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2002 J. Phys. A: Math. Gen. 35 1357

(http://iopscience.iop.org/0305-4470/35/6/303)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS A: MATHEMATICAL AND GENERAL

J. Phys. A: Math. Gen. **35** (2002) 1357–1380 PII: S0305-4470(02)29604-3

Asymptotic solutions of the Becker–Döring equations with size-dependent rate constants

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Received 9 October 2001, in final form 4 December 2001
Published 1 February 2002
Online at stacks.iop.org/JPhysA/35/1357

Abstract

We find the large-time asymptotic behaviour for a number of physically interesting cases of the Becker–Döring equations, allowing both the forward and the backward rates to depend on cluster size in a power-law fashion. We consider in detail the constant monomer form of the equations in the special case where the powers are equal, since the structure of the large-time asymptotic behaviour is then richest. We then turn to cases in which aggregation and fragmentation have different exponents, examining both the fragmentation- and coagulation-dominated cases, again under constant monomer conditions.

PACS numbers: 02.30.Hq, 02.60.−x, 03.65.Sq, 05.45.−a, 61.43.Hv, 68.43.Jr

1. Introduction

Our main aim in this paper is to apply the methods of matched asymptotic expansions to find the large-time asymptotic behaviour of the Becker–Döring system of ordinary differential equations in certain cases of physical interest in which the rate coefficients are allowed to vary with cluster size. This study thus generalizes earlier asymptotic results of the system with constant rates [7]. In particular, we shall be concerned with forward and backward rate coefficients given by

$$a_r = \alpha r^p \qquad \text{and} \qquad b_r = \beta r^q \tag{1.1}$$

respectively, for constant p and q. The exponent p reflects how the rate of coalescence of monomers with clusters scales with the size of cluster. For compact clusters, $p \leqslant 1$ holds since the number of collisions is dependent on the surface area of the cluster and not all collisions lead to the formation of larger clusters; however, $p > 1$ is possible for fractal aggregates (see [3] and references therein). The parameter q determines the relative stability of clusters of different sizes; if $q > 0$ then larger clusters fragment at a faster rate than smaller, whereas it is smaller clusters which have the greater fragmentation rate if $q < 0$. The sign of $p - q$ determines the equilibrium (or steady-state) behaviour of the system; if $q > p$ then large clusters are more likely to fragment than aggregate, corresponding to an undersaturated solution, whereas $q < p$ corresponds to a supersaturated environment in which large clusters are more likely to aggregate than fragment.

The Becker–Döring equations have been studied in two closely related forms; first there is the constant monomer case, as originally proposed by Becker and Döring [2], in which

$$\dot{c}_r = J_{r-1} - J_r \quad (r \geqslant 2) \qquad \text{and} \qquad J_r = a_r c_1 c_r - b_{r+1} c_{r+1} \tag{1.2}$$

are solved with c_1 a prescribed constant for all $t \geqslant 0$. Secondly, and more recently [6], the monomer concentration has been allowed to vary in (1.2), with a constant density condition imposed rather than a prescribed constant monomer concentration. The monomer concentration then satisfies

$$\dot{c}_1 = -J_1 - \sum_{r=1}^{\infty} J_r. \tag{1.3}$$

Since a cluster of size r contains r monomers, the total density in the system is the first moment:

$$\varrho = M_1 = \sum_{r=1}^{\infty} r c_r. \tag{1.4}$$

This quantity is conserved for (1.2), (1.3), at least for $p \leqslant 1$ [1]. Ball *et al* [1] note that for certain initial data the system has no solution if $p > \max(1, q)$ due to the divergence of the sum in (1.3). Brilliantov and Kravitsky [3] observed gelation (that is the loss of mass to a particle of formally infinite size) in numerical simulations of the Becker–Döring equations when $p > 1$ and $q = 0$, but gave no analysis of the phenomenon. We shall include here such an analysis of the simpler constant monomer case.

The system (1.2), (1.3) is nonlinear, due to the appearance of the product of c_1 with c_r in each of the flux functions in (1.2). Viewing r as a spatial variable, equation (1.3) makes the system nonlocal as well as nonlinear. When considering the large-time asymptotics of the system, there are, however, situations in which the two problems are almost identical and many others in which knowledge of the constant monomer problem sheds much light on the harder constant density case. We accordingly concern ourselves here with the constant monomer case, (1.1)–(1.2) with c_1 constant.

There are two important quantities that we should introduce before the analysis of the system proceeds. The first is the partition function Q_r, which is defined by

$$a_r Q_r = b_{r+1} Q_{r+1} \qquad Q_1 = 1. \tag{1.5}$$

It is straightforward to describe the equilibrium solutions of either system in terms of the Q_r, these being the steady-state solutions which satisfy $J_r = 0$ for all r, given by

$$c_r = Q_r c_1^r. \tag{1.6}$$

In the constant density system, the equilibrium monomer concentration is in many cases determined by requiring that the solution defined by (1.6) has the same density (1.4) as the initial data. The other quantity is the function

$$V = \sum_{r=1}^{\infty} c_r \left(\log\left(\frac{c_r}{Q_r c_1^r} \right) - 1 \right) \tag{1.7}$$

which is a Lyapunov function for the system provided it is bounded below, since $\mathrm{d}V/\mathrm{d}t \leqslant 0$ follows from (1.2).

In a previous paper [7], we analysed the constant coefficient case, that is $p = q = 0$. There, we determined the large-time asymptotics of the constant monomer concentration case together with the limit case of the fixed mass system in which the fragmentation rate tends to zero. The purpose of the current paper is to generalize the constant monomer results to variable rate coefficients (1.1); unlike the constant coefficient case, there seem in general to be no exact time-dependent solutions to the variable coefficient system (see section 2.2, however).

Section 2 describes the equilibrium and steady-state solutions which are possible attractors in the large-time limit; in addition, for a very special choice of the rate coefficients, an exact solution is derived. For general rate coefficients, the large-r behaviour of the solutions is then derived using WKBJ methods, in particular. Section 3 concerns the small-time behaviour, which provides important information regarding the qualitative behaviour in the various (p, q) parameter regimes. In section 4 we consider the large-time behaviour, starting by analysing the special case in which the two exponents are equal ($p = q$), so that $Q_r = (\alpha/\beta)^{r-1}/r^p$, the parameter $\theta = \alpha c_1/\beta$ being crucial to the analysis. The resulting balance between coagulation and fragmentation produces some phenomena not seen in cases with $p \neq q$. For $p = q$ we find three subcases: 'E' for $\theta < 1$, where the system tends to an equilibrium solution; 'S' for $\theta > 1$, where a steady-state solution is approached and 'B' for the borderline case $\theta = 1$ in which more complicated phenomena occur. Within each of these categories, there are further subcases depending on the value of the exponent p. The section concludes with brief descriptions of the cases $q > p$ (section 4.6) and $p > q$ (section 4.7). In the former, fragmentation dominates coagulation at large aggregation numbers. We refer to this as the fragmentation-dominated case ('F': $q > p$) and show that, for constant monomer concentration, a well-behaved equilibrium solution is approached. In section 4.7 we consider the case where the aggregation exponent exceeds that of fragmentation ('A': $p > q$), so the system can be viewed as being dominated by aggregation and approaches a steady-state solution. The paper concludes with a discussion of the results and pointers to future work.

2. Preliminaries

2.1. The partition function and equilibrium solutions

With the choice of rate coefficients (1.1), the partition function is given by

$$Q_r = \left(\frac{\alpha}{\beta}\right)^{r-1} \frac{1}{r^p (r!)^{q-p}}. \tag{2.1}$$

This implies that

$$\log Q_r \sim (p-q) r \log r + \left(q - p + \log\frac{\alpha}{\beta}\right) r - \frac{1}{2}(p+q)\log r + \frac{1}{2}(p-q)\log 2\pi - \log\frac{\alpha}{\beta} \qquad \text{as} \quad r \to \infty \tag{2.2}$$

so for $p < q$ the partition function Q_r tends to zero sufficiently fast that the equilibrium distribution (1.6) has a finite total density for any finite value of c_1; if $p > q$, however, then Q_r diverges rapidly.

In the special case $p = q$, the partition function has much weaker large-r asymptotics and the value of the ratio $\theta = \alpha c_1/\beta$ determines whether the system converges to equilibrium or to a steady state (cf [7]). If $\theta > 1$ then the system approaches a steady state solution (i.e. one with J_r constant and strictly positive) in which, for $p > 0$, the concentrations c_r decay algebraically with increasing cluster size (see (2.7)). For $\theta \leqslant 1$, the system converges to its equilibrium solution, which decays exponentially for $\theta < 1$ but has algebraic behaviour when $\theta = 1$; from (1.6) and (2.1) we have

$$c_r = \frac{c_1\theta^{r-1}}{r^p}. \tag{2.3}$$

Thus it is the case $p = q$ which has the richest asymptotic structure and will be the focus of most attention in section 4.

If $\theta > 1$ with $p = q$ then the solution (2.3) diverges as $r \to \infty$ and we must instead consider the more general (one-parameter) family of steady-state solutions

$$J_r = J \qquad c_r = \frac{c_1\theta^{r-1}}{r^p}\left(1 - \frac{J(\theta^r - \theta)}{\beta c_1\theta^r(\theta - 1)}\right) \qquad \theta \neq 1 \tag{2.4}$$

$$J_r = J \qquad c_r = \frac{c_1}{r^p}\left(1 - \frac{J(r-1)}{\beta c_1}\right) \qquad \theta = 1 \tag{2.5}$$

where J is the constant mass flux through the system at steady-state. In order to have the minimal behaviour in c_r as $r \to \infty$, we require for $\theta \leqslant 1$ that $J = 0$, as above, and for $\theta > 1$ that

$$J = c_1(\alpha c_1 - \beta) > 0; \tag{2.6}$$

equation (2.4) then yields the steady-state solution

$$c_r = c_1/r^p. \tag{2.7}$$

This solution coincides with (2.3) in the borderline case $\theta = 1$ and has unbounded mass when $p < 2$. Moreover, it does not necessarily provide a uniform description of the $t \to \infty$ asymptotic behaviour; see section 4.3. For the case of general rate coefficients, the steady-state solution is determined by

$$c_r = Q_r c_1^r J \sum_{k=r}^{\infty} \frac{1}{a_k Q_k c_1^{k+1}} \qquad \text{with} \quad J = 1 \Bigg/ \sum_{k=1}^{\infty} \frac{1}{a_k Q_k c_1^{k+1}}. \tag{2.8}$$

For the rates given by (1.1) with $p > q$ this implies

$$c_r \sim \frac{J}{\alpha c_1 r^p} \qquad \text{as} \quad r \to \infty \quad \text{with} \quad J = \beta c_1 \Bigg/ \sum_{k=1}^{\infty} \frac{1}{\theta^k (k!)^{p-q}}. \tag{2.9}$$

More generally, the former reads $c_r \sim J/a_r c_1$ as $r \to +\infty$.

2.2. Exact solutions

The Becker–Döring system with aggregation rate given by $a_r = \alpha r$ and no fragmentation can in certain cases be solved by the use of generating functions, cf Brilliantov and Krapivsky [3], who derive a closed form solution in the corresponding constant mass case. Introducing

$$G(z, t) = \sum_{r=1}^{\infty} c_r \, e^{-rz} \tag{2.10}$$

in the constant monomer case G satisfies

$$\frac{\partial G}{\partial t} = \alpha \left(c_1(1 - e^{-z})\frac{\partial G}{\partial z} + c_1^2 e^{-z} \right). \tag{2.11}$$

The substitution $e^{\zeta} = e^z - 1$ yields

$$\left(\frac{1}{\alpha c_1}\frac{\partial}{\partial t} - \frac{\partial}{\partial \zeta} \right)\left(G + c_1\zeta - c_1 \log(1 + e^{\zeta}) \right) = 0 \tag{2.12}$$

from which we find

$$G(\zeta, t) = G_0(\zeta + \alpha c_1 t) - c_1\zeta + c_1 \log(1 + e^{\zeta}) \tag{2.13}$$

for some G_0 determined by the initial conditions. For monodisperse initial data, $c_r(0) = 0$ for all $r \geqslant 2$, $G(\zeta, 0) = c_1/(e^{\zeta} + 1)$, we have $G_0(x) = c_1/(1 + e^x) + c_1 x - c_1 \log(1 + e^x)$, so

$$G(z, t) = c_1 e^{-\alpha c_1 t - z}(1 - e^{-z}(1 - e^{-\alpha c_1 t}))^{-1} - c_1 \log(1 - e^{-z}(1 - e^{-\alpha c_1 t})). \tag{2.14}$$

It is then straightforward to find both the moments of the cluster distribution function, for example

$$\varrho = -\left.\frac{\partial G}{\partial z}\right|_{z=0} = c_1(2\, e^{\alpha c_1 t} - 1) \tag{2.15}$$

and the concentrations of clusters of size r, namely

$$c_r(t) = \frac{c_1}{r}(1 - e^{-\alpha c_1 t})^{r-1}(1 + (r-1)\, e^{-\alpha c_1 t}). \tag{2.16}$$

In the large-time limit, this asymptotes to

$$\begin{aligned} c_r &\sim \frac{c_1}{r} && \text{for} \quad r = O(1) \\ c_r &\sim \frac{c_1}{r}(1 + r\, e^{-\alpha c_1 t}) \exp(-r\, e^{-\alpha c_1 t}) && \text{for} \quad r = O(e^{\alpha c_1 t}) \\ c_r &\sim c_1\, e^{-\alpha c_1 t}(1 - e^{-\alpha c_1 t})^r && \text{for} \quad r \gg e^{\alpha c_1 t}. \end{aligned} \tag{2.17}$$

These asymptotic expansions for this integrable case are not, however, generic in systems with rate coefficients given by (1.1), and we shall instead in the remainder of the paper use asymptotic techniques to form a rather complete picture of the phenomena exhibited by the constant monomer Becker–Döring system (1.2). The exponential growth of the density (2.15) reflects the status of the current case as a critical one.

Some further comments about the special case of no fragmentation are in order. Firstly, the system (1.2) can then be solved sequentially through successively larger r, so that for (1.1), if $c_2(0) = 0$, we have that

$$c_2 = c_1 \left(1 - e^{-2^p \alpha c_1 t}\right)\big/ 2^p \tag{2.18}$$

and so on. Moreover, the total number of particles

$$M_0 = \sum_{r=1}^{\infty} c_r \tag{2.19}$$

satisfies

$$\frac{dM_0}{dt} = \alpha c_1^2 - J_\infty. \tag{2.20}$$

$J_\infty = 0$ holds in the 'non-gelating' range $p \leqslant 1$, in which case M_0 grows linearly. Finally, taking p integer (to obviate the need for fractional derivatives) we find that

$$\frac{\partial G}{\partial t} = -(-1)^p \alpha c_1 (1 - e^{-z}) \frac{\partial^p G}{\partial z^p} + \alpha c_1^2\, e^{-z} \tag{2.21}$$

with the initial boundary value problem for (2.21) being somewhat curious: the result noted above that (1.2) can be solved sequentially for $b_r \equiv 0$ implies that the boundary data is all to be imposed as $z \to +\infty$, where

$$G \sim c_1\, e^{-z} \tag{2.22}$$

holds. We also have

$$J_\infty(t) = (-1)^p \alpha c_1 \lim_{z\to 0}\left(z\frac{\partial^p G}{\partial z^p}\right) \tag{2.23}$$

which is equivalent to (2.20) and serves to determine J_∞ (rather than being a boundary condition). The fact that (2.21) is a backward heat equation in $z > 0$ for $p = 2$ indicates the delicacy of such partial differential equation formulations.

2.3. *WKBJ analysis*

2.3.1. Formulation. In the far field, we expect all concentrations to decay to zero. For suitable (p, q), we now find a leading order representation of the solution in this region using a version of the WKBJ method appropriate to discrete systems such as (1.2). We take the rate coefficients to be continuous functions of aggregation size and denote them by $a(r)$, $b(r)$. Substituting $c_r(t) \sim P(r,t)\mathrm{e}^{w(r,t)}$ into (1.2) and naively balancing terms we find that

$$\frac{\partial w}{\partial t} = a(r)c_1\left(\exp\left(-\frac{\partial w}{\partial r}\right) - 1\right) + b(r)\left(\exp\left(\frac{\partial w}{\partial r}\right) - 1\right) \tag{2.24}$$

with correction terms implying

$$\begin{aligned}\frac{\partial P}{\partial t} = c_1\left(\frac{1}{2}aP\frac{\partial^2 w}{\partial r^2} - a\frac{\partial P}{\partial r} - P\frac{\partial a}{\partial r}\right)\exp\left(-\frac{\partial w}{\partial r}\right)\\ + \left(\frac{1}{2}bP\frac{\partial^2 w}{\partial r^2} + b\frac{\partial P}{\partial r} + P\frac{\partial b}{\partial r}\right)\exp\left(\frac{\partial w}{\partial r}\right).\end{aligned} \tag{2.25}$$

We shall not concern ourselves here with the pre-exponential factor $P(r,t)$; moreover, we stress that the full balance in (2.24) is not usually appropriate (particularly when $p \neq q$), with a number of distinct limit cases of it arising below. In most cases only a small subset of the terms present in (2.24) are present in the leading-order balance, the remaining terms being vanishingly small in the limit $r \to \infty$, $t = O(1)$ and so are only relevant if higher order correction terms (for example P) are required. Equation (2.24) is valid for $r \gg 1$ with $t = O(1)$.

2.3.2. Similarity solution for the case $q \leqslant p$. The solution for w which we require to describe certain aspects of the asymptotic behaviour is of the self-similar form

$$w(r,t) \sim t^{1/(1-p)}F(\eta) \qquad \eta = r/t^{1/(1-p)}. \tag{2.26}$$

For $p = q$, $F(\eta)$ is governed by

$$\frac{1}{1-p}(F - \eta F') = \alpha c_1 \eta^p(\mathrm{e}^{-F'} - 1) + \beta\eta^p(\mathrm{e}^{F'} - 1) \tag{2.27}$$

whereas for $p > q$ the b term in (2.24) is negligible as $r \to \infty$, implying

$$\frac{1}{1-p}(F - \eta F') = \alpha c_1 \eta^p(\mathrm{e}^{-F'} - 1). \tag{2.28}$$

For $p < 1$, the similarity solution (2.26) pertains as $t \to \infty$ with $\eta = O(1)$ (see section 4). Here we need the solution of (2.27) with the fastest decay in the large η limit, whereby we find that as $\eta \to \infty$

$$F \sim -(1-p)(\eta\log\eta - \eta) + \eta\log(\alpha c_1) \tag{2.29}$$

so that $F, F' \to -\infty$. The Legendre transform

$$\eta = \hat{F}'(\hat{\eta}) \qquad \hat{\eta} = F'(\eta) \qquad F + \hat{F} = \eta\hat{\eta} \tag{2.30}$$

of (2.27) with boundary condition $\hat{F} \to -\infty$ as $\hat{\eta} \to -\infty$ then yields

$$\hat{F}(\hat{\eta}) = -(1-p)p^{p/(1-p)} \Bigg/ \left\{ \int_{-\infty}^{\hat{\eta}} \frac{e^{u/p}\, du}{[(1-e^u)(\alpha c_1 - \beta e^u)]^{1/p}} \right\}^{p/(1-p)}. \tag{2.31}$$

The solution $F(\eta)$ given parametrically in terms of $\hat{\eta}$ is therefore

$$\eta = p^{1/(1-p)} e^{\hat{\eta}/p} \Bigg/ \left[(e^{\hat{\eta}} - 1)\left(\beta e^{\hat{\eta}} - \alpha c_1\right)\right]^{1/p} \left\{ \int_{-\infty}^{\hat{\eta}} \frac{e^{u/p}\, du}{[(1-e^u)(\alpha c_1 - \beta e^u)]^{1/p}} \right\}^{1/(1-p)} \tag{2.32}$$

$$F = \eta\hat{\eta} - \hat{F}(\hat{\eta}). \tag{2.33}$$

The solution (2.33) exists only for sufficiently large η, i.e. for $\eta \geqslant \eta_c$ where

$$\eta_c = [(1-p)(\beta - \alpha c_1)]^{1/(1-p)} \qquad \theta < 1 \tag{2.34}$$

$$\eta_c = [(1-p)(\alpha c_1 - \beta)]^{1/(1-p)} \qquad \theta > 1 \tag{2.35}$$

corresponding to the integral in (2.31)–(2.32) blowing up as, respectively, $\hat{\eta} \to (\log\theta)^-$ and $\hat{\eta} \to 0^-$; for $\theta < 1$ we have, with η_c given by (2.34),

$$p < 1/2 \qquad F \sim \log\theta\, \eta_c + \log\theta\, (\eta - \eta_c) + O((\eta - \eta_c)^2) \qquad \text{as} \quad \eta \to \eta_c^+ \tag{2.36}$$

$$p = 1/2 \qquad F \sim \log\theta\, \eta_c + \log\theta\, (\eta - \eta_c) + O\left(\frac{(\eta - \eta_c)^2}{\log(\eta - \eta_c)}\right) \qquad \text{as} \quad \eta \to \eta_c^+ \tag{2.37}$$

$$1/2 < p < 1 \qquad F \sim \log\theta\, \eta_c + \log\theta\, (\eta - \eta_c) + O\left((\eta - \eta_c)^{1/(1-p)}\right) \qquad \text{as} \quad \eta \to \eta_c^+. \tag{2.38}$$

In the case $\theta > 1$ the integral in (2.32) diverges in the limit $\hat{\eta} \to 0^-$ and we have

$$p < 1/2 \qquad F \sim -\frac{(\alpha c_1 - \beta)}{(\alpha c_1 + \beta)} \frac{(1-2p)}{2(1-p)} \frac{(\eta - \eta_c)^2}{\eta_c} \qquad \text{as} \quad \eta \to \eta_c^+ \tag{2.39}$$

$$p = 1/2 \qquad F = O\left(\frac{(\eta - \eta_c)^2}{\log(\eta - \eta_c)}\right) \qquad \text{as} \quad \eta \to \eta_c^+ \tag{2.40}$$

$$1/2 < p < 1 \qquad F = O\left((\eta - \eta_c)^{1/(1-p)}\right) \qquad \text{as} \quad \eta \to \eta_c^+ \tag{2.41}$$

where η_c is as defined in (2.35).

The results for the case $q < p < 1$ can be found by setting $\beta = 0$ into (2.35), which gives

$$\eta_c = [(1-p)\alpha c_1]^{1/(1-p)} \qquad F \sim -\frac{(1-2p)}{2(1-p)} \frac{(\eta - \eta_c)^2}{\eta_c} \qquad \text{as} \quad \eta \to \eta_c^+ \tag{2.42}$$

for $0 < p < 1/2$, while for $1/2 \leqslant p < 1$, (2.40), (2.41) remain valid.

For $p > 1$ the similarity solution (2.26) is relevant for small time (see section 3) and the condition (2.29) is instead pertinent as $\eta \to 0^+$. The required solution of (2.27) remains (2.31)–(2.33), the large η asymptotics then being given by expanding the parametric solution (2.32), (2.33) in the limit $\hat{\eta} \nearrow \min(0, \log\theta)$. For $p = q$ with $\theta < 1$, this yields

$$F \sim \eta \log\theta + F_\infty \qquad \text{as} \quad \eta \to \infty \tag{2.43}$$

where

$$F_\infty \equiv -\frac{(p-1)}{\beta^{1/(p-1)} p^{p/(p-1)}} \left\{ \int_{-\infty}^{0} \frac{e^{u/p}\, du}{[(1-e^u)(1-\theta\, e^u)]^{1/p}} \right\}^{p/(p-1)} \tag{2.44}$$

whilst for $p = q$ with $\theta > 1$ we have

$$F \to F_\infty \equiv -\frac{(p-1)}{p^{p/(p-1)}}\left\{\int_{-\infty}^{0}\frac{\mathrm{e}^{u/p}\,\mathrm{d}u}{[\beta(1-\mathrm{e}^u)(\theta-\mathrm{e}^u)]^{1/p}}\right\}^{p/(p-1)} \qquad \text{as} \quad \eta \to \infty. \tag{2.45}$$

By setting $\beta = 0$, this yields the simpler result for $p > q$ that

$$F \to F_\infty \equiv -\frac{(p-1)\pi^{p/(p-1)}\operatorname{cosec}^{p/(p-1)}(\pi/p)}{p^{p/(p-1)}(\alpha c_1)^{1/(p-1)}} \qquad \text{as} \quad \eta \to \infty. \tag{2.46}$$

For $p = q$ with $\theta = 1$ we have

$$1 < p < 2 \qquad F \sim -\frac{\eta^{2-p}}{(2-p)^2\beta} \qquad \text{as} \quad \eta \to \infty \tag{2.47}$$

$$p = 2 \qquad F \sim -\frac{1}{4\beta}\log^2\eta \qquad \text{as} \quad \eta \to \infty \tag{2.48}$$

$$p > 2 \qquad F \sim F_\infty \equiv -\frac{2^{-2/(p-1)}(p-1)}{\pi^{p/2(p-1)}p^{p/(p-1)}}\left(\Gamma\left(\frac{1}{p}\right)\Gamma\left(\frac{1}{2}-\frac{1}{p}\right)\right)^{p/(p-1)} \qquad \text{as} \quad \eta \to \infty. \tag{2.49}$$

2.3.3. Similarity solution for the case $p < q$. Simply setting $\alpha = 0$ in (2.39) does not yield the correct solution for $F(\eta)$ in this case of $p < q < 1$ (cf the far-field analysis of section 2.4). Instead, using (2.2) we substitute

$$w(r,t) = -(q-p)(r\log r - r) + r\log\theta + t^{1/(1-q)}F(\eta) \qquad \eta = r/t^{1/(1-q)} \tag{2.50}$$

into (2.24), the first two terms representing the leading-order equilibrium solution (see (2.2)). This similarity solution is relevant for $q < 1$ as $r \to \infty$ (see section 4) and leads to an ordinary differential equation for $F(\eta)$

$$\frac{1}{(1-q)}(F - \eta F') = \beta\eta^q(\mathrm{e}^{-F'} - 1). \tag{2.51}$$

This equation is of the same form as (2.28) (the equivalence transform of appendix B of [7] shows that this is not a coincidence), so the required results can be deduced immediately from (2.29), (2.31), (2.32), (2.35) and (2.42). The relevant solution has $F \to -\infty$ as $\eta \to \infty$; in fact, in this limit

$$F \sim -(1-q)(\eta\log\eta - \eta) + \eta\log\beta \tag{2.52}$$

as $\eta \to \infty$. The Legendre transform enables a parametric solution of (2.51) to be found in the form

$$\hat{F}(\hat{\eta}) = -(1-q)q^{q/(1-q)} \bigg/ \left\{\int_{-\infty}^{\hat{\eta}}\frac{\mathrm{e}^{u/q}\,\mathrm{d}u}{[\beta(1-\mathrm{e}^u)]^{1/q}}\right\}^{q/(1-q)} \tag{2.53}$$

$$\eta = q^{1/(1-q)}\mathrm{e}^{\hat{\eta}/q} \bigg/ [\beta(1-\mathrm{e}^{\hat{\eta}})]^{1/q}\left\{\int_{-\infty}^{\hat{\eta}}\frac{\mathrm{e}^{u/q}\,\mathrm{d}u}{[\beta(1-\mathrm{e}^u)]^{1/q}}\right\}^{1/(1-q)} \tag{2.54}$$

together with $F = \eta\hat{\eta} - \hat{F}(\hat{\eta})$. Thus we have $\eta_c = [(1-q)\beta]^{1/(1-q)}$, where $F(\eta_c) = 0$ and

$$F \sim -\frac{(1-2q)}{2(1-q)}\frac{(\eta-\eta_c)^2}{\eta_c} \qquad \text{as} \quad \eta \to \eta_c^+ \tag{2.55}$$

for $0 < q < 1/2$, $F = O((\eta-\eta_c)^{1/(1-q)})$ as $\eta \to \eta_c^+$ when $1/2 < q < 1$, and $F = O((\eta-\eta_c)^2/\log(\eta-\eta_c))$ when $q = 1/2$. For $q > 1$ the similarity solution (2.50) is relevant for small time and the condition (2.52) is instead pertinent as $\eta \to 0^+$. The required solution of (2.51) remains (2.53), (2.54), the large η asymptotics then being given by expanding the parametric solution (2.53), (2.54) in the limit $\hat{\eta} \to 0^-$. This yields

$$F \sim F_\infty \equiv -\frac{\pi^{q/(q-1)}(q-1)\,\mathrm{cosec}^{q/(q-1)}(\pi/q)}{q^{q/(q-1)}\beta^{1/(q-1)}} \qquad \text{as} \quad \eta \to \infty. \tag{2.56}$$

2.3.4. The case $q \leqslant p = 1$. Here w takes the form $w \sim rW(t)$ as $r \to \infty$ for all t with

$$\dot{W} = \alpha c_1(\mathrm{e}^{-W} - 1) + \beta(\mathrm{e}^{W} - 1) \tag{2.57}$$

for $p = q = 1$ and

$$\dot{W} = \alpha c_1(\mathrm{e}^{-W} - 1) \tag{2.58}$$

for $p = 1 > q$. Since we require $W \to -\infty$ as $t \to 0^+$, equation (2.57) has the solution

$$\mathrm{e}^W = \theta\left(1 - \mathrm{e}^{-\beta(1-\theta)t}\right)\big/\left(1 - \theta\mathrm{e}^{-\beta(1-\theta)t}\right) \qquad \theta \neq 1 \tag{2.59}$$

$$\mathrm{e}^W = \beta t/(1 + \beta t) \qquad \theta = 1 \tag{2.60}$$

while for (2.58)

$$\mathrm{e}^W = 1 - \mathrm{e}^{-\alpha c_1 t}. \tag{2.61}$$

2.3.5. The case $p < q = 1$. Simply setting $\alpha = 0$ in (2.59) also does not yield a relevant solution in this case; instead, motivated by the form of the equilibrium solution (1.6) for large r, we set

$$w(r, t) \sim -(1 - p)(r \log r - r) + rW(t) \qquad \text{as} \quad r \to \infty. \tag{2.62}$$

Inserting this into (2.24), we find the modified leading-order balance

$$\dot{W} = \beta(\theta\,\mathrm{e}^{-W} - 1). \tag{2.63}$$

Upon imposing the initial data $W(t) \to -\infty$ as $t \to 0^+$, we obtain the solution

$$W(t) = \log\theta + \log(1 - \mathrm{e}^{-\beta t}). \tag{2.64}$$

2.4. Far-field behaviour

2.4.1. The case $p = q$. We are now in a position to outline the behaviour as $r \to \infty$. It follows from (2.24) that, for $p = q$, c_r is rapidly decaying as $r \to \infty$ for $p < 1$, with (provided the initial data decay sufficiently rapidly, which we assume to be the case throughout; cf appendix A of [7])

$$w = -(1 - p)(r \log r - r) + \log(\alpha c_1 t)r + O(1) \qquad \text{as} \quad r \to \infty \quad \text{for} \quad p < 0 \tag{2.65}$$

$$w \sim -(1 - p)(r \log r - r) + \log(\alpha c_1 t)r - \frac{(\alpha c_1 + \beta)}{(p + 1)}tr^p \quad \text{as} \quad r \to \infty \quad \text{for} \quad 0 < p < 1. \tag{2.66}$$

For $p = 1$, the result is as given in section 2.3.4, with

$$w \sim rW(t) \qquad \text{as} \quad r \to \infty \quad \text{for} \quad p = 1 \tag{2.67}$$

where $W(t)$ is given by (2.59), (2.60), so that

$$W \sim \log(\alpha c_1 t) \qquad \text{as} \quad t \to 0 \tag{2.68}$$

$$\begin{array}{lll} \theta < 1 & W \sim \log\theta - (1-\theta)\mathrm{e}^{-\beta(1-\theta)t} & \text{as} \quad t \to \infty \\ \theta = 1 & W \sim -1/\beta t & \text{as} \quad t \to \infty \\ \theta > 1 & W \sim -(\theta - 1)\,\mathrm{e}^{-\beta(\theta-1)t}/\theta & \text{as} \quad t \to \infty. \end{array} \tag{2.69}$$

For $p > 1, \theta \neq 1$ and for $p > 2, \theta = 1$ the far-field balance is quasi-steady, with

$$\begin{array}{llll} \theta < 1 & c_r \sim \dfrac{A(t)}{r^p}\theta^r & \text{as} \quad r \to \infty & p > 1 \\ \theta > 1 & c_r \sim \dfrac{J_\infty(t)}{\beta(\theta - 1)r^p} & \text{as} \quad r \to \infty & p > 1 \end{array} \tag{2.70}$$

where A, J_∞ are positive for $t > 0$ and are determined as part of the solution; for $\theta \leqslant 1$, we have $J_\infty = 0$ but for $\theta > 1$ there is a finite flux of particles (and an infinite flux of mass) to infinity. Finally

$$\begin{array}{llll} \theta = 1 & w \sim -\dfrac{r^{2-p}}{(2-p)^2\beta t} & \text{as} \quad r \to \infty & 1 < p < 2 \\ \theta = 1 & w \sim -\dfrac{\log^2 r}{4\beta t} & \text{as} \quad r \to \infty & p = 2 \\ \theta = 1 & c_r \sim \dfrac{A(t)}{r^p} & \text{as} \quad r \to \infty & p > 2 \end{array} \tag{2.71}$$

the first two of which agree with the large-η limits of the similarity solutions in (2.47), (2.48), and with the second of (2.69) being a special case of the first of (2.71).

2.4.2. The case $p > q$. The relevant expressions are identical to those above, except that β is replaced by zero in (2.66), $W(t)$ in (2.67) is given by (2.64), with (2.69) replaced by

$$W \sim -\mathrm{e}^{-\alpha c_1 t} \qquad \text{as} \quad t \to \infty \tag{2.72}$$

(corresponding to $\beta \to 0, \theta \to \infty$ in (2.69)), and (2.70) is similarly replaced by

$$c_r \sim \frac{J_\infty(t)}{\alpha c_1 r^p} \qquad \text{as} \quad r \to \infty \quad p > 1. \tag{2.73}$$

2.4.3. The case $p < q$. For $q < 1$, the calculation equivalent to that which leads to (2.65), (2.66) implies

$$w = -(1-p)(r\log r - r) + \log(\alpha c_1 t)r + O(1) \qquad \text{as} \quad r \to \infty \quad \text{for} \quad q < 0 \tag{2.74}$$

$$w \sim -(1-p)(r\log r - r) + \log(\alpha c_1 t)r - \frac{\beta}{(q+1)}tr^q \qquad \text{as} \quad r \to \infty \quad \text{for} \quad 0 < q < 1 \tag{2.75}$$

so even though p is less than q, the aggregation terms dominate the far-field behaviour (this is unsurprising, since aggregation effects are evidently solely responsible for the presence of large clusters). For $q = 1$ the analysis of section 2.3.5 pertains, with (2.68) holding and with

$$W \sim \log\theta - \mathrm{e}^{-\beta t} \qquad \text{as} \quad t \to \infty. \tag{2.76}$$

Finally, for $q > 1$ the far-field behaviour of (2.24) is governed by the leading order balance

$$\alpha r^p c_1 \exp\left(-\frac{\partial w}{\partial r}\right) - \beta r^q = 0 \tag{2.77}$$

so that

$$w \sim -(q-p)(r\log r - r) + r\log\theta + w_\infty(t) \qquad \text{as} \quad r \to \infty \tag{2.78}$$

for some $w_\infty(t)$ such that $w_\infty(0) = -\infty$; this is again consistent with the equilibrium solution

$$c_r = \frac{c_1\theta^{r-1}}{r^p(r!)^{q-p}}. \tag{2.79}$$

2.5. Summary

In this section we have defined the equilibrium and steady-state solutions using the partition function and solved exactly the case $p=1$ with $\beta=0$. For general values of p, q, however, there are no such exact solutions and we have used asymptotic methods to analyse the behaviour of the concentrations $c_r(t)$ at large r. For $\max\{p, q\} < 1$, we have identified a power law in t and a critical value of η, namely η_c, which will subsequently prove to determine the position of a wavefront at large values of r and t. This wavefront is located at

$$r = s(t) = \eta_c t^{1/(1-\max\{p,q\})}. \tag{2.80}$$

However, when $\max\{p, q\} = 1$, the WKBJ analysis yields a different decay of the concentrations with increasing size. This behaviour is confirmed by the exact solution available for $p = 1$, $\beta = 0$ (compare equations (2.17) and (2.61)).

3. Small-time behaviour

A small-time analysis is extremely instructive, particularly in clarifying the behaviour as $r \to \infty$. For definiteness we adopt initial data $c_r(0) = 0$ for $r \geqslant 2$; for small-time we then have $c_r \ll c_{r-1}$ for $r = O(1)$, so that

$$\dot{c}_r \sim \alpha(r-1)^p c_1 c_{r-1} \tag{3.1}$$

and hence

$$c_r \sim c_1((r-1)!)^{p-1}(\alpha c_1 t)^{r-1} \qquad \text{as} \quad t \to 0^+. \tag{3.2}$$

For $p \leqslant 1$ this solution decays in a manner consistent with that implied by (2.65), (2.68), (2.74), (2.75) as $r \to \infty$, $t \to 0$, and for $q \leqslant 1$ this representation is then uniform in r for small t. However, for $q > \max(p, 1)$ fragmentation terms contribute at leading order for sufficiently large r, namely $r = O\left(t^{-1/(q-1)}\right)$. This can be described via a balance

$$\frac{\partial w}{\partial t} \sim \alpha r^p c_1 \exp\left(-\frac{\partial w}{\partial r}\right) - \beta r^q \tag{3.3}$$

in (2.24); using the solution (2.50) described in section 2.3.3 to give the small-time behaviour of w we have that

$$w_\infty(t) \sim F_\infty t^{-1/(q-1)} \qquad \text{as} \quad t \to 0 \tag{3.4}$$

where F_∞ is given by (2.56). Moreover, we have

$$F \sim (q-1)(\eta\log\eta - \eta) + \eta\log\beta - \beta\eta^q/(q+1) \qquad \text{as} \quad \eta \to 0. \tag{3.5}$$

If $p > 1$, the solution (3.2) blows up rapidly as $r \to \infty$ and the behaviour in this case is also not described by (3.2) for sufficiently large r. Thus for $p \geqslant q$ with $p > 1$ a non-uniformity occurs at $r = O\left(t^{-1/(p-1)}\right)$ and the leading order solution for w is described by the similarity

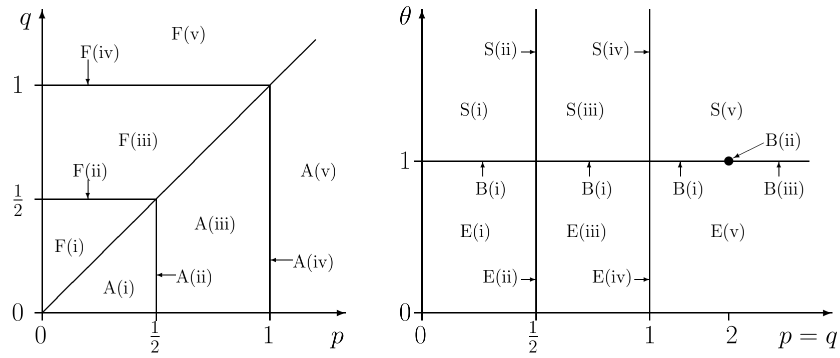

Figure 1. On the left, a diagram of the (p, q) parameter space showing the regions of validity for cases A and F. Cases E, S and B are relevant only when $p = q$, where θ is also relevant for classifying the types of behaviour observed; this is illustrated on the right.

solution of section 2.3.2, whereby (2.29) matches with (3.2) as $\eta \to 0$ and the behaviour (2.45)–(2.46) as $\eta \to \infty$ implies that

$$\log J_\infty \sim F_\infty t^{-1/(p-1)} \qquad \text{as} \quad t \to 0 \tag{3.6}$$

in the second of (2.70) ($p = q, \theta > 1$) and in (2.73) ($p > q$) where the (negative) constant F_∞ is given by (2.45) and (2.46), respectively. Hence the flux of particles to infinity is exponentially small for small t. For $p = q, \theta < 1$ we have (2.43) in the far field, consistent with the first of (2.70) with

$$\log A \sim F_\infty t^{-1/(p-1)} \qquad \text{as} \quad t \to 0 \tag{3.7}$$

where F_∞ is as given by (2.44). For $\theta = 1$, $p > 2$ we also have (3.7) in the third of (2.71), with F_∞ as given in (2.49).

4. Large-time behaviour

4.1. Formulation

We now derive the large-time asymptotics for a constant monomer Becker–Döring system in which the rate coefficients vary in a power-law fashion. Initially, we shall study the special case in which aggregation and fragmentation terms have the same exponent. We thus take $a_r = \alpha r^p$ and $b_r = \beta r^p$ so that $J_r = \alpha c_1 r^p c_r - \beta (r+1)^p c_{r+1}$. The parameter $\theta = \alpha c_1/\beta$, used extensively in [7], remains the crucial quantity in analysing the kinetics of the corresponding system

$$\dot{c}_r = \alpha c_1 (r-1)^p c_{r-1} - \beta r^p c_r - \alpha c_1 r^p c_r + \beta (r+1)^p c_{r+1} \qquad r \geqslant 2 \tag{4.1}$$

where c_1 is a prescribed constant. This system has the equilibrium solution (2.3), so from (1.4) we have density

$$\varrho = (c_1/\theta)\mathrm{polylog}(p-1, \theta) \tag{4.2}$$

for $\theta < 1$, in which case (2.3) describes the behaviour as $r \to \infty$. The polylog function is defined by

$$\mathrm{polylog}(k, z) = \sum_{n=1}^{\infty} \frac{z^n}{n^k} \tag{4.3}$$

which has a singularity at $z = 1$; if $p > 2$ then ϱ is finite for $\theta = 1$. A system with constant density ϱ and $p < 1$ also evolves to (2.3), the monomer concentration at equilibrium being given by (4.2), whereby $\theta = \alpha c_1/\beta$ necessarily satisfies $\theta < 1$. For cases with $\theta > 1$, the system evolves to a steady-state solution (2.7), since in these cases the steady state has faster decay at large r than the equilibrium solution. The case $\theta = 1$ (case B) is more complex and so we consider it last. In case B, the system tends to the equilibrium solution (2.3); however, since it is possible for p to be negative, this solution could be divergent in the limit $r \to \infty$. Case B divides the (θ, p) plane in two distinct regions; in the critical case $\theta = 1$ the equilibrium solution (2.3) and the steady-state solution (2.7) are identical and the system tends to the equilibrium (2.3) for $\theta < 1$ (case E) and to a steady-state (2.7) for $\theta > 1$ (case S). The region in parameter space where each case is relevant is illustrated in figure 1. On the left is the (p, q) parameter space outlining the domains of cases A and F; on the right the (p, θ) plane is given for the case $p = q$ illustrating cases E, S and B. Finally in this section, we generalize the results to the cases where fragmentation dominates aggregation for large r (i.e. where $p < q$ in (1.1)) and the cases where aggregation dominates fragmentation; the form of the solution in this last case differs markedly from that which results from the constant mass formulation of the Becker–Döring equations where conservation of mass results in the monomer concentration decreasing to zero in the large time limit.

4.2. Case E: $\theta < 1$

4.2.1. A continuum limit. Since we expect the system to approach the equilibrium solution $c_r = \theta^{r-1}/r^p$ as $r \to \infty$ with $r = O(1)$, we write $c_r(t) = \theta^{r-1} c_1 \psi(r,t)/r^p$. We aim to provide a full description of the large-time behaviour when the system is started from initial conditions which are non-zero only for some finite range of r (or, more generally, which decay sufficiently rapidly as $r \to \infty$) with boundary data $c_1(t) \equiv 1$. The large-time behaviour is similar to that discussed in [7], with inner solution

$$c_r(t) \sim \frac{\theta^{r-1} c_1}{r^p} \qquad \psi(r,t) \sim 1 \qquad \text{as} \quad t \to \infty \quad \text{with} \quad r = O(1) \tag{4.4}$$

and with an outer region in which ψ varies slowly, so a naive continuum limit of (1.2), namely

$$\frac{\partial \psi}{\partial t} = -\beta(1-\theta) r^p \frac{\partial \psi}{\partial r} \tag{4.5}$$

provides an appropriate description of the leading order behaviour for $r \gg 1$. In view of (4.4), this hyperbolic equation implies

$$\psi(r,t) \sim H(s(t) - r) \qquad \text{as} \quad t \to \infty \quad r = O(s) \tag{4.6}$$

where H is the Heaviside step function and

$$\dot{s} = \beta(1-\theta) s^p \tag{4.7}$$

which is a characteristic projection of (4.5). The nature of the required solution to (4.7) depends on the value of p, and can be split into five cases: (i) $p < 1/2$, (ii) $p = 1/2$, (iii) $1/2 < p < 1$, (iv) $p = 1$ and (v) $p > 1$; (4.7) will in fact prove to be valid only in cases (i)–(iii). We shall give results for all five cases in turn, together with the details of the interior layer around $s(t)$ over which the discontinuity in (4.5) is smoothed. To describe this, we shall (in the usual way) need the second term in the continuum limit $r \to \infty$, whereby

$$\frac{\partial \psi}{\partial t} \sim -\beta(1-\theta) r^p \frac{\partial \psi}{\partial r} + \frac{1}{2}\beta(1+\theta) r^p \frac{\partial^2 \psi}{\partial r^2}. \tag{4.8}$$

Writing $r = s(t) + z$, where s is given by (4.7) we obtain a second continuum limit, namely

$$\frac{\partial \psi}{\partial t} \sim -p\beta(1-\theta)s^{p-1} z \frac{\partial \psi}{\partial z} + \frac{1}{2}\beta(1+\theta)s^p \frac{\partial^2 \psi}{\partial z^2} \tag{4.9}$$

in which the two terms on the right-hand side are in balance if $z = O(\sqrt{s})$.

4.2.2. Case E(i): $\theta < 1$, $p < \frac{1}{2}$. In this case the relevant solution of (4.7) is

$$s(t) = (\beta(1-\theta)(1-p)t)^{1/(1-p)} \tag{4.10}$$

equivalent to (2.80), (2.34), which shows how material is advected to arbitrarily large r-values at an ever-increasing speed. Since s increases monotonically with t, and $s \to \infty$ as $r \to \infty$, we may use s as an internal time variable, so that (4.9) may be rewritten in the form

$$\frac{\partial \psi}{\partial s} = \frac{1}{2}\frac{(1+\theta)}{(1-\theta)}\frac{\partial^2 \psi}{\partial z^2} - \frac{pz}{s}\frac{\partial \psi}{\partial z} \tag{4.11}$$

the required solution to which is

$$\psi \sim \frac{1}{2}\mathrm{erfc}\left(\frac{\sqrt{(1-\theta)(1-2p)}}{\sqrt{2(1+\theta)}}\frac{z}{\sqrt{s}}\right) \qquad \text{for} \quad z = O(\sqrt{s}). \tag{4.12}$$

In terms of the original variables the transition layer is thus described by

$$c_r(t) \sim \frac{\theta^{r-1}c_1}{2r^p}\mathrm{erfc}\left(\frac{\sqrt{(1-\theta)(1-2p)}}{\sqrt{2(1+\theta)}}\frac{(r-s(t))}{\sqrt{s(t)}}\right)$$
$$\text{as} \quad t \to \infty \quad \text{with} \quad r - s(t) = O\left(t^{1/2(1-p)}\right). \tag{4.13}$$

In the outer region $r/s > 1$ the solution is exponentially small and can be described by the WKBJ analysis of section 2.3, thereby giving the transition to the far-field behaviour (2.65), (2.66). Indeed, the factor θ^r in (4.13) provides the required matching with (2.36).

4.2.3. Case E(ii): $\theta < 1$, $p = \frac{1}{2}$. In this case (4.10) still gives the position of the front (namely $s(t) = \beta^2(1-\theta)^2 t^2/4$), but (4.12) evidently does not determine the shape of the wavefront, the width-scaling $z = O(\sqrt{s})$ being inappropriate. Introducing the new variables

$$\tau = \log s \qquad \zeta = z/\sqrt{s} \tag{4.14}$$

(4.11) becomes

$$\frac{\partial \psi}{\partial \tau} = \frac{1}{2}\left(\frac{1+\theta}{1-\theta}\right)\frac{\partial^2 \psi}{\partial \zeta^2} + \left(p - \frac{1}{2}\right)\zeta\frac{\partial \psi}{\partial \zeta} \tag{4.15}$$

a representation which emphasizes the special status of both $\theta = 1$ and $p = 1/2$; hence for $p = 1/2$

$$\psi \sim \frac{1}{2}\mathrm{erfc}\left(\sqrt{\frac{(1-\theta)}{2(1+\theta)}}\frac{\zeta}{\sqrt{\tau}}\right). \tag{4.16}$$

In our original variables the wavefront is thus given by

$$c_r(t) \sim \frac{\theta^{r-1}c_1}{2\sqrt{r}}\mathrm{erfc}\left(\frac{r - \frac{1}{4}\beta^2(1-\theta)^2 t^2}{\beta\sqrt{(1-\theta^2)}t\log^{1/2} t}\right)$$
$$\text{as} \quad t \to \infty \quad \text{with} \quad r - \frac{1}{4}\beta^2(1-\theta)^2 t^2 = O(t\log^{1/2} t). \tag{4.17}$$

The front is thus somewhat thicker than might be expected from the scaling rule for case E(i) ($p < 1/2$); one can think of the material being advected to large aggregation numbers so fast that diffusion is only just able to mould the wavefront into the characteristic erfc shape. The WKBJ analysis again provides the exponentially small solution in $r/s > 1$, the above solution matching smoothly into the WKBJ solution (2.37), with the logarithmic dependence on η in (2.37) corresponding to that on t in (4.17).

4.2.4. Case E(iii): $\theta < 1$, $\frac{1}{2} < p < 1$. With increasing values of p, the front moves faster, still obeying (4.10), but now the 'diffusive' processes are so weak that the wavefront does not adjust to a self-similar shape. In the limit $s \to \infty$, the advective term in (4.11) dominates the diffusive part, its time dependence being of the form

$$\psi \sim \Psi(z/s^p) \qquad \text{as} \quad t \to \infty \tag{4.18}$$

where $\Psi(\xi) \to 1$ as $\xi \to -\infty$ and $\Psi(\xi) \to 0$ as $\xi \to +\infty$, but Ψ is otherwise arbitrary (being dependent on the initial data). The manner in which Ψ decays exponentially as $\xi \to +\infty$ (whereby $-\log \Psi$ grows as $\xi^{1/(1-p)}$) follows by matching into the $(\eta - \eta_c)^{1/(1-p)}$ correction term in (2.38).

4.2.5. Case E(iv): $\theta < 1, p = 1$. Here we have (2.67) with the first of (2.69) in the far-field, which matches directly with (4.4).

4.2.6. Case E(v): $\theta < 1$, $p > 1$. In this case the far-field behaviour is given by the first of (2.70) and (4.4) is uniformly valid in r as $t \to \infty$, with zero flux in the large-r limit, and in (2.70) we have $A \to c_1/\theta$ as $t \to \infty$ (by matching with (4.4)).

4.3. Case S: $\theta > 1$

4.3.1. Preamble. We have already noted the form of the steady-state solution (2.7). As in case E described above, we claim that at large times a front forms and propagates through r-space; as $t \to \infty$ the concentration variables approach the steady-state solution (2.7) behind the front ($r/s(t) < 1$), while c_r is exponentially small ahead of the front ($r/s(t) > 1$). Our aim is to find the position of the front, and its shape.

We use a similar procedure as for case E, whereby, in view of (2.7), we write $c_r = c_1\psi(r, t)/r^p$. The inner solution is thus

$$c_r(t) \sim \frac{c_1}{r^p} \qquad \psi(r, t) \sim 1 \qquad \text{as} \quad t \to \infty \quad \text{with} \quad r = O(1) \tag{4.19}$$

and the outer region in which ψ drops slowly from unity to zero is described (in the first instance) by

$$\frac{\partial \psi}{\partial t} = -\beta(\theta - 1)r^p \frac{\partial \psi}{\partial r} \tag{4.20}$$

a continuum limit of (1.2). In view of the boundary conditions $\psi \to 0$ as $r \to \infty$ and $\psi \to 1$ when $r = O(1)$ (as given in (4.19)) the solution can be described by

$$\psi \sim H(s(t) - r) \qquad \text{as} \quad t \to \infty \quad r = O(s) \tag{4.21}$$

where $r = s(t)$ is the leading order position of the interface and is determined by $\dot{s} = \beta(\theta - 1)s^p$. Once $s(t)$ has been found, higher order terms from the continuum approximation

$$\frac{\partial \psi}{\partial t} \sim -\beta(\theta - 1)r^p \frac{\partial \psi}{\partial r} + \frac{1}{2}\beta(\theta + 1)r^p \frac{\partial^2 \psi}{\partial r^2} \tag{4.22}$$

need to be considered to find the shape of the interface. Writing $r = s(t) + z$, we obtain

$$\frac{\partial \psi}{\partial t} \sim -p\beta(\theta - 1)s^{p-1}z\frac{\partial \psi}{\partial z} + \frac{1}{2}\beta(\theta + 1)s^{p}\frac{\partial^2 \psi}{\partial z^2}. \tag{4.23}$$

4.3.2. Case S(i): $\theta > 1$, $p < \frac{1}{2}$. We start by solving $\dot{s} = \beta(\theta - 1)s^p$ to find, as the large-time solution, that (cf (2.80) and (2.35))

$$s(t) = (\beta(\theta - 1)(1 - p)t)^{1/(1-p)} \tag{4.24}$$

which implies that material is advected to large r-values at a continually increasing speed. Equation (4.23) has the similarity solution

$$\psi = \frac{1}{2}\mathrm{erfc}\left(\sqrt{\frac{(1-2p)(\theta-1)}{2(1+\theta)}}\frac{z}{\sqrt{s}}\right) \tag{4.25}$$

which yields

$$c_r(t) \sim \frac{1}{2r^p}\mathrm{erfc}\left(\sqrt{\frac{(1-2p)(\theta-1)}{2(1+\theta)}}\frac{(r - s(t))}{\sqrt{s(t)}}\right)$$
$$\text{as} \quad t \to \infty \quad \text{with} \quad r - s(t) = O\left(t^{1/2(1-p)}\right). \tag{4.26}$$

In the outer region $r/s(t) > 1$ the solution is exponentially small and can be described by the WKBJ analysis of section 2.3, (4.26) matching in the $r/s(t) > 1$ region with (2.39), which provides the required far-field behaviour (2.65), (2.66). We note that the flux satisfies

$$J_r(t) \sim c_1(\alpha c_1 - \beta)\psi(r, t) \tag{4.27}$$

so (4.25) shows how J_r drops for large r from $c_1(\alpha c_1 - \beta)$ (as in (2.6)) to zero, as required by the far-field behaviour; similar comments apply in the next two subsections.

4.3.3. Case S(ii): $\theta > 1$, $p = \frac{1}{2}$. Equation (4.24) gives the position of the wavefront in this parameter regime, as well as in S(i), so here $s(t) = \frac{1}{4}\beta^2(\theta - 1)^2t^2$. As in case E(ii), the substitutions $\tau = \log s$, $\zeta = z/\sqrt{s}$ again yield a diffusion equation for $\psi(\zeta, \tau)$ though with a modified diffusion constant, namely $(\theta - 1)/2(\theta + 1)$; this has solution (4.16) where $(\theta - 1)$ replaces the factor $(1 - \theta)$. Thus the shape of the wavefront in our original variables is

$$c_r(t) \sim \frac{1}{2\sqrt{r}}\mathrm{erfc}\left(\frac{r - \frac{1}{4}\beta^2(\theta-1)^2t^2}{\beta\sqrt{\theta^2 - 1}\, t\, \log^{1/2} t}\right)$$
$$\text{as} \quad t \to \infty \quad \text{with} \quad r - \tfrac{1}{4}\beta^2(\theta - 1)^2t^2 = O(t \log^{1/2} t). \tag{4.28}$$

As with case E(ii), the front is somewhat thicker than expected from the solution for case S(i), with diffusion only just able to mould the wavefront into the erfc shape. The far-field solution in $r/s(t) > 1$ can again be determined by the WKBJ solution of section 2.3.2, the above solution must match smoothly into the WKBJ solution (2.40) due to the existence of the equivalence transform and the corresponding matching of case E(ii).

4.3.4. Case S(iii): $\theta > 1$, $\frac{1}{2} < p < 1$. As in case E(iii), the large-time asymptotics depend on the initial conditions, the time dependence being of the form

$$\Psi = \Psi(z/s^p) \tag{4.29}$$

where $\Psi(\xi) \to 1$ as $\xi \to -\infty$ and $\Psi \to 0$ as $\xi \to +\infty$ but otherwise depends on the initial conditions since the advective part of (4.22) dominates the diffusive part. The quantity

$s = s(t)$ is as given in (4.24) consistent with the balance (4.20). The flux thus drops from $c_1(\alpha c_1 - \beta)$ to zero over exponentially large cluster sizes $r = O\left(e^{\beta(\theta-1)t}\right)$. The manner in which Ψ decays exponentially as $\xi \to +\infty$, whereby $-\log\Psi$ grows as $\xi^{1/(1-p)}$, follows by matching into (2.41).

4.3.5. Case S(iv): $\theta > 1, p = 1$. Here the far-field is given by (2.67) with the last of (2.69), which matches with (4.19) and implies exponential decay in c_r as $r \to \infty$, albeit at a rate which decays exponentially with t, consistent with the balance (4.20). The flux thus drops from $c_1(\alpha c_1 - \beta)$ to zero over exponentially large cluster sizes $r = O\left(e^{\beta(\theta-1)t}\right)$.

4.3.6. Case S(v): $\theta > 1$, $p > 1$. The far-field from (2.70) applies, implying that (4.19) is uniformly valid in r as $t \to \infty$ with a nonzero flux to infinity,

$$J_\infty \sim \beta c_1(\theta - 1) \qquad \text{as} \quad t \to \infty. \tag{4.30}$$

4.4. Case B: $\theta = 1$

4.4.1. Preliminaries. In this case $\alpha c_1 = \beta$ and a simple rescaling of time removes α and β from the model, leaving

$$\dot{c}_r = (r-1)^p c_{r-1} - 2r^p c_r + (r+1)^p c_{r+1} \qquad r \geqslant 2 \tag{4.31}$$

whose large-time behaviour for $r = O(1)$ is convergence to the equilibrium solution $c_r = 1/r^p$.

We substitute $c_r(t) = \psi(r,t)/r^p$ with $\psi \to 0$ as $r \to \infty$. In the large t limit, (4.31) can be approximated by the continuum formulation

$$\frac{\partial\psi}{\partial t} = r^p \frac{\partial^2\psi}{\partial r^2}. \tag{4.32}$$

4.4.2. Case B(i): $\theta = 1$, $p < 2$. For $p < 2$ we seek a similarity solution

$$c_r(t) \sim \frac{1}{r^p}\Upsilon(\eta) \qquad \eta = \frac{r}{t^{1/(2-p)}} \qquad \text{as} \quad t \to \infty \quad r = O\left(t^{1/(2-p)}\right) \tag{4.33}$$

so $\psi \sim \Upsilon(\eta)$, giving

$$-\eta\Upsilon'(\eta) = (2-p)\eta^p\Upsilon''(\eta). \tag{4.34}$$

When subject to the boundary conditions $\Upsilon(0) = 1$ and $\Upsilon(\eta) \to 0$ as $\eta \to \infty$ this implies

$$\Upsilon(\eta) = \frac{\int_\eta^\infty \exp(-\tilde{\eta}^{2-p}/(2-p)^2)\mathrm{d}\tilde{\eta}}{\int_0^\infty \exp(-\tilde{\eta}^{2-p}/(2-p)^2)\mathrm{d}\tilde{\eta}} = \frac{1}{\Gamma(p)}\Gamma\left(p, \frac{\eta^{2-p}}{(2-p)^2}\right) \tag{4.35}$$

where $\Gamma(p, z)$ is the incomplete Gamma function. This is consistent with the far-field analysis (2.71).

4.4.3. Case B(ii): $\theta = 1$, $p = 2$. It is clear from the definition of η in (4.33) that the similarity approach used in the previous subsection will fail when $p = 2$. Instead, we note that the transformation $R = \log r$ transforms (4.32) into the linear constant coefficient equation

$$\frac{\partial\psi}{\partial t} = \frac{\partial^2\psi}{\partial R^2} - \frac{\partial\psi}{\partial R} \tag{4.36}$$

with large-time solution

$$\psi = \frac{1}{2}\mathrm{erfc}\left(\frac{R-t}{2\sqrt{t}}\right). \tag{4.37}$$

Thus we obtain the leading order large-time solution

$$c_r(t) \sim \frac{1}{2r^2}\mathrm{erfc}\left(\frac{\log r - t}{2\sqrt{t}}\right) \qquad \text{as} \quad t \to \infty \quad \text{with} \quad \log r - t = O(\sqrt{t}). \tag{4.38}$$

This solution is consistent with the far-field analysis given in (2.71).

4.4.4. Case B(iii): $\theta = 1$, $p > 2$. For $p > 2$, (4.19) is consistent with the far-field behaviour described in the last of (2.71) and is uniform in r as $t \to \infty$, with $A(t) \to c_1$ as $t \to \infty$.

4.5. Summary

The equilibrium solution is approached when $\theta \leqslant 1$ and a steady-state solution when $\theta > 1$. The approach to equilibrium or steady-state for $\theta \neq 1$, $p \leqslant 1$ occurs by a diffusive wavefront advecting material to large r as time increases, its position being determined by $s(t)$. For $\theta = 1$ the 'advection' process, present for $\theta < 1$ due to the aggregation coefficient $a_r c_1$ being larger than the fragmentation one b_r, is absent and for $p < 2$ 'diffusion' alone is responsible for the convergence to equilibrium.

Case E concerns $\theta < 1$ and when $p < 1$ the system tends to its equilibrium configuration via a wave travelling into larger r-regions. Only when $p \leqslant 1/2$ does the wavefront adjust to the characteristic erfc shape; when $p > 1/2$ advection dominates diffusion to the extent that the system always retains some knowledge of its initial conditions. For $p > 1$ uniform convergence to equilibrium is observed. The second case considered was $\theta > 1$, where the system approaches the steady-state solution, uniformly for $p > 1$ but through wave propagation to infinity for $p < 1$. In the special case $\theta = 1$, the forward and backward rate coefficients are exactly balanced and so advective forces are, as already noted, significantly weaker; this is manifested in the absence of a wavefront when $p < 2$.

The reason for the strong similarities between cases E and S can be clarified by means of the equivalence transform

$$\hat{a}_r = \frac{1 + Kd_{r+1}}{1 + Kd_r} a_r \qquad \hat{b}_r = \frac{1 + Kd_{r-1}}{1 + Kd_r} b_r \tag{4.39}$$

with

$$d_1 = 0 \qquad d_r = \sum_{k=1}^{r-1} \frac{1}{a_k Q_k c_1^{k+1}} = \frac{1}{bc_1\theta^{r-1}}\left(\frac{\theta^r - 1}{\theta - 1}\right) \tag{4.40}$$

noted in appendix B of [7], which maps case S to case E (and vice versa) if we set $K = -1/d_\infty = -bc_1(\theta - 1)$; this yields $\hat{a}_r = \hat{\alpha} r^p$, $\hat{\alpha} = (a/\theta)$, $\hat{b}_r = \hat{\beta} r^p$, $\hat{\beta} = \beta\theta$. The coefficients $\hat{a}_r$, $\hat{b}_r$ here refer to an associated Becker–Döring system

$$\dot{\hat{c}}_r = \hat{J}_{r-1} - \hat{J}_r \qquad \hat{J}_r = \hat{a}_r \hat{c}_1 \hat{c}_r - \hat{b}_{r+1}\hat{c}_{r+1} \tag{4.41}$$

for $\hat{c}_r = c_r(1 + Kd_r)$ (so that $\hat{c}_1 = c_1$) whereby $\hat{\theta} = \hat{\alpha}\hat{c}_1/\hat{\beta} = 1/\theta$.

4.6. Case F: fragmentation dominated ($p < q$)

We now turn to cases where the fragmentation and coagulation terms have different exponents ($p \neq q$ in equation (1.1)). We first study the case $q > p$ in which fragmentation dominates coagulation at large cluster sizes, and the cluster concentrations decay with increasing size, leading to a well-behaved cluster-size distribution at all times. The system is governed by

$$\dot{c}_r = \alpha(r-1)^p c_1 c_{r-1} - \beta r^q c_r - \alpha r^p c_1 c_r + \beta(r+1)^q c_{r+1} \qquad r \geqslant 2 \quad \dot{c}_1 = 0. \tag{4.42}$$

Since $q > p$, the equilibrium solution $c_r = Q_r c_1^r$ decays with increasing r faster than any exponential. The substitution $c_r = Q_r c_1^r \psi_r$, with Q_r given by (2.1), yields

$$\dot{\psi}_r = \beta r^q \left(\psi_{r-1} - \psi_r - \frac{\theta \psi_r}{r^{q-p}} + \frac{\theta \psi_{r+1}}{r^{q-p}} \right). \tag{4.43}$$

At large times, and for large r, it is admissible to take the continuum limit, which at leading order simplifies (4.43) to, in the first instance,

$$\frac{\partial \psi}{\partial t} = -\beta r^q \frac{\partial \psi}{\partial r}. \tag{4.44}$$

Equation (4.44) can also be derived from (4.5) by taking the limit $\theta \to 0$ and replacing p by q. It supports a wave which travels from small to large values of r at a rate determined, to leading order, by $\dot{s} \sim \beta s^q$. For $q < 1$, this implies the leading order behaviour is given by

$$s(t) \sim (\beta(1-q)t)^{1/(1-q)} \qquad \text{as} \quad t \to \infty. \tag{4.45}$$

Including higher-order correction terms yields

$$\frac{\partial \psi}{\partial t} \sim -\beta r^q \frac{\partial \psi}{\partial r} + \frac{1}{2}\beta r^q \frac{\partial^2 \psi}{\partial r^2} + \beta \theta r^p \frac{\partial \psi}{\partial r}. \tag{4.46}$$

It is now appropriate to introduce $z = r - s(t)$, where $s(t)$ is defined so that all the first-order derivative terms on the right-hand side of (4.46) (the convective terms) are eliminated at leading order, which requires that we define s by

$$\dot{s} = \beta s^q - \beta \theta s^p. \tag{4.47}$$

This can be solved asymptotically as $t \to \infty$, by taking the leading-order solution (4.45) and calculating the first correction term, to give

$$s(t) \sim (\beta(1-q)t)^{1/(1-q)} - \frac{\theta}{p - 2q + 1}(\beta(1-q)t)^{1+p/(1-q)}. \tag{4.48}$$

However, if $p+1 < 2q$ a term $\lambda t^{q/(1-q)}$ where λ is an arbitrary constant whose value depends on the initial data (this term corresponds to the invariance of (4.47) under time translations), intrudes before the second term given in (4.48) (for $p + 1 = 2q$, the correction term has an additional $\log t$ factor). For $q \leqslant 1/2$ the remaining terms from (4.46) imply that the leading-order balance is between the terms

$$\frac{\partial \psi}{\partial t} \sim \frac{\beta s^q}{2} \frac{\partial^2 \psi}{\partial z^2} - \frac{\beta q z}{s^{1-q}} \frac{\partial \psi}{\partial z} \tag{4.49}$$

or some subset thereof, and this enables the shape of the wave to be determined in some cases. Results for the system fall into five categories, depending on the size of q, with a similar classification to cases E and S.

4.6.1. Case F(i): $p < q < 1/2$. For $q < 1/2$ the front's position $s(t)$ is governed by (4.47) and its shape is determined by the leading order terms from (4.49), which are

$$\frac{\partial \psi}{\partial t} \sim \frac{1}{2}\beta s^q \frac{\partial^2 \psi}{\partial z^2} \tag{4.50}$$

leading to

$$c_r(t) \sim \frac{\theta^{r-1}}{2r^p (r!)^{q-p}} \operatorname{erfc}\left(\sqrt{\frac{1-2q}{2}} \frac{r - s(t)}{\sqrt{s(t)}} \right)$$
$$\text{as} \quad t \to \infty \quad \text{with} \quad r - s(t) = O(\sqrt{s(t)}) \tag{4.51}$$

with the WKBJ solution (2.55) holding in $r/s(t) > 1$, giving far-field behaviour (2.74), (2.75).

4.6.2. Case F(ii): $p < q = 1/2$. For $q = 1/2$, the position of the wavefront is given by $s(t) \sim \beta^2 t^2/4$. The wavefront's shape is given by

$$\frac{\partial\psi}{\partial t} \sim \frac{\beta\sqrt{s}}{2}\frac{\partial^2\psi}{\partial z^2} - \frac{\beta z}{2\sqrt{s}}\frac{\partial\psi}{\partial z} \tag{4.52}$$

which on using the transformation (4.14) yields the solution

$$c_r(t) \sim \frac{\theta^{r-1}}{2r^p(r!)^{1/2-p}}\mathrm{erfc}\left(\frac{r-s(t)}{\sqrt{s(t)}\log^{1/2}s(t)}\right)$$
$$\text{as} \quad t\to\infty \quad \text{with} \quad r - s(t) = O(\sqrt{s(t)}\log^{1/2}s(t)). \tag{4.53}$$

4.6.3. Case F(iii): $\max(p, 1/2) < q < 1$. When $1/2 < q < 1$, the position of the wavefront is determined by (4.47). The local behaviour at the wavefront depends on $\xi = z/s^p$ via $\psi \sim \Psi(\xi)$, where $\Psi(\xi)$ is dependent on the initial conditions and satisfies $\Psi \to 0$ as $\xi \to \infty$ and $\Psi \to 1$ as $\xi \to -\infty$.

4.6.4. Case F(iv): $p < q = 1$. In the two remaining cases, the description via a wavefront located about $r = s$ with s given by (4.47) is no longer appropriate. In the current borderline case, we have (2.62), (2.76) in the far field which matches with the equilibrium solution (2.79) which describes the large time behaviour essentially uniformly in r.

4.6.5. Case F(v): $q > \max(q, 1)$. For $q > 1$, (2.78) describes the far-field behaviour, and convergence to the steady-state solution is essentially uniform in r as $t \to \infty$.

4.7. Case A: aggregation dominated ($p > q$)

4.7.1. Formulation. In this case, the system converges to the steady-state solution (2.9) for large time. The behaviour is very similar to case S ($p = q$) in the limit $\theta \to \infty$, corresponding to taking $\beta \to 0$ with $\beta\theta = \alpha c_1$ fixed and $O(1)$. However, in the current case the steady-state solution (2.9) is a little more complex than that in case S. As before, we factor out the steady state by writing

$$c_r(t) = Q_r c_1^r J\sigma(r)\psi(r,t)$$
$$\text{with} \quad J = \beta c_1 \Bigg/ \sum_{k=1}^{\infty}\frac{1}{\theta^k(k!)^{p-q}} \quad \text{and} \quad \sigma(r) = \sum_{k=r}^{\infty}\frac{1}{\beta c_1\theta^k(k!)^{p-q}} \tag{4.54}$$

whereby in the inner region $r = O(1)$ we have $\psi \sim 1$ as $t \to \infty$ and we have an outer region where ψ varies slowly in r. For large r

$$\sigma(r) \sim \frac{1}{\beta c_1\theta^r(r!)^{p-q}}\left(1 + \frac{1}{\theta r^{p-q}} + \cdots\right) \tag{4.55}$$

which can be further simplified using Stirling's formula, while taking the continuum expansion of the system of ordinary differential equations

$$\dot\psi(r,t) = \beta r^q(\psi(r-1,t) - \psi(r,t)) + \alpha c_1 r^p(\psi(r+1,t) - \psi(r+1,t))$$
$$+ \frac{(\psi(r-1,t) - \psi(r+1,t))}{Q_r c_1^r\sigma(r)} \tag{4.56}$$

yields

$$\frac{\partial\psi}{\partial t} \sim -\alpha c_1 r^p\frac{\partial\psi}{\partial r} + (2\alpha c_1 - \beta)r^q\frac{\partial\psi}{\partial r} + \frac{\alpha c_1 r^p}{2}\frac{\partial^2\psi}{\partial r^2}. \tag{4.57}$$

At large r, the leading-order balance is

$$\frac{\partial\psi}{\partial t} = -\alpha c_1 r^p \frac{\partial\psi}{\partial r} \tag{4.58}$$

which determines the position ($r = s(t)$) of the wavefront, the leading-order solution of (4.58) being $\psi = H(s(t) - r)$, where $s(t)$ is determined by

$$\dot{s} \sim \alpha c_1 s^p. \tag{4.59}$$

To determine the solution for $\psi(r, t)$ at higher order we substitute $z = r - s(t)$ in (4.57) and, as before, eliminate the correction terms at leading order by defining $s(t)$ through

$$\dot{s} = \alpha c_1 s^p - (2\alpha c_1 - \beta)s^q \tag{4.60}$$

the dominant balance being

$$\frac{\partial\psi}{\partial t} \sim \frac{\alpha c_1 s^p}{2}\frac{\partial^2\psi}{\partial z^2} - \frac{\alpha c_1 z}{s^{1-p}}\frac{\partial\psi}{\partial z} \tag{4.61}$$

or a subset thereof. For $p \leqslant 1/2$ (4.61) determines the shape of the wavefront as described below. The solution to (4.60) is given for large time by

$$s(t) \sim (\alpha c_1(1-p)t)^{1/(1-p)} + \frac{(1/\theta - 2)}{(q - 2p + 1)}(\alpha c_1(1-p)t)^{1+q/(1-p)} \tag{4.62}$$

(cf (4.48)). However, if $2p > q + 1$ a term of the form $\lambda t^{p/(1-p)}$ where λ depends on the initial conditions, which corresponds to the invariance of (4.60) under time translations, intrudes before the second term given in (4.62).

4.7.2. Case A(i): $p < 1/2$. For $p < 1/2$, the full balance occurs at leading order in (4.61), being solved by

$$\psi \sim \frac{1}{2}\operatorname{erfc}\left(\frac{\sqrt{1-2p}\,z}{\sqrt{2s(t)}}\right) \tag{4.63}$$

thus from (4.54) the solution for large t is

$$c_r \sim \frac{c_1}{2r^p}\operatorname{erfc}\left(\frac{\sqrt{1-2p}(r - s(t))}{\sqrt{2s(t)}}\right) \qquad \text{as} \quad t \to \infty \quad \text{with} \quad r - s(t) = O(\sqrt{s(t)}) \tag{4.64}$$

where $s(t)$ is given by (4.62). In the far-field (where $r/s(t) > 1$), the solution is determined by the WKBJ solution (2.39) with $\beta = 0$. Since we have $J_r(t) \sim J\psi(r, t)$ as $r \to \infty$, (4.63) shows how the flux through the system drops from J to zero for large r.

4.7.3. Case A(ii): $p = \frac{1}{2}$. In this case, solving (4.60) for the position of the diffusive wavefront gives $s(t) \sim \alpha^2 c_1^2 t^2/4$. The shape of the front is clearly not given by (4.64), and we transform (4.61) by introducing the new variables τ, ζ, as defined by (4.14). Thus around the front, the solution in the large-time limit takes the form

$$c_r(t) \sim \frac{c_1}{2\sqrt{r}}\operatorname{erfc}\left(\frac{r - s(t)}{2\sqrt{s(t)}\log^{1/2} s(t)}\right)$$
$$\text{as} \quad t \to \infty \quad \text{with} \quad r - s(t) = O(\sqrt{s(t)}\log^{1/2} s(t)). \tag{4.65}$$

4.7.4. Case A(iii): $\frac{1}{2} < p < 1$. As in cases E(iii) and S(iii), the large-time asymptotics depend on the initial conditions, with the time dependence being of the form

$$\psi \sim \Psi(z/s^p) \tag{4.66}$$

where Ψ is arbitrary (depending on the initial data) subject to $\Psi(\xi) \to 1$ as $\xi \to -\infty$ and $\Psi(\xi) \to 0$ as $\xi \to +\infty$, and where $s = s(t)$ is given by (4.60). The form of decay as $\xi \to +\infty$ can be found by matching into the WKBJ solution (2.41). The advective component of (4.57) in this case dominates the diffusive one, and the details of the initial data are accordingly not all lost.

4.7.5. Case A(iv): $p = 1$. Here (2.67) and (2.72) give the far-field behaviour, matching with the steady-state solution and again implying exponential decay in c_r as $r \to \infty$ at a rate which itself decays exponentially with t.

4.7.6. Case A(v): $p > 1$. As with case S(v), the far-field (2.73) applies, implying that in (4.54) $\psi \to 1$ uniformly in r as $t \to \infty$ with a nonzero flux to infinity, which can be found, using (4.55), to be

$$J_\infty(t) \to J \qquad \text{as} \quad t \to \infty \tag{4.67}$$

where J is as defined in (4.54).

5. Conclusions

Many of the results presented in this paper are applicable to more general forward and backward rate coefficients satisfying $a_r \sim \alpha r^p$, $b_r \sim \beta r^q$ as $r \to \infty$; if (1.1) is valid only for large r then (2.2) is modified solely by a change in the constant term. For a variety of constant monomer Becker–Döring systems we have shown which of the equilibrium solution and the steady-state solution govern the large-time asymptotics, and the manner in which that solution is approached. Depending on the form of the forward and backward rate parameters in the problem, this is often by a wavefront which advects matter to larger aggregation numbers, leaving behind the steady-state or equilibrium solution.

For $p > 1$ with $q < p$ and $p = q > 1$ with $\theta > 1$ a phenomenon akin to gelation (see [4, 5, 8], for example) occurs, whereby there is a finite flux of particles to a particle of infinite size (the 'gel'); unlike the conventional case, however, there is an infinite flux of mass, with new monomers being introduced at an unbounded rate $\left(J_1 + \sum_{r=1}^{\infty} J_r\right)$ in order to maintain the monomer concentration at a fixed level. Although this may appear unphysical, the results are highly instructive for the constant mass formulation of the Becker–Döring equations. We note that for $p > 2$ only a finite amount of mass is present in particles of finite size, while for $1 < p \leqslant 2$ there is an infinite amount; in all cases there is only a finite number of particles of finite size. For the power-law coefficients (1.1) discussed so far, the gel starts to form instantaneously (cf (3.6)). However, there could in principle be classes of rate coefficient for which the onset of gelation may be deferred (finite time gelation, cf [4, 5, 8]); this can be the case if there exists a range of coefficients about the borderline $p = 1$ for which distinct far-field behaviour, one with $J_\infty = 0$ and another with $J_\infty > 0$, are both possible. We now investigate this possibility, considering for brevity the case $b_r \equiv 0$. If $J_\infty > 0$ then

$$c_r \sim \frac{J_\infty(t)}{a_r c_1} \qquad \text{as} \quad r \to \infty \tag{5.1}$$

constructing the first correction term (whereby the continuum limit pertains), we find that

$$c_r \sim \frac{J_\infty}{a(r)c_1} + \frac{\dot{J}_\infty}{a(r)c_1^2}\int_r^\infty \frac{\mathrm{d}r'}{a(r')} \qquad \text{as} \quad r \to \infty \tag{5.2}$$

and this form of the far-field solution is thus self-consistent if the integral in (5.2) converges so, if

$$a_r \sim \alpha r \log^{\hat{p}} r \qquad \text{as} \quad r \to \infty \tag{5.3}$$

say, for some constant $\hat{p}$ then we require $\hat{p} > 1$. In the case (5.3), the far-field balance (2.24) reads

$$\frac{\partial w}{\partial t} = \alpha r \log^{\hat{p}} r c_1 \left(\exp\left(-\frac{\partial w}{\partial r}\right) - 1\right) \tag{5.4}$$

writing

$$w = r\hat{w}(\hat{r}, t) \qquad \hat{r} = \log r \tag{5.5}$$

yields

$$\frac{\partial \hat{w}}{\partial t} = \alpha \hat{r}^{\hat{p}} c_1 \left(\exp\left(-\frac{\partial \hat{w}}{\partial \hat{r}}\right) - 1\right) \tag{5.6}$$

equivalent to the corresponding problem for (1.1) discussed earlier in the paper, with p replaced by $\hat{p}$; thus if $\hat{p} < 1$ a WKBJ approach determines the far-field behaviour of solutions, showing them to be non-gelating. Repeated application of transformations of the form (5.5) enables us to refine iteratively the borderline, below which non-gelating solutions exist, to

$$a_r \sim \alpha r \log r \log\log r \cdots \qquad \text{as} \quad r \to \infty \tag{5.7}$$

coinciding exactly with the borderline for the convergence or otherwise of the integral in (5.2). Since there thus seems to be no overlap between gelating and non-gelating regimes, we conclude that, unlike certain other coagulation models, deferred gelation is not in fact possible for (1.2).

We noted earlier ((4.39), (4.40)) that there is an equivalence transform which maps case S to case E and vice versa. This equivalence transform also yields insight into the relationship between cases F and A; here the coefficients do not map exactly into each other, but the relevant large-r forms do—for example, taking $K = -1/d_\infty$ maps the coefficients $a_r = ar^p$, $b_r = br^q$ with $p > q$ to $\hat{a}_r$, $\hat{b}_r$ which satisfy $\hat{a}_r = (\alpha/\theta)r^q(1 + O(1/r))$ and $\hat{b}_r = \beta\theta r^p(1 + O(1/r))$ as $r \to \infty$ (note the interchange of p and q). Thus case A maps to case F and vice versa.

We have also illustrated the role of some novel forms of self-similarity holding as $t \to \infty$, notably in (4.38).

The results of section 4 also allow us to find the asymptotic behaviour of the mass ($\varrho = M_1(t)$) and total number of clusters, $M_0(t)$. In case E, where $p = q$ and $\theta < 1$ we have

$$M_0 \to \mathrm{polylog}(p, \theta) \qquad M_1 \to \mathrm{polylog}(p-1, \theta) \qquad \text{as} \quad t \to \infty \tag{5.8}$$

since the system converges to the equilibrium solution, whereas for $\theta > 1$ and $p = q$ the system approaches a steady-state according to

$$M_0 \sim \beta c_1(\theta - 1)t \qquad M_1 \sim \frac{c_1}{2-p}(\beta(\theta-1)(1-p)t)^{(2-p)/(1-p)} \qquad \text{as} \quad t \to \infty \tag{5.9}$$

for $p < 1$. In the case $p = 1$ with $\theta > 1$, we have

$$M_0 \sim \beta c_1(\theta - 1)t \qquad M_1 \sim \frac{c_1\theta\, \mathrm{e}^{\beta(\theta-1)t}}{\theta - 1} \qquad \text{as} \quad t \to \infty. \tag{5.10}$$

For $p > 1$ with $\theta > 1$ a phenomenon akin to gelation occurs, so that M_0 and M_1 are thus unable to grow without bound, but instead

$$M_0 \to c_1\zeta(p) \qquad M_1 \to c_1\zeta(p-1) \qquad \text{as} \quad t \to \infty \tag{5.11}$$

where $\zeta(p)$ is the Riemann zeta function; note that $\zeta(p-1)$ is divergent for $p < 2$, the mass in this case being unbounded for all $t > 0$. The borderline case ('B', $p = q$, $\theta = 1$) yields, for $p < 1$,

$$M_0 \sim t^{(1-p)/(2-p)} \int_0^\infty \eta^{-p}\Upsilon(\eta)\,\mathrm{d}\eta \qquad M_1 \sim t \int_0^\infty \eta^{1-p}\Upsilon(\eta)\,\mathrm{d}\eta \qquad \text{as} \quad t \to \infty \tag{5.12}$$

and for $1 < p < 2$,

$$M_0 \sim \zeta(p) \qquad M_1 \sim t \int_0^\infty \eta^{1-p}\Upsilon(\eta)\,\mathrm{d}\eta \qquad \text{as} \quad t \to \infty \tag{5.13}$$

where $\Upsilon(\eta)$ is the similarity solution defined by (4.35) with $\eta = r/t^{1/(2-p)}$. The borderline case for $\theta = 1 = p = q$ has been solved exactly, yielding

$$M_0 = G(0,t) = c_1(1 + \alpha c_1 t) \qquad M_1 = c_1(2\,\mathrm{e}^{\alpha c_1 t} - 1) \tag{5.14}$$

from (2.14) and (2.15) respectively; for case B(ii) ($p = 2$) we have

$$M_0 \to \frac{\pi^2}{6} \qquad M_1 \sim t \qquad \text{as} \quad t \to \infty. \tag{5.15}$$

For $\theta = 1$ with $p > 2$, we have uniform convergence (in r) to the equilibrium solution $c_r = c_1/r^p$, for which $M_0 = c_1\zeta(p)$ and $M_1 = c_1\zeta(p-1)$. Case F ($p < q$) behaves in a similar fashion to case E, with both M_0 and M_1 approaching finite constants as $t \to \infty$, the values of which depend on the details of the equilibrium solution. In case A ($p > q$) with $p < 1$ we have

$$M_0 \sim \alpha c_1^2 t \qquad M_1 \sim \frac{c_1}{2-p}(\alpha c_1(1-p)t)^{(2-p)/(1-p)} \qquad \text{as} \quad t \to \infty \tag{5.16}$$

equivalent to the limit $\beta \to 0$, $\theta \to \infty$ in (5.9).

In a future paper the methodology and results derived here will be applied to the constant mass formulation of the Becker–Döring system of equations to elucidate, in particular, the form of the weak convergence in the case of rate coefficients which yield an aggregation-dominated system.

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