; Mills, M. F.; Sangster, D. F.; Gilbert, R. G.; Napper, D. H. *Macromolecules* **1992**, *25*, 7063.

(27) Maeder, S.; Gilbert, R. G. *Macromolecules* **1998**, *31*, 4410.

(28) Prescott, S. W. *Macromolecules* **2003**, *ASAP*, DOI: 10.1021/ma034845h.

(29) Lansdowne, S. W.; Gilbert, R. G.; Napper, D. H.; Sangster, D. F. *J. Chem. Soc. Faraday Trans. 1* **1980**, *76*, 1344.

(30) Quinn, J. F.; Barner, L.; Davis, T. P.; Thang, S. H.; Rizzardo, E. *Macromol. Rapid Commun.* **2002**, *23*, 717.

(31) Barner-Kowollik, C.; Vana, P.; Quinn, J. F.; Davis, T. P. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 1058.

(32) Barner, L.; Zwaneveld, N.; Perera, S.; Pham, Y.; Davis, T. P. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 4180.

(33) Ballard, M. J.; Napper, D. H.; Gilbert, R. G.; Sangster, D. F. *J. Polym. Sci. Polym. Chem. Edn.* **1986**, *24*, 1027.

(34) De Bruyn, H.; Gilbert, R. G.; Ballard, M. J. *Macromolecules* **1996**, *29*, 8666.