

Point island dynamics under fixed rate deposition

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Abstract

We consider the dynamics of point islands during submonolayer deposition, in which the fragmentation of subcritical size islands is allowed. To understand asymptotics of solutions, we use methods of centre manifold theory, and for globalisation, we employ results from the theories of compartmental systems and of asymptotically autonomous dynamical systems. We also compare our results with those obtained by making the quasi-steady state assumption.

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1. Introduction

Submonolayer deposition, a process in which atoms or molecules are deposited onto a substrate, diffuse and form islands, is a foundational technology in the creation of smart and nanomaterials [11]. A mathematical theory of submonolayer deposition that describes spatial distribution and the size statistics of the islands is an important goal of research. At present there are many competing models to describe the spatial distribution of islands; see, for example [14], and the work that paper has led to.

Size distribution of islands is usually tackled by models that disregard the spatial structure, and deal only with coagulation and fragmentation of clusters composed of adatoms deposited onto a surface. Such models lead to infinite systems of ordinary differential equations (ODEs) for the various species, these are known as rate equations; see, for example, [6, 9].

If furthermore one assumes that the structure of these clusters is also disregarded, one deals with point islands, and then it makes sense to assume that coagulation and fragmentation rates are not size-dependent. Studies of this type of rate equations have been initiated by da Costa *et al.* [4]; see also [3, 5], all of which are relevant to the present work.

^{*}This paper is dedicated to the memory of Jack Carr

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As in [5] we further assume that there exists a *critical island size* i such that islands (adatom clusters) of size $j \geq n := i + 1$ are immobile and can only grow by attachment of single adatoms.

There is a number of possibilities how to model islands of size $1 < j \leq i$. The one considered in [5] is that clusters of size $1 < j \leq i$ simply do not arise. There is one other physically relevant possibility, i.e. that clusters of every size $1 < j \leq i$ are allowed to fragment (at some rate independent of the cluster size, which is consistent with the point-island assumption). This possibility has been considered formally in [1, 12]. In this paper we consider this mechanism, using centre manifold techniques [2] and globalising the results.

In [4] and in [5] as well, it was possible by a change of variables, to decouple the infinite system of ODEs in a way that reduced its analysis to an analysis of a two-dimensional system. In our case, the reduction is to $n = i + 1$ equations, and the remarkable property of these equations is that the complexity of the calculations is independent of n . Furthermore, it appears that computations can be significantly simplified by making a sweeping assumption that all the clusters of size $1 < j \leq i$ are at a quasi-steady state (the quasi-steady state assumption, QSSA). We show that making this assumption results in the same leading term behaviour as the centre manifold computation and emphasise the differences between the two approaches.

The plan of the paper is as follows. In Section 2 we introduce the governing equations, perform the finite-dimensional reduction, and formulate an equivalence theorem between the reduced n -dimensional system of equations and the original infinite-dimensional one. In Section 3 we discuss boundedness and asymptotic behaviour of solutions to our equations. To obtain more precise information about long-time asymptotics, in Section 4 we perform a centre manifold analysis. The results in Section 3 imply that our asymptotics, derived by centre manifold techniques, hold for any positive initial conditions. The monomer asymptotics for large times are computed in Section 5 and are used there to discuss the consequences for the asymptotic behaviour of islands of all sizes and to characterise the similarity profile the solutions converge to. In Section 6 we compare our results to those obtained by making the QSSA, and finally in Section 7 we relate our results to those of [1] and [12] and draw conclusions.

We also comment on the relation between the present paper and [4]. The methods we use to obtain the asymptotics of monomers and hence of the larger clusters (Lemmas 5 and 6) for all positive initial conditions, significantly extend the methods used in [4]. It is in the way we use centre manifold theory and globalise the results using the work of [8, 16] that the main novelty of the paper lies. With the information contained in the above two lemmas, the methods of [4] can be immediately used to discuss similarity solutions (see Theorem 8); where proofs are sufficiently similar to those in [4], we either omit them, or give only the gist as in the proof of Theorem 1.

2. Governing equations

We consider a system containing clusters of any number $j \geq 1$ or monomers. We assume that the following reactions occur:



for $1 \leq j < i$ and



if $j \geq i$. In other words, we allow clusters of size less than $i + 1$ to fragment at a rate $\beta > 0$.

If we set $\tilde{\alpha}$ to be the deposition rate, denote by $C_j(t)$ the concentration of j -mers and use primes for differentiation with respect to time t , the laws of mass kinetics give us the following infinite system of ODEs:

$$\begin{aligned}
C_1' &= \tilde{\alpha} - 2C_1^2 + 2\beta C_2 - C_1 \sum_{k=2}^{\infty} C_k + \beta \sum_{k=3}^i C_k, \\
C_j' &= C_1 C_{j-1} - C_1 C_j - \beta C_j + \beta C_{j+1}, \quad 1 < j < i, \\
C_j' &= C_1 C_{j-1} - C_1 C_j - \beta C_j, \quad j = i, \\
C_j' &= C_1 C_{j-1} - C_1 C_j, \quad j > i.
\end{aligned} \tag{1}$$

It makes sense to scale the variables and the deposition rate to remove β from the equations. Thus scaling $t \rightarrow T := \beta t$, retaining primes for differentiation with respect to the new time scale, setting $C_j(t) = \beta c_j(T)$ and $\alpha = \tilde{\alpha}/\beta^2$, we obtain the system

$$\begin{aligned}
c_1' &= \alpha - 2c_1^2 + 2c_2 - c_1 \sum_{k=2}^{\infty} c_k + \sum_{k=3}^i c_k, \\
c_j' &= c_1 c_{j-1} - c_1 c_j - c_j + c_{j+1}, \quad 1 < j < i, \\
c_j' &= c_1 c_{j-1} - c_1 c_j - c_j, \quad j = i, \\
c_j' &= c_1 c_{j-1} - c_1 c_j, \quad j > i.
\end{aligned} \tag{2}$$

3. Globalisation

In this section we consider the global dynamics of equations (2) satisfied by $c_j(T)$, $1 \leq j \leq i$, and $v(T) = \alpha - c_1(T) \sum_{k=2}^{\infty} c_k(T)$, and establish that all solutions of these equations with non-negative initial data approach the origin. This will show that the flow on the centre manifold, as given by Theorem 4, describes the asymptotics of every non-negative solution of this system of equations.

For that purpose, it is more convenient to rewrite equations (2) formally as follows:

$$\begin{aligned}
c_1' &= \alpha - 2c_1^2 + 2c_2 - c_1 \sum_{k=2}^i c_k + \sum_{k=3}^i c_k - c_1 y, \\
c_j' &= c_1 c_{j-1} - c_1 c_j - c_j + c_{j+1}, \quad 1 < j < i, \\
c_i' &= c_1 c_{i-1} - c_1 c_i - c_i, \\
y' &= c_1 c_i,
\end{aligned} \tag{3}$$

where we have put $y(T) = \sum_{k=i+1}^{\infty} c_k(T)$.

First of all, we have

Theorem 1. *If $\sum_{k=1}^{\infty} c_k(0) < \infty$, a solution of (2) for $j \geq 1$ is also a solution of (3).*

Proof: The argument of the proof is similar to that of [4, Theorem 2.1]; we indicate the main steps.

Let $(c_j)_{j=1}^{\infty}$ be a solution of (2). To show that this is also a solution of (3) we must prove that $\sum_{k=i+1}^{\infty} c_k$ converges to y for all T . We change time from T to $\rho = \int_0^T c_1(s) ds$. This change of variable (also used in [4, Theorem 2.1]) makes the c_j equations of (2) linear in c_j for $j > i$. Keeping primes for differentiation with respect to the new time variable ρ and letting $c_j(T) := \tilde{c}_j(\rho)$, $y(T) := \tilde{y}(\rho)$, these equations become

$$\tilde{c}_j' = \tilde{c}_{j-1} - \tilde{c}_j, \quad j > i, \quad \text{and} \quad \tilde{y}' = \tilde{c}_i. \tag{4}$$

This system of ODEs for \tilde{c}_j , $j > i$, can now be solved in terms of \tilde{c}_i recursively by variation of parameters starting at $j = i + 1$, to give

$$\tilde{c}_j = e^{-\rho} \sum_{k=i+1}^j \frac{\rho^{j-k}}{(j-k)!} \tilde{c}_k(0) + \frac{1}{(j-(i+1))!} \int_0^\rho \tilde{c}_i(\rho-s) s^{j-(i+1)} e^{-s} ds. \quad (5)$$

Introducing the generating function

$$F(\rho, z) := \sum_{n=i+1}^{\infty} \tilde{c}_n z^n,$$

we can use (5) to rewrite F as $F(\rho, z) := G(\rho, z) + H(\rho, z)$, where

$$G(\rho, z) = e^{-\rho} \sum_{n=i+1}^{\infty} \sum_{k=i+1}^n \frac{\rho^{n-k} z^n}{(n-k)!} \tilde{c}_k(0),$$

and

$$H(\rho, z) = \sum_{n=i+1}^{\infty} \frac{z^n}{(n-(i+1))!} \int_0^\rho \tilde{c}_i(\rho-s) s^{n-(i+1)} e^{-s} ds.$$

We now consider these two expressions separately. For G we obtain

$$G(\rho, z) = e^{-\rho(1-z)} \sum_{k=i+1}^{\infty} z^k \tilde{c}_k(0).$$

Since $\sum_{k=1}^{\infty} c_k(0) < \infty$ by assumption, the above series converges when $|z| \leq 1$, and we have

$$G(\rho, z) = e^{-\rho(1-z)} (F(0, z) - \tilde{c}_i(0)z) \quad \text{for } |z| \leq 1.$$

For H , by interchanging the order of summation and integration, we have that

$$H(\rho, z) = z^i \int_0^\rho \tilde{c}_i(s) e^{-(\rho-s)(1-z)} ds.$$

The expression for F at $z = 1$ now becomes

$$F(\rho, 1) = F(0, 1) - \tilde{c}_i(0) + \int_0^\rho \tilde{c}_i(s) ds. \quad (6)$$

Hence, by differentiating with respect to ρ , we see that $F(\rho, 1)$ given by (6) satisfies the same differential equation as \tilde{y} in (4) which proves that $F(\rho, 1) = \tilde{y}$. Thus in the T variables $\sum_{k=i+1}^{\infty} c_k$ converges to y . \square

As a result of Theorem 1, we can use finite-dimensional techniques to discuss the dynamics of $c_j(T)$, $1 \leq j \leq i$.

We begin our analysis of long-time dynamics of (3) by considering the system without outflows through higher clusters, i.e.

$$\begin{aligned} c_1' &= \alpha - 2c_1^2 + 2c_2 - c_1 \sum_{k=2}^i c_k + \sum_{k=3}^i c_k, \\ c_j' &= c_1 c_{j-1} - c_1 c_j - c_j + c_{j+1}, \quad 1 < j < i, \\ c_i' &= c_1 c_{i-1} - c_1 c_i - c_i. \end{aligned} \quad (7)$$

Let us show that the system (7) is a compartmental system in the sense of Jacquez and Simon [8]. To that end, we introduce some notation.

Let $I_1 = \alpha$ and let $I_j = 0$ for all $2 \leq j \leq i$. Now put

$$\begin{aligned} F_{j1} &= c_1 c_{j-1}, \quad j = 2, \dots, i; \\ F_{12} &= 2c_2 \quad \text{and} \quad F_{1j} = c_j, \quad j = 3, \dots, i. \end{aligned}$$

For $k = j - 1$, $2 \leq k \leq i - 1$ put $F_{kj} = c_j$, $F_{jk} = c_1 c_k$ and for $k = j + 1$, $2 \leq j \leq i - 1$, put $F_{kj} = c_j$. Finally, let $F_{0k} = 0$ if $k \neq 1, i$ and $F_{0i} = F_{01} = c_1 c_i$, the only outflows from the system.

Then clearly for each $j = 1, \dots, i$ we can write

$$c'_j = \sum_{k \neq j}^i -F_{kj} + F_{jk} + I_j - F_{0j}, \quad (8)$$

where all the F s and I s are positive, which shows that (7) is a compartmental system in the sense of [8].

Also note that

$$\frac{\partial F_{jk}}{\partial c_m} \geq 0 \quad \text{for all } 1 \leq j, k, m \leq i, \quad j \neq k. \quad (9)$$

Hence we can use the theorem of Maeda, Kodama and Ohta [10]; see also part (i) of Theorem 9 of [8]:

Theorem 2 ([10]). *Given a compartmental system (8) with time-independent inputs I_j that satisfies the monotonicity condition (9), every non-negative solution of the system is bounded iff the system has a positive rest point.*

Since it is not hard to compute that the system (7) admits the unique positive equilibrium

$$(c_1, c_2, \dots, c_i) = (\alpha^{\frac{1}{i+1}}, \alpha^{\frac{2}{i+1}}, \dots, \alpha^{\frac{i}{i+1}}),$$

we conclude using Theorem 2 that all non-negative solutions of (7) are bounded.

Now we consider the first i equations of the system (3). Since the system (3) preserves non-negativity, and $y(T)$ is a positive function, by comparison with solutions of (7) it follows that the (c_1, \dots, c_i) components of non-negative solutions of (3) are bounded for any positive initial condition.

Now consider the dynamics of the last component of (3), $y(T)$. As it is monotone-increasing it can either converge to some limit $l < \infty$ or it can go to infinity.

Let us show that the first possibility cannot occur. If $y(T)$ converges to some limit $l < \infty$, we could use the theorem of Thieme [16, Theorem 4.2] on behaviour as $T \rightarrow \infty$ of asymptotically autonomous systems, combined with the fact that all non-negative solutions of (3) are bounded and the uniqueness of the positive equilibrium, to conclude that the ω -limit set of every orbit of (3) would be the same as that of the system

$$\begin{aligned} c'_1 &= \alpha - 2c_1^2 + 2c_2 - c_1 \sum_{k=2}^i c_k + \sum_{k=3}^i c_k - c_1 l, \\ c'_j &= c_1 c_{j-1} - c_1 c_j - c_j + c_{j+1}, \quad 1 < j < i, \\ c'_i &= c_1 c_{i-1} - c_1 c_i - c_i. \end{aligned} \quad (10)$$

But if $y(T) \rightarrow l$ as $T \rightarrow \infty$, we must have that either $c_1(T) \rightarrow 0$ or $c_i(T) \rightarrow 0$. If we suppose, for example, that $c_i(T) \rightarrow 0$, we see from the c'_i equation of (10) that either $c_1(T)$ or $c_{i-1}(T)$ must go to zero. Continuing

in this way, we see that all $c_j(T)$ must go to zero as $T \rightarrow \infty$, but the origin is not a rest point of the first i equations of (10). Hence we conclude that $y(T) \rightarrow \infty$.

Furthermore, since the positive orthant of \mathbb{R}^{i+1} is invariant under the flow of (3), this means that $c_1(T) \rightarrow 0$ as $T \rightarrow \infty$.

Now, from the equations for c_i, c_{i-1}, \dots, c_2 it follows consecutively that for all $2 \leq k \leq i$, $c_k(T) \rightarrow 0$ as $T \rightarrow \infty$, again using the same result of Thieme [16] for asymptotically autonomous differential equations. Applying these results to the equation for c_1 in (3), we finally conclude that $c_1(T)y(T) \rightarrow \alpha$ as $T \rightarrow \infty$. If we now set

$$v(T) := \alpha - c_1(T) \sum_{k=2}^{\infty} c_k(T), \quad (11)$$

this is equivalent to saying that $v(T) \rightarrow 0$ as $T \rightarrow \infty$.

We collect these results as a theorem:

Theorem 3. *As $T \rightarrow \infty$, for all non-negative initial data, $c_k(T) \rightarrow 0$, $1 \leq k \leq i$, and $v(T) \rightarrow 0$.*

To understand better the dynamics of $c_j(T)$ as $T \rightarrow \infty$ for all $j \geq 1$, we first use centre manifold techniques to understand the rate of approach of $c_j(T)$ to zero, $1 \leq i$ as $T \rightarrow \infty$.

4. Centre manifold analysis

The variable $v(T)$ defined by (11) satisfies the equation

$$\begin{aligned} v' = & -\frac{1}{c_1} \left[c_1^4 - c_1^2 c_2 + \alpha v - v^2 - 2\alpha c_1^2 + 2c_1^2 v + 2\alpha c_2 \right. \\ & \left. - 2c_2 v + \alpha \sum_{k=3}^i c_k - v \sum_{k=3}^i c_k \right]. \end{aligned} \quad (12)$$

In terms of v , the equation for c_1 becomes

$$c_1' = v - 2c_1^2 + 2c_2 + \sum_{k=3}^i c_k. \quad (13)$$

We now change time from T to $\tau = \int_0^T \frac{1}{c_1(s)} ds$. This change of variable (also used in [4, p. 377] and [3, system (3.3)]) is needed to desingularise the v equation when $c_1 = 0$. Note that by the result of Theorem 3, $\tau \rightarrow \infty$ as $T \rightarrow \infty$. Letting dots represent derivatives with respect to τ , the $i+1$ ODEs for c_j , $1 \leq j \leq i$, and for v become

$$\begin{aligned} \dot{c}_1 &= c_1 \left(v - 2c_1^2 + 2c_2 + \sum_{k=3}^i c_k \right), \\ \dot{c}_j &= c_1 (c_1 c_{j-1} - c_1 c_j - c_j + c_{j+1}), \quad 1 < j < i, \\ \dot{c}_i &= c_1 (c_1 c_{i-1} - c_1 c_i - c_i), \end{aligned} \quad (14)$$

and

$$\begin{aligned} \dot{v} = & -c_1^4 - c_1^2 c_2 + \alpha v - v^2 - 2\alpha c_1^2 + 2c_1^2 v \\ & + 2\alpha c_2 - 2c_2 v + \alpha \sum_{k=3}^i c_k - v \sum_{k=3}^i c_k. \end{aligned} \quad (15)$$

Note that $0 \in \mathbb{R}^{i+1}$ is now a rest point of the system of equations (14)–(15). The object of interest is to establish stability properties of this rest point and the way in which it is approached.

It is useful to make another change of variable. We set

$$w = v + 2c_2 + \sum_{k=3}^i c_k.$$

In the $(c_1, c_2, \dots, c_i, w)$ variables the equation (13) for c_1 becomes conveniently

$$\dot{c}_1 = c_1(w - 2c_1^2), \quad (16)$$

the equations for c_2, \dots, c_i remain as before in (14) and obviously we have

$$\begin{aligned} \dot{w} = \dot{v} + 2\dot{c}_2 + \sum_{k=3}^i \dot{c}_k &= -\alpha w + 2\alpha c_1^2 - 2c_1 c_2 + 2c_1^3 + c_1 c_3 + 4c_1^2 c_2 - 2c_1^2 w \\ &\quad - 2c_2 w - c_1^2 c_i - w \sum_{k=3}^i c_k + 2c_1^2 \sum_{k=3}^i c_k - c_1^4 + w^2. \end{aligned} \quad (17)$$

Now we appeal to centre manifold theory [2]. In the language of that theory, for the equations (16), (14), (17), the variables c_j , $1 \leq j \leq i$ are “centre” variables while w is a “stable” variable, so that according to centre manifold theory, in a neighbourhood of the origin in \mathbb{R}^{i+1} , equations (16), (14) for $1 < j \leq i$ and (17) admit an i -dimensional centre manifold, $w = h(c_1, c_2, \dots, c_i)$. Furthermore, from Theorem 3 it follows that the centre manifold attracts all solutions in a neighbourhood of the origin in \mathbb{R}^{i+1} .

On this centre manifold, the flow is given by

$$\begin{aligned} \dot{c}_1 &= c_1(h(c_1, c_2, \dots, c_i) - 2c_1^2), \\ \dot{c}_j &= c_1(c_1 c_{j-1} - c_1 c_j - c_j + c_{j+1}), \quad 1 < j < i, \\ \dot{c}_i &= c_1(c_1 c_{i-1} - c_1 c_i - c_i). \end{aligned} \quad (18)$$

Remarkably, we can reparameterise time by going back to the variable T to obtain on the centre manifold $w = h(c_1, c_2, \dots, c_i)$ the equations

$$\begin{aligned} c_1' &= h(c_1, c_2, \dots, c_i) - 2c_1^2, \\ c_j' &= c_1 c_{j-1} - c_1 c_j - c_j + c_{j+1}, \quad 1 < j < i, \\ c_i' &= c_1 c_{i-1} - c_1 c_i - c_i. \end{aligned} \quad (19)$$

Since by centre manifold theory the asymptotic expansion of $h(c_1, c_2, \dots, c_i)$ contains only quadratic terms and above in c_j , $j \geq 1$, the $i \times i$ Jacobian matrix $J(0)$ of equations (19) around the origin in \mathbb{R}^{i+1} has the following structure:

$$J(0) = \left[\begin{array}{c|c} 0 & 0 \\ \hline 0 & A \end{array} \right],$$

with the first row being made of zeros, and the $(i-1) \times (i-1)$ bi-diagonal matrix A having -1 on the main diagonal and 1 in the $(j, j+1)$ positions, $2 \leq j \leq i-1$. It is easily seen that all eigenvalues of A are negative. Such structure of the Jacobian matrix means that for the equations of the flow on the centre manifold $w = h(c_1, c_2, \dots, c_i)$, c_j , $2 \leq j \leq i$ are “stable” variables and c_1 is a “centre” variable, so that inside the i -dimensional centre manifold there is another, one-dimensional, centre manifold parameterised

by c_1 , i.e., a curve with components $c_j = g_j(c_1)$, $1 < j \leq i$. We will write $g_w(c_1) = h(c_1, g_2(c_1), \dots, g_i(c_1))$. Furthermore, we also know by centre manifold theory that as $c_1 \rightarrow 0$,

$$g_j(c_1) \sim \sum_{k=2}^{\infty} \gamma_{j,k} c_1^k, \quad (20)$$

where we use \sim to mean “is asymptotic to as $c_1 \rightarrow 0$ ”. We also have

$$g_w(c_1) \sim \sum_{k=2}^{\infty} \gamma_{w,k} c_1^k. \quad (21)$$

Hence (see [2]) the flow on the one-dimensional centre manifold is given by

$$c_1' = g_w(c_1) - 2c_1^2, \quad (22)$$

and as the rest point at the origin of the one-dimensional ODE (22) is asymptotically stable by Theorem 3, the one-dimensional centre manifold $(g_2(c_1), \dots, g_i(c_1))$ attracts nearby solutions, so all (apart possibly from sets of zero $(i+1)$ -dimensional Lebesgue measure) approach the origin along this curve.

We have

Theorem 4. c_1 asymptotically satisfies the differential equation

$$c_1' \sim \frac{1}{\alpha} (-c_1^{i+3} + c_1^{i+4} - c_1^{2i+3}) + O(c_1^{2i+4}).$$

Proof: Before we start the computation of the coefficients $\gamma_{j,k}$ and $\gamma_{w,k}$, let us indicate the flow of logic. The equations we are dealing with, (19) and (17), have a very special structure that we are going to exploit.

On the centre manifold, the equations determining $g_j(c_1)$, ($2 \leq j \leq i$), have the form

$$\begin{aligned} \frac{dg_2}{dc_1}(c_1)(g_w(c_1) - 2c_1^2) &= c_1^2 - c_1 g_2(c_1) + c_1 g_3(c_1) - g_2(c_1) + g_3(c_1), \\ \frac{dg_j}{dc_1}(c_1)(g_w(c_1) - 2c_1^2) &= c_1 g_{j-1}(c_1) - c_1 g_j(c_1) - g_j(c_1) + g_{j+1}(c_1), \quad 2 < j < i, \\ \frac{dg_i}{dc_1}(c_1)(g_w(c_1) - 2c_1^2) &= c_1 g_{i-1}(c_1) - c_1 g_i(c_1) - g_i(c_1), \end{aligned}$$

to which we, denoting the right-hand side of (17) by $F(c_1, c_2, \dots, c_i, w)$, add the equation

$$\frac{dg_w}{dc_1}(c_1)(g_w(c_1) - 2c_1^2) = F(c_1, g_2(c_1), \dots, g_i(c_1), g_w(c_1)).$$

Now, using the expansions (20) and (21), we have a system of equations from which we can, in theory, find as many of the coefficients $\gamma_{j,k}$ and $\gamma_{w,k}$ as we wish. The order of the computation is as follows:

By inspection, one can immediately determine $\gamma_{w,2}$, then consecutively $\gamma_{i,2}$, $\gamma_{i-1,2}$ and all the way to $\gamma_{2,2}$. Once this is done, we can find $\gamma_{w,3}$ and proceed in this way to find as many terms of the expansion as required. See Appendix A for the MAPLE code to do the computation for $i = 5$.

Following the algorithm, we find that for all j , $2 \leq j \leq i$, $g_j(c_1) = O(c_1^j)$ and $\gamma_{j,j} = 1$. The final result of this computation is that the functions $g_j(c_1)$, $2 \leq j < i$, $g_i(c_1)$, and $g_w(c_1)$ have the following asymptotic expansions as $c_1 \rightarrow 0$:

$$g_j(c_1) \sim c_1^j - c_1^{i+1} + c_1^{i+j} + O(c_1^{i+j+2}), \quad g_i(c_1) \sim c_1^i - c_1^{i+1} + c_1^{2i} + O(c_1^{2i+1}), \quad (23)$$

and

$$g_w(c_1) \sim 2c_1^2 + \frac{1}{\alpha} (-c_1^{i+3} + c_1^{i+4} - c_1^{2i+3}) + O(c_1^{2i+4}).$$

From these representations, Theorem 4 follows immediately. \square

Note that beyond terms of $O(c_1^{i+j})$ the interplay among $g_j(c_1)$, $1 < j \leq i$, and $g_w(c_1)$ becomes complex, and that the later coefficients of these functions depend on α . Computations using the MAPLE code in Appendix A indicate that the radius of convergence of the expansions is 0 for all $\alpha > 0$.

5. Asymptotics of solutions

Armed with Theorem 4, which holds for any non-negative solution of (2) by the globalisation results of Section 3, we can discuss asymptotics of solutions of (1), using the methods of [3, 4], which were also used in [5]. As proofs are similar to those used in the above papers, we indicate only the main ideas. Further terms in the expansions in this section can be computed using the machinery of [3]; here we only determine the leading terms, denoting higher order terms by ‘‘h.o.t.’’. Going back to our original variables $C_j(t)$ to exhibit the complicated dependence of the results on β , from Theorem 4 we have the following statement:

Lemma 5. *As $t \rightarrow \infty$, the asymptotics of $C_1(t)$ are given by*

$$C_1(t) \sim \left(\frac{\tilde{\alpha}\beta^{i-1}}{(i+2)t} \right)^{\frac{1}{i+2}} + \text{h.o.t.}$$

Note that if we set $\beta = 1$ in the equation above we obtain the same result as in [5]. Already at the level of $C_1(t)$ one sees that the influence of the fragmentation rate β is not intuitive.

Once we know the asymptotics of $C_1(t)$ from Lemma 5, the asymptotics of $C_j(t)$ when $1 \leq j \leq i$ follow from (23).

Lemma 6. *For $1 < j \leq i$, the asymptotics of $C_j(t)$ as $t \rightarrow \infty$ are given by*

$$C_j(t) \sim \left(\frac{\tilde{\alpha}\beta^{\frac{i-3j+2}{j}}}{(i+2)t} \right)^{\frac{j}{i+2}} + \text{h.o.t.}$$

Hence we are now in a position to express the asymptotics of $C_j(t)$ when $j > i$ by solving linear non-homogeneous ODEs using the same change of variable as in the proof of Theorem 1.

Lemma 7. *For $j > i$, the asymptotics of $C_j(t)$ as $t \rightarrow \infty$ are given by*

$$C_j(t) \sim \left(\frac{\tilde{\alpha}\beta^{\frac{-2i+2}{i}}}{(i+2)t} \right)^{\frac{i}{i+2}} + \text{h.o.t.}$$

From this information we have the equivalent of [4, Theorem 5.1] and, to which it is more directly comparable, [5, Theorem 6] concerning similarity solutions of (1). These references should be consulted for the required computations. To formulate the theorem, we first compute the asymptotics of the average cluster size $\langle j \rangle$ using the information in Lemmas 5–7:

$$\langle j \rangle = \frac{\sum_{j=1}^{\infty} j C_j(t)}{\sum_{j=1}^{\infty} C_j(t)} \sim \left(\frac{\tilde{\alpha}\beta^{i-1}}{i+2} \right)^{\frac{1}{i+2}} t^{\frac{i+1}{i+2}} + \text{h.o.t.}$$

Next, we define the function Ψ by

$$\Psi(r) = \begin{cases} (1-r)^{-\frac{i}{i+1}} & \text{if } r \leq 1, \\ 0 & \text{otherwise.} \end{cases}$$

Finally, define the similarity variable η by

$$\eta = \frac{(i+1)\beta^{-\frac{i+1}{i+2}} j}{i+2} \frac{j}{\langle j \rangle}.$$

Then we have that the solutions of (1) converge to a (discontinuous) similarity profile:

Theorem 8. $C_j(t) = \langle j \rangle^{-\frac{i}{i+1}} \Psi(\eta)$ as $t \rightarrow \infty$.

The profile obtained in this theorem can be further analysed by the methods of [4, Section 6].

6. Quasi-steady state assumption

In this section we would like to investigate whether the asymptotics of solutions obtained in Section 5 based on the centre manifold analysis of Section 4 can be recovered more easily by combining centre manifold reasoning with a technique that is often used in the engineering community, the quasi-steady state approximation (QSSA; see [7, 13, 15]). As in the famous example from enzyme kinetics due to Segel and Slemrod [15], we show that QSSA correctly captures the leading term asymptotics, though of course there will be differences in higher order terms.

We restart with equations (2), but now we immediately make the QSSA assumption that $c'_j = 0$ for $1 < j \leq i$. We solve the i algebraic equations for c_j , $1 < j \leq i$, in terms of c_1 . This clearly can be done consecutively, by starting with the c_i equation and solving it in terms of c_1 and c_{i-1} , substituting the expression we get for c_i into the c_{i-1} equation and continuing in this way, till c_2 has been solved in terms of c_1 , after which we back-substitute.

This procedure gives us that under the QSSA assumption

$$c_j = \frac{\sum_{k=1}^{i-j+1} c_1^{k+j-1}}{\sum_{k=1}^i c_1^{k-1}}, \quad j = 2, \dots, i.$$

Note that these are global objects, defined for all values of $c_1 > 0$ unlike the centre manifold expansions (23) which have zero radius of convergence. We will need the MacLaurin series expansions of these objects,

$$c_j = c_1^j + \sum_{k=1}^n \left(-c_1^{ki+1} + c_1^{ki+j} \right) + O\left(c_1^{(n+1)i+1}\right). \quad (24)$$

Now we can go back to the equation for \dot{w} (17), write $w = g_w(c_1)$, remember that by the centre manifold theorem g_w contains terms that are at least quadratic in c_1 , and substituting instead of c_j , $1 < j \leq i$, the expressions from (24), obtain that

$$g_w(c_1) \sim 2c_1^2 + \frac{1}{\alpha} \sum_{k=1}^n \left(-c_1^{ki+3} + c_1^{ki+4} \right) + O\left(c_1^{(n+1)i+3}\right).$$

In the series above we can take n as large as we wish. Hence under the QSSA assumption, setting $h(c_1, \dots, c_i) = g_w(c_1)$ in the first equation of (19), the dynamics of c_1 is governed by the equation

$$c_1' \sim \frac{1}{\alpha} (-c_1^{i+3} + c_1^{i+4} - c_1^{2i+3} + c_1^{2i+4}) + O(c_1^{3i+3}),$$

which by inspection yields the same first three terms as the centre manifold computation of Theorem 4 for a fraction of the effort.

7. Conclusions

In this paper we complemented the analysis of [5] by considering a more realistic dynamics of nucleating point islands with critical island size i by allowing subcritical islands of size $2 \leq j \leq i - 1$ to form and fragment. The mathematics of this new system of equations is more challenging than the fundamentally 2-dimensional system considered in [5] and we had to use both centre manifold techniques and a sophisticated globalisation argument using ideas from theories of compartmental systems and of asymptotically autonomous differential equations; the globalisation methods used in this paper are in our opinion more elegant than the “brute-force” asymptotics in [5].

Our asymptotic results in Section 5 are consistent with the leading term asymptotics for $c_1(t)$ of [12] (see our Lemma 5) and for $c_j(t)$, ($1 \leq j \leq i$), of [1] (see Lemma 6), as well as with the conjecture in [12] about the behaviour of $c_j(t)$, $j > i$ (see Lemma 7). Of course our methods are not restricted to the computation of leading terms of the asymptotics.

Appendix A. Computations of Theorem 4

In this Appendix we supply the code implementing the computations described in the proof of Theorem 4. We compute 15 terms in the expansion of the one-dimensional centre manifold with components given by (20) of a system with $i = 5$.

n:=15:

First of all we set up the equations:

```

eqc1 := a-2*c1^2-c1*z+2*b*c2+b*c3+b*c4+b*c5:
eqc2 := c1^2-c1*c2-b*c2+b*c3:
eqc3 := c1*c2-c1*c3-b*c3+b*c4:
eqc4 := c1*c3-c1*c4-b*c4+b*c5:
eqc5 := c1*c4-c1*c5-b*c5:

eqz := c1^2-b*c2:

z := (a-v)/c1:

eqv := -eqc1*z-c1*eqz:

eqc1s := eqc1*c1:
eqc2s := eqc2*c1:

```

```

eqc3s := eqc3*c1:
eqc4s := eqc4*c1:
eqc5s := eqc5*c1:

eqvs := simplify(eqv*c1):

v := w-2*b*c2-b*c3-b*c4-b*c5:

eqws := simplify(eqvs+2*b*eqc2s+b*eqc3s+b*eqc4s+b*eqc5s):

eqws := expand(eqws):

```

Now we use the expansions (20) and (21) and remove all the higher order terms that are not needed in the computation to save time:

```

c2 := sum('g2||j*c1^j', 'j'=2..n):
c3 := sum('g3||j*c1^j', 'j'=2..n):
c4:= sum('g4||j*c1^j', 'j'=2..n):
c5 := sum('g5||j*c1^j', 'j'=2..n):
w := sum('gw||j*c1^j', 'j'=2..n):

aw := collect(simplify(eqc1s*diff(w,c1)-eqws),c1):
ac2 := collect(simplify((w-2*c1^2)*diff(c2,c1)-eqc2),c1):
ac3 := collect(simplify((w-2*c1^2)*diff(c3,c1)-eqc3),c1):
ac4 := collect(simplify((w-2*c1^2)*diff(c4,c1)-eqc4),c1):
ac5 := collect(simplify((w-2*c1^2)*diff(c5,c1)-eqc5),c1):
aw:= convert(taylor(aw,c1=0,n+1),polynom):

ac2:= convert(taylor(ac2,c1=0,n+1),polynom):
ac3:= convert(taylor(ac3,c1=0,n+1),polynom):
ac4:= convert(taylor(ac4,c1=0,n+1),polynom):
ac5:= convert(taylor(ac5,c1=0,n+1),polynom):

```

Finally, we compute the coefficients of the expansion in the order indicated in the proof of Theorem 4.

```

for k from 2 to n do
  gw||k:= solve(coeff(aw,c1,k),gw||k):
  g5||k:= solve(coeff(ac5,c1,k),g5||k):
  g4||k:= solve(coeff(ac4,c1,k),g4||k):
  g3||k:= solve(coeff(ac3,c1,k),g3||k):
  g2||k:= solve(coeff(ac2,c1,k),g2||k):
od:

```

Now we print out the asymptotic ODE equation for c_1 :

```

odec1 := w-2*c1^2;

```

The result is

$$c_1' \sim -\frac{c_1^8}{\alpha\beta^4} + \frac{c_1^9}{\alpha\beta^5} - \frac{c_1^{13}}{\alpha\beta^9} + \frac{(30\beta^2 + \alpha)c_1^{14}}{\alpha^2\beta^{10}} - \frac{80c_1^{15}}{\alpha\beta^9} + O(c_1^{16}).$$

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